Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

Synthesis by combustion in solution of Zn_2TiO_4+Ag for photocatalytic and photodynamic applications in the visible

IOP Conf. Series: Journal of Physics: Conf. Series **935** (2017) 012013 doi:10.1088/1742-6596/935/1/012013

Synthesis by combustion in solution of Zn_2TiO_4+Ag for photocatalytic and photodynamic applications in the visible

A A Lopera[1], **A M Velásquez**[2], **E A Chavarriaga**[1], **S Ocampo**[1], **M A Zaghete**[2], **M A Graminha**[2] **and C P Garcia**[1]

[1] Universidad Nacional de Colombia, Bogotá, Colombia

[2] Universidade Estadual Paulista Júlio de Mesquita Filho, Araraquara, Brasil

E-mail: aalopera@unal.edu.co

Abstract. Zn_2TiO_4 + Ag compounds were synthesized by the solution combustion path seeking to enhance their photocatalytic and photodynamic response in the visible. X-ray diffraction tests confirmed the formation of the phase and the presence of metallic silver. Field emission electron microscopy evidenced the formation of aggregates formed by grains lower than 100nm. The diffuse reflectance tests allowed to detect compound absorption in the visible region and activation energy of 2.8eV. The evaluation of the photocatalytic properties was performed by the degradation of methylene blue while the photodynamic response in biological systems was performed by the antilesihmanicidal response of the compounds in promastigotes of Leishmania amazonensis. Indirect measurement of ROS species confirmed the formation of oxygen singlets and OH radicals of the compounds when subjected to the action of visible light.

1. Introduction

Semiconductor ceramic materials with photocatalytic properties are of great interest due to their multiple applications in different areas, from waste water treatment to applications such as photodynamic therapy. These applications are based on the principle of the production of ROS reactive species, which can interact with different types of inorganic and organic molecules until their breakdown. It allows applications in photodynamic systems for the treatment of skin diseases such as cancer or parasitic diseases such as cutaneous leishmaniasis. One of the main interests in photocatalytic and photodynamic systems is that their activation could do it in the visible spectrum and thus enhance their applications because approximately 40% of sunlight is within the range of 400-700nm while UV only covers about 4%.

The zinc titanate Zn_2TiO_4 is an inverse spinel often reported as a secondary or resulting phase of the TiO_2/ZnO system. It has an excellent thermal stability and is interesting in different applications such as pigments, catalysts, sensors, dielectric materials [1,2] adsorbent systems [3], and degradation of dyes by UV irradiation [4]. On the other hand, Ag is a material with excellent antimicrobial and antiparasitic properties. Silver nanoparticles have been used in multiple investigations against different strains of E.Coli, Stapilococcus aureous, and antileishmanial response [5,6]. Recently, a study of the antimicorbial and photocatalytic properties of the Ag/TiO_2/ZnO system under visible irradiation was carried out [7,8], reiterating their properties and potential use in water decontamination and disinfection. In the present work, we synthesized Zn_2TiO_4+Ag through combustion in solution and evaluated its potential photocatalytic response in the visible by the degradation of methylene blue and its photodynamic response in the visible with the effect aintilehismania in promastigotes L. amazonensis.

IOP Conf. Series: Journal of Physics: Conf. Series **935** (2017) 012013 doi:10.1088/1742-6596/935/1/012013

