Manufacturing of patterned ZnO films with application for photoinitiated decolorization of malachite green in aqueous solutions

NINA V KANEVA, GEORGI G YORDANOV and CECO D DUSHKIN*

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

MS received 30 December 2008; revised 11 July 2009

Abstract. Patterned thin films, ZnO, are successfully prepared on glass substrates by the sol–gel method using dip-coating technique. The films, formed of ZnO nanocrystallites with hexagonal crystal structure, are characterized by means of scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. The as obtained ZnO films are studied with respect to photo-initiated bleaching of malachite green in aqueous solutions. The bleaching process is investigated at various initial concentrations of malachite green in the aqueous solutions by using ZnO films of different thicknesses. The obtained results are promising for the development of ZnO photocatalysts by the sol–gel method.

Keywords. ZnO; zinc oxide; sol–gel; thin films; nanostructures; catalytic properties; photocatalysis; malachite green.

1. Introduction

From an ecological viewpoint, the elimination of toxic chemicals from wastewater is currently one of the most important subjects in pollution control. Universal attention has been given to the application of photocatalysis in environmental water treatment and energy development fields. In the recent years, the most environmentally friendly pollution-treatment method is the elimination of low-concentration organic pollutants in water by oxidation through molecular oxygen and sunlight (Asahi *et al* 2001; Malato *et al* 2002; Bouras *et al* 2004; Comparelli *et al* 2005a, b; Evgenidou *et al* 2007; Kositzi *et al* 2007; Mascolo *et al* 2007; Strataki *et al* 2007; Vlachos *et al* 2008; Kitsiou *et al* 2009; Pelentridou *et al* 2009). For this purpose, photocatalysts with a high activity should be developed in order to utilize more effectively the photocatalytic reactions for elimination of the organic waste.

The photocatalysis with ZnO represents a perspective field, because ZnO can be more efficient than TiO₂ in the photocatalytic degradation of some dyes in aqueous solution (Gouvea *et al* 2000; Dindar and Icli 2001). As a well-known photocatalyst, ZnO gained much attention in the degradation and complete mineralization of environmental pollutants (Yeber *et al* 2000). ZnO thin films have been found to decompose aqueous solutions of reactive dyes (Gouvea *et al* 2000; Lizama *et al* 2002), phenol (Dindar and Icli 2001), chlorophenol (Lathasree *et al*

2004), methyl-orange (Wang *et al* 2004), methyl-blue (Jang *et al* 2006) and other organic environmental pollutants (Khalil *et al* 1998; Akyol *et al* 2004; Daneshvar *et al* 2004; Sirtori *et al* 2006). However, ZnO has not been used until now for the degradation of malachite green dyes as the one utilized by us here. Furthermore, ZnO is of special interest, because of the possibilities for modification and control of various ZnO-based nanostructures (Andres-Verges *et al* 1989; Haile *et al* 1989; Andres-Verges and Martinez-Gallego 1992). The use of conventional powder catalyst has disadvantages in stirring during the reaction and in separation of powder after the reaction. The preparation of film catalyst makes it possible to overcome these disadvantages and extend the industrial applications (Iketani *et al* 2004). The sol–gel process and the utilization of dip-coating technique are two of the versatile strategies to prepare thin films of particles. ZnO thin films are prepared by different techniques such as metal organic chemical vapour deposition (Yang *et al* 2004), sol–gel (Pal and Sharon 2002; Peng *et al* 2005), thermal evaporation, oxidation and anodization (Yamaguchi *et al* 1998; Alivov *et al* 2005; Fouad *et al* 2006). Recent research demonstrates the possibilities for the utilization of ZnO thin films prepared by the sol–gel method (Peng *et al* 2006; Delgado *et al* 2008).

In this paper we demonstrate the successful preparation of thin films of ZnO on glass substrates by the sol–gel method using dip-coating technique. We used Zn(CH₃COO)₂·2H₂O, 2-methoxyethanol and monoethanolamine (MEA) to prepare the sol precursor. The films are prepared on glass substrates by dip coating (by one

*Author for correspondence (nhtd@wmail.chem.uni-sofia.bg)

and five coatings) and annealed at 500°C for 1 h. Further, we characterized the as obtained ZnO films with respect to the photo-initiated bleaching of malachite green (MG) oxalate in aqueous solutions. The obtained results are promising for the development of ZnO photocatalysts by the sol-gel method.

