Research Article

Preparation of Glass Plate-Supported Nanostructure ZnO Thin Film Deposited by Sol-Gel Spin-Coating Technique and Its Photocatalytic Degradation to Monoazo Textile Dye

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Glass plate-supported nanostructure ZnO thin films were deposited by sol-gel spin coating. Films were preheated at 275°C for 10 minutes and annealed at 350, 450, and 550°C for 80 minutes. The ZnO thin films were transparent ca 80–90% in visible range and revealed that absorption edges at about 370 nm. The *c*-axis orientation improves and the grain size increases which was indicated by an increase in intensity of the (002) peak at 34.4° in XRD corresponding to the hexagonal ZnO crystal. The photocatalytic degradation of X6G an anionic monoazo dye, in aqueous solutions, was investigated and the effects of some operational parameters such as the number of layer and reusability of ZnO nanostructure thin film were examined. The results showed that the five-layer coated glass surfaces have a very high photocatalytic performance.

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1. INTRODUCTION

Textile industry wastewater is heavily charged with unconsumed dyes, surfactants, and sometimes traces of metals. These effluents cause a lot of damage to the environment. Many methods, including biosorption [1], conventional activated sludge treatment process [2], electrochemical technologies [3, 4], and reverse osmosis, [5] have been applied on wastewater treatment. However, new environmental laws may consider the spent adsorbents or sludge as hazardous wastes that require further treatment. Consequently, intensive researches on novel technologies with more efficiency and less energy consumption have been stimulated. Photocatalysis using a semiconductor as a photocatalyst is an alternative to conventional methods [6–11]. As a well-known photocatalyst, ZnO has been paid much attention in the degradation and complete mineralization of environmental pollutants. Since ZnO has approximately the same band gap energy (3.2 eV) as TiO₂, its photocatalytic capacity is anticipated to be similar to that of TiO₂. However, the greatest advantage of ZnO is that it absorbs large fraction of the solar spectrum and more light quanta than TiO₂ [12]. Some

researches have highlighted the performance of ZnO on degrading some organic compounds [13]. On the other hand, the use of conventional powder catalyst results in disadvantages in stirring during the reaction and in the separation of powder after the reaction. Preparation of film catalysts will make it possible to overcome these disadvantages and to extend the industrial applications [14]. The sol-gel process, as a simple and easy dip-coating means, is one of the versatile methods to prepare thin film-supported nanosized particles without complicated instruments such as CVD. Thin film photocatalysts, with their high photocatalytic ability, high stability, and convenient reuse, have received more and more attention. However, there has been little success in finding thin film photocatalyst that can operate effectively with visible light as yet. In this context, we have paid much attention in preparing thin films of ZnO on glass plates by a sol-gel process and studying its photocatalytic ability for the degradation of X6G an anionic monoazo textile dye. In this paper, a commercial glass-plate was successfully used as substrate to prepare highest *c*-axis oriented ZnO nanostructure thin film by sol-gel dip-coating process. The ZnO/glass films have been employed in photocatalytic degradation of textile dye.

FIGURE 1: Chemical structure of commercial diazo dye of light yellow (X6G).

FIGURE 2: Schematic diagram of photoreactor for degradation.

The result shows that the ZnO/glass film is a photocatalyst with higher activity. It is very interesting and significant to research promising photocatalysts.

2. EXPERIMENTAL

2.1. Preparation of sol

All the chemicals were analytic grade reagents without further purification, and purchased from Merck Company. Light YellowX6G dye (C. I. Reactive Yellow 2, Rmm872.5) was obtained from Youhao (China) and has chemical structure shown in Figure 1. Nanocrystalline ZnO films were prepared on microscope glass slide (75 mm $\times$ 25 mm $\times$ 1 mm) substrate (washed with ethanol and dilute acid) by a sol-gel method. Sol solution was prepared by adding 3.10 g Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$: ZnAc $\cdot$ 2H $_2$ O), 0.86 g monoethanolamine (MEA), and adequate deionized water to 15 mL isopropanol alcohol, then heated to 60°C with continuous stirring for 60 minutes. The coating substrate (microscope glass slid) was preheated at 275°C for 10 minutes in air after each coating. The sol-gel coating was made usually a day after the sol solution was prepared and the molar ratio of MEA to Zinc acetate was maintained at 1 : 1.

