Zinc oxide nanocolloids prepared by picosecond pulsed laser ablation in water at different temperatures

Luisa D'Urso^{1,*}, Salvatore Spadaro², Martina Bonsignore², Saveria Santangelo³, Giuseppe Compagnini¹, Fortunato Neri², and Enza Fazio^{2*}

¹Dip. di Scienze Chimiche, Università di Catania, Catania, Italy

²Dip. di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra (MIFT), Università di Messina, 98166 Messina, Italy

³Dip. di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università Mediterranea, 89122 Reggio Calabria, Italy

Abstract. Zinc oxide with wide direct band gap and high exciton binding energy is one of the most promising materials for ultraviolet (UV) light-emitting devices. It further exhibits good performance in the degradation of non-biodegradable pollutants under UV irradiation. In this work, zinc oxide (ZnO) and zinc oxide/gold (ZnO/Au) nanocolloids are prepared by picosecond pulsed laser ablation (ps-PLA), using a Zn and Au metallic targets in water media at room temperature (RT) and 80°C. ZnO and Au nanoparticles (NPs) with size in the 10–50 nm range are obtained at RT, while ZnO nanorods (NRs) are formed when water is maintained at 80°C during the ps-PLA process. Au NPs, added to ZnO colloids after the ablation process, decorate ZnO NRs. The crystalline phase of all ZnO nanocolloids is wurtzite. Methylene blue dye is used to investigate the photo-catalytic activity of all the synthesised nanocolloids, under UV light irradiation.

1 Introduction

Photo-catalysis has been emerged as a viable route to decrease the damage caused by dye pollution to environment and humans [1]. The removal of persistent and toxic organic compounds (TOCs) from contaminated water occurs through oxidation and reduction processes. Several kinds of semiconductor-based photo-catalysts, such as titania (TiO₂), zirconia (ZrO₂), tungsten trioxide (WO₃), tantalum pentoxide (Ta₂O₅), hematite (Fe₂O₃) and zinc oxide (ZnO), have been applied in wastewater treatment to convert non-biodegradable TOCs into non-toxic chemicals under UV irradiation [2,3].

Among them, ZnO looks as a very promising candidate for environmental applications because it is cheap, and has a great photo-catalytic activity, a strong oxidation ability, a direct and wide band-gap energy in the near-UV spectral region (3.3 eV at 300K), higher quantum efficiency compared to other wide band-gap semiconductors, and a large free-exciton binding energy (60 meV) so that exciton emission processes can persist at or even above the room temperature. Moreover, being compatible with living organisms, ZnO is currently employed in a broad range of daily applications without risks to human health and environmental impact [4].

Many works in the literature deal with the utilisation of ZnO for UV lasers, high power light emitting diodes, solar cells, heterogeneous catalysis and antibacterial treatments and the effective degradation of harmful and toxic pollutants present in the wastewater [5]. Nonetheless, the photo-catalytic activity of ZnO nanomaterials is limited under the sun irradiation because the solar spectrum contains only 5–7% of the UV component. The relatively high recombination rate of generated electron-hole pairs also reduces the efficiency of this photo-catalyst. A large number of factors, such as crystallinity, crystallite size, crystal phase, and porosity, as well as specific surface area, can further affect the performance of ZnO [6].

Different strategies have been employed in order to improve the photo-catalytic performance of semiconductor materials. The nanostructuration, resulting in a high surface-area/volume ratio, enhances the amount of the photo-generated charge carriers, whereas the addition of metal NPs on the photo-catalyst surface reduces recombination rate of the excited photoelectron-hole pairs. Gold NPs have been successfully utilised by several groups. The addition of Au NPs shifts the optical absorption into the visible region, hence enabling a more efficient utilisation of the solar energy. Au NPs can act as a sink for photo-induced charge carriers, thus promoting interfacial chargetransfer processes. Moreover, receiving electrons from the Au NPs surface, oxygen can trap electrons and becomes the active O_2^- species with consequent enhancement of the photo-catalytic activity [7].

