

Lanthanide-based upconverting and chromium-based persistent luminescence nanoparticles for optical applications involving NIR illumination

Ph.D. thesis

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illumination

Thesis presented to the Institute of
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Advisor: Prof. Dr. Sidney José Lima Ribeiro

Co- Advisor: Prof. Dr. Sajjad Ullah

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Nanopartículas de conversão ascendente de energia baseadas em lantanídeos e de luminescência persistente baseadas em crômio para aplicações ópticas envolvendo radiação no infravermelho próximo

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I definitely dedicate this and each one of my achievements to my parents Cesar and Alba, my brothers Cesar and Keybis, and my darling wife Nayara. I admire them and they are my main source of inspiration.

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DATA

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- XIX Brazil MRS Meeting (Sep 25 – 29, 2022, Foz do Iguaçu - Pr – Brasil). Synthesis, surface modification, and functionalization of $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ persistent luminescence nanoparticles for biosensing (poster presentation).
- XXX International Materials Research Congress and International Conference on Advanced Materials (Aug 14 – 19, 2022, Cancun, Mexico). A UV-visible-NIR active photocatalytic system based on $\text{NaYbF}_4:\text{Tm}^{3+}/\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ for broad spectrum photocatalysis (oral presentation)
- XIX Brazil MRS Meeting (Aug 30 – Sep 03, 2021, online format). Photocatalytic system based on upconverting particles/photocatalyst/oxidant Thulium-doped sodium ytterbium fluoride/silver phosphate/hydrogen peroxide activated under visible and near infrared light (poster presentation).
- 42^a Reunião Anual da Sociedade Brasileira de Química (May 27 - 30, 2019, Joinville - SC - Brasil). Multicolor Emission through Bi-directional Energy Transfer in Nd^{3+} -Sensitized Gd^{3+} -based Core/Shell/Shell Upconverting Nanoparticles (oral and poster presentation).
- 8th International Conference on Optical, Optoelectronic and Photonic Materials and Applications (Aug 26 - 31, 2018, Maresias – SP - Brasil). Nd^{3+} -Sensitized Gd^{3+} -based Core/Shell/Shell Upconverting Nanoparticles: A Platform for Multicolour Emissions through Bi-directional Energy Transfer (poster presentation).
- 10th International Conference on Nanophotonics (Jul 02 - 05, 2017, Recife-Pe-Brasil) Size-controlled synthesis of Nd^{3+} -sensitized Core@shell Upconversion Particles (poster presentation).
- XI Encuentro Departamental de Semilleros de Investigación (May 16 - 17, 2014, Barranquilla - Colombia. Evaluación del Carácter Generador de Oxígeno Singlete por Derivados Pirido[2,3-d]Pirimidínicos (oral presentation).
- X Encuentro Departamental de Semilleros de Investigación (May 29 - 31, 2013, Barranquilla - Colombia. Determinación del Rendimiento Cuántico de Producción de Oxígeno Singlete de 7-Indolilpirido[2,3-d]Pirimidinas (oral presentation.

Scientific Productions

- **Y.E. Serge-Correales**, D. Neumeyer, S. Ullah, R. Mauricot, Q. Zou, S.J.L. Ribeiro, M. Verelst, Size control and improved aqueous colloidal stability of surface-functionalized $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ bright persistent luminescence nanoparticles. *Langmuir*. Accepted manuscript. Doi: 10.1021/acs.langmuir.2c02871
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FOREWORD

This thesis was written in the format of chapters/articles in accordance with the presentation of dissertations and theses norms of the Chemistry Graduate Program at the Institute of Chemistry, UNESP – Araraquara – SP.

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The content of Chapter 6 has not yet been submitted to any journal because it is not fully completed.

The results corresponding to Chapters 3 and 4 were collected at the host institution. Meanwhile, most of the results corresponding to Chapters 5 and 6 were collected during the studies abroad at CEMES–CNRS in Toulouse–France, and a little part at the host institution. More detailed information about the manuscripts that make up this thesis is presented below.

Chapter 3 Precisely tailored shell thickness and Ln^{3+} content to produce multicolor emission from Nd^{3+} -sensitized Gd^{3+} -based core/shell/shell UCNPs through bi-directional energy transfer

Authors York E. Serge Correales, Chanchal Hazra, Sajjad Ullah, Laís R. Lima, and Sidney J. L. Ribeiro

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Chapter 4 A UV-visible-NIR active smart photocatalytic system based on NaYbF₄:Tm³⁺ upconverting particles and Ag₃PO₄/H₂O₂ for photocatalytic processes under light on/light off conditions

Authors York E. Serge-Correales, Sajjad Ullah, Elias P. Ferreira-Neto, Hernan D. Rojas-Mantilla, Chanchal Hazra, and Sidney J. L. Ribeiro

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Chapter 5 Size control and improved aqueous colloidal stability of surface-functionalized ZnGa₂O₄:Cr³⁺ bright persistent luminescence nanoparticles

Authors York E. Serge-Correales, David Neumeyer, Sajjad Ullah, Robert Mauricot, Qilin Zou, Sidney J. L. Ribeiro, and Marc Verelst

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Chapter 6 Coupling of NaYbF₄:Tm³⁺ upconverting nanoparticles with ZnGa₂O₄:Cr³⁺ persistent luminescence nanoparticles

Authors York E. Serge-Correales, David Neumeyer, Sajjad Ullah, Robert Mauricot, Sidney J. L. Ribeiro, and Marc Verelst

Journal This work is expected to be submitted to ACS Applied Nano Materials upon completion.

ABSTRACT

This work reports the development of luminescent materials with upconversion (UC) and persistent luminescence (PL) properties for optical applications involving near-infrared (NIR) illumination. The following are described and discussed: 1) controlled synthesis to obtain uniform and monodisperse nano- and micro-particles; 2) surface modification to provide hydrophilic functional groups, making them dispersible and stable in aqueous media; 3) the structural, morphological, optical and photoluminescent characterizations; 4) potential applications.

Sub-20 nm core/multishell $\text{NaGdF}_4:\text{Yb}^{3+}/\text{Ca}^{2+}/\text{Nd}^{3+}/\text{Tm}^{3+}@\text{NaGdF}_4:\text{Nd}^{3+}/\text{Ca}^{2+}@\text{NaGdF}_4:\text{Yb}^{3+}/\text{Ca}^{2+}/\text{Er}^{3+}/\text{Nd}^{3+}$ UC nanoparticles (UCNPs) were obtained by seed-mediated growth *via* high-temperature co-precipitation route. Through simple and precise control of the shell thickness along with tuning the content of lanthanide ions in each domain (core, middle shell, and outermost shell) it was possible to obtain multicolored and tunable luminescence from blue to white under 808 nm laser excitation.

$\text{NaYbF}_4:\text{Tm}^{3+}$ UC particles (UCPs) with microrod shape of 8 μm in length and 2.5 μm in diameter were also synthesized. These microrods in conjunction with Ag_3PO_4 particles (photocatalyst) and H_2O_2 (oxidizing agent) were used in the development of a broad-spectrum photocatalytic system, active in the UV-Vis-NIR region. This photocatalytic system showed high photocatalytic activity in crystal violet (CV) dye degradation under both direct excitation with visible light (complete dye removal in less than 8 min) and indirect excitation of Ag_3PO_4 in the NIR due to photons emitted by the UCPs under 980 nm laser irradiation (almost total dye removal in approximately 90 min).

Furthermore, uniform OA-capped $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell UCNPs were synthesized. The UC property of these nanoparticles was improved by increasing the protection of the $\text{NaYbF}_4:\text{Tm}^{3+}$ core nanoparticles with a NaYF_4 protective layer of different thickness. Increasing shell thickness led to a concomitant decrease in energy quenching associated with surface defects of the unprotected nanoparticles.

To enhance the applications of these $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ UCNPs, their coupling with PL nanoparticles (PLNPs) was investigated, aiming at obtaining a system that presents UC and PL (UC-PL) with excitation and emission in the NIR, which may find

potential applications in deep tissue luminescence bioimaging or in the activation of photosensitizers in the photodynamic therapy.

As a result, OA-coated $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ (ZGO) PLNPs were first synthesized. The synthesis was carried out by solvothermal treatment at 210 °C, without the need for further calcination. Tunable size from 7 to 21 nm was achieved using different alcohols in the synthesis and a seed-mediated nanoparticle growth approach. The PL was nanoparticle size-dependent (PL lasting over 1000 s).

After improving the optical properties of the OA-coated nanoparticles, the ligand exchange process for surface modification was carried out. This allowed removing hydrophobic ligands and anchoring hydrophilic groups provided by poly(acrylic acid) (PAA) polymer and cysteamine (Cys) molecules on the surface of the nanoparticles, ensuring their redispersion in aqueous media, as well as providing long-term colloidal stability.

Finally, the coupling reactions of hydrophilic nanoparticles were investigated through the formation of covalent bonds between surface-functionalized UCNPs and PLNPs, on the basis of EDC/NHS (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride)/(N-Hydroxysuccinimide) coupling chemistry. The results obtained suggest that the coupling reaction was successfully performed. However, new coupling conditions and characterizations are needed, as well as the study of the energy transfer between the nanoparticles for a better understanding of this coupling process and to guarantee future applications.

RESUMO

Neste trabalho é relatado o desenvolvimento de materiais luminescentes com propriedades de UC e PL envolvendo radiação no NIR. São descritas e discutidas: 1) a síntese controlada para a obtenção de nano e micropartículas monodispersas e de tamanho uniforme; 2) a modificação da superfície para fornecer grupos funcionais hidrofílicos, tornando-as dispersíveis e estáveis em meio aquoso; 3) caracterizações: estrutural, morfológica, óptica e fotoluminescente; 4) as potenciais aplicações.

UCNPs com tamanho menor que 20 nm, estrutura do tipo núcleo/multicamada e de composição/design representado como $\text{NaGdF}_4:\text{Yb}^{3+}/\text{Ca}^{2+}/\text{Nd}^{3+}/\text{Tm}^{3+}@\text{NaGdF}_4:\text{Nd}^{3+}/\text{Ca}^{2+}@\text{NaGdF}_4:\text{Yb}^{3+}/\text{Ca}^{2+}/\text{Er}^{3+}/\text{Nd}^{3+}$ foram obtidas por crescimento mediado por sementes através de uma rota de coprecipitação a 300 °C. Mediante o controle simples e preciso da espessura das diferentes camadas, juntamente com ajuste do conteúdo dos íons lantanídeos em cada domínio (núcleo, camada intermediária e camada mais externa) foi possível obter luminescência multicolorida e sintonizável do azul ao branco sob excitação laser de 808 nm.

Também foram sintetizadas UCPs de $\text{NaYbF}_4:\text{Tm}^{3+}$ em formato de microbastões de 8 µm de comprimento e 2,5 µm de diâmetro. Estes microbastões, juntamente com partículas de Ag_3PO_4 (fotocatalisador) e H_2O_2 (agente oxidante) foram utilizados no desenvolvimento de um sistema fotocatalítico de amplo espectro, ativo no UV-Vis-NIR. O sistema fotocatalítico desenvolvido apresentou alta atividade fotocatalítica na degradação do corante cristal violeta (CV) sob irradiação com luz visível (remoção total do corante em menos de 8 min) e no NIR usando um laser de 980 nm (quase total remoção do corante em aproximadamente 90 min).

Além disso, foram sintetizadas UCNPs de tamanho uniforme, de estrutura do tipo núcleo/casca e de composição/design representado como $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$. A propriedade de UC destas nanopartículas foi aprimorada mediante o aumento da proteção das nanopartículas centrais (núcleo) de $\text{NaYbF}_4:\text{Tm}^{3+}$ com uma camada protetora de NaYF_4 cada vez maior. O aumento da espessura da casca levou a uma diminuição concomitante da supressão da energia associada aos defeitos de superfície das nanopartículas sem revestimento.

Para potencializar as aplicações destas UCNPs de $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ foi investigado seu acoplamento com nanopartículas de PL (PLNPs), visando a obtenção de um sistema que apresente UC e PL (UC-PL) com excitação e emissão no NIR, que

podem encontrar aplicações potenciais em bioimagem de tecido profundo baseado em luminescência ou na ativação de fotosensibilizadores na terapia fotodinâmica.

Em decorrência disso, primeiramente foram sintetizadas PLNPs de composição $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ (ZGO) revestidas com OA. A síntese foi realizada pelo tratamento solvotérmico a 210 °C, sem a necessidade de calcinação adicional. Foi possível controlar o tamanho de 7 a 21 nm usando diferentes álcoois na síntese e uma abordagem de crescimento de nanopartículas mediada por sementes. A luminescência persistente foi dependente do tamanho das nanopartículas (PL com duração acima de 1000 s).

Após do aprimoramento das propriedades ópticas das nanopartículas revestidas com OA foi realizada a modificação de superfície mediante troca de ligante com PAA e Cys. Isto permitiu remover os ligantes hidrofóbicos e fornecer grupo funcionais hidrofílicos na superfície das nanopartículas, garantindo sua redispersão em meios aquosos, além de proporcionar estabilidade coloidal a longo prazo.

Finalmente, as reações de acoplamento das nanopartículas hidrofílicas foi investigado através da formação de ligação covalente entre as UCNPs e as PLNPs funcionalizadas na superfície, com base na química de acoplamento EDC/NHS. Os resultados obtidos sugerem que a reação de acoplamento foi realizada com sucesso. Com tudo, são necessárias novas condições de acoplamento e caracterizações, bem como o estudo da transferência de energia entre as nanopartículas para melhor entendimento desse processo de acoplamento e para garantir futuras aplicações.

SYMBOL TABLE

$^1\text{O}_2$	Singlet oxygen
$^{2S+1}\text{L}_J$	Notation for energy levels
BG	Background
CB	Conduction band
CIE	Commission Internationale de l'Eclairage'
CR	Cross relaxation
CSU	Cooperative sensitization upconversion
CV	Crystal violet
Cys	Cysteamine
DC	Downconversion
DLS	Dynamic light scattering
DMF	N,N-Dimethylformamide
DRS	Diffuse reflectance spectra
DS	Downshifting
e^-	Electron
E1	First excited state
E2	Second excited state
EDC	1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride
EDS or EDX	Energy-dispersive X-ray spectroscopy
EDTA	Ethylenediaminetetraacetic acid
E_g	Band gap energy
EPR	Electron paramagnetic resonance
ESA	Excited-state absorption
ET	Energy transfer

ETU	Energy transfer upconversion
ExpDec2	Bi-exponential decay function
FEG-SEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared
GO	Graphene oxide
GS	Ground state
h^+	Oxidative hole
HO $\cdot$	Hydroxyl radical
HRTEM	High resolution transmission electron microscopy
$h\nu$	Photon energy
I_l	Integrated luminescence intensity
J	Electronic angular momentum
k	Photodegradation rate constant
L	Orbital angular momentum
LED	Light-emitting diode
Ln	Lanthanide
m	Number of electrons in 5d orbitals
MRI	Magnetic resonance imaging
n	Number of electrons in 4f orbitals
n	Number of the laser photons required to populate the upper emitting state
NHS	N-Hydroxysuccinimide
NIR	Near-Infrared
NPEGN	Poly(ethylene glycol) bis(amine)
O $_2^{\cdot-}$	Superoxide radical
OA	Oleic acid

OAm	Oleylamine
ODE	1-Octadecene
P	Pump laser power
PAA	Poly(acrylic acid)
PDI	Polydispersibility index
PDT	Photodynamic therapy
PEG	Poly(ethylene glycol)
PES	Polyethersulfone
PL	Persistent luminescence
PLE	Photoluminescence emission
PLNPs	Persistent luminescence nanoparticles
PS	Photosensitizer
PVP	poly(vinylpyrrolidone)
r	Average donor–acceptor distance
RE	Rare-earth
ROS	Reactive oxygen species
S	Total electron spin
SEM	Scanning electron microscopy
SNPs	Sacrificial nanoparticles
t or τ	Luminescence lifetime
t_1 or τ_1	First decay luminescence lifetime
t_2 or τ_2	Second decay luminescence lifetime
TEM	Transmission electron microscopy
UC	Upconversion or upconverting
UCL	Upconversion luminescence
UCNPs	Upconverting nanoparticles

UC-PL system	System resulting from the coupling of UC and PL materials
UCPs	Upconverting particles
UV	Ultraviolet
VB	Valence band
Vis	Visible
XRD	X-ray diffraction
ZGO	$\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$
α -	Cubic phase of NaLnF_4
β -	Hexagonal phase of NaLnF_4
ζ potential	Zeta potential
λ_{em}	Emission wavelength
λ_{ex} or λ_{exc}	Excitation wavelength

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CHAPTER 1

INTRODUCTION

1 INTRODUCTION

1.1 Luminescence materials

A luminescent material, also called a phosphor, is any substance capable of emitting electromagnetic radiation, usually accompanied by the emission of thermal radiation, after being externally excited by some type of energy, such as electromagnetic radiation (photoluminescence), energetic electron beams (catholuminescence), energy of a chemical reaction (chemiluminescence), mechanical energy (triboluminescence), electrical voltage (electroluminescence), among others.^{1–4} The type of excitation energy indicates the type of luminescent material. For example, a photoluminescent material composed of a host lattice and an emitting center (activator) absorbs photons of light of a certain wavelength and emits photons of another wavelength, either longer [downshift (DS), downconversion (DC)] or shorter [upconversion (UC)].^{2,3,5}

Although the emitting center can be directly excited by incident light, in most cases the function of a host lattice is to absorb that radiation and transfer it to the activator ion.⁶

Some characteristics of a good host matrix include high thermal and chemical stability, being transparent in the region of interest, having low to relatively low phonon energies, being resistant to photobleaching, etc.

Different inorganic materials have been widely used as host lattice, such as oxides, fluorides, phosphates, sulfides, silicates, aluminates, gallates, borates, aluminosilicates, selenides, sulfates, titanates, etc.^{3,7–12}

The function of the emitting center or activator ion is mainly to emit photons, commonly in the UV, Visible and NIR regions. The most commonly used activators are lanthanide (Ln) ions such as Eu^{2+} , Eu^{3+} , Tb^{3+} , Er^{3+} , Tm^{3+} , Ho^{3+} , Nd^{3+} , Sm^{3+} , Dy^{3+} and Pr^{3+} ,^{13–22} and some transition metal ions, such as Cr^{3+} , Cr^{4+} , Mn^{2+} , Mn^{3+} , Mn^{4+} ,^{23–27} among others,^{19,28} which have emission peaks mainly in the visible and NIR regions, suitable for several applications^{28–34}

Since the absorption and emission properties of a luminescent material are generally determined by the type of host lattice and the characteristics of the activator ion, it is extremely important to choose them properly to ensure their successful

application. Similarly, the regions or wavelengths of excitation and emission for a given material also play a vital role for its appropriate and relevant use.

Typically, luminescent materials absorb and emit in the UV-Vis and Vis region, respectively. However, excitation and/or emission in the UV-Vis region presents some disadvantages for certain bioapplications, for example, various constituents of biological tissues absorb and/or emit significantly in this region, which leads to a very limited penetration depth of photons into biological tissues, as well as a high autofluorescence signal.^{35–38}

Meanwhile, biological tissues show greater transparency in the NIR window (also called optical window or therapeutic window), between 650–950 nm (NIR-I), 1–1.35 μm (NIR-II), and 1.5–1.8 μm (NIR-III).^{35–42} In addition, the autofluorescence signal is practically insignificant, because the chromophores present in the components of biological tissues are not excited by light beyond the visible region, making the development of materials that absorb and/or emit in those regions of the NIR highly interesting.^{43–51}

Ln-doped materials with UC properties from NIR to UV-Vis-NIR, and materials presenting persistent luminescence (PL) properties with NIR emission have attracted great research attention in recent years due to their interesting optical properties and will be discussed in the next topics.

1.2 General introduction to trivalent lanthanide ions

Ln elements represent a group of 15 chemically similar elements in the periodic table from lanthanum (La) to lutetium (Lu), that are associated with the progressive filling of the 4f orbitals. These 15 elements, along with the chemically similar elements scandium (Sc) and yttrium (Y), are often collectively known as rare-earth (RE) elements (see Figure 1.1).^{3,52–54}

seven 4f wavefunctions and may have a spin of $\pm \frac{1}{2}$.⁵⁶ The way to associate the n electrons with the 4f orbitals, considering the spin, can be calculated using the expression:

$$\frac{(4l + 2)!}{n!(4l + 2 - n)!} = \frac{14!}{n!(14 - n)!} \quad \text{if } l = 3 \quad (1.1)$$

For example, the number of microstates for Tm^{3+} , electronic configuration $[\text{Xe}] 4f^{12}$, is 91. Each energy level is characterized by three quantum numbers, S , L , and J , and is labeled as $^{2S+1}L_J$, according to Russel-Saunders' theory.⁵⁷ S denote the total electron spin, and results from the vector sum of the spins of the individual electrons. The value of S is used to obtain the total spin multiplicity according to the equation $2S + 1$. For example, if $S = 5$, the multiplicity of the spectroscopic term or level is quintet. Meanwhile, L denote orbital angular momentum, and results from the sum of the magnetic orbital momentum of each individual electron. Each value of L is assigned a capital letter of the Latin alphabet to obtain the different spectroscopic terms: S ($L = 0$), P ($L = 1$), D ($L = 2$), F ($L = 3$), G ($L = 4$), H ($L = 5$), I ($L = 6$), K ($L = 7$), and so on. Vector addition of L and S affords the resulting quantum number, J , which can have values of $(L + S)$, $(L + S) - 1$, ...($L - S$).⁵⁷⁻⁵⁹ Since the 4f orbitals do not directly participate in chemical bonding due to shielding effect by the fully filled 5s and 5p orbitals, their energy levels $^{2S+1}L_J$ are well defined and poorly sensitive to chemical environment.^{60,61} This shielding effect is mainly responsible for the luminescent properties associated with the forbidden 4f-4f transitions of the lanthanides ions, for example, their multiple narrow and sharp emission bands, long excited-state lifetimes, high resistance to photobleaching.

Furthermore, the highly complex energy levels of the lanthanide ions may be suitable for giving rise to several optical processes during electronic transitions, including DS, DC, and UC (Figure 1.2).⁶²⁻⁶⁸ DS is a process that converts a high-energy excitation photon, usually in the UV, into a lower energy emission photon, usually in the visible region.⁶²⁻⁶⁵ DC is a process in which one high-energy excitation photon, typically in the UV-Vis region, results in two or more lower-energy emission photons, commonly in the Vis-NIR region.^{62,66} In particular, the UC process allows the conversion of two or more low energy excitation photons, usually in the NIR, to generate a higher energy emission photon, typically in the UV-Vis-higher energy NIR region.^{62-65,67-69} Through these well-established optical processes, lanthanide ions can

have multiple and tunable emissions over a wide range of the electromagnetic spectrum, from UV to NIR.

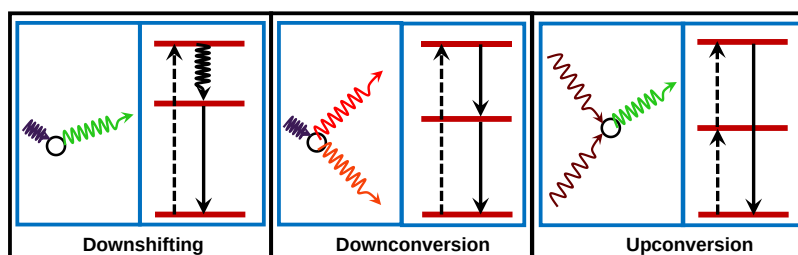


Figure 1.2 Simplified scheme of photon conversion processes.

1.3 Lanthanide-doped UC materials

Ln^{3+} ions can be incorporated as dopants into different nanomaterials including upconverting nanoparticles (UCNPs) to achieve unique luminescent optical properties. Ln^{3+} -doped UCNPs are diluted guest-host systems where Ln^{3+} ions are spatially distributed as guest in an appropriate dielectric crystal host lattice.⁷⁰ Typically, Ln^{3+} -doped UCNPs are composed of one or more sensitizer ions, with sufficiently large absorption cross-sections, and activators, which are optically active centers that produce emission when excited, e.g. Er^{3+} , Tm^{3+} , and/or Ho^{3+} . Interestingly, by proper control of Ln^{3+} dopants, UCNPs can emit at specific and tunable wavelengths, thus the color of the resulting emitted light can also be controlled.

1.3.1 UC Mechanisms

Several basic mechanisms have been identified by which UC luminescence (UCL) processes associated with Ln^{3+} ions can be achieved (Figure 1.3),^{29,69,71–74} including:

1.3.1.1 Excited-state absorption (ESA)

For ESA process, Ln^{3+} ions with ladder-like energy levels, such as Er^{3+} , Tm^{3+} , Ho^{3+} , and Nd^{3+} , under 980 or 800 nm excitation, are often used. In this process, the Ln^{3+} ions in the ground state (GS) absorb photons and are promoted to the first excited state (E1), which must be a metastable level. Subsequently, the ions in E1 absorb another photon and are promoted to a second excited state E2, from which the ions decay to the ground state, emitting light of shorter wavelength.

1.3.1.2 Energy transfer upconversion (ETU)

The ETU process is probably the most studied today due to its high conversion efficiency. Basically, two different types of Ln^{3+} ions are needed in this process, sensitizers (usually Yb^{3+} or $\text{Yb}^{3+}/\text{Nd}^{3+}$) and activators (for example Tm^{3+} , Er^{3+} or Ho^{3+}). The successive absorption of two or more NIR photons by the sensitizer ions (ion 1), with subsequent energy transfer (ET) from the E1 of the sensitizer ions to the E1 (long-lived intermediate energy states of activator ions) and subsequent E2 of the activator ions (ion 2), is followed by the emission of higher energy photons than the excitation photons (NIR $\rightarrow$ UV-Vis-NIR).

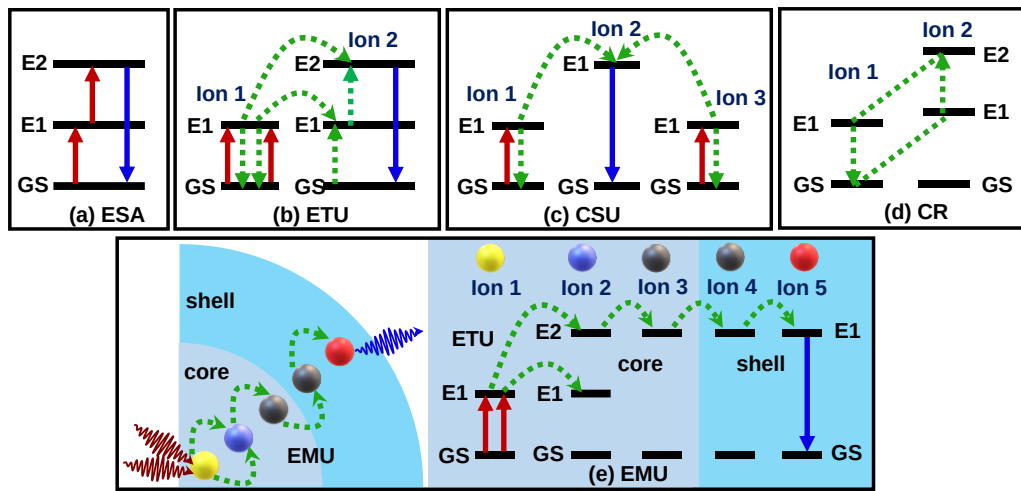


Figure 1.3 Schematic diagrams of different photon UC processes.

1.3.1.3 Cooperative sensitization upconversion (CSU)

CSU is a process that involves three ions, two sensitizers (ion 1 and 3), which are generally of the same type, and one activator (ion 2). This mechanism has been reported for materials containing Yb^{3+} ions as sensitizer and Pr^{3+} , Eu^{3+} , or Tb^{3+} , as activator ion. The process begins with the excitation of the sensitizer ions, which simultaneously transfer the excitation energy from their E1 to the E1 of the activator ion, resulting in the emission of light of wavelength shorter than the wavelength of the excitation light during radiative decay from the E1 to the GS of the activator ion. The activator ion does not have an intermediate energy level that matches the energy transferred by only one of the sensitizer ions, therefore, the efficiency of this process is very low.

1.3.1.4 Cross relaxation (CR)

CR is a process of energy transfer between two equal or different neighbor ions, but with similar energy differences between two energy levels of both, in such a way that an ion (ion 1) transfers its energy from an excited level E1 to a second ion (ion 2) that is already in its excited level E1. As a result, ion 1 decays to the GS (or to a lower energy excited level) and ion 2 is promoted to a higher energy excited level (E2). The process can be represented as $E1 (\text{ion 1}) + E1 (\text{ion 2}) \rightarrow \text{GS} (\text{ion1}) + E2 (\text{ion 2})$. This process depends on the distance of the dopant ions and requires high concentrations of them. It should be noted that in general it is a detrimental process of luminescence extinction, however, in optimal concentrations of dopants it can help in other UC processes, for example, to populate the $^1D_2$ (and higher) state of Tm^{3+} ions, through the process of $^3F_{2,3} (\text{Tm}^{3+}) + ^3H_4 (\text{Tm}^{3+}) \rightarrow ^3H_6 (\text{Tm}^{3+}) + ^1D_2 (\text{Tm}^{3+})$, during ETU.

1.3.1.5 Energy migration upconversion (EMU)

EMU has been reported for core/shell nanoparticles and starts with an ETU process between a sensitizer ion (ion 1) and an accumulator ion (ion 2) in the core domain. Subsequently, instead of being emitted, the energy is transferred to a migrator ion (ion 3). After that, the energy migrates through the core-shell interface by transfer between migrator ions (ion 3 - ion 4). Subsequently, ion 4 transfers the energy to an activator ion (ion 5), which finally decays radiatively, emitting a photon of shorter wavelength than the wavelength of the excitation photons. To avoid detrimental cross-relaxation processes, the sensitizer/accumulator and activator ions are spatially separated and confined in different layers of the core/shell structure. Usually Yb^{3+} , Tm^{3+} , and Gd^{3+} ions are incorporated as ions sensitizer, activator, and migrator ions, respectively, while Dy^{3+} , Sm^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} , Ce^{3+} ions are commonly incorporated as activator ions (ion 5).^{75–80}

In general, the UC process in this work refers to ETU mechanism, unless otherwise specified.

1.3.2 Design and fabrication of UCNPs

As UCL efficiency and the optical properties of UCNPs are generally affected by several parameters, such as types and concentration of dopant ions, host lattice, crystal phase as well as the architecture of the nanoparticles; this requires rationally designed UCNPs to ensure their successful use in various applications.^{71,74,81–83}

1.3.2.1 Host lattice

The host lattice determines the local symmetry, the spatial distribution of the dopant Ln^{3+} ions, as well as the crystalline field strength in its environment, and consequently, the ability to relax Laporte-forbidden f–f transitions; therefore, its proper selection is essential to obtain high UCL efficiency. The selection of the host lattice material proceeds to fulfill a primordial set of criteria, including being transparent in the spectral range of interest, non-hygroscopic, chemically stable, and photobleaching resistant. Additionally, to achieve high UCL efficiency the host lattice must have low lattice phonon energies.^{70,74,83–86}

Phonon-mediated non-radiative relaxation is one of the detrimental luminescence suppression pathways that affect the efficiency of the UC process.^{87,88} The smaller the gap between two energy levels or the higher the energy of the phonons, the greater the probability that the phonons can fill the gap between them by multiphonon emission and, consequently, the probability of driving the excited electrons to the lower energy level without radiative emission.

Since many energy levels of the sensitizer and activator ions participate in the UC process, it is necessary for the host lattice to have sufficiently low phonon energies, especially when conversions of three or more photons are required. Although bromides and chlorides of Ln^{3+} generally exhibit low phonon energies, e.g., 175 and 240 cm^{-1} , respectively for LaBr_3 and LaCl_3 ,^{89,90} they are generally highly hygroscopic, water soluble, and deliquescent, which limits their use as host lattices in UC processes.^{90–92} In contrast, oxides, and phosphates of Ln^{3+} meet high chemical stability but their phonon energies are relatively high, e.g., 600, 700, and 1050 cm^{-1} , for Y_2O_3 , Gd_2O_3 , and LaPO_4 , respectively,^{89,93–95} leading to relaxation of the excited states by phonon-mediated nonradiative decays, and making the UC process inefficient. Fluoride-based host lattice systems, for example, NaLnF_4 and LnF_3 , meet the prerequisite of chemical stability, non-hygroscopic nature, transparency in the UV-Vis-NIR region, resistance to photobleaching, as well as relatively low phonon energies ($\sim 350 \text{ cm}^{-1}$) to achieve high UC efficiency, thus are often used as host lattice materials for the synthesis of Ln-based UCNPs.^{70,89,90,95–97}

As mentioned above, the local symmetry of the dopant ions at the lattice sites of the inorganic host material has a prominent impact on the optical properties of the UCNPs, which is correlated to the difference in crystal fields in the dopant ions vicinity

generated in different crystal symmetries. NaYF₄, NaYbF₄ and NaGdF₄, which are the most representative host lattice materials for UC, are known to crystallize in two different crystal phases,^{67,98–104} the cubic phase (α -NaLnF₄) and the hexagonal phase (β -NaLnF₄). The last one is thermodynamically more stable at room temperature⁹⁸ and generally exhibits much stronger and sharper UCL, as well as higher quantum yield and UC efficiency than the cubic phase, due to the lower crystal symmetry which increases the 4f-4f transition probabilities by relaxing forbidden selection rules.^{67,70,99,105} However, there is a greater tendency for the formation of the cubic rather than the hexagonal phase.^{99,106–108} The cubic phase can be obtained at room temperature. However, obtaining the hexagonal phase requires a phase transition from the cubic one, demanding more energy because the free energy barrier for that phase transition is remarkably high.^{99,106,107,109–111} In most cases, the hexagonal phase can be obtained by thermal treatment, which require elevated temperature conditions accompanied by long reaction times.

1.3.2.2 Dopant ions

Sensitizer and activator ions are mostly responsible for the UC process to occur, and their type and content can directly determine the efficiency of the process, as well as the color of the emitted light.^{89,112–114} Sensitizer ions allow the UCNPs to absorb the excitation photons, while activator ions help in the UC process thanks to their ladder-like arrangement of levels with similar energy differences between them and relatively long lifetimes of their excited states, which allow the population of higher energy states, and the subsequent emission of higher energy photons.

Only a few sensitizer-activator ion pairs are suitable for UC process, including Yb³⁺-Er³⁺, Yb³⁺-Tm³⁺, and Yb³⁺-Ho³⁺, which can operate successfully under 980 nm thanks to the relatively large absorption cross section of Yb³⁺ ions in that region, due to the electronic transition $^2F_{7/2} \rightarrow ^2F_{5/2}$.^{70,89,90,96,112–114}

Additionally, several of the transitions between the ladder-like arranged energy levels of Er³⁺, Tm³⁺ and Ho³⁺ ions are closely resonant with the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb³⁺ ions, favoring the successive energy transfers between sensitizer and activator. In particular, Er³⁺ and Tm³⁺ ions have large enough energy gaps between various energy levels to decrease the probability of phonon-mediated nonradiative relaxation and increase the UC efficiency along with the probability of radiative transitions in the visible region for Er³⁺ ions and UV-Vis (blue)-NIR for Tm³⁺ ions (Figure 1.4).^{74,81,115–117}

Er^{3+} ions have three main UCL emission bands, including a red emission band around 660 nm and two fairly close green emission bands around 525 and 545 nm, which involve the UC of two photons. During sample excitation, a first photon is absorbed mainly by Yb^{3+} ions through $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition. Yb^{3+} ions in the $^2\text{F}_{5/2}$ excited state transfer the energy nonradiatively to Er^{3+} ions in the $^4\text{I}_{15/2}$ GS, leading to the $^4\text{I}_{11/2}$ excited level population of Er^{3+} ions and the return of Yb^{3+} ions to $^2\text{F}_{7/2}$ GS. After that Er^{3+} ions can either decay nonradiatively to the $^4\text{I}_{13/2}$ excited state or be promoted to the $^2\text{H}_{5/2}$ excited state mediated by a second ET from excited Yb^{3+} ions after absorption of a new photon. Er^{3+} ions in the $^2\text{H}_{5/2}$ excited state decay nonradiatively to either the $^2\text{H}_{11/2}$ state (responsible for emission at 525 nm) or the $^4\text{S}_{3/2}$ state (responsible for emission at 545 nm) (Figure 1.4). Similarly, Er^{3+} ions in the $^4\text{I}_{13/2}$ excited state can be promoted to the $^4\text{F}_{9/2}$ excited state (responsible for emission at 660 nm) after a second ET from the excited Yb^{3+} ions. The radiative decay from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ excited states to the $^4\text{I}_{15/2}$ GS of Er^{3+} ions produces the characteristic green and red emissions of these ions, according to the literature.^{118–121}

Meanwhile, the main UC emission bands of the Tm^{3+} ions are located in the NIR (~800 nm), blue (around 475 and 450), and UV (near 360, 345, and 290 nm) regions, for this reason Tm^{3+} -doped UCNPs are suitable for applications in deep tissues bioimaging or in the activation of photocatalysts, photosensitizers (PS), or PL nanoparticles (PLNPs).

As in the UC mechanism based on Er^{3+} ions, the UC process based on Tm^{3+} ions starts with the absorption of the excitation light at 980 nm by Yb^{3+} ions leading to population of the excited state ($^2\text{F}_{5/2}$) as a result of the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition. The excited Yb^{3+} ions transfer their energy to Tm^{3+} ions through successive energy transfer (ET) steps, resulting in the population of its higher energy levels. The excited Tm^{3+} ion then relaxes by emitting upconverted photons of shorter wavelengths (than the excitation wavelength of 980 nm) at around 290, 345, 360, 450, 475, and 800 nm which are, respectively, attributed to the $^1\text{I}_6 \rightarrow ^3\text{H}_6$, $^1\text{I}_6 \rightarrow ^3\text{F}_4$, $^1\text{D}_2 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^3\text{F}_4$, and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transitions of Tm^{3+} ions (Figure 1.4).^{105,122–124}

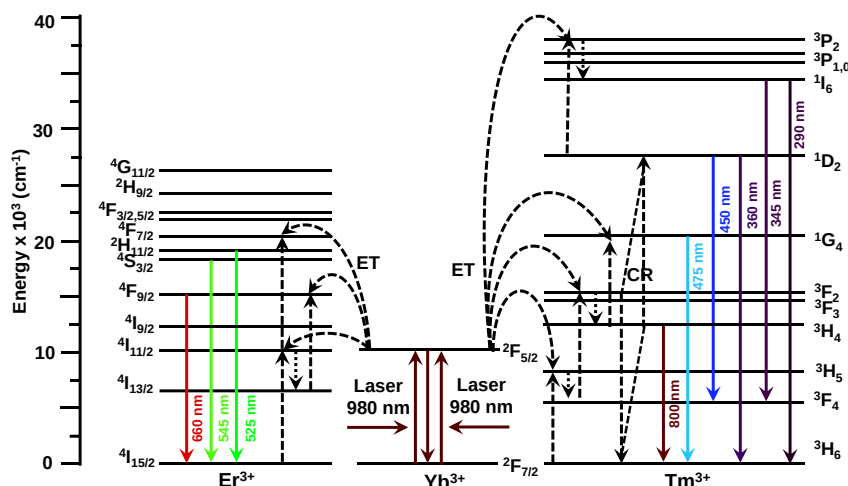


Figure 1.4 Schematic diagram of the mechanism of the UC process between the $\text{Yb}^{3+}\text{--Er}^{3+}$ and $\text{Yb}^{3+}\text{--Tm}^{3+}$ pairs involving their energy level diagrams to explain the main UC emissions of the Er^{3+} and Tm^{3+} ions. ET: Energy transfer; CR: Cross relaxation.

It is worth mentioning that increasing the concentration of sensitizer and activator ions will always lead to an increase in the UCL intensity of UCNPs. Of course, higher the concentration of Yb^{3+} ions, greater the intrinsic absorption cross-section of the UCNPs. However, a very high concentration of Yb^{3+} ions could lead to non-radiative relaxation by energy migration to quenching sites on UCNPs surface.^{125–127}

On the other hand, although the increase in activator ions concentration shortens the distance between sensitizer-activator ions, a highly doped system with activator ions irremediably leads to deleterious cross-relaxation processes and, consequently, to non-radiative decay;^{84,125–127} therefore, an adequate control of the elemental composition of UCNPs is essential to avoid energy losses due to non-radiative decay and maximize the emissions of upconverted photons.^{29,128,129}

In addition, doping a suitable host material with different types of activators (e.g., $\text{Er}^{3+}/\text{Tm}^{3+}$) in conjunction with Yb^{3+} as the sensitizer, ensuring precise control of their concentration, can produce multicolor UCL under 980 nm diode laser excitation.^{113,117,130–132} However, this strategy can also lead to cross-relaxation processes between the different types of activators, resulting in low UCL efficiency.

To address the problem of non-radiative decay associated with energy migration to quenching sites on UCNPs surface and achieve multicolor UCL by simultaneous doping with different activator ions it is necessary to design the nanoparticle with a core/shell architecture,^{133–135} where the protective shell prevents the migration of energy from Yb^{3+} ions in the core region to quenching sites on nanoparticle surface, in

addition to allowing the activator ions to be separated into two different domains, the core and shell region.

1.3.2.3 Nd³⁺-sensitized core/shell/shell UCNPs

In the Yb³⁺-sensitized UC process, the excitation wavelength (980 nm) may be strongly absorbed by water molecules in biological environment, which could cause local heating problems in the vicinity of cells and tissues, thus damaging them.¹³⁶ To solve this problem, some research has been focused on the extension of the UC excitation spectrum to shorter wavelengths (especially, in the vicinity of 808 nm using Nd³⁺ ions as sensitizers), where water molecules do not absorb significantly.^{136–143}

Nevertheless, efficient multicolor UCL output from Nd³⁺-sensitized UCNPs remains vague until this point. The UC mechanism under 800 nm laser excitation differs basically from the UC mechanism based on the excitation of Yb³⁺ ions under 980 nm laser irradiation in the first step. Specifically, the electrons of Nd³⁺ ion in the ⁴I_{9/2} GS are excited to the ⁴F_{5/2} level by the 808 nm laser. After a non-radiative decay of Nd³⁺ ions from the ⁴F_{5/2} excited level to the ⁴F_{3/2} excited level, an energy transfer occurs between the excited Nd³⁺ ions and the Yb³⁺ ions in the GS, causing the population of the excited level ²F_{5/2} of Yb³⁺ ions and the return of Nd³⁺ ions to the GS (Figure 1.5).¹⁴¹ After that, the energy transfer from the Yb³⁺ ions to the activator ions occurs as mentioned above.

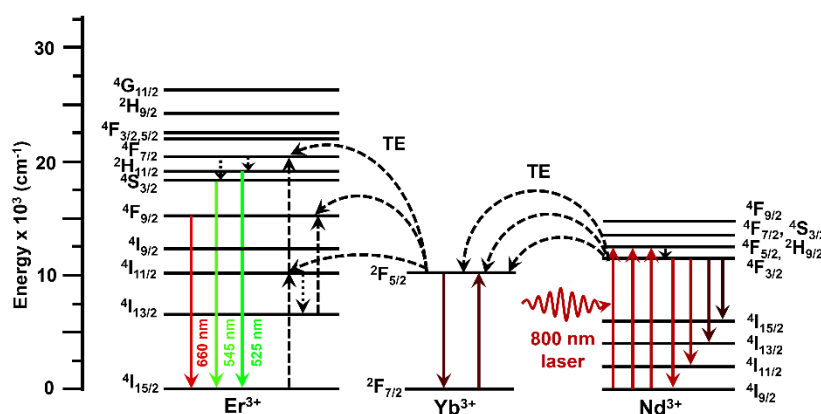


Figure 1.5 Schematic illustration of the UC process involving Nd³⁺, Yb³⁺, and Er³⁺, based on the excitation of Nd³⁺ ions at 800 nm.

In Chapter 3 of this work, Nd³⁺-sensitized UCNPs, using NaGdF₄ as host matrix, are further explored, and a detailed study of the synthesis is conducted, controlling the core/multishell architecture and the lanthanide contents to obtain multicolor UCL. Such

tunable multicolor UCL emission makes these Nd^{3+} -sensitized Gd^{3+} -based core/multishell UCNPs potential candidates for bioimaging and magnetic resonance imaging (MRI) dual modal application.

1.3.3 Synthesis of UCNPs

The optical properties and, in general, the successful application of UCNPs in different fields, depend largely on obtaining monodisperse UCNPs, with adequate control of size, shape, elemental composition, and crystalline phase during synthesis.

The most common methods for the synthesis of high-quality Ln^{3+} -doped core-only, core/shell, and core/multishell UCNPs include high-temperature coprecipitation and thermal decomposition methods, hot-injection strategies, and conventional and microwave-assisted hydrothermal treatment,^{8,13,122,144–148}

Additionally, the seed-mediated growth via high-temperature co-precipitation route and ripening-mediated self-focusing method for layer-by-layer epitaxial shell growth allow optimal control of the growth of one or more layers on the core (seed) nanoparticles and obtain high-quality core/shell and/or core/multishell structured UCNPs.^{135,149–151}

For developing of this thesis, high-temperature co-precipitation methods, microwave-assisted hydrothermal treatment, seed-mediated growth via high-temperature co-precipitation route and ripening-mediated self-focusing method with injections of small sacrificial nanoparticles for layer-by-layer epitaxial shell growth were followed, and therefore, only the fundamentals of these methods will be described here.

1.3.3.1 High-temperature coprecipitation method for the synthesis of core UCNPs

High-temperature coprecipitation method for the synthesis of UCNPs is based on the formation of small amorphous coprecipitates of fluoride-based nanoparticles at room temperature, followed by growth and ripening at high temperatures (280–315 °C) for a relatively short time, ranging from minutes to a few hours. Although other co-precipitating (stabilizing) agents/high boiling solvents could also be used, oleic acid (OA) as the stabilizing agent and 1-octadecene (ODE) as the solvent are the most widely used as they allow obtaining uniform, high-quality UCNPs and because of their cost-effectiveness, biocompatibility, and efficiency^{133,152–154}

1.3.3.2 Microwave-assisted hydrothermal treatment for the synthesis of core UCNPs

Hydrothermal treatment is a synthesis strategy that employs a Teflon-lined sealed autoclave reactor that allows obtaining UCNPs from aqueous solutions of the precursors at lower temperatures (180–220 °C) than those needed in the high-temperature coprecipitation method, but with much longer reaction times (12–24 h) and much higher pressures (0.3–4 MPa).

In addition, the microwave-assisted hydrothermal approach is a fast and simple method that drastically reduces the reaction time (0.5–1 h), even at temperatures lower than 200 °C. It also provides an excellent control over experimental parameters and a uniform distribution of energy inside the sample due to the high penetrability of microwave radiation, achieving a low thermal gradient and uniform heating. Micrometric size UC particles (UCPs), which can be used in heterogeneous photocatalysis processes for the activation of photocatalysts under NIR excitation, can be synthesized by microwave-assisted hydrothermal treatment.^{105,122}

1.3.3.3 Methodologies for the synthesis of core/shell and core/multishell UCNPs

Epitaxial shell growth on UCNPs is a widely used strategy to spatially separate the optically active core from the surrounding environment, reducing non-radiative decays caused by energy migration to quenching sites on its surface and improving the efficiency of the UC process. Furthermore, shell growth is an attractive option to fabricate UCNPs with multifunctionality.

1.3.3.3.1 Seed-mediated growth via high-temperature co-precipitation route

This strategy is a powerful and versatile approach to synthesize high quality core/shell structure UCNPs with a relatively uniform morphology and size. Similar to the high temperature coprecipitation method, this is based on the coprecipitation of lanthanide fluorides and their subsequent growth and ripening at high temperatures, but in this case the coprecipitation is carried out in the presence of small crystals as seeds (core UCNPs), which are used as seed nuclei for the epitaxial growth of the outer shell layer.^{76,151} However, in the widely used seed-mediated shell growth on β -NaLnF₄, the shell precursors preferentially nucleate as α -NaLnF₄ and thus a ripening-mediated process is necessary to lead to the formation of β -core/ β -shell UCNPs. By consecutively repeating the coprecipitation/ripening of new precursors using the

core/shell nanocrystals as seeds, it is possible to obtain UCNPs in core/multishell architecture. The shell thickness can be controlled by controlling the molar ratio of core to shell precursor.^{153,154}

1.3.3.3.2 Ripening-mediated self-focusing method for layer-by-layer epitaxial shell growth

This approach consists in that larger particles with smaller surface-to-volume ratios are favored over energetically less stable smaller particles, resulting in the growth of larger particles at the expense of smaller ones. When small α -phase nanoparticles, called sacrificial nanoparticles (α -SNPs), are injected at high temperature into a mixture containing OA, ODE, and larger β -phase core UCNPs (defocusing process), the thermodynamically less stable α -SNPs dissolve rapidly, forming shell monomers. The fast release of these monomers results in a supersaturation of monomers which are then deposited on the larger stable core nanoparticles forming the β -core/ β -shell structure (self-focusing). The most interesting point of this approach comes mainly from the high degree of control that can be achieved over the size, shape, and structure of the UCNPs without the need for vigorous control during synthesis. Additionally, this strategy saves time by repeating the defocusing and self-focusing cycle, which allow layer-by-layer growth during the same synthesis, enabling to evaluate the shell thickness and synthesize core/multishell UCNPs more efficiently.¹⁵⁰

1.3.4 Surface Modification

Most of the synthetic methodologies mentioned above produce UCNPs with hydrophobic surfaces, exclusively dispersible in nonpolar organic solvents, due to the hydrophobic nature of the capping ligands used during the synthesis (e.g., OA). The resulting non-dispersibility nature of these nanoparticles in aqueous media limits their use in bioapplications, where hydrophilicity is essential.

Since surface properties determine the biocompatibility of nanoparticles *in vitro* and *in vivo*, a crucial step in the use of UCNPs in bioapplications is the surface hydrophilic modification to make them water-dispersible, provide both a stable aqueous colloidal dispersion, and anchor suitable ligands to the surface for subsequent conjugation with biomolecules and/or other ligands.

A wide variety of surface modification strategies have been developed to fulfill this prerequisite and can be categorized into four groups: chemical modification of the

original hydrophobic ligand on the surface, amphiphilic coatings, encapsulation with inorganic materials forming a hydrophilic shell and complete exchange of the original ligand by another.^{155–160}

Here only the ligand exchange strategy will be discussed since it was the only one used in the development of this thesis, and because it is usually the simplest, fastest, and most cost-effective strategy.

1.3.4.1 Ligand exchange strategy

Ligand exchange is a versatile strategy for modifying the surface of UCNPs, which is usually quite simple, fast, and cost-effective. It is based on the replacement of the original hydrophobic ligands by others of a hydrophilic nature. Ligand exchange can be achieved in two ways: by direct exchange of the original hydrophobic ligands for the new ones and by two-step strategies using NOBF_4 (or acid treatment with HCl) to remove the hydrophobic ligands, followed by coating with the new hydrophilic ones.^{155–157,161}

1.3.4.1.1 Direct exchange of the original hydrophobic ligands

For this purpose, ligands that have a higher coordination capacity with the lanthanide ions than the original ligands are used, in many cases in excess. The protocols are quite simple, but the elaboration is tedious and more challenging than the chemical reaction itself. Typically, oleate-capped UCNPs and the hydrophilic ligands are mixed in a suitable solvent under continuous stirring, generally at high temperature for a few hours or days.