2.2. Film deposition

The films of ZnO were prepared by spin coating method onto substrate with 3000 rpm for 45 seconds (the spinner reached 3000 rpm after 5 s which was maintained for 40 s). Films were annealed at furnace at 550°C for 80 minutes. Precursor solution did not produce any precipitation after 30 days. This spinning-drying procedure was repeated from 2 to 10 times. The microscope glass slide (75 mm $\times$ 25 mm $\times$ 1 mm: cleaned in dilute HCl solution and ethanol) was used as sub-

strate. Film deposition was carried out in air at room temperature by a rate 3000 rpm for 30 s. After each coating, the films were preheated at 275°C for 10 minutes, and postheated at 550°C for 80 minutes. The deposition was repeated for 2, 4, 5, 6, 8, and 10 times to obtain a film with different thickness.

2.3. Characterization of thin films

The structure and crystalline size were determined by XRD diffraction (Bruker D8 advanced X-ray diffractometer: Cu K $_{\alpha}$ radiation, Scan rate 0.03 2 θ s $^{-1}$). X-ray diffraction shows zincite structure with *c*-axis orientation (002). Optical transmittance was measured by spectrophotometer (Varian Cary 500 Scan).

2.4. Photocatalytic degradation

The photocatalytic degradation experiments were carried out in a simple (40 cm $\times$ 15 cm $\times$ 15 cm) oxidation reactor (see Figure 2), placed in a 25°C water bath. Slide with 5 layers that placed in 25 mL 10 ppm X6G solution was irradiated with two 8 W lamps (Philips; λ = 365 nm) placed 5 cm above the solutions. Concentration is measured by spectrophotometer (Varian Cary 500 Scan). In all experiments, 25 mL of 10 ppm X6G solution was used with stirring during the irradiation.

3. RESULTS AND DISCUSSION

3.1. Stability of sol

Sol was prepared by altering the ratio of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$: MEA. In this work, the best sol was obtained with a $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$: MEA molar ratio 1 : 1 in isopropanol. Increasing the

FIGURE 3: XRD pattern of the ZnO thin films on microscope glass slide by five spin-coatings (5 layers), preheated at 275°C for 10 minutes and postheated for 80 minutes at different temperature.

water content and decreasing the time of reflux may change the sol to gel immediately. MEA was added to keep the sol solutions stable and clear for a long period (more than 30 days). There are many factors affecting the crystallization behavior of the films such as substrate, the time and temperature of reflux, molar ratio of starting material, and composition of stabilizers such as MEA. In this work, sol was prepared at 60°C for 60 minutes until a clear homogeneous solution appeared. The XRD pattern of the ZnO thin films on microscope glass slide by five spin-coating (5-layer) preheated at 275°C for 10 minutes and postheated for 80 minutes at different temperature, 350°C, 450°C, and 550°C, was shown in Figure 3. There are three distinct differences between the XRD of thin films and ZnO powder. Firstly, diffraction peaks of thin films have lower intensity and higher FWHM (Fully Width at Half Maximum) compared to powder; secondly, the films are predominantly (002) oriented, and finally films are crystallized (wurtzite) at comparatively higher temperature as compared to powder that has been prepared from chemical producers. Increase of annealing temperature affected the intensity of (002) peak which was the highest at 550°C. The ZnO films grow with a (002) orientation is kinetically preferred, which in turn likely reflects the fact that the highest density of Zn atoms is found along the (002) plane [15].

Figure 4 shows the XRD pattern of the ZnO thin film on microscope glass for various layers by spin-coating (2, 4, 6, 8, and 10 layers), preheated at 275°C for 10 minutes and postheated for 80 minutes at 550°C.