2. Experimental

2.1 Preparation of ZnO films

The materials used to manufacture the ZnO thin films are described as follows: Zinc acetate dihydrate (>99.5%), 2-methoxyethanol (>99.5%) and monoethanolamine (>99%) were from Fluka. Malachite green (MG) oxalate was from Croma-Gesellschaft mbH & Co. Glass slides (~76 × 26 mm) used for substrates of ZnO films were from ISO-LAB (Germany).

For the deposition of ZnO films, we had to prepare first the precursor solution. Zinc acetate dihydrate (10 g), 2-methoxyethanol (20 ml) and monoethanolamine (3.2 ml) were mixed together in a round-bottomed flask and stirred at room temperature for 15 min. The obtained clear solution was heated up at 60°C upon magnetic stirring for 60 min and let overnight. The resultant solution was clear and homogenous, and served as the coating substance for film preparation. No visible changes were observed upon standing of the precursor at room temperature for at least 2 months.

The coating process for ZnO films consisted of dip coating, drying and sintering of the material. Dipping a glass substrate in the precursor solution and withdrawing it at rates of 0.9 cm/min at room temperature prepared the gel films. It was found that higher withdrawal rates resulted in films of lower quality. Films with various numbers of coatings (1–5) were deposited. The films were dried at 80°C for 30 min after each successive coating. The final gel films were preheated at 350°C for 15 min and then sintered at 500°C for 60 min in order to obtain the ZnO films for photocatalytic tests. The mass of ZnO deposited on films prepared with a single and 5 coatings were 2.9 mg (± 11%) and 5.2 mg (± 8%), respectively. The film area was about 14.5 cm² on each side of the glass plate.

2.2 Characterization of ZnO films

The obtained ZnO thin films and powders were first imaged by a 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 X-ray diffraction (XRD) spectra were recorded at room temperature on a powder diffractometer (Siemens D500 with CuK α radiation within 2 θ range 10–80 deg at a step of 0.05 deg 2 θ and counting time 2 s/step).

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 activities of the ZnO films were assessed by the photoinitiated bleaching of malachite green (MG) dye in aqueous solution. The photocatalytic reaction was conducted in a cylindrical glass vessel of volume 150 ml, equipped with a magnetic stirrer (rotating speed controlled by stroboscope) and UV-lamp (maximum emission at 370 nm; the light power density at the sample position was 0.66 mW/cm² 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. Control experiments without UV light (the reaction system kept in dark) were also performed. Experiments were carried out with two series of ZnO films, prepared with 1 and 5 coatings, respectively. The effect of initial concentration of MG (for 3, 5 and 10 ppm) was also evaluated. All photocatalytic tests were performed at constant stirring rate (500 rpm) at room temperature (25°C).

The optical absorbance spectra were measured by spectrophotometer Jenway 6400 in the wavelength range from 400–800 nm.

3. Results and discussion

3.1 Structure characterization

The thickness of the as obtained ZnO films and the mass of deposited material is found to depend reproducibly on the number of coatings (figure 1). As seen, the mass/area (mg/cm²) of the gel precursor deposited on glass sub-

Figure 1. Dependence of the film mass per area (mg/cm²) before sintering on the number of coatings. The films are dried for 30 min at 80°C before each coating. The bars represent the standard error estimated for 3 experiments at least. The solid line is a linear fit by (1).

strates, m , depends linearly on the number of coatings, x , according to the equation

$$m(x) = m_0 + \Delta m x. \quad (1)$$

Here $m_0 = 0.43 \text{ mg/cm}^2$ is the intercept with the ordinate axis (formally corresponding to $x = 0$) and $\Delta m = 0.093 \text{ mg/cm}^2$ is the slope of line (the mass per unit area added by each subsequent coating to the previous one). Since $m_0 \neq 0$, (1) reflects the fact that the ZnO material is added to the preexisting layers of numbers $x \geq 2$ in smaller portions than to the bare glass for the first layer of $x = 1$. This might be due to dissolution of a part of the previous coating while depositing the new one. From the mass balance of coated material one gets

$$m = m_1 + \Delta m(x - 1), \quad (2)$$

where m_1 is the mass of the first coated layer. Comparing (1) and (2), we obtain $m_1 = m_0 + \Delta m$, which gives that indeed $m_1 = 0.52 \text{ mg/cm}^2$.

The mass of deposited material is reduced with about 56–58% after annealing at 500°C for 1 h.

Figure 2. SEM images of ZnO film annealed for 1 h at 500°C . Images of (a) surface topology and (b) cross-sections are given.