A major disadvantage is that protocols must be optimized for each type/family of ligands because each requires specific reaction conditions. Furthermore, the particles tend to agglomerate during ligand exchange.^{155,162}

1.3.4.1.2 Two-step strategies

This is a widely applicable strategy for nanoparticle surface modification. In a first step, the hydrophobic ligands are removed from the surface of UCNPs in the presence of an excess of NOBF_4 , resulting in the stabilization of the nanoparticles by BF_4^- ions. Although the nanoparticles are stabilized by BF_4^- ions instead of NO^+ ions, the

participation of the latter is important, since it has been shown that other fluoroborates work much less well, or even not at all in this strategy.

Total exchange of OA molecules by BF_4^- ions usually takes 20 minutes or less at room temperature, without the use of large amounts of solvents, requiring only stirring or sonication, thus resulting in an easy, fast, and cost-effective method, as well as being a general ligand-exchange strategy that may also be applied to other types of nanoparticles and enables their sequential surface functionalization.

In addition to the above, the aggregation during the ligand exchange process is considerably reduced compared to other protocols, and the resulting nanocrystal dispersions in aprotic polar solvents such as dimethylformamide (DMF) have long-term colloidal stability.¹⁵⁷

In a second step, by simply adding and stirring, new molecules or polymers with functional groups of a hydrophilic nature can be anchored to the surface of the nanoparticles, resulting in the exchange of BF_4^- ions for new ligands, such as poly(acrylic acid) (PAA), poly(vinylpyrrolidone) (PVP), poly(ethylene glycol) (PEG), citrate, etc.^{157,163}

1.3.5 Application of UCNPs and UCPs

The unique luminescent properties of UCNPs and UCPs make them attractive for various interesting bioapplications, such as nanothermometry, photoluminescence bioimaging, in bioassays for the detection of viruses, bacteria, and cancer cells, treatment of some diseases including cancer, photoinduced drug delivery, etc.^{164–169} Furthermore, Ga^{3+} -based UCNPs can be used as dual-mode imaging contrast agents.¹⁷⁰

In addition to their multiple bioapplications, UCNPs and UCPs can also be used in heterogeneous photocatalysis, to obtain UV-Vis-NIR active broad-spectrum photocatalytic systems by coupling UCNPs or UCPs with UV-Vis active photocatalysts, since the emitted photons by the UC materials in the UV-Vis region can activate photocatalysts with appropriate bandgap energy.^{105,122,171} Furthermore, the combination of broad-spectrum photocatalytic systems with other advanced oxidation processes, including the heterogeneous Fenton-like process, seems a highly promising strategy to achieve more efficient degradation results, and even to improve the photostability of photoinstable photocatalysts, such as Ag_3PO_4 , which has high photocatalytic activity, but suffers from photoreduction when exposed to UV-Vis light.

The two main objectives of Chapter 4 of this work were (i) the development of a broad-spectrum photocatalytic system by combining UCPs with Ag_3PO_4 , photocatalyst, and (ii) the improvement of Ag_3PO_4 photostability using H_2O_2 , which allows Ag_3PO_4 oxidation back/regeneration while leading to the formation of reactive oxygen species through Fenton-like reactions.

Moreover, increasing attention has been paid to the use of UCNPs in the activation of PL materials,^{172,173} to simultaneously explore the advantages offered by the individual use of each of the two types of materials. For example, excitation of UCNPs at NIR allows deep penetration into biological tissues, while afterglow emission of PL materials could prevent damage to biological tissues by avoiding the continuous use of the excitation laser irradiation.

1.4 PL materials

PL materials, also called long-lasting or afterglow materials, have drawn considerable attention in the field of luminescence bioimaging and other bioapplications since they allow decreasing the exposure time of tissues to the excitation radiation, in addition to considerably reducing the autofluorescence background signal.^{174–176} This is due to the inherent ability of PL materials to function as optical batteries, storing excitation energy and eventually emitting lower energy photons for a long time after removing the excitation source, which in many cases can even be seen with the naked eye for several hours.

Generally, two kinds of active centers are involved in PL process: traps and emitters. Trap levels originate because of lattice defects, impurities, or co-dopants in the material, mainly just below the conduction bands.^{177–179}

Excitation with suitable energy leads to the separation of electron-hole pairs, forming holes in the valence band and electrons in the conduction band, the latter are captured in the trap levels.

The traps operate as deposits that store the excitation energy. When the excitation light is switched off, the charge carriers are gradually released from such traps and recombine radiatively or non-radiatively with the emitters (e.g., activator dopant ions) to emit PL^{177,180} as schematically shown in Figure 1.6.

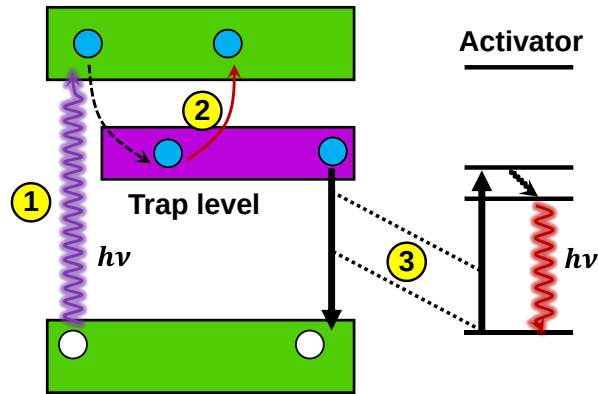


Figure 1.6 Schematic representation of a PL mechanism.

The characteristics of the emission center mainly determine the emitting wavelength region of interest, while those of the trap center determine the intensity and duration of PL.^{179,181}

Various types of lattice defects such as cation or anion substitution, interstitial impurities, cation or anion vacancies, and antisites act as electron and hole traps in the host material (Figure 1.7).^{182,183}

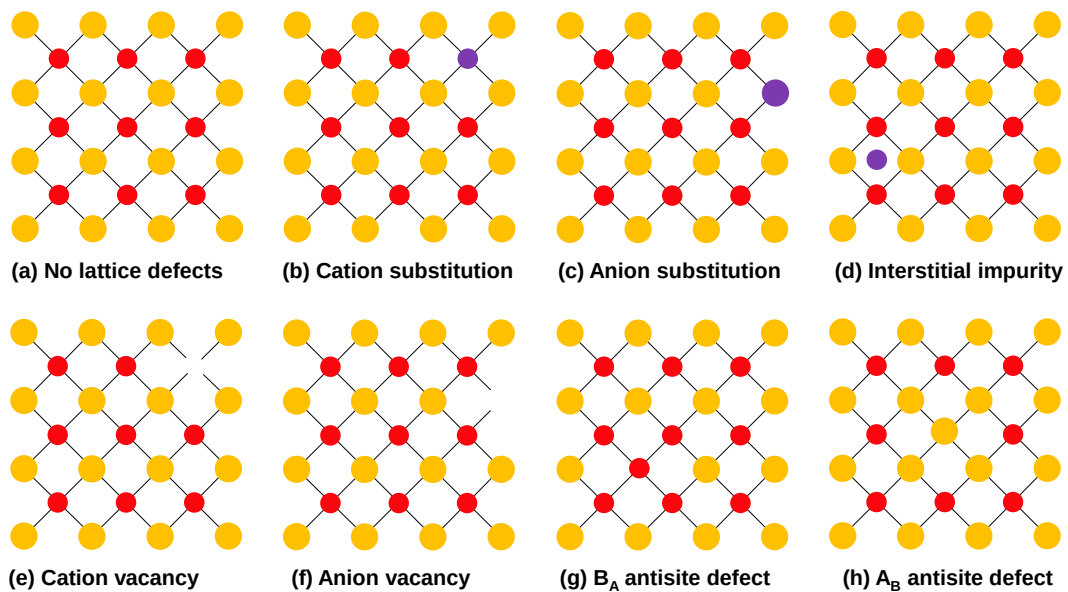


Figure 1.7 Examples of different types of point defects in a crystal lattice.

Emission centers can be lanthanide ions (e.g., Ce^{3+} , Eu^{2+} , Nd^{3+} , Er^{3+} , Pr^{3+} , Sm^{3+}) with $5d \rightarrow 4f$ or $4f \rightarrow 4f$ transitions, transition metal ions (e.g., Cr^{3+} , Mn^{2+} , Mn^{4+} , Ni^{2+}) with $d \rightarrow d$ transitions, or other metal ions (e.g., Pb^{2+} , Bi^{3+}) with $p \rightarrow s$ transitions, etc. However, only a few have PL emissions in the NIR region.^{177,179,181,184}

Nevertheless, several challenges to ensure the application of these materials in bioapplications remain unresolved. One of the major challenges related to the use of PL materials in bioapplications is the lack of crystal size control, since high calcination temperatures (above 1000 °C) are needed to induce lattice defect formation and increase PL signal, leading to exaggerated particle growth and poor size distribution.^{12,193–195} In addition, the large size of the particles and the lack of ligands on the surface make their redispersion in aqueous media practically impossible.

These challenges have been the subject of various studies in recent years. For example, by combining sol-gel and calcination procedures, several researchers obtained PL nanomaterials at lower temperatures (around 1000 °C), but the problem of agglomeration remained unsolved.^{196,197}

Particularly, hydro(solvo)thermal treatments allow obtaining ZGO particles at much lower temperatures. In addition, they offer the possibility of obtaining PL nanoparticles (PLNPs) with better control of size and morphology, thus being of greater relevance for bioapplications.^{189,198–201}

Until now, the hydro(solvo)thermal strategies that allow better control of size and morphology in the synthesis of PLNPs and other nanomaterials are those that use long-chain fatty acids, such as OA, to coat the nanoparticles,^{189,199–201} since a lower degree of polydispersity is obtained and agglomeration between them can be avoided, as mentioned above for the synthesis of UCNPs.

Srivastava *et al.*¹⁹⁹ obtained 6.1 nm ZGO nanoparticles through a biphasic synthesis route, heating a mixture formed by an aqueous solution of $\text{Zn}(\text{NO}_3)_2$, $\text{Ga}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$ and an organic solution of OA and toluene at 160 °C in an autoclave reactor. However, there was still a need for subsequent calcination at 750 °C to obtain PL emission.

Also using OA as a stabilizing agent, Yeh *et al.*¹⁸⁹ synthesized ZGO concave nanocubes with an edge length of 30 nm through a solvothermal process at 220 °C, which showed afterglow emission for more than 6 h without the need for additional calcination.

Similarly, Chen *et al.*²⁰⁰ synthesized ZGO PLNPs by a liquid-solid-solution hydro(solvo)thermal method at 210 °C using $\text{Zn}(\text{NO}_3)_2$, $\text{Ga}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, and a mixture of OA, ethanol, water, and sodium hydroxide. Due to the oleate molecules on the surface the PLNPs produced were monodisperse and flexible for surface functionalization, however they emphasized that their optical properties need to be improved.

More recently, Gao *et al.*²⁰¹ reported a solvothermal synthesis route, based on methanol-mediated pyrolysis of zinc, gallium, and chromium acetylacetonates to synthesize size-adjustable ZGO in a mixture of OA and ODE. Interestingly, the authors used smaller nanoparticles as seeds to obtain larger nanoparticles by seed-mediated growth, which allowed them to achieve an almost 10-fold increase in luminescence lifetime. They concluded that the increase in size favors the storage and release of

electrons captured by relatively deep traps, which leads to an increase in the luminescence lifetime (τ).

In addition to the controlled synthesis of ZGO PLNPs with suitable morphological characteristics and good optical properties, other prerequisites must be resolved before the proper use of these nanocrystals in bioapplications. For example, nanoparticles must have good redispersibility in aqueous media, long-term colloidal and gravitational stability, and functional groups anchored to their surface to enable their subsequent conjugation with biomolecules.

In Chapter 5 of this thesis, hydrophilic NIR-emitting ZGO PLNPs with improved afterglow properties that fulfill several fundamental requirements for optical bioapplications were obtained; therefore, the aforementioned challenges were well addressed here.

In addition to the advances related to the development of PLNPs suitable for bioapplications obtained in this thesis, these ZGO PLNPs may be appropriate for coupling with UCNPs to develop biocompatible UC-PL systems, thus opening new research horizons.

1.5 NIR-activated PL materials

Taking into account the above considerations on the advantages of using near-infrared excitation/emission in bioapplications, the interesting optical properties of UCNPs, and the inherent ability of PL materials to function as optical batteries and emit for a long post-excitation time, the development of UC-PL systems activated by NIR radiation and presenting PL in the NIR has attracted great research interest.^{172,173}

A great advantage of developing UC-PL materials is the possibility of obtaining NIR-rechargeable “optical batteries”, which can find interesting applications including the activation of PS in photodynamic therapy (PDT) or deep tissue luminescence bioimaging.

Unlike conventional PDT, for example, a UC-PL-PS system achieves a deeper penetration of the excitation light (980 nm laser), which is absorbed and upconverted by the UC materials. The photons emitted in the UV-Vis region by the UC materials activate the PL materials, which continue to emit for a long post-excitation period after which a new recharge takes place. In parallel, the photons emitted by the PL materials

lead to the excitation of PS responsible for producing singlet oxygen ($^1\text{O}_2$) capable of killing cancer cells.

However, most of the works published so far on the subject use PL materials obtained by calcination at high temperatures and even UCPs with several micrometers in size, which makes their real use in bioapplications practically impossible.^{173,202,203}

Therefore, it is of paramount importance to develop novel UC-PL systems that are properly sized and fulfill the fundamental prerequisites for their potential bioapplications.

For this reason, the NIR-emitting PLNPs obtained in Chapter 5 of this work have been used in conjunction with sub-40 nm size UCNPs obtained in Chapter 6 of this work to investigate their coupling in order to develop a UC-PL system with suitable properties for bioapplications.

1.6 References

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CHAPTER 2

OBJECTIVES

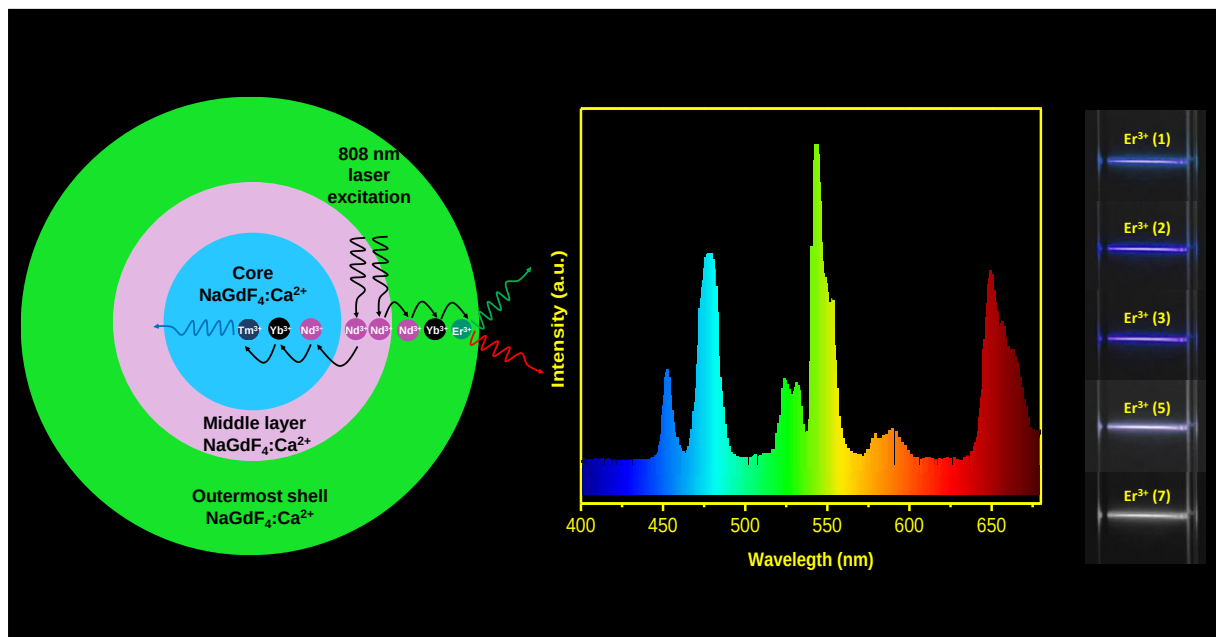
2 OBJECTIVES

The general objective of this thesis is the synthesis, surface modification and characterization of Ln^{3+} -doped UCNPs and Cr^{3+} -doped PLNPs for optical applications involving NIR illumination in view of its deep penetration into biological tissues. In this context, the PhD research activities developed in this thesis can be summarized as the following specific objectives:

- ✓ Control of size, morphology, crystal phase and optical properties of UCNPs and PLNPs through different synthetic routes.
- ✓ Characterize the synthesized nanoparticles through different instrumental techniques (excitation and emission spectra, TEM, SEM, EDS, DRS, XRD, FTIR, among others) and associate their structural characteristics with their optical properties.
- ✓ Evaluate the lanthanide content, core/shell architecture and shell thickness of UCNPs with the aim of improving their optical properties under 800 or 980 nm laser excitation.
- ✓ Investigate different surface modification strategies to convert the synthesized hydrophobic nanoparticles into hydrophilic ones, guaranteeing their dispersion in aqueous media and anchoring functional groups to their surface suitable for subsequent ligand reactions.
- ✓ Investigate the indirect photoexcitation of photocatalysts and PLNPs through the UV-Vis photons upconverted/emitted by the UCNPs under NIR irradiation.
- ✓ Explore applications involving the use of the synthesized nanoparticles under NIR illumination.

CHAPTER 3

PRECISELY TAILORED SHELL THICKNESS AND Ln^{3+} CONTENT TO PRODUCE MULTICOLOR EMISSION FROM Nd^{3+} - SENSITIZED Gd^{3+} -BASED CORE/SHELL/SHELL UCNPS THROUGH BI- DIRECTIONAL ENERGY TRANSFER



Precise control of the lanthanide content (activators and sensitizer ions) ✓

Suitable nanoparticle architecture (core/multishell) ✓

Control of shell thickness ✓

Multicolor UC luminescence ✓

Bi-directional energy transfer ✓

Biologically relevant excitation wavelength (808 nm) ✓

3 PRECISELY TAILORED SHELL THICKNESS AND Ln^{3+} CONTENT TO PRODUCE MULTICOLOR EMISSION FROM Nd^{3+} -SENSITIZED Gd^{3+} -BASED CORE/SHELL/SHELL UCNPS THROUGH BI-DIRECTIONAL ENERGY TRANSFER†

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Abstract

Lanthanide (Ln^{3+})-doped upconversion nanoparticles (UCNPs) have been paid great attention as multiplexing agents due to their numerous uses in biological and clinical applications such as bioimaging and magnetic resonance imaging (MRI), to name a few. To achieve efficient multicolor emission from UCNPs under single 808 nm excitation and avoid detrimental cross-relaxations between the Ln^{3+} activator ions (positioned in either the core and/or shell in the core/shell), it is essential to design an adequate nanoparticle architecture. Herein, we demonstrate the tailoring of multicolor upconversion luminescence (UCL) from Nd^{3+} -sensitized Gd^{3+} -based core/shell/shell UCNPs with an architecture represented as $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Ca}^{2+}(7)/\text{Nd}^{3+}(1)@\text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)@\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Ca}^{2+}(7)/\text{Nd}^{3+}(1)/\text{Er}^{3+}(X = 1, 2, 3, 5, 7)$ [hereafter named CSS ($\text{Er}^{3+} = 1, 2, 3, 5$ and 7 mol%)]. Such UCNPs can be excited at a single wavelength (~ 808 nm) without generation of any local heat. Incorporation of substantial Nd^{3+} -sensitizers with an appropriate concentration in the middle layer allows efficient harvesting of excitation light which migrates bi-directionally across the core/shell interfaces in sync to produce blue emission from Tm^{3+} (activator) ions in the core as well as green and red emission from Er^{3+} (activator) ions in the outermost shell. Introduction of Ca^{2+} lowers the local crystal field symmetry around Ln^{3+} ions and subsequently affects their intra $4f-4f$ transition probability, thus enhancing the upconversion efficiency of the UCNPs. By simple and precise control of

the shell thickness along with tuning the content of Ln^{3+} ions in each domain, multicolor UCL can be produced, ranging from blue to white. We envision that our sub-20 nm sized Nd^{3+} -sensitized Gd^{3+} -based UCNPs are not only potential candidates for a variety of multiplexed biological applications (without impediment of any heating effect), but also can act as MRI contrast agents in clinical diagnosis.

3.1 Introduction

In view of the recent research upsurge, multicolor luminescence from photoluminescent probes is of great interest due to its widespread use in chemical and biological sciences.^{1–7} The multicolor luminescence provides remarkable insight into molecular biological processes, and, using a number of color-encoded probes, makes a large number of biochemical entities feasible for high-throughput sequencing technologies together with brief sequencing chemistry.^{8–10} Along with multicolor luminescence, multiplexing experiments are adequately used in human genome decoding, and biological and clinical applications.^{11–13} To date, there are several reports available on photoluminescent probes that have been used as multiplexing agents in bio-system analysis and therapy applications.^{14–18} Among them, Ln^{3+} -doped UCNPs hold promise because of their unique anti-Stokes [known as upconversion (UC)] optical properties.^{19–24} Typically, these Ln^{3+} -doped nanoparticles are composed of sensitizers (e.g., $\text{Yb}^{3+}/\text{Nd}^{3+}$) and activators ($\text{Er}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$) which are spatially distributed in an appropriate host matrix or in a dilute host–guest system. Successive absorption of near infrared (NIR) photons and/or energy transfer (ET) generally promote the activators to higher excited states and concurrently lead to the emission of higher energy radiation spanning over a wide region, from the ultraviolet (UV) to NIR spectral regions.^{25–29} The relatively high penetration depth of NIR light in biological structures causes a minimal autofluorescence background signal and low biotoxicity, which again make UCNPs ideal candidates for a wide range of biological applications such as sensing, imaging and therapy, among others.^{30–38} Moreover, compact, inexpensive continuous-wave NIR diode lasers can be used to excite UCNPs, leading to the generation of multiphoton UCL which is an important additive to conventional multiphoton microscopy. This characteristic physiochemical property of UCNPs also allows their extensive use in biological domains.^{39–41}

Doping different types of activators (e.g., $\text{Er}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$) together with sensitizers (e.g., Yb^{3+}) with a precise concentration in a suitable host matrix can produce multicolor

UCL under single NIR wavelength excitation at 980 nm, which corresponds to the absorption of Yb^{3+} ions.^{42,43} However, this strategy can lead to cross-relaxation processes between the different types of activators, resulting in lower UCL efficiency from the UCNPs.^{44–46} Moreover, in the Yb^{3+} -sensitized UC process, the excitation wavelength (980 nm) is strongly absorbed by water molecules in biological environment which causes local heating problems in the vicinity of cells and tissues, thus damaging them.^{42,47} To address this problem, recent research has been focused on the extension of the UC excitation spectrum to shorter wavelengths (especially, in the vicinity of 808 nm), where water molecules do not absorb significantly.^{48–52} Nevertheless, efficient multicolor UCL output from Nd^{3+} -sensitized UCNPs remains vague until this point.

Furthermore, the multicolor UCL from Nd^{3+} -sensitized UCNPs, obtained through a combination of different types of activators (such as Er^{3+} and Tm^{3+}) in a single domain, can introduce deleterious cross-relaxation quenching processes, leading to low UCL efficiency from UCNPs. Therefore, it is necessary to separate different types of activators at a nanoscale distance. Moreover, to date, Nd^{3+} -sensitized core/shell UCNPs have typically been exploited to transfer the energy from a Nd^{3+} -doped light-harvesting layer across the core/shell interface to a $\text{Yb}^{3+}/\text{X}^{3+}$ ($\text{X} = \text{Er}, \text{Ho}$ or Tm) co-doped layer in one single direction. This uni-directional ET process provides no plausible scope to sensitize two different types of activators in separated layers which again leads to the decrease in UCL efficiency, knowing that the efficiency depends on the distance between the Nd^{3+} -doped layer and the activator-doped layer. It is worth mentioning that the efficiency of $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ non-radiative ET is directly proportional to the number of Yb^{3+} ions per Nd^{3+} ion in the doped region. In fact, the ability to harvest light most efficiently by UCNPs at 808 nm is also directed by the total number of doped Nd^{3+} ions. Thus, to achieve efficient multicolor UCL, it is essential to optimize the concentration of Yb^{3+} ions and Nd^{3+} ions in their defined domains. Recently, Hao *et al.* reported that the Tm^{3+} and Er^{3+} ions doped into sandwich-structured UCNPs of core/shell/shell $\text{NaYbF}_4:\text{Tm}^{3+}@\text{CaF}_2:\text{Nd}^{3+}@\text{CaF}_2:\text{Er}^{3+}$ effectively produce multicolor UCL via a bi-directional ET process.⁵³ However, to our knowledge, there is no report available on the use of a bi-directional ET process along with precise control of the shell thickness and proper tuning of the content of Ln^{3+} ions in each domain to produce bright multicolor emission from Nd^{3+} -sensitized Gd^{3+} -based core/shell/shell UCNPs.

Such strategies could be a potential tool for bio-imaging and MRI dual modal applications in the near future.

In this context, we report Nd³⁺-sensitized Gd³⁺-based core/shell/shell (CSS) UCNPs to achieve multicolor UCL under single wavelength excitation at 808 nm. In particular, NaGdF₄ has been selected as a host matrix (both as the core and the shell layer) as it allows the formation of small sized nanoparticles. In small sized UCNPs, the surface-to-volume ratio is very high and a large portion of dopant ions are located at the surface. Moreover, with proper functionalization, Gd³⁺-based core/shell/shell UCNPs could effectively serve as MRI contrast agents in medical diagnosis. Ca²⁺ was chosen as it has lower valence than Gd³⁺ ions. Upon replacement of some Gd³⁺ ions by Ca²⁺ ions, a charge imbalance in NaGdF₄ occurs which lowers the local crystal field symmetry around Yb³⁺, Er³⁺ and Tm³⁺ ions and subsequently affects the intra 4f–4f transition probability of the Ln³⁺ ions, thus enhancing the UC efficiency.^{34,54–56} The Nd³⁺ sensitizer is doped at a high concentration (30 mol%) in the middle layer to effectively and efficiently absorb the excitation light in this region and simultaneously conveys it to core and outermost shell in a bi-directional manner to emit efficient multicolor emissions from the nanoparticles. Tm³⁺ and Er³⁺ activators are separated into the inner core and the outermost shell, respectively, to prevent deleterious cross-relaxation processes between them. Moreover, the core/shell/shell nanoconfiguration allows simultaneous non-radiative ET from the middle layer to both the Tm³⁺-doped core and Er³⁺-doped outermost shell. Since high concentrations of Yb³⁺ ions (40 mol%) are incorporated in both the outermost shell and core domain, efficient core/shell interface energy migration takes place from the Nd³⁺ ions to the Yb³⁺ ions, which then sensitizes the activator ions (both Er³⁺ and Tm³⁺) to produce bright UCL. A lower doping of Nd³⁺ (1 mol%) in the outermost shell and in the core region is expected to assist the energy migration across the core/shell interfaces through a resonant ET process between Nd³⁺ ions. We demonstrated that the CSS (Er³⁺ = 1, 2, 3, 5 and 7 mol%) UCNPs are able to emit efficient multicolor UCL, ranging from blue to white under laser excitation at 808 nm. Tailoring the shell thickness, along with a precise control of the concentration of sensitizers and activators in their defined domains, allows us to achieve such tunable multicolor UCL from our designed sub-20 nm sized core/shell/shell UCNPs.

3.2 Experimental

3.2.1 Materials

Gd₂O₃ (99.99%, Sigma-Aldrich), Yb₂O₃ (99.99%, Sigma-Aldrich), Er₂O₃ (99.99%, Sigma-Aldrich), Nd₂O₃ (99.99%, Sigma-Aldrich), Tm₂O₃ (99.99%, Sigma-Aldrich), CaCl₂ (Synth), NaOH (Synth), NH₄F (Merck), methanol (CH₃OH, Synth), 1-octadecene (ODE, Aldrich), oleic acid (OA, Aldrich), cyclohexane (Synth, Brazil), and ethanol (C₂H₅OH, Synth, Brazil) were used in this work. All chemicals were used without further purification.

3.2.2 Methods

3.2.2.1 Synthesis of core NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7).

The core NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7) UCNPs were synthesized following a modified co-precipitation method according to a literature report.⁵⁷ In a typical experiment, 4 mL aqueous solution (0.2 M) of LnCl₃·6H₂O (Ln = Gd, Yb, Nd and Tm) and CaCl₂ were added to a 100 mL three-necked flask containing OA (6 mL) and ODE (14 mL). The resulting mixture was heated to 150 °C and kept for 1 h to form lanthanide oleate complexes and then cooled down to room temperature. Subsequently, a methanol solution (10 mL) containing NH₄F (3.25 mmol) and NaOH (2.0 mmol) was added and the mixture was stirred at 50 °C for 30 min. The temperature of the reaction mixture was then increased to 110 °C to remove methanol. Upon removal of methanol and keeping the reaction mixture at 110 °C under vacuum for 15 min, the solution was heated to 300 °C under a N₂ atmosphere and kept for 30 min before cooling down to room temperature naturally. The resulting nanoparticles were precipitated out by the addition of ethanol, collected by centrifugation, washed with cyclohexane, ethanol and methanol and finally redispersed in 4 mL cyclohexane.

3.2.2.2 Synthesis of core/shell NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)@NaGdF₄:Ca²⁺(7)/Nd³⁺(X) (X = 5, 10, 20, 30 and 50 mol%) [hereafter named CS (Nd³⁺ = 5, 10, 20, 30 and 50 mol%)]

In a typical experiment, a 4 mL solution (0.2 M) of LnCl₃·6H₂O (Ln = Gd, Nd) and CaCl₂ in water was added to a 100 mL three-necked flask containing OA (6 mL) and ODE (14 mL). The mixture was then heated to 150 °C and kept for 1 h with magnetic

stirring and then cooled down to 50 °C naturally. NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7) core UCNPs in 4 mL cyclohexane were then added along with 10 mL methanol solution of NH₄F (3.25 mmol) and NaOH (2.0 mmol). The resulting mixture was stirred at 50 °C for 30 min. The temperature of the reaction mixture was increased to 110 °C to remove the methanol. Upon removal of the methanol and keeping the reaction mixture at 110 °C under vacuum for 15 min, the solution was then heated to 300 °C under a N₂ atmosphere and kept for 45 min before cooling down to room temperature naturally. The resulting nanoparticles were precipitated out by the addition of ethanol, collected by centrifugation, washed with cyclohexane, ethanol, and methanol and finally redispersed in 4 mL cyclohexane.

3.2.2.3 Synthesis of core/shell/shell [CSS (Er³⁺ = 1, 2, 3, 5 and 7 mol%)]

In a typical experiment, a 4 mL solution (0.2 M) of LnCl₃.6H₂O [Ln = Gd, Nd, Yb, Er (X = 1, 2, 3, 5, 7)] and CaCl₂ in water was added to a 100 mL three-necked flask containing OA (6 mL) and ODE (14 mL). The mixture was then heated to 150 °C and kept for 1 h with magnetic stirring and then cooled down to 50 °C naturally. The CS (Nd³⁺ = 30 mol%) UCNPs in 4 mL cyclohexane were then added along with a 10 mL methanol solution of NH₄F (3.25 mmol) and NaOH (2.0 mmol). The resulting mixture was stirred at 50 °C for 30 min. The temperature of the reaction mixture was increased to 110 °C to remove the methanol. Upon removal of the methanol and keeping the reaction mixture at 110 °C under vacuum for 15 min, the solution was then heated to 300 °C under a N₂ atmosphere and kept for 1 h before cooling down to room temperature naturally. The resulting nanoparticles were precipitated out by the addition of ethanol, collected by centrifugation, washed with cyclohexane, ethanol, and methanol and finally redispersed in 4 mL cyclohexane. Different shell thickness controlled CS (Nd³⁺ = 30 mol%) and CSS (Er³⁺ = 5 mol%) UCNPs were synthesized following identical procedures to those mentioned above, except for a change in the amount of shell precursors and methanolic solution of NH₄F and NaOH.

3.2.3 Characterization

3.2.3.1 Structure and morphology

Fourier transform infrared (FTIR) spectra were collected using a PerkinElmer Spectrum 1000 FTIR spectrometer with a resolution of 2 cm⁻¹ and averaged over four

scans. Room temperature optical absorption spectra of the samples were recorded on a Varian model Cary 5000 spectrophotometer. The samples were taken in a 3 mL quartz cuvette (path length, 2 cm). The XRD measurements were performed on a powder X-ray diffractometer (Rigaku-RINT 2000) using Ni-filtered Cu K α X-ray radiation (1.540 Å) from a rotating Cu anode operated at 30 mA and 30 kV. The diffracted X-rays in the 2-theta range of 10–60° were monitored with a linear D/Tex detector at a scan rate of 1° min⁻¹. TEM analyses of the samples supported on holey carbon-coated copper grids were carried out using an FEI TECNAI (G2 F20) transmission electron microscope operated at an accelerating voltage of 200 kV. Before the imaging, each sample was further diluted in cyclohexane and sonicated for 1 min. One drop of the dispersion was deposited on a carbon-coated copper grid and the solvent was allowed to slowly evaporate.

3.2.3.2 Optical properties

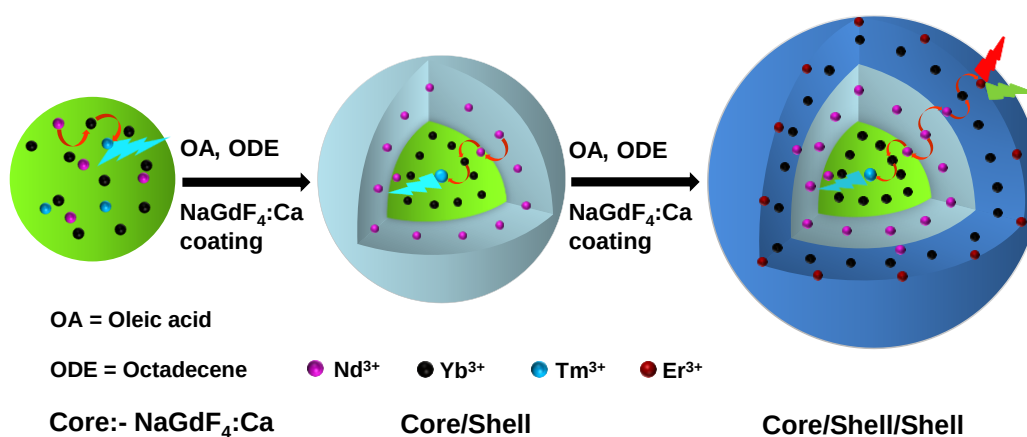
UC emission spectra of the core, core/shell and core/shell/shell UCNPs were acquired using a Horiba Jobin Yvon spectrofluorometer (model fluorolog-3 FL3-122) equipped with a photomultiplier tube (model R 928 P, Spex) sensitive between 250 and 850 nm. An 808 nm laser diode (from DMC, Brazil) coupled with an optical fiber (200 μ m diameter) was utilized as the excitation source. All spectra were acquired in identical fashion under the same experimental conditions. The laser power used in all measurements was 7 W cm⁻², determined using a Newport power meter, model 2935-C.

3.3 Results and discussion

3.3.1 Structural characterization of materials

Nd³⁺-sensitized Gd³⁺-based CSS UCNPs were successfully synthesized following a modified seed-mediated layer-by-layer growth method according to a literature report⁵⁷ (Scheme 3.1). Phase analysis of the core, CS (30 mol% Nd³⁺) and CSS (5 mol% Er³⁺) UCNPs was carried out using powder X-ray diffraction (XRD) measurements (Fig. 3.1a). All diffraction peaks perfectly match with the standard diffraction pattern of hexagonal NaGdF₄ crystals (JCPDS no: 27-0699). The shape and size of the nanoparticles were examined by TEM. TEM images indicate the formation of uniform and monodisperse nanoparticles with an average diameter of 7 nm, 12 nm and 19 nm for core [NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)], CS (30 mol% Nd³⁺)

and CSS (5 mol% Er^{3+}) UCNPs, respectively (Fig. 3.1b, c and d). The shell thickness of the CS and CSS UCNPs is thus estimated to be around 2.5 and 3.5 nm, respectively. Monodispersity in the size of these core, CS and CSS UCNPs is evident from the size distribution histograms shown in Fig. 3.S1.† Along with the size increase (core $\rightarrow$ CS $\rightarrow$ CSS), there is hardly any change in the morphology observed, indicating the homogeneous nature of shell growth over core and CS UCNPs. The high resolution TEM results further supported the formation of high quality hexagonal phase core, CS and CSS UCNPs (Fig. 3.S2†). The qualitative chemical composition of these UCNPs was studied by energy-dispersive X-ray spectroscopy (EDS) (Fig. 3.S3†). The EDS spectra of the samples show the presence of Gd, Nd, Ca, Yb, and Tm, Gd, Nd, Ca, Yb, and Tm and Gd, Nd, Ca, Yb, Tm, and Er for core, CS and CSS UCNPs, respectively, implying the layer-by-layer growth of shells on core nanoparticles. The capping of core, CS and CSS UCNPs with OA onto the surface of the same is confirmed by the appearance of strong carbonyl stretching vibration near 1500 cm^{-1} (Fig. 3.S4†). This frequency is much lower than that observed for the free OA molecules (1700 cm^{-1}), indicating strong binding of the ligands (OA) onto the surface of the nanoparticles.



Scheme 3.1 Schematic illustration of the synthesis of CSS UCNPs following a seed-mediated layer-by-layer growth method.

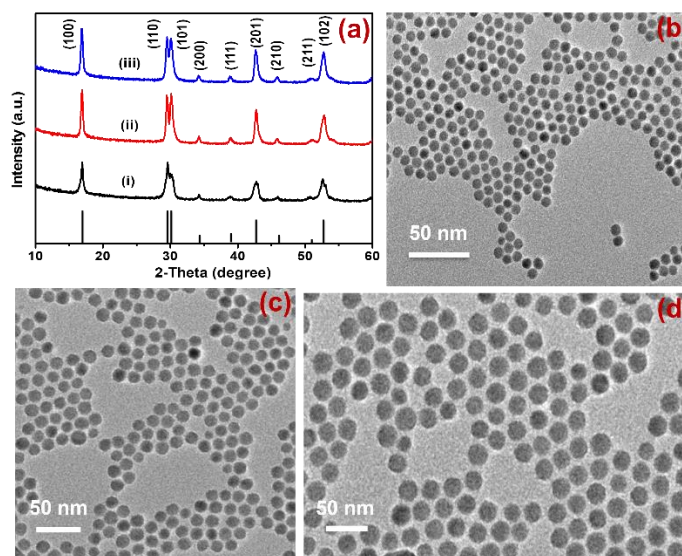


Figure 3.1 (a) XRD patterns of the NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7) core (i), CS (30 mol% Nd³⁺) (ii) and CSS (5 mol% Er³⁺) (iii) UCNPs. (b, c, and d) present the TEM images of these core, CS and CSS UCNPs, respectively.

3.3.2 Study of optical properties

The presence of Yb³⁺ ions (along with 1 mol% Nd³⁺ ions) in core, (Yb³⁺ + Nd³⁺) ions in CS (30 mol% Nd³⁺) and (Yb³⁺ + Nd³⁺) ions in CSS (5 mol% Er³⁺) UCNPs is confirmed by the presence of their characteristic peaks in the electronic absorption spectra of the samples (Fig. 3.S5†). In comparison to core UCNPs, the absorption intensity of the characteristic peaks of Nd³⁺ ions increases with increase in the Nd³⁺ concentration in the CS and CSS UCNPs, suggesting efficient incorporation of Nd³⁺ ions in the shell of CS and in the middle layer of CSS UCNPs. To justify the importance of a Nd³⁺-enriched shell to efficiently harvest light at 808 nm for simultaneous sensitization of both Tm³⁺ and Er³⁺ activators to produce bright multicolor UCL, we first prepared the core-NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7), CS (30 mol% Nd³⁺) and CSS (5 mol% Er³⁺) UCNPs. Fig. 3.2 shows the UC emission spectra for these core and CS UCNPs obtained using 808 nm laser excitation. The UCL peaks centered around 451 and 477 nm are assigned to the ¹D₂ → ³F₄ and ¹G₄ → ³H₆ transitions of Tm³⁺ ions, respectively. The calculated integrated UCL intensity of the blue (442–505 nm) emission of CS UCNPs is 77 times higher than that of core UCNPs. The reason behind this observation might be explained on the basis of two factors. First, surface related harsh quenching of the core NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7) is diminished by coating the NaGdF₄:Nd³⁺(30)/Ca²⁺(7) shell over the former. Secondly, the high concentration of Nd³⁺ ions (30 mol%) in the shell of the core/shell UCNPs might harvest the light at 808

nm more efficiently and subsequently transfer it to the core region to sensitize Yb^{3+} ions and simultaneously the Tm^{3+} ions (activator) to produce blue emission.

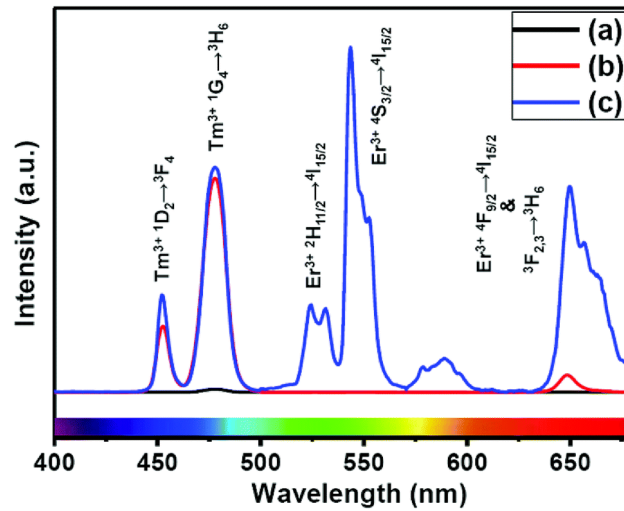


Figure 3.2 UCL spectra of the (a) core $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$, (b) CS (30 mol% Nd^{3+}) and (c) CSS (5 mol% Er^{3+}) UCNPs.

To understand the effect of shell thickness on the UCL intensity from CS (30 mol% Nd^{3+}), the core particles were coated with a shell of variable thickness (*i.e.*, 1.3, 1.8, 2.5, 3.9 and 4.8 nm) using epitaxial growth (Fig. 3.3C and D). As shown in Fig. 3.3A, the luminescence intensity first increases, reaching a maximum for a shell thickness of 2.5 nm, and then decreases. From Fig. 3.3B, it could be noted that the calculated integrated intensity of the blue (462–505 nm) emission of CS UCNPs with 2.5 nm shell thickness is 7.6 and 3.5 times higher than that of CS nanoparticles with 1.3 and 4.8 nm shell thickness, respectively. This result clearly suggests that shell thickness plays a pivotal role in the UCL intensity of CS UCNPs. Thinner shells (*i.e.*, shell thickness < 2.5 nm) allow the activator (Tm^{3+} , 0.75 mol% in the core) and the sensitizer (Nd^{3+} , 30 mol% in the shell) to come closer in proximity.

Hence, a good overlap between emission of Tm^{3+} ions and the absorption of Nd^{3+} ions could be expected which assures an efficient back ET from Tm^{3+} ions to Nd^{3+} ions, leading to a decrease in blue UCL from the CS UCNPs.

On the other hand, with an increase in the shell thickness (>2.5 nm), though the shell with 30 mol% Nd^{3+} efficiently harvests excitation light, it does not allow it to migrate effectively to Yb^{3+} ions (in core) across the core/shell interfaces to produce efficient blue emission from Tm^{3+} (activator) ions in the core. In fact, such CS UCNPs with a thicker shell (>2.5 nm) enable excitation energy to travel a long $\text{Nd}^{3+}\text{--Yb}^{3+}$

distance, which again leads to the decrease in the UCL intensity from the nanoparticles.

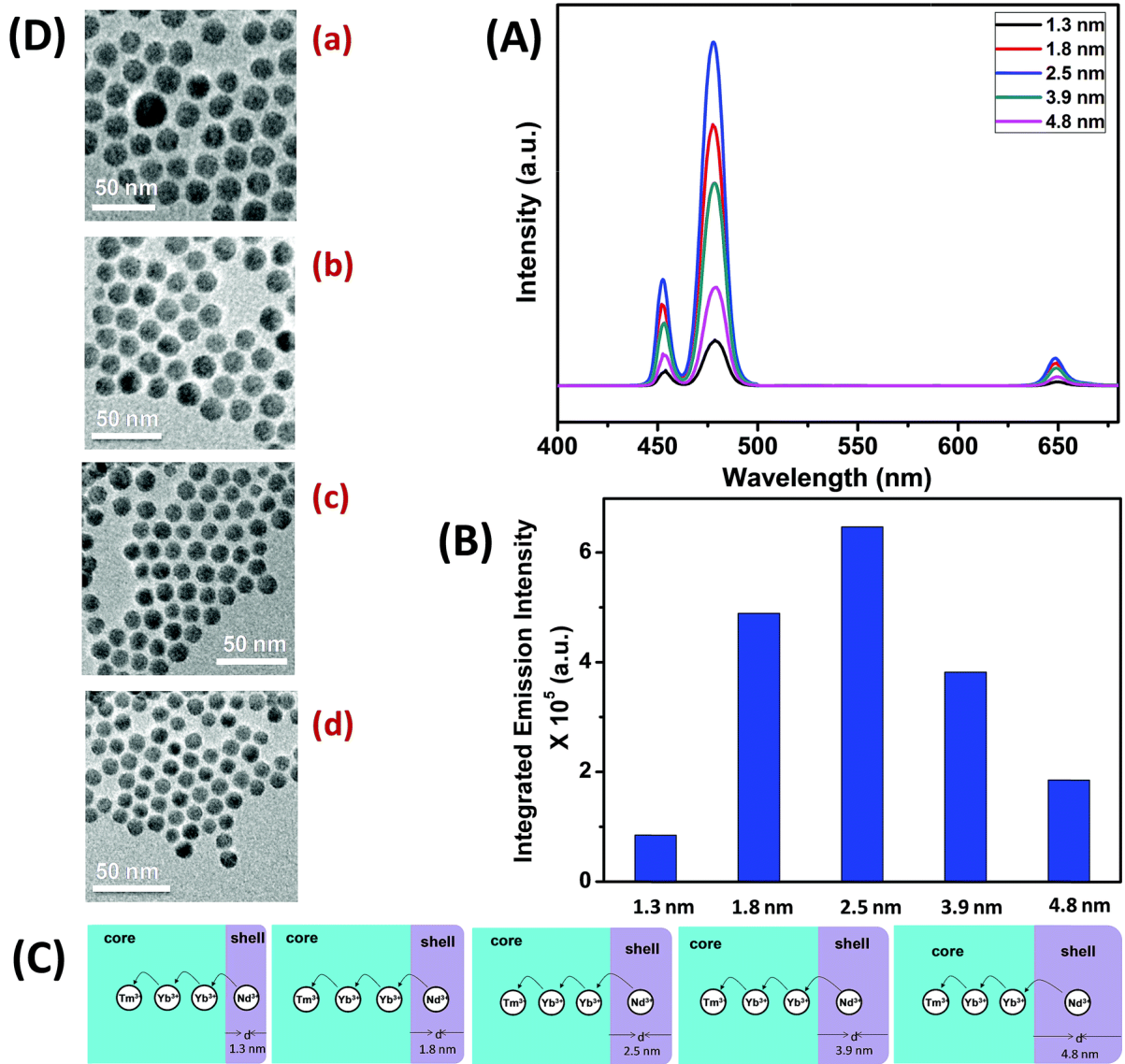


Figure 3.3 (A) UCL spectra of CS (30 mol% Nd³⁺) UCNP with different thickness of the NaGdF₄:Ca²⁺(7)/Nd³⁺(30) shell ($d = 1.3$ – 4.8 nm). (B) Integrated intensity of the blue (462–505 nm) emission of CS (30 mol% Nd³⁺) UCNP with different shell thickness ($d = 1.3$ – 4.8 nm). (C) Mechanistic investigation of interfacial ET from the Nd³⁺-containing shell to the Tm³⁺ containing core in different shell thickness controlled ($d = 1.3$ – 4.8 nm) CS (30 mol% Nd³⁺) UCNP. (D) TEM images of CS (30 mol% Nd³⁺) UCNP with different shell thickness [(a) 1.3 nm, (b) 1.8 nm, (c) 3.9 nm and (d) 4.8 nm].

Upon growth of the second shell (*i.e.*, NaGdF₄:Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)/Er³⁺(5) onto the surface of CS (30 mol% Nd³⁺) UCNP, the UCL from both activators (Er³⁺ and Tm³⁺) was observed together (Fig. 3.2, spectrum c). Along with the ¹D₂ → ³F₄ and ¹G₄ → ³H₆ transitions of Tm³⁺ ions, the green emission peak centered at 544 nm (⁴S_{3/2} → ⁴I_{15/2}) and the red emission peak centered at 650 nm (⁴F_{9/2} → ⁴I_{15/2}) from Er³⁺ ions are

also observed. This result substantiates that the Nd^{3+} enriched shell can harvest excitation light more efficiently and allows migration of energy across the core/shell interface to both Tm^{3+} ions in the core and Er^{3+} in the outermost shell to produce multicolor UCL from CSS UCNPs.

Similar to CS (30 mol% Nd^{3+}), to examine the effect of shell thickness on the UCL intensity from CSS (5 mol% Er^{3+}), CS (30 mol% Nd^{3+}) was used as a seed for the epitaxial growth of outermost shells with different thickness (1.2, 2.5, 3.5, 5 and 5.7 nm) (Fig. 3.4C and D). From Fig. 3.4A, a shell thickness of 3.5 nm results in the highest UCL. From Fig. 3.4B, it can be clearly observed that the calculated integrated intensity of the green (536–570 nm) emission of these CSS UCNPs with 3.5 nm shell thickness is 2.3 and 4.5 times higher than that of CSS nanoparticles with 1.2 and 5.7 nm outermost shell thicknesses, respectively. A similar trend was observed for red (630–680 nm) emission too.

Thinner outermost shells (*i.e.*, shell thickness 1.2 and 2.5 nm) allow the activator (Er^{3+} , 5 mol% in the outermost shell) and the sensitizer (Nd^{3+} , 30 mol% in the middle shell layer) to come closer in proximity. Therefore, in this case too, a good overlap between emission of Er^{3+} ions and the absorption of Nd^{3+} ions can be expected which manifests itself in the form of an efficient back ET from Er^{3+} ions to Nd^{3+} ions, leading to the decrease in UCL (green + red) from the CSS UCNPs. On the other hand, with an increase in the outermost shell thickness (>3.5 nm), the shell with 30 mol% Nd^{3+} , despite efficiently harvesting excitation light, does not allow it to migrate efficiently to Yb^{3+} ions (40 mol%, outermost shell) concurrently to produce green and red emissions from Er^{3+} (activator) ions in the outermost shell.

