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Nanosized composite thin films of SiO_2-ZnO for photocatalytic decomposition of organic dyes – structure and characterization

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In this study we present pure ZnO and $20SiO_2$–80ZnO (mol %) nanocomposite photocatalysts, prepared on glass substrates via spin coating technique and sol-gel method from starting solutions of zinc nitrate and tetraethoxysilane. The as-prepared films are annealed in air at 500 °C for 1 h. The films are characterized by XRD and SEM analysis. The photocatalytic action of the films is checked and compared in photodegradation of two organic dyes Malachite Green and Methylene Blue under UV and visible light illumination. The change in dye concentration with time of irradiation is monitored by UV-visible spectroscopy.

Key words: SiO_2–ZnO films, photocatalytic degradation, sol–gel, spin coating, Malachite Green, Methylene Blue.

INTRODUCTION

The organic dyes belong to one of the most common and large group of pollutants in wastewaters from textile industries, dye manufacturing, and various other industrial processes such as food and paper production, pharmaceuticals, cosmetics and etc. The worldwide dye production is more than 7.10^5 tones per year. The losses in wastewaters at different stages of manufacturing and during application are about 10–15% of the total produced amount [1]. Organic dyes can undergo transformation in aquatic media and can form harmful carcinogenic and mutagenic intermediates, this way causing a serious risk for survival of microorganisms, aquatic life and environmental media – water and soil [2, 3]. The effect of such contamination on human health may be unpredictable hazardous inflicting different diseases like immune-suppression, respiratory, central nervous, neurobehavioural disorders presage as allergy, tissue necrosis, skin or eye infections and irritation and even lung edema [4, 5].

Different biological, physical and chemical methods have been successfully applied to solve the problems in purification of dye contaminated wastewaters. All these conventional methods have also some disadvantages: large amounts of biological sludge and the problem of their disposal; transfer of the toxic compounds just from one phase to another instead of their decomposition; need of regular regeneration of the adsorbents. Recently the advanced oxidation processes based on generation of highly reactive species (hydroxyl radicals, superoxide anion radicals or hydrogen peroxide as initiators of oxidative degradation), are an attractive alternative to traditional methods for wastewaters purification. Among these processes, heterogeneous photocatalysis seems to be promising advanced method and has been successfully applied in photodecomposition of large number organic pollutants including dyes [6, 7]. In general the photocatalytic process is governed by combined interaction between semiconductor catalyst and light irradiation, which leads to formation of free radicals from the photogenerated on the catalysts surface charge carriers and further degradation of the organics. One of the most popular semiconductor catalysts is ZnO. Zinc oxide is a natural compound with band gap energy of 3.2 eV, which makes it an alternative potential catalyst due to its high quantum efficiency. For that

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reasons ZnO has been applied and studied in various organic pollutants photodegradation [2, 8]. The surface modification [9–11], semiconductor coupling [12–14], metal [15–17] and non-metal [18–20] doping of ZnO also have been investigated in terms of their influence on the catalyst effectiveness.

In this work we present a study on photocatalysis with films, prepared of ZnO and ZnO–SiO_2 heterostructures, aimed to enhance the degradation efficiency and activity in visible region as well as solar irradiation in future applications. The organic dyes malachite green (MG) and methylene blue (MB) are chosen as modal pollutants for dye contaminated wastewaters.

EXPERIMENTAL

The reagents and materials, used in the experiments, were as follows: zinc nitrate ($Zn(NO_3)_2.6H_2O$, Fluka); tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, Sigma-Aldrich); microscopic glass slides (25×75 ×1.2 mm, ISOLAB Germany). Prior films deposition the glass substrates were thoroughly cleaned by ultrasound with acetone, ethanol and deionized water. As model pollutant were chosen the commercial dyes malachite green oxalate ($C_{48}H_{50}N_4O_4.2C_2H_2O_4$, dye content >90%, λ_{max} = 618 nm) and methylene blue ($C_{16}H_{18}ClN_3S.\times H_2O$, dye content >95%, λ_{max} = 665 nm) supplied from Sigma-Aldrich. All dye solutions, used in the photocatalytic tests, were prepared with distilled water.