In this paper, we propose a simple and cheap physical approach to the synthesis of ZnO and Audecorated ZnO nanorods with no environmental impact.

Corresponding author: ldurso@unict.it; enfazio@unime.it

[©] The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (http://creativecommons.org/licenses/by/4.0/).

Materials produced are tested as catalysts for environmental applications, showing relatively high photo-degradation efficiency of methylene blue (MB) in aqueous solution under UV light irradiation.

2 Experimental

2.1 Synthesis of the ZnO-based nanocolloids

Figure 1a displays the experimental setup utilised for the synthesis of nanocolloids. The second harmonic (532 nm) of a laser operating at 100 kHz repetition rate with a pulse width of 6–8 ps was used for the ablation experiments (Fig. 1b). The laser beam was focused to a spot of about 70 μ m in diameter on the surface of the target with a galvanometric scanner having a telecentric objective with a focal length of 163 mm.



Fig. 1. (a) Experimental setup utilised for the synthesis of nanocolloids, (b) during laser irradiation.

Gold and metallic zinc targets with a thickness of 3 mm (99.99% purity) were positioned on a holder within a glass vessel and ablated in distilled water. In an experiment, the water was maintained at RT, in the other one it was heated at 80°C before the ps-PLA process. ZnO and Au nanocolloids were produced by separate ablation processes. The ZnO and Au targets were irradiated, at a typical laser power density of 2.0 W/cm², for 30 min and 5 min, respectively. Au decorated ZnO nanostructures were obtained by mixing ZnO and Au colloidal solutions, in 1:1 volume ratio, immediately after their production. After preparation, all the solutions were stirred at RT in an ultrasonic bath for about 15 min.

2.2 Nanocolloids characterisation and photocatalytic activity evaluation

The morphology of the samples was investigated by scanning electron microscopy (SEM). SEM analyses were carried out with a Zeiss-Gemini 2 electron microscope, operating at 150 kV. The apparatus was coupled with a Quantax EDX spectrometer to carry out energy dispersive X-ray (EDX) analysis. The EDX detected pear-shaped dimension is about 0.7 μ m. The crystal structures of the ZnO and ZnO/Au nanocolloids

were investigated by X-ray diffraction (XRD) analysis. XRD patterns were recorded by using using the $CuK_{\alpha 1}$ wavelength (1.5405 Å) by means of a Bruker D8 Advance diffractometer. UV-vis absorption response of the Au and ZnO nanostructures was investigated by means of a Perkin-Elmer Lambda 750 UV-vis spectrometer in the 190-1100 nm range. Analyses were carried out in the colloidal phase immediately after the ablation process. Methylene blue (MB), from Sigma Aldrich, was used as a probe molecule for the preliminary evaluation of the photocatalytic activities of ZnO and ZnO/Au nanostructures. The reaction was conducted in an aqueous solution containing MB at a 1.5 · 10⁻⁵ M concentration. The photocatalytic reaction was carried out, under stirring, using an UV lamp (100W), emitting mainly at 365 nm. The reaction beaker was located at a distance of about 15 cm from the irradiation source. The lamp energy density, measured by a power meter source, is of 30mW/cm²; 0.5 mg of catalyst were dispersed in 3 ml of MB aqueous solution. The photo-degradation was monitored by recording the UV-Vis spectrum during the irradiation and following the optical density at 662 nm.

3 Results and discussion

Figure 2 displays the morphology of the samples as resulting from SEM analysis. Regardless of the water temperature, rounded Au NPs, with size narrowly distributed around 9 nm, are obtained (Fig.2a). Conversely, the morphology of ZnO is found to depend on the water temperature. NPs are formed at RT (not shown for briefness), whereas NRs are obtained at 80°C (Figs. 2b–c). Au NPs decorate the NRs in ZnO/Au colloids (Fig. 3).



Fig. 2. SEM images of (a) Au colloids prepared at RT. Similar features characterize Au colloids synthesized at 80° C. (b) ZnO/Au colloids synthesized at 80° C; (c) a morphological detail of the sample prepared at 80° C at higher magnification.



