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Original Paper

Synthesis of ZnO films in different solvents and their photocatalytic activities

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ZnO thin films have been successfully synthesized via the chemical bath deposition (CBD) method without using any catalysts or templates. The effects of solvents (such as water, ethanol and *n*-propanol) on structure and morphology of ZnO thin films have been studied. XRD analysis showed that all ZnO thin films with wurtzite crystal structure were obtained via various solvents. SEM images showed that ZnO thin films prepared in different solvents have different sizes and morphologies. TEM images showed that crystalline ZnO samples prepared in different solvents have different growth habits. Photoluminescence and photocatalysis properties have been investigated at room temperature. ZnO thin films prepared in water showed superior photocatalytic activity in the degradation of rhodamine B (RhB) compared to other samples.

1 Introduction

Dye wastewater from the textile industry causes a lot of damage to the environment, and wastewater pollution has always been a major problem throughout the world [1]. In most countries, researchers are looking for appropriate treatments in order to purify the contaminated water. Some traditional purification procedures often transfer organic pollutants to another collecting phase and do not degrade completely to nontoxic substances [2–4]. Therefore, finding an effective method to remove hazardous organic dyes from industrial effluents still remains a great challenge. Recently, semiconductor photocatalytic processes have received increasing attention for complete elimination of environmental pollutants from water due to its efficiency [5–7]. Among the various semiconductors, ZnO is well known as a promising photocatalyst because of its typical properties such as wide direct bandgap (3.37 eV) and large exciton binding energy (60 meV) at room temperature, and widely applied for wastewater treatments because of its high activity, low cost and nontoxicity [8, 9].

Originally, ZnO was used in powder form for water treatment. However, some serious practical problems arose from the use of ZnO powder in the photocatalytic processes. For example, powder must be kept stirred during the reaction process and it is difficult to separate powder from wastewater after the reaction. In order to solve these problems, the immobilization photocatalyst such as ZnO thin film was prepared. Up to now, many different methods were used to obtain ZnO thin film, such as the chemical bath deposition method (CBD) [10–12], pulsed laser deposition (PLD) [13, 14], the hydrothermal method [15, 16], the sol-gel process [17], metal-organic chemical vapor deposition (MOCVD) [18], radio-frequency magnetron sputtering [19], molecular beam epitaxy [20, 21] and so on. Among these techniques, the CBD method is an attractive technique to prepare ZnO films due to its great advantages in both low cost and environment friendliness, and this technique is a process well suited to large-scale production.

In addition, the photocatalytic activity of ZnO photocatalyst has a very close relationship with its morphology [22–24]. Also, ZnO morphology is determined by synthesis parameters in the preparation process. Some

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researchers have shown that the choice of solvent has a profound influence on the growth of polar crystals [25, 26]. As is well known, ZnO is a polar crystal and the relative growth rates of various crystal planes are different in solvents with different polarities. Therefore, the solvent is an important parameter in the synthesis of ZnO photocatalysts by liquid-chemistry methods.

In this study, ZnO thin films were prepared by using a low-cost and environmentally friendly procedure through the chemical bath deposition (CBD) method. The effect of solvents on the sizes and morphologies of ZnO was investigated. The photocatalytic activities of the obtained thin films were evaluated by the photodegradation of rhodamine B (RhB) aqueous solution as a model of the pollutant.

2 Experimental section

2.1 Preparation

All reagents were analytical grade, purchased from Sinopharm Chemical Regent Co., Ltd., and used without further purification. ZnO thin films were prepared by chemical bath deposition (CBD) method. The Si wafers with size of 10 × 10 mm (length × width) were used as the substrates. And the preparation of seeds layer on the Si substrates was described in our previous work [27]. In a typical synthesis: 0.1 mol $Zn(NO_3)_2{\cdot}6H_2O$ and 0.1 mol $C_6H_{12}N_4$ were dissolved in 100 ml the same solvents, respectively. The solvents could be deionized water, absolute ethanol or absolute *n*-propanol. Then the two solutions were mixed with vigorous stirring for 30 min. The Si substrates were immersed into a beaker with the above mixture. The beaker was put into an oven which was maintained at 80 °C for 5 h. Finally, the substrates were taken out and washed with deionized water and ethanol, respectively, and then dried in an oven at 60°C for 5 h.

