ZnO thin films preparation on glass substrates by two different sol-gel methods

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Here we present thin films of ZnO with photocatalytic application in purifying water from organic pollutants. The films were obtained from stable colloidal precursor sol, prepared by two sol-gel methods (*A* and *B*) using zinc acetate and varying the solvents. These sols are deposited on glass substrates via dip-coating technique. The films are characterized by different methods (XRD, SEM, FTIR). By XRD was established that the zinc oxide is of hexagonal crystal structure.

A comparison of the determined morphology, composition and structure for the prepared by two different method films is studied. The morphology of films obtained with 1-propanol and 1-butanol, as shown is not homogeneous. The film surface is not uniform and there are many cracks and bubbles. Layers in such films is very easy to peel off after their ignition. Therefore, a third synthesis of the sol-gel method *A* is performed, with any changes in the formulation, only alcohol is substituted by 2-propanol. There is ganglia typical surface structure of the so obtained film, which is established by SEM. They are evenly distributed over the entire film surface. The film surface in the sol-gel *B* was investigated by SEM. The film surface has characteristic ganglia-like patterns. The resulting samples are more uniform, show much better adhesion of the layers and higher density, compared to films from the sol-gel method *A*. The difference in the films morphology has influence their photocatalytic performance.

Key words: zinc oxide, thin films, crystallites, glass substrate, dip coating, sol-gel method.

INTRODUCTION

The zinc oxide (ZnO) is an important II–VI group semiconductor material, with a hexagonal wurtzite crystal structure (c = 5.21 Å and a = 3.25 Å) [1], wide and direct band gap of 3.37 eV (at 300 K), large free-exciton binding energy (60 meV) [2], strong cohesive energy of 1.89 eV [3], high mechanical and thermal stabilities [4], and radiation hardness [5–7]. ZnO possesses a wurtzite structure similar to GaN [8, 9], which is widely used in high-performance optoelectronic devices.

Undoped and doped zinc oxide thin films have many interesting properties, such as, transparency in the visible and high infrared reflectivity [10], excellent piezoelectrical properties [11], hexagonal wurtzite structure n-type conductivity [12], etc. All these properties make them widely applied in many fields, such as, transparent conductors [13], solar cells [14], electrical, piezoelectric or luminescent devices and also as gas sensors, chemical sensors, surface acoustic wave devices (SAW) [15], UV laser and catalysts. Semiconductor catalysts have been studied extensively [16–18] to promote the degradation of potential organic pollutants present in waste water [19, 20].

ZnO films can be prepared by various methods, including vapor deposition [21], pulsed laser deposition [22], molecular beam epitaxy [23], metal organic chemical vapor deposition (MOCVD) [24], sputtering [25], electron beam evaporation [26], spray pyrolysis [27] and sol–gel [28,29]. Sol–gel is an attractive method for films preparation because of its easy control, low cost and low fabricating temperature [30]. It is well known that the sensing mechanism of semiconducting oxide gas sensors is based on the surface reaction and a high surface–volume ratio. The grain size and the porosity of the sensing material are the most important factors for high sensitivity and short response time sensors.

This paper presents preliminary results on the crystalline structure, morphology and photocatalytic properties of nanocrystalline ZnO thin films prepared by both sol–gel methods. When dip-coating sol–gel technique is used, the withdrawal

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speed is the most important processing parameter affecting the porosity of the films. It was found that higher withdrawal rates resulted in films of lower quality. The surface of films obtained with 1-butanol and 1-propanol were observed bubbles, cracks and haven't good photocatalytic properties. While films with 2-propanol manifest homogeneous ganglia-like surface structure. Nanostructured zinc oxide films with 2-methoxyethanol have improved ganglia-like structure, but much more developed. They degrade most completely the dye (97% for 3 hours) and have the highest photocatalytic activity.

EXPERIMENTAL SECTION

Preparation of ZnO films

Materials: Zinc acetate dihydrate $Zn(CH_3COO)_2$.$2H_2O$ (>99.5%), n-propanol (>99.0%), 2-propanol (>99.0%), n-butanol (>99.0%), glycerol (>99,0%), ethylene glycol (>99,0%), triethylamine (>99.5%), 2-methoxyethanol (>99.5%) and monoethanolamine (>99%) were supplied from Fluka. Malachite green

(MG) oxalate was from Croma-G mbH & Co. The glass slides (ca. 76×26 mm), used for substrates of the ZnO films, were from ISO-LAB (Germany). All other reagents were of analytical grade. The soda-lime microscope glasses were cleaned with a chromerge solution (H_2SO_4/Cr_2O_3), then with a mixture of hydrochloric and nitric acid and finally with ethanol and acetone successively.