Figures 5(a)–5(c) show the scanning electron microscopy (SEM) image of the nanostructure ZnO thin films at various temperatures, and Figure 5(d) shows atomic force microscopy (AFM) image of ZnO thin film at 450°C that prepared by spin coating method on a glass substrate. The average grain size of nanostructure ZnO thin films was near 40 nm, and the crystal size increased with increasing the annealing temperature. As shown in Figures 5(a)–5(d), thin films of ZnO prepared by spin coating reveal the formation of a porous granular surface.

FIGURE 4: XRD pattern of the ZnO thin films on microscope glass with different layers (2, 4, 6, 8, and 10 layers), preheated at 275°C for 10 minutes and postheated for 80 minutes at 550°C.

TABLE 1: The grain size (crystalline size) of ZnO thin films with various times of coating, postheated at 550°C.

Samples of thin film	2θ	$\text{FWHM} = \beta$	D (nm)
2-layer	34.484	0.350	23.9
4-layer	34.471	0.342	24.7
6-layer	34.743	0.358	23.5
8-layer	34.443	0.335	25.1
10-layer	34.462	0.332	25.1

Optical transmittance of ZnO thin films with 5 times spin coating, preheated at 275°C for 10 minutes and postheated at various temperatures, 350°C, 450°C, and 550°C, is shown in Figure 6. The absorption at about 370 nm corresponds to an electronic transition beyond the bandgap, 3.2 eV of the wurtzite crystalline phase of ZnO.

The crystalline size of ZnO in the films was calculated by Scherrer's formula $D = 0.9\lambda/\beta\cos\theta$, where D is the grain size, λ (1.548 Å) is the wavelength of X-ray radiation used, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle of the XRD peak. The average crystalline size of ZnO in the films annealed at 350°C, 450°C, and 550°C was about 16, 23 and 25 nm, respectively. The average crystalline size of ZnO in the films with various times of coating annealed at 550°C is shown in Table 1. It was observed that the c -axis orientation improves, and the grain size increases as indicated by an increase in intensity of the (002) peak and the decrease in the FWHM (Fully Width at Half Maximum) high with the increase of annealed temperature. An average grain size was about 25 nm.

3.2. Photocatalytic activity

Evaluation of the films as potential photocatalyst for water pollutant purification was based on the degradation of a

FIGURE 5: ((a)–(c)) SEM images of the ZnO thin film at different temperature ((a) = 350°C, (b) = 450°C, and (c) = 550°C), (d) AFM image ZnO thin film prepared at 450°C.

FIGURE 6: Optical transmittance of ZnO thin films, postheated at various temperatures (a = 350°C, b = 450°C, and c = 550°C).

FIGURE 7: UV-visible spectra of X6G (initial concentration of X6G = 0.013 mM) in deionized water after photocatalytic degradation under UV irradiation on ZnO film with 5 layers.

model azo dye, X6G. The results showed that nanostructure ZnO thin film and UV light (365 nm) had a negligible effect when they were used on their own after 240 minutes. Figure 7

shows the degradation of 10 ppm X6G under UV irradiation (365 nm) using ZnO thin film. Glass plate supported ZnO thin films with different layers (2, 4, 5, 6, 8, and 10 layers)

FIGURE 8: X6G concentration (ppm) (initial concentration of X6G = 0.013 mM) after photocatalytic degradation under UV irradiation for 80 minutes on ZnO films with various layers.

FIGURE 9: X6G concentration (ppm) (initial concentration of X6G = 0.013 mM) after photocatalytic degradation under UV irradiation for 80 minutes on ZnO film with 5-layer six-cycle reuse.

were tested for degradation of the X6G dye for 80 minutes (see Figure 8).

Thin films with 5 layers were reused five times and did not show much catalytic activity change (see Figure 9).

4. CONCLUSION

Zinc acetate and MEA have proved to be suitable compounds to obtain high quality pure coatings. These precursor compounds and the proper annealing conditions have proved to be suitable to produce stable guest oxide nanocrystalline size. The thin films show good photocatalytic activity for degradation of X6G dye solution.

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