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Nanosized composite ZnO/TiO_2 thin films for photocatalytic applications

S. A. Siuleiman, D. V. Raichev, A. S. Bojinova*,
D. T. Dimitrov, K. I. Papazova

Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Bourchier Blvd., Sofia 1164, Bulgaria

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This study is focused on preparation, characterization and photocatalysis with ZnO, TiO_2 and nanocomposite thin films of ZnO/TiO_2, prepared by spin coating method from suspensions of the commercial metal oxide powders in ethanol, with addition of PEG as stabilizer. The content of ZnO in the composite samples is selected to be 90%. The phase composition and morphology of the ZnO, TiO_2 and mixed composite thin films of ZnO/TiO_2 is characterized by X-Ray Diffraction and SEM analysis. The photocatalytic efficiency of the prepared films is tested in photooxidation of organic azo dye Orange II from aqueous solutions under irradiation with UV and visible light. The influence of the number of coated layers on the efficiency of dye photodegradation is also investigated. Comparative photocatalytic experiments with ZnO and TiO_2 films are performed. It is found out that the nanocomposite film of 90% ZnO content with 3 coated layers manifests the highest photocatalytic efficiency under UV irradiation.

Key words: ZnO/TiO_2 composite film, spin coating, photocatalysis, Orange II, UV, visible light.

INTRODUCTION

Heterogeneous photocatalysis is an attractive advanced technology for removal of organic pollutants from water and air under light illumination. Titania and zinc oxide are the most popular semiconductor oxides used as photocatalysts due to their unique blend of properties [1]. The coupling of two semiconductors, possessing different energy levels for their corresponding conduction and valence bands, provides an approach to achieve a more efficient charge separation, an increased lifetime of the charge carriers and an enhanced interfacial charge transfer to the adsorbed species favoring their photooxidation and further mineralization [2]. There is significant interest in the scientific research on nanostructured ZnO/TiO_2 composites with different configurations and morphologies in order to obtain more efficient photocatalytic degradation [3–5]. In addition to classical mechanochemical processing used to manufacture nanoparticulate $(TiO_2)_x(ZnO)_{1-x}$ photocatalytic powders [6], the photocatalityc performance is investigated for coated with titania shell ZnO nanorods [7], junction type p-ZnO/n-TiO_2 powder photocatalyst [8], powdered $ZnO–TiO_2$ nanocomposites prepared by wet chemical methods [9–11], nanosized ZnO/TiO_2 [12] and Zn-TiO_2-ZnO [13] nanocomposite films. To the best of our knowledge, we have not found in the available literature, investigation on ZnO/TiO_2 films, prepared via spin coating method from suspensions.

In this study we present a procedure for obtaining thin solid films of TiO_2/ZnO from slurry by spin coating and their characterization as a first step to enhance the photocatalitic efficiency of the composite film under UV-light. For this reason, our goal is to find the conditions for preparation of good and reproducible coatings by studying the influence of different factors on the photocatalytic properties of the composite films.

EXPERIMENTAL

The reagents and materials used in the experiments were as follows: TiO_2 anatase from KRONOS-Germany, ZnO and Orange II (O II) ($C_{16}H_{11}N_2NaO_4S$, dye content ~85%, absorption

* To whom all correspondence should be sent:
E-mail: nhasb@wmail.chem.uni-sofia.bg

maximum at λ_{max} = 484 nm) from Sigma Aldrich. Absolute ethanol and PEG (2000) were purchased from the Institute of Pure Substances, University of Sofia. Standard microscopic glass slides of dimensions 75×26×1 mm (Isolab, Germany) were used as substrates of the coatings. The glass slides were preliminary cleaned thoroughly with detergent and then consecutively rinsed with isopropanol, acetone and ethanol in order to eliminate organic residues and assure better adhesion of the coatings [14].

