

ZnO/TiO₂ coupled semiconductor photocatalysts

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The present study is directed to clarify the influence of the ratio of TiO₂ to ZnO, containing in the nanocomposite powder samples, on their activity as photocatalysts in slurry. A series of samples corresponding to different percentages of titania are prepared from commercial brands. The phase composition and crystallinity of the samples is characterized by X-ray diffraction. The surface morphology of the samples is observed via scanning electron microscope. The photocatalytic action of the composites is tested in UV and visible light induced degradation of two model pollutants: azo dye Orange II (O II) used as cosmetic colorant CI 15510 and triarylmethane dye Brilliant Green (BG), used as food colorant E142.

Key words: ZnO/TiO₂ composite, photocatalysis, Orange II, Brilliant Green, UV, visible light

INTRODUCTION

Photocatalysis is an attractive solution for water and air purification from various pollutants in low concentrations under light illumination. Titania and zinc oxide are the most popular oxides used in heterogeneous photocatalysis due to their unique properties [1, 2].

TiO₂ has relatively large band gap (3.2 eV for anatase modification). It is most widely used photocatalyst since it is chemically stable, nontoxic and natural material [3]. ZnO has also been considered as a suitable alternative of TiO₂ because of its comparability with TiO₂ band gap energy and its relatively lower cost of production [4, 5]. 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 [6]. The band gaps values of TiO₂ and ZnO show that near UV irradiation is needed for photo activation of both oxides.

The photoactivity of a photocatalysts depends on several key properties: crystal phase, light exposed surface area, uncoordinated surface sites, lattice defects and degree of crystallinity. The application of composite materials allows morphology control, improvement and fine tuning of most of the above properties. Additionally, composite heterostructures can create suitable mid-band-gap electronic states which can alter charge migration or produce a red shift in the absorption spectrum. Further, formation of heterojunctions between the materials can yield visible light absorption. The application of heterostructured catalysts with adjustable bandgaps, enhanced stability and photocatalytic performance, gives the possibility to realize sufficient charge

separation, an increased lifetime of the charge carriers and enhanced interfacial charge transfer to the adsorbed species favoring their photooxidation and further mineralization [7-11]. A plenty of investigations on nanostructured ZnO/TiO₂ composites with different configurations and morphologies are performed in order to obtain more efficient photocatalytic degradation [9, 12-14].

It is of interest to understand how the differences between TiO₂ and ZnO may affect the overall catalytic processes. As the first step, this investigation is focused on the influence of the ZnO and TiO₂ content in the heterostructured composite on the UV and visible light induced degradation of two model pollutants: azo dye Orange II (O II) used as cosmetic colorant CI 15510 and triarylmethane dye Brilliant Green (BG), used as food colorant E142.

EXPERIMENTAL

The oxides TiO₂ anatase from KRONOS-Germany and ZnO from Sigma Aldrich were used for the composite ZnO/TiO₂ powders preparation. The initial charge for the composite was prepared from thoroughly homogenized commercial oxide powders. Seven series of samples with composition corresponding to 10, 25, 40, 50, 60, 75 and 90% ZnO content were prepared. As mixing media a small quantity of ethanol (Institute of Pure Substances, Sofia University) was added to assure better contact between both oxides. Then the mixtures were sonicated for 10 min, after that thermally treated for 2 h at 200°C to assure complete removal of the ethanol residue and finally well stirred in a glass mortar to obtain fine powder.

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The phase composition and crystallinity of as-prepared composites was identified by X-Ray analysis (diffractometer Siemens D 500 CuK α source of radiation at a step of 0.05 deg for 2 θ and counting time 2 s/step). The surface area of the dry composite powders, was determined by BET analyses using N₂ adsorption. The surface morphology of the samples was observed via scanning electron microscopy (JSM-5510 JEOL).

The characteristics of two model pollutants Orange II and Brilliant Green are presented in Table 1.