Sol-gel method (A): The sol was prepared using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), ethylene glycol ($C_2H_6O_2$), alcohols (1-propanol, 2-propanol, 1-butanol), glycerol ($C_3H_8O_3$) and triethylamine ($C_6H_{15}N$) (Fig. 1a). Ethylene glycol (2.5 ml) and zinc acetate dihydrate (10 g) were mixed in a round-bottomed flask and heated at 100 °C for 15 min to obtain a uniform transparent mixture. During the heating, water vapor evolved from the mixture equivalent to the water of hydration of zinc acetate dihydrate. After cooling down to room temperature the content of the flask solidifies to a transparent brittle solid, which is then dissolved in alcohol. The addition of glycerol (0.5 ml) enhances the solubility of zinc acetate as well as the film formation property of the sol. Triethylamine (1 mol eq.) is also added
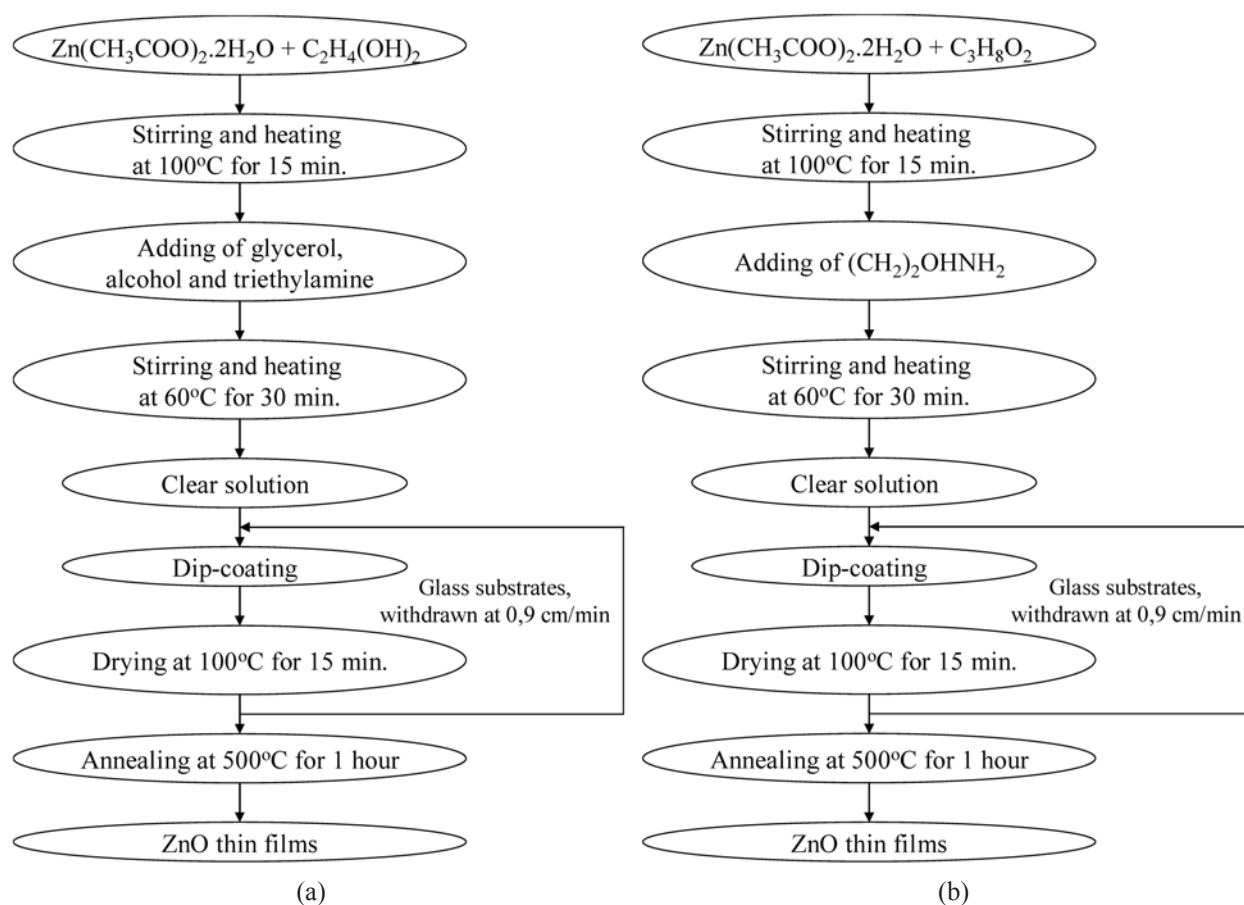