The coating suspension, containing commercial TiO_2 or ZnO powders, was obtained by addition of the corresponding metal oxides (7% weight ratio) to ethanol. The ZnO content in the composite TiO_2/ZnO film samples was selected to be 90% with respect to titanium oxide, based on our previous investigation [15]. To assure better films adhesion and porosity, 7% (weight) polyethylene glycol 2000 was also added to the slurry [16]. Then the coating suspension was homogenized by ultrasonic bath (IKEDARIKA BU95001) for 20 minutes and was let to age overnight. The substrates were coated using spin-coater (KW-4A, Chemat Technology Inc) at two speeds of rotation: first – 1000 rpm (3 sec) and second – 2000 rpm (30 sec). Three series of film samples of each composition were prepared – with one, two and three coated layers. The films were allowed to dry at 100 °C for 10 min between the successive coating cycles. The as-coated substrates were finally annealed in a high temperature oven (Barnstead Thermolyne, Furnace 1400) for 1.5 h at 500 °C in air atmosphere to obtain complete organics decomposition and crystalline films.

The phase composition and crystallinity of as-prepared thin films was established by Siemens D 500 diffractometer (CuKα source of radiation at a step of 0.05 deg for 2Θ and counting time 2s/step). The surface morphology of the samples was observed via scanning electron microscope (SEM) (JSM-5510 JEOL). The film thickness was determined by weight method for series of films from ZnO, TiO_2 and TiO_2/ZnO, prepared with 1, 2 and 3 spin coated layers.

The as-prepared ZnO, TiO_2 and TiO_2/ZnO films were tested in photodegradation of Orange II from water solution by a standard testing procedure [14]. The volume of dye solution was 100 ml. The initial O II concentration was 8 ppm. The sources of irradiation were as follows: UVA lamp (Sylvania 18W BLB T8, emitting mainly in the range 315–400 nm) placed 10 cm above and a linear Tungsram lamp (500 W K1R7s 9700 Lm, maximal emission at 700 nm) for the visible irradiation fixed at 25 cm above the investigated solution. Aliquot samples were regularly taken from the dye solution at fixed time intervals and analyzed for absorption at the maximal absorption of O II by UV-VIS spectrophotometer (Thermo scientific, Type Evolution 300 BB). After absorption measurement, the aliquots were immediately returned back to the treated solution. The solution was constantly stirred by electromagnetic stirrer at constant rotation speed of 400 rpm. All photocatalytic experiments were conducted at constant temperature of 23±2 °C.

RESULTS AND DISCUSSION

The crystalline phase of the prepared ZnO, TiO_2 and TiO_2/ZnO films, identified by X-ray diffraction analysis is represented in Fig. 1. It is clear from the XRD pattern that zinc oxide is well crystallized and can be classified as hexagonal wurtzite modification, with dominating (101) peak. The titanium dioxide, in the thin films, is of anatase form (with main peak at (101)). The diffractogram of mixed TiO_2/ZnO composite film with pointed characteristic peaks of anatase and zinc oxide is presented also in Fig. 1. The intensities of the main peaks of ZnO and TiO_2 in case of composite do not differ from those in case of pure ZnO or TiO_2 film – both oxides are present in the composite as separate phases, there is no indication for formation of mixed compound. The size of crystallites is calculated following Sherrers equation (k = 1.5406 Å) for ZnO from the (101) peak and for TiO_2 from the (101) peak (Fig. 1) as they are relatively strong and single for the respective metal oxide. The sizes of crystallites are found to be 40.7 nm for TiO_2 and 24 nm for ZnO.

The surface morphology of TiO_2 and TiO_2/ZnO composite film is represented in Fig. 2. From the SEM images in Fig. 2 is seen that the films are uni-

