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Synthesis and characterization of ZnO and TiO_2 powders, nanowire ZnO and TiO_2/ZnO thin films for photocatalyc applications

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The study concerns vertically well-aligned ZnO nanowires and TiO_2–ZnO films on Si substrates. They were prepared by a two-step chemical bath deposition (CBD) method, witch includes seed deposition and growth of ZnO nanowires. SEM and X-ray diffraction are used for the ZnO and TiO_2/ZnO thin films characterization. The film thickness is of 3–3.5 μm and the average diameter of ZnO nanowires is 100-150 nm, as determinated by SEM. Thus prepared films (pure ZnO nanowires and mixed with TiO_2 nanoparticles) are tested in comparison to TiO_2 and ZnO powder catalysts. TiO_2 doped ZnO nanowire films show a significant rise in the photocatalytic efficiency. The photocatalytic tests are performed in cylindrical glass reactors under UV and visible light irradiation. The effect is due to the successful separation of photogenerated charge carriers in the prepared TiO_2/ZnO photocatalytic film. The pollutants concentrations are 20 ppm Orange II for slurry and 10 ppm for film photocatalysis. The photodegradation of organic dye Orange II is observed spectrophotometrically.

Key words: ZnO nanowires, TiO_2, composite films, Orange II, photocatalysis.

INTRODUCTION

Nanomaterials are of tremendous interest due to their noticeable application in electronics, optics, and photonics. Nanomaterials are generaly classified into three groups: 0-dimensional, 1-dimensional, and 2-dimensional. Zero-dimensional nanostructures, referred to as quantum dots or nanoparticles with an aspect ratio near unity, have been extensively used in biological applications [1]. Two-dimensional nanomaterials, such as thin films, have also been widely used as optical coatings, corrosion protection, and semiconductor thin film devices. One-dimensional (1D) semiconductor nanostructures such as nanowires, nanorods (short nanowires), nanofibres, nanobelts, and nanotubes have been of intense interest in both academic research and industrial applications. This is due to their potential as building blocks for other structures [1]. 1D nanostructures are useful materials for investigating the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement) [2]. They are also important because of their interconnections and functional units in the fabrication of electronic, optoelectronic, electrochemical, and electromechanical nanodevices [3]. In todays research zinc oxide (ZnO) nanowire is one of the most important among the one-dimensional (1D) nanostructures [4].

The band gap energy plays a significant role in the photocatalytic process. Figure 1 shows the band gap energies and the band edge positions of a common semiconductor photocatalysts [5–7]. It is important to have in mind that, the band gap values of ZnO, reported in the literature, are not all equivalent due to the different levels of the O vacancyes in ZnO [8]. ZnO has also been considered as a suitable alternative of TiO_2 because of its comparability with TiO_2 band gap energy and its relatively lower cost of production [9, 10].

ZnO is a semiconductor with a direct wide band gap energy (3.37 eV) and has a large exciton binding energy (60 meV) at room temperature [11]. TiO_2 has similar large band gap – 3.2 eV for anatase modification. It is most widely used photocatalyst since it is chemically stable, nontoxic and natural

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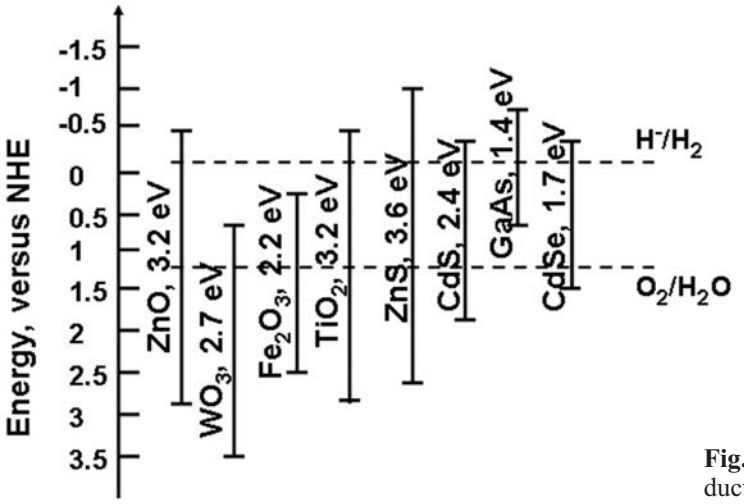

Fig. 1. Band edge positions of common semiconductor photocatalysts (data from [5–7])

material [12].The band gaps values of TiO_2 and ZnO show that near UV irradiation is needed for photo activation of both oxides.