Fig. 3. Elemental dispersion in ZnO/Au colloids synthesised at 80 °C.

The samples high crystallinity, regardless of the water temperature, is evidenced by strong intensity peaks appearing in the XRD patterns (Fig. 4). The diffraction peaks can be indexed to the hexagonal wurtzite ZnO structure (JCPDS card No.36–1451). The mean crystallite size calculated from the most intense (101) peak by using the Scherrer's formula is 35.0 nm.



Fig. 4. XRD pattern of ZnO/Au colloids synthesised at RT.

The optical gap (E_{σ}) of the synthesised colloids was estimated from their UV-Vis absorption spectra (Fig. 5), by applying to the Tauc relationship, namely $(\alpha hv)^{1/n} = C(hv - E_g)$, where α is the absorption coefficient, C is a constant, hv is the energy of incident photons, and n an exponent whose value depends on the type of transition (the value of 2, typical of direct allowed transitions, can be used for n in the case of ZnO and ZnO/Au). Accordingly, by plotting $(\alpha hv)^2$ as a function of hv, a linear region is observed, which denotes the onset of absorption. The extrapolation of this region to the abscissa axis yields the energy value of the optical band gap of the material. By this procedure the values of 3.31 and 3.24 eV were found for ZnO and ZnO/Au colloids, respectively. The presence of surface and intrinsic defects might be responsible for the E_{g} lowering with respect to the bulk ZnO (3.37 eV). Moreover, no substantial difference emerges from the comparison between ZnO based colloids prepared in water at RT or 80°C.



Fig. 5. Plot of $(\alpha h v)^2$ as a function of hv in colloids prepared at RT.

In order to explore the photocatalytic activity of assynthesized ZnO and ZnO/Au nanostructures towards organic pollutants, an aqueous solution containing MB at a $1.5 \cdot 10^{-5}$ M concentration was employed as standard model water-contaminant. For this study, samples were irradiated by an UV light source emitting at 365 nm. Under UV irradiation, the MB aqueous solution undergoes degradation and its optical absorption spectrum changes. Figure 6 shows the spectral changes produced by the ZnO/Au photo-catalyst prepared by ps-PLA at 80°C water temperature.



Fig. 6. Photo-degradation of $1.5 \cdot 10^{-5}$ M MB in presence of ZnO/Au (water temperature at 80°C) nanoparticles under UV lamp.

The characteristic absorption peak of MB appears at 662 nm, whereas the optical response of the mixed ZnO/Au colloids gives rise to a shoulder at 530 nm, which is associated to Au characteristic plasmon resonance peak. Under UV irradiation, a decrease and a blue shift of the maximum of the absorbance take place with increasing irradiation time. The absorbance decrease is indicative of the ability of catalyst to reduce MB, whereas the energy shift is probably due to the concomitant de-methylation of MB [8]. The photocatalytic process was monitored by measuring the absorbance spectra for all samples as a function of the irradiation time. Figure 7a gives the UV irradiation time

$$D\% = (\frac{A_t}{A_0} - 1) \times 100$$

In addition, the semilogarithmic plot of A_t/A_0 as a function of the irradiation time *t* (Fig. 7b) evidences the existence of a satisfactory linear correlation between $\ln(A_t/A_0)$ and *t* in our experiments. This indicates that the kinetics of photo-bleaching can be represented as a pseudo-first order law and can be expressed by the Langmuir-Hinshelwood equation [9] as follows:

$$\ln(\frac{A_t}{A_0}) = -k_a t.$$



Fig. 7. (a) Photo-degradation percentage of $1.5 \cdot 10^{-5}$ M MB under UV irradiation; (b)The linear fitting of $\ln(A_t/A_0)$ versus irradiation time (t).