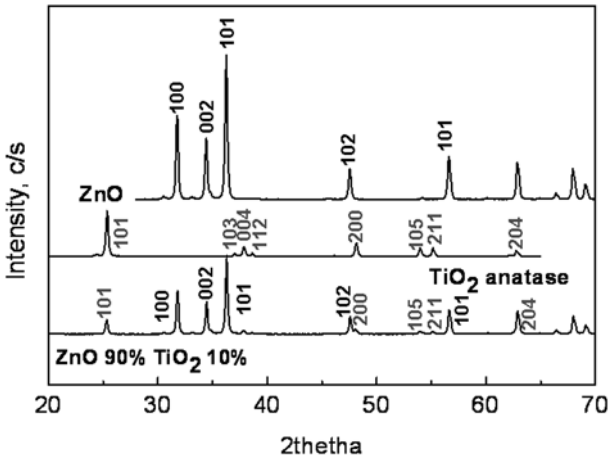

Fig. 1. Comparative XRD pattern of TiO_2, ZnO and composite TiO_2/ZnO thin films

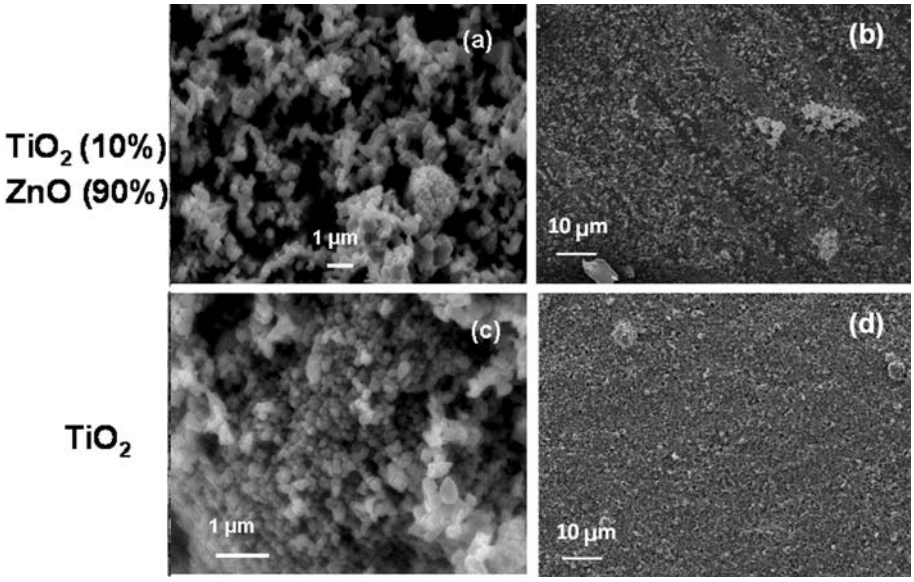

Fig. 2. SEM images of the prepared catalysts in form of thin films at different magnifications

form and homogeneous. The size of the particles in the films is calculated following the equation:

$$D_{av} = \sum_{N}^{i=1} \left(D_{i\max} + D_{i\min}\right)/2N \qquad (1)$$

Where N is the number of observed particles, and D_{av}, D_{max} and D_{min} are the average, maximum and minimum diameter of the particle, respectively. In our case N=300–500. The average particle size is found to be 0.2 µm for TiO_2 and 0.45 µm for ZnO in all the prepared films. The observed film thickness by SEM is 2.5 µm.

Series of experiments are made in order to obtain the optimal number of coated layers of the prepared films. The dependence of the film weight on the number of spin coating cycles is presented in Fig. 3. As seen from Fig. 3a, in case of ZnO and TiO_2 films, the weight of the first layer is greater, compared to that of the next ones. The second and third coatings, for each of the pure oxide films, have approximately equal weigh. In general – the ZnO films have greater weight (0.49 µg.cm^{-2} per 3 coatinds), than these of TiO_2 (0.43 µg.cm^{-2}) due to the different density of the respective oxides (ρ_{ZnO} = 5.6 g.cm^{-3}, ρ_{TiO2} = 3.9 g.cm^{-3}). The average film weight in case of 3 coated film of TiO_2/ZnO composite (Fig. 3b) is found to be 0.43 µg.cm^{-2}.

The photocatalytic action of the titania, zinc oxide and titania/zinc oxide nanocomposite films is investigated, as mentioned above, in the photo initi-