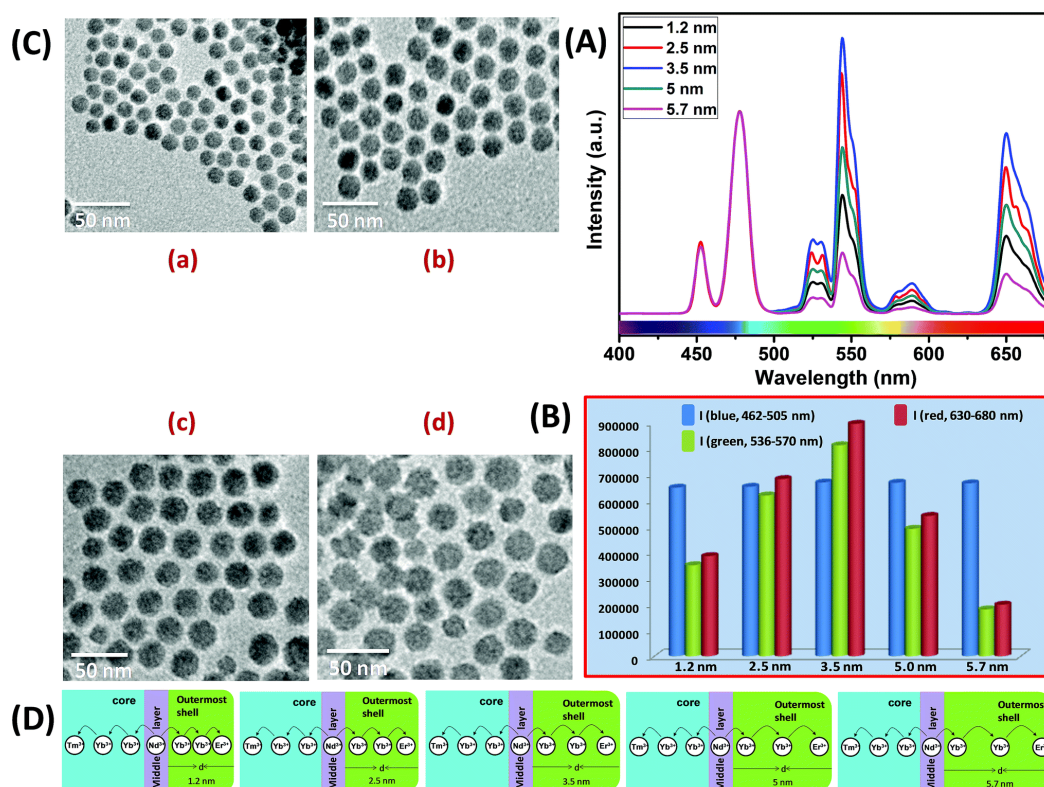


Figure 3.4 (A) UCL spectra of CSS UCNPs (5 mol% Er³⁺) with different thickness of the outermost shell over CS (30 mol% Nd³⁺) UCNPs ($d = 1.2$ – 5.7 nm). (B) Integrated intensity of blue (Tm³⁺, 462–505 nm), green (Er³⁺, 536–570 nm) and red (Er³⁺, 630–680 nm) emissions of CSS UCNPs with different outermost shell thickness ($d = 1.2$ – 5.7 nm). Note that, the UCL spectra and integrated emissions in (A) and (B), respectively, are normalized to the blue (462–505 nm) emission. (C) TEM images of CSS (5 mol% Er³⁺) UCNPs with different outermost shell thickness [(a) 1.2 nm, (b) 2.5 nm, (c) 5.0 nm and (d) 5.7 nm]. (D) Mechanistic investigation of interfacial ET from the Nd³⁺-containing middle shell layer to the Tm³⁺ containing core (with defined shell thickness $d = 2.5$ nm) and Er³⁺ containing outermost shell (with different shell thickness $d = 1.2$ – 5.7 nm) in CSS (5 mol% Er³⁺) UCNPs

Moreover, like the CS UCNPs, the CSS UCNPs with a thicker shell (>3.5 nm) make the excitation energy travel a long Nd³⁺–Yb³⁺ distance, which again leads to a decrease in the green and red UCL intensity from the nanoparticles. The UCL spectra and integrated emissions in Fig. 3.4A and B, respectively, are normalized to the blue (462–505 nm) emission. Actually, to prepare CSS nanoparticles *via* the epitaxial growth mechanism, we used CS nanoparticles with similar size in each reaction. We only varied the amount of outermost shell precursor to deposit an outermost shell (with different thickness) over CS nanoparticles. All other synthesis parameters (time, temperature, *etc.*) were kept constant. Hence, there was no remarkable change in the blue emission intensity as the energy transfer efficiency of Nd $\rightarrow$ Yb $\rightarrow$ Tm remained unaltered in each case. Though we acquired all the spectra under identical experimental conditions, still we observed a slight change in the blue emission. To

further clarify the effect of outermost shell thickness on the green and red emission of Er^{3+} ions (doped in outermost shell), we normalized the whole spectra and intensity with respect to the blue emission. The original spectra and intensity (without normalization) are shown in Fig. S6 and Table 3.S1,† respectively.

The CSS (5 mol% Er^{3+}) nanostructure thus plays an important role in separating two activators (Tm^{3+} and Er^{3+}) to mitigate deleterious cross-relaxation processes between them. Fig. 3.5a depicts a schematic route of nonradiative ET processes of $\text{Tm}^{3+} \leftarrow \text{Yb}^{3+} \leftarrow \text{Nd}^{3+} \rightarrow \text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ in the CSS UCNPs, upon 808 nm excitation. The schematic illustration of ET pathways to produce bright UCL from both the core and the outermost shell in the designed CSS UCNPs (upon 808 nm excitation) is shown in Fig. 3.5b. Moreover, to better understand, we recorded the UCL spectra of three different $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@\text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$, $\text{NaGdF}_4:\text{Er}^{3+}(2)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@\text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$ and $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Er}^{3+}(2)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@\text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$ core/shell UCNPs to verify the adverse cross-relaxation processes between the activator ions (Tm^{3+} and Er^{3+}). From Fig. 3.6A, it is clearly observed that the UCL intensity is significantly reduced when Tm^{3+} and Er^{3+} ions are doped together in the core region (spectrum c), indicating the unwanted cross-relaxation process between them.

As a reasonable explanation of our observation, a simplified energy level diagram depicting the cross-relaxation quenching mechanisms between Tm^{3+} and Er^{3+} (under 808 nm excitation) in Nd^{3+} -sensitized Gd^{3+} -based core/shell UCNPs is shown in Fig. 3-6B. In order to achieve efficient multicolor UCL from CSS (5 mol% Er^{3+}) UCNPs, it is essential to first optimize the concentration of Tm^{3+} ions in the core region of CS (30 mol% Nd^{3+}) nanoparticles. To achieve the utmost blue emission (808 nm excitation), the optimal concentration of Tm^{3+} ions in CS nanoparticles (against 40 mol% Yb^{3+} ions) was found to be 0.75 mol% (Fig. 3.S7†). The reason behind the use of such high mol% of Yb^{3+} ions has also been explained in this article (*vide infra*). We also investigated the effect of Nd^{3+} concentration in the middle layer of CS UCNPs and the optimum concentration of Nd^{3+} ion was determined to be 30% (Fig. 3.S8†). The gradual increase of Nd^{3+} concentration in the middle layer is consistent with the overall increase in absorption of excitation energy, leading to the utmost photon harvesting efficiency and, concurrently, the strongest UCL intensity from the UCNPs. However, at a Nd^{3+} concentration higher than 30 mol%, the mutual interaction between Nd^{3+} ions increases in the shell. This enhanced interaction consumes the excitation energy,

leading to less efficient energy migration across the core/shell interface to the Tm^{3+} -doped core. We believe that a similar phenomenon might occur in the Er^{3+} -doped outermost shell in CSS UCNPs. Thus, multicolor UCL intensity from the UCNPs is greatly reduced. Moreover, a good overlap between the emission of Tm^{3+} and Er^{3+} ions with the absorption of Nd^{3+} ions ensures an efficient back ET from Tm^{3+} or Er^{3+} ions to Nd^{3+} ions which again leads to a decrease in UCL from the nanoparticles.

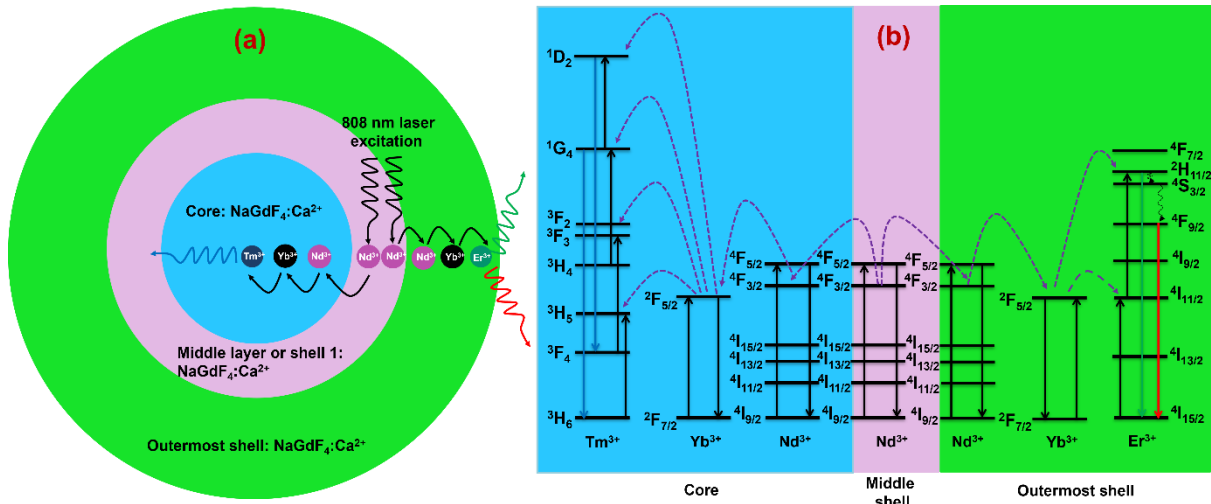


Figure 3.5 (a) Schematic illustration of the non-radiative ET mechanism of $\text{Tm}^{3+} \leftarrow \text{Yb}^{3+} \leftarrow \text{Nd}^{3+} \rightarrow \text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ in CSS (5 mol% Er^{3+}) UCNPs (808 nm laser excitation). (b) Schematic illustration of ET pathways to produce bright UCL from both the core (blue, Tm^{3+}) and the outermost shell (red and green, Er^{3+}) in the same CSS UCNPs upon 808 nm excitation.

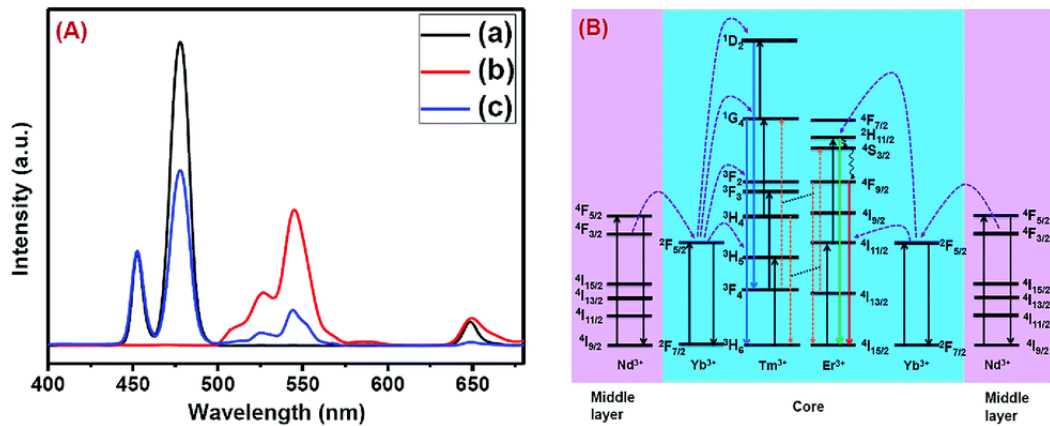


Figure 3.6 (A) Comparison of UCL spectra of (a) $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$, (b) $\text{NaGdF}_4:\text{Er}^{3+}(2)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$ and (c) $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Er}^{3+}(2)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$ core/shell UCNPs, upon 808 nm laser excitation, to verify the cross-relaxation between Tm^{3+} and Er^{3+} ions. (B) Energy level diagram indicating the cross-relaxation mechanism between Tm^{3+} and Er^{3+} ions in $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Er}^{3+}(2)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Ca}^{2+}(7)/\text{Nd}^{3+}(30)$ core/shell UCNPs, upon 808 nm laser excitation.

Upon variation in the concentration of Nd^{3+} ions in the shell, the crystalline phase and size of the CS UCNPs remain intact (Fig. 3.S9†). It is worth mentioning that the coating of at least one inert shell over CS UCNPs is necessary to preserve excitation energy and simultaneously achieve strong luminescence from the nanoparticles. In this work, we did not follow the growth of any inert shell over CS (30 mol% Nd^{3+}) UCNPs as our goal was to allow the excitation energy to migrate along the core/shell interface to both the core and the outermost shell to produce efficient multicolor UCL. Though Nd^{3+} – Nd^{3+} energy migration is not reported in the literature, using lower doping of Nd^{3+} ions (1 mol%) in the core and outermost shell is due to two reasons: (i) to systematically follow the UCL spectra of UCNPs upon growth of shells in a layer-by-layer fashion, under single 808 nm excitation and (ii) to help the energy transfer (Nd^{3+} – Yb^{3+}) across the core/shell interfaces through a resonant ET process between Nd^{3+} ions.

It is interesting to note that, in the core and outermost shell, a relatively high concentration (40 mol%) of Yb^{3+} ions was used in our designed CSS (5 mol% Er^{3+}) UCNPs. To examine the impact of Yb^{3+} concentration in the outermost shell on the complete UCL spectrum of these CSS UCNPs, we varied the concentration of Yb^{3+} ions in the outermost shell, while the Yb^{3+} concentration (40 mol%) in the core was kept fixed. As shown in Fig. 3.7A, maximum green and red emission intensities are observed with an increase in Yb^{3+} ions concentration (in the outermost shell) up to 40 mol%, whereas the intensity of blue emissions remains almost unchanged. From Fig. 3.7B, it is clear that the calculated integrated intensity of the green (536–570 nm) emission of CSS UCNPs with 40 mol% Yb^{3+} concentration in the outermost shell is 4.4 and 1.2 times higher than that of CSS nanoparticles with 10 and 50 mol% Yb^{3+} concentration in the outermost shell, respectively. The change in the calculated integrated intensity of red (630–680 nm) emission was similar to that of green emission.

Furthermore, we examined the impact of Yb^{3+} ions in the core on the complete UCL spectrum of our designed CSS UCNPs. We varied the concentration of Yb^{3+} ions in the core while fixing its concentration at 40 mol% in the outermost shell. As shown in Fig. 3.7C, as the concentration of Yb^{3+} ions is increased, the UCL intensity of blue emission increased concomitantly, reaching a maximum at 40 mol% concentration of Yb^{3+} ions, while hardly any change in the green and red emission intensity was observed.

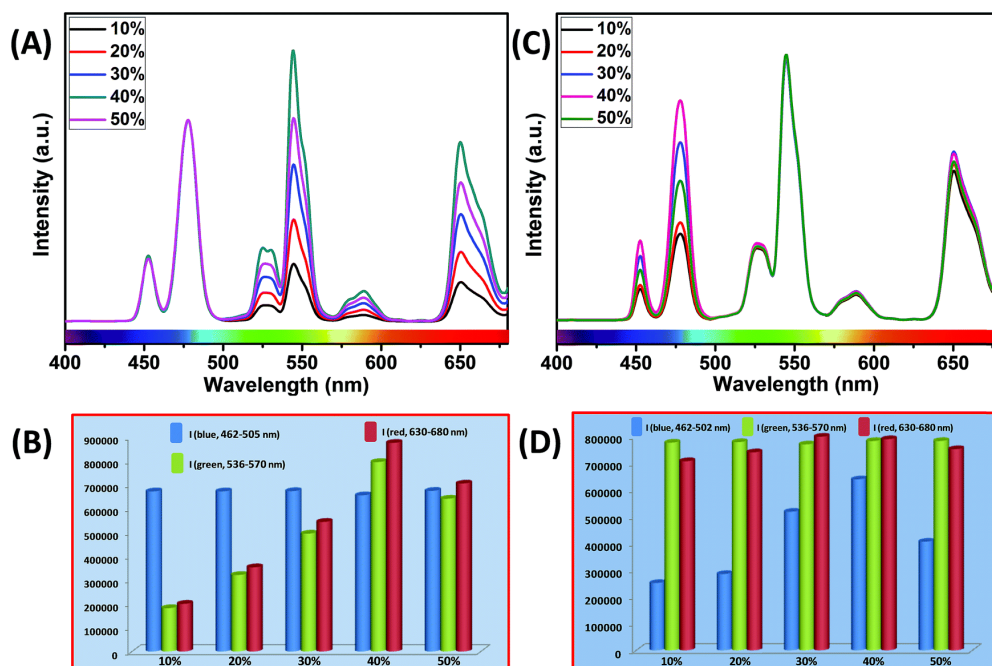


Figure 3.7 (A) UCL spectra of CSS (5 mol% Er^{3+}) UCNP with different Yb^{3+} concentrations in the outermost shell, where the Yb^{3+} concentration in the core remains unchanged at 40 mol%. Note that the UCL spectra are normalized to the blue (Tm^{3+} , 462–505 nm) emission. (B) Integrated intensity of blue (Tm^{3+} , 462–505 nm), green (Er^{3+} , 536–570 nm) and red (Er^{3+} , 630–680 nm) emissions of CSS UCNP with different Yb^{3+} concentrations in the outermost shell. Note that integrated emissions are normalized to the blue (Tm^{3+} , 462–505 nm) emission. (C) UCL spectra of CSS (5 mol% Er^{3+}) UCNP with different Yb^{3+} concentrations in the core, where the Yb^{3+} concentration in the outermost shell remains intact at 40 mol%. Note that the UCL spectra are normalized to the green (Er^{3+} , 536–570 nm) emission. (D) Integrated intensity of blue (Tm^{3+} , 462–502 nm), green (Er^{3+} , 536–570 nm) and red (Er^{3+} , 630–680 nm) emissions of CSS UCNP with different Yb^{3+} concentrations in the core. Note that integrated emissions are normalized to the green (Er^{3+} , 536–570 nm) emission.

From Fig. 3.7D, it is quite clear that the calculated integrated intensity of the blue (462–502 nm) emission of CSS UCNP with 40 mol% Yb^{3+} concentration in the core is 2.5 and 1.6 times higher than that of CSS nanoparticles with 10 and 50 mol% Yb^{3+} concentrations in the core, respectively. In fact, the use of a high concentration of Yb^{3+} ions is expected to strongly affect the UCL intensity of the nanoparticles as Yb^{3+} -mediated sub-lattice enables excitation energy migration from the primary sensitizer to the activator. Upon increase in Yb^{3+} concentration, the total absorption cross-section of the same increases which again leads to the enhanced efficiency of ET from Nd^{3+} (middle layer domain) to Tm^{3+} (core region) and Er^{3+} (outermost shell). Moreover, a higher concentration of Yb^{3+} ions resulted in shorter Yb^{3+} – Yb^{3+} interionic distance within the sublattice ensuring an efficient ET from Nd^{3+} to both the Tm^{3+} -doped core and Er^{3+} -doped outermost shell in CSS UCNP. To our knowledge, literature reports suggest that the ET rate is proportional to r^{-6} (where, r is the average donor–acceptor distance) within the dipole interaction.^{58,59} Based on this fundamental, we assume that

a suitable shell thickness (2.5 nm for CS and 3.5 nm for CSS, in our work) and high concentration of Nd^{3+} ions in the middle layer along with a high concentration of Yb^{3+} ions in both the core and outermost shell not only allow our designed UCNPs to migrate excitation energy directionally across the core/shell interface but also prevent the excitation energy from travelling long Nd^{3+} – Nd^{3+} , Yb^{3+} – Yb^{3+} and Nd^{3+} – Yb^{3+} distances. However, when the Yb^{3+} – Yb^{3+} interionic distance exceeds the optimal value, back ET might occur from Tm^{3+} or Er^{3+} to Yb^{3+} ions, leading to the reduction of the UCL intensity from the nanoparticles. In this point of view, a high concentration of Yb^{3+} ions played a pivotal role in limiting the possibility of producing unwanted cross-relaxation pathways, while also affecting the process of bridging efficient ET from Nd^{3+} (middle layer) to Tm^{3+} (core region) and Er^{3+} (outermost shell) to produce efficient multicolor UCL from CSS UCNPs. Now, to check whether the use of a higher concentration of Yb^{3+} ions leads to the formation of bigger sized nanoparticles and simultaneously affect the UCL intensity of the same, we performed TEM measurements of core nanoparticles where the Yb^{3+} concentration was varied from 20 to 50 mol% while the concentration of other ions was kept unchanged. Almost no change in the size of the core nanoparticles was observed (Fig. 3.S10†). Hence, from Fig. 3.7, we believe that the change in the UCL intensity of CSS (5 mol% Er^{3+}) UCNPs is not related to the variation in size of the core but with the variation of Yb^{3+} ions in the core as well as in the outermost shell.

In addition, in our work, the Ca^{2+} ion has been chosen as dopant in each domain as the UCL intensity (438–503, blue emission) of the CS (30 mol% Nd^{3+}) UCNPs with 7 mol% Ca^{2+} (in both core and shell) showed an around 1.4 times enhancement as compared to the same sample prepared without Ca^{2+} (Fig. 3.S11†).

Very small sized NaGdF_4 UCNPs possess a very high surface-to-volume ratio and, at the same time, a large portion of dopant ions occupy positions at the surface of the nanoparticles. Thus, the excitation energy is easily quenched either by surface defects or surface capping ligands. Therefore, it is essential to modify the host lattice and this is possible while Ca^{2+} ions are introduced into the NaGdF_4 core (and even into the shell). Due to the lower valence, when Ca^{2+} is introduced to replace Gd^{3+} , a charge imbalance occurs in NaGdF_4 . In addition, F^- vacancies play an important role in charge compensation inside the crystal lattice. This induces the formation of transient electric dipoles with positive poles pointing outward on the grain surfaces. These transient electric dipoles accelerate the diffusion of ions for the crystal growth, needing F^- ions from the solution to the grain and thus promoting the growth of NaGdF_4 . In this case,

the growth of NaGdF₄ nanoparticles is indeed a diffusion-controlled process, resulting in better size-uniformity and fewer surface defects which lead to the enhancement of the UCL intensity of the UCNP.

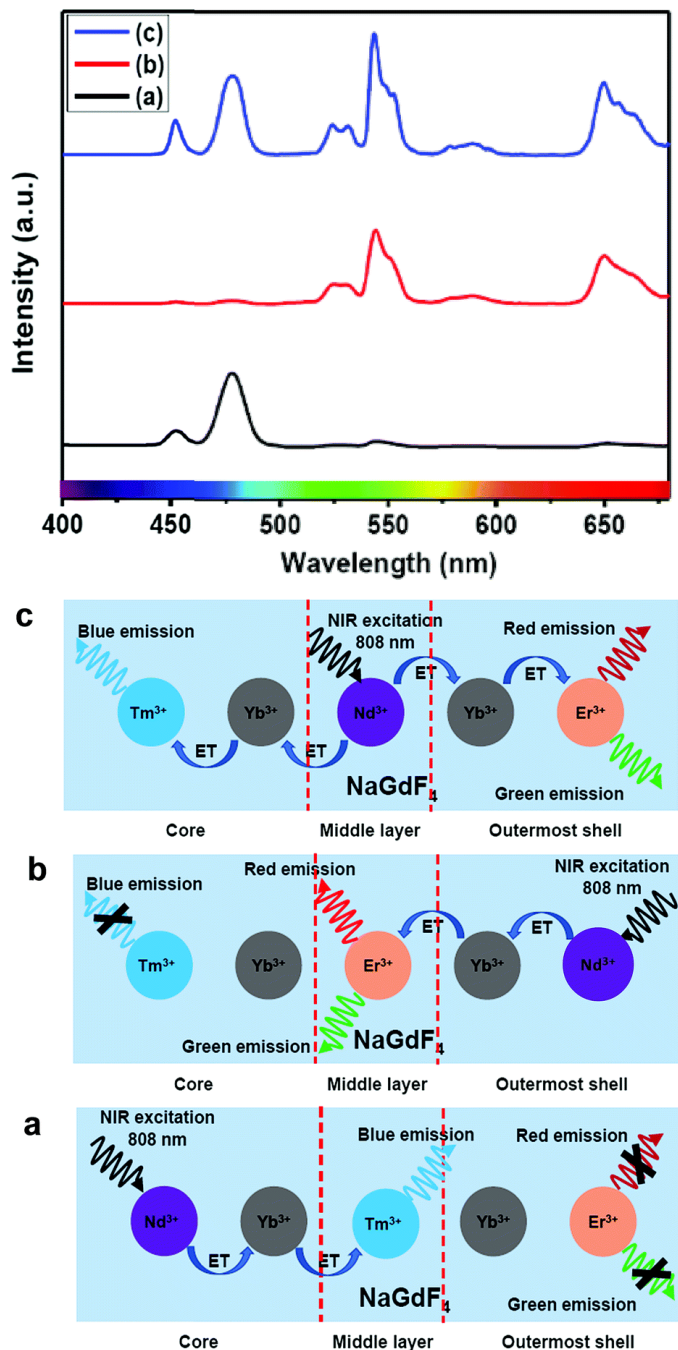


Figure 3.8 UCL spectra of (a) NaGdF₄:Nd³⁺(30)/Ca²⁺(7)@NaGdF₄:Nd³⁺(1)/Ca²⁺(7)/Tm³⁺(0.75)/Yb³⁺(40)@NaGdF₄:Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)/Er³⁺(5), (b) NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)@NaGdF₄:Nd³⁺(1)/Ca²⁺(7)/Yb³⁺(40)/Er³⁺(5)@NaGdF₄:Nd³⁺(30)/Ca²⁺(7) and (c) NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)@NaGdF₄:Nd³⁺(30)/Ca²⁺(7)@NaGdF₄:Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)/Er³⁺(5) core/shell/shell UCNP (808 nm laser excitation). Schematic illustration of the switching of the Nd³⁺-enriched domain to emit multicolor UCL from corresponding core/shell/shell UCNP

Moreover, the formation of F^- vacancies induced by the substitution of Gd^{3+} with Ca^{2+} in the host lattice lowers the local crystal field symmetry around Yb^{3+} , Nd^{3+} , Er^{3+} and Tm^{3+} ions, which in turn affects the intra 4f–4f transition possibility of Ln^{3+} ions and subsequently enhances the UCL intensity from the CSS UCNP.

Furthermore, to shed light on the position of the Nd^{3+} -enriched harvesting layer (*i.e.*, first shell or middle layer) in the CSS (5 mol% Er^{3+}) UCNP, we synthesized $NaGdF_4:Nd^{3+}(30)/Ca^{2+}(7)@NaGdF_4:Nd^{3+}(1)/Ca^{2+}(7)/Tm^{3+}(0.75)/Yb^{3+}(40)@NaGdF_4:Yb^{3+}(40)/Nd^{3+}(1)/Ca^{2+}(7)/Er^{3+}(5)$ CSS and $NaGdF_4:Tm^{3+}(0.75)/Yb^{3+}(40)/Nd^{3+}(1)/Ca^{2+}(7)@NaGdF_4:Nd^{3+}(1)/Ca^{2+}(7)/Yb^{3+}(40)/Er^{3+}(5)@NaGdF_4:Nd^{3+}(30)/Ca^{2+}(7)$ CSS UCNP, whereas the Nd^{3+} -enriched domain was placed in the core and outermost shell, respectively, and the energy transfer process ($Nd^{3+} \rightarrow Yb^{3+} \rightarrow Er^{3+}/Tm^{3+}$) was uni-directional. Fig. 3.8 clearly depicts that the UCL [blue or (red + green)] is only generated from Tm^{3+} or Er^{3+} ions from those CSS UCNP. On the other hand, the Nd^{3+} -enriched middle shell along with separation of Tm^{3+} (in core) and Er^{3+} ions (in outermost shell) enable the CSS UCNP to produce efficient multicolor UCL (Fig. 3.8c). These results suggest that the ET in a bi-directional manner dominates the uni-directional one to achieve efficient multicolor UCL without implication of any deleterious cross-relaxation mechanism between the activator ions.

Precise control of the concentration of Er^{3+} (activator) ions in the outermost shell of CSS UCNP makes them potential candidates to produce efficient multicolor UCL output. There is hardly any change in the size (Fig. 3.S12†) and size distribution (Fig. 3.S13†) observed for CSS UCNP with varying Er^{3+} concentration in the outermost shell. Moreover, it is evident from Fig. 3.9A that the appropriate tuning of the concentration of Er^{3+} ions in the outermost shell plays a vital role in the change in relative intensities of the green ($^4S_{3/2} \rightarrow ^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow ^4I_{15/2}$) emissions of Er^{3+} ions, resulting in the continuous production of UCL colors ranging from blue to white. Such spectral changes could also be observed by the naked eye (Fig. 3.9B, right side).

Furthermore, the calculated chromaticity coordinates (Fig. 3.9B) reveal a similar trend of the emission colors as perceived through spectroscopic study and naked eye visualization. It is worth mentioning that control in the use of each activator (*e.g.*, Tm^{3+} or Er^{3+}) in the CSS UCNP allows manipulating and producing different UCL spectra with different colors. From Fig. 3.S14,† it is quite clear that the core/shell/shell UCNP (analogues to CSS and without Er^{3+} in the outermost shell) show pure blue emission at 451 and 477 nm from Tm^{3+} ions positioned in the core. However, core/shell/shell

UCNPs (analogues to CSS and without Tm^{3+} in the core) exhibit both green (540 nm) and red (650 nm) emissions, which originate from Er^{3+} ions present in the outermost shell. On the other hand, our designed CSS (5 mol% Er^{3+}) shows a three primary color (blue, green and red) blended spectrum responsible for generating white UCL light.

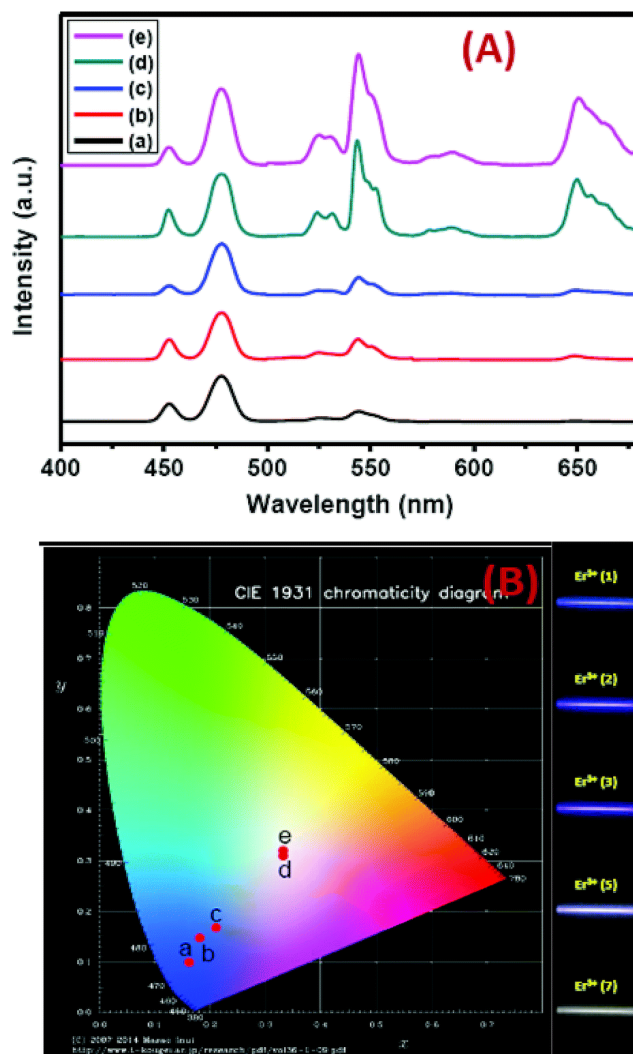


Figure 3.9 (A) UCL spectra (B) corresponding ‘Commission Internationale de l’Eclairage’ (CIE) and digital images of CSS UCNPs. a, b, c, d and e in the CIE diagram indicate the corresponding UCNPs, having Er^{3+} concentrations 1, 2, 3, 5 and 7 mol%, respectively, in the outermost shell. Digital images are taken using an 808 nm laser, 10 W cm^{-2} (without using any filter).

To understand whether the middle shell layer-to-core (Nd^{3+} to Tm^{3+}) ET or the middle shell layer-to-outermost shell (Nd^{3+} to Er^{3+}) ET has higher contribution to the overall UCL to produce multicolor emission, as a control experiment, Tm^{3+} ions in the core and Er^{3+} ions in the shell of the CSS (5 mol% Er^{3+}) were subjected to the corresponding direct excitations at 357 and 488 nm, respectively. As shown in Fig. 3.S15,† the integrated photoluminescence emission (PLE) intensity of Tm^{3+} ions ($\lambda_{\text{ex}} = 357 \text{ nm}$) was slightly higher (1.3 times) than that of Er^{3+} ions ($\lambda_{\text{ex}} = 488 \text{ nm}$). As the

absorption coefficients of Tm^{3+} and Er^{3+} ions are lower and similar ($\sim 2\text{--}10 \text{ M}^{-1} \text{ cm}^{-1}$),⁶⁰ we may conclude that Tm^{3+} excited states favour a radiative decay pathway slightly more compared to that of Er^{3+} ions. However, the ratio between the integrated area of green + red (510–570 nm + 630–680 nm, Er^{3+}) and blue (436–500 nm, Tm^{3+}) regions in the UCL spectrum of the same CSS UCNP was found to be 2.4 indicating higher contribution from Er^{3+} . This is only possible if the ET from Nd^{3+} to Er^{3+} is more compared to Nd^{3+} to Tm^{3+} in the UCNP.

Furthermore, to investigate the number of photons involved to produce white UCL, the power dependence of UCL was measured from CSS (5 mol% Er^{3+}) UCNP. Fig. 3.S16† shows that the number of photons involved in multicolor UCL is 3 (slope, 3.01), 2 (slope, 1.98) and 2 (slope, 1.76) for blue, green and red emissions, respectively. These results are in good agreement with the literature reports.

3.4 Conclusion

In summary, we have successfully illustrated multicolor UCL from Nd^{3+} -sensitized Gd^{3+} -based core/shell/shell UCNP under biologically relevant, single wavelength excitation (808 nm) which, unlike 980 nm excitation, does not cause biological heating problems that could damage cells and tissues. The separation of Tm^{3+} (in the core) and Er^{3+} (in the outermost shell layer) in the core/shell/shell UCNP effectively alleviates the deleterious cross-relaxation processes between them. The doping of a Nd^{3+} sensitizer (30 mol%) in the middle layer, on the other hand, enables efficient harvesting of excitation light and concurrent migration of the energy across the core/shell interfaces to both Tm^{3+} in the core and Er^{3+} in the outermost shell layer. Precise control of the shell thickness and judicious manipulation of Ln^{3+} ions (activators and sensitizers) along with their spatial distribution in their defined layer domain provide a broad range of multicolor UCL (from blue to white) through a bi-directional ET process. Such tuneable multicolor UCL makes these sub-20 nm sized Nd^{3+} -sensitized Gd^{3+} -based core/shell/shell UCNP potential candidates for bioimaging and MRI dual modal applications.

Conflicts of interest

There are no conflicts to declare.

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Footnotes

† Electronic supplementary information (ESI) available: Histograms, TEM, infrared spectra, EDS, absorption spectra, XRD, UCL spectra, PLE spectra, and calculation of the number of photons. See DOI: 10.1039/c9na00006b

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Electronic Supporting Information

PRECISELY TAILORED SHELL THICKNESS AND Ln^{3+} CONTENT TO PRODUCE MULTICOLOR EMISSION FROM Nd^{3+} -SENSITIZED Gd^{3+} -BASED CORE/SHELL/SHELL UCNPS THROUGH BI-DIRECTIONAL ENERGY TRANSFER

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Table 3.S1 Calculation of UCL intensity (integrated area) of the blue, green and red emissions against different thickness of the outermost shell of CSS (5 mol % Er^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)]$ UCNP.

Outermost shell thickness	Intensity (462-505 nm)	Intensity (536-570 nm)	Intensity (630-680 nm)
1.2 nm	649492.32	350358.44	385910.01
2.5 nm	646365.80	612980.09	676026.64
3.5 nm	668118.19	811079.78	894514.75
5 nm	648936.87	476545.11	524901.11
5.7 nm	658374.04	178068.93	9228.86

Histogram of core, core/shell and core/shell/shell UCNP

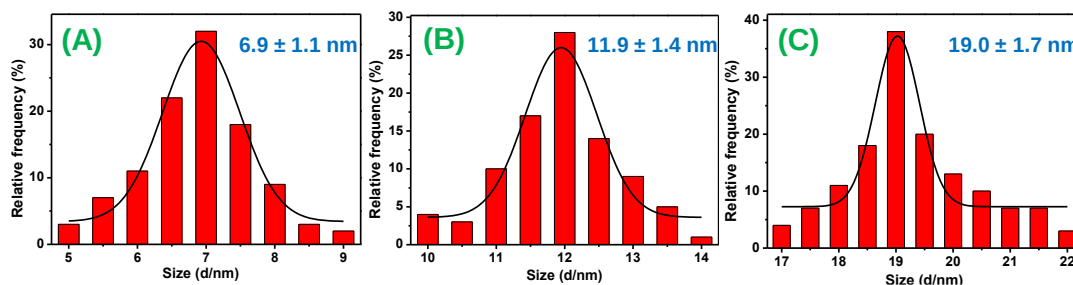


Figure 3.S1 Size distribution of (A) core $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ (B) CS (30 mol % Nd^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]$ and (C) CSS (5 mol % Er^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)]$ UCNP. Statistical analysis was performed on 100 particles in each of the two batches, recurring the respective size distributions of the corresponding nanoparticles. Average diameter (d/nm) of the corresponding core, core/shell and core/shell/shell UCNP is shown with significant error.

High resolution TEM images of core, core/shell and core/shell/shell UCNP

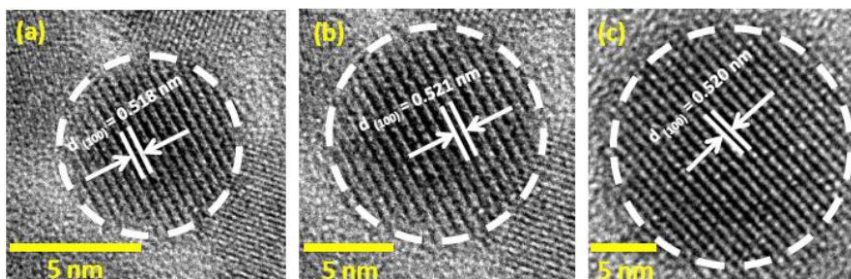


Figure 3.S2 High resolution TEM (HRTEM) images of (a) core $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ (b) CS (30 mol % Nd^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]$ and (c) CSS (5 mol % Er^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)]$ UCNP. The HRTEM images present the lattice fringes with an observed d-spacing of ~ 0.52 nm, which is in agreement with the lattice spacing in the (100) plane of hexagonal-phase NaGdF_4 , indicating a high crystallinity of the corresponding core, core/shell and core/shell/shell nanoparticles.

EDS spectra of core, core/shell and core/shell/shell UCNPs

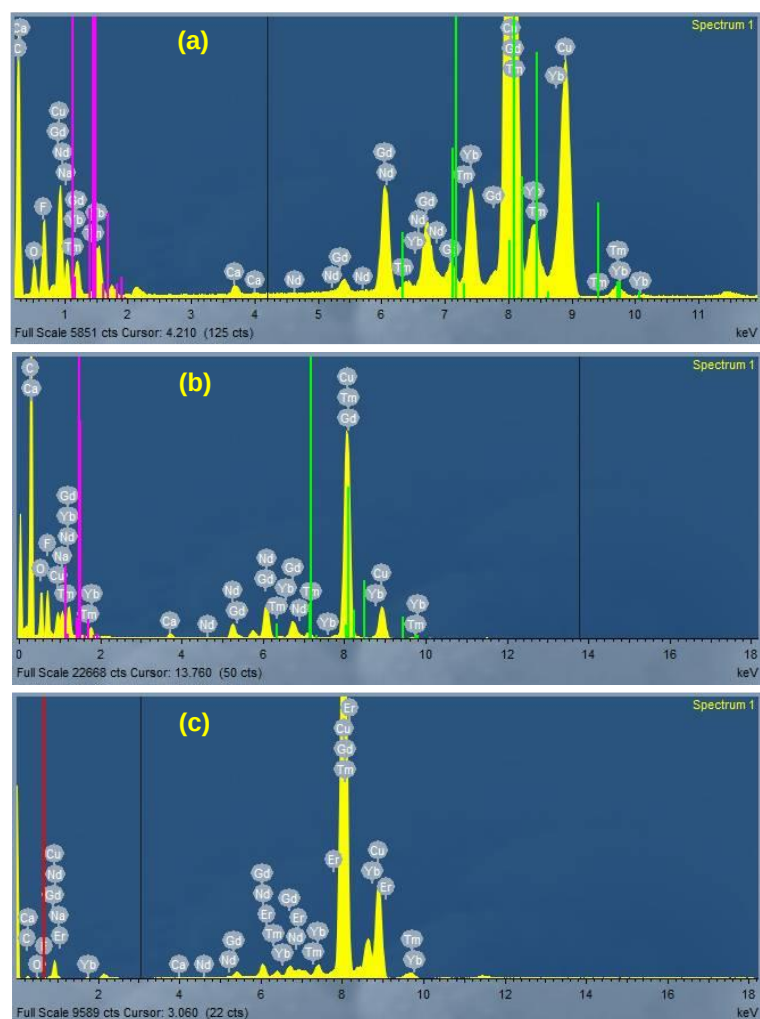


Figure 3.S3 EDS spectra of (a) core $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ (b) CS (30 mol % Nd^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]$ and (c) CSS (5 mol % Er^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)@\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)]$ UCNPs. The spectra show the presence of (Gd, Nd, Ca, Yb, Tm), (Gd, Nd, Ca, Yb, Tm) and (Gd, Nd, Ca, Yb, Tm, Er) for core, core/shell and core/shell/shell UCNPs, respectively, suggesting the growth of shells on core nanoparticles layer-by-layer. In each spectrum, Cu element appears due to the use of carbon coated copper grid during TEM measurements.

Comparison of IR spectra of free OA and OA capped UCNPs

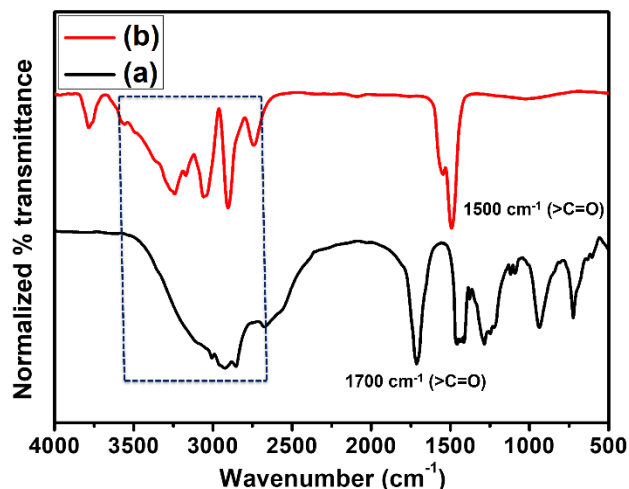


Figure 3.S4 FTIR spectra of (a) pure OA molecules and (b) OA capped CSS (5 mol % Er^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)]$ UCNPs. Selected area indicates the presence of stretching vibration of $-\text{CH}_2$ units in OA. Decrease in the broadness of $-\text{CH}_2$ stretching vibration also indicates the strong attachment of OA molecules onto the surface of the core/shell/shell UCNPs.

Absorption spectra of core, core/shell and core/shell/shell UCNPs

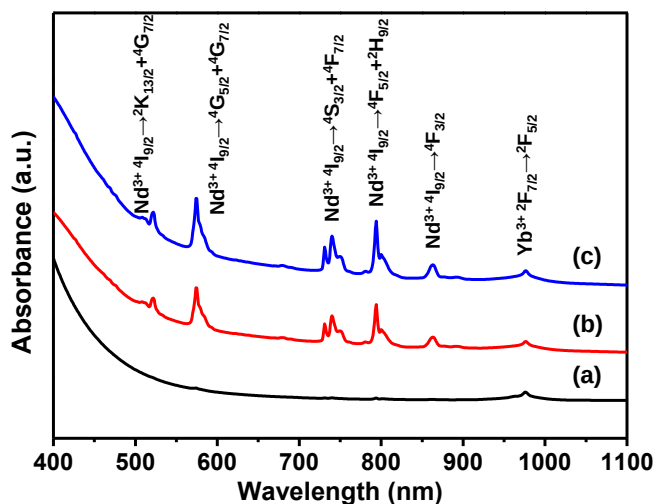


Figure 3.S5 The absorption spectra of the (a) core $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ (b) CS (30 mol % Nd^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]$ and (c) CSS (5 mol % Er^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)]$ UCNPs. Absorption peak around 980 nm was observed, assigning to the ground state absorption of the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition of Yb^{3+} ions. A strong absorption peak (for b and c) at ~ 800 nm was observed, corresponding to the ground state absorption of the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}/^2\text{H}_{9/2}$ transition of Nd^{3+} ions. Very small absorption peak (for a) at ~ 800 nm (i.e. $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}/^2\text{H}_{9/2}$ transition of Nd^{3+} ions) was observed, indicating the presence of small 1 mol% of Nd^{3+} ions in the core nanoparticles.

UCL spectra of core/shell/shell UCNPs (without normalization) with different thickness of outermost shell

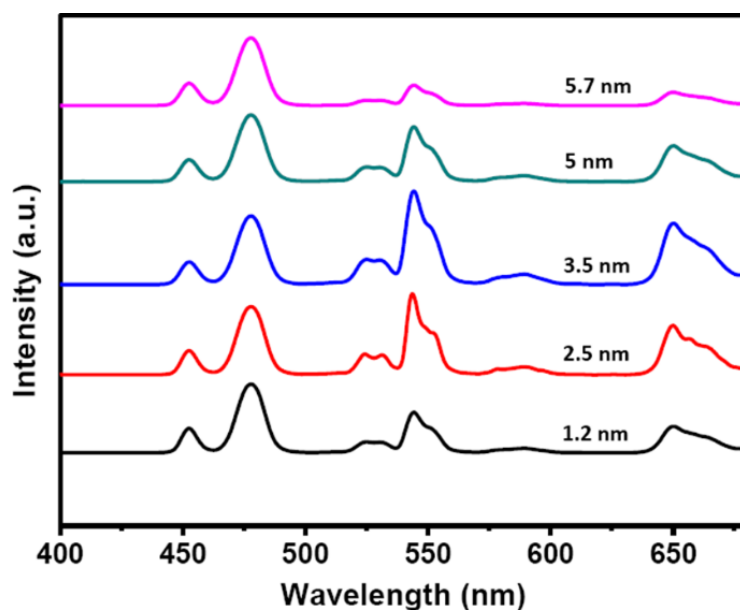


Figure 3.S6 UCL spectra (without normalization) of CSS UCNPs (5 mol % Er^{3+}) with different thickness of outermost shell over CS (30 mol % Nd^{3+}) UCNPs ($d = 1.2 - 5.7$ nm).

Optimization in the concentration of Tm^{3+} ions in core/shell UCNPs

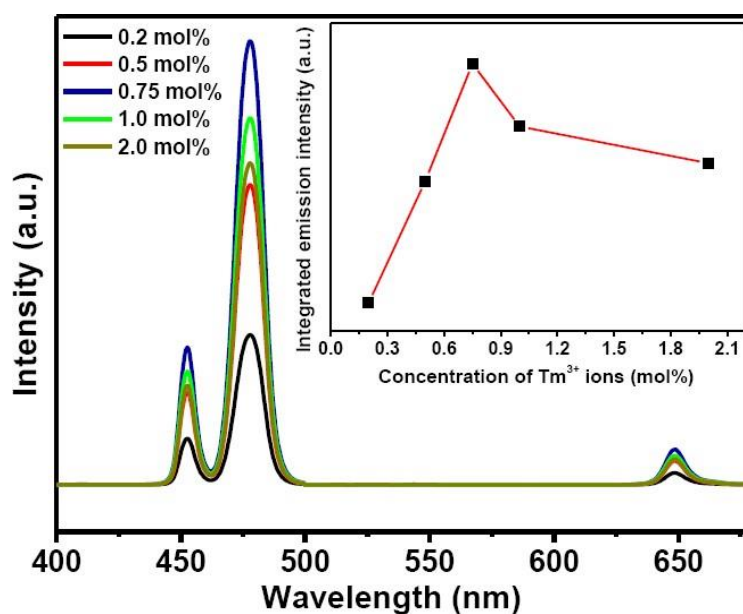


Figure 3.S7 Optimization in the concentration of Tm^{3+} ions (against 40 mol% Yb^{3+} ion) in the CS (30 mol % Nd^{3+}) $[\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)]@[\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)]$ UCNPs. The optimized concentration of Tm^{3+} ions leads to produce strongest UCL from the core nanoparticles. Beyond the optimized concentration of Tm^{3+} ions, the integrated emission intensity decreases because of the self-quenching of the activator (i.e. Tm^{3+}) ions.

Optimization of Nd^{3+} ion concentration in the shell of core/shell UCNPs

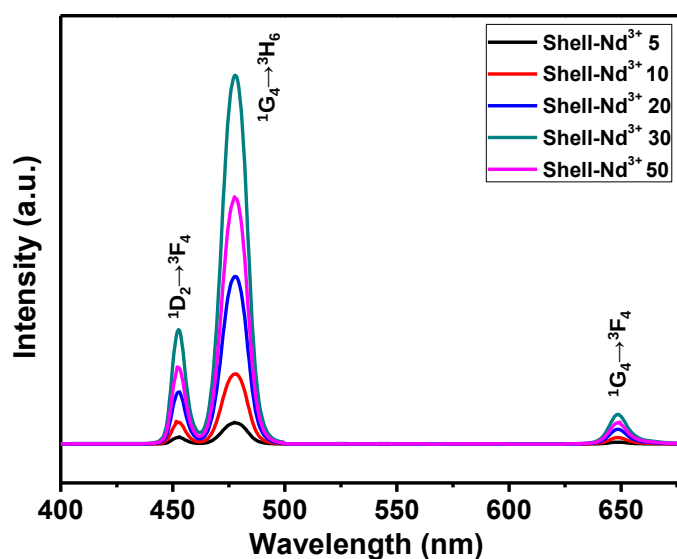


Figure 3.S8 The UCL spectra from CS (Nd^{3+} = 5, 10, 20, 30 and 50 mol %) UCNPs. The optimized Nd^{3+} content was determined to be 30 mol%. Upon 808 nm excitation, the integrated UCL intensity at ~477 nm of the $^1\text{G}_4 \rightarrow ^3\text{H}_6$ of Tm ions from CS (30 mol % Nd^{3+}) UCNPs enhanced by 17.5 times, compared with the sample doped with 5 mol % Nd^{3+} in the shell.