Fig. 1. Scheme of experimental procedures: (a) *sol A* and (b) *sol B*

to assist the hydrolysis of zinc acetate. The resultant solution is stirred at 60 °C for 1h to yield a clear and homogeneous solution, which serves as precursor coating sol.

Sol-gel method (B): The scheme of *sol B* is shown in Fig. 1b. Zinc acetate dihydrate (10 g) and 2-methoxyethanol (20 ml) are mixed together in a round-bottomed flask and heated at 100 °C for 15 min to obtain a uniform transparent mixture. Monoethanolamine (3.2 ml) is also added to assist the hydrolysis of zinc acetate. The obtained clear solution was heated up at 60 °C upon magnetic stirring for 1h and let aging overnight. The resultant solution was clear and homogenous to serve as the coating substance for film preparation.

The *sol A* and *sol B* was strongly hydrolyze and formed a thick gel after the addition of water. No visible changes were observed in the solution stored at room temperature for at least 2 months.

The deposition of ZnO films consisted of dip coating, drying and annealing of the material. The gel films were prepared by dipping glass substrates in the precursor solutions and next withdrawing at rates of 0.9 cm/min at room temperature. It was found that higher withdrawal rates resulted in films of lower quality. The films were deposited with 5 coatings and dried at 80 °C for 15 min after each successive coating. The final gel films were annealed at 500 °C for 60 min in order to obtain photocatalytic ZnO films.

Characterization of ZnO films

The obtained ZnO thin films were analyzed by scanning electron microscope (SEM) JSM-5510 (JEOL), operated at 10 kV of acceleration voltage. The investigated samples were coated with gold by JFC-1200 fine coater (JEOL) before observation. The phase composition and crystallinity of the samples is determined by XRD.

X-Ray diffraction (XRD) spectra were recorded at room temperature on a powder diffractometer (Siemens D500 with CuKα radiation within 2θ range 10–80 deg and step 0.05 deg 2θ and counting time 2 s/step). The average crystallite size was estimated according to Scherrer's equation:

$$d_{hkl} = k\lambda / \beta \cos(2\theta) \qquad (1)$$

where d_{hkl} is the average crystallite size (nm), λ is the wavelength of CuKα radiation applied (λ = 0.154056 nm), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the peak observed at $2\theta = 25.20$ (converted to radians) and k is a constant usually chosen ~0.9.

Fourier transform infrared (FTIR) spectra were taken with Bruker Tensor 27 spectrometer, using KBr tablet technique. Spectra were taken in the interval 400–4400 cm^{-1}.

The photocatalytic action of the ZnO films was tested in photoinitiated bleaching of malachite green (MG) dye in aqueous solution. The photocatalytic reaction was conducted in a cylindrical glass reactor (volume 150 ml), equipped with a magnetic stirrer (rotating speed controlled by stroboscope) and UV-lamp (emission maximum at 370 nm; the light power density at the sample position was 0.66 mW/cm^2 as measured with Research Radiometer of Ealing Electro-optics, Inc.). The decay of MG concentration during the bleaching process was monitored by UV-vis absorbance spectroscopy after aliquot sampling at regular time intervals. Experiments were carried out with two series of ZnO films, prepared with *sol A* and *sol B*, respectively.

The decolorization and degradation efficiency, *D (%)*, was calculated as:

$$D = \left[\frac{C_0 - C}{C_0}\right] \times 100 \qquad (2)$$

where C_0 is the initial concentration of dye and C is the dye concentration after UV irradiation in selected time interval, t.

The initial concentration of MG is 10 ppm. All photocatalytic tests were performed at constant stirring rate (500 rpm) and room temperature (23±2 °C). The optical absorbance spectra were measured by spectrophotometer Jenway 6400 in the wavelength range from 400 to 800 nm.