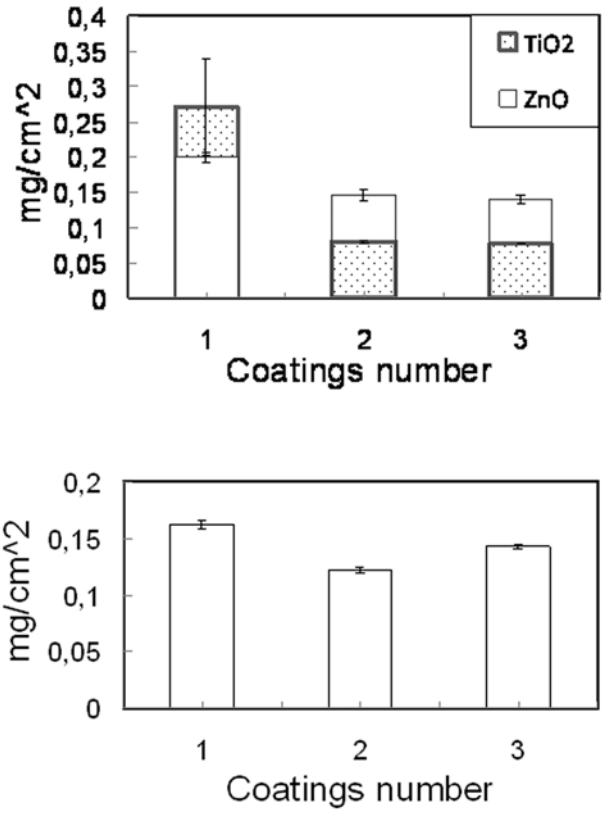

Fig. 3. Weight of the successive coatings for the films of: (a) TiO_2 and ZnO; (b) thin composite films of 90% ZnO content. The experimental data points represent the average from three independent measurements; the error bars show the respective deviations

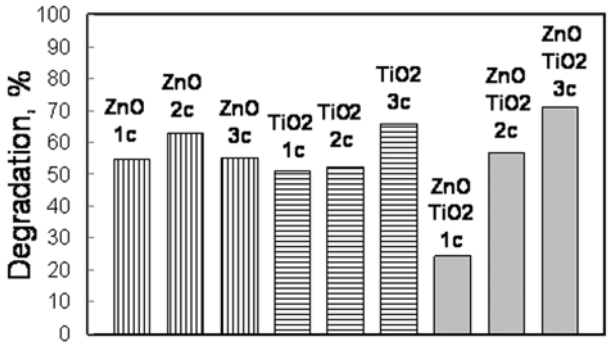

Fig. 4. Comparison of the achieved degree of photocatalytic decomposition of O II in 8 ppm water solution with all film samples at 3th h of UV light irradiation

ated decomposition of Orange II from 8 ppm water solutions. The photocatalytic experiments are carried out with films coated by 1, 2 and 3 spin coated layers. The results of the photocatalytic experiments after 180 min of UV illumination are shown in Fig. 4. The experimental data in case of TiO_2 and TiO_2/ZnO composite films show clear tendency for higher photocatalytic efficiency with the number of film coatings. The effect is most expressive for the TiO_2/ZnO composite films. The photocatalytic activity of ZnO films undergoes maximum (62% dye degradation) for the film prepared with 2 spin coatings and then slightly decreases. Higher degree of pollutants photodegradation (65%) is observed with TiO_2 films, prepared with 3 layers. The titania/zinc oxide films, prepared with 3 coatings, manifest the best photocatalytic efficiency (72% O II degradation) under UV irradiation due to successful charge separation in the prepared composite and therefore avoiding losses from recombination of the photogenerated charge carriers.

The experimental results from the photocatalytic tests at the 180th minute of visible light illumination are presented in Fig. 5. Generally the photocatalytic activity of all film samples under visible light is lower, compared to the results obtained upon UV irradiation. In this case a trend, reverse to the case of photocatalysis under UV light, is observed for the TiO_2 and TiO_2/ZnO film samples – the photocatalytic activity decreases with the number of coated layers. Here the TiO_2 and TiO_2/ZnO films have lower efficiency in comparison with the ZnO films. In case of films of zinc oxide, the photodegradation efficiency regularly increases with the number of the film coatings. The ZnO films prepared with 3 coated layers have the highest efficiency – 14% Orange II photodegradation.

The apparent rate constants of photocatalytic process are determined following the equation:

$$C = C_{in}.e^{-kt} \qquad (2)$$

where C is the concentration of the dye solution at the moment t, C_{in} – the initial dye concentration and t is the illumination time in minutes.

The rate constants values (K), calculated by Eq. (2) with the data, obtained from the photocatalytic experiments under both types of illumination, are plotted in Fig. 6. From the figure one can see, that highest rate constants values are observed in case of photocatalysis under UV light with TiO_2/ZnO nanocomposite films, where the process of photocatalysis is the most effective.