Crystalline phase and size investigation of core/shell UCNPs with different concentration of Nd^{3+} ions in the shell

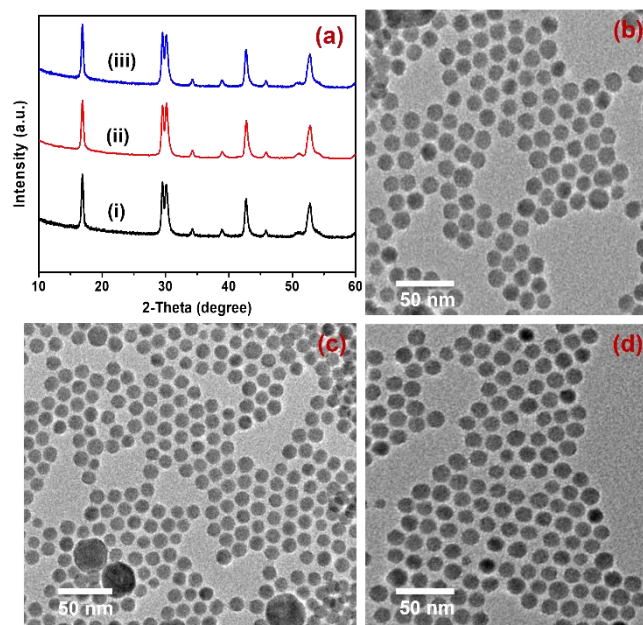


Figure 3.S9 (a) XRD of CS (Nd^{3+} = 10, 20 and 50 mol %) UCNPs [10 (i), 20 (ii) and 50 mol % (iii)]. The core/shell nanoparticles with different Nd^{3+} concentration in the shell remain intact along with hexagonal phase (JCPDS No: 27-0699). TEM images of CS (Nd^{3+} = 10, 20 and 50 mol%) UCNPs [10 (b), 20 (c) and 50 mol % (d)]. From these images, it is clearly noted that

the all as-prepared core/shell UCNPs have uniform spherical shape with an average diameter ~ 12 nm.

TEM images of core UCNPs with different concentration of Yb^{3+} ions

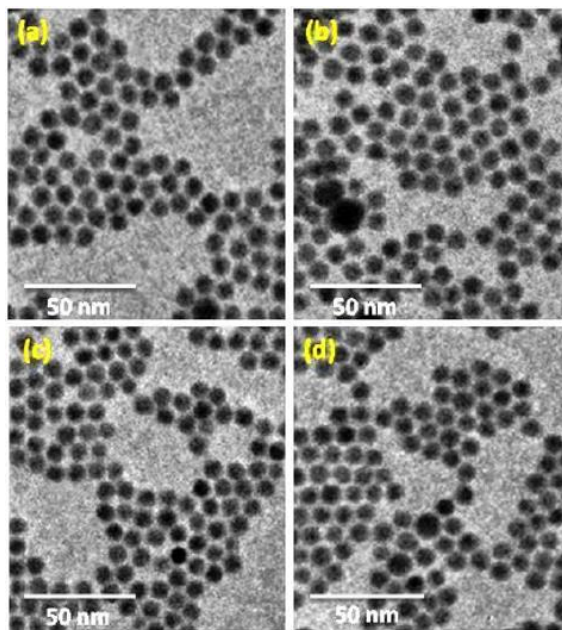


Figure 3.S10 TEM images of core $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ UCNPs with different (a – 10, b – 20, c – 40 and d – 50) mol % Yb^{3+} concentration. There is hardly any change in the size of the nanoparticles observed, indicating that the change in the UCL intensity of CS and CSS nanoparticles are not due to the size of the core but rather associated with other parameters like variation of Yb^{3+} concentration in core as well as in outermost shell, shell thickness, etc.

UC comparison of Ca^{2+} -doped and un-doped core/shell/shell UCNPs

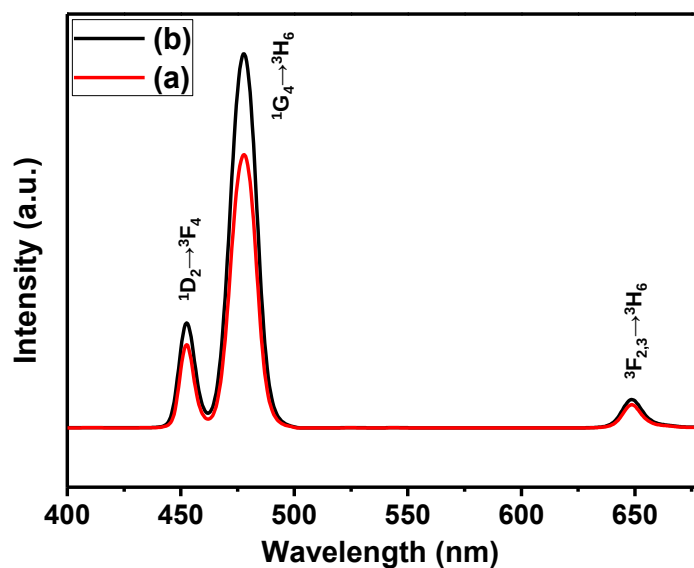


Figure 3.S11 The UCL spectra of (a) NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)@NaGdF₄:Nd³⁺(30) and (b) NaGdF₄:Tm³⁺(0.75)/Yb³⁺(40)/Nd³⁺(1)/Ca²⁺(7)@NaGdF₄:Nd³⁺(30)/Ca²⁺(7) core/shell UCNPs. Ca²⁺ -dopants modified the lattice defects and concurrently enhanced the energy transfer efficiency. All samples were dispersed in cyclohexane.

TEM images of core/shell/shell UCNPs with different Er³⁺ concentration in the outermost shell

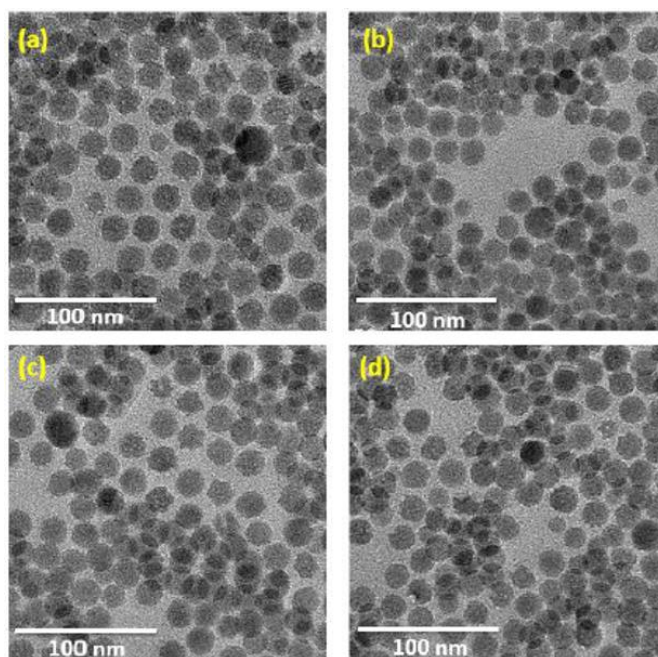


Figure 3.S12 TEM images of CSS (Er³⁺ = 1, 2, 3 and 7 mol %) UCNPs [(a) = 1 %, (b) = 2 %, (c) = 3 % and (d) = 7 %]. It can be seen that all the obtained core/shell/shell UCNPs have a uniform spherical shape with an average diameter ~19 nm.

Histogram of core/shell/shell UCNPs with different Er³⁺ concentration in the outermost shell

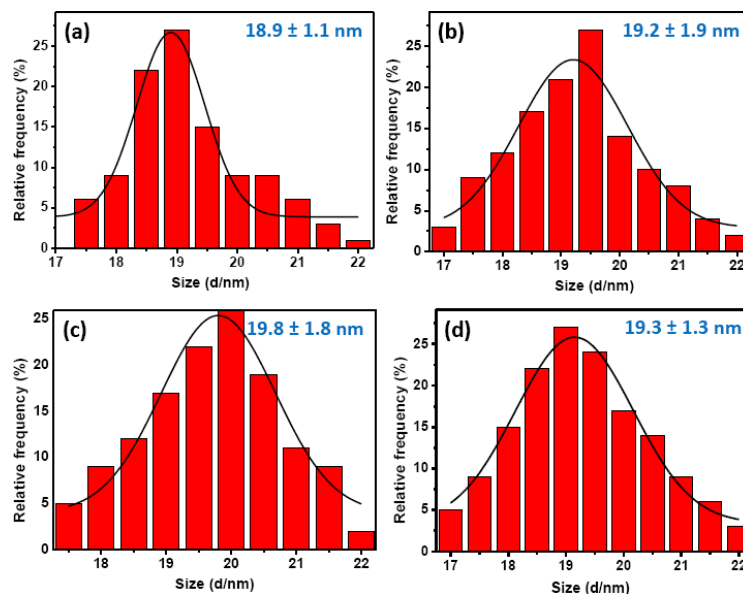


Figure 3.S13 Size distribution of CSS (Er^{3+} = 1, 2, 3 and 7 mol %) UCNPs [(a) = 1 %, (b) = 2%, (c) = 3 % and (d) = 7 %]. Statistical analysis was performed on 100 particles in each of the two batches, recurring the respective size distributions of the corresponding nanoparticles. Average diameter (d/nm) of the core/shell/shell UCNPs is shown with significant error.

UCL Comparison of Tm^{3+} -doped, Er^{3+} -doped and $\text{Tm}^{3+}/\text{Er}^{3+}$ co-doped core/shell/shell UCNPs

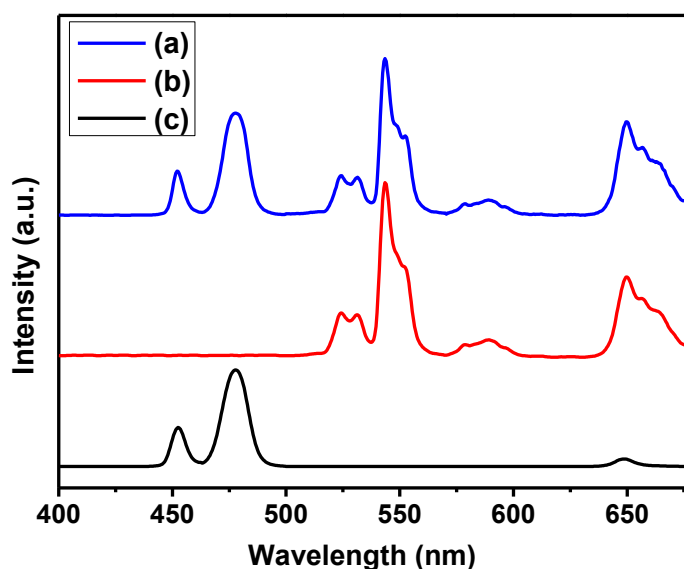


Figure 3.S14 UCL spectra of (a) $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)$, (b) $\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)$ and (c) $\text{NaGdF}_4:\text{Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ core/shell/shell UCNPs in cyclohexane.

PLE spectra of core/shell/shell nanoparticles using direct excitation of Tm^{3+} ion and Er^{3+} ion

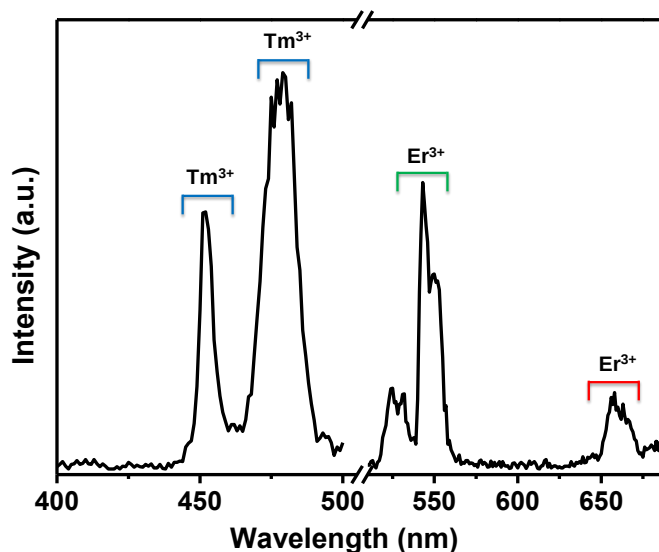


Figure 3.S15 PLE spectra of CSS (5 mol % Er^{3+}) [$\text{NaGdF}_4\text{:Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ @ $\text{NaGdF}_4\text{:Nd}^{3+}(30)/\text{Ca}^{2+}(7)$ @ $\text{NaGdF}_4\text{:Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)$] nanoparticles using direct excitation of Tm^{3+} ions ($\lambda_{\text{ex}} = 357 \text{ nm}$) and Er^{3+} ions ($\lambda_{\text{ex}} = 488 \text{ nm}$). The integrated PLE intensity of Tm^{3+} ion ($\lambda_{\text{ex}} = 357 \text{ nm}$) was slightly higher (1.3 times) than that of Er^{3+} ion ($\lambda_{\text{ex}} = 488 \text{ nm}$). All measurements were carried out under identical condition.

Calculation of photons involved in the white UCL

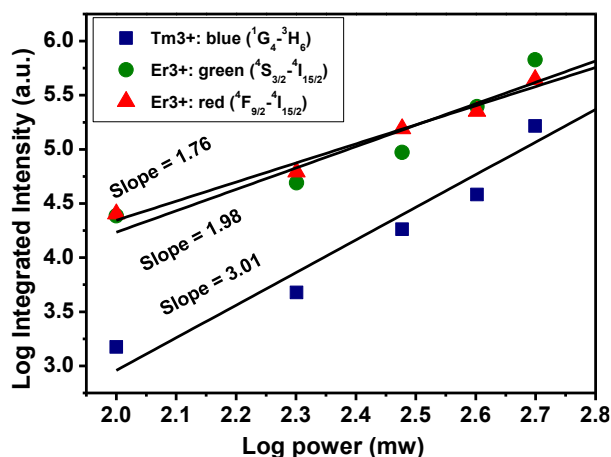
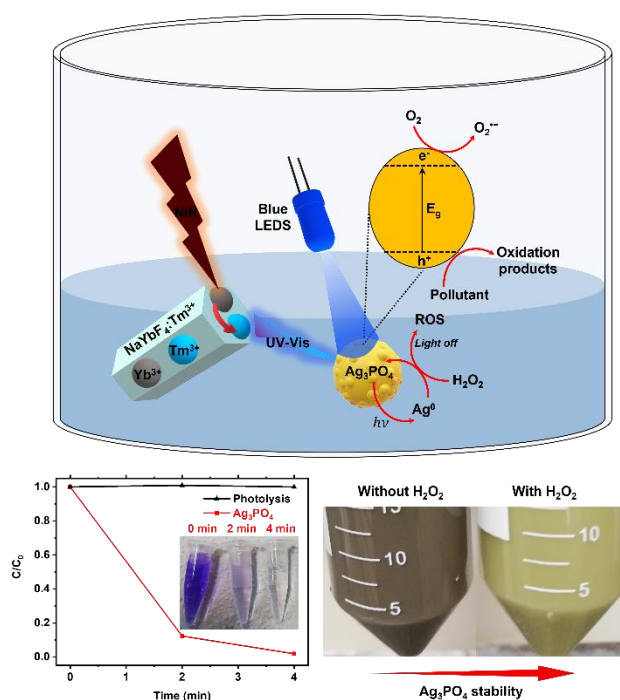


Figure 3.S16 The dependence of the intensities of UCL at 477 nm (Tm^{3+}), 544 nm (Er^{3+}) and 650 nm (Er^{3+}) on the excitation power in colloidal CSS (5 mol % Er^{3+}) [$\text{NaGdF}_4\text{:Tm}^{3+}(0.75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ @ $\text{NaGdF}_4\text{:Nd}^{3+}(30)/\text{Ca}^{2+}(7)$ @ $\text{NaGdF}_4\text{:Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)$] UCNPs. The number of photon process can be derived from the relation, $I_i \propto P^n$, where I_i is the integrated luminescence intensity and P is the pump laser power and n is the number of the laser photons required to populate the upper emitting state. The value of n can be obtained from the slope of the fitting line in the plot of $\log I_i$ versus $\log P$. A slope value of 3.01, 1.98, and 1.76 are observed for the blue emission (Tm^{3+}), green emission (Er^{3+}) and red emission (Er^{3+}), illustrating an involvement of three, two and two-photon process in the generation of UCL at 477 nm, 544 nm and 650 nm, respectively.

CHAPTER 4

A UV-VISIBLE-NIR ACTIVE SMART PHOTOCATALYTIC SYSTEM BASED ON NaYbF₄:Tm³⁺ UPCONVERTING PARTICLES AND Ag₃PO₄/H₂O₂ FOR PHOTOCATALYTIC PROCESSES UNDER LIGHT ON/LIGHT OFF CONDITIONS



Development of a highly efficient photocatalytic system ✓

Pathway to broad spectrum photocatalysis: extending to the NIR Region ✓

Improved photostability of the Ag₃PO₄ photocatalyst ✓

4 A UV-VISIBLE-NIR ACTIVE SMART PHOTOCATALYTIC SYSTEM BASED ON NaYbF₄:Tm³⁺ UPCONVERTING PARTICLES AND Ag₃PO₄/H₂O₂ FOR PHOTOCATALYTIC PROCESSES UNDER LIGHT ON/LIGHT OFF CONDITIONS†

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Abstract

The development of broad-spectrum photocatalytic materials that allow the use of a larger portion (UV to NIR) of the solar spectrum for photocatalytic processes has attracted great attention. Among visible light-active photocatalysts, silver phosphate (Ag₃PO₄) stands out prominent for its high photocatalytic activity towards the degradation of different pollutants. However, the full potential of this photocatalyst is limited by its inherent low photostability arising from self-photo-reduction and its inability to efficiently use light beyond the UV-Vis range of the solar spectrum. To address these fundamental limitations of Ag₃PO₄, we have developed a smart photocatalytic system by combining the interesting upconversion property of NaYbF₄:Tm³⁺ upconverting particles (UCPs) with the exceptionally high photocatalytic activity of Ag₃PO₄ and the oxidizing capacity of H₂O₂. In this UCPs/photocatalyst/oxidant (NaYbF₄:Tm³⁺/Ag₃PO₄/H₂O₂) system, the NIR-to-UV/visible UCPs can convert low energy NIR photons into high energy UV-visible photons that can be absorbed by Ag₃PO₄, thus photo-exciting (activating) it indirectly under NIR illumination. Similarly, the oxidant (H₂O₂) prevents self-reduction and/or assists in regeneration of Ag₃PO₄ through a Fenton-like process, thus ensuring the photostability and recyclability of

Ag₃PO₄. Interestingly, the Ag₃PO₄/H₂O₂ system remains active generating reactive oxygen species even after the photoexcitation process is turned off (dark conditions). The proposed broad spectrum photocatalytic system (UCPs/Ag₃PO₄/H₂O₂) was found to exhibit a high photocatalytic response (98% degradation of crystal violet dye in 90 min) under NIR illumination from a 980 nm laser and still a higher response (100% removal in less than 8 min) under direct visible light from low-cost blue emitting LEDs.

4.1 Introduction

Considering the growing environmental problems caused by anthropogenic activities as a global concern,^{1–4} the development of strategies and methods to counter these problems has become an active research area.^{5–12} Among environmental remediation strategies, heterogeneous photocatalysis based on semiconductor photocatalysts has so far been the most promising strategy with greater potential for combating environmental pollution on one hand and clean energy generation on the other.^{13–18} Unfortunately, most of the best known and commonly used semiconductor oxide photocatalysts are wide band semiconductors (TiO₂ and ZnO, for example) and thus can only be photoactivated using ultraviolet (UV) radiation^{17,19–24} which is only around 5–6% of the solar spectrum. On the other hand, relatively narrow band photocatalysts (BiVO₄, CdS, ZnSe, Ag₃PO₄ and Ag₂O) exhibit photocatalytic activity under UV and visible (Vis) light,^{25–28} but often suffer from fast electron–hole recombination and limited photostability. For example, Ag₃PO₄ has been found to exhibit high photoactivity and thus high contaminant removal performance, but it shows low photostability and is photo(self)reduced ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$) during the photocatalytic process by the photoexcited conduction band (CB) electrons,^{29–32} thus limiting the recyclability of the photocatalysts.

One of the strategies to inhibit photocorrosion of Ag₃PO₄ is to prepare its composites with other electron-acceptor materials of adequate conductivity such as graphene oxide (GO) which can remove the photoexcited electrons from the CB of Ag₃PO₄. For instance, Q. Xiang and co-workers prepared GO-Ag₃PO₄ composites in which the photoactive component (Ag₃PO₄) exhibited improved photostability, a smaller particle size and reduced charge carrier recombination, thus leading to enhanced overall photocatalytic activity.³³ The same results can be achieved and photo(self)reduction of Ag₃PO₄ can be prevented if the photocatalytic experiments are

performed in an oxidizing environment, such as in the presence of H_2O_2 discussed in this article.

Furthermore, the presence of GO also provides additional active adsorption sites for effective adsorption of target molecules. Since adsorption plays an important role in photocatalytic reactions, enhanced photocatalytic degradation of pollutants has been reported for GO supported Ag_3O_4 and silica-supported TiO_2 materials.^{33,34} Similarly, the enhanced CO_2 photoreduction capability of nanosheet-assembled g- C_3N_4 has been associated with its high specific surface area and number of active sites and/or improved adsorption capacity towards CO_2 .^{35,36} Moreover, supported photocatalysts often exhibit increased active sites accessible for surface reactions. For instance, EPR studies of the mechanism of enhanced photocatalytic activity showed that the number of spins per gram (representing active sites) on the surface of silica-supported TiO_2 ($1.6 \pm 0.3 \times 10^{18}$ spin g^{-1} of TiO_2) is higher as compared to pure or unsupported TiO_2 (0.6×10^{18} spins g^{-1} of TiO_2), which partly explains the higher photoactivity of the former.³⁴

Like any photocatalyst, the photocatalytic activity of Ag_3PO_4 strongly depends on its particle size and the rate of charge carrier recombination, and decreasing these two parameters leads to improved photocatalytic activity.³³ Although a narrow band gap is often useful for utilization of visible light, the position of the valence band (VB) and CB plays an important role in the formation of reactive oxygen species (ROS) and consequently the redox reactions of target molecules on the surface of the photocatalyst. For instance, the VB potential of Ag_3PO_4 is not positive enough to produce hydroxyl radicals ($\text{OH}^\cdot$) from $\text{H}_2\text{O}/\text{OH}^-$, but Ag_3PO_4 can produce superoxide ($\text{O}_2^{\cdot-}$) radicals from the reduction of O_2 present on or in the vicinity of the photocatalyst surface.³³

Many attempts have been made to prepare new or modified and recyclable broad spectrum photocatalytic systems that can make use of a wider range of solar radiation (from UV to NIR), especially the NIR range which constitutes ~50% of incident solar radiation.^{37–40} One promising strategy to extend the absorption/application range of UV-visible active photocatalysts is to couple them with lanthanide-based upconverting particles (UCPs) such as $\text{NaYbF}_4:\text{Tm}^{3+}$ and $\text{NaYF}_4:\text{Yb}^{3+}/\text{Tm}^{3+}$.^{41–45} The UCPs can successively absorb two or more relatively low energy photons (NIR photons) *via* intermediate long-lived energy states and then emit higher energy photons (in the UV-Vis region) upon relaxation through a non-linear optical process known as UC.^{41–45}

During this anti-Stokes ($\lambda_{\text{em}} < \lambda_{\text{ex}}$) process, the UCPs are excited to a higher energy level through the population of intermediate energy levels and subsequently emit a higher energy photon.^{44–52} The photons emitted by the UCPs in the UV-Vis region can be exploited to photo-excite any photocatalysts with an adequate band gap (E_g) that matches the energy of the emitted photon ($E_g = h\nu$). Photoexcitation of the photocatalysts and interband transitions then result in the production of oxidative holes in VB and reductive electrons in the CB for the subsequent redox reaction on the photocatalyst surface responsible for the degradation of pollutants.^{45,53,54} Despite the theoretical feasibility of the NIR active UCPs/photocatalyst system, reported literature on this topic demonstrates the limited practical success and lower contaminant removal efficiency of the system, often requiring several hours of NIR illumination.^{54–58} The combination of different advanced oxidation processes such as photocatalysis and Fenton-like processes using H_2O_2 as an oxidizing agent is a possible strategy to address the problem of low photoactivity under NIR irradiation.^{59–61}

In this work, we report a smart photocatalytic system based on $\text{NaYbF}_4:\text{Tm}^{3+}$ UCPs/ $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ that can be activated under both direct visible light illumination from low-cost blue LEDs (460 ± 10 nm) as well as NIR illumination, thanks to the NIR-to-UV/visible UC by the UCPs. Moreover, not only the presence of H_2O_2 improves the photoactivity and photostability of Ag_3PO_4 (by oxidizing back/regenerating the photo-(self)reduced Ag back to Ag^+), but also the process of regeneration/oxidation leads to the formation of reactive oxygen species through a Fenton-like process, even when the photoexcitation process is stopped (light off condition). The strategy proposed herein may be extended to other photocatalytic systems for improving their photocatalytic activity and recyclability under a broad range of solar radiation and illumination modes.

4.2 Experimental

4.2.1 Reagents

Yb_2O_3 (99.99%), Tm_2O_3 (99.99%), sodium fluoride (NaF) and bovine catalase enzyme (>10 000 units per mg protein) were supplied by Sigma-Aldrich (USA). Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA-Na_2) was acquired from Merck. Nitric acid (HNO_3) and crystal violet (CV) were purchased from Qhemis (Brazil). Hydrogen peroxide (H_2O_2 , 50%), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and silver acetate

(CH₃COOAg, 98%) were supplied by Synth (Brazil). All chemicals were used without further purification.

4.2.2 Synthesis of the Ag₃PO₄ photocatalyst

The Ag₃PO₄ photocatalyst was synthesized by a facile precipitation process at room temperature,⁶² followed by thermal treatment at 200 °C.⁶³ Briefly, 125 mL (7.5 mmol) of silver acetate solution was added dropwise under continuous stirring to a 100 mL (2.5 mmol) Na₂HPO₄·12H₂O solution. The resulting yellow suspension was stirred for 30 min and the Ag₃PO₄ particles were then recovered by centrifugation at 7500 rpm. The precipitated particles were washed several times with deionized water, dried in a vacuum oven at 80 °C and finally calcined at 200 °C for 1 h.

4.2.3 Synthesis of NaYbF₄:Tm³⁺(0.5) UCPs

The NaYbF₄:Tm³⁺(0.5) UCPs were synthesized by a microwave-assisted hydrothermal methodology developed by our group.^{44,45} A commercial microwave synthesizer (Discover SP model 909 150, CEM Corp.) with a 35 mL pressure vessel (CEM Part no. 909 036) covered with a special cap (CEM part no. 909 235) provided by the manufacturer was used. Briefly, Ln(NO₃)₃·6H₂O solutions (Ln = Yb³⁺, Tm³⁺) were prepared separately from the reaction of the respective oxides with concentrated nitric acid, followed by repeated addition/evaporation of water until the pH of the solution was around 3. The resulting solutions were standardized by titrating with a standard 0.01 mol L⁻¹ EDTA solution. Then, appropriate amounts of Ln(NO₃)₃·6H₂O solutions (total Ln³⁺ content = 1 mmol) were added to 10 mL (2 mmol) of EDTA solution. After stirring for 30 min, 15 mL (15 mmol) of NaF was added to the above Ln³⁺–EDTA solution and the resulting mixture was vigorously stirred for 30 min. The obtained colloidal suspension was subjected to microwave-assisted hydrothermal treatment for 1 h at 190 °C, 250 psi and 200 W of microwave power. The NaYbF₄:Tm³⁺(0.5) UCPs were recovered by centrifugation at 7500 rpm and then vacuum-dried after being washed once with ethanol and twice with deionized water following centrifugation–resuspension cycles. To remove EDTA from the particle surface, the UCPs were calcined at 400 °C for 90 min.

4.2.4 Photocatalytic experiments

The photocatalytic experiments were carried out under two different illumination modes, namely blue LED illumination (direct photoexcitation of Ag_3PO_4) and 980 nm laser irradiation (indirect photoexcitation of Ag_3PO_4 by the upconverted UV-visible radiation from UCPs).

4.2.4.1 Visible light photocatalytic activity under 460 ± 10 nm LED irradiation

The photocatalytic activity of the synthesized Ag_3PO_4 photocatalyst (25 mg) under blue light irradiation provided by LEDs (460 ± 10 nm) was evaluated through photodegradation of CV dye solution (7.5 mg L^{-1} , 30 mL). The photocatalyst/CV mixture in a glass-cylindrical-reactor (10.4 cm in diameter, 5.9 cm in height) was allowed to stir in the dark for 8 min and then exposed to blue light for another 8 min. An aliquot of 1.2 mL was collected every 2 min and centrifuged to monitor changes in the electronic absorption spectrum of the supernatant part. The experiments in the presence of H_2O_2 were carried out using the same procedure but with the addition of 110 μL or 200 μL of 1 mol L^{-1} H_2O_2 (final H_2O_2 concentration of 3.6 or 6.6 mmol L^{-1}) to the 30 mL CV- Ag_3PO_4 mixture just before starting irradiation. Sample aliquots were withdrawn at regular intervals and 30–40 μL of bovine catalase solution (0.4 g L^{-1}) was added to each aliquot withdrawn to consume any residual H_2O_2 and interrupt the reaction. Regeneration of the Ag_3PO_4 photocatalysts once used in the dye degradation test (in the absence of H_2O_2 in the reaction mixture) was performed. For this purpose, 200 μL of H_2O_2 was added to the photocatalytic mixture at the end of degradation experiments and the photocatalyst/ H_2O_2 mixture was kept under stirring for several hours. Finally, the regenerated photocatalyst was recovered by centrifugation and washed several times with ethanol and water.

4.2.4.2 NIR photocatalytic activity evaluation.

The photocatalytic activity of the UCPs/ Ag_3PO_4 photocatalyst and UCPs/ Ag_3PO_4 / H_2O_2 systems under NIR excitation (980 nm laser) was evaluated using 3 mL of CV dye solution (4 mg L^{-1}) and 10 mg of photocatalysts (mixture of UCPs + Ag_3PO_4 in different ratios) in a 4 mL glass vial. The CV/UCPs/ Ag_3PO_4 mixture was left in the dark overnight and then irradiated with NIR radiation using a 980 nm diode laser (DMC, Brazil) coupled to a 1.5 mm diameter optical fiber at a 2 W laser power. Sample aliquots were collected for the measurement of UV-visible absorption spectra as

described in Section 2.4.1, after which the sample was transferred back to the photoreactor. Different ratios of UCPs/Ag₃PO₄ were considered to find the optimal UCPs/photocatalyst ratio for effective dye degradation under 980 nm laser irradiation. Once the optimum ratio was found (6 mg UCPs/4 mg Ag₃PO₄), further experiments were carried out using this ratio in the presence of 6.6 mmol L⁻¹ of H₂O₂ to analyze its influence on the degradation of CV dye under 980 nm laser irradiation and the stability/recyclability of Ag₃PO₄.

4.2.5 Characterization techniques

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy measurements were performed using a field emission scanning electron microscope (FEG-SEM) (JEOL, model JSM-7500 F). Powder X-ray diffractograms (XRD) were acquired using a D8 Advance X-ray diffractometer (Bruker) operating at 40 mA and 40 kV and employing Ni-filtered Cu K α X-ray radiation ($\lambda = 1.540 \text{ \AA}$). Fourier transform infrared (FTIR) spectra were obtained using a PerkinElmer Spectrum 1000 FTIR spectrometer with a resolution of 2 cm⁻¹ and averaged over four scans. Raman spectra were measured in the 100–1000 cm⁻¹ range with an acquisition time of 50 s and 2 cycles using a LabRAM HR 800 Raman spectrophotometer (Horiba Jobin Yvon) equipped with a CCD detector (model DU420A-OE-325) and a He–Ne laser (632.81 nm). The diffuse reflectance spectra (DRS) of the powder samples against a background of MgO were obtained using a Cary 5000 UV-Vis-NIR spectrophotometer (Varian). The UCL spectra of UCPs (8 mg of NaYbF₄:Tm³⁺(0.5) in 10 mL of water) with an optical spectral resolution of 0.5 nm were acquired using a Horiba Jobin Yvon spectrofluorometer (Fluorolog-3 model FL3-122) equipped with a Hamamatsu R-928 photomultiplier tube. A 980 nm laser diode (DMC, Brazil) coupled with an optical fiber (1.5 mm diameter) was used as the NIR excitation source.

4.3 Results and discussion

4.3.1 Characterization of the Ag₃PO₄ photocatalyst

The morphological, compositional, crystallographic, and optical properties of the calcined Ag₃PO₄ particles, previously prepared by a facile room temperature method, were studied using SEM, EDX, XRD, and DRS, respectively. The Ag₃PO₄ particles are micrometric (mean: 475 $\pm$ 182 nm) with their surface decorated with small

(approximately 16 ± 4 nm size) nanospheres (Fig. 4.1a), as also previously observed by P. Dong and collaborators.⁶³ They reported the formation of small Ag nanoparticles, promoted by heat treatment, on the surface of calcinated Ag_3PO_4 .⁶³ The EDS spectrum (Fig. 4.1b) shows clear emission lines of Ag, P and O, confirming the presence of these elements in the samples.

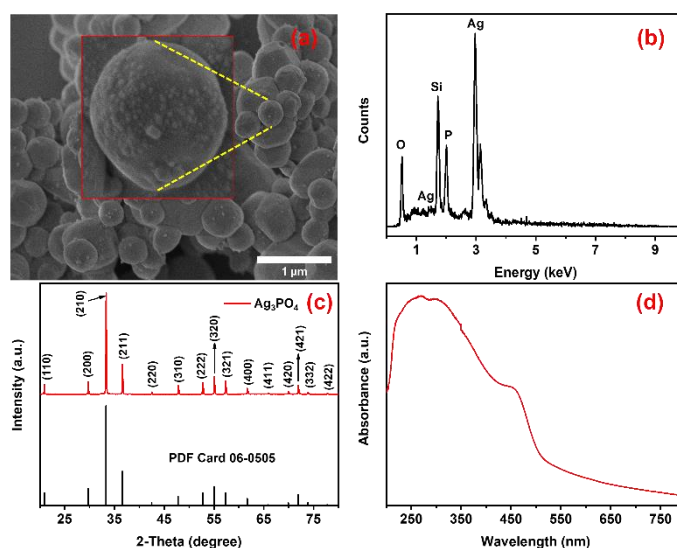


Figure 4.1 (a) SEM image, (b) EDS spectrum, (c) XRD pattern and (d) UV-Vis-NIR absorption spectrum of the Ag_3PO_4 photocatalyst. The Si signal in the EDX spectrum comes from the sample holder. The inset in a shows a magnified view of the Ag_3PO_4 photocatalyst.

As shown in Fig. 4.1c, all the diffraction peaks in the diffractogram of the sample perfectly match with those of the body-centered cubic phase of Ag_3PO_4 with the space group $P\bar{4}3n$ (PDF no. 06-0505). The optical absorption property is an important factor that can determine the photocatalytic efficiency of materials under irradiation in a certain part of the electromagnetic spectrum and, therefore, the absorption spectrum of Ag_3PO_4 powder was measured by diffuse reflectance spectroscopy (Fig. 4.1d). The absorption transformed DRS spectrum of the Ag_3PO_4 particles shows strong absorption in the UV-Vis region (Fig. 4.1d), attributed to the intrinsic charge transfer of Ag_3PO_4 from the VB to the CB,^{29,63–65} with an indirect band-gap of 2.30 eV, as estimated from the Kubelka–Munk plot shown in Fig. 4.S1a (ESI†). The strong absorption in the visible region (540–400 nm) overlaps well with the emission from blue LEDs (460 ± 10 nm), allowing effective photoexcitation of Ag_3PO_3 and photodegradation of pollutants using low-cost commercial LEDs as the illumination source (*vide infra*). The Ag_3PO_4 samples were also characterized by vibrational spectroscopy. The FTIR spectrum of the sample exhibits four typical FTIR bands of

Ag_3PO_4 (Fig. 4.S1b, ESI†), two of which lying around 560 cm^{-1} and 1010 cm^{-1} are of medium/high intensity and can be attributed to the $\text{O}=\text{P}-\text{O}$ bending vibration in the plane and the asymmetric stretching of $\text{P}-\text{O}-\text{P}$ groups, respectively.^{66–68} The other two bands of low intensity, situated at 850 and 1385 cm^{-1} , are related to the symmetric stretching vibration of $\text{P}-\text{O}-\text{P}$ bonds and the stretching vibration of the $\text{P}=\text{O}$ bonds in the Ag_3PO_4 structure.^{67,69} Additionally, the vibrational bands around 3390 cm^{-1} and 1650 cm^{-1} are attributed to the stretching vibrations of $\text{O}-\text{H}$ groups and $\text{H}-\text{O}-\text{H}$ bending vibrations of the adsorbed water molecules, respectively.^{67,69} Similarly, the Raman spectrum of Ag_3PO_4 samples exhibits the characteristic vibrational modes of the PO_4^{3-} groups in a T_d symmetry around 405 , 550 , 907 , 950 and 1000 cm^{-1} ,^{64,70} confirming the formation of Ag_3PO_4 (Fig. 4S1c, ESI†).

4.3.2 Morphological/structural characterization and optical properties of $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)$ UCPs

The structural, morphological and optical properties of the $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)$ UCPs, synthesized by a facile microwave-assisted hydrothermal method,^{44,45} were studied using XRD, SEM and photoluminescence spectroscopy, respectively (Fig. 4.2). The X-ray diffraction patterns of UCPs perfectly match with the standard diffraction pattern of the hexagonal $\beta\text{-NaYbF}_4$ phase (PDF no. 27-1427) (Fig. 4.2a) which is usually associated with stronger UCL than its cubic ($\alpha\text{-NaYbF}_4$) counterpart. This UCP sample consists of microrods of around $7.9 \pm 1.4\text{ }\mu\text{m}$ length and $2.5 \pm 0.5\text{ }\mu\text{m}$ diameter (Fig. 4.2b). A magnified view of a vertically oriented microrod reveals its hexagonal shape (inset in Fig. 4.2b), in accordance with the results of the XRD analysis (Fig. 4.2a). The presence of Yb^{3+} ions and/or NIR absorption properties of the UCPs are evident from the characteristic absorption peak of Yb^{3+} at around 975 nm in the electronic absorption spectrum, obtained by measuring the diffuse reflectance from the powder sample (Fig. 4.2c, dotted line).⁷¹ The presence of Yb^{3+} thus allows the UCPs to absorb the NIR photons from a 980 nm laser while doping with Tm^{3+} ions as the emitters assists in obtaining upconverted light in the UV and visible region of the spectrum (Fig. 4.2c, solid line). The UCL spectrum of an aqueous suspension of UCPs, measured under 980 nm laser excitation, thus shows emission peaks centered around 286 , 344 , 361 , 452 , and 477 nm which are, respectively, attributed to the $^1\text{I}_6 \rightarrow ^3\text{H}_6$, $^1\text{I}_6 \rightarrow ^3\text{F}_4$, $^1\text{D}_2 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transitions of Tm^{3+} ions (Fig. 4.2c, solid line),^{44–48} as explained later.

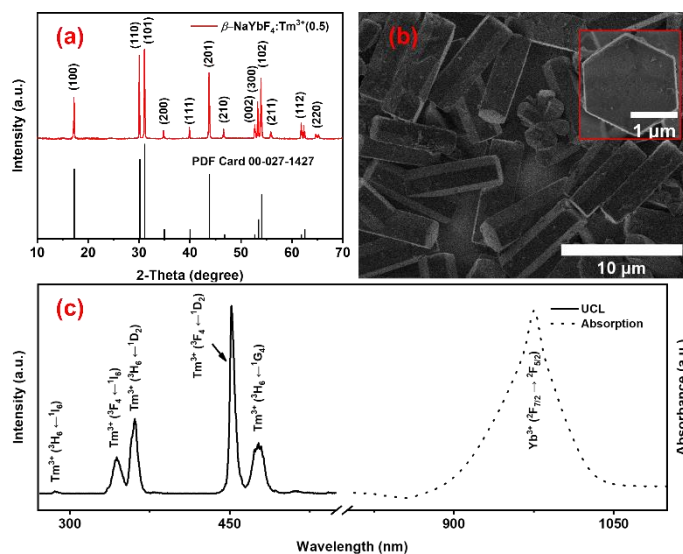


Figure 4.2 (a) XRD pattern, (b) SEM image and (c) UV-Vis-NIR absorption spectrum (dotted line) and UCL spectrum under 980 nm laser irradiation (black solid line) of NaYbF₄:Tm³⁺ UCPS. The inset in b shows a magnified view of a single NaYbF₄:Tm³⁺ UCP.

4.3.3 Photocatalytic activity evaluation

Two main objectives of the present study were to improve the photostability of Ag₃PO₄ (by employing H₂O₂) and extend the application of this photocatalyst beyond the UV-visible region and into the NIR region (by coupling UCPs with Ag₃PO₄). Thus, detailed photocatalytic assays were performed employing Ag₃PO₄ and Ag₃PO₄-UCP samples in the presence and absence of H₂O₂ using either visible light from low-cost blue (460 ± 10 nm) commercial LEDs or NIR light from a laser. Evolution of the photocatalytic degradation process by the Ag₃PO₄-H₂O₂ system under light ON/light OFF modes was also studied.

4.3.3.1 Photocatalytic activity of Ag₃PO₄/H₂O₂ under visible light from blue LEDs.

The visible photocatalytic activity of Ag₃PO₄ particles was examined under direct excitation from blue (460 ± 10 nm) LEDs (Fig. 4.3). No significant decrease in the absorbance of CV dye was observed in the absence of Ag₃PO₄, suggesting that direct photolysis does not degrade the dye. On the other hand, in the presence of Ag₃PO₄, the normalized absorbance of the dye at around 582 nm exhibits a drastic decrease within just 2 min of LED illumination (Fig. 4.3a, red line) and almost 100% dye discoloration is achieved in less than 8 min (see the inset in Fig. 4.3a), indicating the high visible light photocatalytic activity of the prepared Ag₃PO₄ particles.

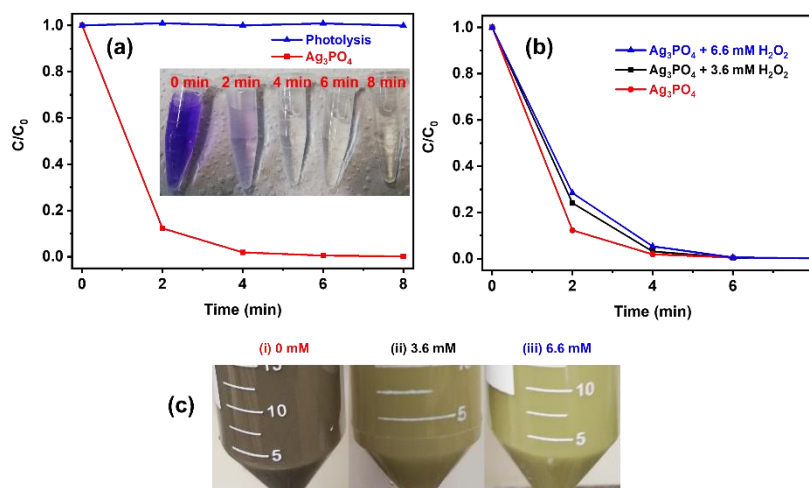


Figure 4.3 Temporal change in the concentration of CV dye as a function of irradiation time with blue LEDs in the (a) absence (blue line) and presence (red line) of the Ag_3PO_4 photocatalyst, and in the (b) absence and presence of H_2O_2 in the dye– Ag_3PO_4 mixture. The inset in (a) shows the digital images of CV dye solution at different irradiation times (marked on the images) in the presence of the Ag_3PO_4 photocatalyst. (c) Digital images of aqueous dispersions of the Ag_3PO_4 photocatalyst recovered and washed after four photocatalytic cycles corresponding to the experiments carried out in the absence of H_2O_2 (i) and with the addition of 3.6 mmol L^{-1} (ii) and 6.6 mmol L^{-1} (iii) of H_2O_2 .

Unfortunately, the high photocatalytic activity was accompanied by a change in both the morphology (Fig. 4.S2a and b, ESI†) and color (from yellow to black) of the used photocatalyst [Fig. 4.3c(i)], suggesting the decomposition of the photocatalysts and/or self-reduction of Ag^+ to Ag by the photoexcited CB electron.²⁹ The presence of H_2O_2 in the photocatalytic reaction media, however, prevented any change in the morphology of the particles (Fig. 4.S2c and d, ESI†) as well as the darkening of the photocatalyst suspension during the photocatalytic experiments [Fig. 4.3c(ii/iii)], without significantly affecting the original photocatalytic activity of the sample (Fig. 4.3b). The change in the color and morphology of the Ag_3PO_4 photocatalyst during the photocatalytic experiments in the absence of H_2O_2 is also accompanied by a loss in photocatalytic activity (green bar in Fig. 4.4), thus negatively affecting the recyclability of the photocatalyst. In fact, the observed photodegradation rate constant (k) decreases around 10 times, going from 0.853 min^{-1} (first cycle) to 0.088 min^{-1} (4th cycle). The loss in photocatalytic activity in the absence of H_2O_2 after repeated photodegradation cycles is attributed to the photo-assisted self-reduction of Ag^+ to Ag, mediated by the photoexcited electrons in the CB of Ag_3PO_4 [eqn (4.1)–(4.5)].^{29–32}

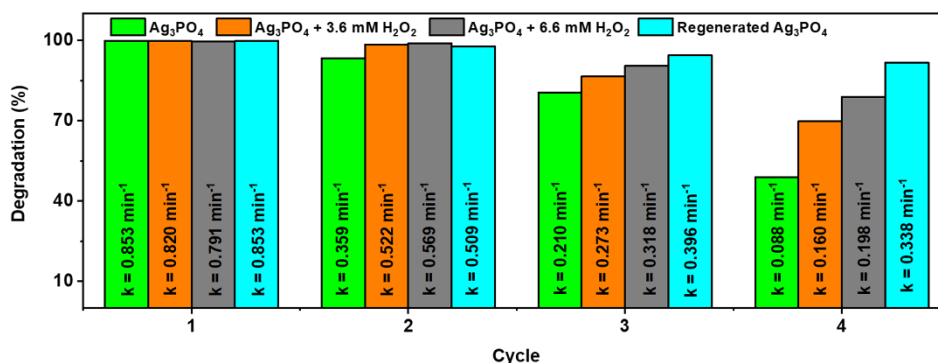
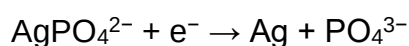
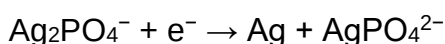
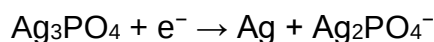
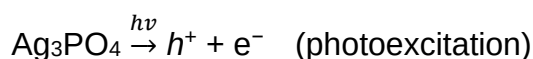


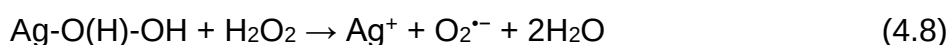
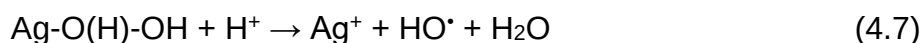
Figure 4.4 Evaluation of the effect of H₂O₂ as an auxiliary oxidizing agent on the photostability and recyclability of Ag₃PO₄ during repeated photocatalytic degradation cycles under blue LED irradiation.

The photoassisted self-reduction of Ag₃PO₄ occurs according to the following reactions:



In fact, the XRD patterns of the used Ag₃PO₄ show the presence of a diffraction peak of Ag⁰ at around 38.1° (PDF no. 65-2871) when no H₂O₂ is used during the photocatalytic tests (Fig. 4.S4, ESI†). However, the intensity of this peak is much lower when H₂O₂ is added to the Ag₃PO₄/dye mixture during photocatalytic tests (Fig. 4.S4, ESI†), indicating the importance of H₂O₂ for the photostability and recyclability of Ag₃PO₄.

During the photocatalyst regeneration process, H₂O₂ can oxidize the Ag back to Ag⁺ and thus reform Ag₃PO₄ through a Fenton-like process [eqn (4.6)–(4.9)],^{72–76} as shown below.



Control experiments in the absence of Ag_3PO_4 in the reaction mixture or in the absence of LED illumination showed no significant decreases in the absorbance of the CV dye in 8 min (Fig. 4.S3, ESI†). Although the presence of H_2O_2 slightly decreased the dye degradation rate in the first photocatalytic cycle (Fig. 4.3b), it significantly improved the structural stability (Fig. 4.S2 and S4, ESI†) and recyclability of Ag_3PO_4 as mentioned above (Fig. 4.3c, 4 and Fig. 4.S2, S4, ESI†). These results demonstrate that the presence of H_2O_2 had a positive influence on the photocatalytic performance during repeated cycles of use (orange and gray bars in Fig. 4.4). The slight decrease in the photoactivity of the $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ system after repeated photocatalytic cycles may be related to the incomplete recovery of the photocatalyst or partial photoreduction of Ag_3PO_4 to Ag^0 . Previous studies have shown that the oxygen vacancies present on the surface of Ag_3PO_4 play an important role in its photocatalytic activity and the slight decrease in photoactivity upon repeated use may also be related to the loss of these vacancies.⁶³ Furthermore, the Ag_3PO_4 used in the degradation experiments, without the addition of H_2O_2 , was recovered and then regenerated with H_2O_2 in an *ex situ* manner (Fig. 4.S2e and f, ESI†). This regenerated photocatalyst was as efficient as the freshly prepared new photocatalysts (cyan bar in Fig. 4.4), thus demonstrating a remarkable recovery of its photocatalytic activity.

4.3.3.2 Photocatalytic activity of the $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ system after turning off the excitation light (dark)

Fig. 4.5 shows that, in the presence of both Ag_3PO_4 and H_2O_2 , the absorbance or concentration of CV dye continues to decrease even when the LED illumination is turned off at the end of the 4th photodegradation cycle. On the other hand, no significant post-irradiation change in concentration was observed in the absence of H_2O_2 in the reaction mixture. Since Ag_3PO_4 can be charged with photoinduced reductive energy by the excitation light from LEDs [eqn (4.1)–(4.5)], this energy can then be used to produce reactive oxygen species (ROS) in the presence of H_2O_2 , even in the dark, as can be observed from Fig. 4.5. The results of Fig. 4.5 can thus be explained based on eqn (4.6)–(4.8)^{72–76} where the peroxide-induced oxidation of Ag^0 to Ag^+ or regeneration of Ag_3PO_4 is accompanied by the generation of ROS ($\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$) that can take part in the photodegradation of the dye even after the excitation light is turned off. Although previous studies suggest that Ag_3PO_4 cannot produce $\text{HO}^\bullet$ radicals from $\text{H}_2\text{O}/\text{OH}^-$ as its VB edge potential is not enough, $\text{HO}^\bullet$ radicals can be

produced in the presence of H_2O_2 , even in the dark [eqn (4.7)]. Under adequate light illumination, Ag_3PO_4 has been found to produce superoxide radicals ($\text{O}_2^{\cdot-}$) and oxidative holes that degrade the organic dye molecules.³³

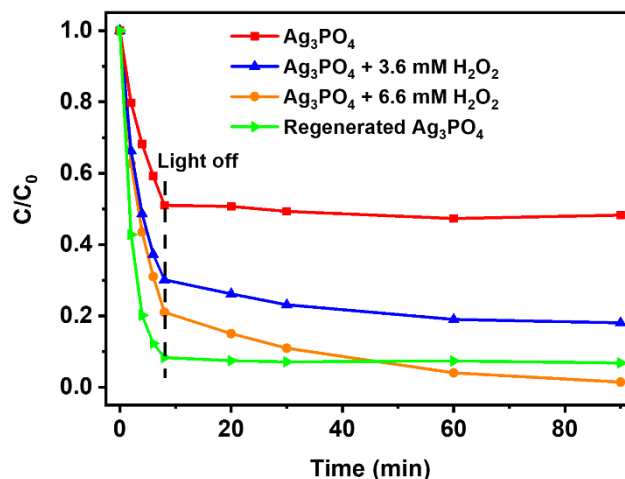


Figure 4.5 Changes in the concentration of CV dye during the fourth photocatalytic cycle under irradiation (the first 8 min) and in the dark (after 8 min) using the photocatalyst recovered in the experiments performed in the absence of H_2O_2 (red line) and in the presence of 3.6 mmol L^{-1} (blue line) and 6.6 mmol L^{-1} of H_2O_2 (orange line) and the regenerated material (green line).