Different authors apply various methods of modification like ball-milling [13], doping and co-doping [14, 15] to obtain efficient photocatalysis under visible light with ZnO and TiO_2. Composite materials are another approach to achieve this goal. There is a number of investigations reporting such effect, achieved by addition of variety of oxides such as SnO_2 [16, 17], SiO_2 [18], CeO_2 [19], ZnO [20–23], WO_3 [24] and ZrO_2 [25]. Application of supported bycomponent catalysts from two semiconductor oxides also alters the electronic properties, as compared to the initial material, in turn affecting charge photogeneration, charge separation and transfer, as found for ZnO overlayers on TiO_2 [26]. Other study reports about significant inhibition of the particle-to-particle electron transfer established for thin ZnO shell on a TiO_2 core [27].

To clarify this effect, ZnO films with TiO_2 overlayer have been studied. The new element here is investigation of the photocatalytic effect due to the combination of the two semiconductors, presented in different forms as nanowires and nanoparticles. This effect is checked in degradation of the commonly used organic dye Orange II in aqueous solution and compared using TiO_2 and ZnO nanowire film. The aim is to prepare and characterize ZnO nanowire film and TiO_2/ZnO photocatalyc film, suitable for application under illumination with UV and visible light irradiation.

EXPERIMENTAL

The reagents and materials used in the experiments were: Zn $(CH_3COO)_2.2H_2O$ and 2 methoxyethanol from Fluka, methenamine from Reidel de Haen, TiO_2 anatase and Orange II (λmax = 484 nm) from Sigma Aldrich. Si substrates (50×50×2 mm) from ISO-LAB (Germany) were used as supports for the films. The ZnO nanorods used in this investigation were grown on Si substrates by chemical bath deposition (CBD). It is a two step process, on a substrate treatment prior to the CBD growth. The first stage was ZnO seed deposition for next growth of nanowires. The pretreatment of the substrates is conducted by spin-coating (spin coater KW-4A, Chemat Technology Inc, 2200 rpm). A substrate with a solution of zinc acetate dihydrate ($Zn(C_2H_3O_2)_2 2H_2O$), dissolved in pure ethanol with a concentration of 5 mM, was used to control the diameter of ZnO nanorods. Then the seeded substrate was rinsed with distilled water, dried and annealed at 320 °C for 20 min. The next step was growth of ZnO nanowires on the as-prepared seeds. For this purpose the seeded substrates were kept for 3h placed in aqueous solutions of zinc nitrate hexahydrate [$Zn(NO_3)_2 6H_2O$, 99.9% purity grade] and methenamine ($C_6H_{12}N_4$, 99.9% purity grade) containing also methenamine (25 mM). After that the substrates were rinsed with distilled water and placed again in new precursor solution. In the CBD growth, the concentrations of both reagents were fixed at 0.1M. The pretreated Si substrates were immersed into the aqueous solution, and ZnO was grown at an constant temperature of 93 °C. This step was repeated 8 times and the final films were dried in air [28]. The mixed films were prepared by impregnation of the ZnO coating with TiO_2 suspension in ethanol in selected ZnO:TiO_2 ratio 3:1 (weight) [27].

The prepared ZnO and mixed films were characterized by X-ray analysis (diffractometer Siemens D 500, CuKα source radiation at a step of 0.05Θ for 2h and counting time 2 s/step) and scanning electron microscopy (SEM, JEOL JSM-5510).

