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Bacterial cellulose and silk fibroin biopolymers: Biotemplates to design nanostructured materials for optical applications.

MOLÍRIA VIEIRA DOS SANTOS

Ph.D thesis
2016

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Biopolímeros de celulose bacteriana e fibroína da seda: biotemplates para a preparação de materiais nanoestruturados para aplicações ópticas

Tese apresentada ao Instituto de Química,
Universidade Estadual Paulista,
como parte dos requisitos para obtenção
do título de Doutor em Química.

Orientador: Prof. Dr. Sidney José Lima Ribeiro.

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MOLÍRIA VIEIRA DOS SANTOS

Bacterial cellulose and silk fibroin biopolymers: Biotemplates to design nanostructured materials for optical applications.

Thesis presented to the Institute of Chemistry,
São Paulo State University "Júlio de Mesquita Filho",
to obtain the Ph.D in Chemistry.

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Tese apresentada ao Instituto de Química, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Doutora em Química.

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1) SANTOS, M. V.; TOLENTINO, C.; RIBEIRO, S.; BARUD, H.; DE ARAUJO, C. B.; GOMES, A.; DE MELO, L. **Biopolymer Random Laser Consisting of Rhodamine 6G and Silica Nanoparticles Incorporated to Bacterial Cellulose**. In: Conference on Lasers and Electro-Optics 2012. Washington: OSA, 2012. p. JW4A.51.

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“The mind that opens up to a new idea never returns to its original size.”

Albert Einstein

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ABSTRACT

Among all natural polymers, bacterial cellulose and silk fibroin offer unlimited opportunities for processing, functionalization, and biological integration. This thesis presents the preparation and characterization of nanostructured materials based on bacterial cellulose produced by *Gluconacetobacter xylinus* bacteria, as well as regenerated silk fibroin stemmed from the cocoons of silkworms (*Bombyx mori*) for optical applications.

Firstly, dried bacterial cellulose membranes were utilized to prepare cellulose nanocrystals (CNC). CNC were casted in the form of thick iridescent films whose color originates in the periodic patterning of layers in a chiral nematic texture created by self-assembly of rod crystallites. Once the CNC films were obtained, self-sustainable films were coated with a low molecular weight nematic liquid crystal (LC), 4′-(hexyloxy)-4-biphenylcarbonitrile (HOBC). The materials were obtained as free-standing iridescent films, with chiral nematic structure that exhibited modulated optical properties, in response to external stimulus, such as thermal gradient or relatively small electrical voltage. The scanning electron microscopy (SEM) confirmed that the composite film structure comprises the multi-domain Bragg reflectors. The relationship between the surface structure and thermo-responsive properties of investigated HOBC coated with CNC film was examined using transmission optical microscopy (TOM). Additionally, electrostatic force microscopy (EFM) measurement was employed to prove the effect of external stimuli, in this case applied voltage, on the HOBC liquid crystal coated with CNC film.

The second part of this thesis involves the design of luminescent iridescent films through the combination of CNC suspension with tetraethoxysilane (TEOS) and ethanolic solutions of Rhodamine 6G (Rh6G). These materials were obtained as freestanding composite films with chiral nematic organization. The optical properties of such films can be tuned through changes in the silica/CNC proportion during the preparations. Photoluminescence measurements, as function of the detection angle, were realized in order to investigate the influence of photonic structure in the light emission of composite films. Our findings demonstrated that the photonic structure of the film acts as an inner- filter, causing selective suppression of the light emitted with a variation of the detection angle. This behavior was found to be dependent of the bandgap position on the photonic structure of these materials.

Lastly, we designed structured organic-inorganic hybrids (OIH) based on silica and silk fibroin. The materials were obtained as robust monoliths possessing different fibroin fractions. The SEM images demonstrated in-situ self-assembly of fibroin nanofibers dispersed into the

IOH monoliths. Structural characterization of OIH monoliths was performed by Raman and solid state NMR spectroscopies. Our findings demonstrated that precipitated fibroin presented prevailing β-sheet conformation. Furthermore, we demonstrated that the fibroin nanofibers can be used as biotemplates, acting as a sacrificial material to development porous silica monoliths. The porous silica monoliths doped with rhodamine 6g (Rh6G) exhibited efficient RL action with low threshold power excitation and narrowing linewidth. From the spectral behavior, it is inferred that the RL operates in the diffusive regime in hierarchical macro–mesoporous network. In addition, analysis of the emission spectra showed two gain mechanisms coupled, specifically the random lasing and the stimulated Raman scattering, which suggest that designed materials can also be promising for random Raman laser applications.

