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Review

ZnO for application in photocatalysis: From thin films to nanostructures

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ABSTRACT

In this research work, we report the photocatalytic properties of ZnO synthesized in several forms: ZnO thin films deposited by atomic layer deposition (ALD), ZnO nanofibers synthesized by electrospinnig, and ZnO nanorods realized by chemical bath deposition onto ZnO thin films grown by ALD. The methylene blue was employed as a representative dye pollutant to evaluate the photocatalytic activity of the samples. All the nanostructured materials showed an enhancement of the photocatalytic activity with respect to the thin films. It was found that ZnO nanorods deposited onto 3 nm thin film showed the best photocatalytic activity. The relevance of the results is discussed, opening the route for the application of ZnO in photocatalysis.

1. Introduction

One of the most abundant clean energy source available in the world is the solar energy. Lewis in 2007 estimated that the solar energy striking our Earth in an hour is higher than the energy consumed by humans for an entire year [1]. For this reason, recently, the researcher's studies are focused on the development of materials that can efficiently harvest solar irradiation and use it for green environmental pollution management. In this field, photocatalysis is an interesting solution because it can use the renewable solar energy to activate the oxidation and reduction processes responsible for the removal of persistent and toxic organic compounds, and microorganisms in water [2]. During a typical photocatalytic process two different reactions occurs at the surface of the materials in contact with the wastewater: 1) an oxidation reaction, thanks to the photo-induced positive holes, 2) a reduction reaction, thanks to the photo-induced negative electrons [3]. Several kinds of semiconductor-based photocatalysts, such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron(III) oxide (Fe_2O_3), zirconia (ZrO_2), tungsten trioxide (WO_3), and tantalum pentoxide (Ta_2O_5) have been applied in wastewater treatment [2,4–14].

In this field, ZnO has emerged as a promising candidate for environmental applications because it has a direct and wide band-gap energy in the near-UV spectral region, a strong oxidation ability, a great photocatalytic property, and a large free-exciton binding energy [15–19] so that exciton emission processes can persist at or even above the room temperature. The ZnO is easy to grow, and its thermodynamically stable phase is the hexagonal wurtzite structure [20–22]. In addition, the ZnO is an environmental friendly material as it is compatible with living organisms, which lending itself nicely to a broad range of daily applications that will not leave any risks to human health, and environmental impacts [21]. The ZnO has the same band-gap of TiO_2 (~ 3 eV) and for this reason it is expected a similar photocatalytic efficiency of TiO_2. Moreover, ZnO is relatively cheaper compared to TiO_2, whereby the usage of TiO_2 are uneconomic for large scale water treatment operations [23].

In order to improve the photocatalytic performance of semiconductor materials, different strategies can be employed, such as the nanostructuration, that offers a high surface-area–to-volume ratio, enhancing in this way the amount of the photo-generated charge carriers [6,24–26]; or the use of metal nanoparticles in order to increase the electron-hole separation [5,27].

In this work we presented the photocatalytic activity of ZnO. Several kinds of ZnO were investigated: thin films deposited by atomic layer deposition (ALD), ZnO nanofibers (hereafter simply called "ZnO NFs") synthesized by electrospinning, and ZnO nanorods (hereafter simply called "ZnO NRs") synthesized by chemical bath deposition (CBD) on ZnO thin films grown by ALD. The idea was to follow the effect of the nanostructuration of the material on its photocatalytic response. Fig. 1 reports a schematic of the materials presented in this review.

2. Experimental

ZnO films with different thicknesses (from ~ 3 to ~ 30 nm) were deposited by ALD using the Picosun R-200 Advanced reactor. During the deposition the temperature was fixed at 300 °C, or 80 °C in the case

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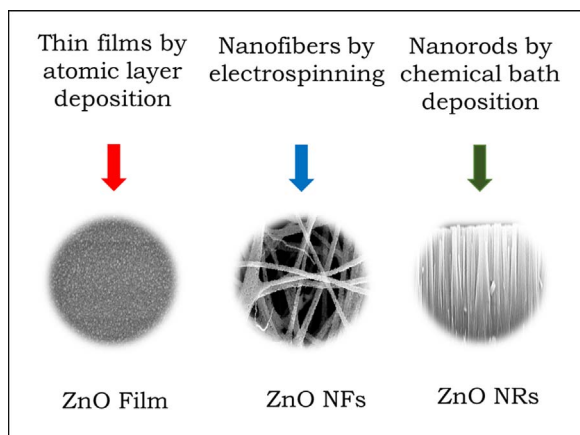
Fig. 1. Schematic of ZnO nanomaterials presented in the review: thin films deposited by atomic layer deposition, nanofibers (ZnO NFs) deposited by electrospinning, and nanorods (ZnO NRs) realized by chemical bath deposition.

of deposition on thermally-fragile plastic. Diethyl zinc (DEZ, purity 99.9999%) and de-ionized water were used as precursors, while N_2 was used as carrier and purge gas (purity $\geq 99.999\%$). The pulse and purge time were kept constant at 0.1/3/0.1/5 s for $DEZ/N_2/H_2O/N_2$. Three different substrates were used: silicon for the morphological and structural analyses, and for the photocatalytic tests; quartz for the optical measurements; poly methyl methacrylate (PMMA) in order to transfer the process on a flexible support. The PMMA film used as substrate was prepared according to the method of sonication and solution casting [28]. In detail, 800 mg of PMMA powders (molecular weight: 120000 a.m.u., transition temperature: 105 °C, density: 1.188 g/ml, as provided by Sigma-Aldrich) were dissolved in 4 ml of acetone. After that, the mixture was cast into a Petri dish (6 cm in diameter) and dried overnight to produce a PMMA film that was peeled off from the Petri dish.