The scanning electron microscopy (SEM) images of ZnO films are shown in figure 2. The cross-section of the films is also characterized by means of SEM. The results show that the average thickness of the films is about $2 \mu\text{m}$ and $5 \mu\text{m}$ as obtained by one and five coatings, respectively. Different ganglia-like hills are seen of typical width, $1 \mu\text{m}$ and length from 5 – $15 \mu\text{m}$. The ganglia are located on the surface of film being of typical height about 2.5 – $3 \mu\text{m}$. They are reproducible irrespective of the conditions of film deposition and we can see them in different films. In cross-section, a ganglion comprises nanograins of ZnO similar to those in the continuous film in-between.

The phase structure of glass-supported ZnO thin films is observed by XRD (figure 3). The XRD pattern confirms the formation of hexagonal ZnO ($2\theta = 31.9, 34.6, 36.4, 47.6, 56.7, 63.1$ and 68.1°) with average size of the crystallites of about 30 nm . An interesting phenomenon is the change in relative intensity of the diffraction peak at 34.6° , which increases for the films, prepared with 5 coatings in comparison with the ones prepared with one coating.

The FTIR spectra of the dried gel films are shown in figure 4. The FTIR spectrum shows few interesting regions. The first in the range 3000 – 3750 cm^{-1} with a maximum at 3436 cm^{-1} , arises from the absorption of O–H groups. The second region in the range 1250 – 1750 cm^{-1} , originates from the absorption of COO^- (1620 cm^{-1}). The third region with bands at 1000 – 1300 cm^{-1} , is assigned to the absorption of C–O stretching vibrations (1021 cm^{-1}).

Figure 3. XRD spectra of ZnO films annealed for 1 h at 500°C after: (a) one coating and (b) five coatings. The crystallite sizes are about 30 nm in both cases.

The absorption band at $440\text{--}450\text{ cm}^{-1}$ is attributed to ZnO. Some other absorption bands are also found in the dried gel, for example, the bands at 2988 and 1381 cm^{-1} for C–H, which indicates the presence of some organic by-products.

3.2 Characterization of photocatalytic activity

Three sets of experiments are performed in order to confirm the photocatalytic activity of ZnO films and to com-

Figure 4. FTIR spectrum of ZnO film annealed for 1 h at 500°C .

pare the MG degradation rates with and without UV light illumination. (i) The first type consists of experiments on the exposure of MG to ZnO films in the presence of UV illumination (the photocatalysis condition). At that, three different initial MG concentrations are tested (close to 3, 5, and 10 ppm) for each film, while the catalyst films are of one and five coatings. (ii) The second type of experiments are performed at the same conditions as in (i), but without UV illumination. (iii) The third type of experiments expose MG aqueous solutions to UV light without ZnO (the photolysis condition). We record the time-dependent absorbance of the water solutions of MG in all types of experiments. To convert it in dye concentration, we obtain the respective calibration straight line shown in Appendix A.

Now let us consider the decolorization of MG by ZnO films under UV illumination. The results from the experiments under the photocatalysis conditions are presented in figures 5–7. Figure 5 demonstrates the bleaching kinetics of MG aqueous solutions by ZnO films (prepared by one coating) with and without UV light illumination. No bleaching of the MG solution is observed in the absence of ZnO films. The process is studied at three different initial concentrations of MG, as shown in figure 5. On the other hand, figure 6 demonstrates the results from similar

Figure 5. Decrease of MG concentration in aqueous solutions by ZnO films (a) with and (b) without UV light illumination at various initial MG concentrations (given in the legend). The films were prepared by one coating and annealed at 500°C for 1 h.

Figure 6. Decrease of MG concentration in aqueous solutions by ZnO films (a) with and (b) without UV light illumination at various initial MG concentrations (given in the legend). The films were prepared by five coatings and annealed at 500°C for 1 h.

experiments carried out with ZnO films prepared by five coatings. The decolorization of MG by ZnO films under UV illumination follows kinetics with reaction orders $n = 0.75$ and 0.69 for films obtained by one and five coatings, respectively. The rate constant is higher for the

Figure 7. The plot of $\ln(v_0)$ against $\ln(C_0)$ for MG bleaching with ZnO films, prepared by (a) one coating, and (b) five coatings. Experiments were carried out with and without UV-illumination. The respective kinetic parameters from the linear plots are given in table 1.

Table 1. Kinetic parameters of MG bleaching rate at various experimental conditions. Different films were prepared by one and five coatings and tested upon UV-light illumination (UV on) and without UV-light (UV off). The rate constant, k and the reaction order, n , were calculated by the method of initial rates (see Appendix B for details).