2.2 Characterization

The crystallographic information of the prepared samples was analyzed by X-ray power diffraction (XRD) pattern using a D/max-RA XRD diffraction spectrometer (MAC Science, MXP18, Japan) with a Cu Kα line at 1.5406 Å. The sizes and morphologies of the samples were analyzed by field emission scanning electron microscopy (FESEM, JEOL JEM-2010HR) and transition electron microscopy (TEM, JEOL JEM-2010HR). Photoluminescence (PL) properties were studied at room temperature in a spectral range of 350–750 nm using a He-Cd Laser with a wavelength of 325 nm at a power of 50 mW.

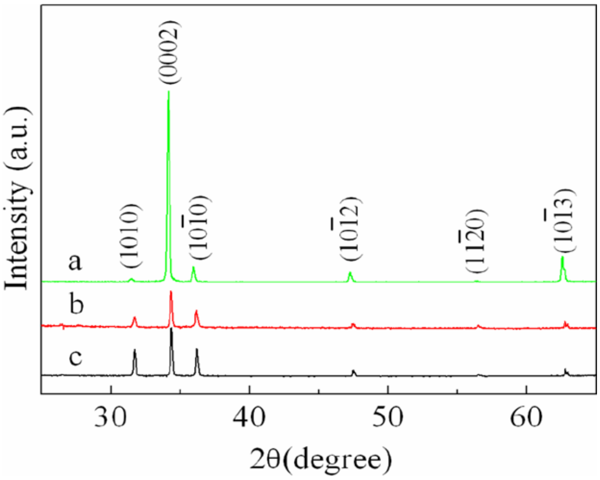

Fig. 1 XRD patterns of ZnO thin films prepared in different solvents. (a) water, (b) ethanol, and (c) propanol.

2.3 Photocatalysis

The photocatalytic activities of ZnO thin films were investigated by decomposition of RhB aqueous solution (10 mg/L) under UV irradiation. A 250 W high-pressure mercury lamp (main emission wavelength $\lambda = 365$ nm) was used as UV light source. All experiments were carried out at ambient temperature. For comparison, blank photodegradation experiment was performed without adding photocatalyst. Before and after different irradiation intervals, the solution concentration of RhB was analyzed by a UV-vis spectrophotometer (UV-5800PC, Shanghai Metash Instruments Co., Ltd.).

3 Results and discussion

3.1 Characterization

Figure 1 shows XRD patterns of ZnO thin films prepared in different solvents. All diffraction peaks shown in figure 1 can be indexed as ZnO with wurtzite structure, which are in a good agreement with JCPDS card No. 36-1451. No characteristic diffraction peaks from other phases or impurities are found in all samples. In addition, compared to the standard pattern of hexagonal phase ZnO, the relative intensity of the peaks corresponding to (0002) planes is significantly enhanced in the thin film prepared in water, suggesting that ZnO

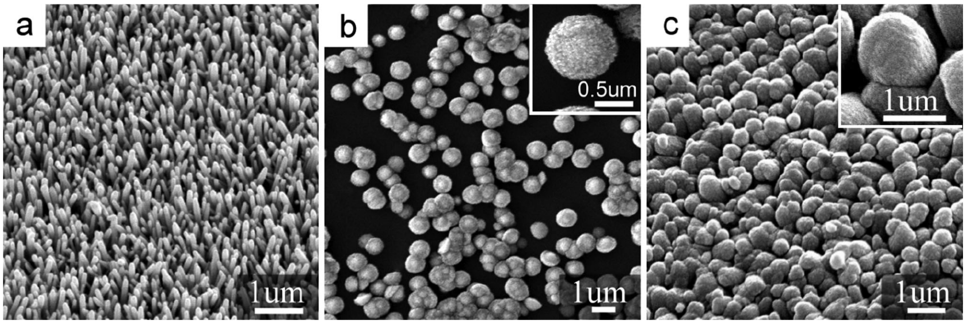

Fig. 2 SEM images of ZnO thin films prepared in different solvents. (a) water, (b) ethanol, and (c) propanol. Insets in (b) and (c) are the enlarged figure of individual crystal, respectively.

crystal grown used water as solvent are preferential orientation grew along the <0001> direction.