The ZnO and $20SiO_2$–80ZnO nanocomposite films were deposited by sol gel method [21, 22] from sol solutions, based on binary heterochain inorganic polymers. The 20:80 (SiO_2 to ZnO) ratio of the composite is selected based on our previous morphological study on porous silicon with embedded metal oxide nanocomposites [22]. In this case more uniform coatings with better adhesion to substrate were achieved. The films were finally annealed at 520 °C 1.5 h in air for complete organics decomposition. The initial precursors contain easily hydrolyzed components, such as TEOS, which interact with water with formation of polymolecules. For the preparation of the two-component oxide coatings, based on silica and zinc oxide, the hydrolysis and polycondensation of TEOS was carried out in the presence of the zinc inorganic salt $Zn(NO_3)_2$. The precursor sols were deposited onto glass substrates via spin coating technique at rotation speed of 3000 $rpm.min^{-1}$. The as-obtained gel films were finally annealed at 500 °C for 1.5 h in air for completing the organics decomposition.

The as-obtained ZnO and ZnO–SiO_2 films were checked for photocatalysis by standard testing procedure in photodegradation of 5 ppm MG or MB in water solutions under UV or visible-light illumination. The volume of treated dye solution was 150 ml. The sources of radiation were as follows: (i) for the UV light – Sylvania 18W BLB T8, emitting mainly in the range 315–400 nm UVA lamp fixed 10 cm above the pollutants solution; (ii) for the visible light – linear Tungsram lamp 500 W K1R7s 9700 Lm, maximal emission at 700 nm placed at 25 cm above the treated solution. The photocatalytic tests were carried out in four series. Photocatalysis with composite ZnO–SiO_2 thin and thick films under UV and visible light irradiation was compared to photocatalytic experiments with ZnO thin and thick films and under both types of illumination. Regularly taken aliquot samples from the pollutants aqueous solution at determined time intervals were analyzed by spectrophotometer (Jenway 6400) at the maximal absorption of the dye. After the measurements the aliquots were returned back to the purified solution. The solution was constantly stirred by electromagnetic stirrer at constant rotation speed of 400 rpm. The experiments were conducted at constant temperature of 23±2 °C.

The samples surface morphology was observed by scanning electron microscopy (SEM) (JSM-5510 JEOL). The phase composition and crystallinity of ZnO and ZnO-SiO_2 films was characterized by X-ray diffraction (Siemens D 500 diffractometer, CuKα source of radiation at a step of 0.05 deg for 2Θ and counting time 2s/step).

RESULTS AND DISCUSSION

The comparison of surface morphology observation by SEM shows that the ZnO and ZnO–SiO_2 film samples are textured, the effect is more pronounced in the case of composite film (Figs. 1 and 2). The porous structure of the nanocomposite is formed as a result from spinoidal decomposition of the sol, with a simultaneous release of the solvent by evaporation from the formed gel net. The latter leads to formation of macropores with overall size of 0.2–0.5 μm (Fig. 2a). The conductive branches of the macropores are from unhomogeneous mesoporous material, build by conducting ZnO spherical structures and insolating SiO_2 grains. The film thickness of the composite coatings is found to be 200 nm (Fig. 2b).

The nanostructured films are analyzed by X-ray diffraction in order to determine the phase composition of the samples (Fig. 3). The ZnO in the films is identified as wurtzite, with main characteristic peaks at 32.1, 34.8 and 36.5 2θ degrees. The SiO_2 in the composite structures is amorphous and therefore is not represented in the XRD spectrum.