The as-prepared ZnO/TiO₂ samples were tested in photodegradation of O II or BG from water solution by a standard testing procedure [15]. The dye solution volume was 250 ml. The catalysts loading was 1g L⁻¹. The initial concentration was 20 ppm for O II and for BG. The sources of light

illumination were as follows: UVA lamp (Sylvania 18W BLB T8, emitting mainly in the range of 315-400 nm) placed at 10 cm above and linear Tungfram lamp (500 W K1R7s 9700 Lm, maximal emission at 700 nm) for the visible irradiation fixed at 25 cm above the treated solution. Aliquot samples from the investigated solution were taken regularly at fixed time intervals and analyzed by UV-VIS spectrophotometer (Thermo scientific, Type Evolution 300 BB) at the maximal absorption of the contaminants. After the measurement, the aliquots were returned back to the pollutants solution. The solutions were stirred constantly by electromagnetic stirrer (rotation speed of 400 rpm). All the photocatalytic tests were performed at room temperature of 23±2°C.

Table 1. Characteristic data of the organic dyes used in the photocatalytic experiments

Contaminant	O II	BG
Empirical formula:	C ₁₆ H ₁₁ N ₂ NaO ₄ S	C ₂₇ H ₃₃ N ₂ .HO ₄ S
Molar mass:	350.32 g/mol	482.64 g/mol
Absorption maximum (in water):	484 nm	
Minimum dye content:	85%	90%
Synonyms:	4-(2-Hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt, Acid Orange 7, Acid Orange A, Orange II, Tropaeolin 000 No. 2	Astradiamant green GX, Basic Green 1, Diamond Green, Emerald Green, Solid green JJO, Diamond green G, Ethyl Green, Aniline green, Benzaldehyde green, Fast green J

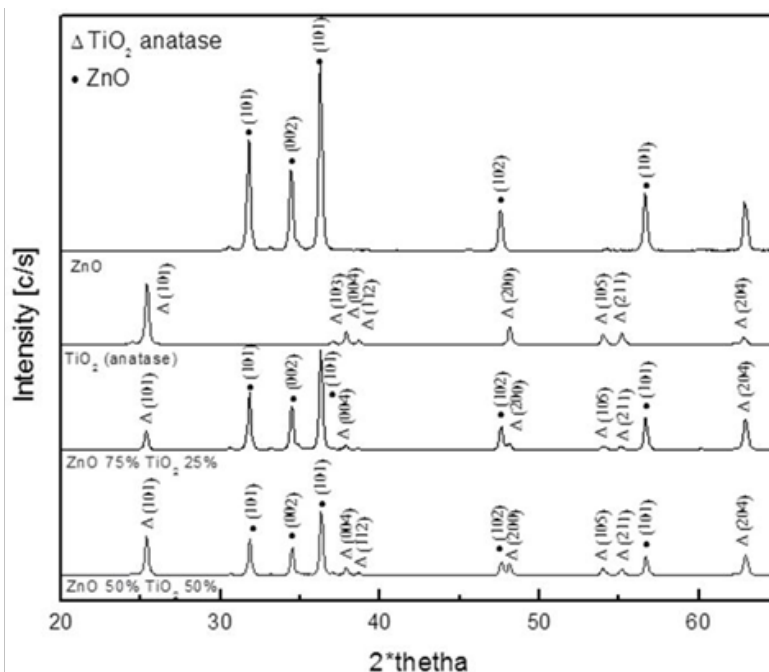


Fig. 1. Comparative XRD pattern of TiO₂, ZnO and ZnO/TiO₂ composites.

RESULTS AND DISCUSSION

The crystalline phase composition of the ZnO/TiO₂ nanocomposite and pure oxide samples is

verified by X-ray analysis (Fig. 1). From the XRD it is clearly seen that ZnO is crystalline, in form of hexagonal wurtzite with dominating peak (101). The titania has main peak at (101) and is in form of

anatase modification. Comparing the XRD patterns in Fig. 1 one can see that ZnO and TiO₂ are present in the composite as separate phases, there is no indication for formation of mixed compound: the main peaks of both oxides in case of composite sample do not differ in width and intensity from these in the case of pure ZnO or TiO₂ phases. The crystallites size, calculated following Sherrers equation ($k = 1.5406 \text{ \AA}$) is found to be 24 nm for ZnO and 17 nm for TiO₂. The calculation is made from the peaks (101) for ZnO and (101) for TiO₂ (relatively strong and single for the respective oxide - Fig. 1).