The presence of H_2O_2 thus not only ensures the improved photostability and recyclability of Ag_3PO_4 , but also allows photoinduced electron storage and harnessing of the stored chemical energy for redox processes even after the photoexcitation light is turned off.

4.3.3.3. Photocatalytic activity of UCPs/ Ag_3PO_4 / H_2O_2 under NIR illumination.

After confirming the excellent inherent photocatalytic activity of the prepared Ag_3PO_4 under visible light, we evaluated the NIR photoactivity of the UCPs– Ag_3PO_4 system under 980 nm illumination from a laser (Fig. 4.6). A clear decrease in the absorbance of CV dyes as a function of NIR irradiation time in the presence of UCPs– Ag_3PO_4 (Fig. 4.6a) and/or UCPs– Ag_3PO_4 – H_2O_2 (Fig. 4.6b) confirms the NIR-based photoactivity of the systems.

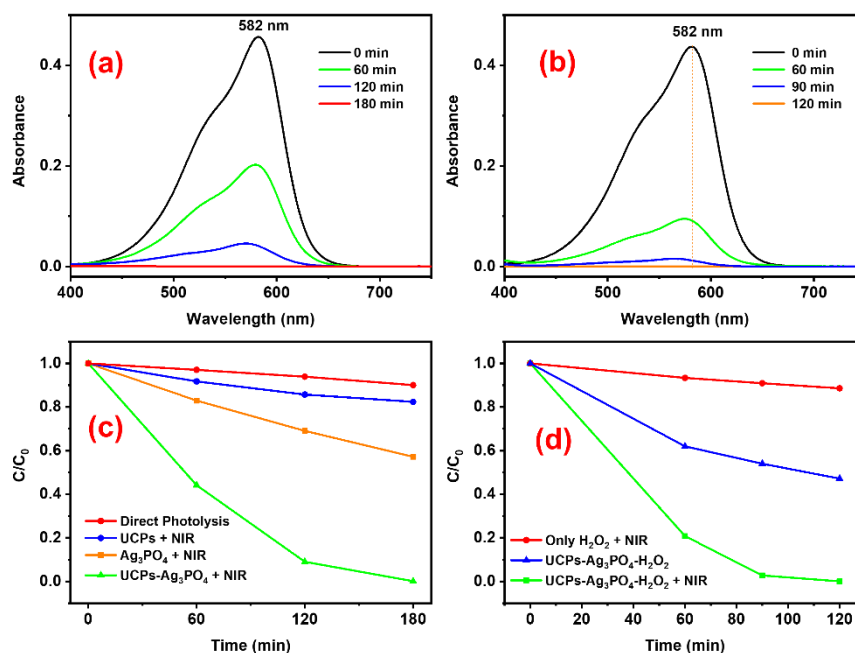


Figure 4.6 Temporal evolution of the absorbance of CV under 980 nm laser irradiation in the presence of (a) UCPs-Ag₃PO₄ and (b) and UCPs-Ag₃PO₄-H₂O₂ systems. Concentration profiles showing a decrease in the concentration of CV dye as a function of NIR irradiation time in the presence of (c) UCPs-Ag₃PO₄ and (d) UCPs-Ag₃PO₄-H₂O₂ systems. Different controls are also shown in (c and d).

An important factor determining the degradation efficiency of a certain pollutant using the UCPs-Ag₃PO₄ photocatalytic system is the ratio between the UCPs and the Ag₃PO₄ photocatalyst. A suitable UCP/Ag₃PO₄ ratio may allow efficient absorption of the excitation (NIR) light by the UCPs, leading to their strong UCL emission which, in turn, may efficiently photoactivate the photocatalyst particles for effective photodegradation of the pollutants in the vicinity of UCP-Ag₃PO₄ particles. Therefore, we evaluated the efficiency of different UCP/Ag₃PO₄ ratios keeping the total amount of the photocatalyst system (UCPs + Ag₃PO₄) fixed at 10 mg (Fig. 4.S5, ESI†). It turns out that this ratio really plays an important role in the degradation of CV dye under 980 nm laser irradiation (Fig. 4.S5, ESI†) and an increase in the degradation rate was clearly observed until reaching a maximum for the 6/4 UCPs/Ag₃PO₄ ratio (Fig. 4.S5e, ESI†). Thus, further photocatalytic experiments presented in Fig. 4.6 were performed using the 6/4 ratio of UCPs/Ag₃PO₄ and an almost 100% degradation of the dye was achieved in 180 min (Fig. 4.6c). Additionally, the presence of H₂O₂ led to a considerable improvement in the degradation of the dye under 980 nm laser irradiation, reaching almost 100% degradation of the dye in just 90 min of NIR illumination (Fig. 4.6b and d).

Control experiments were performed to better understand the photocatalytic process and evaluate the contribution of different possible factors to it. For example, it may be noted that direct photolysis (DP) of the dye by the NIR laser, irrespective of the absence or presence of H_2O_2 (red lines in Fig. 4.6c and d, respectively), is insignificant. Similarly, we observed an around 40% decrease in the concentration of CV dye in the presence of only Ag_3PO_4 (orange line in Fig. 4.6c), possibly due to direct excitation of the highly photoactive Ag_3PO_4 by the NIR laser. Likewise, a significant reduction in the concentration of CV dye by the UCPs– Ag_3PO_4 – H_2O_2 system in the absence of NIR illumination was observed (blue line in Fig. 4.6d), which might be attributed to the production of ROS by a Fenton-like reaction between H_2O_2 ^{72–76} and the Ag particles on the surface of Ag_3PO_4 formed during the calcination process.^{63,77} In either case, the decrease in the concentration of CV dye in the presence of UCPs– Ag_3PO_4 and/or UCPs– Ag_3PO_4 – H_2O_2 systems under NIR illumination is much higher (100%), confirming the NIR photocatalytic activity of these two systems.

4.3.3.4. Mechanism of the NIR based photocatalytic activity.

As shown earlier in Fig. 4.2c, the $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)$ UCPs could efficiently convert the 980 nm NIR light into UV-visible light at 286, 344, 361, 452, and 477 nm, thanks to the presence of Yb^{3+} ions (sensitizer/NIR absorber) and Tm^{3+} ions (UV-visible emitters). As schematically presented in Fig. 4.7a, the Yb^{3+} ion absorbs the NIR photons (980 nm) from the laser leading to population of the higher energy state ($^2\text{F}_{5/2}$) as a result of the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition. The excited Yb^{3+} transfers its energy to the emitter Tm^{3+} ion through successive energy transfer (ET) steps, resulting in the population of its higher energy levels. The excited Tm^{3+} ion then relaxes by emitting upconverted photons of shorter wavelengths (than the excitation wavelength of 980 nm) at around 286, 344, 361, 452, and 477 nm which are, respectively, attributed to the $^1\text{I}_6 \rightarrow ^3\text{H}_6$, $^1\text{I}_6 \rightarrow ^3\text{F}_4$, $^1\text{D}_2 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transitions of Tm^{3+} ions (Fig. 4.7a).^{44–48}

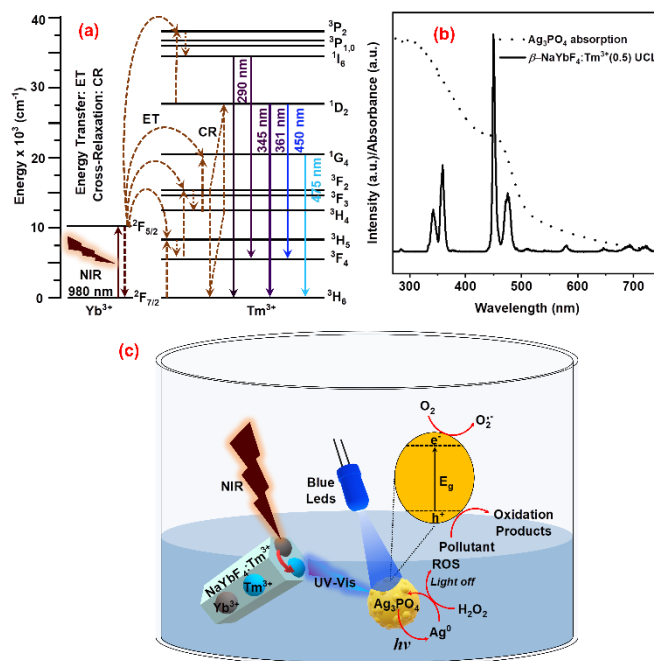


Figure 4.7 (a) UC mechanism of Tm^{3+} doped NaYbF_4 UCPs under 980 nm laser excitation, (b) comparison between the absorption spectrum of the Ag_3PO_4 photocatalyst and the UCL spectrum of $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)$ UCPs, and (c) photoactivation of the Ag_3PO_4 photocatalyst under UV-Vis/NIR irradiation and its regeneration with H_2O_2 .

These upconverted photons with a wavelength shorter than 500 nm can be absorbed by Ag_3PO_4 ($E_g = 2.3$ eV), as suggested by the excellent overlap between the absorption spectrum of Ag_3PO_4 and the UCL spectrum of UCPs (Fig. 4.7b). Absorption of the upconverted photons of suitable energy by Ag_3PO_4 is then followed by its photoexcitation, generating oxidative holes (h^+) and reductive electrons (e^-) as a result of typical interband transitions. The oxidative holes in the VB and reductive electrons in the CB then take part in a series of redox processes on the surface of the semiconductor photocatalyst particles which ultimately leads to photodegradation of pollutants. It may be noted that the reductive electrons take part not only in redox processes (such as the formation of superoxide radicals, $\text{O}_2 + e^- \rightarrow \text{O}_2^{\cdot-}$) but also in the self-reduction of Ag_3PO_4 [see eqn. (4.5)], leading to the formation of metallic Ag and hence the photocorrosion of the photocatalysts (Fig. 4.7c). Then the addition of H_2O_2 not only prevents photocorrosion and/or assists in photocatalyst regeneration, but also produces ROS through a Fenton-like process, even in the dark. Fig. 4.7 schematically summarizes the mechanism of the photocatalytic activity of the UCPs– Ag_3PO_4 system under direct UV-vis light (direct excitation from LEDs) and/or upconverted UV-vis light obtained from UCPs under NIR illumination (indirect excitation), as well the process of photocatalyst regeneration using H_2O_2 .

4.4. Conclusions

Taking advantage of the high photocatalytic activity of Ag_3PO_4 , the interesting NIR-to-UV/vis UC ability of $\text{NaYbF}_4:\text{Tm}^{3+}$ UCPs and the oxidizing power of H_2O_2 , we successfully developed a smart photocatalytic system that shows distinct features including (i) high photoactivity under both NIR and UV-vis light, (ii) better photostability of the otherwise photounstable Ag_3PO_4 and its regeneration for effective recycling and (iii) the possibility of achieving photocatalytic processes after the excitation light is turned off (light off mode). Highly photoactive Ag_3PO_4 particles were prepared by a simple precipitation method at room temperature. The UCPs were prepared by a facile MW-assisted hydrothermal method which allowed their crystallization in the hexagonal β -phase with a high NIR-to-UV/vis UCL intensity under 980 nm laser irradiation. The upconverted UV-vis light obtained from UCPs under NIR excitation was successfully used to photoactivate the Ag_3PO_4 photocatalyst, achieving a high degradation rate of crystal violet dye. It was demonstrated that the presence of H_2O_2 has a positive influence on the stability of Ag_3PO_4 , preventing its photocorrosion and regenerating the used photocatalysts. Importantly, the photocatalyst regeneration process also simultaneously produces reactive oxygen species in a Fenton-like manner which help in the degradation of the pollutants even when the excitation light is turned off. Moreover, the presence of H_2O_2 also increased the degradation rate of the crystal violet (CV) dye under NIR irradiation, reaching an almost complete degradation of the dye in 90 min. These results indicate that the coupling between UCPs and suitable photocatalysts, in combination with other advanced oxidation processes, may allow the application of photocatalytic processes in an extended region of the electromagnetic spectrum.

Author contributions

Y. E. Serge Correales: conceptualization, methodology, investigation, visualization, writing – original draft, writing – review & editing. S. Ullah: conceptualization, methodology, visualization, writing – review & editing, supervision. E. P. Ferreira-Neto: methodology, writing – review & editing. H. D. Rojas-Mantilla: design and construction of the blue emitting LED reactor. C. Hazra: conceptualization, methodology. S. J. Lima Ribeiro: writing – review & editing, supervision, acquisition of funds, project management.

Conflicts of interest

There are no conflicts to declare.

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Footnote

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ma01028j

Supplementary Material

UV-visible-NIR active smart photocatalytic system based on $\text{NaYbF}_4\text{:Tm}^{3+}$ upconverting particles and $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ for photocatalytic processes under both light on/light off conditions

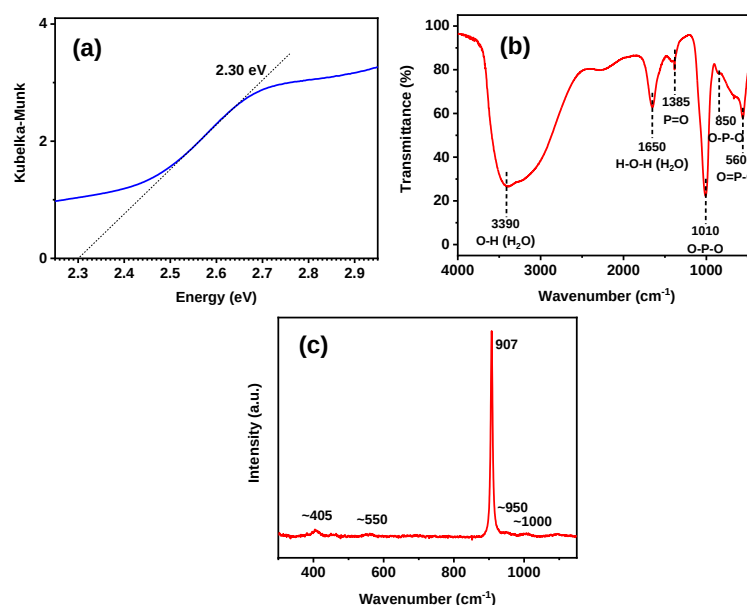


Figure 4.S1 (a) Kubelka-Munk transformed reflectance spectrum and estimated optical bandgap, (b) FTIR spectrum and (c) Raman spectrum of Ag_3PO_4 photocatalyst.

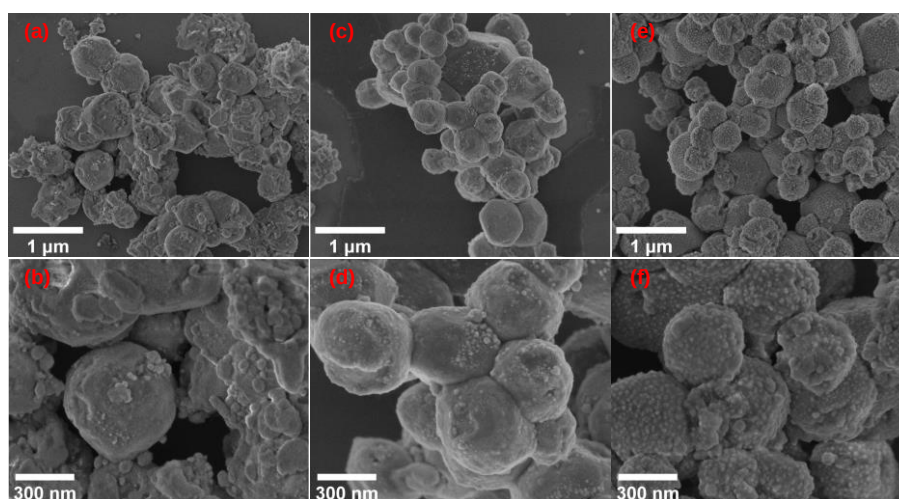


Figure 4.S2 SEM images of Ag_3PO_4 photocatalyst after four photocatalytic cycles (a, b) in the absence of H_2O_2 , (c, d) in the presence of 6.6 mmol L^{-1} of H_2O_2 and (e, f) regenerated photocatalyst. Figs. S2a,b show that in the absence of H_2O_2 , the surface of the Ag_3PO_4 particles was severely deformed, while the presence of 6.6 mmol L^{-1} of H_2O_2 during the degradation experiments apparently prevented the damage to the photocatalyst surface (Figs. S2c,d). Additionally, the regenerated Ag_3PO_4 photocatalysts presented small particles on the surface, which might have formed from the oxidation of the photodeposited small Ag nanoparticles back to Ag^+ (Ag_3PO_4) by H_2O_2 employed as an oxidizing agent during the regeneration process.

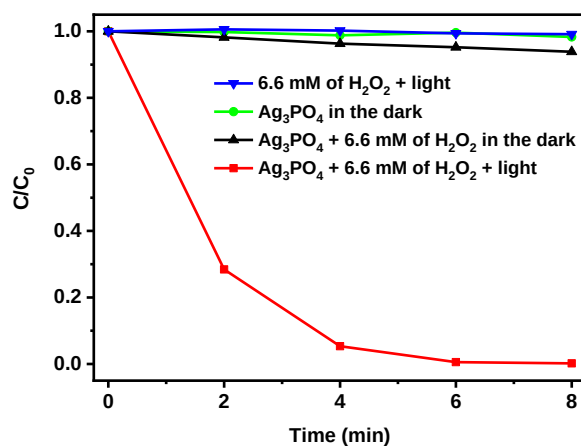


Figure 4.S3 Temporal change in concentration of CV dye under different experimental conditions (shown in Figure labels) including illumination with blue LEDs in the presence of only H₂O₂ or Ag₃PO₄ + H₂O₂ as well under dark conditions (control experiments).

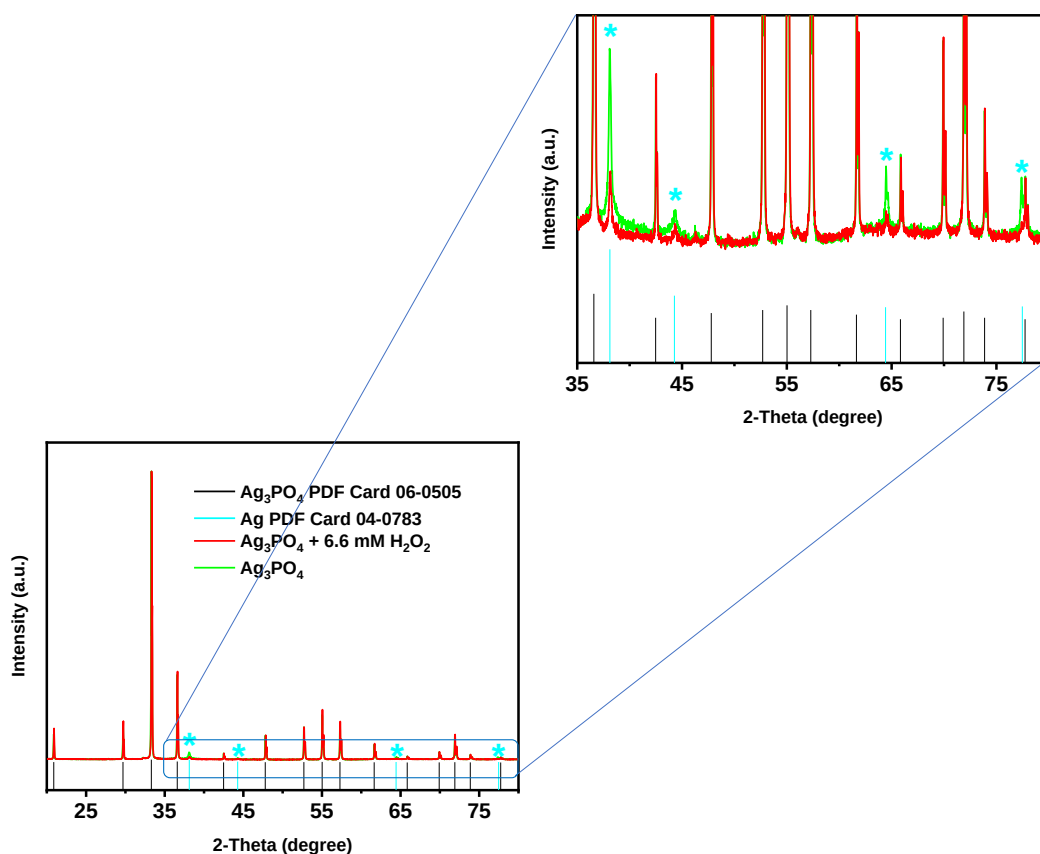


Figure 4.S4 X-ray powder diffractograms of the recovered Ag₃PO₄ samples compared to the diffraction patterns of pure Ag₃PO₄ and Ag. The upper panel shows a zoom of the 2-theta region (35–80°) for better visualization of the peaks pertaining to metallic silver. The intensity of the characteristics diffraction peaks of Ag⁰ (marked with asterisks) are much lower for the binary Ag₃PO₄-H₂O₂ system than the one single component Ag₃PO₄ system, indicating the importance of H₂O₂ for the stability recyclability of Ag₃PO₄ during degradation tests.

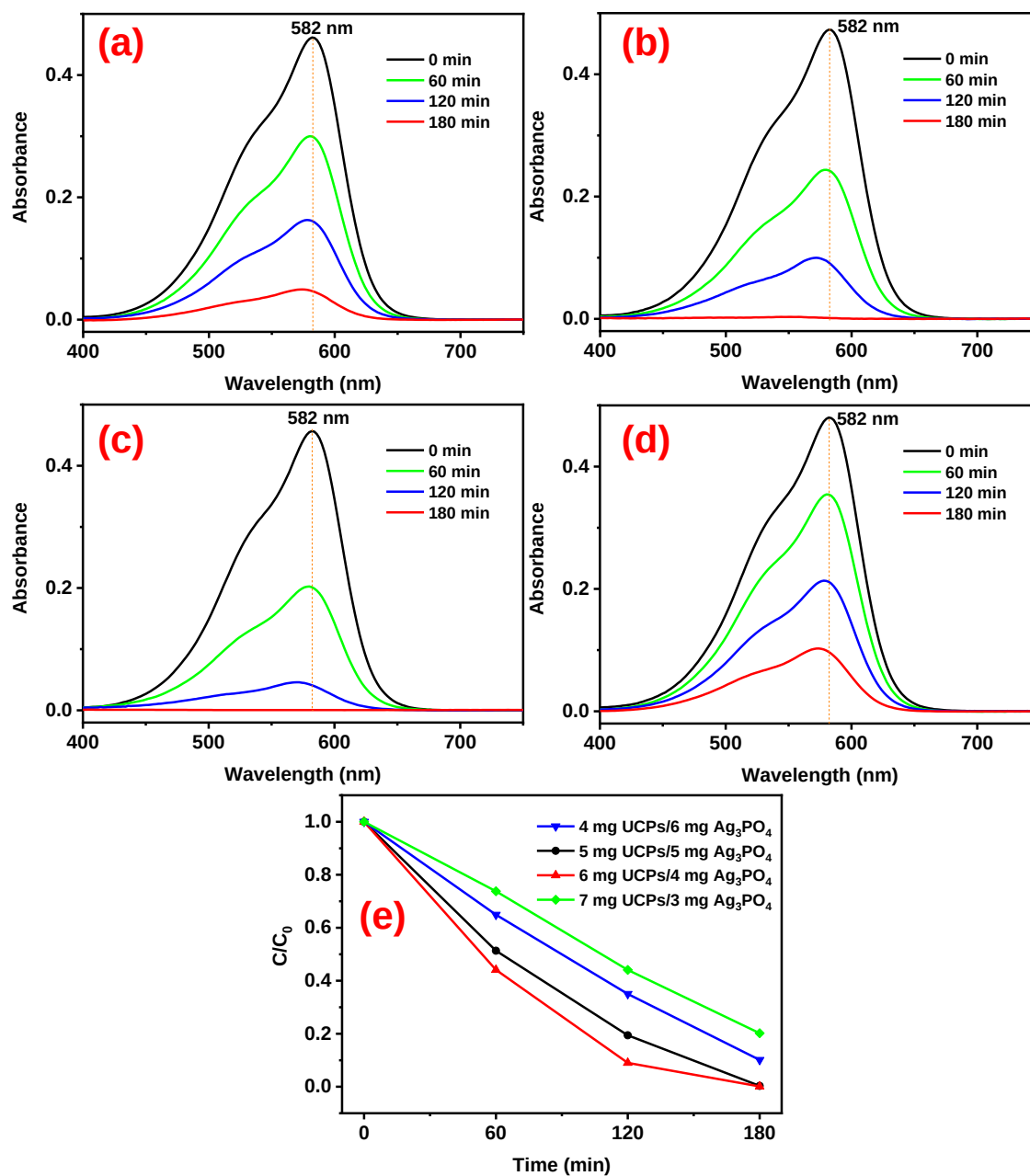
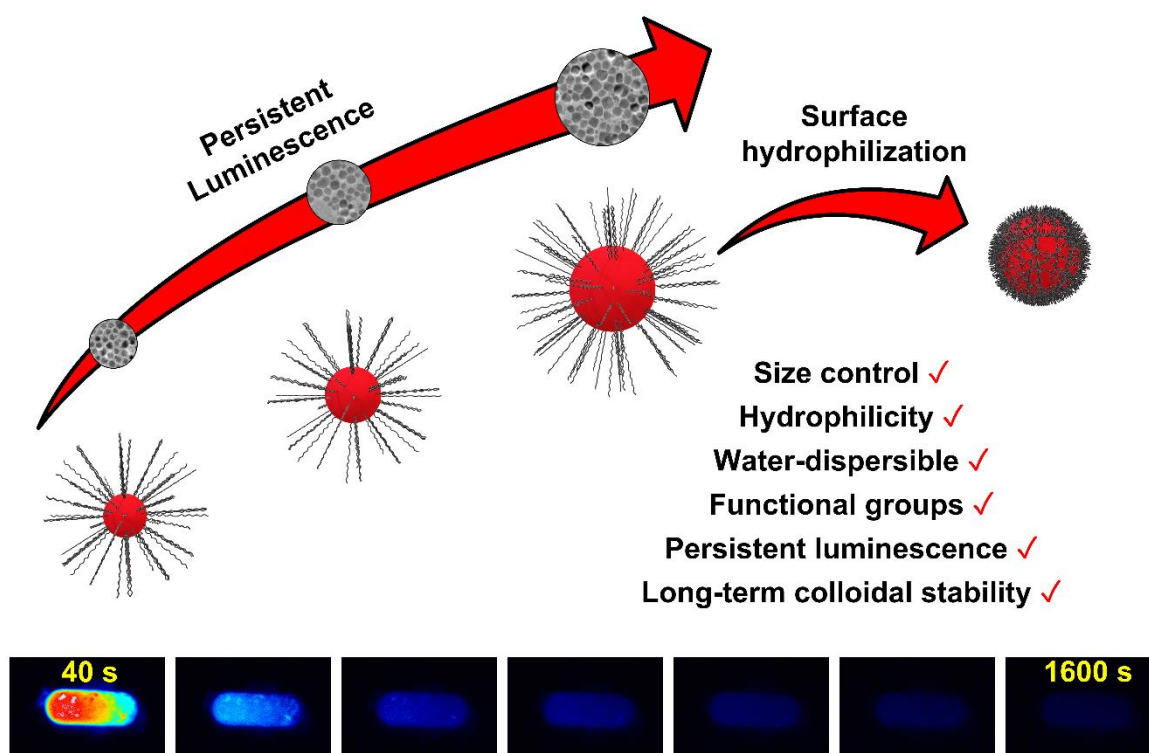


Figure 4.S5 Temporal decrease in the absorbance of CV dye under 980 nm laser irradiation in the presence of different UCPS/Ag₃PO₄ ratios (total amount of UCPS+Ag₃PO₄ = 10 mg): (a) 4 mg/6 mg, (b) 5 mg/5 mg, (c) 6 mg/4 mg and (d) 7 mg/3 mg. (e) Comparison of the decrease in concentration of CV dye as a function of 980 nm laser irradiation time in the presence of the above ratios.

CHAPTER 5

SIZE CONTROL AND IMPROVED AQUEOUS COLLOIDAL STABILITY OF SURFACE-FUNCTIONALIZED $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ BRIGHT PERSISTENT LUMINESCENCE NANOPARTICLES



5 SIZE CONTROL AND IMPROVED AQUEOUS COLLOIDAL STABILITY OF SURFACE-FUNCTIONALIZED $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ BRIGHT PERSISTENT LUMINESCENCE NANOPARTICLES

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Abstract

Near-infrared (NIR)-emitting persistent luminescent nanoparticles (PLNPs) especially those doped with chromium (Cr^{3+}), such as $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ (ZGO), have recently attracted considerable attention for diverse optical applications. The widespread use and promising potential of ZGO in different applications arise from their prolonged post-excitation emission (several minutes to hours for ZGO) that eliminates the need for continuous *in situ* excitation and the possibility of their excitation in different regions (X-rays and UV–Vis) of the electromagnetic spectrum. However, the lack of precise control over particle size/distribution and their poor water dispersibility and/or limited colloidal stability required for certain biological applications are the major bottlenecks that limit their practical applications. To address these fundamental limitations, herein, we have prepared OA-stabilized ZGO PLNPs with controlled size (7–12 nm, depending on the type of alcohol used in synthesis) and monodispersity. A further increase in size (8–21 nm), with a concomitant increase in persistent luminescence, could be achieved using a seed-mediated approach, employing the as-prepared ZGO PLNPs from the first synthesis as the seed and growing layers of the same material by adding fresh precursors. To remove the oleate groups from the surface and make the nanoparticles hydrophilic, two surface modification strategies were evaluated: modification with only poly(acrylic acid) (PAA) as the hydrophilic capping agent and modification with either PAA or cysteamine (Cys) as the hydrophilic capping agent in conjunction with BF_4^- as the intermediate surface modifier. These later surface modifications involving BF_4^- conferred long-term colloidal stability to the nanoparticles in aqueous media (60 days and longer), which is related to their favorable ζ potential values (-46 and +40 mV, for PAA/ BF_4^- and Cys/ BF_4^- , respectively). The proposed generalized strategy could be used to prepare different kinds of surface-functionalized PLNPs with control of size, hydrophilicity and colloidal

stability and enhanced/prolonged persistent luminescence for diverse potential applications.

5.1 Introduction

Chromium (Cr^{3+})-doped persistent luminescent nanoparticles (PLNPs) have attracted great research interest due to their long-lasting near-infrared (NIR) persistent emission after the cessation of the excitation light.^{1–9} Their long-lasting persistent emission around 700 nm, which falls within the first optical biological window [650–950 nm],^{10–15} presents high penetration into biological tissues, making them highly relevant for biological applications including bioimaging.^{16–25} ZnGa_2O_4 is considered one of the most appropriate host lattices for obtaining Cr^{3+} -doped persistent luminescent materials [such as $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ (ZGO)] because its UV-triggered emission spectrum overlaps well with the absorption range of Cr^{3+} ions, thus allowing a non-radiative resonant energy transfer between the host and Cr^{3+} .^{2,9,26–33}

Several strategies for the synthesis of ZGO particles have been reported, including solid-state, hydrothermal, solvothermal, and sol–gel methods.^{2,18,34–38} Each of these strategies offers its own advantages and limitations. For example, solid-state synthesis leads to the preparation of materials with strong emission and a longer luminescence lifetime (hours to days) but with a lack of size control and often bulk materials inadequate for bio-applications are obtained due to the high calcination temperatures used.

Alternatively, sol–gel and hydrothermal methods allow the synthesis of materials at lower temperatures; however, the formation of agglomerates during synthesis and in some cases, the need for post-synthesis calcination limit the use of these materials in biomedical applications.

In this context, solvothermal methods allow obtaining ZGO particles at relatively low temperatures and provide better control in size (down to nano-regime) and morphology and is thus relevant for preparing PLNPs for bio-applications. Such size/morphology control in the solvothermal approach is often achieved by coating the target nanoparticles with long-chain fatty acids (e.g., OA).^{39–42} The long hydrophobic chain of the fatty acid keeps the nanoparticles away from each other, thus hindering their agglomeration and lowering their degree of polydispersity. For instance, Srivastava *et al.*³⁹ obtained 6.1 nm ZGO nanoparticles through a biphasic (OA + toluene)

solvothermal route at 160 °C in an autoclave reactor. However, the small ZGO exhibited low emission intensity and a short luminescence lifetime, and post-synthesis calcination of the nanoparticles at 750 °C was necessary to improve their optical properties but with an inevitable loss of dispersibility and colloidal stability of the nanoparticles.

Using a higher temperature (210–220 °C) during the solvothermal step leads to the formation of uniform and monodisperse OA-capped PLNPs that do not require post-synthesis calcination.^{40–42} Furthermore, an increase in size following seed-mediated nanoparticle growth can improve their optical properties.⁴² The increase in PLNP size favors the storage and release of electrons captured by relatively deep traps, which leads to an increase in the luminescence lifetime.⁴²

Unfortunately, the nanoparticles synthesized using OA as a stabilizing agent are hydrophobic and thus irrelevant for biological applications involving aqueous media. Such bio-applications demand stable, water-dispersible hydrophilic PLNPs with reactive surface functional groups for subsequent conjugation with other relevant molecules.^{43–48} Fortunately, certain post-synthetic treatments and surface modification with different hydrophilic functional groups (–NH₂ and –COO, for instance) can be employed to allow easy bioconjugation with other target molecules and transform the hydrophobic surface of nanoparticles into a hydrophilic one, thus improving water dispersibility. For instance, Yeh *et al.*⁴⁰ carried out a surface modification of ZGO PLNPs through a silanization process with (3-aminopropyl)triethoxysilane and subsequent PEGylation using amine–PEG–acid. The resulting PLNPs were water dispersible, but their low ζ potential values (~20 mV) and large hydrodynamic size (132 nm) are not suitable for long-term colloidal stability.

It is clear that surface modification strategies are the most widely used post-synthetic treatments for transferring hydrophobic nanocrystals into aqueous media and different types of OA-capped nanomaterials, including quantum dots, UCNPs, iron oxides, TiO₂ nanorods, FePt nanocrystals and Bi₂S₃ nanorods have been successfully surface-modified with hydrophilic molecules or polymers via ligand exchange strategies.^{49–56} However, the conversion of OA-coated ZGO PLNPs to hydrophilic ZGO PLNPs using the surface modification strategies has largely remained understudied and deserves a better investigation.

With this aim, in this study, we report the solvothermal preparation of small (7–12 nm) ZGO PLNPs using OA as the stabilizing agent⁴¹ in the presence of different

alcohols. A further systematic increase in size (8–21 nm) and hence persistence luminescence response was achieved using a seed-mediated growth strategy.⁴²

Finally, we transformed the OA-capped ZGO into water dispersible PLNPs through surface modification with hydrophilic molecules (PAA or Cys, in conjunction with BF_4^-), based on widely used modification strategies for lanthanide-doped fluoride-based UCNPs, such as $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$,^{52,57–61} and performed a detailed study on the water-dispersibility, colloidal/gravitational stability in aqueous media and afterglow luminescence as a function of time. Fulfilling the essential requirements of PLNPs for bioapplications, PAA/ BF_4^- stabilized ZGO particles exhibited excellent colloidal stability and strong PL as discussed in the results and discussion section.

5.2 Experimental Section

5.2.1 Chemicals and materials

N,N-Dimethylformamide (DMF, $\geq 99\%$, ReagentPlus, Sigma-Aldrich), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich), poly(acrylic acid) (PAA, Mw ~ 2000 , product code 323,667, batch no. SLBZ5278, Sigma-Aldrich), nitrosyl tetrafluoroborate (NOBF_4 , Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), cysteamine hydrochloride (Cys, $\geq 98\%$ titration, Sigma-Aldrich), Vivaspin 6 100 kDa MWCO (Sigma-Aldrich), boric acid (99.5%, ACS reagent, Sigma-Aldrich), ethanol ($\geq 99.5\%$ ACS reagent, Sigma-Aldrich), diethylene glycol (99%, ReagentPlus, Sigma-Aldrich), KBr (for spectroscopy, Merck), methanol (GPR Rectapur, VWR Chemicals), 1-propanol (ACS reagent, Acros Organics), toluene (99.9%, Chromasolv, HPLC, Sigma-Aldrich), cyclohexane ($\geq 99.8\%$, HPLC grade, Fisher), chloroform ($\geq 99.8\%$, HPLC grade, Fisher), sodium hydroxide (NaOH, Panreac).

5.2.2 Synthesis of $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ PLNPs

ZGO PLNPs were synthesized following a solvothermal liquid–solid–solution method according to a literature report with some modifications.⁴¹ In a typical experiment, 5.3 g of OA and 14.2 g of alcohol [ethanol (ZGOE), methanol (ZGOM), or propanol (ZGOP)] were mixed at room temperature; then 8.6 g of NaOH solution (7% w/w) was added to it (Solution A) and left to stir for 1 h. Then, 2 mL of a solution containing 0.2975 g (1 mmol) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5475 g (2 mmol) of $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$,

and 0.0024 g (0.006 mmol) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Solution B) were added dropwise to Solution A under vigorous stirring. The resulting mixture was stirred for 30 min, subjected to solvothermal treatment for 16 h at 210 °C in a 50 mL Teflon-lined autoclave, and finally naturally cooled down to room temperature. ZGO PLNPs were precipitated by the addition of ethanol, collected by centrifugation at 5000 rpm, and washed following three cycles of redispersion (in cyclohexane)/precipitation (with ethanol)/centrifugation (at 5000 rpm). ZGOE, ZGOM and ZGOP PLNPs were redispersed in 5 mL cyclohexane (seed suspension) for further experiments. Furthermore, ZGOE PLNPs from the first synthesis (now denoted as ZGOE1) were used as seeds to prepare larger nanoparticles. Briefly, 1.25 mL of the above ZGOE1 PLNP seed suspension was added to 5.3 g of OA under constant agitation. Then, cyclohexane was evaporated by heating the mixture at 85 °C under an argon atmosphere. Next, 14.2 g of ethanol and 8.6 g of aqueous NaOH solution (7% w/w) were added to the above mixture (OA + seed suspension) followed by the addition of a solution containing 0.2231 g (0.75 mmol) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.4106 g (1.5 mmol) of $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and 0.0018 g (0.0045 mmol) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After the hydrothermal treatment and washing process as described above for ZGOE1, the size-grown nanoparticles were redispersed in 5 mL of cyclohexane and labeled as ZGOE2. The same procedure was applied to prepare still bigger PLNPs (ZGOE3) using the prepared ZGOE2 sample as the seed.

5.2.3 Surface modification of $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ PLNPs

To achieve dispersion of the hydrophobic OA-capped ZGO PLNPs in aqueous medium, the ZGOE3 PLNPs were either coated with PAA polymer by a one-step (direct) ligand exchange strategy [route (i), Figure 5.1] or a two-step ligand exchange strategy [route (ii), Figure 5.1]. In the latter case, the original OA molecules were replaced by BF_4^- ions using NOBF_4 in DMF and subsequently replacing the BF_4^- ions either with PAA polymer at pH 9 [route (ii-a)] or cysteamine molecules [route (ii-b)]. The samples were coded as ZGOE3-PAA, ZGOE3-B, ZGOE3-B-PAA, and ZGOE3-B-Cys after surface modifications with PAA [route (i)], NOBF_4 [route (ii)], NOBF_4/PAA [route (ii-a)], and NOBF_4/Cys [route (ii-b)], respectively.

5.2.3.1 One-step ligand exchange reaction

OA was replaced with a hydrophilic PAA polymer through a modified ligand exchange in diethylene glycol at 240 °C⁶² [route (i) in Fig. 5.1]. First, 1.25 mL of size-grown ZGOE3 were precipitated with ethanol, and after centrifugation, the precipitated particles were resuspended in 5 mL of toluene. This toluene suspension was then added to a three-necked flask containing 30 mL of diethylene glycol and 200 mg of PAA at 110°C, and the mixture was stirred for 1 h, followed by heating it at 140 °C and then 240 °C for 1 h and 1.5 h, respectively. The resulting solution was naturally cooled down to room temperature, and the PAA-coated ZGOE3 PLNPs were recovered by centrifugation at 13300 rpm and washed twice with water. Finally, the resulting hydrophilic PLNPs were dispersed in 10 mL of water and centrifuged at 2500 rpm for 3 min in order to get rid of larger agglomerates.

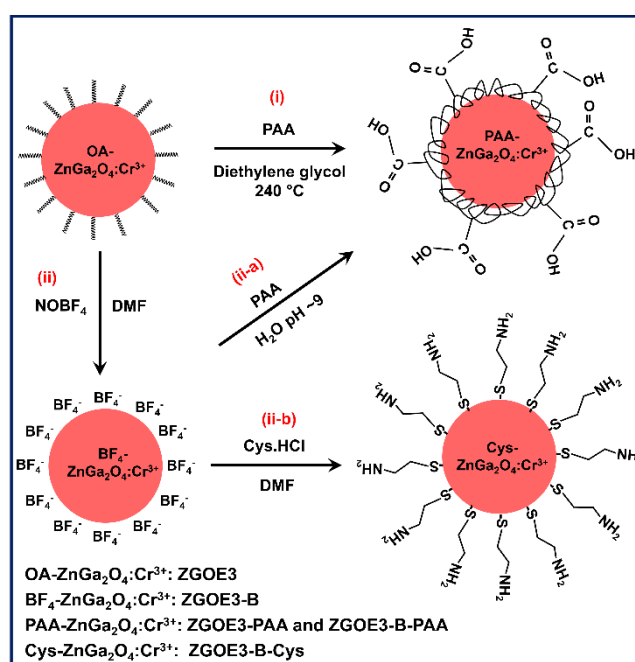


Figure 5.1 Schematic diagram of the surface modification of ZnGa₂O₄:Cr³⁺ through different strategies.

5.2.3.1 Two-step ligand exchange reaction

As shown in route (ii) of Figure 5.1, in this method, 3 mL of the ZGOE3 PLNP suspension in cyclohexane, 2 mL of cyclohexane, and 5 mL of DMF were mixed in a 20 mL glass vial at room temperature to form a two-phase system consisting of an upper cyclohexane layer containing the OA-coated ZGOE3 PLNPs and a bottom DMF layer. Subsequently, 180 mg of NOBF₄ was added under gentle agitation for 2 min. The resulting cloudy mixture was sonicated for 20 min, whereby a layer of hydrophilic

BF_4^- replaced the original hydrophobic OA-coating of the ZGOE3 PLNPs, resulting in the transfer of the nanoparticles from the upper cyclohexane layer to the bottom DMF layer. After allowing the mixture to stand for a few minutes, the upper cyclohexane layer was carefully removed. The BF_4^- -coated ZGOE3 (ZGOE3-B) PLNPs in the DMF layer were precipitated by adding an excess of chloroform and collected by centrifugation at 2500 rpm for 10 min. The samples were washed twice with 0.5 mL of DMF, precipitated by adding 5 mL of chloroform, and centrifuged at 2500 rpm for 10 min. The resulting ZGOE3-B PLNPs were then redispersed in 3 mL of DMF and centrifuged at 2500 rpm for 3 min to remove any larger agglomerates present. Next, the ZGOE3-B particles were modified with PAA (route ii-a) or cysteamine (route ii-b).

To prepare PAA-coated PLNPs (route ii-a), 2 mL of PAA solution (50 mg/mL at pH 9) were added to 1 mL of the above ZGOE3-B DMF suspension, left to stir for 20 min, and then centrifuged at 13300 rpm for 20 min. The resulting particles were then redispersed in 2 mL of water, transferred to a centrifuge filter [membrane: 100 kDa Mw cut off, polyethersulfone (PES), Vivaspin], diluted to 6 mL with water, and preconcentrated through filtration-centrifugation at 2000 rpm until a final volume of approximately 200 μL was obtained. The reservoir of the filter was immediately refilled with 6 mL of borate buffer (pH 9), and the pre-concentration of the diluted solution was repeated by filtration-centrifugation. The dilution-concentration sequence was repeated three times. Between each step, the remaining ZGOE3-B-PAA dispersion in the reservoir was vigorously shaken to prevent agglomeration. In the final step, the sample solution was dispersed in 2 mL of pH 9 borate buffer.

To prepare Cys-coated PLNPs (route ii-b), 2 mL of a freshly prepared solution of cysteamine hydrochloride in DMF (150 mg/mL) were added dropwise to 0.5 mL of the ZGOE3-B PLNPs dispersed in DMF. After 20 min of vigorous stirring, the mixture was centrifuged at 13300 rpm for 20 min. Two washing cycles were carried out by redispersing the Cys-coated ZGOE3 (ZGOE3-B-Cys) nanoparticles in 2 mL of water and centrifugation at 13300 rpm for 20 min. Finally, the ZGOE3-B-Cys particles were redispersed in 1 mL of water and centrifuged at 2500 rpm for 3 min to get rid of any larger agglomerates present.

5.2.4 Evaluation of colloidal and gravitational stability of $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ PLNPs in aqueous dispersion

To evaluate their colloidal/gravitational stability, 2 mL of aqueous dispersion of the surface-modified PLNP samples prepared above were kept undisturbed in quartz cuvettes for 60 days. After 60 days, the hydrodynamic diameters and photoluminescence spectra of each sample were measured and compared with the corresponding freshly prepared samples measured initially to investigate the possible changes due to sedimentation or agglomeration/sedimentation processes and correlate them with the gravitational and colloidal stability of the samples.

5.2.5 Characterizations

TEM images were obtained using a transmission electron microscope (CM20 Philips) operated at 200 kV and equipped with a LaB_6 electron source. The number-based particle size distributions of the PLNPs were determined from the TEM images (at least 300 nanoparticles were measured to obtain the histograms) using ImageJ software. Powder X-ray diffractograms (XRD) were acquired using a D8 Advance X-ray diffractometer (Bruker) (Bragg-Brentano geometry) employing Ni-filtered $\text{Cu K}\alpha$ X-ray radiation ($\lambda = 1.540 \text{ \AA}$). The dynamic light scattering (DLS) and ζ potential measurements were performed on a Zetasizer Nano ZS (Malvern). Fourier transform infrared (FTIR) spectra of the powder samples diluted in KBr Merck for spectroscopy and pressed in a pelletizer for 1 min under a pressure of 5 tons were obtained using a Thermo Scientific Nicolet iS5 FTIR spectrometer, set up with the iD1 Transmission Module. 4000–400 cm^{-1} scan, 32 background (BG) scan, 32 scan sample analyses, 2 cm^{-1} resolution. Emission and excitation spectra of the synthesized PLNPs were acquired at room temperature using a Horiba Jobin Yvon spectrofluorometer (Fluorolog-3 Model FL3-122) equipped with a Hamamatsu R-928 photomultiplier tube. For afterglow experiments, samples in powder or dispersion form were irradiated for 120 s either at the maximum excitation wavelength in the UV or using a white light emitting diode (LED), followed by room temperature measurement of the emission decay (697 nm) or the fully integrated emission band using a Horiba Jobin Yvon spectrofluorometer. For luminescence image acquisition, a CCD camera (iKon-M 934; Andor, Toulouse, France) equipped with a 35-mm focal length lens (LM35XC; Kowa, Toulouse, France), two bandpass filters (FF01-842/SP25; Semrock, Toulouse,

France), one short pass blocking edge filter (FF01-890/SP25; Semrock, Toulouse, France), and a dichroic filter (DMSP950R; Thorlabs, Toulouse, France) were used.

5.3 Results and discussion

5.3.1 Synthesis of $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ PLNPs

The as-prepared OA-coated ZGO PLNP samples synthesized in a mixture of OA, short-chain alcohol, and water⁴¹ exhibit certain changes in their morphology, particle size, crystallite size, as well as luminescent properties depending on the type of alcohol used in their synthesis (Figure 5.2). The PLNPs synthesized in the presence of propanol (ZGOP, Figure 5.2a) and ethanol (ZGOE, Figure 5.2b) present a quasi-spherical morphology and a unimodal distribution with average particle diameters of 7.1 and 7.7 nm, respectively. On the other hand, the sample prepared using methanol (ZGOM, Figure 5.2c) exhibits a bimodal distribution with the co-existence of small (10.6 nm) spheroidal and large (64.4 nm) triangular PLNPs.

The X-ray powder diffraction analysis in Figure 5.2d shows all the ZGO samples crystallized in the cubic ZnGa_2O_4 phase (PDF Card 00-038-1240), without the presence of any phase impurities. The crystallite sizes obtained from the XRD using Scherrer's equation are 6.9, 7.2, and 14.2 nm for ZGOP, ZGOE, and ZGOM, respectively, in agreement with the particle sizes calculated from the corresponding TEM images (Figure 5.2a–c).

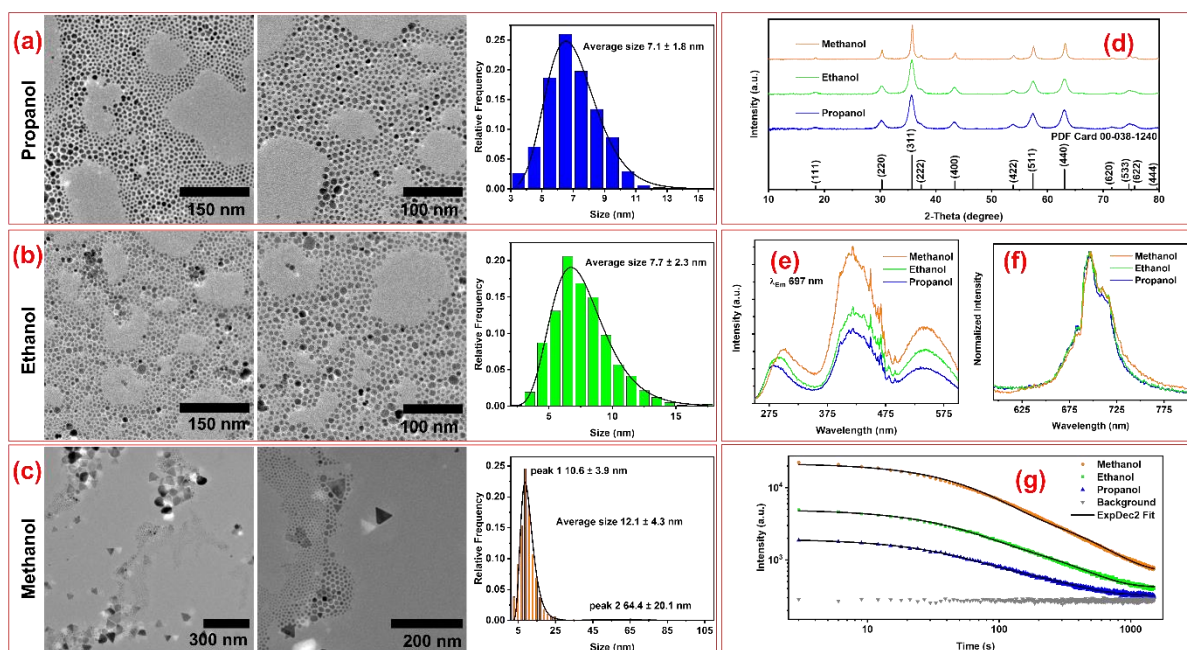


Figure 5.2 TEM images at two different magnifications and the corresponding size distribution extracted from the TEM images (a–c) of ZGO PLNPs prepared in the presence of propanol (a), ethanol (b), and methanol (c); the corresponding powder X-ray diffractograms (d), excitation spectra (e), normalized emission spectra ($\lambda_{exc} = 291$ nm) (f), and afterglow decay curve (g) of different ZGO PLNPs synthesized in the presence of different alcohols. The afterglow decay curve and emission and excitation spectra were obtained from the powder samples.