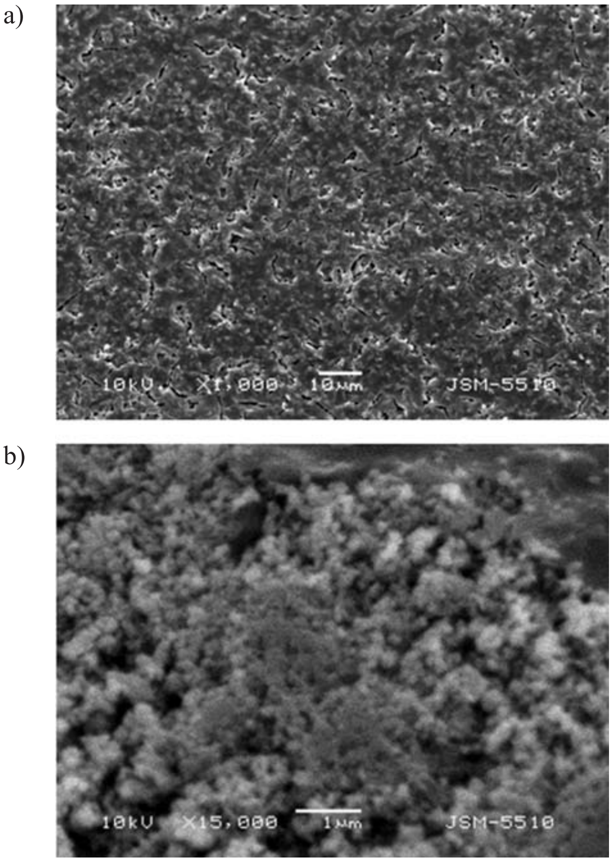

Fig. 1. SEM micrographs of zinc oxide films: (a) typical top view of the films surface at lower magnification; (b) a structure of spherical particles inside the pores at higher magnification

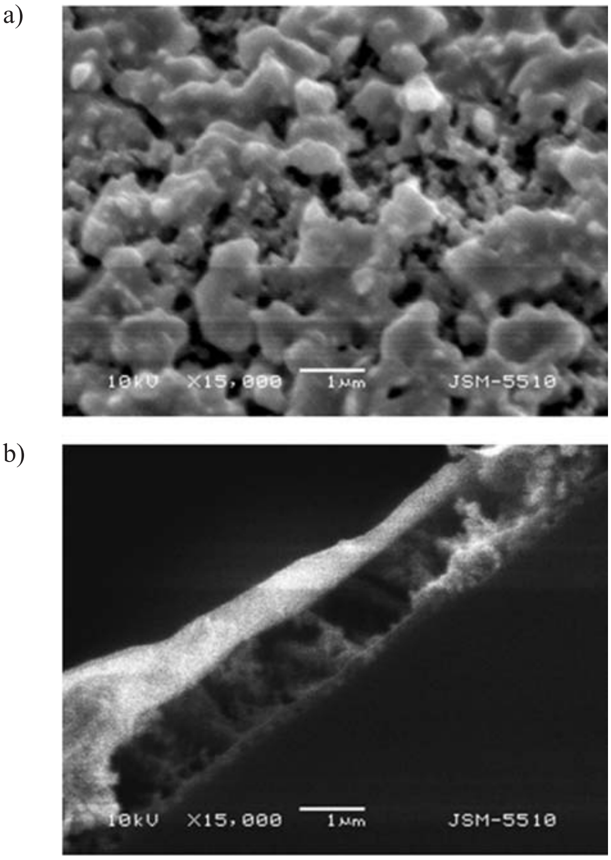

Fig. 2. SEM images of $20SiO_2$–80ZnO films: (a) top view of the coatings surface morphology; (b) cross section of the nanocomposite film

Two series of photocatalytic experiments are performed upon UV and visible light irradiation – with methylene blue and with malachite green aqueous solutions. The results from the photocatalytic tests for MB degradation with the ZnO and composite films are presented in Figure 4. As seen from the experimental data, the photocatalytic efficiency of all the films (ZnO and ZnO–SiO_2) is low. In case of visible light illumination the ZnO thin film is more effective than the composite one. Similar trend is observed from the tests under UV illumination – all the thin film samples manifest higher rates of MB photodegradation in comparison to the thicker ones irrespective of type of light irradiation. From the comparison of visible light induced photocatalysis by samples with thicker layers is seen that the ZnO-SiO_2 composite sample shows higher degree of pollutants degradation than the ZnO film. The rate constants values of photocatalysis, calculated following the equation $\ln (C/C_0) = -kt$ are given in Table 1.