2. Experimental

2.1. Samples preparation and morphological - structural characterization

Zn_2TiO_4+Ag powders were synthesized by means of combustion in solution route. Titanium isopropoxide (Alfa Aesar) Zinc nitrate hexahydrate (Merck), commercial silver metal, nitric acid and glycine (Sigma Aldrich) were used as reagents. Titanium nitrate was initially obtained from titanium isopropoxide using the appropriate amount of water and nitric acid. Silver nitrate was obtained by reacting commercial silver and nitric acid. Zinc nitrate and silver nitrate were added to Titanyl nitrate solution. Glycine was used as fuel and the molar ratio between nitrates-fuel was adjusted to the previously reported parameter $\varphi=1$ [9]. The system was heated and magnetic stirred at 80°C and 300rpm respectively until combustion was reached. The ashes obtained were macerated in agate mortar and calcinated at 700°C for 2 hours. For crystalline phase identification, X-ray diffraction with a double circle multipurpose Xpert-Pro PANanalytical Radiation Cu-Ka (λ=0.15406nm) diffractometer in a range of diffraction of 0-80°(2θ) was used. The optical properties of powders were analysed by spectrophotometry measurements of diffuse reflectance UV-VIS using a Perkin Helmer equipment with a spectral range between 280-800nm. The powder morphology was analysed in a Scanning Electron Microscope JEOL JSM-7610F (FE-SEM).

2.2. Assessment of photocatalytic activity by indirect measurement of ROS species and degradation of methylene blue

For the photodynamic activation, a white led light source was used with an irradiation power of 100mW/cm^2. The detection of ROS species was performed indirectly by fluorescence of the probe 2',7'-dichlorofluorescein diacetate (H_2DCFDA) and Singlet Oxygen Sensor Green (SOSG) for hydroxyl radicals and singlet oxygen respectively. For the measurement of the hydroxyl radicals the compound was suspended in 200µl of deionized water and in 10µg/mL H_2DCFDA. For the detection of the oxygen singlets, 3µM of the SOSG probe dissolved in ethanol was used. The compounds were immediately exposed to visible irradiance by led light and the fluorescence was monitored for 60 minutes at excitation/emission in an equipment Infinite M200Pro, TECAN with wavelengths of 488/520nm and 505/525 nm respectively.

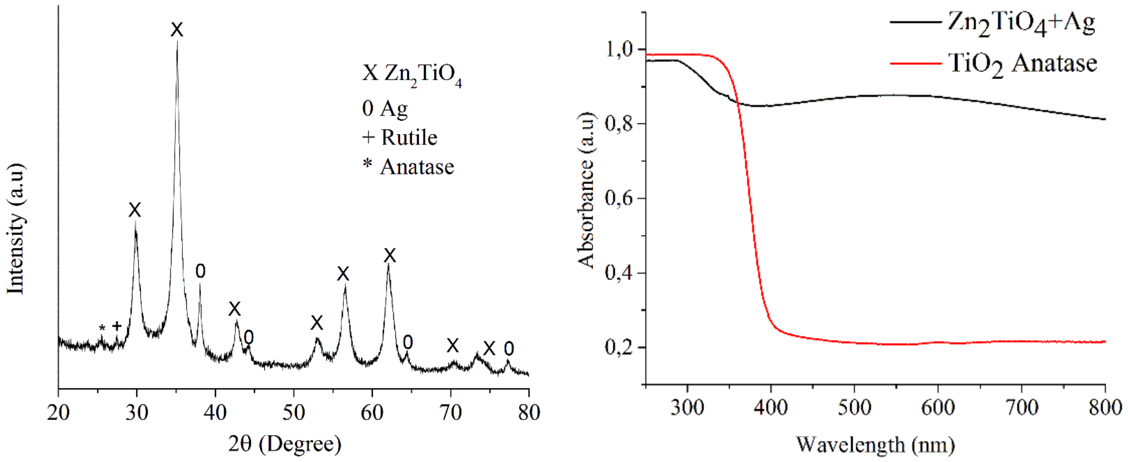
For the photocatalytic evaluation, a stock solution of methylene blue at 1mmol in water was prepared. 20mg of the compound were added. The system was sonicated for 20 minutes and subsequently was placed in a reactor under constant stirring and visible irradiation. The degradation of methylene blue was monitored by spectrophotometry at 670nm.

2.3. Assessment of the activity by measuring antipromastigotes of Leishmania amazonensis

Promastigotes of L. amazonensis MPRO/BR/1972/M1841-LV-79 were used for the photodynamic tests. The parasites were kept in culture medium at 28°C. 96-well plates and a concentration of parasites of 5×10^5 were used. A stock solution of Zn_2TiO_4+Ag with a concentration of 20mg/mL was prepared. This solution was added to the wells with Leishmania in the respective amounts starting from a concentration of 1000µg/mL to 25µg/mL. The plates with Leishmania+compounds were exposed to visible irradiation for 40 minutes (the tests were performed in triplicate) and incubated in a humid chamber at 27°C for 24 hours. Subsequently a cell viability test was performed [10].