A comparison of the surface morphology of TiO₂ to that of ZnO/TiO₂ nanocomposite observed by SEM is shown in Fig. 2. From the micrographs is seen that the samples are uniform and homogeneous. The size of the particles grains of the samples is

calculated following the equation:

$$D_{av} = \sum_{i=1}^N (D_{i_{max}} + D_{i_{min}}) / 2N ,$$

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 particles. In this case $N=350 \div 520$. The average grain size is found to be approximately 0.45 μm for ZnO and 0.02 μm for TiO₂ for all of the investigated samples.

The results from BET analysis are presented in Table 2.

As shown in the table, the surface area in the composites increases with the TiO₂ content from 23.03 m^2/g in case of 90%ZnO/10%TiO₂ to 37.89 m^2/g for the 90%ZnO/10%TiO₂ composite. The latter is greatest among all samples. The pure oxide phases have approximately equal surface area.

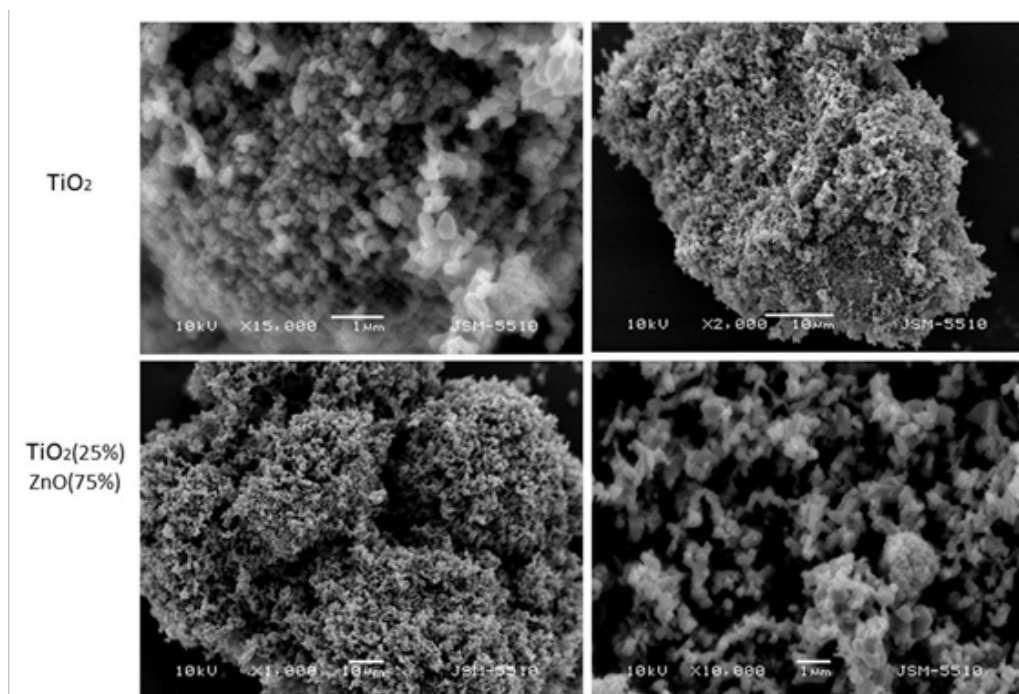


Fig. 2. SEM images of the powdered catalysts at different magnifications: (a) and (b) pure TiO₂; (c) and (d) ZnO(75%)/TiO₂(25%) composite.

Table 2. Specific surface area S of the commercial (pure ZnO and TiO₂) and prepared ZnO/TiO₂ powder catalysts

ZnO, %	TiO ₂ , %	$S, \text{m}^2/\text{g}$
100	0	35.76
90	10	23.03
75	25	26.55
60	40	30.81
50	50	31
40	60	33.45
25	75	34.35
10	90	37.89
0	100	35.52