From the linear fitting to the $\ln(A_t/A_0)$ versus *t* data (Fig. 7b), the rate constant (k_a) can be directly obtained. The values of k_a inferred from the fitting procedure as well as the degradation percentage of MB after 15 min of reaction and the time necessary to reach the 50% of the MB degradation ($t_{1/2}$), are reported in Table 1. The data reported in Table 1 prove that, under UV irradiation, all the synthesised nanostructures show a photo-catalytic activity towards the selected dye molecules with the highest k_a value (0.162 min⁻¹), pertaining to Audecorated ZnO nanorods (ZnO/Au 80°C). This value is 14 times higher than that obtained for the MB photodegradation in absence of any catalysts, and 1.6 times higher than for ZnO nanorods (ZnO 80°C).

Table 1. Photo-degradation rate constants of MB with different
catalysts using $\ln(A_t/A_0) = k_a t$ as fitting equation model,
R-square value R^2 , degradation percentage (D%) of MB and
time $(t_{1/2})$ for D%=50%.

Sample	ka	R^2	D%	t _{1/2}
	(\min^{-1})		(t=15min)	(min)
MB	0.011	0.99	19.96	46
ZnO RT	0.089	0.98	81.61	5
ZnO 80°C	0.097	0.99	68.23	7
ZnO/Au RT	0.064	0.97	82.49	3
ZnO/Au 80°C	0.162	0.98	89.21	3

The calculated k_a values confirm that Au NPs act as effective catalysts in the reduction of MB under UV irradiation. Moreover, the presence of Au NPs on the surface of ZnO nanorods (as proven by STEM images) is probably responsible for the improved photo-catalytic activity (i.e. increase of photo-degradation rate) of the ZnO/Au sample. This behaviour is explained in terms of a "doping action" of Au nanoparticles on the photocatalytically active metal oxides. The accepted mechanism for the enhancement is the transfer of the excited electrons from the ZnO conduction band to the Au nanoparticles. Trapping of the electrons on the Au particles then slows down the recombination process [10].

4 Conclusion

ZnO and Au nanocolloids were successfully synthesised by picosecond pulsed laser ablation, using Zn and Au metallic targets, in water media at RT and 80°C. ZnO and Au nanoparticles were formed at RT with size in the 10–50 nm range, while ZnO nanorods were obtained when water was maintained at 80°C during the ablation process. By adding Au NPs to ZnO colloids after the ablation process, Au-decorated ZnO nanorods were attained. Under UV irradiation, all the produced nanostructures show a photo-catalytic activity towards the used dye molecule. An improvement of the catalytic efficiency was observed in the presence of Au NPS, specially when ZnO sample was characterized by welldefined nanorod structures.

References

- 1. V. Binas, D. Venieri, D. Kotzias, G. Kiriakidis, Journal of Materiomics, **3** (1), 3 (2017)
- 2. M. Anijum, R. Miandad, M. Waqas, F. Gehany, M.A. Barakat, Ar. J. of Chemistry, (to be published)
- Y.S. Song, N.I. Cho, M.H. Lee, B.Y. Kim, D.Y. Lee, J Nanosci. Nanotechnol. 16 (2), 1831 (2016)
- C. Wang, J. Lu, L. Zhou, J. Li, J. Xu, W. Li, L. Zhang, X. Zhong, T. Wang, PLoS One. 11(10), e0164434 (2016)
- M. T. Amin, A. A. Alazba, and U. Manzoor, AdV in Mat. Sci. and Eng., 24, 6 (2014)

- 6. C. Chen, J. Liu, P. Liu, B. Yu, Advances in Chem.Eng. and Sci., **1**, 9 (2011)
- 7. J. Manna, T.P. Vinod, K.Flomin, R. Jelinek, J. Colloid and Interface Sci. 460, 113 (2015)
- T. Zhang , T. Oyama, A. Aoshima , H. Hidaka, J. Zhao, N. Serpone J. Photochem. Photobio. A Chem 140, 163 (2001)
- 9. A. Nezamzadeh-Ejhieh, H. Z. Mobarakeh, J. of Ind. and Eng.Chem., **20** (4) 1421 (2014).
- 10. K.-J. Kim, B. Kreider, C.-H. PChang, C.-M. Park, H.-G. Ahn, J. Nanopart. Res. 15, 1 (2013).