RESULTS AND DISCUSSION

Structure characterization

The morphology of both films from *sol A* with 1-propanol and 1-butanol determined by scanning electron microscope is shown in Fig. 2a and b.

The SEM images of both films were made at the same magnification (x 1000) and the marker is 10 μm. As seen from the picture their morphology is not homogeneous. Even the appearance of the films does not look good, their surface is not uniform and there are many cracks and bubbles. Layers are very easy to peel off after their ignition. The photocatalytic tests with such films showed very low photocatalytic activity. Therefore, a third synthesis was performed – no other changes in the formulation only alcohol is 2-propanol. The as-prepared samples are more uniform and show much better adhesion of the layers and the higher density of the film. There is ganglia typical surface structure of the film. The surface morphology of the films (Fig. 2c) is represented by different ganglia-
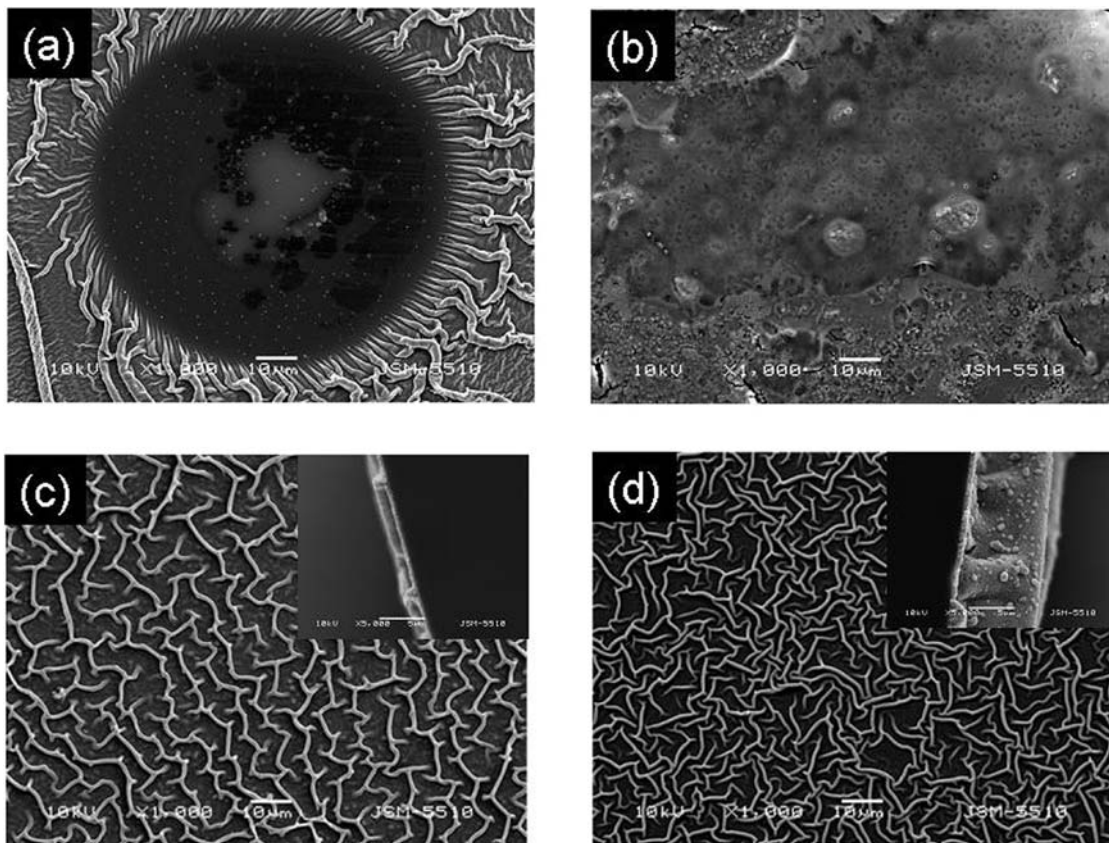
Fig. 2. SEM images of ZnO film prepared by *sol A* with (a) 1-propanol, (b) 1-butanol, (c) 2-propanol, (d) *sol B* with 2-methoxyethanol. The inset SEM images show the cross-section of the both last films

like hills with typical width of about 1 μm and a height of 1–2 μm. They are evenly distributed over the entire surface of the film. Cross-sectional SEM image inset picture allows us to determine the film thickness, which is about 0.5 μm. At the places whit intensively formed ganglia, the thickness can reach 2–2.5 μm.