Kinetic parameters	Reaction conditions			
	One coating		Five coatings	
	UV on	UV off	UV on	UV off
$-\ln(k)$	5.23	5.27	4.11	4.49
n	0.75	0.73	0.69	0.62

films obtained by five coatings (table 1), which is probably due to the larger amount of ZnO catalyst in this case.

Finally, we compare the above results with the decolorization of MG by ZnO films without UV illumination. The experiments without UV light are compared with the respective photocatalytic experiments in figures 5 and 6. The concentration of MG decreases without UV illumination, but slower in comparison with the respective photocatalytic reactions. The rate of MG decolorization by ZnO films without UV light is slowing down with the time of experiment, reaching almost a constant value after about 6 h. The decrease of MG concentration in this case is most probably due to the adsorption of MG on the ZnO films. The sol-gel process usually leads to the formation of highly porous materials, which may be the reason for the intense decolorization.

The results from determination of the rate law by the method of initial rates, considered in Appendix B, are shown in figure 7. For one-layer coating of ZnO the two processes (with and without UV-lighting) are almost indistinguishable (figure 7a). In spite of the small film mass, this implies on an intrinsic property of ZnO films to remove dyes from water even without UV-light (for example, by adsorption). However, for five-layer films of ZnO the two processes could be clearly distinguished (figure 7b). Under UV-light the dye-removal is much better pronounced than in the case without UV, which means that a MG destruction process takes place on the ZnO films even without UV illumination. This assumption needs further proofs and will be a subject of future studies.

4. Conclusions

We have synthesized dense and crackfree ZnO thin films by the sol-gel process from zinc acetate, 2-methoxy-ethanol and monoethanolamine. 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 by 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. Further the obtained ZnO films are characterized by photo-initiated bleaching of malachite green in aqueous solutions. The kinetic parameters are determined by the method of initial rates. The reaction rate is faster when using thicker ZnO films prepared by five coatings compared to one-coating films. The ZnO thin films prepared by us are found promising and efficient catalyst to degrade organic pollutants by means of photocatalytic decomposition.

Acknowledgements

The financial support by the Bulgarian Ministry of Education and Science (Project TK-X-1702/07) is greatly

acknowledged. One of the authors (CD) is indebted also to the COST D43 Project of the European Community.

Appendix A. Calibration of absorbance versus dye concentration

The malachite green dye exhibits two maxima of absorbance at 405 nm and 620 nm. For the purpose of measurements we utilized the second maximum since it is much better pronounced thus allowing a better sensitivity of detection. Figure 8 plots the absorbance maximum, A , at 615 nm versus the dye concentration in solution C (in ppm). The calibration plot (correlation coefficient, 0.998) shows the linear dependence of the optical absorbance on the dye concentration expressed as

$$A = 0.14C. \quad (\text{A1})$$

This equation confirms the validity of the Bouguer–Lambert–Beer law for our system in the form

$$A = \varepsilon LC, \quad (\text{A2})$$

where $L = 1$ cm is the width of glass cuvette and ε the molar absorption coefficient. By comparing (A1) and (A2), one gets $\varepsilon = 0.14 \text{ cm}^{-1} \cdot \text{ppm}^{-1}$. This fact is used further to obtain the actual dye concentration in the solution.

Appendix B. Determination of reaction rate law

The rate law of photocatalytic reaction is determined by the method of initial rates. In this method the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with MG is

$$\nu = k[\text{MG}]^n, \quad (\text{B1})$$

Figure 8. The calibration line of the absorbance maxima at wavelength, 615 nm, versus the dye concentration.

with n being the reaction order. Then its initial rate, ν_0 , is given by the initial values of the molar concentration of MG, $[\text{MG}]_0$, and we can write

$$\nu_0 = k[\text{MG}]_0^n. \quad (\text{B2})$$

Taking logarithms from both sides of (B2) gives

$$\ln(\nu_0) = \ln(k) + n\ln([\text{MG}]_0). \quad (\text{B3})$$

For a series of initial concentrations, a plot of the logarithms of the initial rates against the logarithms of the initial concentrations of MG should be a straight line with slope, n . We determine the initial rates by fitting the data in figures 5 and 6 with polynomials of the type

$$[\text{MG}] = at^2 + bt + [\text{MG}]_0. \quad (\text{B4})$$

Here t is the time, a and b are parameters obtained from the fit. By differentiation of (B4), we find that

$$\nu = -\frac{d[\text{MG}]}{dt} = -2at - b.$$

At $t = 0$, $\nu = \nu_0$ and we obtain that actually $b = \nu_0$.