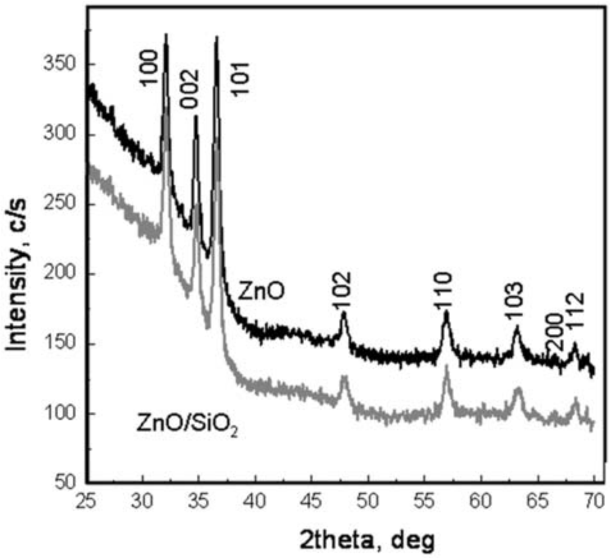

Fig. 3. Comparative XRD of ZnO and ZnO–SiO_2 composite films

Figure 5 represents kinetics of photocatalysis of MG with the ZnO and ZnO–SiO_2 film samples under UV and visible light illumination. In general an increased photocatalytic efficiency of all samples is observed in this case. From the presented data one can see clear tendency for regular rise in the samples photocatalytic efficiency with the film thickness irrespective of the type of light irradiation. Double layered films reach 43.45% of dye degradation under UV and 55.70% under visible light irradiation. This effect can be seen also from the rate constants of photocatalysis, presented in Table 1. The differ-

Table 1. Rate constants of photodegradation, calculated from the tests, conducted with different film samples

Samples	Rate constants, min^{-1}			
	Methylene Blue		Malachite Green	
	UV	Visible	UV	Visible
ZnO, thin	0.0009	0.0014	0.001	0.0014
ZnO, thick	0.0003	0.0005	0.0021	0.0031
SiO_2-ZnO, thin	0.0003	0.001	0.0007	0.0013
SiO_2-ZnO, thick	0.0002	0.0006	0.0024	0.0033

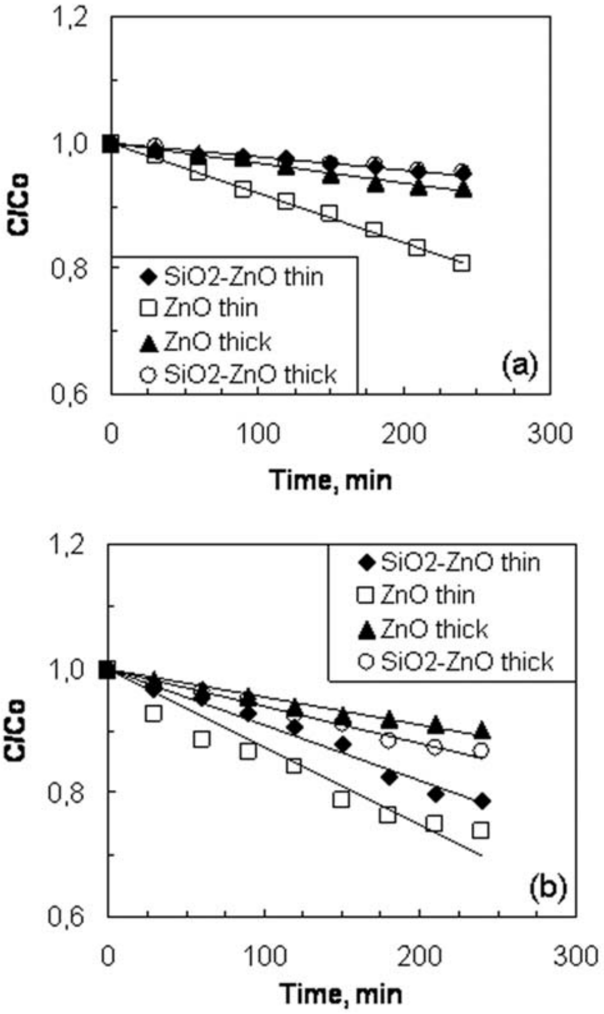

Fig. 4. Change in methylene blue concentration versus time of photocatalysis with the different film samples under: (a) UV illumination and (b) visible light. The initial MB concentration is 5 ppm