Keywords: bacterial cellulose, silk fibroin, cellulose nanocrystals, nematic liquid crystal, silica, organic-inorganic hybrids, photonic devices and random lasers.

RESUMO

Entre os polímeros naturais, celulose bacteriana e fibroína da seda oferecem inúmeras oportunidades para funcionalização, processamento e integração biológica. Esta tese apresenta a preparação e caracterização de novos materiais nanoestruturados para aplicações ópticas utilizando celulose bacteriana produzida pela bactéria *Gluconacetobacter xylinus*, como também em fibroína regenerada extraída de casulos do bicho da seda (*Bombyx mori).*

Primeiramente, membranas de celulose bacteriana secas foram utilizadas para a preparação de nanocristais de celulose (NCC). Os nanocristais de celulose foram processados na forma de filmes espessos e iridescentes nos quais a cor tem origem de padrões periódicos de camadas em uma estrutura nemática quiral criada pelo alto montagem dos bastões cristalinos. Uma vez obtido o filme de NCC, o mesmo foi revestido com um cristal líquido nemático de baixo peso molecular, 4'- (hexiloxi) - 4 - bifenilcarbonitrila (HOBC). O material foi obtido como um filme auto-suportado, iridescente, formado por uma estrutura nematic quiral e que exibe moduladas propriedades em resposta a estímulos externos, tais como, gradiente de temperatura e relativa pequena voltagem elétrica. Imagens de microscopia eletrônica de varredura (MEV) confirmaram a estrutura do filme formada por múltiplos domínios refletores de Bragg. A relação entre a estrutura da superfície e as propriedades de resposta térmica do revestimento de HOBC no filme foram investigadas utilizando microscopia óptica de transmissão (TOM). Além disso, medidas de microscopia de força eletrostática foram empregadas para provas o efeito do estímulo externo, neste caso da voltagem aplicada, no revestimento de cristal líquido HOBC no filme.

A segunda parte desta tese envolve a preparação de filmes iridescente luminescentes através da combinação da suspensão de NCC com tetraetoxisilano (TEOS) e uma solução etanólica de rodamina 6G (Rh6G). Estes materiais foram obtidos como filmes compósitos auto suportados com ordenação nemática quiral. As propriedades ópticas dos filmes foram sintonizadas através de mudanças na proporção de sílica/NCC na preparação. Medidas de fotoluminescência em função do ângulo foram realizadas a fim de investigar a influência da estrutura fotônica com ordenação nemática quiral na emissão de luz pelos filmes compósitos. Os resultados demonstraram que a estrutura fotônica dos filmes atuam como um filtro interno causando supressão seletiva da luz emitida com a variação do ângulo de detecção. Este comportamento mostrou-se dependente da posição da banda proibida destes materiais.

Por fim, nós preparamos híbridos orgânico - inorgânicos (HOI) baseados em sílica e fibroína da seda. Os materiais foram obtidos em forma de monolitos robustos conte

diferentes concentrações de fibroína. As imagens de MEV apresentam a precipitação de nanofibras de fibroína dispersas dentro dos HOIs. A caracterização estrutural das amostras foi realizada por espectroscopia Raman e ressonância magnética nuclear (RMN) do estado sólido. Os resultados demonstraram que a fibroína precipitada apresenta preferencial conformação folha- β. Nós demonstramos ainda que as nanofibras de fibroína podem ser utilizadas como moldes, atuando com um material de sacrifício para a produção de monolitos de sílica porosos. Os monolitos de sílica porosa dopados com rodamina 6G (Rh6G) exibiram eficiente ação laser aleatório (LA), com baixo limiar laser e estreita largura de banda. A partir do comportamento espectral, infere-se que o LA opera no regime difusivo na rede hierarquia formada por macro e mesoporos. Além deste comportamento, através de análise do espectro de emissão foi observado o acoplamento de dois mecanismos, laser aleatório e espalhamento Raman estimulado, o que sugere que o material obtido também pode ser promissor para aplicações em laser aleatório Raman.