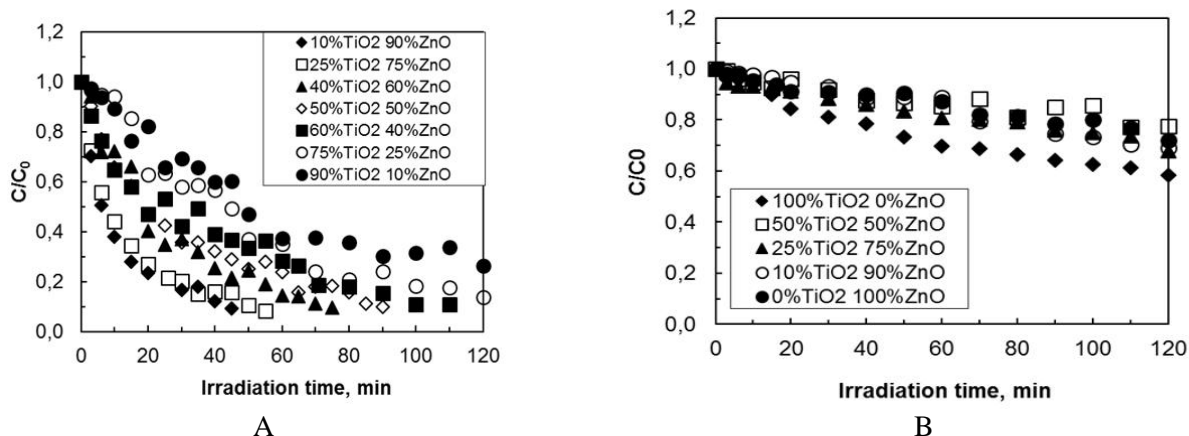


Fig. 3. Photodegradation kinetics of O II colorant from 20 ppm aqueous solutions by the different samples under: (a) UV and (b) visible light illumination.

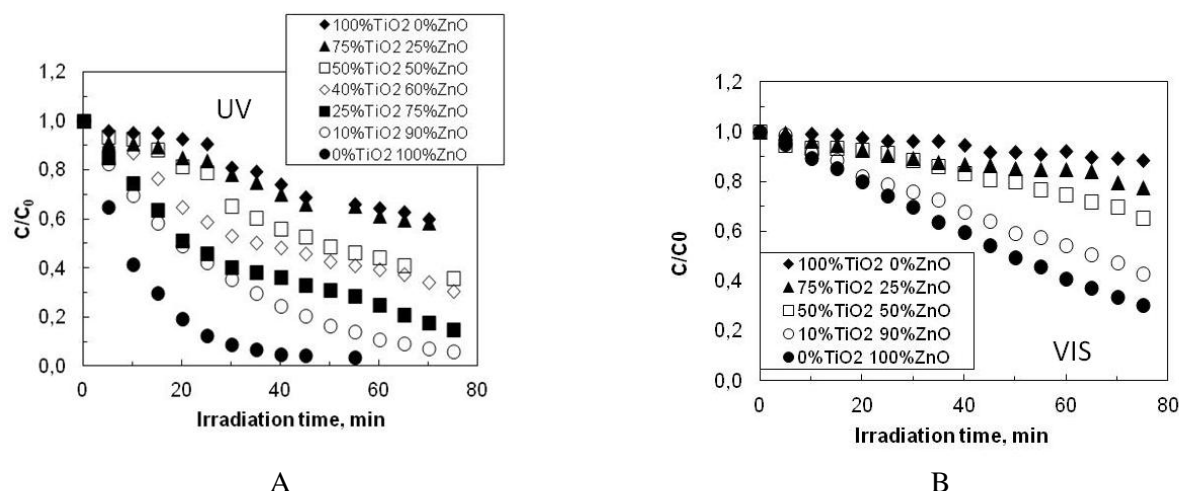


Fig. 4. Kinetics of BG colorant photodecomposition by the different powder catalysts from 20 ppm water solutions under irradiation with: (a) UV and (b) visible light.

The kinetics of colorants degradation in the photocatalytic experiments is presented in Fig. 3 for O II and in Fig 4 for BG. The colorants concentration in the water solutions is 20 ppm. Figs. 3a. and 4a show the experimental runs under UV illumination. The photocatalytic tests carried out with visible light irradiation are presented in Figs. 3b. and 4b. In general - higher rates and degrees of photodegradation under UV and visible light are achieved in case of BG in comparison to these in case of O II. The differences between the investigated heterocomposite samples are more pronounced and can be better observed also in the case of BG (Fig 4.). The experimental data in case of ZnO/TiO₂ heterocomposites show clear tendency for higher photocatalytic efficiency with the ZnO content in the sample irrespective of type of pollutant or illumination. Pure ZnO is the most efficient photocatalysts in comparison to the rest of the samples in all the photocatalytic tests. Pure TiO₂ sample always has the lowest efficiency among all tested photocatalysts.