Scanning electron microscope was also used to monitor and study the surface of films obtained by method B (Fig. 2d). Cross section of the films was also characterized using SEM. The SEM images show that the surface is homogeneous and much more developed. There are different ganglia with a typical width of about 1 μm and a length of 5 μm to 15 μm. The results show that the average film thickness is about 5–10 μm. Ganglia-like hills along the entire surface of the film and have a height of about 2.5–3μm. They are reproducible, regardless of the conditions under which films are obtained. They can be seen on the surface of various other movies. An example can be given to the first synthesis of films of ZnO. The surface of the samples obtained using different reagents can be observed ganglia similar entities. With the difference that in the

first case they are not as wide and thick, but smaller and not so expressed. From cross section of the two films is clearly evident that ganglia-like formations are composed of very small nano-sized particles of ZnO.

The XRD spectra of thin ZnO films are presented in Figure 3. The blades resemble many spectra of literature on thin films of zinc oxide. The spectrum of both types nanostructured films consist of well-defined diffraction peaks showing good crystallinity. The three characteristic peaks clearly proof the existence of ZnO, which correspond to different crystallographic orientations of the crystal lattice of wurtzite (from left to right) (100) – at ($2\theta = 31.76°$); (002) – at ($2\theta = 34.39°$) and (101) – at $2\theta = 36.24°$. Almost the same peak height shows that the nanocrystallites are with different orientations of the axes. Crystalline structure of both films is hexagonal wurtzite. The size of crystallites, calculated by Scherer (Equation 1) is 30 nm. We assume that annealing for 1h at 500 °C leads to decomposition of Zn (II) hydroxide and its transformation into ZnO with hexagonal structure, which can be seen from diffraction spectra.
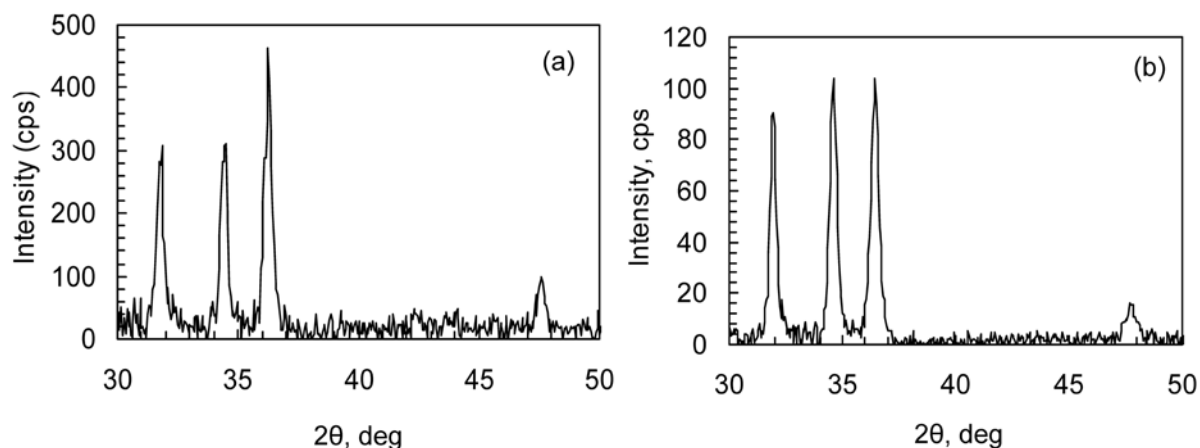
Fig. 3. XRD spectra of nanostructured films annealed for 1 hour at 500 °C (*sol A* with 2-propanol) (a) and *sol B* (b). The crystallite sizes are about 30 nm in both cases

Figure 3 are compared to the first peaks of spectrums of ZnO, obtained by both methods. The paintings are completely identical and correspond to the zinc oxide. Attempt was made to find, even small differences in half-width of the major peaks and their positions. For this purpose, the peaks were approximated with a Gaussian function. Within experimental error has been found only difference either in width or in the angular positions of the more intensive (three) peaks. An interesting phenomenon is the observed change in the relative intensity of three diffraction peaks, which increase with the movies, the first synthesis compared with those of the second method. The latter can be attributed to the different precursors, used in methods A and B (2-propanol and 2-metoxyethanol), favoring different orientation of the as grown crystallites.