Palavras-chaves: Celulose bacteriana, fibroína da seda, nanocristais de celulose, sílica, híbridos orgânicos-inorgânicos, dispositivos fotônicos e lasers aleatórios.

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LIST OF ABBREVIATIONS

AFM- Atomic Force Microscopy

8CB - 4-Cyano-4′octylbiphenyl

BC - Bacterial cellulose

BET- Brunauer, Emmett, Teller

CNC - Cellulose nanocrystal

DP- Degree of polymerization

DSC- Differential scanning calorimetry

EFM - Electrostatic force microscopy

EPE- Excitation pulse energy

HOBC- 4'-(hexyloxy)-4-biphenyl carbonitrile

IOH- Inorganic organic hybrids

LCs - Liquid crystals

MFC - Microfibrillated cellulose

NFC - Nanofibrillated cellulose

M_W - Molecular weight

NMR - Nuclear magnetic resonance spectroscopy

PLA - Poly(l-lactic acid)

PL- Photoluminescence

POM- Polarized optical microscopy

RL- Random laser

Rh6G- Rhodamine 6G

SF- Silk Fibroin

SEM - Scanning electron microscopy

TOM - Transmission optical microscopy

TEOS - Tetraethylorthosilicate

TEM - Transmission electron microscopy

TG- Thermogravimetric

UV - Ultraviolet

CONTENTS

Organization of the thesis

In light of recent studies, cellulose nanocrystals extracted from bacterial cellulose and regenerated silk fibroin from silkworm cocoons are attractive alternatives to design multifunctional materials, reason why this is the focus of such thesis.

Therefore, this study is divided into four chapters. The first chapter is devoted to introduce cellulose nanocrystals and silk fibroins, their preparation, properties and recent applications. Subsequently to the introductory section, the preparation of multifunctional materials based on cellulose nanocrystal is presented on second and third chapter.

Further, the second chapter presents the preparation of free-standing CNC films coated with low molecular weight nematic liquid crystal (LC), 4′-(hexyloxy)-4-biphenylcarbonitrile (HOBC), which integrate iridescence, conductive and thermal response. Such composite films were morphologically characterized by the SEM and POM, and optically by electron spectroscopy. Emphasis is given to the characterization of morphological and optical properties of the composite in function of the temperature. Additionally, the conductive response brush surface was evaluated using electrostatic force microscopy (EFM) measurements.

Afterwards, the third chapter encompasses the preparation and characterization of iridescent luminescent films based on dye-doped CNC/silica composites. Such composite films were morphologically characterized through SEM and POM, and optically by electron spectroscopy. In this section, the focus is given to the investigation of the influence of photonic structure of films on light emission from dye-doped CNC/HOBC composites, using luminescence spectroscopy measurements in function of the detection angle.

Finally, in the last chapter, the synthesis of organic inorganic hybrids monoliths based on silica and silk fibroin is described. The hybrids monoliths were morphologically characterized by SEM and structural characterized by Raman, and solid state RMN spectroscopies. Additionally, the chapter also describes the preparation of porous silica monoliths using the fibroin nanofibers as a biotemplate. The silica monoliths were morphologically characterized by SEM and their porous structure were characterized via nitrogen adsorption experiments. Moreover, the random laser action of silica monoliths was investigated.

1. INTRODUCTION

Commonly, natural materials provide a convincing template to reinterpretation and, in some cases, simplification of modern manufacturing, while rendering them sustainability and green. Biopolymers, produced and modified by living organisms are the pillars of self-assembly on structurally hierarchical micro and nanoscale systems, which occur naturally, such as chitin of butterfly wings, beetles exoskeletons, keratin in peacock feathers (PENNISI, 2013; WEAVER et al., 2012; YANG et al., 2013), and so forth. From the material science perspective, biopolymers can be a versatile source to design structured inorganic or inorganic/organic materials in the laboratory. The interest in the direct use and re-engineering of natural polymers as platforms for the development of technology materials has been growing in recent years. The challenge using these materials is to identify, among the options available, materials that present adequate properties to interface with current technology. In addition, such materials should be widely available and have competitive costs in the world market. Thus, in this thesis, there is an interest in the opportunities offered by bacterial cellulose produced through the *Gluconacetobacte*r *xylinus* bacteria and silk fibroin extracted from *Bombyx mori* silkworm cocoons biopolymers as platforms for technological applications.