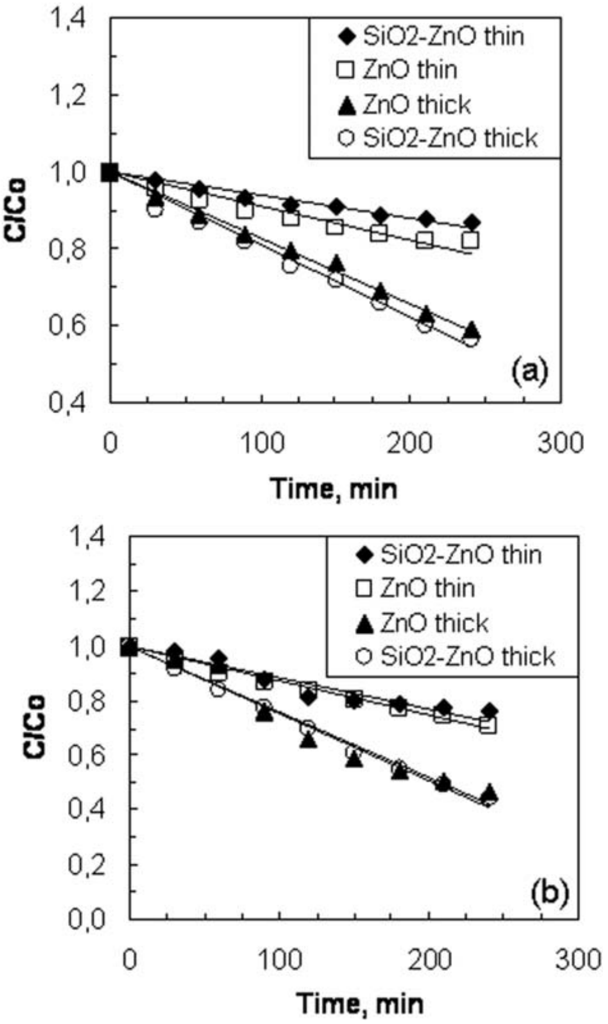

Fig. 5. Comparison of the photodegradation kinetics of malachite green with the photocatalytic films under catalytic action under: (a) UV irradiation and (b) visible light. The initial MG concentration is 5 ppm

ences, observed in photocatalytic decomposition of both pollutants can be attributed to geometrical factor, which is different for the different dye molecules. The structural formulas of Methylene blue and Malachite green oxalate are shown in Fig. 6.