Figure 5.2e–g shows the photoluminescence excitation (e) and emission (f) spectra, as well as the afterglow luminescence decays corresponding to the emission at 697 nm after excitation for 2 min with a white LED and a delay of 20 s (g) for the samples synthesized in the presence of the three different alcohols. As can be observed from the excitation spectra (Figure 5.2e), the samples exhibit three characteristic broadbands, located in the UV (250–350 nm), blue (420 nm), and orange (540 nm) regions. The bands located around 420 and 540 nm are attributed to the spin-allowed transitions from the ground state [$^4A_2$ (^4F)] of Cr^{3+} ions in an octahedral symmetry to the excited states $^4T_1$ (^4F) and $^4T_2$ (^4F), respectively.^{2,63–66} The other band in the UV region results from a partial overlapping of the ZGO host matrix bandgap edge with the spin-allowed transition from the ground state [$^4A_2$ (^4F)] to the excited state [$^4T_1$ (^4P)] of Cr^{3+} ions.^{2,29,35,67} It can be noted that ZGOM and ZGOE samples present a higher intensity of the excitation peaks, probably due to the larger particle size accompanied by the little increase in crystallinity, as observed from the XRD (Figure 5.2d) and TEM images (Figure 5.2c). Interestingly, the change of alcohol (from propanol to methanol) also caused a redshift of the UV band, attributed to the decrease

in energy between the valence and conduction bands of ZGO associated with an increase in crystal size.

Analyzing the emission characteristics, the emission spectra (Figure 5.2f) ($\lambda_{\text{exc}} = 291$ nm) show a band in the NIR-I region centered around 697 nm, which is assigned to the spin-forbidden ^2E_g (^2G) $\rightarrow$ $^4A_{2g}$ (^4F) transition of Cr^{3+} ions in an octahedral symmetry.^{65,66,68}

All the samples exhibit a similar decay profile (Figure 5.2g) which can be best fitted with a bi-exponential decay function (ExpDec2), indicating two different lifetimes according to the decay ramp (see Table 5.S1). Although the ZGOM sample apparently has a higher energy storage capacity, all further experiments in this work were performed using the ZGOE sample that exhibits a higher degree of monodispersity and better energy storage capacity than the ZGOP sample.

To prepare slightly larger particles with enhanced luminescent properties, we employed the small (7.7 nm) ZGOE (now denoted as ZGOE1) nanoparticles as seeds to synthesize larger (12 nm) ZGOE2 nanoparticles, and the resulting ZGOE2 was subsequently used as seeds to prepare still larger nanoparticles (ZGOE3) (Figure 5.3a,b, and Table 5.S2). However, the ZGOE3 sample showed a bimodal size distribution (9.5 and 24 nm), suggesting that crystal growth is accompanied by fresh nucleation. The gradual increase in the size of the nanoparticles as a result of seed-mediated growth was also confirmed by measurements of the hydrodynamic sizes of ZGOE1, ZGOE2, and ZGOE3 samples (Figure 5.3c and Table 5.S2).

From the results summarized in Table 5.S2, it can be seen that the hydrodynamic diameters measured by DLS (19.1, 26.1, and 35.6 nm, respectively, for ZGOE1, ZGOE2, and ZGOE3) are larger than the respective particle sizes obtained from the respective TEM images. The difference arises from the fact that while the TEM images show the sizes of bare core particles, the DLS measures the hydrodynamic diameters, consisting of the core particles covered with oleate molecules as well as solvent molecules present around the coated particles. Nevertheless, the relatively low values of the polydispersity index (PDI) in Table 5.S2 suggest a homogeneous size distribution and a satisfactorily low degree of agglomeration.

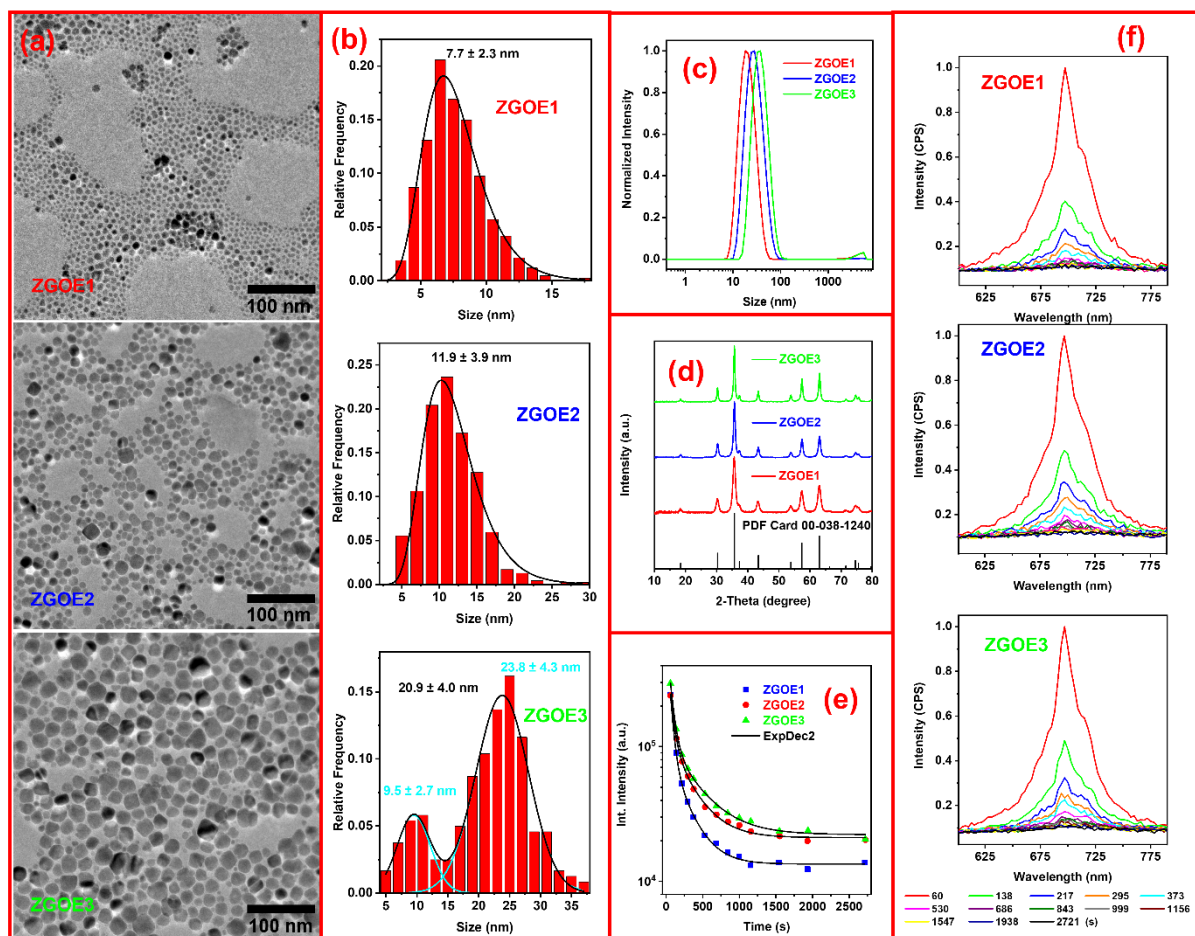


Figure 5.3 TEM images (a) and the corresponding size distribution calculated from TEM images (b), solvodynamic particle size distribution in cyclohexane (c), powder XRD patterns (d), PL decay curves in cyclohexane, (e) and afterglow luminescence spectra (f) of ZGO PLNPs with different sizes obtained using seed-mediated growth process.

Phase analysis by XRD (Figure 5.3d) confirmed that, regardless of size, all ZGO PLNPs crystallized in the cubic ZnGa_2O_4 phase (PDF Card 38–1240), without impurities. Furthermore, the crystallite sizes calculated from the XRD of ZGOE1, ZGOE2, and ZGOE3 samples were 7.2, 10.4, and 13.9 nm, respectively, which also confirms the successive and successful growth of the crystals by the seed-mediated growth process.

Next, the samples dispersed in cyclohexane were irradiated at 291 nm (λ_{exc}) for 120 s and, after a delay time of 25 s, the afterglow spectra (601–790 nm) were recorded at different time intervals (Figure 5.3f). The integrated intensities (Figure 5.3e) obtained from the afterglow spectra (Figure 5.3f) show a slower decay for the larger particles (ZGOE2 and ZGOE3), which can be attributed to a decrease of the defects/interferences of the surface states for the larger nanoparticles, in agreement with the observations made by Gao M. et al.⁴² In fact, as the nanocrystal size increased

from 8 to 21 nm, the lifetime (t) obtained by fitting the data to a biexponential decay function increased from 45 to 56 s (t_1) for the first decay and from 233 to 375 s (t_2) for the second decay (Table 5.S3), thus demonstrating the positive impact of the increase in particle size, via seed-mediated growth, on the luminescent properties of the PLNPs.

Similarly, after the excitation of the ZGO samples of different sizes in cyclohexane for 120 s with a white LED and a delay time of 5 s, the afterglow emission (697 nm) decay curves were recorded (Figure 5.S1). As a higher emission intensity was observed for samples with larger particle sizes (ZGOE3 and ZGOE2), it can be safely inferred from Figure 5.S1 that an increase in nanoparticle size allows for higher energy storage of visible light. Furthermore, the ZGOE3 and ZGOE2 samples continued to emit for a longer time compared to the ZGOE1 sample, which again supports the importance of increasing nanoparticle size by seed-mediated growth in improving the optical properties of ZGO PLNPs.

5.3.2 Surface modification of $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ PLNPs

Since the surface characteristics of nanomaterials determine their *in vitro* and *in vivo* biocompatibility, it is inevitable to convert the hydrophobic nanoparticles into hydrophilic ones *via* surface modification and thus ensure their adequate dispersion in aqueous solutions or biological buffers. Furthermore, the hydrophilic nanoparticles must present high stability in aqueous dispersion to avoid their agglomeration and sedimentation.^{43–48} To this end, surface modifications of ZGOE3 PLNPs were performed through different ligand exchange strategies, as schematically illustrated in Figure 5.1 and discussed in the experimental section.

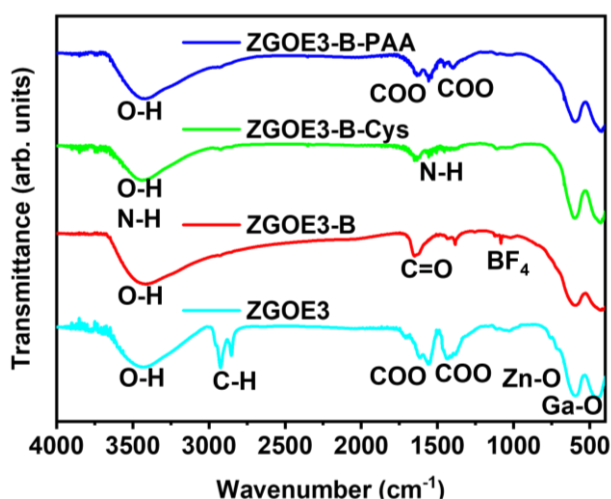


Figure 5.4 FTIR spectra of ZGOE3 before and after surface modifications.

We used FTIR spectroscopy to confirm the successful surface modification of the ZGOE3 PLNPs. The FTIR spectra ($400\text{--}4000\text{ cm}^{-1}$) of the ZGOE3 PLNPs coated with OA, BF_4^- , Cys, and PAA are presented in Figure 5.4. Most importantly, a comparison of the FTIR spectra of ZGOE3 and ZGOE3-B shows that the intensity of characteristic C–H stretching vibrations ($2800\text{--}3000\text{ cm}^{-1}$) belonging to the oleate anions was markedly reduced after NOBF_4 treatment. Additionally, the appearance of a new peak (1084 cm^{-1} , attributed to BF_4^- anions) and the absence of characteristic vibrational modes ($\sim 2100\text{--}2200\text{ cm}^{-1}$) of NO^+ cations after surface modification reactions confirm a successful ligand exchange (oleate with BF_4^- anions) process.^{52,69,70} The vibrational bands around 1435 and 1554 cm^{-1} in the spectrum of ZGOE3 are attributed to the symmetric and asymmetric stretching vibrations, respectively, of carboxylic groups ($-\text{COO}$) present in the OA molecules. The broadband observed around 3435 cm^{-1} comes from the stretching vibrations of the hydroxyl groups ($-\text{OH}$) of adsorbed water molecules. The new peak around 1650 cm^{-1} for ZGOE3-B can be attributed to stretching vibrations of the carbonyl group of DMF solvent molecules.⁵² The metal–oxygen signals are observed around 595 cm^{-1} and 445 cm^{-1} , for Zn–O and Ga–O, respectively.⁷¹ In the same way, the absence of the peak corresponding to BF_4^- ions at 1084 cm^{-1} in the FTIR spectra of ZGOE3-B-Cys and ZGOE3-B-PAA confirms the successful modification of ZGOE3-B nanoparticles with Cys and PAA, respectively. The band beyond 3000 cm^{-1} in the FTIR spectrum of ZGOE3-B-Cys is due to O–H (H_2O) and/or N–H ($-\text{NH}_2$) stretching vibrations. Furthermore, the absence of a band at approximately $2340\text{--}2360\text{ cm}^{-1}$ ($-\text{SH}$ group vibration) and the presence of a small band near 1560 cm^{-1} suggest the presence of Cys on the surface of ZGOE3-B-Cys PLNPs bound through the $-\text{SH}$ group.^{72–75} On the other hand, the band beyond 3000 cm^{-1} in the FTIR spectrum of ZGOE3-B-PAA can be attributed to the vibrations of the hydroxyl groups of the adsorbed water molecules and those present in the PAA polymer. Moreover, the peaks around 1456 and 1556 cm^{-1} in the spectrum of ZGOE3-B-PAA are attributed to the symmetric and asymmetric stretching vibrations of $-\text{COO}$ groups of PAA, confirming the coating of PLNPs by PAA polymer.

The TEM images in Figure 5.5 show that ZGOE3 PLNPs retained their shape after surface modification with the different ligands. As shown in Figure 5.5b, large nanoparticle agglomerates were obtained after surface modification with only PAA (ZGOE3-PAA) through the one-step strategy (route i, Figure 1), while all other surface modifications allowed an optimal dispersion of the nanoparticles (Figure 5.5c–e).

These observations were also confirmed by measuring the corresponding hydrodynamic diameters in terms of intensity (Figure 5.5f) and number (Figure 5.S2) size distribution, summarized in Table 5.S4, which shows that the samples obtained by the two-step ligand exchange strategy (route ii, Figure 5.1) show smaller hydrodynamic sizes and narrower size distributions. Moreover, the ZGOE3-PAA sample presented a bimodal hydrodynamic size profile and a significantly higher PDI value.

Finally, the luminescence decay curves of ZGOE3-B-Cys and ZGOE3-B-PAA were measured (Figure 5.6) in the same manner as described above for the OA-coated ZGO PLNPs. The hydrophilic PLNPs retain their PL in polar aqueous media, and only a slight decrease in its duration is seen, which may be related to the difference in solvent/media or the presence of a capping agent. In fact, Cys molecules are smaller and may not provide the nanoparticles with the same protection as larger OA molecules or PAA polymers against interactions with the solvent, causing energy dissipation on the surface by interactions with O–H groups of water molecules.

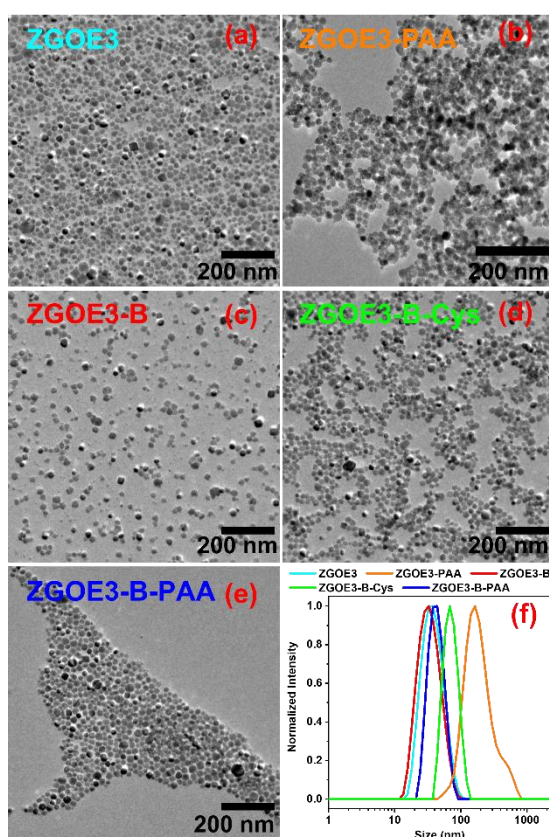


Figure 5.5 TEM images (a-e) and corresponding hydro(solvo)dynamic diameter in terms of intensity size distribution of ZGOE3 PLNPs before and after surface modifications. Solvent: cyclohexane (a), water (b,d,e), and DMF (c).

On the other hand, the decay of the afterglow intensity of the ZGOE3-B-Cys powder sample, after irradiation for 120 s with a white LED, was also followed from luminescence images (Figure 5.7). The luminescence images (Figure 5.7a) and the corresponding mean intensity values (Figure 5.7b) for the region of interest extracted from the luminescence images show the possibility of detection up to and beyond 1500 s. The luminescence decay fitted to a biexponential curve ($t_1 = 74$ s and $t_2 = 418$ s) again suggests that there are at least two pathways for the radiative recombination of charge carriers in the long-lasting luminescence of synthesized nanoparticles, independent of the capping molecules that cover their surface.

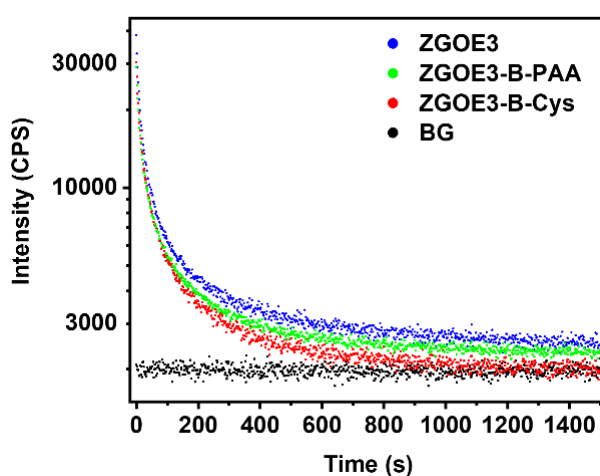


Figure 5.6 Afterglow decay curves of ZGOE3 (in cyclohexane), ZGOE3-B-PAA (in buffer pH 9), and ZGOE3-B-Cys (in water). Excitation: 120 s with a white LED; post-irradiation delay of 5 s.

Additionally, a luminescence image of a ZGOE3-B-Cys sample in water was recorded at a post-illumination interval of 40 s (Figure 5.7c). The detectable signal suggests the possibility of using these nanoparticles for obtaining luminescence images (bioimaging) without any significant autofluorescence signal, which is attributed to the ability of these nanoparticles to function as “optical batteries” storing excitation energy and, subsequently, emitting NIR photons for a long post-excitation period.

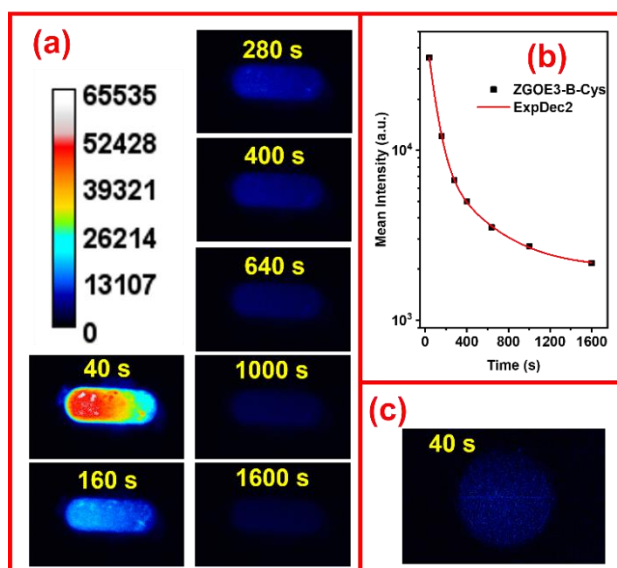


Figure 5.7 Luminescence images recorded at different post-illumination intervals (a) and the decay of the corresponding mean intensity values of the region of interest extracted from the luminescence images as a function of time (b) of ZGOE3-B-Cys in powder. Luminescence image of ZGOE3-B-Cys in water recorded 40 s postexcitation (c). The irradiation was performed with a white LED for 120 s. The luminescence images against a black BG are represented with a false color, where the color indicates the scale of luminescence intensity from black to white.

5.3.3 Colloidal and gravitational stability of $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ PLNPs in aqueous medium

As mentioned above, the stability of hydrophilic nanoparticles in aqueous dispersion or buffer solutions is another important prerequisite for their practical use in biological applications. The gravitational and colloidal stability of the nanoparticles was evaluated by measuring their photoluminescence emission spectra and hydrodynamic size distribution at different times (days) after their preparation. Nanoparticles with poor gravitational stability and poor colloidal stability are prone to sedimentation and agglomeration, respectively, in a less defined manner (Figure 5.8a). On the other hand, nanoparticles with good gravitational and/or colloidal stability do not undergo sedimentation in aqueous suspension (Figure 5.8a) and hence no changes in their emission spectra over time.

Figure 5.8b shows the emission spectra and the integrated emission intensity of the aqueous dispersions of ZGOE3-PAA, ZGOE3-B-PAA, and ZGOE3-B-Cys after 0, 10, 15, 20, 30, and 60 days, without any external disturbances (no shaking). A comparison of the emission band and the corresponding integrated emission intensity of different samples suggests the best, good, and poor gravitational stability of ZGOE3-B-PAA, ZGOE3-B-Cys, and ZGOE3-PAA nanoparticles, respectively (Figure 5.8b). For instance, the decrease in the emission band and the corresponding integrated

emission intensity as a function of time is faster/larger for ZGOE3-PAA nanoparticles (within 10–15 days), small for ZGOE3-B-Cys nanoparticles, and very slight for the ZGOE3-PAA sample after the same period, in agreement with the results of the DLS analysis (Figure 5.8c).

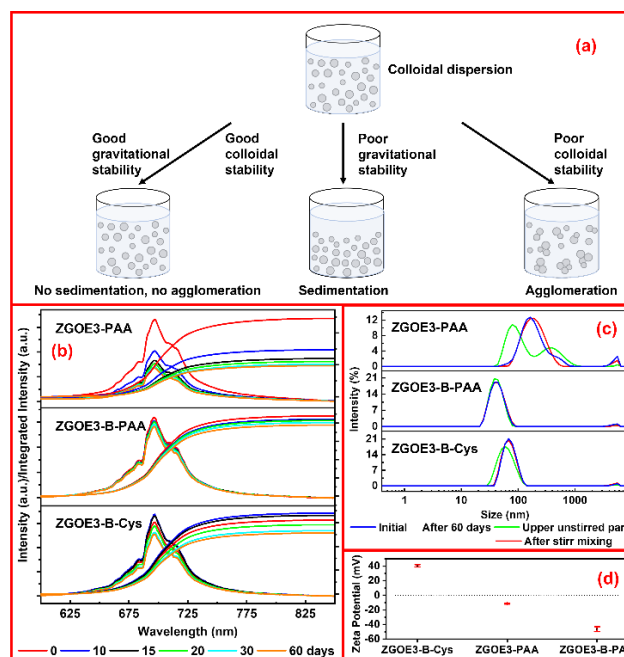


Figure 5.8 Schematic diagram of the behavior of a colloidal dispersion according to its colloidal and gravitational stability (a). Emission spectra and their corresponding integrated intensities of the unstirred colloidal dispersions of the samples on different days (b). Hydrodynamic size in terms of intensity size distribution of the hydrophilic ZGO samples: as prepared (blue line) and after 60 days of standing without shaking (green line), followed by stir mixing (red line) (c). ζ potential values of ZGOE3-B-Cys, ZGOE3-PAA, and ZGOE3-B-PAA samples (d).

DLS measurements in terms of the intensity size distribution (Figure 5.8c) and number size distribution (Figure 5.S3) of the aqueous dispersions after 60 days of undisturbed storage (without shaking) showed no significant changes in the hydrodynamic diameter of the ZGOE3-B-PAA sample, demonstrating its good colloidal and gravitational stability and hence a reasonably stable luminescence response (Figure 5.8b). These observations and the high stability of the ZGOE3-B-PAA sample are related to its high ζ potential value (−46 mV) (Figure 5.8d).

Concerning the ZGOE3-B-Cys sample, there was a decrease in the hydrodynamic diameter in terms of intensity size distribution (Figure 5.8c) from 72 to 63 nm and in terms of number size distribution (Figure 5.S3) from 54 to 42 nm, which agrees with the previous results of the emission spectra and the corresponding integrated intensities in Figure 5.8b, showing that indeed the sample has slightly less gravitational stability than the ZGOE3-B-PAA sample.

On the other hand, the ZGOE3-PAA sample exhibits a lower ζ potential value (-11 mV, implying limited colloidal stability) (Figure 5.8d) and hence a multimodal distribution/polydispersity of its hydrodynamic size (Figure 5.8c). For this sample, the bimodal hydrodynamic diameters (intensity size distribution) change significantly when the as-prepared (184 and 462 nm) sample is stored for 60 days (95 and 408 nm). Similarly, a change in hydrodynamic size in terms of the number size distribution (Figure 5.S3) occurs, with the sizes being 58 and 108 nm for the initial sample and 60 nm for the sample after 60 days, confirming that this sample has poor colloidal and gravitational stability.

The observed changes in hydrodynamic diameters over time could be related to gravitational stability (sedimentation) or colloidal stability (agglomeration followed by sedimentation). To verify which one of these factors plays a prominent role, we measured the hydrodynamic diameters of the 60 days old samples after mechanical shaking (Figure 5.8c, red lines). From Figure 5.8c, the ZGOE3-B-PAA sample (60 days) after simple shaking (red line overlaid with the blue line) exhibits the same size distribution as that of the initially prepared one (blue line), further testifying its high dispersion stability. Similarly, the 60 days old ZGOE3-B-Cys after simple mechanical shaking (red line overlaid with the blue line) exhibits the same size as that of the initially prepared sample, suggesting that the change in hydrodynamic size distribution over 60 days' was simply due to sedimentation and not agglomeration-sedimentation or corrosion of the nanoparticles. Such excellent colloidal stability and the relatively good gravitational stability of ZGOE3-B-Cys sample are again related to the high ζ potential value ($+40$ mV) (Figure 5.8d). On the contrary, ZGOE3-PAA sample with lower colloidal stability (ζ potential = -11 mV) could not resume its initial hydrodynamic size.

5.4 Conclusions

OA-coated hydrophobic Cr^{3+} -doped ZGO PLNPs with a controlled size 7–21 nm were successfully synthesized using a solvothermal/seed-mediated growth approach. An increase in PLNP size led to enhanced PL response of the particles. Subsequently, the hydrophobic ZGO PLNPs with larger sizes and better afterglow luminescence properties were transformed into water-dispersible hydrophilic ones employing two distinct surface/ligand-modification strategies (one step or two steps), the best of which involved replacement of the hydrophobic OA first with BF_4^- ions and then hydrophilic

polymer (PAA) or molecules (Cys), which exhibited long persistence luminescence and long-term colloidal/gravitational stability (60 days and beyond), as a result of their favorable ζ potential values. The resulting PAA- or Cys-coated ZGO PLNPs offer several advantages relevant to biological applications, including (i) excellent hydrophilicity/water dispersibility, (ii) adequate colloidal/gravitational stability in aqueous media (60 days or longer), (iii) good persistence luminescence, and (iv) the availability of surface functional groups (carboxylic groups of PAA and amine groups of Cys) for subsequent functionalization/anchoring with other functional molecules. The proposed generalized strategy, which satisfies several prerequisites in relation to biological/biomedical applications of PLNPs, could be used to prepare different kinds of surface-functionalized PLNPs with control of size, hydrophilicity, and colloidal stability and enhanced/prolonged PL for diverse potential applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.2c02871>

Details of fitting parameters of luminescence decay curves, nanoparticle size tables, afterglow emission decay curves, hydrodynamic sizes in terms of number size distribution (PDF)

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Author Contributions

Y.E.S.-C.: conceptualization, methodology, investigation, visualization, writing—original draft, and writing—review and editing. D.N.: conceptualization and writing—review and editing. S.U.: conceptualization, visualization, and writing—review and editing. R.M.: conceptualization. Q.Z.: methodology. S.J.L.R.: writing—review and editing, supervision, acquisition of funds, and project management. M.V.: conceptualization, methodology, writing—review and editing, supervision, acquisition of funds, and project management. All authors have given their approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information

Size control and improved aqueous colloidal stability of surface-functionalized $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ bright persistent luminescence nanoparticles

Table 5.S1 Fitting of the experimental afterglow luminescence (697 nm) decay spectra with a bi-exponential decay function (ExpDec2) and the resulting lifetimes (t_1 and t_2) values for the ZGO samples synthesized in the presence of the three different alcohols. The powder samples were excited for 120 s with a white LED.

Model			ExpDec2		
Equation			$y = A1 \cdot \exp(-x/t_1) + A2 \cdot \exp(-x/t_2) + y0$		
	y0	A1	t_1 (s)	A2	t_2 (s)
Propanol	326 ± 1	1053 ± 12	40 ± 1	576 ± 12	237 ± 5
Ethanol	419 ± 2	3050 ± 20	44 ± 1	1527 ± 19	275 ± 4
Methanol	684 ± 1	16698 ± 102	55 ± 1	4424 ± 57	367 ± 5

Table 5.S2 Comparison of the size obtained from TEM images, the hydrodynamic diameter in terms of intensity size distribution obtained by DLS, and the crystallite size obtained from the X-ray diffractograms of the ZGOE1, ZGOE2, and ZGOE3 nanoparticles.

Sample	TEM (nm)	DLS (nm) (PDI)	Crystallite size (nm)
ZGOE1	7.7	19.1 (0.12)	7.2
ZGOE2	11.9	26.1 (0.13)	10.4
ZGOE3	20.9	35.6 (0.16)	13.9

Table 5.S3 Fitting of the experimental afterglow integrated intensity decay curves with a biexponential decay function (ExpDec2) and the resulting lifetime (t_1 and t_2) values for ZGOE1, ZGOE2, and ZGOE3 samples in cyclohexane. The integrated intensities were calculated from the emission spectra (601 – 790 nm) of the samples obtained at different post-excitation ($\lambda_{\text{exc}} = 291$ nm) times intervals.

Model			ExpDec2		
Equation			$y = A1 \cdot \exp(-x/t_1) + A2 \cdot \exp(-x/t_2) + y0$		
	y0	A1	t_1 (s)	A2	t_2 (s)
ZGOE1	13435 ± 449	615012 ± 23668	45 ± 2	86415 ± 9869	233 ± 20
ZGOE2	21110 ± 742	405408 ± 17076	54 ± 4	103155 ± 11246	289 ± 26
ZGOE3	22244 ± 665	556665 ± 11735	56 ± 2	94241 ± 5375	375 ± 23

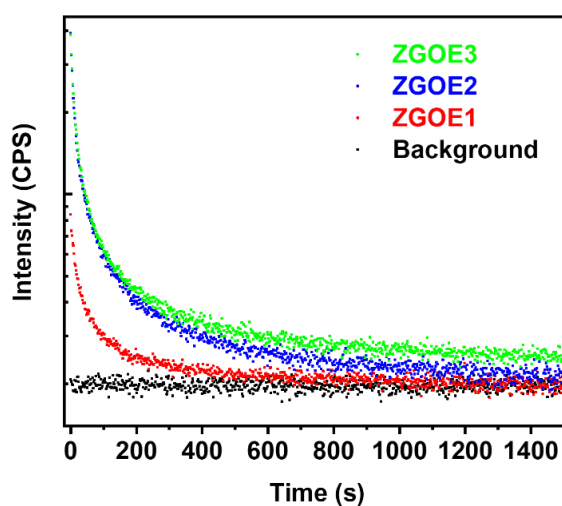


Figure 5.S1 Afterglow emission (697 nm) decay curves of ZGOE1, ZGOE2, and ZGOE3. Excitation with a white LED for 120 s, 5 s delay.

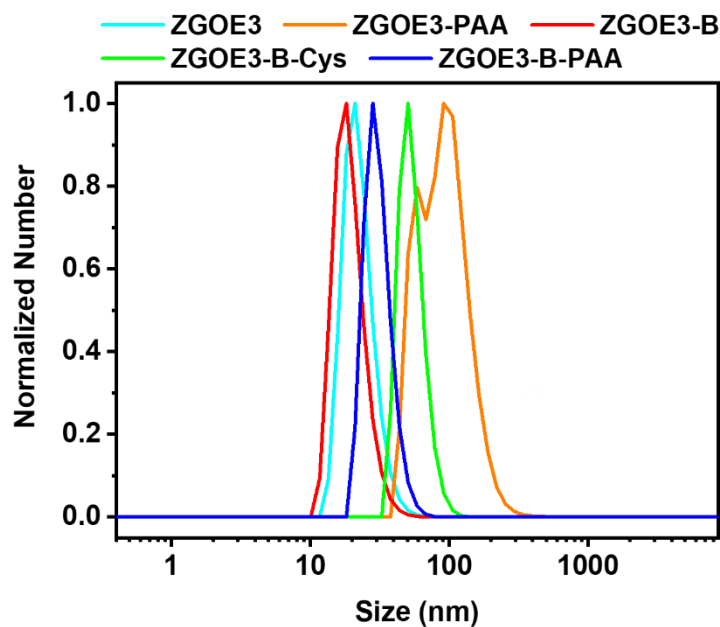


Figure 5.S2 Hydrodynamic sizes in terms of number size distribution of ZGOE3 sample before and after surface modifications.

Table 5.S4 Hydrodynamic diameter in terms of intensity and number size distribution obtained by DLS.

Sample	Intensity size distribution (nm)	Number size distribution (nm)	PDI
ZGOE3	35.6	22.7	0.16
ZGOE3-PAA*	245 (184 and 462)	(58 and 108)	0.49
ZGOE3-B	31.2	19.5	0.14
ZGOE3-B-Cys	72.0	54.2	0.18
ZGOE3-B-PAA	43.4	31.1	0.19

* ZGOE3-PAA sample presented a bimodal size distribution profile with an average diameter of 245 nm. For this sample, the values in parentheses are the corresponding peaks of the two size populations.

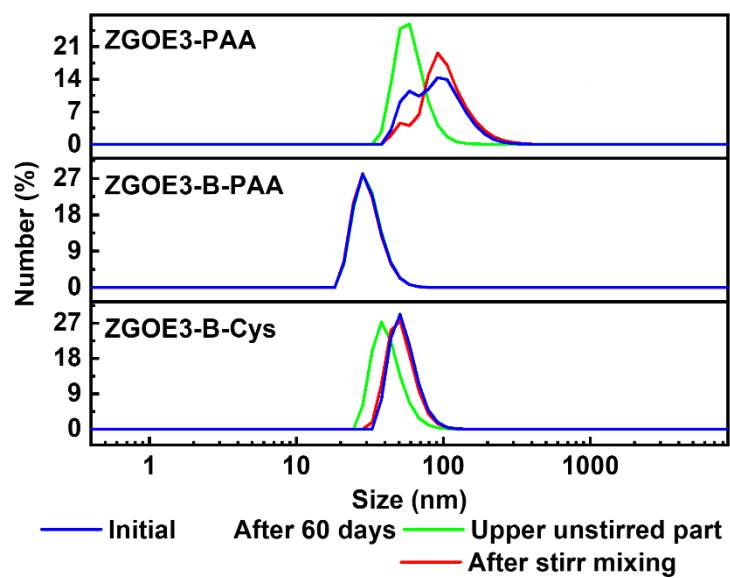
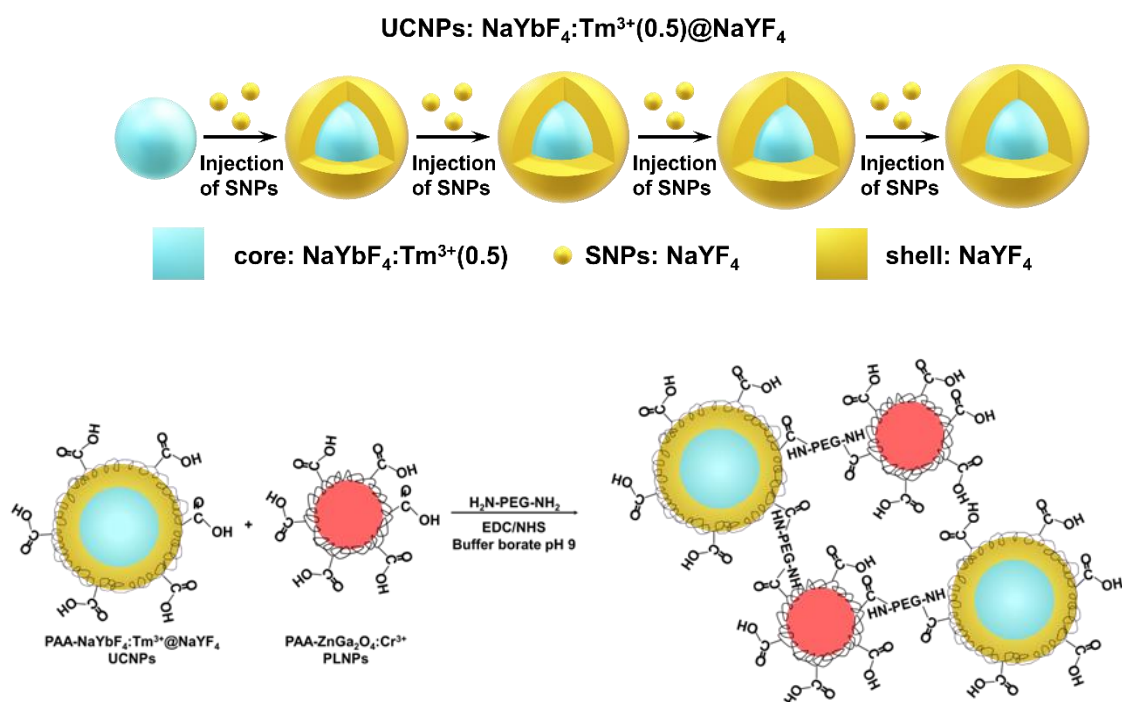


Figure 5.S3 Hydrodynamic sizes in terms of number size distribution of the samples before and after 60 days of undisturbed storage (no shaking). The green and red lines in the ZGOE3-B-PAA plots are overlapped by the blue line.

CHAPTER 6

COUPLING OF $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ UPCONVERTING NANOPARTICLES WITH $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ PERSISTENT LUMINESCENCE NANOPARTICLES



Control of the lanthanide content, size and shell thickness of core/shell UCNPs ✓

Surface hydrophilization – functional groups ✓

Coupling reactions of UCNPs with PLNPs ✓

6 COUPLING OF NaYbF₄:Tm³⁺@NaYF₄ UPCONVERTING NANOPARTICLES WITH ZnGa₂O₄:Cr³⁺ PERSISTENT LUMINESCENCE NANOPARTICLES

Abstract

Ln³⁺-based UCNPs and Cr³⁺-doped PL materials have unique optical properties that make them attractive for a wide variety of biomedical applications. Even more interesting, the coupling of these two types of materials to obtain a system that presents UC e PL (UC-PL) could allow to take advantage of the optical properties of both simultaneously, such as NIR excitation/UV-Vis emission of the UCNPs, and long-lived NIR afterglow emission of the Cr³⁺-doped PL materials, which in turn could drastically decrease the BG and autofluorescence signals, as well as allowing reactivation using NIR irradiation with considerably high penetration into biological tissues. However, there are some problems that limit the obtaining and application of UC-PL systems, including: i) The low efficiency of UCL emission in the UV-Vis region of small UCNPs, necessary for the activation of PL materials. ii) Obtaining hydrophilic PL materials that fulfill the fundamental prerequisites for bioapplications. iii) The difficulty in chemically coupling two types of materials avoiding the formation of large agglomerates.

To address the first problem, in this work core/shell UCNPs with high concentration of Yb³⁺ as sensitizing agent were synthesized, and the shell thickness was evaluated to improve the UV-Vis emission properties. The second problem was addressed in the Chapter 5 of this thesis. To address the third problem, the coupling of UCNPs and PLNPs based on EDC/NHS coupling chemistry was investigated here.

The results reported in this thesis show some progress regarding obtaining UC-PL systems; however, new conditions for coupling and the energy transfer between UCNPs and PLNPs must be investigated to guarantee potential applications.

6.1 Introduction

In recent years, several researchers focused their interests on combining UCNPs with PLNPs to obtain UC-PL systems for medical and biological applications, due to their interesting optical properties.¹⁻⁴ In this way it has been possible to achieve a decrease in the exposure time of the tissue to the excitation radiation and, additionally, decrease the autofluorescence background signal compared to the particular use of

UCNPs, that is due to the unique ability of PLPs to work as optical batteries (*i.e.* storing excitation energy) and emitting lower energy photons for a long time after turning off the external excitation light.^{5,6}

The characteristics resulting from the combination of UCNPs with PL materials may overcome several drawbacks related to different bioapplications such as luminescence bioimaging and photodynamic therapy.

For example, it allows obtaining a sequence of luminescence images for several minutes to hours after turning off the external excitation, which completely suppresses the background fluorescence signal, further improving the signal-to-noise ratio.

In addition, the NIR absorption of UCNPs and the NIR afterglow emission of some Cr³⁺-doped gallates⁷ increases the interest of their combination because both are found in the first biological window, that is, in a region of low absorption by biological tissues, remarkably increasing the depth of detection and improving therapeutic effectiveness.

Moreover, the possibility of re-activation of the UC-PL system through the excitation of UCNPs under NIR irradiation, which can emit photons with the energy necessary to excite the PLNPs, thus being recharged. Therefore, multiple cycles of luminescent imaging for diagnosis, or prolonged treatment using photodynamic therapy can be carried out.¹⁻⁴

However, most of the work published so far on the subject uses considerably large UC materials (several micrometers in size), and PL materials obtained after calcination at high temperatures.^{8,9} These do not fulfill the fundamental prerequisites for bioapplications, since, for example, present poor hydrophilicity and limited colloidal stability in aqueous media, which makes their real use in bioapplications practically impossible.

There are many well-known methodologies to obtain small-sized Ln³⁺-based UCNPs that meet fundamental prerequisites for bioapplications.¹⁰⁻¹³ Nevertheless, the concentration of Yb³⁺, sensitizer, usually used for doping the UCNPs is not high enough to capture/absorb the excitation energy efficiently.

On the contrary, although a high concentration of Yb³⁺ leads to a higher absorption of excitation photons, it also increases energy migration towards the surface defects of small nanoparticles, which consume the excitation energy and decrease the UC efficiency for UV-Vis photon emission.¹⁴ Therefore, it is necessary to coat the

nanoparticles with inactive layers of different thicknesses (e.g., NaYF₄) to improve the emission properties.^{15–18}

For this reason, in this work, small core/shell UCNPs with improved UC properties were first obtained. A high concentration of Yb³⁺ was used and different shell thicknesses were investigated to avoid the previously mentioned problems.

On other hand, the PLNPs that meet the prerequisites for bioapplications can be obtained through the synthesis-surface modification approach reported in Chapter 5 of this thesis.

Finally, the fabrication of the UC-PL system could be carried out by obtaining a membrane containing the two types of materials,² or by physical mixing of the powders, which are immediately ground in a ball mill.¹⁹ However, some applications require that the nanoparticles be in aqueous dispersion. Therefore, in this work, the coupling of the synthesized UCNPs and PLNPs was investigated in aqueous media, taking advantage of the carboxylic and/or amino functional groups present on the surface of the nanoparticles after surface modification. Coupling reactions were performed based on well-known EDC/NHS coupling chemistry for amide functional group formation.

6.2 Experimental procedures and methodologies

6.2.1 Materials and methods

Yttrium(III) acetate hydrate (99.9%, Sigma-Aldrich), Ytterbium(III) acetate tetrahydrate (99.9%, Sigma-Aldrich), Thulium(III) acetate hydrate (99.9%, Sigma-Aldrich), N,N-Dimethylformamide (DMF, ≥99%, ReagentPlus, Sigma-Aldrich), Zn(NO₃)₂·6H₂O (Sigma-Aldrich), Ga(NO₃)₃·xH₂O (99.9%, Sigma-Aldrich), Cr(NO₃)₃·9H₂O (Sigma-Aldrich), poly(acrylic acid) (PAA, Mw 1800, Sigma-Aldrich), nitrosyl tetrafluoroborate (NOBF₄, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), cysteamine hydrochloride (Cys, ≥98% titration, Sigma-Aldrich), Vivaspin 6 100 kDa MWCO (Sigma-Aldrich), boric acid (99.5%, ACS reagent, Sigma-Aldrich), ethanol (≥99.5% ACS reagent, Sigma-Aldrich), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, ≥98%, Sigma-Aldrich), poly(ethylene glycol) bis(amine) (NPEGN, Mw 2000, Sigma-Aldrich), toluene (99.9%, Chromasolv, HPLC, Sigma-Aldrich), diethylene glycol (99%, ReagentPlus, Sigma-Aldrich), 1-Octadecene (ODE, 90%, tech, Acros Organics), cyclohexane (≥99.8, HPLC grade, Fisher),

chloroform ($\geq 99.8\%$, HPLC grade, Fisher), sodium hydroxide (NaOH, Panreac), oleylamine (OAm, $>50\%$, TCI), N-hydroxysuccinimide (NHS, $>97\%$, Fluka).

6.2.2 Synthesis of β -NaYF₄:Yb³⁺/Tm³⁺ and NaYbF₄:Tm³⁺ core UCNPs by co-precipitation method at 310 °C

β -NaYF₄:Yb³⁺/Tm³⁺ and β -NaYbF₄:Tm³⁺ core UCNPs were synthesized following a previously reported procedure.^{15,16} Briefly, in a three-necked flask containing 5.34 g of OA and 11.84 g of ODE, $1 - x - 0.005$ mmol ($x = 0.4, 0.7, \text{ and } 0.995$) of Y(CH₃COO)₃·4H₂O, x mmol of Yb(CH₃COO)₃·4H₂O, and 0.005 mmol of Tm(CH₃COO)₃·4H₂O were added. The mixture was kept under argon flow and heated at 160 °C for 40 min. After a cooling period, 3.125 mmol of sodium oleate and 4 mmol of NH₄F were added in solid form. After completing 20 min of stirring at 50 °C under argon flow, a second heating process was carried out for 1 h at 160 °C and 40 min at 310 °C. The resulting mixture was cooled down to room temperature naturally. The resulting nanoparticles were precipitated by adding ethanol, collected by centrifugation, washed with cyclohexane and ethanol following cycles of precipitation, centrifugation and redispersion before being redispersed in 10 mL of cyclohexane and labeled as CYYb40Tm ($x = 0.4$), CYYb70Tm ($x = 0.7$) and CYbTm ($x = 0.995$).

6.2.3 Seed-mediated heat-up synthesis of NaYF₄:Yb³⁺/Tm³⁺@NaYF₄ and NaYbF₄:Tm³⁺@NaYF₄ core/shell UCNPs via high-temperature co-precipitation route.

These core/shell syntheses were based on a previously reported procedure.²⁰ The synthesized core UCNPs were used as seeds to obtain core/shell UCNPs. In a typical experiment, 1 mmol of Y(CH₃COO)₃·4H₂O was added to a 100 mL three-necked flask containing 7.1 g OA and 13.4 g ODE. The resulting mixture was heated to 160 °C, maintained for 40 min, and then cooled down to room temperature. Subsequently, 5 mL of cyclohexane dispersion of the respective core UCNPs were added, followed by the addition of 10 mL of a methanol solution containing NH₄F (4 mmol) and NaOH (2.5 mmol). The mixture was stirred at 60 °C for 40 min under argon flow. Subsequently, the mixture was heated to 105 °C, kept under stirring and vacuum for 10 min and then heated to 310 °C under argon flow. After 1 h under continuous stirring, the resulting mixture was cooled down to room temperature naturally. The nanoparticles were

recovered and washed as described in section 6.2.2, and finally labeled CYYb40TmSY1 ($x = 0.4$), CYYb70TmSY1 ($x = 0.7$), and CYbTmSY1 ($x = 0.995$).

6.2.4 Ripening-mediated self-focusing method for layer-by-layer epitaxial shell growth

The synthesis of NaYbF₄:Tm³⁺@NaYF₄ core/shell UCNPs was also carried out using the ripening-mediated self-focusing method on which the core NaYbF₄:Tm³⁺ nanoparticles were coated by successive layers of α -NaYF₄ sacrificial nanoparticles (SNPs), based on a previously reported procedure.¹⁸

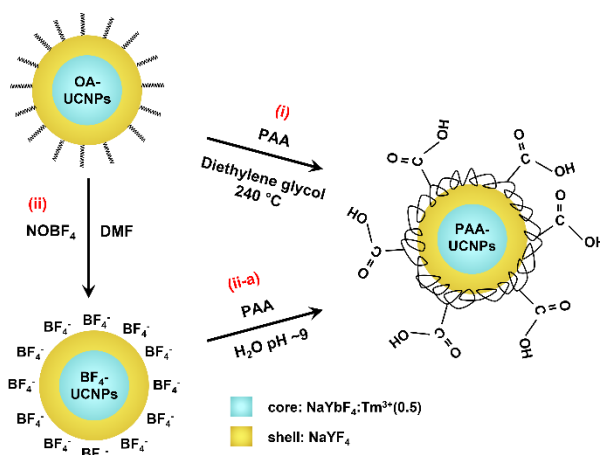
Initially, small α -NaYF₄ SNPs were prepared by thermal decomposition of yttrium and sodium trifluoroacetates. Briefly, 2.5 mmol of Y(CF₃COO)₃·H₂O and 2.5 mmol of sodium trifluoroacetate were mixed with 7.5 mL of OA, 7.5 mL of OAm, and 12.5 mL of ODE in a three-necked flask. The mixture was subjected to two heating processes under argon flow and continuous stirring, first at 120 °C for 45 min and then at 280 °C for 45 min. The mixture was then cooled to room temperature naturally and the nanoparticles were recovered and washed as described above.

The synthesis of NaYbF₄:Tm³⁺ core UCNPs was carried out as described in section 6.2.2, but after 40 min at 310 °C, the temperature was decreased to 300 °C instead of room temperature. Immediately, about 2 mL of the reaction mixture was recovered ($t = 0$ core) and then 1 mL of octadecene containing 0.25 mmol (regarding the amount of Y³⁺) of SNPs was injected in one-shot (~1 sec for the injection volume of 1 mL) every 5 min using a syringe with a stainless-steel cannula until the desired amount was injected for ripening and the layer-by-layer growth process. According to Johnson N.J. *et al.*,¹⁸ in 2012 this layer-by-layer successive epitaxial shell growth methodology does not require precise injection control to obtain a unimodal size distribution of core/shell nanoparticles.¹⁸ Injection of SNPs and ripening cycles were performed for a total injection of 0.75 (CYbTmSY2), 1.0 (CYbTmSY3), 1.25 (CYbTmSY4), and 1.5 (CYbTmSY5) mmol of SNPs, that is, three, four, five, and six injection cycles, respectively. After the last ripening process, the reaction mixture was cooled down to room temperature naturally and the core/shell UCNPs were recovered and washed as described above, and finally redispersed in 10 mL of cyclohexane.