The apparent rate constants of photocatalysis are calculated following the equation:

$$C = C_{in} \cdot e^{-Kt}$$

where C is the concentration of the contaminants solution at the moment t , C_{in} – the initial dye concentration and t is the irradiation time in minutes. The rate constants values (K), calculated by the above equation with the data, obtained from the photocatalytic experiments under both types of illumination, are plotted in Fig. 5. From the figure one can see, that highest rate constants values are observed in case of photocatalysis under UV light (Fig. 5a), where the process of photocatalysis is most effective. In comparison with O II, the BG photodegradation is always faster, irrespective of irradiation wavelength - UV or visible light.

The experimental data confirm other researchers viewpoint [16] that for some applications where the process of ZnO photocatalysis is the most effective, zinc oxide is a suitable alternative to TiO₂.

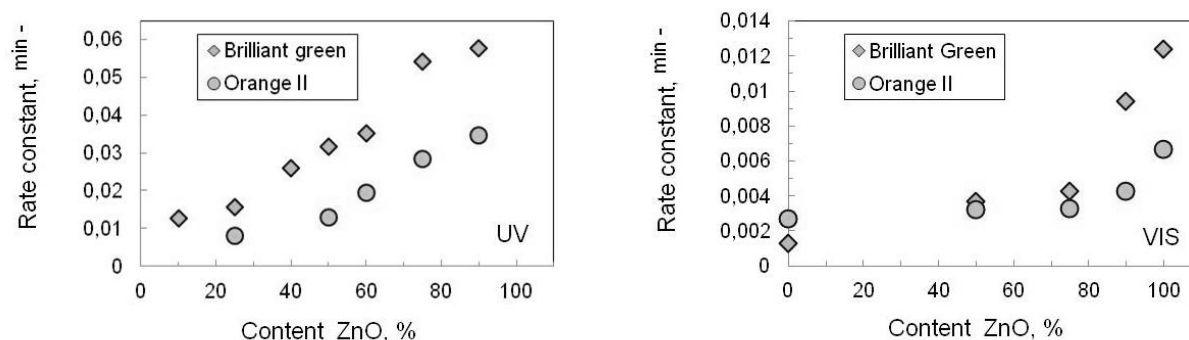


Fig. 5. Rate constant values of O II and BG photodegradation versus the ZnO content in the composite samples in case of: (a) UV and (b) visible light induced photocatalysis.

CONCLUSIONS

The photocatalytic action of the ZnO/TiO₂ samples is tested and compared to that of pure commercial oxides in UV and visible light induced purification of aqueous solutions from the organic colorants Orange II and Brilliant Green. The photocatalytic effectiveness of the composites increases regularly with the ZnO content in the powders. Most efficient colorants photodegradation is achieved in case of BG. The best photocatalyst in all the experiments is pure ZnO in comparison to the rest of the samples. The above effects are established irrespective of the type of illumination or type of purified solution. The experimental data show that in the particular purification ZnO is the suitable alternative to TiO₂.

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ZnO/TiO₂ композитни фотокатализатори

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(Резюме)

Настоящата работа има за цел изследване на влиянието на съотношението на TiO₂ към ZnO, в състава на нанокмозитни прахове, върху тяхната ефективност като фотокатализатори в суспензия. Серия от проби, съответстващи на различно съдържание на титанов диоксид са получени от търговските марки на двата оксида. Фазовият състав и кристалността на пробите са характеризирани с рентгенова дифракция. Морфологията на повърхността на пробите е наблюдавана чрез сканираща електронна микроскопия. Фотокаталитичната активност на композитите е тествана под действието на ултравиолетова и видима светлина, при фотокаталитичното разграждане на два моделни замърсителя: азо багрилото Оранжево II (O II), използвано като козметичен оцветител CI 15510 и триарилметановото багрило, Брилянтно зелено (BG), използвано като оцветител на храни E142.