References

- Akyol H, Yatmaz C and Bayramoglu M 2004 *Appl. Catal. B Environ.* **54** 19
- Alivov Ya I, Chernykh A V, Chukichev M V and Korotkov R Y 2005 *Thin Solid Films* **473** 241
- Andres-Verges M, Mifsud A and Serna C 1989 *Mater. Letts.* **8** 115
- Andres-Verges M and Martinez-Gallego M 1992 *J. Mater. Sci.* **27** 375
- Asahi R, Morikawa T and Ohwaki T 2001 *Science* **293** 269
- Bouras P, Stathatos E, Lianos P and Tsakiroglou C 2004 *Appl. Catal. B: Environ.* **51** 275
- Comparelli R, Fanizza E, Curri M L, Cozzoli P D, Mascolo G, Passino R and Agostiano A 2005a *Appl. Catal. B: Environ.* **55** 81
- Comparelli R, Fanizza E, Curri M L, Cozzoli P D, Mascolo G and Agostiano A 2005b *Appl. Catal. B: Environ.* **60** 1
- Daneshvar N, Salari D and Khataee A 2004 *Appl. Catal. B Environ.* **162** 317
- Delgado G, Romero C I, Hernandez S A, Perez R and Angel O 2008 *Solar Energy Materials & Solar Cells* **93** 55
- Dindar B and Icli S 2001 *J. Photochem. Photobiol. A: Chem.* **140** 263
- Evgenidou E, Konstantinou I, Fytianos K, Poullos I and Albanis T 2007 *Catalysis Today* **124** 156
- Fouad O A, Ismail A A, Zaki Z I and Mohamed R M 2006 *Appl. Catal. B: Environ.* **62** 144
- Gouvea C A K, Wypych F, Moraes S G, Duran N, Nagata N and Peralta-Zamora P 2000 *Chemosphere* **40** 433
- Haile S, Johnson D, Wisemen G and Bowen H 1989 *J. Am. Ceram. Soc.* **72** 2004
- Iketani K, Sun R D, Toki M, Hirota K and Yamaguchi O 2004 *Mater. Sci. Eng.* **B108** 187
- Jang Y, Simer C and Ohm T 2006 *Mater. Res. Bull.* **41** 67
- Khalil L B, Mourad W E and Rophael M W 1998 *Appl. Catal. B: Environ.* **17** 267

- Kitsiou V, Filippidis N, Mantzavinos D and Poullos I 2009 *Appl. Catal. B: Environ.* **86** 27
- Kositzi M, Poullos I, Samara K, Tsatsaroni E and Darakas E 2007 *J. Hazard. Mater.* **146** 680
- Lathasree S, Rao A N, Siva-Sankar B, Sadasivam B and Rengaraj K 2004 *J. Mol. Catal. A: Chem.* **223** 101
- Lizama C, Ferrer J, Baeza J and Mansilla H D 2002 *Catal. Today* **76** 235
- Malato S, Blanco J, Vidal A and Richter C 2002 *Appl. Catal. B: Environ.* **37** 1
- Mascolo G, Comparelli R, Curri M L, Lovecchio G, Lopez A and Agostiano A 2007 *J. Hazard. Mater.* **142** 130
- Pal B and Sharon M 2002 *Mater. Chem. Phys.* **76** 82
- Pelentridou K, Stathatos E, Karasali H and Lianos P 2009 *J. Hazard. Mater.* **163** 756
- Peng F, Chen S H, Zhang L, Huang H J and Xie Z Y 2005 *Acta Phys. Chem. Sin.* **21** 944
- Peng F, Wang H, Yu H and Chen S 2006 *Mater. Res. Bull.* **41** 2123
- Sirtori C, Altwater P K, de Freitas A M and Peralta-Zamora P G 2006 *J. Hazardous Mater.* **129** 110
- Strataki N, Bekiari V, Stathatos E and Lianos P 2007 *J. Photochem. Photobiol. A: Chem.* **191** 13
- Vlachos P, Stathatos E, Lyberatos G and Lianos P 2008 *Catal. Commun.* **9** 1987
- Wang C, Wang X, Xu Bo-Qing, Zhao J, Mai B, Peng Ping'an, Sheng G and Fu J 2004 *J. Photochem. Photobiol. A Chem.* **168** 47
- Yamaguchi Y, Yamazaki M, Yoshihara S and Shirakashi T 1998 *J. Electroanal. Chem.* **442** 1
- Yang J L, An S J, Park W I, Yi G Y and Choi W 2004 *Adv. Mater.* **16** 1661
- Yeber M C, Rodriguez J, Freer J, Duran N and Mansilla H D 2000 *Chemosphere* **41** 1193