6.2.5 Surface modification of NaYbF₄:Tm³⁺@NaYF₄ core/shell UCNPs

Using the direct (route (i) of Scheme 6.1) and two-step (route (ii) of Scheme 6.1) ligand exchange strategy, as described in Chapter 1, the original hydrophobic ligands

(OA and OAm) on the surface of $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell nanoparticles were replaced by PAA polymer.^{10–13}



Scheme 6.1 Illustrative diagram of the surface modification of $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYbF}_4$ core/shell UCNP with PAA.

6.2.5.1 Direct ligand exchange strategy

Briefly, 200 mg of PAA were added in a three-necked flask containing 30 mL of diethylene glycol. The mixture was heated to 110 °C under an argon atmosphere to form a clear solution. Next, 5 mL of toluene containing 0.25 mmol of $\text{NaYbF}_4:\text{Tm}^{3+}(0.5)@\text{NaYF}_4$ (regarding the total millimole of Yb^{3+} and Tm^{3+} used during the synthesis) was slowly added to the mixture. After 1 h of continuous stirring, the mixture was heated to 140 °C and kept for one more hour, before heating to 240 °C for 1.5 h. The resulting solution was naturally cooled down to room temperature. The nanoparticles were recovered by centrifugation at 13300 rpm and washed twice with water. Finally, the PAA-coated UCNP (CYbTmSY1-PAA) were redispersed in 10 mL of water and centrifuged at 2500 rpm for 3 min in order to get rid of larger agglomerates.

6.2.5.2 Two-step ligand exchange strategy

In a typical process, 4 mL of the above CYbTmSY5 cyclohexane dispersion, 2 mL of cyclohexane, and 6 mL of DMF were added together into a glass vial of 20 mL at room temperature to form a two-phase system consisting of an upper layer of cyclohexane (containing the OA-capped $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell UCNP) and a bottom layer of DMF. Subsequently, 120 mg of NOBF_4 were added at once under gentle agitation for 2 minutes. The resulting cloudy mixture was sonicated for 20 min whereby the original hydrophobic OA molecules on $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell

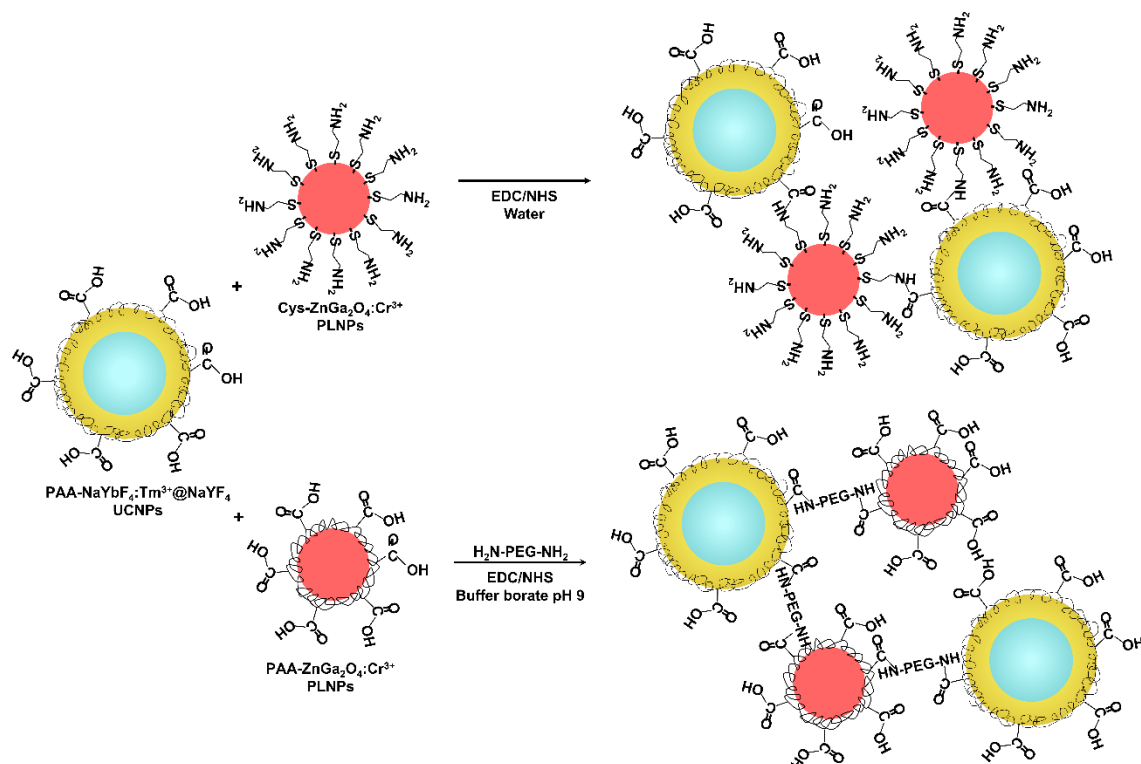
UCNPs surface were replaced by a layer of hydrophilic BF_4^- [route (ii-1)], resulting in the transfer of the nanoparticles from the upper cyclohexane layer to the bottom DMF layer. After letting the mixture stand for a few minutes, the cyclohexane (upper layer) was carefully removed. The BF_4^- -coating $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell UCNPs (CYbTmSY5-B) in the DMF layer were precipitated by adding an excess of chloroform and collected by centrifugation at 2500 rpm for 10 min. After washing twice with 0.5 mL of DMF, precipitating by adding 5 mL of chloroform and centrifuging at 2500 rpm for 10 min, CYbTmSY5-B UCNPs were redispersed in 4 mL of DMF and centrifuged at 2500 rpm for 3 minutes to get rid of larger agglomerates. After that, 2 mL of PAA (5%v/v at pH 9) solution was added into 2 mL of the above CYbTmSY5-B UCNPs dispersion in DMF [route (ii-2)]. After 20 min under vigorous stirring, the mixture was centrifuged at 13300 rpm for 30 min. The resulting particles were then redispersed in 2 mL of water, transferred to a centrifuge filter (membrane: 100 kDa Mw cut off, polyethersulfone (PES), Vivaspin), diluted to 6 mL with water and preconcentrated through filtration-centrifugation at 2000 rpm until a final volume of approximately 200 μL was obtained. The reservoir of the filter was immediately refilled once with 6 mL of water and three times with 6 mL of borate buffer (pH 9). The pre-concentration of the diluted solution was repeated by filtration-centrifugation. Between each step, the remaining PAA-capped UCNPs (CYbTmSY5-B-PAA) dispersion in the reservoir was vigorously shaken to prevent agglomeration. In the final step, the CYbTmSY5-B-PAA sample was dispersed in 4 mL of borate buffer pH 9.

6.2.6 Synthesis and surface modification of $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$

The synthesis and surface modification of ZGO PLNPs (ZGOE3-B-PAA and ZGOE3-B-Cys) was performed using the liquid-solid-solution solvothermal method and the two-step ligand exchange strategy, respectively, as described in Chapter 5 of this work.

6.2.7 Coupling reaction between $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell UCNPs and $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ PLNPs

Coupling reactions between PAA-coated $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ core/shell UCNPs with either PAA- or Cys-coated ZGO PLNPs were performed based on EDC/NHS coupling chemistry for amide group formation from the reaction between amino and carboxyl functional groups (see Scheme 6.2 and Table 6.1 for details).



Scheme 6.2 Illustrative diagram of the coupling reactions between the surface-functionalized UCNPs and PLNPs on the basis of EDC/NHS coupling chemistry.

Table 6.1 Experimental conditions of the coupling reactions between UCNPs and PLNPs.

Coupling reaction	1st	2nd	3rd	4th
Sample code	UC-PL	UC-NPEGN-PL-1	UC-NPEGN-PL-2	UC-NPEGN-PL-3
UCNPs	CYbTmSY1-PAA	CYbTmSY5-B-PAA		
mmol of UCNPs	0.00875	0.025		
PLNPs	ZGOE3-B-Cys	ZGOE3-B-PAA		
mmol of PLNPs	0.0125	0.02	0.1	0.05
mmol of EDC	0.007	0.1	0.15	
mmol of NHS	0.007	0.04	0.08	
mmol of NPEGN	0	0.001	0.003	
Medium	Water	Buffer borate pH 9		

6.2.8 Characterizations

Powder X-ray diffractograms (XRD) were obtained using a D8 Advance X-ray diffractometer (Bruker) (Bragg-Brentano geometry) employing Ni-filtered Cu K α X-ray radiation ($\lambda = 1.540 \text{ \AA}$). TEM images were acquired in a Transmission Electron Microscope (CM20 Philips) operated at 200 kV and equipped with LaB $_6$ electron source. The number-based particle size distributions of the UCNPs and PLNPs were determined from their TEM images (at least 300 nanoparticles were measured to obtain the histograms) using ImageJ software. The dynamic light scattering (DLS) and ζ potential measurements were carried out using a Zetasizer Nano ZS (Marvern). Fourier transform infrared (FTIR) spectra of the powder samples diluted in KBr Merck for spectroscopy and pressed in a pelletizer for 1 min under a pressure of 5 tons were obtained using a Thermo Scientific Nicolet iS5 FTIR Spectrometer, set up with the iD1 Transmission Module. 4000–400 cm^{-1} scan, 2 cm^{-1} resolution. The UC luminescence spectra and the luminescence decay curves at 697 nm were acquired at room temperature using a Horiba Jobin Yvon spectrofluorometer (Fluorolog-3 Model FL3-122) equipped with a Hamamatsu R-928 photomultiplier tube. A 980 nm laser diode coupled with an optical fiber was used as the NIR excitation source.

6.3 Results and discussions

6.3.1 NaYF $_4$:Yb $^{3+}$ /Tm $^{3+}$ @NaYF $_4$ and NaYbF $_4$:Tm $^{3+}$ @NaYF $_4$ core/shell UCNPs (high-temperature co-precipitation route).

The concentration of Yb $^{3+}$ is critical to the UC process since a higher concentration allows an increase in the absorption properties at 980 nm. However, two major problems have been widely reported for especially high concentrations of Yb $^{3+}$ ions in UC systems: 1) the difficulty of obtaining the β phase for small nanoparticles, as well as the poor control of size and morphology;¹⁷ 2) non-radiative energy losses due to energy migration to quenching sites on the surface of nanoparticles.²¹ The first problem can be solved by using sodium oleate instead of the conventionally used NaOH as the sodium source. While coating the core nanoparticle with a shell to form a core/shell structure prevents or reduces the occurrence of the second problem. Figure 6.1 shows the formation of monodisperse and uniform nanoparticles with average sizes of 19, 21, 27, 27, 28, and 34 nm for CYYb40Tm, CYYb70Tm, CYbTm, CYYb40TmSY1,

CYYb70TmSY1, and CYbTmSY1, respectively, which have different concentrations of Yb^{3+} in the core region.

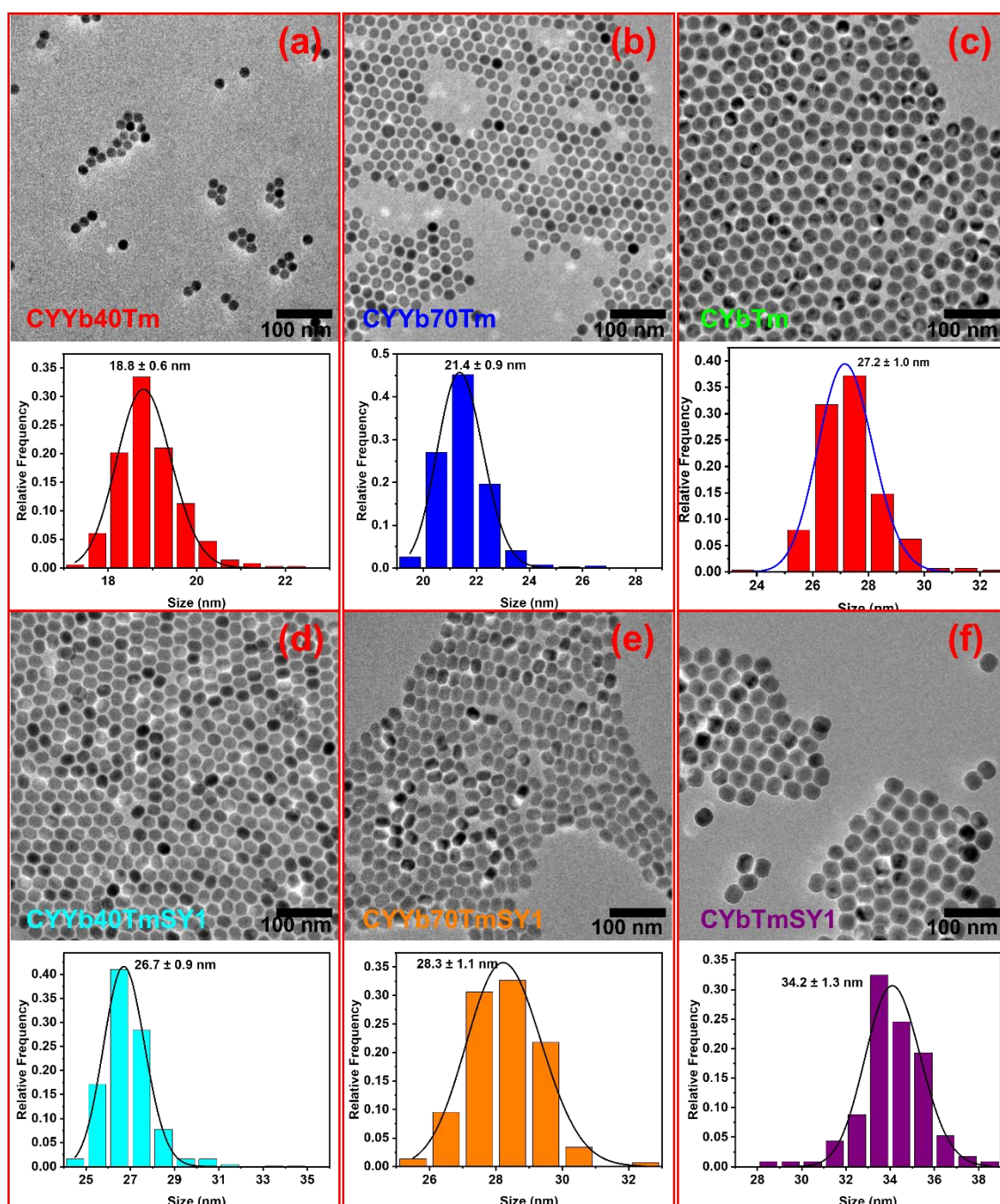


Figure 6.1 TEM Images and the corresponding size distributions calculated from the TEM images of the core and core/shell UCNPs with different concentration of Y^{3+} and Yb^{3+} in the core region.

The UC luminescence spectra of the UCNPs (Figure 6.2) clearly show the importance of the coating of the nanoparticles with the inactive NaYF_4 shell. In fact, the integrated UC luminescence intensities from 275 to 500 nm were approximately 80-, 45-, and 20-fold higher for CYbTmSY1, CYYb70TmSY1, and CYYb40TmSY1

core/shell UCNP than for the corresponding core nanoparticles, respectively. It is wrong to say that the increase in the concentration of Yb^{3+} led to an increase in the intensity of UC luminescence (although it appears to be the case), since it could also be attributed to the difference in the sizes of the nanoparticles with different concentrations of Yb^{3+} , as shown in Figure 6.1.

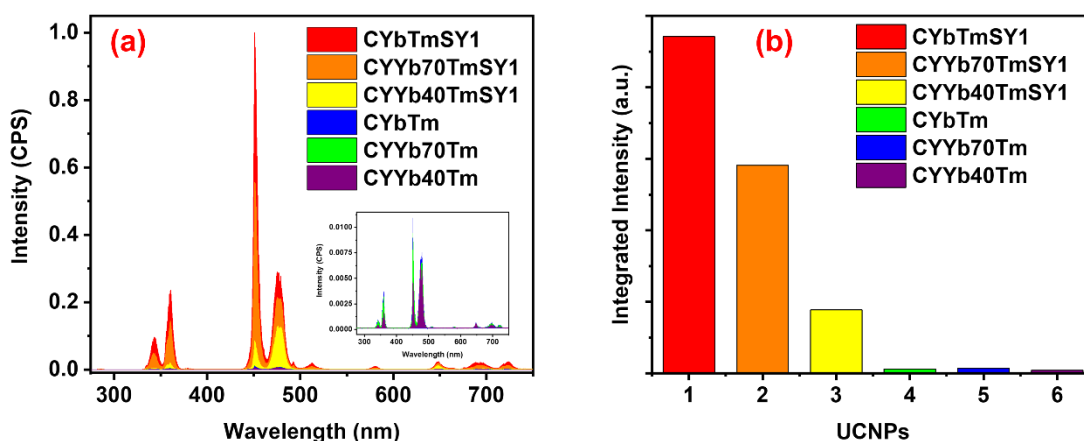


Figure 6.2 UCL spectra (a) and the corresponding integrated UCL intensity in the region from 275 to 500 nm (b) of the core and core/shell UCNP (in powder form) synthesized with different concentrations of Y^{3+} and Yb^{3+} . The spectra were measured under 980 nm laser irradiation.

6.3.2 $\text{NaYbF}_4\text{:Tm}^{3+}\text{@NaYF}_4$ core/shell UCNP (Ripening-mediated self-focusing method for layer-by-layer epitaxial shell growth)

It is well known that shell thickness plays an important role in the luminescence intensity of the UCNP; therefore, $\text{NaYbF}_4\text{:Tm}^{3+}\text{@NaYF}_4$ core/shell UCNP with different shell thicknesses were synthesized by injecting different amounts of small NaYF_4 SNPs directly into the $\text{NaYbF}_4\text{:Tm}^{3+}$ core reaction mixture at 300 °C. $\text{NaYbF}_4\text{:Tm}^{3+}$ core UCNP of approximately 27.2 nm (see Figures 6.1c and 6.3c) are favored over the energetically less stable NaYF_4 small SNPs of approximately 9.5 nm (see Figures 6.3b), resulting in the growth of larger particles ($\text{NaYbF}_4\text{:Tm}^{3+}$) at the expense of smaller ones (NaYF_4), forming the $\text{NaYbF}_4\text{:Tm}^{3+}\text{@NaYF}_4$ core/shell structure. Here, 0.75 mmol, 1 mmol, 1.25 mol and 1.5 mmol of NaYF_4 were injected, resulting in the formation of core/shell nanoparticles with shell thicknesses of 1.4, 2.4, 2.8, and 3.4 nm, respectively (Figures 6.3 d-g). Additionally, as shown in Figure 6.4, the SNPs crystallized in the α phase, while the core and core/shell nanoparticles crystallized in the β phase, which proves that the sacrificial nanoparticles effectively dissolved when injected into the mixture of reaction and immediately recrystallized in the β phase, forming the shell of the core/shell nanoparticles.

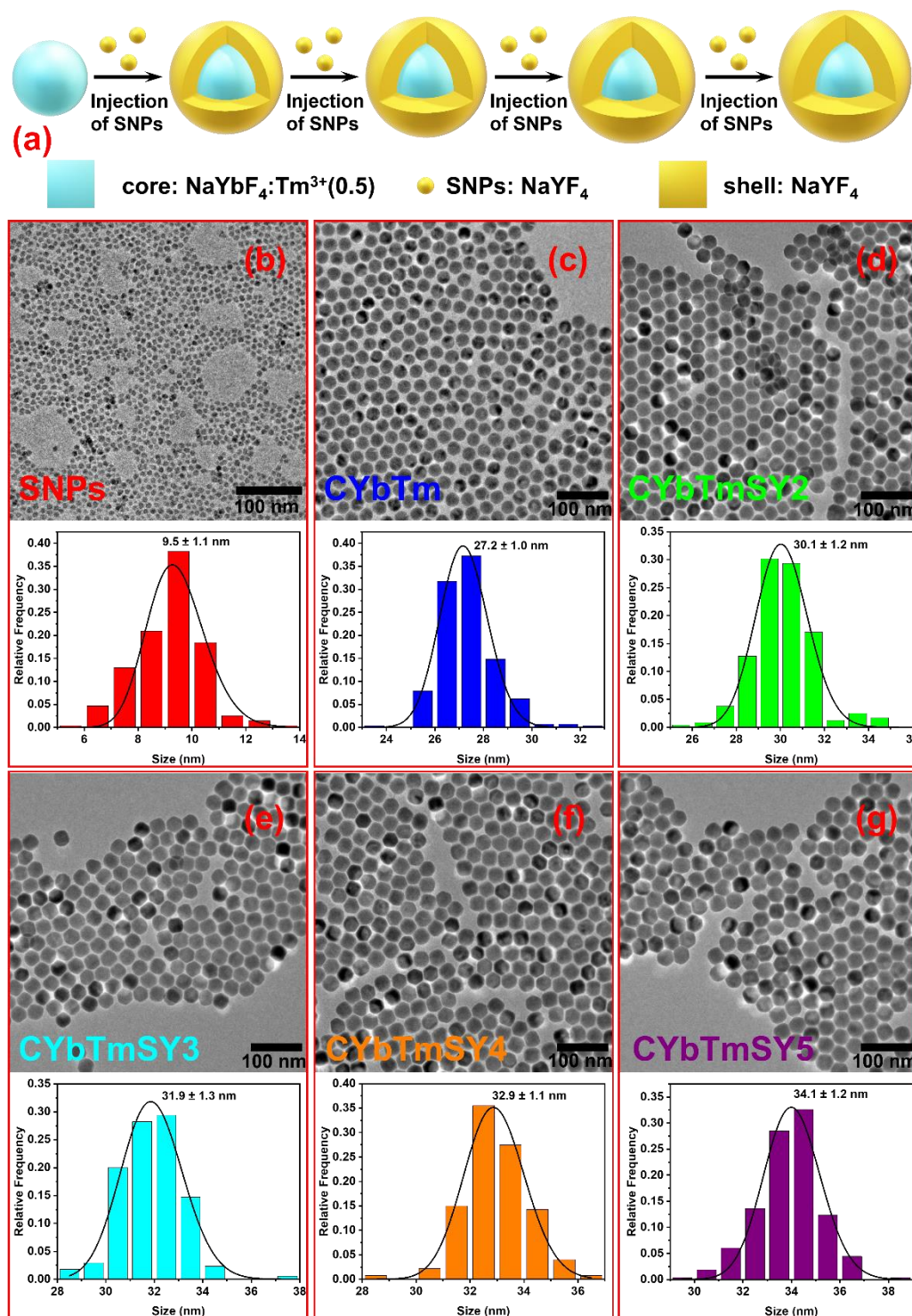


Figure 6.3 Schematic diagram of shell growth from core UCNP and SNPs based on the Oswald ripening process (a). TEM images and corresponding size distribution (b-g) of SNPs, core and core/shell UCNP with different sizes.

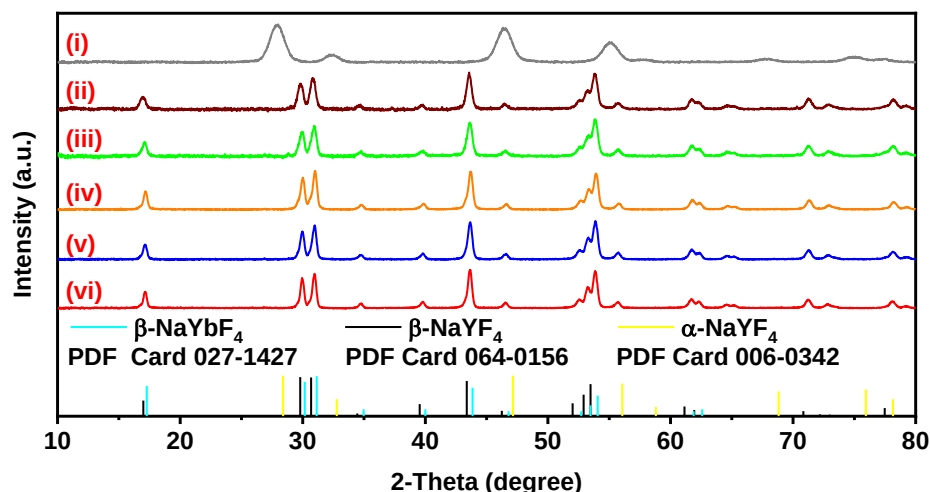


Figure 6.4 XRD analysis of NaYF₄ SNPs (i), CYbTm (ii), CYbTmSY2 (iii), CYbTmSY3 (iv), CYbTmSY4 (v), and CYbTmSY5 (vi).

To compare the effect of shell thickness on luminescent properties, the emission spectra of core/shell nanoparticles with different shell thicknesses were measured under 980 nm laser excitation (Figure 6.5). It can be clearly seen that the shell thickness had a positive influence on the UC luminescence intensity. The explanation behind this observation lies in the fact that the coating of the core nanoparticles with an increasingly larger shell allows a concomitant reduction in energy migration to the surface, due to the greater distance between the core and the surface.

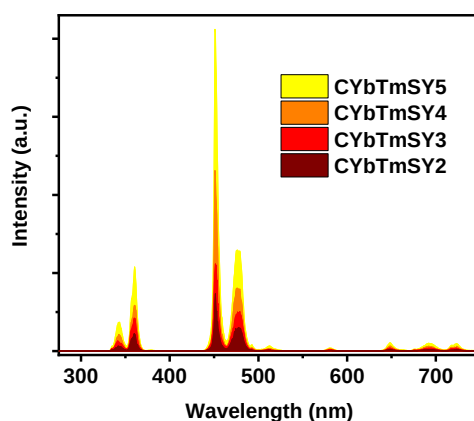


Figure 6.5 UCL spectra of NaYbF₄:Tm³⁺@NaYF₄ core/shell UCNP samples (powder samples) with different shell thicknesses. The spectra were measured under 980 nm laser irradiation.

6.3.3 Surface modification of NaYbF₄:Tm³⁺@NaYF₄ core@shell UCNP

To make our nanoparticles dispersible in water and add functional groups to their surface for coupling reaction with ZGO PLNPs, we performed surface modification of NaYbF₄:Tm³⁺@NaYF₄ core/shell UCNP *via* one- and two-step ligand exchange strategies, as illustrated in the Scheme 6.1, section 6.2.5. Figures 6.1 f, 6.3 g, and 6.6

a-c show that the nanoparticles retained their shape and size after the surface modification; however, the CYbTmSY1-PAA sample showed some precipitate after a few days, suggesting low stability of this dispersion, which can be attributed to its low negative ζ potential value (-12.4 mV) (Figure 6.6 d), while the high negative ζ potential value (-35.4 mV) (Figure 6.6 d) of CYbTmSY5-B-PAA is adequate enough to confer good colloidal stability to the nanoparticles. All these samples were stored for further experiments.

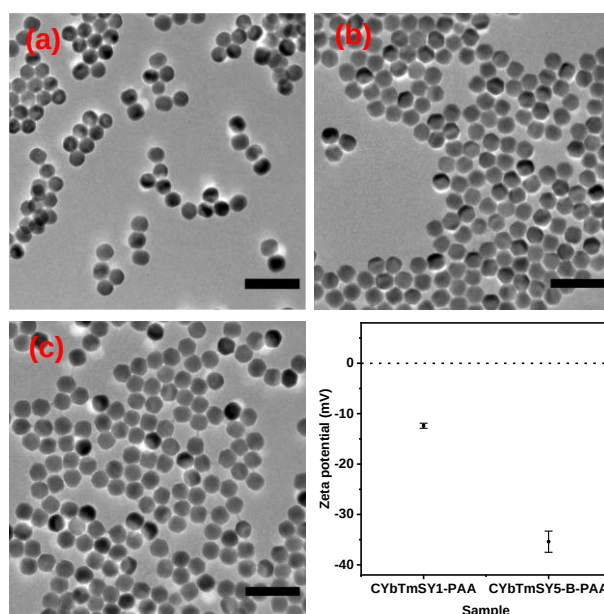


Figure 6.6 TEM images of CYbTmSY1-PAA (a), CYbTmSY5-B (b), and CYbTmSY5-B-PAA (c) samples. ζ potential values of PAA-coated UCNPs. Scale bar in the TEM images: 100 nm.

6.3.4 Coupling reaction between NaYbF₄:Tm³⁺@NaYF₄ core/shell UCNPs and ZnGa₂O₄:Cr³⁺ PLNPs

Coupling reactions between PAA-coated NaYbF₄:Tm³⁺@NaYF₄ UCNPs with either PAA- or Cys-coated ZGO PLNPs were performed on the basis of EDC/NHS coupling chemistry for the amide group formation from the amino and carbonyl functional group reaction. As shown in Figure 6.7a, the coupling reaction between ZGOE3-B-Cys and CYbTmSY1-PAA to obtain UCNPs linked to PLNPs (UC-PL) led to the formation of small agglomerates of nanoparticles, which suggests that the coupling reaction between the amino groups on the surface of the PLNPs and the carboxylic groups on the surface of the UCNPs was successfully performed. However, due to the stability problem of the CYbTmSY1-BPAA dispersion in water, it was not possible to reproduce this reaction more than once, leading to large agglomerates on several occasions (see

Figure 6.7b). In an attempt to solve this problem, the coupling reactions were carried out between the CYbTmSY5-B-PAA sample dispersed in borate buffer pH 9 and the ZGOE3-B-Cys dispersed in water; even so, again the formation of large agglomerates was observed (Figure 6.7c). In fact, just the addition of the pH 9 buffer solution to the aqueous dispersion of ZGOE3-B-Cys caused a visible change in the dispersion, turning it quite cloudy, probably due to the change of the ζ potential of these nanoparticles because of the difference of the pH of the media.

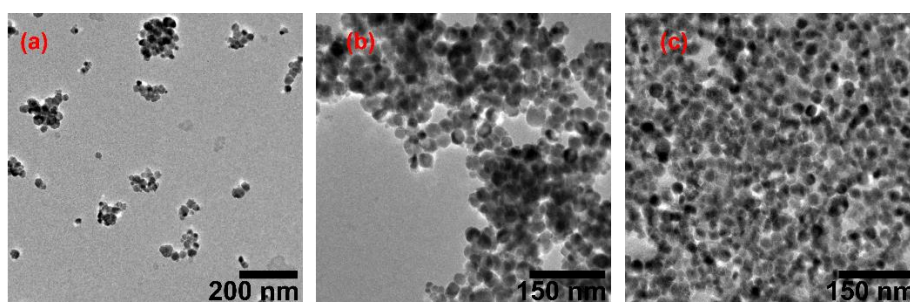


Figure 6.7 TEM images of the UC-PL coupling products (a and b) between ZGOE3-B-Cys and CYbTmSY1-PAA in water, and (c) between ZGOE3-B-Cys and CYbTmSY5-B-PAA in borate buffer pH 9, based on EDC/NHS coupling chemistry. The coupling reactions in (a), (b), and (c) were performed 1, 3, and 5 days, respectively, after obtaining the corresponding PAA-coated UCNPs.

Then, a new coupling strategy was followed, in this case using ZGOE3-B-PAA and CYbTmSY5-B-PAA, both dispersed in borate buffer pH 9 in the presence of polyethylene glycol bis(amine) polymer (NPEGN), in conjunction with EDC and NHS reagents (see Table 6.1). NPEGN polymer was used to link the two types of PAA-coated nanoparticles, through the formation of amide groups from the carboxylic groups on their surface with the amino groups of NPEGN polymer.

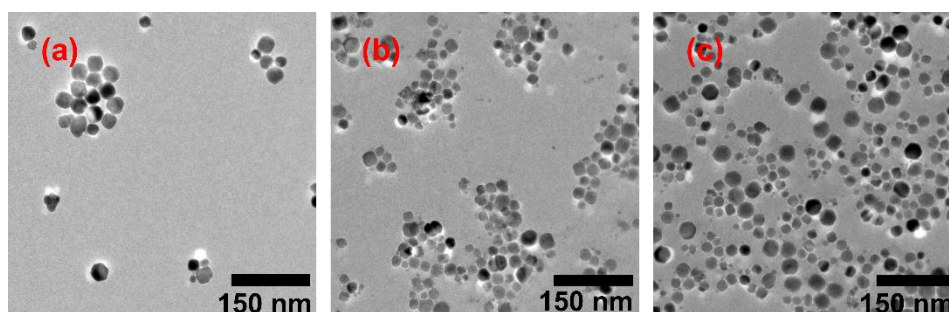


Figure 6.8 TEM images of (a) UC-NPEGN-PL-1, (b) UC-NPEGN-PL-2, and (c) UC-NPEGN-PL-3 coupling products between ZGOE3-B-PAA and CYbTmSY5-B-PAA on the basis of EDC/NHS coupling chemistry in borate buffer pH9.

In all cases, the amount of CYbTmSY5-B-PAA was fixed, while the amounts of ZGOE3-B-PAA and NPEGN used were varied (see Table 6.1). Figure 6.8 shows that using this second strategy, large agglomeration due to the difference in pH and/or ζ potentials of the nanoparticles can be avoided. In addition, the TEM images in Figure 6.8 suggests that for UC-NPEGN-PL-1 the amount of ZGOE3-B-PAA may be very low regarding the amount of CYbTmSY5-B-PAA, while for UC-NPEGN-PL-3 the amount of ZGOE3-B-PAA regarding the amount of CYbTmSY5-B-PAA seems to be adequate. However, when comparing the Figures 6.8 (b) and (c), it can be observed that the same amount of NPEGN (0.003 mmol), leads to the formation of some agglomerates (may be due to the formation of the covalent bonds between the UCNPs and the PLNPs) for UC-NPEGN-PL-2, but not for UC-NPEGN-PL-3. It may be because for UC-NPEGN-PL-3 the amount of ZGOE3-B-PAA used (half than for UC-NPEGN-PL-2) is low enough to allow the amount of NPEGN to link to all the available carboxylic groups on the surface of CYbTmSY5-B-PAA and ZGOE3-B-PAA, thus coupling between these nanoparticles does not occur or occurs to a lesser extent. Meanwhile, for UC-NPEGN-PL-2, the amount of ZGOE3-B-PAA may be large enough that more carboxylic groups are available than amino groups of the NPEGN polymer. Consequently, some carboxylic groups are free for coupling. Finally, it is possible to observe individual nanoparticles even for UC-NPEGN-PL-2, which may indicate that not all nanoparticles were bound by carrying out this coupling strategy and further experiments and characterizations will probably be necessary.

6.4 Conclusions

In summary, this chapter presents some advances achieved in relation to the development of UC-PL systems, through the controlled coupling between small and uniform UCNPs and PLNPs on the basis of EDC/NHS coupling chemistry for amide group formation.

Furthermore, due to the importance for the coupling to the PLNPs and their subsequent activation, the synthesis of NaYF₄:Yb³⁺/Tm³⁺@NaYF₄ core/shell UCNPs with high content of Yb³⁺, different sizes (from 19 to 34 nm), and different shell thicknesses (from 1.4 to 3.4 nm) to improve their UC optical properties, as well as their surface modification to anchor hydrophilic carboxylic groups to the surface of the nanoparticles, is shown in detail.

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7 GENERAL CONCLUSION

Briefly, materials with UC and PL properties involving NIR illumination (excitation and emission) were successfully developed here.

The lanthanide-doped fluoride-based UCNPs showed high degree of monodispersity, uniform size and mainly spherical shape.

The vital role that different factors have on the morphological, structural, optical, and photoluminescent properties of UCNPs was demonstrated. The content of the activator ions directly determines the color of the light emitted by the UCNPs. It is important to choose the activator ion according to the required applications. For this, it must be considered if the wavelength emitted by them fits the needs. In addition, the adequate concentration can avoid cross-relation processes between the dopant ions. On the contrary, high concentrations can negatively affect emission processes due to non-radiative relaxation processes such as cross-relaxation or energy migration to surface quenching sites.

Particularly high concentrations of Yb^{3+} can induce further growth of nanocrystals. Higher concentrations of Yb^{3+} and larger sizes of the nanoparticles may be suitable for the UC under 980 nm laser excitation, especially when the conversion of three or more photons is required. However, coating of the core nanoparticle with an inactive layer is generally necessary to prevent surface migration to surface quenching sites. Therefore, coating the core nanoparticle with a shell can increase several times the UC luminescence intensity.

Regarding the PLNPs, a relationship was found between the nanoparticle/crystallite size and the PL properties. In addition, it was shown that the synthesis conditions (for example, variation in the type of solvent), influence the growth of the nanoparticles and, consequently, the PL properties.

The main conclusions of each chapter of this thesis are shown below. First, in Chapter 3, sub-20 nm Nd^{3+} -sensitized Gd^{3+} -based core/shell/shell UCNPs showed simultaneous emission of Tm^{3+} (blue) and Er^{3+} (green and red) ions under 808 nm laser irradiation. The color of the emitted light was thus tuned from blue to white by controlling the concentration of the dopant ions. It was demonstrated that the doping of Tm^{3+} and Er^{3+} ions in the core and outermost shell domains, respectively, as well as the enrichment of the intermediate shell with Nd^{3+} , prevents cross-relaxation processes between them. Furthermore, the precise control of the content and concentration of

the dopant ions in each domain, as well as the thickness of each layer, plays a vital role in the energy transfer process. These results contribute to the development of new materials with multicolor emission and the understanding of energy transfer mechanisms between sensitizer and activator ions. In addition, it helps to understand possible routes to alleviate deleterious processes that decrease the radiative emission *via* quenching the excitation energy.

Chapter 4 addresses and offers solutions to two major problems associated with the use of otherwise very photoactive and promising Ag_3PO_4 photocatalyst: (i) the *lack of photoactivity in the NIR region* and (ii) *limited photostability due to self(photo)reduction involving reduction from Ag^+ to Ag^0* . Problem (i) is addressed here by combining Ag_3PO_4 with $\text{NaYbF}_4:\text{Tm}^{3+}$ UCPs. These UCPs showed quite intense UC luminescence in the UV-Vis region under NIR irradiation using a 980 nm laser. The photons emitted by the UCPs have enough energy to photoexcite Ag_3PO_4 , thus extending its application to the NIR region. Consequently, the activation of Ag_3PO_4 can occur indirectly with NIR light, in addition to its direct photoexcitation using low-cost commercial LEDs. The problem of limited photostability and poor recyclability of Ag_3PO_4 is addressed here using a minute quantity of hydrogen peroxide (H_2O_2) as the oxidant and photocatalyst regenerating agent that prevents the reduction of Ag^+ and/or assists in the oxidation of Ag^0 back to Ag^+ , thus ensuring the structural integrity and recyclability of the photocatalyst. Interestingly, the H_2O_2 -induced photocatalyst regeneration process produces reactive oxygen species long after the photoexcitation process has been turned off (light off condition) and thus the photocatalytic system remains active even under dark conditions, leading to the photodegradation of CV dye both under light on and light off conditions. The simple but practical approach introduced in Chapter 4 marks a significant advancement in the development of recyclable photoactive materials for diverse photo(electrochemical) applications.

UCNPs or UCPs can also be implemented to develop many other systems based on the UC process, for example, they could be combined with ZGO PLNPs to develop NIR rechargeable optical batteries, which may find potential applications in bioimaging and photodynamic therapy. Therefore, the synthesis of ZGO PLNPs and their coupling with UCNPs was also investigated here.

Regarding the obtaining of ZGO PLNPs, Chapter 5 addresses and offers solutions to three fundamental limitations of PL materials: (i) the *lack of precise control over particle size/distribution*, (ii) the *short-lived PL for small nanoparticles*, and (iii) their

poor water dispersibility and/or limited colloidal stability required for certain biological applications. *Problem (i)* have been addressed by using a solvothermal synthesis approach employing OA as the nanoparticle stabilizing/capping agent, which prevents their agglomeration and irregular growth. *Problem (ii)* have been addressed by increasing the nanoparticle size in a controlled way using a seed-mediated growth approach, which was accompanied by an increase in PL. *Problem (iii)* have been addressed using surface modification strategies through ligand exchange of the hydrophobic OA molecules, anchored to the nanoparticles surface, by hydrophilic molecules (PAA and Cys, in conjunction with NOBF_4), which allows its redispersion in aqueous media and confers long-term colloidal stability. Furthermore, the carboxyl and amino groups anchored to the surface of these nanoparticles are suitable for functionalization with various biomolecules or other types of materials including UCNPs, and thus are relevant for biological applications.

The proposed generalized strategy, which satisfies several prerequisites in relation to bioapplications, could be employed to prepare different kinds of surface-functionalized PLNPs for bioapplications.

Finally, for developing an UC-PL system the coupling of hydrophilic UCNPs and PLNPs was investigated here. An UC-PL system may be able to function as an "optical battery", rechargeable under NIR irradiation and with PL emission also in the NIR region, which makes it attractive for applications requiring deep penetration of the excitation and emission light. The coupling reactions were performed based on EDC/NHS coupling chemistry for the formation of amide groups. The results suggest that the carboxylic and/or amino functional groups anchored to the surface of the nanoparticles are essential for the formation of covalent bonds in the coupling process between them. However, new coupling conditions and the study of resonant energy transfer between UCNPs and PLNPs should be better investigated to ensure possible applications.

8 RESUMO EXPANDIDO DA TESE EM PORTUGUÊS

Esta seção apresenta resumidamente os principais resultados desta tese de doutorado.

Inicialmente, foram obtidas nanopartículas de conversão ascendente de energia (UCNPs) baseadas em Gd^{3+} e sensibilizadas com Nd^{3+} para emissão simultânea dos íons Tm^{3+} (azul) e Er^{3+} (verde e vermelho) sob excitação de 808 nm.

Para obter uma emissão multicolorida eficiente dos UCNPs e evitar relaxações cruzadas deletérias entre os íons Ln^{3+} ativadores (localizados no núcleo e/ou na casca), é essencial obter nanopartículas com nanoestrutura adequada.

A Figura 1a esquematiza um design apropriado para obter emissão multicolorida a partir dos íons Tm^{3+} e Er^{3+} sob excitação em 808 nm dos íons Nd^{3+} .

A separação dos íons ativadores em diferentes camadas (Tm^{3+} no núcleo e Er^{3+} na casca2), juntamente com a dopagem relativamente alta de Nd^{3+} na casca1 permite a transferência de energia de maneira bidirecional, evitando processos de relaxação cruzadas entre esses íons.

A Figura 1b mostra o diagrama ilustrativo da obtenção das nanopartículas com nanoestrutura do tipo núcleo/casca/casca com composição $\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Ca}^{2+}(7)/\text{Nd}^{3+}(1)/\text{Tm}^{3+}(0,75)@ \text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)@ \text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Ca}^{2+}(7)/\text{Nd}^{3+}(1)/\text{Er}^{3+}(X = 1, 2, 3, 5, 7 \text{ mol\%})$ [doravante referido como CSS ($\text{Er}^{3+} = 1, 2, 3, 5$ e 7)] mediante o crescimento das respectivas nanopartículas núcleo e núcleo/casca (doravante referido como CS).

As imagens de TEM na Figura 1c revelam a formação de nanopartículas esféricas de 7, 12 e 19 nm, respectivamente, para as nanopartículas com estrutura do tipo núcleo (i), CS (ii) e CSS (iii).

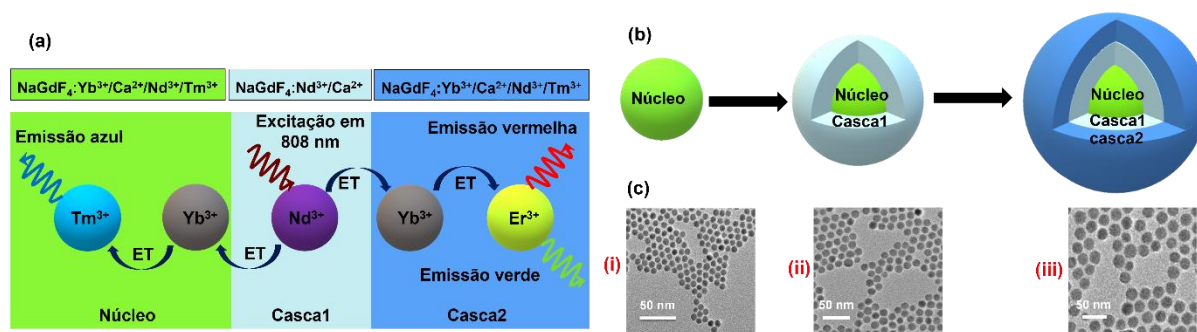


Figura 1 Diagrama esquemático do design do tipo núcleo/casca/casca para emissão multicolorida a partir dos íons Tm^{3+} (no núcleo) e Er^{3+} (na casca2) sob excitação dos íons Nd^{3+} em 808 nm (a). Ilustração esquemática da síntese das UCNPs CSS seguindo um método de crescimento camada por camada mediado por sementes (b). Imagens de microscopia.

Para investigar o efeito das cascas sobre as propriedades óptica foram medidos os espectros de UC das UCNPs de estrutura do tipo núcleo, CS e CSS($\text{Er}^{3+} = 5$) sintetizadas sob excitação de laser de 808 nm (Figura 2a).

Os picos de luminescência de UC centrados em torno de 451 e 477 nm são atribuídos às transições $^1\text{D}_2 \rightarrow ^3\text{F}_4$ e $^1\text{G}_4 \rightarrow ^3\text{H}_6$ dos íons Tm^{3+} , respectivamente. A intensidade de luminescência de UC integrada na faixa de 442 a 505 nm é 77 vezes maior após o revestimento da nanopartícula núcleo com a casca. A razão por trás dessa observação pode ser explicada com base em dois fatores. Primeiro, a severa supressão da energia relacionada à superfície das nanopartículas núcleo $\text{NaGdF}_4:\text{Tm}^{3+}(0,75)/\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)$ é diminuída pelo revestimento com a camada de $\text{NaGdF}_4:\text{Nd}^{3+}(30)/\text{Ca}^{2+}(7)$. Em segundo lugar, a alta concentração de íons Nd^{3+} (30 mol%) na casca das UCNPs CS pode coletar a luz em 808 nm de forma mais eficiente e posteriormente transferi-la para a região central (núcleo) para sensibilizar os íons Yb^{3+} e simultaneamente a íons Tm^{3+} (ativador) para produzir emissão azul.

Após o crescimento da segunda casca (ou seja, $\text{NaGdF}_4:\text{Yb}^{3+}(40)/\text{Nd}^{3+}(1)/\text{Ca}^{2+}(7)/\text{Er}^{3+}(5)$ na superfície das nanopartículas CS, a luminescência de UC de ambos os ativadores (Er^{3+} e Tm^{3+}) foi observada em conjunto (espectro azul na Figura 2a). Junto com as transições $^1\text{D}_2 \rightarrow ^3\text{F}_4$ e $^1\text{G}_4 \rightarrow ^3\text{H}_6$ dos íons Tm^{3+} , o pico de emissão verde centrado em 544 nm ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) e o pico de emissão vermelho centrado em 650 nm ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) dos íons Er^{3+} também são observados. Esses resultados comprovam que a casca enriquecida com Nd^{3+} pode coletar a luz de excitação de forma eficiente e permite a migração de energia através da interface núcleo/casca para íons Tm^{3+} no núcleo e Er^{3+} na camada mais externa para produzir luminescência de UC multicolorido a partir das nanopartículas CSS.

O controle preciso da concentração dos íons Er^{3+} na camada mais externa das nanopartículas CSS os torna candidatos potenciais para produzir eficiente luminescência de UC multicolorida. É evidente a partir da Figura 2b que o ajuste apropriado da concentração de Er^{3+} na camada mais externa desempenha um papel essencial na mudança nas intensidades relativas das cores de emissão verde ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) e vermelha ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) dos íons Er^{3+} , resultando na produção de cores luminescência que variam do azul ao branco. Tais mudanças espectrais também podem ser observadas a olho nu como mostrado nas imagens digitais inseridas na Figura 2b.

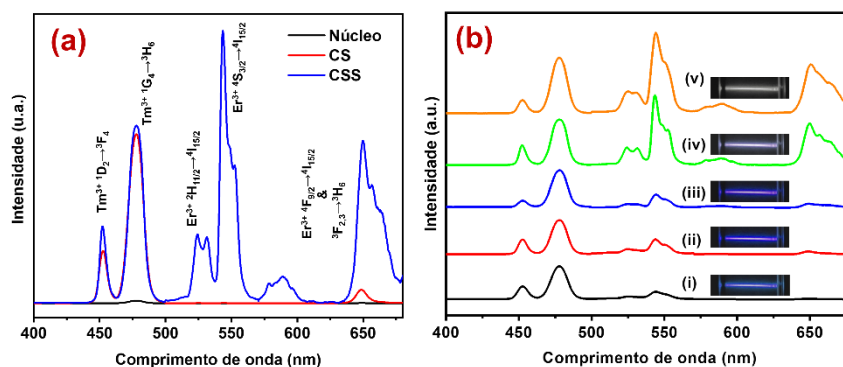


Figura 2 (a) Espectros de luminescência de UC das nanopartículas com estrutura do tipo núcleo, CS (30 mol% de Nd^{3+} na casca) e CSS (5 mol% de Er^{3+} na camada mais externa). (b) Espectros de luminescência de UC das nanopartículas com estrutura CSS com diferentes concentrações de Er^{3+} [(i) = 1, (ii) = 2, (iii) 3, (iv) = 5 e (v) = 7 mol%]. Estão inseridas em (b) às respectivas imagens digitais das correspondentes nanopartículas. Os experimentos foram realizados sob excitação laser de 808 nm.

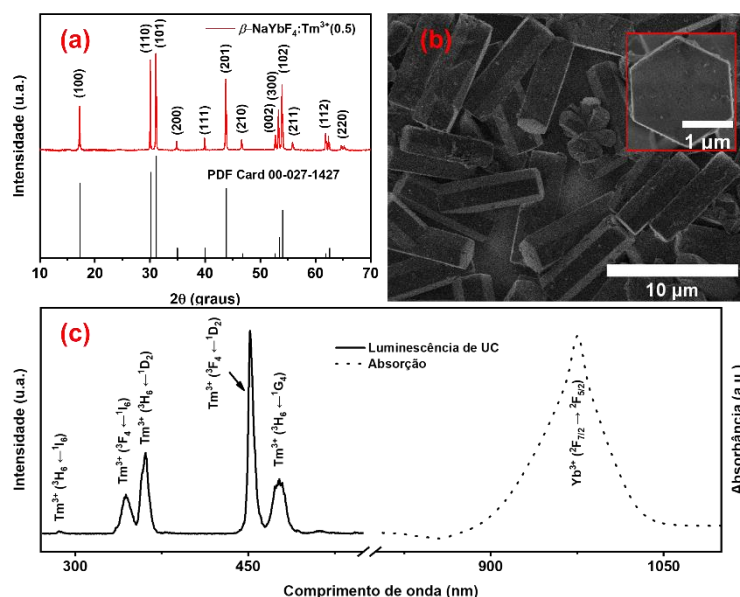


Figura 3 (a) padrão DRX, (b) imagem MEV e (c) espectro de absorção UV-Vis-NIR (linha pontilhada) e espectro de luminescência de UC sob irradiação laser de 980 nm (linha sólida preta) das UCPs de composição $\text{NaYbF}_4:\text{Tm}^{3+}$. A inserção em (b) mostra uma visão ampliada de uma única partícula orientada verticalmente.