The photocatalytic action of the films was examined in photoinitiated degradation of the organic dye Orange II in water solution (10 ppm, 150 ml) under UV (Sylvania 18 W BLB T8 lamp, emitting mainly in the range 315–400 nm) and visible (linear TUNGSRAM lamp 500 W K1R7 s, 9700 Lm) light irradiation. Three series of experiments were performed with the powder and with the film samples: under UV and visible light irradiation. Photocatalytic experiments with commercial and prepared by us powder samples were conducted prior testing of the films. The detailed procedure of photocatalytic experiments is described elsewhere [29, 30]. Spectrophotometer (Jenway 6400) determined the change in the dye concentration within the time of photocatalysis.

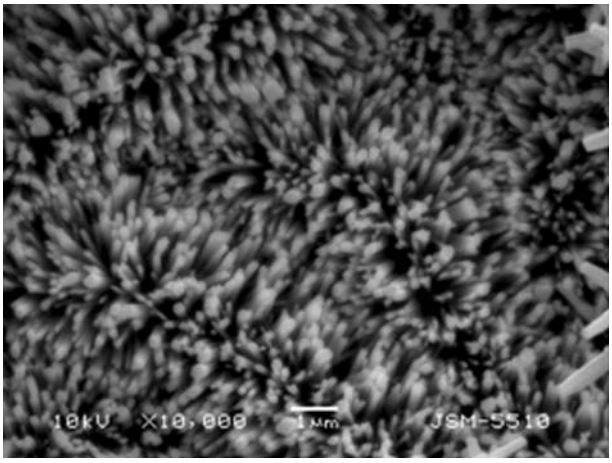

Fig. 2. SEM images of top view of the ZnO nanowires

RESULTS AND DISCUSSION

SEM analysis is used to study the morphology of as-prepared films. Figure 2 shows a schematic view of ZnO nanowires film produced by chemical bath deposition (CBD). The ZnO nanowires obtained are of hexagonal crystal structure. The SEM micrographs show uniform films of high density (3.1×10^9 numbers of nanowires per cm^{-2}). The ZnO nanowires grown on Si substrate are of approximately 3–3.5 μm length and 100-150 nm in diameter.

The microscopic observations of the ZnO nanowires and TiO_2 nanoparticles in the TiO_2/ZnO film on Si substrate are shown in Fig. 3.