The thickness of the ZnO films deposited on silicon substrates by ALD was evaluated by the M-2000 spectroscopic ellipsometer by Woollam, by applying a Cauchy model.

The synthesis of ZnO NFs was achieved by electrospinning. A solution containing 1 g of polyvinylpyrrolidone (PVP) polymer (molecular weight: 1300000 a.m.u.), and 0.36 g of zinc acetate (Zn $(CH_3COO)_2 \cdot H_2O$) in 2 ml of dimethylformamide (DMF) (all reagents were purchased from Sigma Aldrich), was electrospun using the electrospinning equipment EC-DIG Electrospinning by the IME Technologies. The composite was ejected from the needle (21 gauge) of a syringe applying an electrical field as high as several kV/cm; in detail, the depositions were achieved by using a negative and positive voltage of −4 and 18 kV, respectively. Nanofibers were collected (in a stationary mode) on the surface of silicon substrates clamped on top of a conductive circular collector. In order to remove the PVP matrix, the ZnO nanofibers were annealed at 500 °C for 1 h, in a conventional horizontal furnace under a controlled oxygen atmosphere (O_2 flow: 2.5 l/min) [29].

Well-aligned ZnO NRs arrays were synthesized using the CBD method. ZnO thin films deposited by ALD were used as seeds for the CBD. The seed layers were dipped horizontally (with the face down) in a 0.025 M zinc acetate dehydrate and 0.025 M ethylenediamine aqueous solutions under mild stirring at 80 °C for 3 h [30,31]. The obtained ZnO NRs were washed with de-ionized water and sonicated for 3 min, so to clean the surface, and then dried by blowing N_2.

A schematic of the ZnO materials is reported in Fig. 1.

All the synthesized materials were observed by the Zeiss Supra-55 field emission scanning electron microscope (SEM), operating at 5.0 keV, equipped with an Oxford solid state detector for energy dispersed X-ray spectroscopy (EDS).

The crystallographic structure of the materials was analyzed by X-ray diffraction (XRD) with a Brucker D-500 diffractometer (detector scan mode) at 0.8° angle of incidence, and 2θ from 20° to 60°. The XRD spectra were analyzed by the Bruker software suite, including ICSD structure database.

The optical characterization was obtained by extracting both the normal transmittance (T) and the 8° reflectance (R) spectra in the 200–800 nm wavelength range, by using a Perkin-Elmer Lambda 40 UV/VIS/NIR spectrophotometer.

The photocatalytic activity of the investigated materials was tested by the degradation of methylene blue (MB) dye. Before starting the MB degradation experiments, the samples were irradiated by an UV lamp for 60 min in order to remove the hydrocarbons from the sample surfaces [32]. ZnO thin films, ZnO NFs and ZnO NRs arrays deposited on Si substrates (1 cm^2 in size) were immersed in 2 ml of dye aqueous solutions (1.5×10^{-5} M). The pH of the aqueous solution is one of the most important operating parameter that affects the heterogeneous photocatalysis, since it influences the surface-charge properties of the photocatalyst, and the position of the conductance and valence bands. Some papers reports the effects of the pH on the photocatalytic activity of ZnO (the reader can refer to Refs. [33–35]). It is shown that the ZnO photocatalytic rate increases with the pH, reaching high rate for 7.5 pH. For this reason, the measurements were performed at a fixed pH value of 7.5, using NaOH to control its value. The dye solution containing the samples was irradiated by an UV lamp with the irradiance of 2 mW/cm^2, which simulate the UV irradiance of the Sun on the Earth. The irradiated solution was measured at regular time intervals with the Lambda 45 Perkin-Elmer UV/VIS/NIR spectrophotometer, in a wavelength range of 500–800 nm. The degradation of MB was quantitatively evaluated by the absorbance peak at 664 nm in the Lambert-Beer regime [36]. The photo-degradation reaction rate was calculated from the linear plot of $-\ln(C_0/C)$ versus the irradiation time (where C_0 is the starting concentration of the MB, C is the concentration of the MB at the time t) [37]. The decomposition of the MB dye in the absence of any photocatalyst materials was always checked as a reference. Control experiments in the dark for 60 min were conducted in order to clarify the contribution of the adsorption of the MB at the beaker walls and at the sample surface.

3. Results

Several films of ZnO were deposited by ALD at 300 °C with different thickness: 3, 5, 10, 20, and 30 nm, by simply varying the number of the ALD cycles. The surface morphology of the 3, 10, and 30 nm thick films was reported in Fig. 2.

The plan-view SEM images showed a high uniformity of the ALD films, with a granularity that increases with the thickness (see Fig. 2(a), (b), and (c)), in good agreement with what reported in literature for atomic layer deposition of ZnO [38]. The EDS analysis of the 30 nm thick sample (Fig. 2(d)) shows the typical peak of the Zn (at ~ 1.0 keV), O (at ~ 0.5 keV) both coming from the ZnO, and the peak of the Si (at ~ 1.7 keV) due to the silicon substrate. The films with lower thickness showed similar spectra, for this reason they are not reported.

The XRD spectra of the ZnO films are reported in our previous article [39], showing the typical pattern of the wurtzite structure.

The ZnO films were also analyzed by optical characterization, so to evaluate the band-gap energy of the films. In Fig. 3 the absorbance (A) of the films as a function of the wavelength is reported. The absorbance was calculated by the transmittance (T) and the reflectance (R) spectra through to the following equation:

$$A\% = 100\% - T\% - R\% \tag{1}$$

All the films showed the typical optical absorption in the UV part of the spectrum. Moreover, the intensity of the absorbance increases with the film thickness, as expected. The optical spectra were analyzed by the Tauc model in order to evaluate the band-gap energy of the ZnO films. The model was born for the description of the light absorption