Por outro lado, também foram sintetizadas partículas de conversão ascendente de energia (UCPs) de composição $\text{NaYbF}_4:\text{Tm}^{3+}$. Estas UCPs foram obtidos pelo tratamento hidrotérmico assistido por micro-ondas, usando ácido etilenodiaminotetracético (EDTA) como agente coprecipitante. Suas propriedades estruturais, morfológicas e ópticas, foram estudadas usando espectroscopia de XRD, SEM e fotoluminescência (PL), respectivamente (Figura 3).

Os padrões de difração de raios-X das UCPs encaixam perfeitamente com o padrão de difração padrão da fase hexagonal dos cristais de $\beta\text{-NaYbF}_4$ (PDF nº 27-

1427) (Figura 3a) que geralmente está associada a luminescência de UC mais forte do que a fase cúbica (α -NaYbF₄).

Esta amostra consiste em microbastões de cerca de $7,9 \pm 1,4$ μm de comprimento e $2,5 \pm 0,5$ μm de diâmetro (Figura 2b). Uma vista ampliada de um microbastão orientado verticalmente revela a sua forma hexagonal (inserção na Figura 3b), de acordo com os resultados da análise de XRD (Figure 3a).

A presença de íons Yb³⁺ e/ou propriedades de absorção NIR das UCPs são evidentes a partir do pico de absorção característico do Yb³⁺ em cerca de 975 nm no espectro de absorção eletrônico, obtido pela medição da refletância difusa da amostra em pó (Figura 3c, linha pontilhada).

A presença do Yb³⁺ permite assim que as UCPs absorvam os fótons NIR fornecidos pelo laser de 980 nm, enquanto a dopagem com o íon Tm³⁺ como ativador auxilia na obtenção de luminescência de UC na região UV e visível do espectro (Figura 3c, linha contínua).

O espectro de UC das UCPs em suspensão aquosa, medido sob excitação de laser de 980 nm, mostra assim picos de emissão centrados em torno de 286, 344, 361, 452 e 477 nm que são, respectivamente, atribuídos às transições $^1\text{I}_6 \rightarrow ^3\text{H}_6$, $^1\text{I}_6 \rightarrow ^3\text{F}_4$, $^1\text{D}_2 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^3\text{F}_4$ e $^1\text{G}_4 \rightarrow ^3\text{H}_6$ dos íons Tm³⁺ (Figure 3c, linha contínua).

Seguidamente, os microbastões de UC sintetizados foram usados na ativação do Ag₃PO₄, fotocatalisador altamente fotoativo na região UV-Vis, mediante os fótons emitidos sob excitação no NIR. O Ag₃PO₄ foi sintetizado mediante uma metodologia fácil de precipitação usando acetato de prata (CH₃COOAg) e Na₂HPO₄.12H₂O como precursores. Após calcinação a 200 °C, as propriedades morfológicas, composicionais, cristalográficas e ópticas das partículas de Ag₃PO₄ foram estudadas usando SEM, EDX, XRD e DRS, respectivamente. A imagem de SEM do Ag₃PO₄ revela a formação de partículas quase esféricas de tamanho micrométrico (diâmetro médio: 475 ± 182 nm) (Figura 4a). Também se observa que a superfície destas partículas está decorada com pequenas nanoesferas (diâmetro médio aproximado: 16 ± 4 nm) (Figura 4a), que podem corresponder à formação de nanopartículas de Ag na superfície do Ag₃PO₄ calcinado, promovidas pelo tratamento térmico. O espectro de EDS (Figure 4b) mostra claras linhas de emissão de Ag, P e O, confirmando a presença desses elementos nas amostras. O difratograma de XRD na Figure 4c, mostra que todos os picos de difração da amostra encaixam perfeitamente com os da fase cúbica de corpo centrado de Ag₃PO₄ (PDF no. 06-0505).

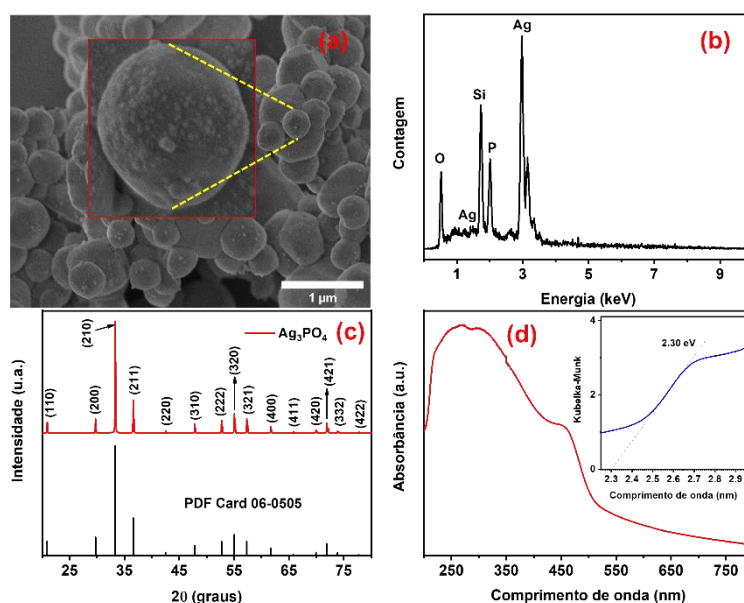


Figure 4 (a) imagem de SEM, (b) espectro de EDS, (c) padrão DRX e (d) espectro de absorção UV-Vis-NIR do fotocatalisador Ag_3PO_4 . O sinal do Si no espectro EDS é atribuído ao porta-amostra. A inserção em (a) mostra uma visão ampliada de uma partícula de Ag_3PO_4 . A inserção em (c) mostra o valor do band-gap obtido a partir do gráfico da função de Kubelka-Munk contra a energia (eV).

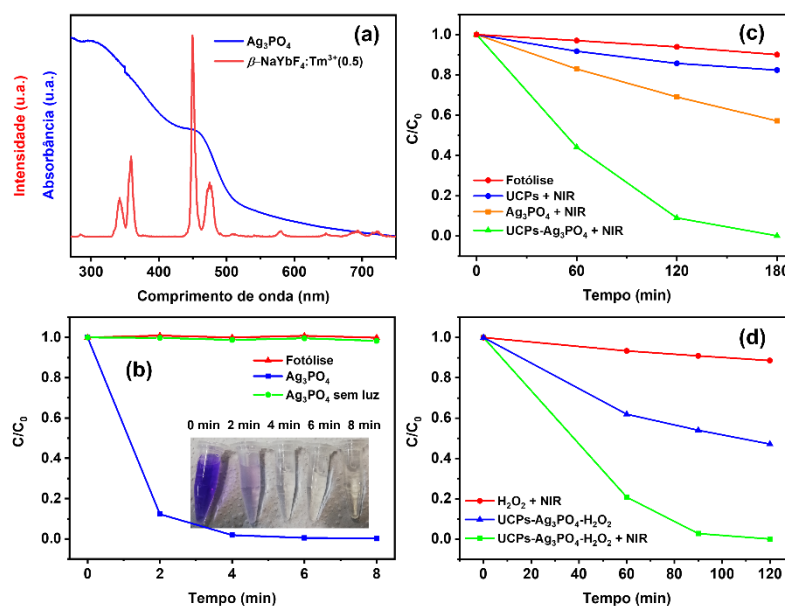


Figura 5 Sobreposição do espectro de absorção do fotocatalisador Ag_3PO_4 com o espectro de luminescência de UC dos microbastões de $\text{NaYbF}_4:\text{Tm}^{3+}(0,5)$ sob irradiação com laser de 980 nm (a). Mudança temporal na concentração do corante CV em função do tempo de irradiação com LEDs azul (b). Diminuição na concentração do corante CV em função do tempo de irradiação com laser de 980 nm na presença dos sistemas fotocatalíticos UCPs- Ag_3PO_4 (c) e UCPs- $\text{Ag}_3\text{PO}_4\text{-H}_2\text{O}_2$ (d). Além dos experimentos fotocatalíticos na presença de somente Ag_3PO_4 em (b), UCPs- Ag_3PO_4 em (c) e UCPs- $\text{Ag}_3\text{PO}_4\text{-H}_2\text{O}_2$ em (d), diferentes controles também são mostrados.

O espectro de absorção da amostra de Ag_3PO_4 em pó foi medido por espectroscopia de refletância difusa (Figura 4d). Este apresenta forte absorção na

região UV-Vis, atribuída à transferência de carga intrínseca de Ag_3PO_4 da banda de valência (VB) para a banda de condução (CB), com um band-gap indireto de 2,30 eV, como estimado a partir do gráfico de Kubelka-Munk (inserção na Figura 4d).

A forte absorção do Ag_3PO_4 se sobrepõe bem com a emissão de diodos emissores de luz (LEDs) azul (460 ± 10 nm) e com o espectro de emissão dos microbastões de $\text{NaYbF}_4:\text{Tm}^{3+}$ sob excitação no NIR (Figure 5a), permitindo a fotoexcitação efetiva do Ag_3PO_4 e a fotodegradação de poluentes de maneira direta com os LEDs azul, e de maneira indireta sob irradiação no NIR devido aos fótons emitidos pelas UCPs.

A resposta fotocatalítica do Ag_3PO_4 foi, portanto, avaliada na degradação do corante violeta cristal (CV) sob dois modos de iluminação diferentes, a saber, iluminação com LEDs azul (fotoexcitação direta do Ag_3PO_4) (Figura 5b) e irradiação laser de 980 nm (fotoexcitação indireta de Ag_3PO_4 pelos fótons UV-visível emitidos pelas UCPs) (Figura 5c).

A absorbância normalizada do corante exibiu uma diminuição drástica em apenas 2 min de iluminação com os LEDs (Figure 5b, linha vermelha) e quase 100% de descoloração do corante foi alcançado em menos de 8 min (veja a inserção na Figura 5b), indicando a alta atividade fotocatalítica sob luz visível das partículas de Ag_3PO_4 preparadas.

Depois de confirmar a excelente atividade fotocatalítica inerente do Ag_3PO_4 sob luz visível foi avaliada a fotoatividade no NIR do sistema composto pelas UCPs e o fotocatalisador (UCPs- Ag_3PO_4) (Figura 5c). Foi observada uma degradação de quase 100% do corante em 180 min sob na presença do sistema UCPs- Ag_3PO_4 sob irradiação laser (Figura 5c), confirmando, portanto, sua fotoatividade baseada no NIR. Além disso, a presença de H_2O_2 levou a uma melhora considerável na degradação do corante sob irradiação de laser de 980 nm, atingindo quase 100% de degradação do corante em apenas 90 min de iluminação no NIR (Figura 5d).

Experimentos controle foram realizados para entender melhor o processo fotocatalítico e avaliar a contribuição de diferentes fatores. Por exemplo, pode-se notar que a diminuição da absorbância do corante no experimento de adsorção (Ag_3PO_4 sem luz) (Figura 5b, linha verde) e a fotólise direta do corante sob irradiação com luz visível (Figura 5b, linha vermelha) e com laser de 980 nm, independentemente da ausência (Figura 5c, linha vermelha) ou presença de H_2O_2 (Figuras 5 d, linha vermelha), é insignificante.

Da mesma forma, observamos uma diminuição de cerca de 40% na concentração do corante CV na presença de apenas Ag_3PO_4 (linha laranja na Figura 5c) sob irradiação laser de 980 nm. Isso pode ser atribuído à excitação direta no NIR do Ag_3PO_4 altamente fotoativo.

De maneira similar, foi observada uma redução significativa na concentração do corante CV pelo sistema UCPs- Ag_3PO_4 - H_2O_2 na ausência de iluminação NIR (linha azul na Figura 5d), o que pode ser associado à produção de espécies reativas de oxigênio, mediante reação do tipo Fenton entre H_2O_2 e as partículas de Ag na superfície de Ag_3PO_4 formadas durante o processo de calcinação. Em todos os casos, a diminuição da concentração do corante CV na presença do sistema UCPs- Ag_3PO_4 e/ou UCPs- Ag_3PO_4 - H_2O_2 sob irradiação com laser de 980 é muito maior (~100%), confirmando a atividade fotocatalítica baseada no NIR desses dois sistemas.

Além do uso na fotocatalise heterogênea, os materiais com propriedades de UC também podem ser empregados na excitação de outros materiais, por exemplo, PLNPs. As características resultantes da combinação de UCNPs com PLNPs podem oferecer vantagens proeminentes para bioaplicações. As PLNPs possuem a capacidade única de funcionar como baterias ópticas (ou seja, armazenar energia de excitação) e emitir fótons de energia mais baixa por um longo tempo após desligar a luz de excitação externa. Isso permite uma diminuição no tempo de exposição do tecido à radiação de excitação e, adicionalmente, à diminuição do sinal de fundo de autofluorescência em comparação com o uso particular das UCNPs.

Em particular o galato de zinco dopado com cromo ($\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$, doravante nomeado como ZGO) apresenta luminescência persistente no NIR entorno de 700 nm. Da mesma forma que a radiação de excitação das UCNPs em 980 nm a emissão do ZGO encontra-se na primeira janela biológica, ou seja, em uma região de baixa absorção pelos tecidos biológicos, aumentando notavelmente a profundidade de detecção e melhora da eficácia terapêutica.

Devido ao mencionado anteriormente, neste trabalho também foram sintetizadas PLNPs de ZGO para posteriormente investigar o acoplamento com UCNPs.

As PLNPs de ZGO foram sintetizados mediante um método solvotérmico líquido-sólido-solução de acordo com metodologias adaptadas da literatura. Usou-se uma mistura de OA, NaOH, álcoois de cadeia curta, água e os nitratos de Zn^{2+} , Ga^{3+} e Cr^{3+} . Estas amostras revestidas com OA exibiram algumas mudanças em sua morfologia, tamanho de partícula, tamanho de cristalito, bem como nas suas propriedades

luminescentes, dependendo do tipo de álcool usado na síntese (Figure 6). Os PLNPs sintetizados na presença de propanol (ZGOP, Figura 6a) e etanol (ZGOE, Figura 6b) apresentaram uma morfologia quase esférica e uma distribuição de tamanho unimodal, com diâmetro médio de partícula de 7,1 e 7,7 nm, respectivamente. Por outro lado, a amostra preparada com metanol (ZGOM, Figura 6c) apresentou uma distribuição bimodal com a coexistência de nanopartículas pequenas (10,6 nm) e grandes (64,4 nm), de formato esferoidal e triangular, respectivamente.

A análise de XRD em pó na Figura 6d mostra que todas as amostras de ZGO cristalizaram na fase cúbica do ZnGa_2O_4 (PDF Card 00-038-1240), sem a presença de quaisquer impurezas de fase. Os tamanhos de cristalitos obtidos a partir dos difratogramas da Figura 6d, usando a equação de Scherrer são 6,9, 7,2 e 14,2 nm para ZGOP, ZGOE e ZGOM, respectivamente, de acordo com os tamanhos de partículas calculados a partir das imagens TEM correspondentes (Figura 6a-c).

A Figura 6 e-g mostra os espectros de excitação (e) e emissão (f), bem como os decaimentos da luminescência pós-excitação correspondentes à emissão em 697 nm (g). Os decaimentos da luminescência em (g) foram obtidos após excitação das amostras sintetizadas na presença dos três álcoois diferentes durante 2 min com um LED branco e um atraso de 20 segundos. Como pode ser observado a partir dos espectros de excitação (Figura 6e), as amostras apresentam três bandas características, localizadas nas regiões UV (250–350 nm), azul (420 nm) e laranja (540 nm). As bandas localizadas em torno de 420 nm e 540 nm são atribuídas às transições permitidas por spin do estado fundamental [$^4\text{A}_2$ (^4F)] dos íons Cr^{3+} em uma simetria octaédrica para os estados excitados $^4\text{T}_1$ (^4F) e $^4\text{T}_2$ (^4F), respectivamente. A outra banda na região UV resulta de uma sobreposição parcial do band gap da matriz hospedeira de ZnGa_2O_4 com a transição permitida por spin do estado fundamental [$^4\text{A}_2$ (^4F)] para o estado excitado [$^4\text{T}_1$ (^4P)] de Cr^{3+} íons. Todas as amostras exibiram um perfil de decaimento semelhante (Figure 6g), que foi ajustado em uma função de decaimento biexponencial (ExpDec2 Fit), indicando dois tempos de vida diferentes e sugerindo que existem pelo menos dois caminhos para a recombinação radiativa dos portadores de carga na produção de luminescência persistente dessas nanopartículas.

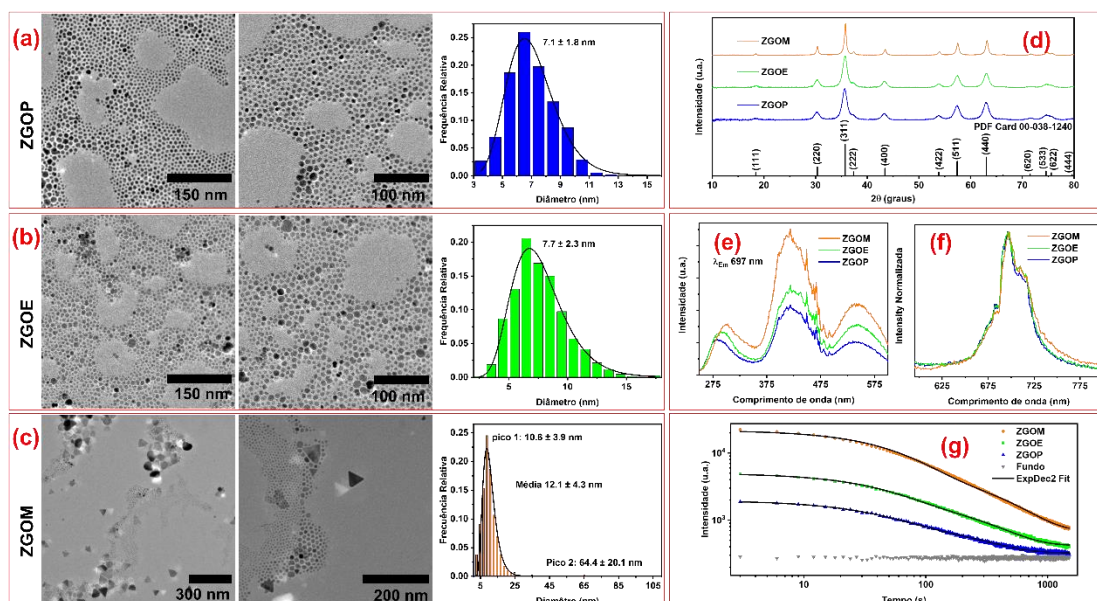


Figura 6 Imagens de TEM em duas ampliações diferentes e a correspondente distribuição de tamanho extraída das imagens de TEM (a-c) das amostras de ZGO preparadas na presença de propanol (a), etanol (b) e metanol (c). XRD (d), espectros de excitação ($\lambda_{\text{em}} = 697 \text{ nm}$) (e), espectros de emissão ($\lambda_{\text{exc}} = 291 \text{ nm}$) (f) e curva de decaimento de luminescência pós-excitação (g) das correspondentes amostras em pó.

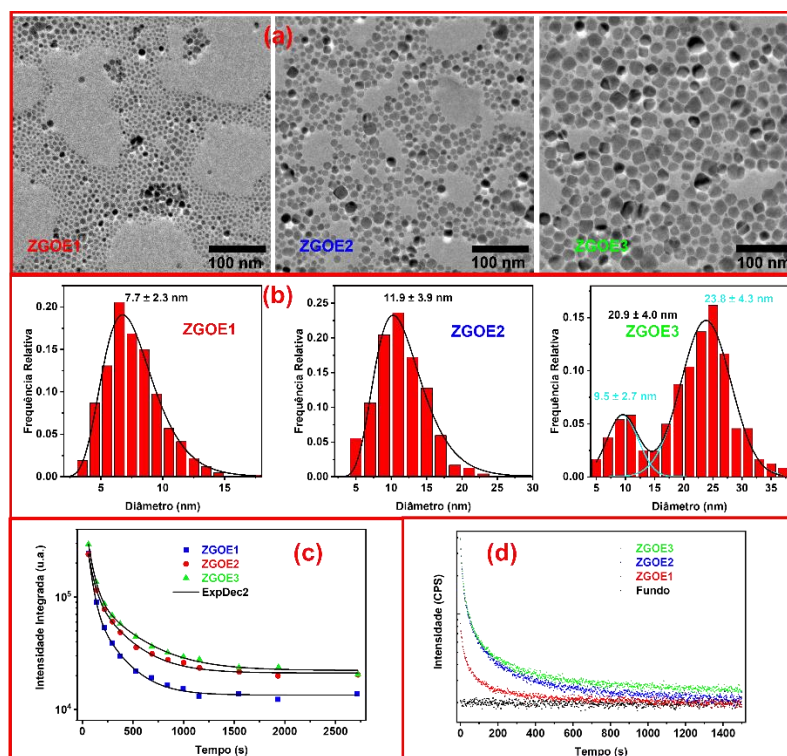


Figura 7 Imagens de TEM (a), distribuição de tamanho calculada a partir das correspondentes imagens de TEM (b) e curvas de decaimento da luminescência persistente (c e d) das mostras de ZGO com diferentes tamanhos. As curvas em (c) foram obtidas a partir do cálculo das intensidades integradas dos espectros de emissão (601–790 nm) em diferentes intervalos de tempo pós-excitação ($\lambda_{\text{exc}} = 291 \text{ nm}$). As curvas em (d) correspondem ao decaimento da emissão ($\lambda_{\text{em}} = 697 \text{ nm}$) pós-excitação (LED branco). A excitação das amostras realizou-se durante 120 s; atraso pós-irradiação de 25 e 5 s para (c) e (d), respectivamente. Todos os experimentos foram realizados em ciclohexano.

Para preparar partículas ligeiramente maiores com propriedades de luminescência aprimoradas, foram empregadas as pequenas nanopartículas ZGOE (7,7 nm) (agora denominadas ZGOE1) como sementes para sintetizar nanopartículas maiores (ZGOE2) de aproximadamente 12 nm (veja Figura 7 a,b). Subsequentemente, as ZGOE2 resultantes foram usadas como sementes para preparar nanopartículas ainda maiores (ZGOE3) (veja Figura 7 a,b). No entanto, a amostra ZGOE3 mostrou uma distribuição de tamanho bimodal (9,5 nm e 24 nm), sugerindo que o crescimento do cristal é acompanhado por nucleação fresca.

Seguidamente, as amostras dispersadas em ciclohexano foram irradiadas a 291 nm (λ_{exc}) durante 120 s. Os espectros de luminescência (601–790 nm) pós-excitação começaram ser registrados 25 s após desligar a luz de excitação. Em seguida, foram calculadas as intensidades integradas (Figura 7c) obtidas a partir desses espectros em diferentes intervalos de tempo pós-excitação. À medida que o tamanho médio de partícula aumentou de 8 para 21 nm, os tempos de vida (t) do primeiro (t_1) e segundo decaimento (t_2) (ajuste ExpDec2) aumentaram de 45 para 56 s e de 233 a 375 s, respectivamente. Esses resultados demonstram o impacto positivo do aumento do tamanho das partículas, via crescimento mediado por sementes, nas propriedades luminescentes das PLNPs.

Da mesma forma, as amostras em ciclohexano foram irradiadas com um LED branco durante 120 s. As curvas de decaimento de luminescência pós-excitação (λ_{em} 697 nm) foram registradas 5 s depois de remover a excitação (Figura 7d). A partir da Figura 7d pode-se inferir que o aumento no tamanho das nanopartículas permite maior armazenamento da energia de excitação. Adicionalmente, as amostras ZGOE3 e ZGOE2 continuaram emitindo fotoluminescência por mais tempo em comparação com ZGOE1, o que novamente apoia a importância de aumentar o tamanho das nanopartículas pelo crescimento mediado por sementes para melhorar as propriedades ópticas das PLNPs de ZGO.

Depois de aprimorar as propriedades de PL das nanopartículas de ZGO revestidas com OA foi realizada a modificação de superfície para remover os ligantes hidrofóbicos e fornecer grupos hidrofílicos na sua superfície. As nanopartículas ZGOE3 foram revestidos com ácido poliacrílico (PAA) mediante uma estratégia de troca de ligante de uma etapa (direta) (rota 1, Figura 8a) e através de uma estratégia de troca de ligante de duas etapas (rota ii, Figura 8a). Neste último caso, as moléculas de OA originais são substituídas por íons BF_4^- usando $NOBF_4$ em N,N-

dimetilformamida (DMF). Posteriormente, os íons BF_4^- são também substituídos pelo polímero PAA em pH 9 (rota ii-a) ou moléculas de cisteamina (rota ii-b). As amostras foram nomeadas como ZGOE3-PAA, ZGOE3-B, ZGOE3-B-PAA e ZGOE3-B-Cys após as modificações de superfície com PAA (rota i), NOBF_4 (rota ii), NOBF_4/PAA (rota ii-a), e NOBF_4/Cys (rota ii-b), respectivamente.

As imagens de TEM na Figura 8b-e mostram que as nanopartículas ZGOE3 mantiveram seu formato após a modificação da superfície com os diferentes ligantes. Conforme mostrado na Figura 8b, grandes aglomerados de nanopartículas foram obtidos após a modificação de superfície com apenas PAA (ZGOE3-PAA) através da estratégia de uma etapa (rota i). Entretanto, todas as outras modificações de superfície permitiram uma boa dispersão das nanopartículas (Figura 8c-e).

Adicionalmente, as modificações de superfície em duas etapas envolvendo BF_4^- conferiram estabilidade coloidal de longo prazo às nanopartículas em meio aquoso (60 dias ou mais), como evidenciado na Figura 8f (i e ii).

As medições de espalhamento dinâmico de luz (DLS) (Figura 8f) das dispersões aquosas após 60 dias de armazenadas em repouso (sem agitação e após agitação) não mostraram alterações importantes no diâmetro hidrodinâmico das amostras ZGOE3-B-Cys (i) e ZGOE3-B-PAA (ii), em relação ao DLS inicial (antes do período de 60 dias), demonstrando sua boa estabilidade coloidal. A alta estabilidade destas amostras está relacionada ao seu alto valor de potencial ζ (-46 e +40 mV, para ZGOE3-B-PAA e ZGOE3-B-Cys, respectivamente) (Figure 8g).

Por outro lado, a amostra ZGOE3-PAA exibiu um valor de potencial ζ mais baixo (-11 mV, implicando estabilidade coloidal limitada) (Figura 8g) e, portanto, uma distribuição de tamanho hidrodinâmico multimodal [Figura 8f (iii)]. Para esta amostra, os diâmetros hidrodinâmicos bimodais mudam significativamente quando a amostra preparada (184 e 462 nm) é armazenada por 60 dias sem agitação (95 e 408 nm), confirmando que de fato esta amostra tem pobre estabilidade coloidal.

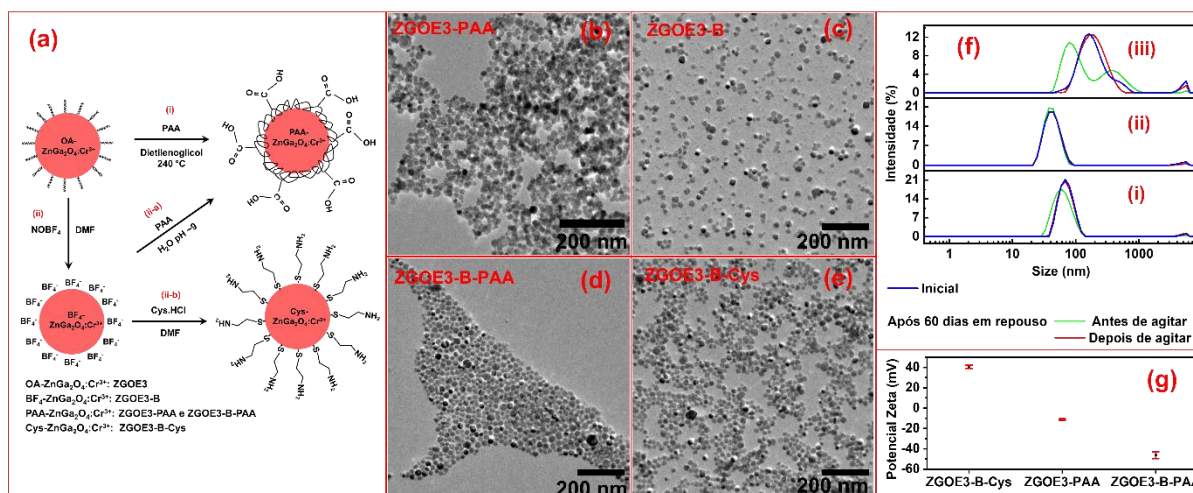


Figura 8 Diagrama esquemático da modificação da superfície das nanopartículas de ZGO através de diferentes estratégias (a). Imagens de TEM ZGOE3 antes e depois das modificações de superfície (b-e). Tamanho hidrodinâmico das amostras antes e após 60 dias em repouso sem agitação e após agitação (f). Valor de potencial ζ das amostras ZGOE3-B-Cys, ZGOE3-PAA e ZGOE3-B-PAA.

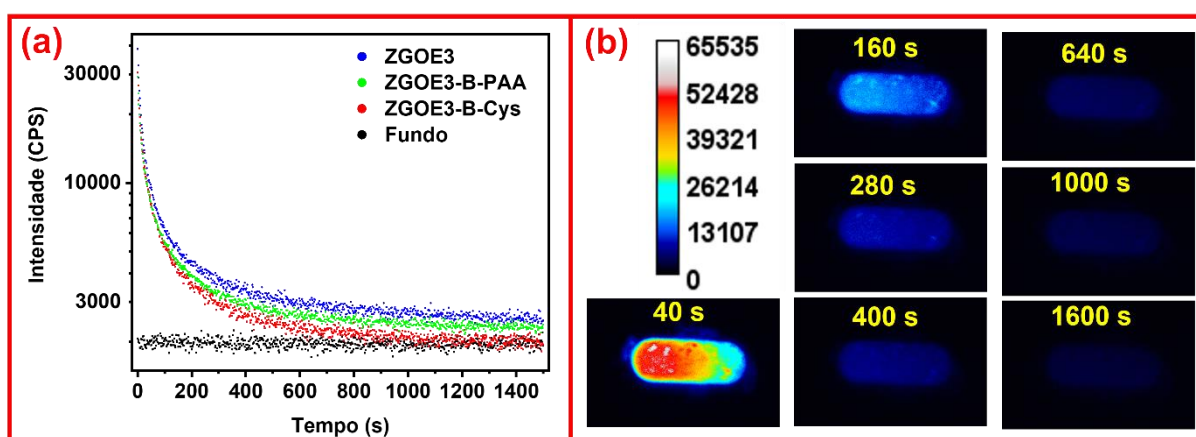


Figura 9 Curvas de decaimento pós-excitação de ZGOE3 (em ciclohexano), ZGOE3-B-PAA (em tampão pH 9) e ZGOE3-B-Cys (em água) (a). Imagens de luminescência da amostra ZGOE3-B-Cys em pó registradas em diferentes intervalos pós-excitação (b). Excitação: 120 s com LED branco; atraso pós-irradiação de 5 s. As imagens de luminescência em (b) contra um fundo preto são representadas com cores falsas onde a cor indica a escala de intensidade de luminescência de preto a branco.

Seguidamente, as curvas de decaimento de luminescência de ZGOE3-B-Cys e ZGOE3-B-PAA foram medidas (Figura 9a) da mesma maneira descrita acima para as amostras revestidos com OA.

As PLNPs hidrofílicos retêm a PL em meio aquoso, e observa-se apenas uma pequena diminuição em sua duração, o que pode estar relacionado à diferença de solvente/meio ou do agente de revestimento das nanopartículas. De fato, as moléculas de Cys são menores e, provavelmente, não fornecem às nanopartículas a mesma proteção que as moléculas maiores de OA ou PAA contra interações com o

solvente, causando dissipação de energia na superfície por interações com grupos O–H de moléculas de água.

Por outro lado, após irradiação da amostra ZGOE3-B-Cys em pó durante 120 s com o LED branco seguiu-se o decaimento da intensidade de luminescência pós-excitação a partir das imagens de luminescência (Figura 9b). Essas imagens mostram a possibilidade de detecção acima de 1500 s, o que é interessante para obtenção de bioimagens de luminescência com baixo sinal de autofluorescência.

Uma vez que se conseguiu boa luminescência persistente e estabilidade coloidal de longo prazo das nanopartículas de ZGO em meio aquoso, o seguinte passo foi a investigação do acoplamento dessas nanopartículas com os materiais com propriedades de UC. Entretanto, as UCPs de $\text{NaYbF}_4:\text{Tm}^{3+}$ sintetizados anteriormente, que apresentaram forte sinal de luminescência de UC na região UV-Vis, não apresentam um tamanho adequado para esse objetivo.

Por isso procedeu-se sintetizar nanopartículas com estrutura do tipo núcleo/casca e composição $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$. A emissão UV-Vis foi aprimorada mediante o controle da espessura da casca. Para controlar adequadamente a espessura dessa camada injetou-se diferentes quantidades de pequenas nanopartículas de NaYF_4 , denominadas *sacrificial nanoparticles* (SNPs), diretamente na mistura de reação das UCNPs centrais (núcleo) de $\text{NaYbF}_4:\text{Tm}^{3+}$ a 300 °C (veja Figura 10a). As UCNPs de $\text{NaYbF}_4:\text{Tm}^{3+}$ de aproximadamente 27,2 nm (veja as Figuras 10c) são favorecidas sobre as SNPs de NaYF_4 energeticamente menos estáveis de aproximadamente 9,5 nm (veja as Figuras 10b), resultando no crescimento de partículas maiores ($\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$) às custas das menores (NaYF_4), formando a estrutura núcleo/casca de $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ com diferentes espessuras da casca, desde 1,4 até 3,4 nm, como mostrado na Figura 10 d-g.

Pode-se observar na Figura 11 que o aumento da espessura da casca teve uma influência positiva na intensidade de luminescência de UC medida sob excitação laser de 980 nm. A explicação para esta observação reside no fato de que o revestimento das nanopartículas centrais (núcleo) com uma casca cada vez maior permite uma concomitante redução da dissipação da energia por migração para a superfície, devido à maior distância núcleo-superfície.

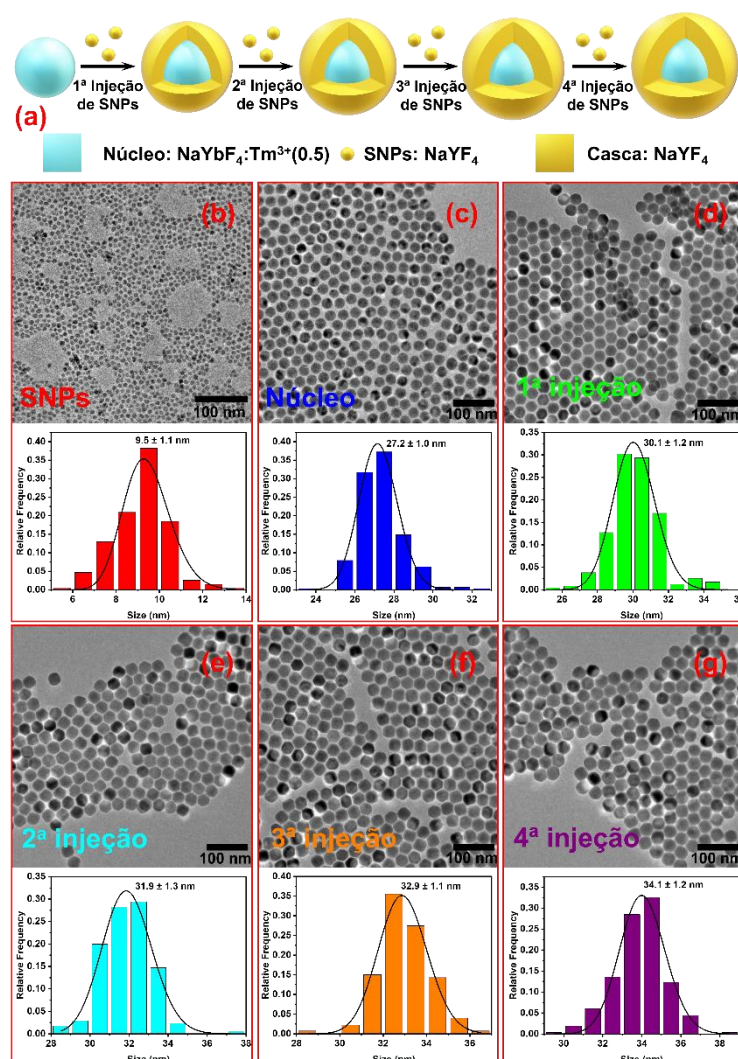


Figura 10 Diagrama esquemático do crescimento da casca a partir das UCNPs de apenas núcleo com injeção de SNPs com base no processo de amadurecimento de Oswald (a). Imagens de TEM e as correspondentes distribuições de tamanho (b-g) das SNPs (b) e as UCNPs de apenas núcleo (c) e de estrutura núcleo/casca com diferentes espessuras da camada de acordo com o número de injeções de SNPs.

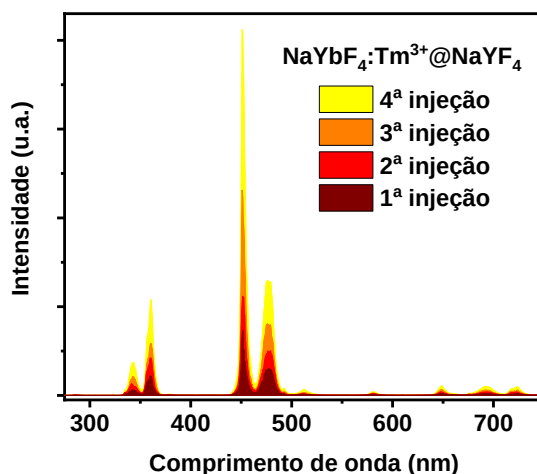


Figura 11 Espectros de luminescência de UC das amostras núcleo/casca de $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4$ com diferentes espessuras de casca. Os espectros foram obtidos sob irradiação com laser de 980 nm.

Após a troca dos ligantes hidrofóbicos por PAA, como foi descrito acima para as PLNPs, procedeu-se com as reações de acoplamento entre as PLNPs e as UCNPs hidrofílicas, usando as nanopartículas com as propriedades ópticas aprimoradas.

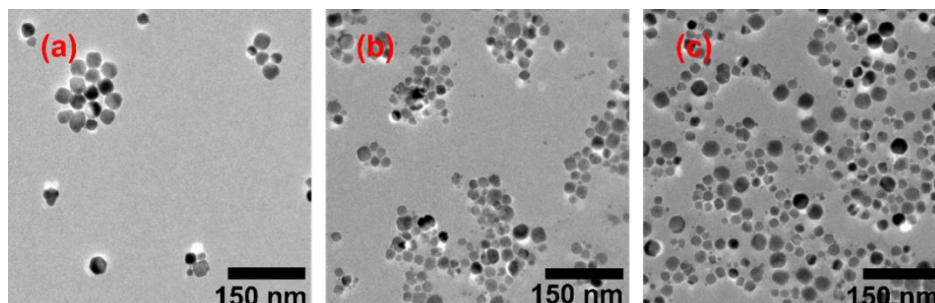


Figura 12 (a-c) Imagens de TEM das nanopartículas produtos das reações de acoplamento dos experimentos (a), (b) e (c), respetivamente, com base na química de acoplamento EDC/NHS em tampão borato pH = 9.

As imagens de TEM na Figura 12, são os resultados do acoplamento entre as PLNPs e as UCNPs com base na química de acoplamento EDC/NHS para a formação de grupo amida. Para o acoplamento entre as nanopartículas revestidas com PAA usou-se o polímero poli(etilenoglicol)bis(amina) (NPEGN), em conjunto com os reagentes EDC e NHS.

Em todos os casos, a quantidade de UCNPs foi fixa, enquanto a quantidade de PLNPs e NPEGN utilizadas foram variadas (ver Tabela 1).

As imagens de TEM sugerem que para a quantidade de PLNPs no experimento da Figura 12a pode ser muito baixa em relação à quantidade de UCNPs, enquanto no experimento da Figura 12c a quantidade de PLNPs em relação à quantidade de UCNPs parece ser adequada. No entanto, ao comparar as Figuras 12 b e c, pode-se observar que a mesma quantidade de NPEGN (0,003 mmol) leva à formação de alguns aglomerados no experimento da Figura 12b (que podem ser devido à formação de ligações covalentes entre os UCNPs e PLNPs), mas não no experimento da Figura 12c. É provável que para o experimento da Figura 12c a quantidade de PLNPs usada (metade do que no experimento da Figura 12b) seja baixa o suficiente para permitir que a quantidade de NPEGN seja ligada a todos os grupos carboxílicos disponíveis na superfície das UCNPs e PLNPs, portanto, o acoplamento entre essas nanopartículas não ocorre ou pode ocorrer em menor proporção. Enquanto isso, no experimento da Figura 12b a quantidade de PLNPs pode ser grande o suficiente para que mais grupos carboxílicos estejam disponíveis do que grupos amino do polímero

NPEGN. Consequentemente, alguns grupos carboxílicos estão livres para a reação de acoplamento.

Além disso, é possível observar nanopartículas individuais, inclusive na Figura 12b, o que pode indicar que nem todas as nanopartículas foram ligadas ao realizar esta estratégia de acoplamento.

Por fim, como perspectivas futuras para melhor entendimento desse processo e obtenção de sistemas UC-PL, novos experimentos de acoplamento, assim como caracterizações, incluindo o estudo da transferência de energia entre as nanopartículas será necessário.

Tabela 1 Condições experimentais das reações de acoplamento entre UCNPs e PLNPs.

Experimento de acoplamento	(a)	(b)	(c)
mmol das UCNPs revestidas com PAA	0.025		
mmol das PLNPs revestidas com PAA	0.02	0.1	0.05
mmol de EDC	0.1	0.15	
mmol de NHS	0.04	0.08	
mmol de NPEGN	0.001	0.003	
Médio	Tampão borato pH 9		

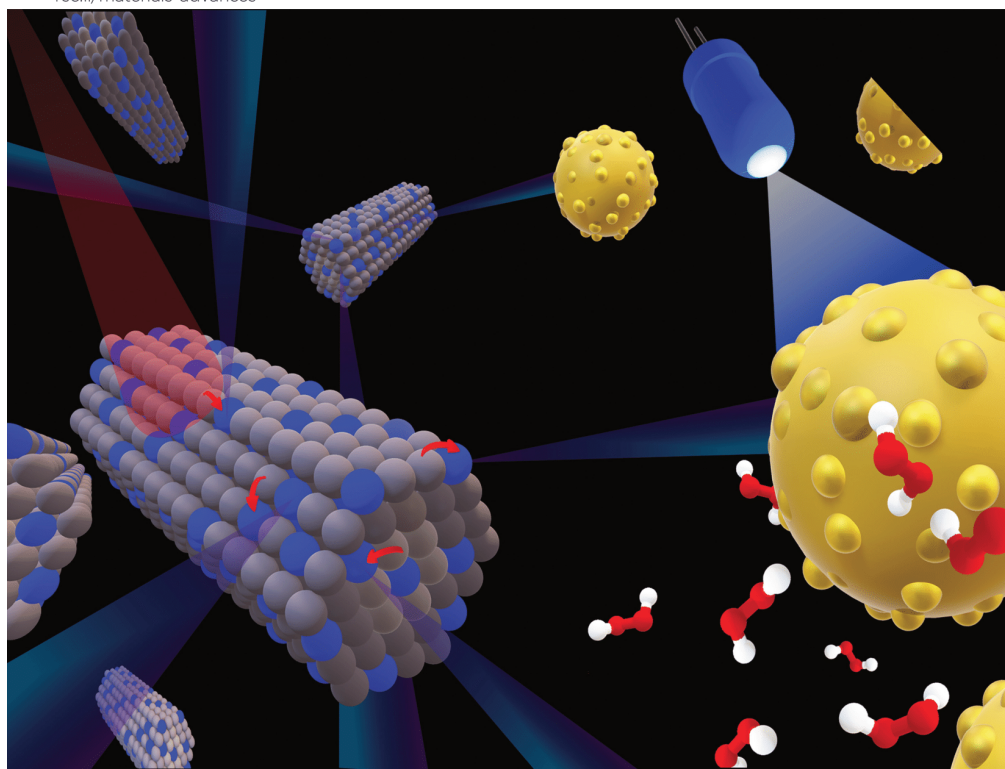
ATTACHMENTS

The article corresponding to Chapter 4 of this thesis “A UV-visible-NIR active smart photocatalytic system based on $\text{NaYbF}_4\text{:Tm}^{3+}$ upconverting particles and $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ for photocatalytic processes under light on/light off conditions” was front cover of Materials Advances journal of Royal Society of Chemistry.

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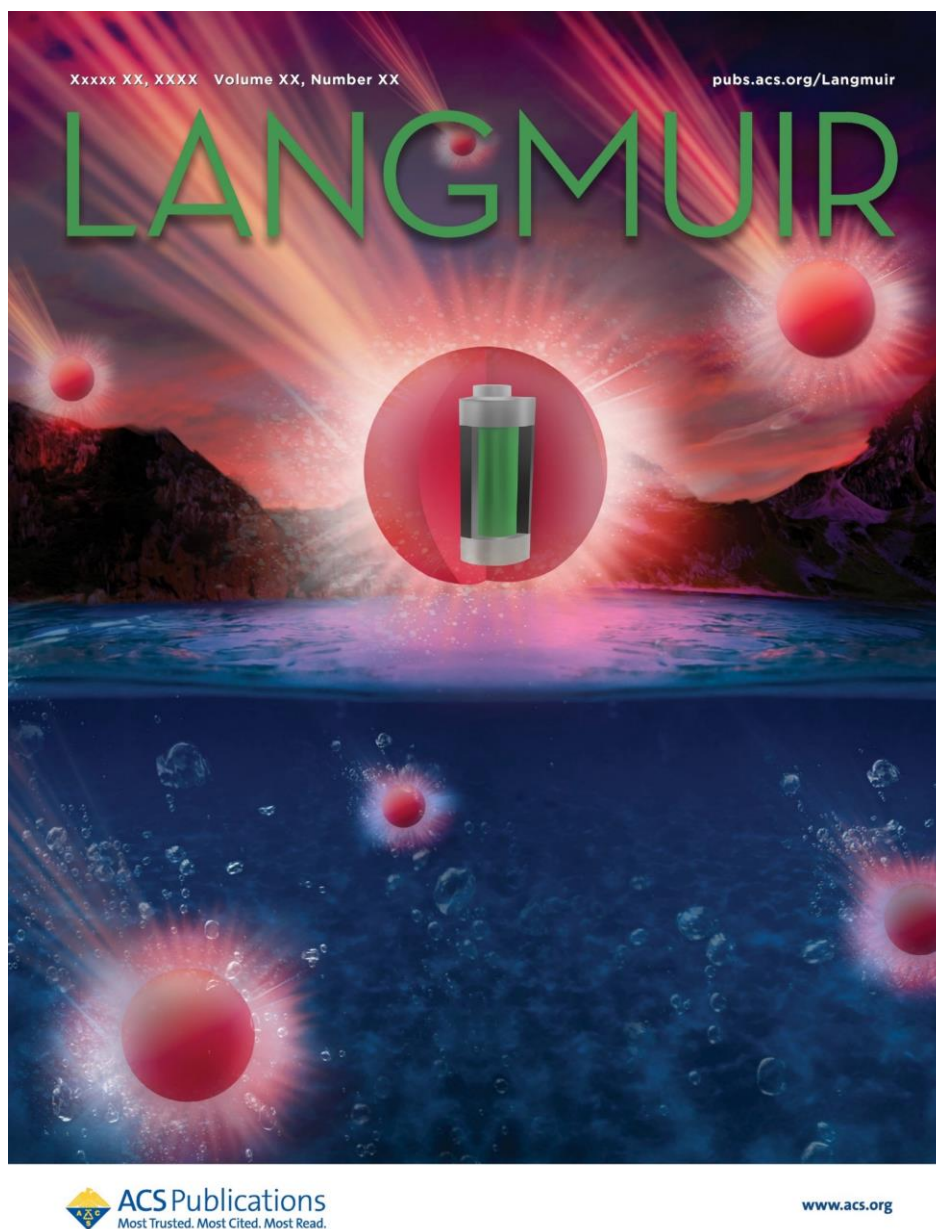


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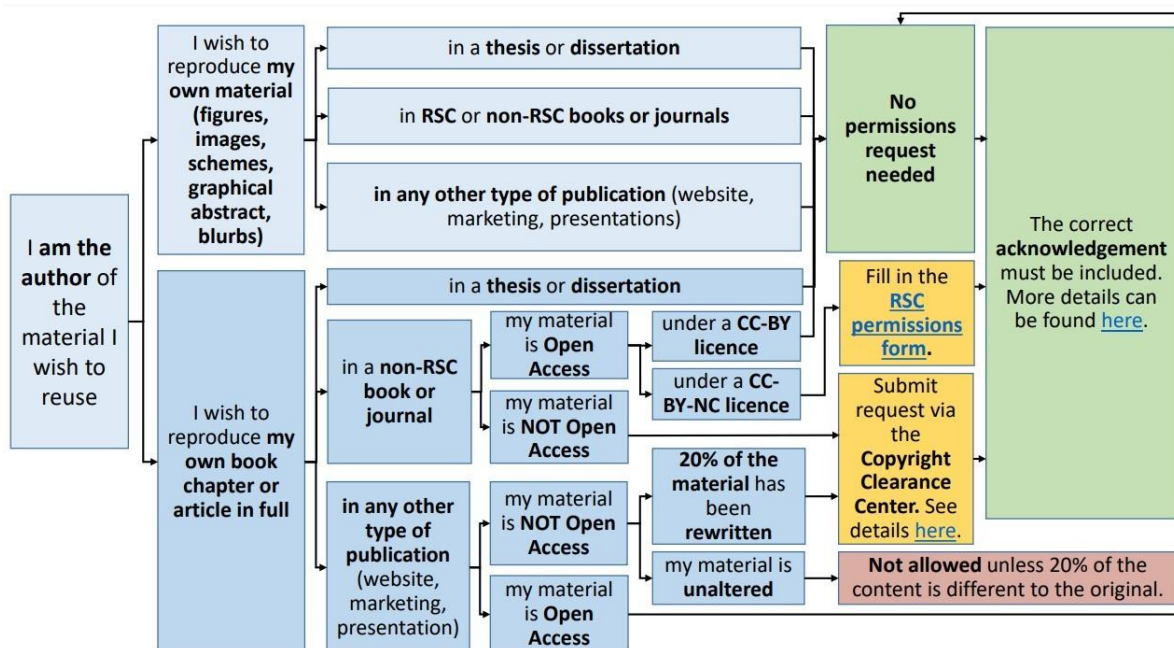
Sajjad Ullah, Sidney J. L. Ribeiro *et al.*
A UV-visible-NIR active smart photocatalytic system based on $\text{NaYbF}_4\text{:Tm}^{3+}$ upconverting particles and $\text{Ag}_3\text{PO}_4/\text{H}_2\text{O}_2$ for photocatalytic processes under light on/light off conditions

The article corresponding to Chapter 5 of this thesis “Size control and improved aqueous colloidal stability of surface-functionalized $\text{ZnGa}_2\text{O}_4\text{:Cr}^{3+}$ bright persistent luminescence nanoparticles” will be cover of Langmuir journal of American Chemical Society.



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Size Control and Improved Aqueous Colloidal Stability of Surface-Functionalized ZnGa₂O₄:Cr³⁺ Bright Persistent Luminescent Nanoparticles

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