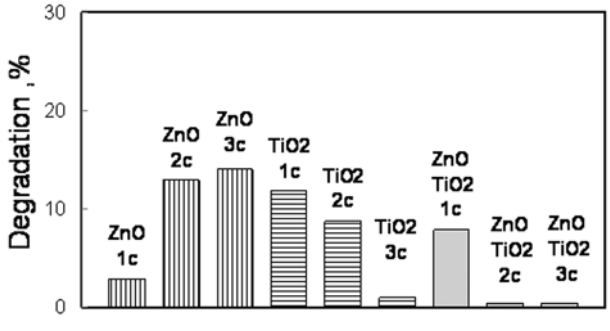

Fig. 5. Degradation degree (%) of Orange II after 3 h photocatalysis with the different film samples under visible light illumination. The initial dye concentration is 8 ppm

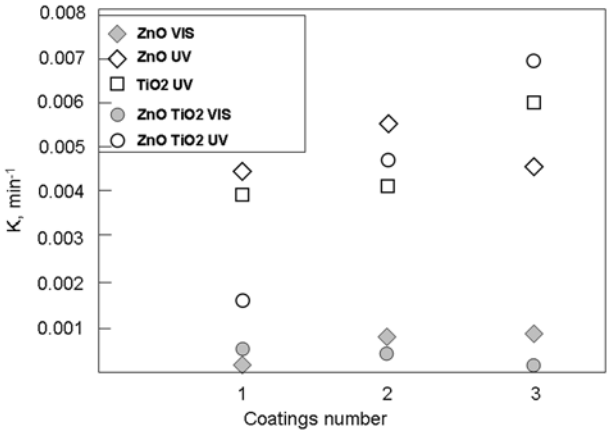

Fig. 6. Rate constants of photocatalysis versus number of the films coatings

CONCLUSIONS

Nanocomposite films of TiO_2/ZnO are prepared using for the first time dip coating method from ethanol suspensions. The films exhibit a good homogeneity and nanocrystallinity as shown by XRD and SEM analysis. The titania and zinc oxides in the composite film exist as separate phases in form of anatase and wurtzite modification, respectively. The determined by weight method composite film weight is found to be 0.43 μg.cm^{-2}. The photocatalytic action of the TiO_2/ZnO films is tested and compared with that of ZnO and TiO_2 films in UV and visible light induced purification of aqueous solutions from the organic dye Orange II. Most efficient dye photodegradation is achieved with the composite films of TiO_2/ZnO under UV irradiation. The investigation will be developed further upon visible light illumination, where a better photocatalytic performance of the composite TiO_2/ZnO films might be expected.

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НАНОРАЗМЕРНИ КОМПОЗИТНИ ТЪНКИ ФИЛМИ ОТ ZnO/TiO_2 ЗА ФОТОКАТАЛИТИЧНИ ПРИЛОЖЕНИЯ

Ш. А. Сюлейман, Д. В. Райчев А. С. Божинова*,
Д. Ц. Димитров, К. И. Папазова

Лаборатория по наука и технология на наночастици, катедра Обща и неорганична химия, Факултет по химия и фармация, Софийски университет, София 1164, България

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(Резюме)

Представеното изследване е насочено към синтез, характеризиране и фотокаталитична активност на ZnO, TiO_2 и нанокомпозитни тънки филми от ZnO/TiO_2, отложени по метода на центробежно въртене (spin coating) от етанолни суспензии на търговските прахове метални оксиди, съдържащи стабилизираща добавка от полиетиленгликол. Избраното съдържание на ZnO в композитните проби е 90%. Фазовият състав и морфологията на ZnO, TiO_2 и смесените композитни тънки филми от ZnO/TiO_2 са характеризирани с рентгенова дифракция и сканираща електронна микроскопия. Фотокаталитичното поведение на получените филми е изпитано при фотоокислението на органичното азо багрило Оранжево II във воден разтвор при облъчване с ултравиолетова и видима светлина. Изследвано е и влиянието на броя на покритията върху ефективността на фоторазграждане на багрилото. Проведени са сравнителни фотокаталитични тестове с филми от чистите ZnO и TiO_2. Установено е, че филмите със съдържание на 90% ZnO и 3 покрития показват най-висока фотокаталитична ефективност под действието на ултравиолетова светлина.