3. Results and discussion

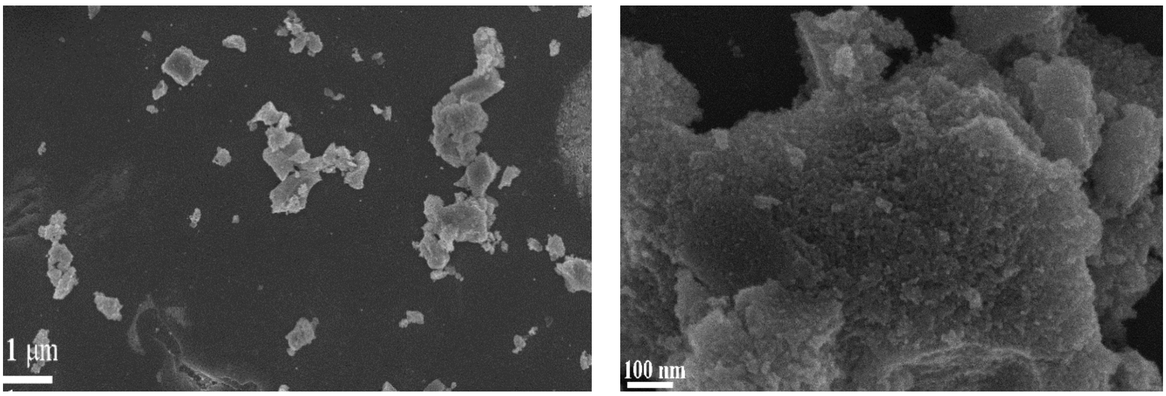
Figure 1(a) shows the diffractograms of the obtained powders subjected to 700°C for 2 hours. The predominant phase was the spinel Zn_2TiO_4 indexing with the pattern JDPCS 00-013-0536. It is possible to identify metallic silver indexed with the pattern JCPDS 04-0783 and anatase and rutile as the main titanium phases. Zn_2TiO_4 is usually formed under temperatures close to 1000°C when is obtained by solid state. Using the combustion route the temperature of the phase was 700°C. Other works report 900°C as the minimal temperature to obtain this phase by combustion route during 4 hours when urea was used as fuel [3]. In our case the fuel used was glycine, which could result in a more exothermic combustion reaction that makes easier the formation of the phase. Synthesis of the Ag/TiO_2/ZnO system by a sol gel route was performed by Shalaby et al. finding that the Zn_2TiO_4 phase was not formed for temperatures lower than 800°C and only from this temperature appeared that phase associated to other secondary phases of ZnO, $ZnTiO_3$ and metallic silver [7]. UV-Vis spectrophotometry (Figure 1(b)) showed that the Zn_2TiO_4+Ag compounds showed visible absorption unlike the commercial TiO_2. The compounds Zn_2TiO_4+Ag presented an energy band gap of 2.8eV. The absorbance of the sample in the visible can be related to the formation of intermediate states of energy due to the possible doping of the structure with C and N atoms from the combustion reaction in solution [11]. This kind of reactions are characterized by releasing large amounts of CO_2 and NO_x. Similar behaviours had already been observed in synthesis of TiO_2 structures by combustion in solution [12].



(a) (b)

Figure 1. (a) X-ray diffractograms for the sample treated at 700°C for two hours (b) diffuse reflectance of the calcined powders at 700°C.

Field emission microscopy showed micrometric aggregates with sizes ranging from 0.5 to 3µm (see Figure 2(a)). These aggregates are composed of small particles with geometries tending to be granular and lower than 100nm (Figure 2(b)). The combustion route is characterized by the facility to obtain nanometric systems with geometries tending to be spherical but with a considerable degree of aggregation [9]. In the combustion routes, the production of nanoparticles depends mainly on the local temperature and the distribution of it in the medium. Choosing an adequate fuel and an adequate ignition mechanism play a decisive role in the final product morphology [9].