FTIR spectra of gel films are shown in Figure 4. FTIR spectrum shows several interesting areas in both cases. The first is in the range 3000–3750 cm^{-1} with a maximum of 3436 cm^{-1} due to the absorption of O-H groups. The second area of absorption (in the range 1250–1750 cm^{-1}) corresponds to COO^{-} (1620 cm^{-1}) group. The third absorption region with a peak between 1000–1300 cm^{-1} due to CO stretching vibration absorption (1021 cm^{-1}). The maximum absorption peak in the range 440–450 cm^{-1} is attributed to ZnO. Some other groups absorption can also be found in the well ignited movies, for example, can give the group between 2988 and 1381 cm^{-1} CH, which indicates the presence of some organic products. The lack of such groups in the range 500–3000 cm^{-1} shows that there are only traces of other organic substances. Both films contain only ZnO.
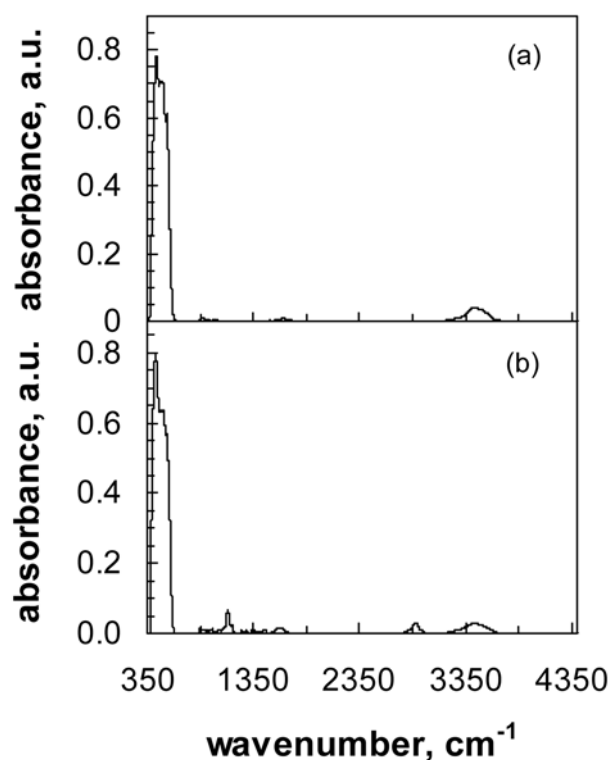
Characterization of the photocatalytic activity

The purification of wastewater from dyes in the textile industry is becoming a serious environmental problem because of their unacceptable color need high oxygen content, and their resistance to different methods of destruction – chemical, photochemical and biological. We have chosen photocatalytic degradation of malachite green (as a representative
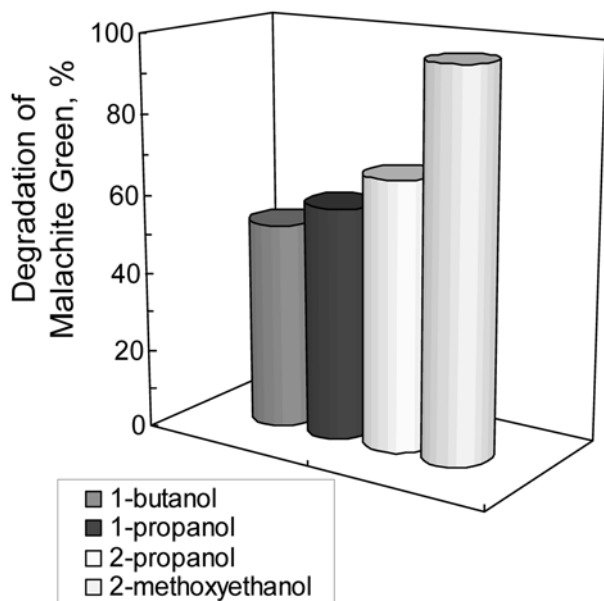

Fig. 4. FTIR spectrum of ZnO films obtained by *sol A* with 2-propanol (a) and *sol B* (b)

Fig. 5. Photocatalytic degradation of MG solution at 3 hour by ZnO films under UV-light illumination. The initial concentration of MG is 10 ppm

of such dyes) in the presence of a catalyst under UV-light illumination. This will be assessed the influence of photocatalysts. The initial dye concentration in these experiments is constant – 10 ppm.