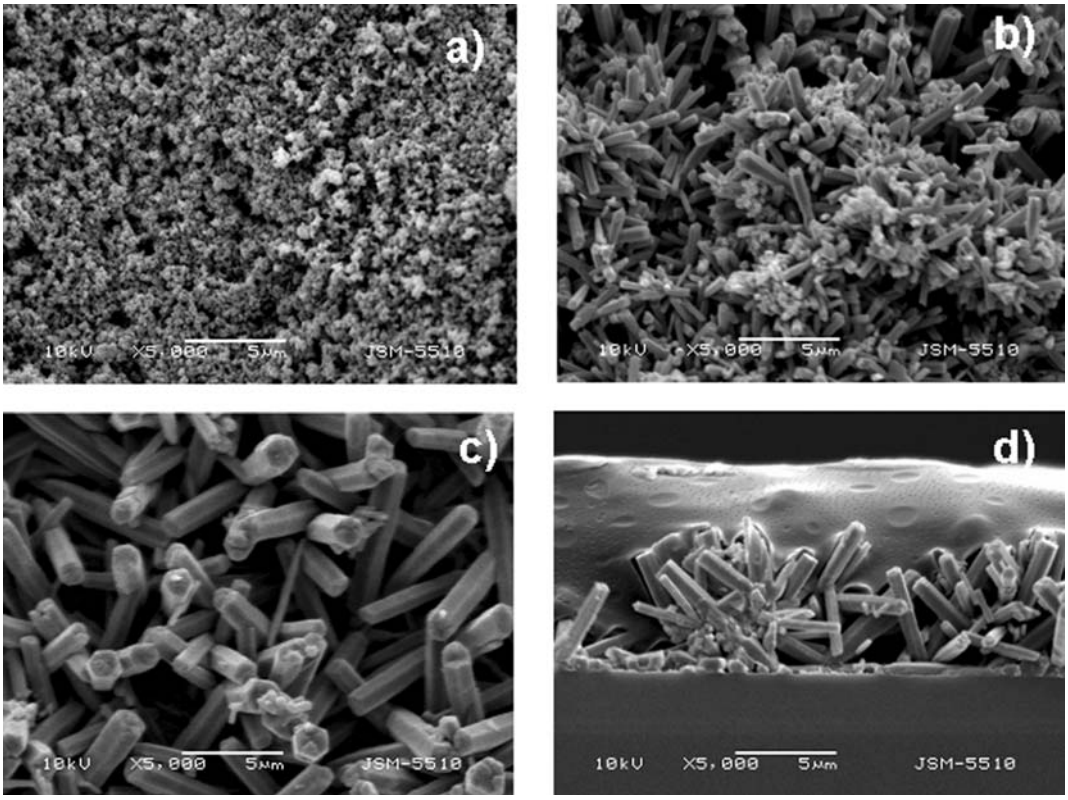

Fig. 3. SEM images of TiO_2/ZnO nanowire arrays: (a), (b), (c) TiO_2/ZnO arrays (top view) at different magnifications; (d) shows films cross section – TiO_2/ZnO nanowire array with TiO_2 nanoparticles film on the top

Figure 3 shows impregnated ZnO:TiO_2 of weight ratio 3:1. Samples are 100% crystalline. TiO_2 nanoparticles of about 0.05 μm average diameter can be clearly seen unevenly distributed between the ZnO nanowires along the entire films surface (Fig. 3a). The bottom layer of ZnO nanowires and upper layer of TiO_2/ZnO nanoparticles can be clearly seen in Fig. 3b and 3c. Figure 3d shows the composite films cross section.

Figure 4 represents XRD patterns of commercial TiO_2 anatase, ZnO powder from Aldrich and ZnO nanowire films.

It is clear from Fig. 4a that the nanowires can be classified as hexagonal wurtzite ZnO, and the dominating (002) peak at 34.4° indicates that the nanowire is well crystallized and grows in preferred orientation perpendicular to the substrate, which is in perfect agreement with the data from SEM observations. The XRD of mixed TiO_2/ZnO powder and nanosized film with pointed characteristic peaks of anatase and zinc oxide is presented in Fig. 4b. The intensities of the main peaks of ZnO differ from those of a mechanical mixture. After addition of TiO_2, the two ZnO peaks (100) and (002) are the strongest, indicating a slight change of the preferred orientation. The size of crystallites is calculated following Sherrers equation for ZnO from the (100) peak and for TiO_2 from the (101) peak (Fig. 4b) as they are relatively strong and single for the respective metal oxide. The crystallite size in direction perpendicular to the (101) plane remains the same (33.9 nm) as in the nanowire ZnO film, whereas the crystallite size in direction (100) changes from 33.0 before the preparation procedure to 35.9 nm after it.

The results from the photocatalytic experiments with commercial powders of TiO_2 and ZnO samples are shown in Table 1. The adsorption degree of Orange II onto different catalysts surface at 30th minute of contact without any illumination are also presented. Blank experiments with pure dye solutions, irradiated with the respective lamps (UV or visible), are performed prior the photocatalytic tests. No significant photobleaching of the pollutants solution is observed upon UV or visible light illumination, meaning that the direct dye photoly-