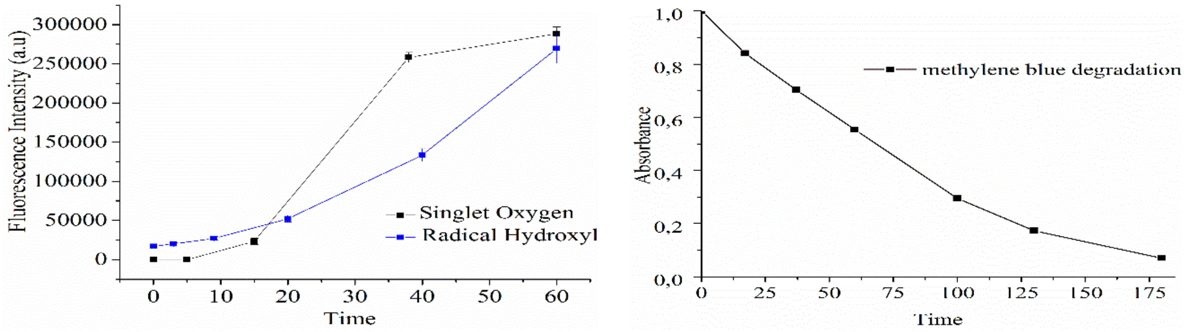
(a) (b)

Figure 2. Electron emission field photomicrographs for calcined powders.

IOP Conf. Series: Journal of Physics: Conf. Series **935** (2017) 012013 doi:10.1088/1742-6596/935/1/012013

Figure 3 (a) shows the fluorescence intensity of the test molecules over time, evidencing the formation of reactive oxygen species, both for the production of oxygen singlets and hydroxyl radicals. The fluorescence increases with the time of exposure to the light source corroborating the electronic excitation and the production of electron hole pairs in the structure of the Zn_2TiO_4.

Figure 3 (b) shows the absorbance measurements as a function of time for the solution of methylene blue exposed to visible irradiance by led light. The degradation measurements showed 50% of methylene blue decomposition at 70 minutes of irradiation and almost total discoloration at 180 minutes of irradiation. Figure 4 shows the percentage of cell viability of L amazonensis promastigotes incubated with different concentrations of the compound and irradiated with visible light during 40 minutes.



(a) (b)

Figure 3. (a) Fluorescence intensity of the molecules used to detect ROS species. (b) Photocatalytic degradation of methylene blue undo visible radiation.

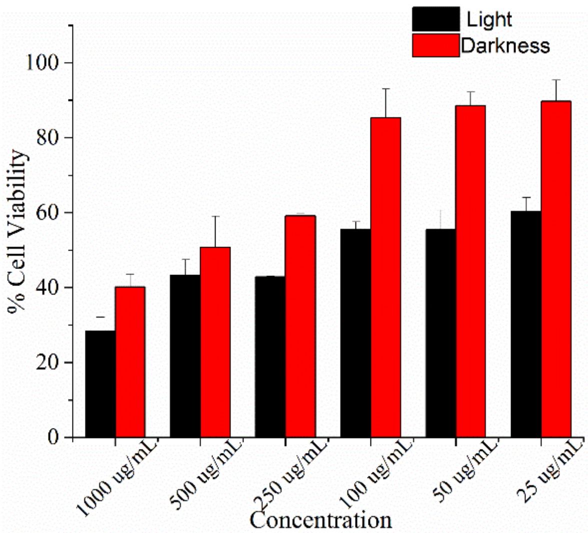


Figure 4. Cell viability of L. amazonensis promastigotes incubated with the compound at different concentrations and subjected to visible light.