Four types of experiments were made with four different types of films, obtained using different alcohols (*sol A* and *sol B*) for preparation of the precursor sol: 1-propanol, 2-propanol, 1-butanol and 2-methoxyethanol. The aim is to investigate kinetics of decolorization of the dye and to determine which of the four types of samples manifests higher photocatalytic effeciency and rates of dye photodegradation. Nanostructured films made with 2-methoxyethanol rapidly degrade dye (96.77%) and have the best photocatalytic efficiency compared to films with 2-propanol (67.88%). All the rates of dye degradation are calculated using (Equation 2) and the results are presented in Figure 5. Very clearly and distinctly visible trend of rapid degradation of the dye films with 2-methoxyethanol is seen from the date in Fig. 5. Thin films with 1-butanol degraded dye most slowly about 54% for period of three hours. Films with 2-methoxyethanol are better catalysts than those prepared with 2-propanol, are consistent with the observed surface morphology (SEM images). They have formation of ganglia-like hills on the films surface. The difference in morphology is that the ganglia formed in films obtained by the second method are larger in width, height and length as well as cash. This has a decisive influence on their photocatalytic properties.

The results show that the films that have significantly developed surface area are better photocatalysts. Thin ZnO films are promising and efficient catalysts for the decomposition of organic pollutants by photocatalytic oxidation.

CONCLUSION

Thin films of nanostructured ZnO are successfully prepared by two sol-gel methods from zinc acetate and different solvents. The sol is deposited on glass substrates by dip coating method and the obtained films are dried and annealed to form nanostructured zinc oxide. The film structure is characterized be means of XRD, FTIR spectroscopy and SEM. It is shown that the thin films are porous and formed of zinc oxide nanoparticles with an average diameter of 30 nm. The morphology of films obtained with 1-propanol and 1-butanol, as shown is not homogeneous. The film surface is not uniform and there are many cracks and bubbles. The prepared with 2-propanol and 2-methoxyethanol samples have typical ganglia structure, which is established by SEM. The resulting samples from *sol B* are more uniform show much better adhesion of the layers and higher density, compared to films from the first sol-gel method. All films pertain to the hexagonal wurtzite structure without preferred orientation irrespective to the manner of film preparation.

Further the obtained ZnO films are characterized by photo-initiated bleaching of malachite green in aqueous solutions. The photocatalytic activities of the films obtained by *sol A* are lower than those of the films obtained by *sol B*. The results obtained show that the films morphology has significant influence on the photocatalytic properties. The ZnO thin films prepared by us are promising and efficient catalyst for photocatalytic degradation of malachite green.

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ПОЛУЧАВАНЕ НА ТЪНКИ ФИЛМИ ОТ ZnO ВЪРХУ СТЪКЛО ПО ДВА РАЗЛИЧНИ ЗОЛ–ГЕЛ МЕТОДА

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(Резюме)

В настоящето изследване представяме фотокаталитичното приложение на тънки филми от ZnO за пречистване на вода от органични замърсители. Филмите са получени от стабилен колоиден прекурсорен зол, приготвен по два различни зол-гел метода (*A* и *B*) от цинков ацетат и при вариране на разтворителите. Покритията са отложени на стъкло по метода на потапяне на подложката. Филмите са характеризирани чрез различни методи на анализ (XRD, SEM, FTIR). XRD показват, че цинковият оксид е с хексагонална кристална структура.

Сравнени са морфологията, състава и структурата на получените по двата метода филми. Морфологията на филмите, получени с 1-пропанол и 1-бутанол е нехомогенна. По повърхността се наблюдават множество балончета и пукнатини. Затова е направен трети синтез по метод *A*, като е използван 2-пропанол. Ганглийната структура на повърхността на така получените филми е установена със SEM. Подобна ганглийна структура е наблюдавана и при филмите, получени по метод *B*. was investigated by SEM. Получените образци са хомогенни, с по-добра адхезия и по-висока плътност, в сравнение с филмите, получени по метод *A*. Разликата в морфологията на филмите оказва влияние върху фотокаталитичната им ефективност.