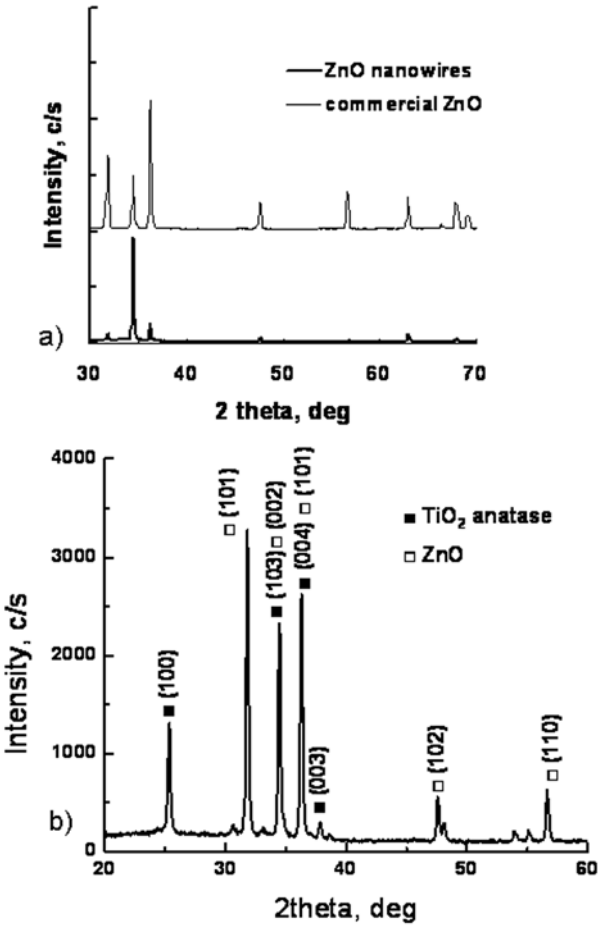

Fig. 4. Comparative XRD patterns of (a) commercial ZnO powder to nanowire ZnO film and (b) XRD pattern of mixed TiO_2/ZnO film of weight ratio 3:1

Table 1. Rate constants, adsorption and photodegradation degrees reached in the experiments with different photocatalytic samples. The duration of photocatalytic tests is 1 h for all powders (denoted as *) and 2.5 h for film samples (denoted as **)

Type of Illumination	Darkness (0.5 h)	UV		VIS	
Sample \ Quantity	Absorption, %	Degradation, %	Rate constant, min^{-1}	Degradation, %	Rate constant, min^{-1}
Orange II	0	0	–	0	–
ZnO powder*	5	98	0.157	21	0.028
TiO_2 powder*	2	100	0.162	2	–
ZnO nanowire film**	15	29	0.0015	35	0.0019
TiO_2/ZnO nanowire film**	20	53	0.0038	73	0.0058

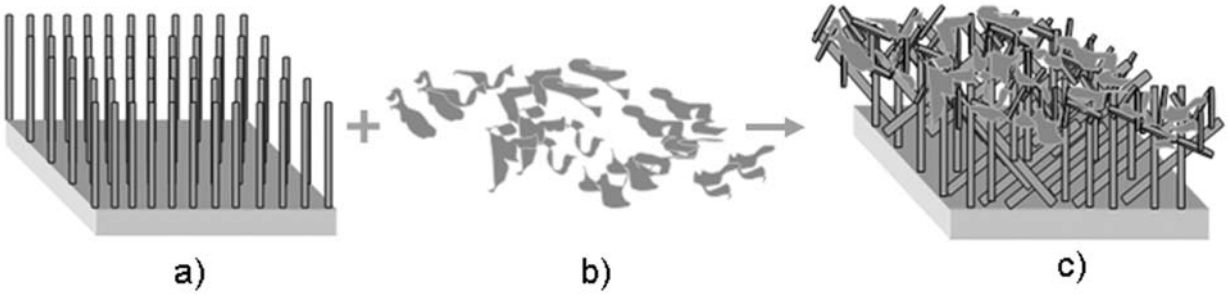

Fig. 5. Schematic illustration of (a) ZnO nanowires; (b) TiO_2 suspension in ethanol; (c) ZnO nanowires with TiO_2 nanoparticles

sis of is negligible at the particular experimental conditions.