6. GENERAL CONCLUSION.

The main goal of this PhD research was to exploit the self-assembly properties of cellulose nanocrystals (CNC) extracted from bacterial cellulose produced by *Acetobacter xylinum* bacteria, as well as, regenerated silk fibroin (SF) stemmed from the cocoons of the silkworm (*Bombyx mori*) in order to prepare nanostructured materials for optical applications. In this context, different multifunctional materials were prepared.

Initially, a composite structure formed from two different liquid crystal forming materials, a low molecular weight 4′-(hexyloxy)-4-biphenylcarbonitrile (HOBC) and cellulose nanocrystals (CNC), was prepared. The HOBC was applied on a CNC film by simple painting. In this case, HOBC liquid crystal was used as a functional compound to promote new properties of the CNC films. The new material here proposed was obtained as a free-standing iridescent film, with chiral nematic structure. The films exhibited modulated optical properties, in response to thermal gradient or relatively small electrical voltage, in addition to liquid crystal properties of the CNC films. Further, the HOBC coating did not change the morphological and optical properties of the cellulose nanocrystal film. It is noteworthy that, for this record, cellulose nanocrystals iridescent films with thermochromic or conductive properties have not been reported in the literature yet. This work presented a new platform for utilization of CNC film, which opens the possibility of applications for this material in the field of thermo- and electro optical devices.

Moreover, still in the field of optical applications of CNC, the preparation of iridescent luminescent composite films by combining tetraethoxysilane (TEOS) to a CNC suspension and to ethanolic solutions of a broad band emitter (Rhodamine 6G (Rh6G)) was demonstrated. The composites were obtained as free-standing films with chiral nematic organization. The morphological and optical characterization demonstrated that the insertion of silica in the composites implies in the control of optical film properties, as well as in the improvement in the quality of the photoluminescence material. The cellulose based photonic materials also displayed modulated photoluminescence with detecting angle. This behavior suggests that the photonic structure with chiral nematic ordering has a strong effect in the emission spectra. In addition, it was demonstrated that this effect is tuned with the stop band position of composite films. Taken the advantages of the luminescence and chiral nematic ordering integration of the CNC films, some examples have been reported in the literature. However, in all of them, their focus was given to the modulating spontaneous emission through circularly polarized excitation of the samples. In this thesis, it is suggested a novel strategy to modulate the emission of

luminescent species exploring the inner filter effect of the periodic structure of films. Thus, it holds that this multifunctional material can be attractive to develop new optical devices with potential for various applications, such as, sensors, lasers or tunable filters.

Finally, multifunctional organic inorganic hybrids based on silica and silk fibroin were developed. Although there are several reports on the literature that present design silica/fibroin hybrids materials, this was the first time the preparation of robust monoliths containing until 15.8 wt% of fibroin was demonstrated. In addition, it was exhibited that these unique materials are formed by 3D network silica gel reinforced by the interpenetrated fibroin nanofibers with preferential crystalline β-sheet conformation, which can lead to an improve of the robustness and the hardness of monoliths when compared with silica xerogel. Likewise, considering the biocompatible property of these materials, the combination of silica and silk leads to very promising and versatile materials with foreseen application in a variety of domains, including bone regeneration. However, it was also possible to demonstrate that the fibroin nanofibers can be used as biotemplates, acting as a sacrificial material to develop porous silica monoliths. These porous monoliths demonstrated efficient RL action, operating in a diffusive regime in hierarchical macro–mesoporous network. In addition, when higher values of EPE are inserted, the emission spectra obtained present the stimulated emission and stimulated Raman scattering mechanisms coupled. These results suggest that designed materials can be promising for new applications of the RL phenomenon, such as specklefree laser imaging and random Raman laser.

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