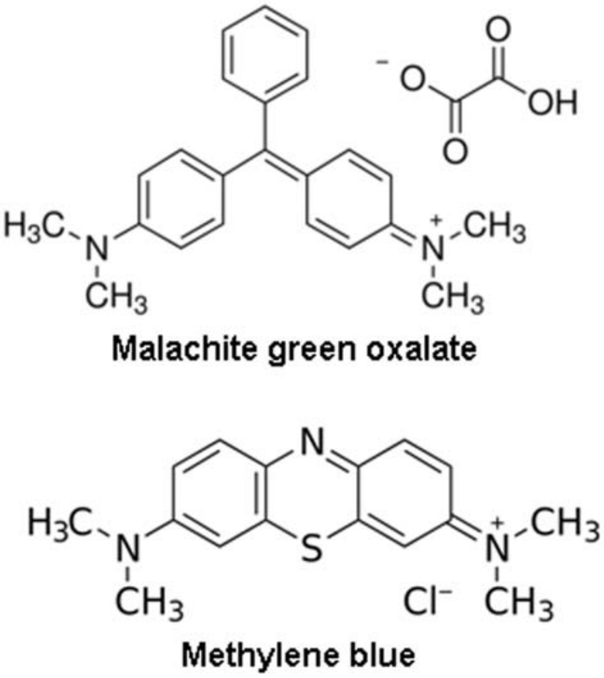

Fig. 6. Structural formulas of Methylene blue and Malachite green oxalate

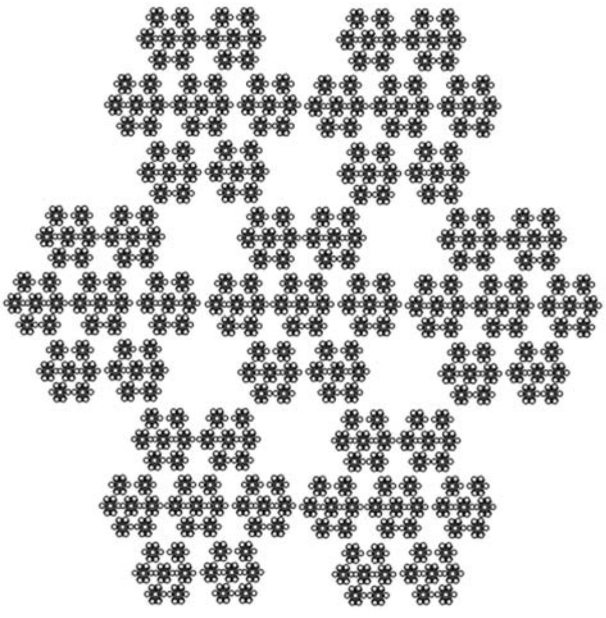

Fig. 7. Scheme of 3-D Julien fractal

The main advantages of using hierarchical assembled SiO_2/ZnO nanocomposite photocatalyst, consisting micro- and nanocrystals, are connected with the possible control over size and morphology towards desirable chemical properties of the obtained materials. The hierarchical self-assembly materials consist of constructive “blocks” with different sizes and shapes (and size-dependent properties) and have hierarchical porous structure. Hierarchical self-assembly can be a multilevel one, when the integrated blocks are basic elements for larger consolidations (with lager interaction radius). Figure 7 represents Julien fractal, which is one of the simplest idealized examples of self-assembly [22]. It is an appropriate example for understanding of the principal possibility to obtain materials with calibrated pores size. That is very important for development of new-generation devices, because the pores with different sizes have different functions (adsorption centers, canals for import and export of reaction products, nanoreactors with different capillary phenomena etc.).

CONCLUSIONS

Thin solid films of ZnO–SiO_2 are prepared via sol-gel process and spin coating technique. The films consist of micro- and nanostructures as shown by SEM and XRD investigations. The photocatalytic tests with respect to destruction of MG prove that of best performance is always the composite ZnO–SiO_2 thick film sample. This result is confirmed with both UV and visible light illumination using lamps of different power. The double layered films manifest much higher photocatalytic efficiency, compared with the rest film samples under UV and visible light irradiation. All films have higher photocatalytic efficiency in malachite green degradation in comparison to methylene blue.

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НАНОРАЗМЕРНИ КОМПОЗИТНИ ТЪНКИ ФИЛМИ ОТ SiO_2–ZnO ЗА ФОТОКАТАЛИТИЧНО РАЗЛАГАНЕ НА ОРГАНИЧНИ БАГРИЛА – СТРУКТУРА И ХАРАКТЕРИЗИРАНЕ

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(Резюме)

В това изследване ние представяме чист ZnO и нанокомпозитни фотокатализатори $20SiO_2$–80ZnO (мол. %), получени върху стъклени подложки чрез техника на цетробежно отлагане (spin coating) и золгелен метод от изходни разтвори на цинков нитрат и тетраетоксисилан. Така получените филми са накалени при 500 °С за 1 час. Филмите са характеризирани чрез рентгенова дифракция и СЕМ анализи. Фотокаталитичното действие на филмите е изпитано и сравнено при фоторазграждането на две органични багрила Малахитово Зелено и Метиленово Синьо под облъчване с УВ и видима светлина. Промяната в концентрацията на багрилото с времето на облъчване е проследена с УВ-видима спектроскопия.