As seen from the experimental data, both TiO_2 and ZnO successfully degrade Orange II under UV illumination approximately – the achieved after 1 h of photocatalysis dye degradation is 100% and 98% respectively. Zinc oxide has also photocatalytic activity under visible light irradiation (19% dye degradation at 1st h of illumination).

A comparison of the photocatalytic tests, conducted with prepared by us ZnO nanowire and mixed TiO_2/ZnO films is presented in Table 1. As seen from the Table, the ZnO films have not very high efficiency: 28% of Orange II degradation is reached for the UV and 35% for the visible light photocatalysis at 2.5 h of irradiation. The composite TiO_2/ZnO films express more efficient degradation of Orange II in aqueous solutions in both cases of UV or visible illumination. Highest degree of dye degradation for UV (53%) and for visible light (72%) irradiation, are achieved with the mixed TiO_2/ZnO photocatalytic films.

The observed higher rate of degradation with mixed TiO_2/ZnO than that with ZnO films is a complex result of at least two effects and can be explained by the change in the surface morphology as represented in the scheme of the mixed photocatalyst below (Fig. 5). As seen from the scheme, the addition of titania nanoparticles to the dense nanowire structure drastically increases the amount of illuminated catalysts surface and allows more efficient utilization of ZnO nanowires in the photocatalytic reaction. On another hand, the combination of two nanosized semiconductors with close band gaps (Fig. 1) in form of wires and particles increases the contact between TiO_2 and ZnO and favors effective charge separation of the photogenerated charge carriers under light excitation and therefore reduces the losses of recombination.

CONCLUSIONS

Nanowire TiO_2/ZnO films of 3–3.5 μm thickness are prepared on Si substrate. The zinc and titania oxides are present in the composite film as wurtzite and anatase respectively. The films exhibit a good homogeneity and nanocrystallinity as shown by SEM and XRD analysis. The average diameter of ZnO nanowires is 100–150 nm, as determined by SEM. The as-prepared films (pure and mixed with TiO_2) are tested in light induced degradation of the organic dye Orange II from water solutions. Significant rise in the photocatalytic efficiency is established with the composite TiO_2/ZnO nanowire film. The trend is confirmed under both sources of illumination – UV and visible light and is due to composites morphology and successful charge separation.

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СИНТЕЗ И ХАРАКТЕРИЗИРАНЕ НА ПРАХОВЕ ОТ ZnO И TiO_2, ТЪНКИ ФИЛМИ ОТ ZnO НАНОЖИЧКИ И TiO_2/ZnO ЗА ФОТОКАТАЛИТИЧНИ ПРИЛОЖЕНИЯ

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(Резюме)

Обект на настоящата работа са филми от вертикално подредени ZnO наножички върху Si подложка, както и такива дотирани с TiO_2. Изследваните образци са получени по метода на химично отлагане чрез двуетапна процедура, включваща зародишообразуване и последващ кристален растеж на наножичките от ZnO. Тънките филми от ZnO и TiO_2/ZnO са характеризирани със сканираща електронна микроскопия (СЕМ) и рентгенова дифракция. Определената със СЕМ дебелина на филма е 3–3.5 μm, а средният диаметър на наножичките от ZnO е 100–150 nm. Получените от нас филми (от чисти ZnO наножички и дотирани с наночастици TiO_2) са изпитани за фотокатализа и действието им е сравнено с това на каталитични прахове от TiO_2 и ZnO. Фотокаталитичните експерименти са проведени в цилиндричен стъклен реактор при облъчване с УВ или видима светлина. Изходната концентрация на замърсителя Оранжево II е 20 ppm за суспензия и 10 ppm за фотокатализа с филми. Фоторазграждането на багрилото е проследено спектрофотометрично. Дотираните с TiO_2 филми от ZnO наножички показват значително повишена фотокаталитична ефективност. Наблюдаваният ефект се дължи на успешно реализирано разделение на фотогенерираните заряди в синтезираните TiO_2/ZnO филми.