A dose-dependent response was shown. Even for concentrations greater than 1000µg/mL cell viability was reduced by more than 50%. This behaviour could be associated with Ag properties acting as anti-parasitic agent. The anti-leishsmania capacity of the Ag nanoparticles and Ag/ZnO nanocomposites is well known [5]. The photodynamic effect of the compounds was higher with lower concentrations (25, 50, 100µg/mL). At these values the cell viability decreased between 25-30% with respect to controls when the systems were irradiated, whereas for the higher concentrations (250, 500, 1000µg/mL) the viability cell decreased between 5-10% with respect to the controls. This could be explained by assuming an antileishmanicide effect corresponding to the sum of the effect due to light irradiation (photodynamic response) and the independent effect of the silver particles. At low concentrations the photodynamic effect is greater than the cellular inhibition of Ag and in the case of high concentrations the antiparasitic response is due to a greater extent to the Ag present in the compounds. The antileishmania response of these compounds is related to the production of reactive species of oxygen both singlet oxygen and hydroxyl radicals which can interact with different biological molecules producing membrane peroxidation and stimulating the immune response of the cell. A. Nadhaman *et. al*. [13] reported that materials that can produce these reactive species are interesting as antilehismania compounds. Other studies as cytotoxicity, genotoxicity and hepatoxicity are required in order to support the biological safety of these compounds to be used as photodynamic systems.

4. Conclusions

Zn_2TiO_4+Ag compounds were synthesized by combustion in solution. The X-Ray diffractograms showed the presence of peaks associated with metallic silver. The compounds showed a visible absorption spectrum and a band gap of 2.8V. The compounds showed production of single ROS species of oxygen and hydroxyl radicals upon irradiation. These species were responsible for the degradation of methylene blue dye in 180 minutes and the photodynamic response antileishmaniasis. The presence of silver also plays an important role because of its antiparasitic capacity.

Acknowledgements

This work was partially funded by CNPq-TAWS of Brazil, Colciencias, Project "National Doctorates Call for 6172" and the National University of Colombia, Medellín.

References

[1] A C Chaves, S J Lima, R C Araújo, M A M Maurera, E Longo, P S Pizani, L G Simões, L E Soledade, A G Souza and I M G dos Santos 2006 *J. Solid State Chem.* **179** 985-992
[2] H T Kim, Y Kim, M Valant and D Suvorov 2001 *J. Am. Ceram. Soc.* **84** 1081-1086
[3] R Raveendra, P Prashanth and B Nagabhushana 2015 Synthesis, Characterization of Combustion Derived Zn 2 TiO 4 Nanocrystals and Its Application to Adsorption of Azo Dye *International Journal of Advanced Scientific and Technical Research* **5** 129-137
[4] P Zhang, C Shao, M Zhang, Z Guo, J Mu, Z Zhang, X Zhang, P Liang and Y Liu 2012 *J. Hazard Mater.* **229** 265-272
[5] P Baiocco, A Ilari, P Ceci, S Orsini, M Gramiccia, T Di Muccio and G Colotti 2011 *ACS. Med. Chem. Lett.* **2** 230-233
[6] I Sondi and B Salopek-Sondi 2004 *J. Colloid Interf. Sci.* **275** 177-182
[7] A Shalaby, A Bachvarova-Nedelcheva, R Iordanova, Y Dimitriev, A Stoyanova, H Hitkova, N Ivanova and M Sredkova 2015 *J. Optoelectron. Adv. M.* **17** 248-256
[8] S Manik and S Pradhan 2006 *Physica E.* **33** 69-76
[9] K C Patil, S T Aruna and T Mimani 2002 *Curr. Opin. Solid St. M.* **6** 507-512
[10] T Mosmann 1983 *J Immunol. Methods* **65** 55-63
[11] K Nagaveni, G Sivalingam, M Hegde and G Madras 2004 *Appl. Catal. B-Environ.* **48** 83-93
[12] A D Mani, V Laporte, P Ghosal and C Subrahmanyam 2012 *Mater. Res. Bull.* **47** 2415-2421
[13] A Nadhman, S Nazir, M I Khan, S Arooj, M Bakhtiar, G Shahnaz and M Yasinzai 2014 *Free Radical Bio. Med.* **77** 230-238