Figure 2 illustrates SEM images of ZnO thin films obtained in different solvents. As shown in figure 2a, ZnO thin film is composed of rodlike structure in high orientated with the average diameter of ~80 nm. When organic solvents (ethanol or propanol) were used as solvents, the morphologies of ZnO thin films were changed. The sizes of ZnO thin film synthesized in ethanol solvent are nonuniform, as shown in figure 2b. ZnO disklike structure crystals grown on the edge of the film are sparse and the average diameter is about 0.8 μm. An amplified SEM image of an individual disk in figure 2b indicates that the disk is composed of nanoparticles with mean particle size of ~20 nm. However, disk-like ZnO grown in the center of the film are dense and the diameters are around 0.4 μm. This is because ZnO grown in the center of the thin film have not enough space to grow up. As a whole, a majority of surface of the thin film prepared in ethanol is covered with the disk-like ZnO with the diameters ~0.4 μm under the observation of SEM. ZnO thin film synthesized in propanol solvent exhibits fungus morphology (figure 2c), and the average size of fungus is about 0.5 μm. The enlarged view of individual fungus shows that the surface is rough, suggesting that the fungus may consist of nanoparticles.

To better understand the microstructure of ZnO crystalline, further characterization by using TEM was performed and the results are shown in figure 3. Figure 3a shows a typical TEM image of ZnO rods grown in water. The diameter is about 80 nm, which is in good agreement with SEM observation in figure 2a. Figure 3b is HRTEM image from the solid-lined square in figure 3a. HRTEM result displays that the lattice spacing of 0.26 nm agrees with the distance between two (0002) crystal planes of wurtzite ZnO, indicating that ZnO rods grew along c-axis. Figure 3c shows a typical TEM image of an isolated ZnO disk with a diameter of approximate 0.8 μm. The surface of the disk is relatively rough. The lattice fringes shown in figure 3d have a spacing of 0.28 nm corresponding to the interplanar spacing of $(10\bar{1}0)$ plane of ZnO. The single crystal-like SAED pattern consisting of individual diffraction spots implies that the nanoparticles of the whole

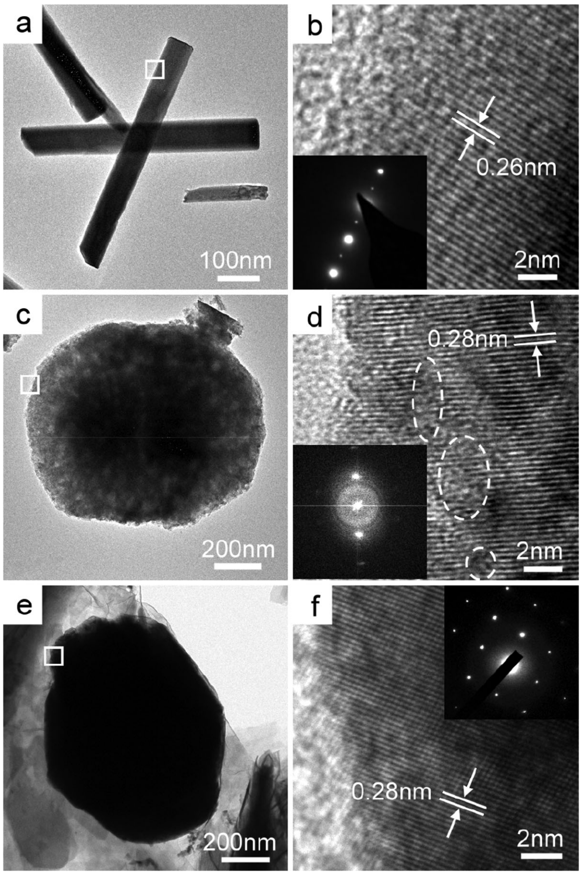

Fig. 3 TEM (left) and HRTEM (right) images of ZnO thin films prepared in different solvents. (a, b) water, (c, d) ethanol, (e, f) propanol. Insets are the corresponding SAED pattern. The white circles point to the defects.

ZnO disk assemble in the same orientation. Some defects of ZnO crystal is clearly observed in the HRTEM image (dashed white circles). Figure 3e shows the TEM image of ZnO prepared in propanol solvent. As shown in figure 3e, the morphology of ZnO is ellipse rather than fungus. The HRTEM and SAED pattern in figure 3f show that this structure is single crystal-like structure. Like ZnO disk, the nanoparticles of the ellipse are in the high orientation.

Obviously, solvents play a significant effect on the sizes and morphologies of ZnO crystal. As we know, ZnO is a polar crystal and the relative growth rate of the various crystal planes is influenced by the polarity of solvents [25, 28, 29]. The dielectric constants of water, ethanol and *n*-propanol are 80.1, 25.3 and 20.3, respectively. And the higher dielectric constant is corresponding to a higher polarity. In higher polarity solvents, such as water, ZnO rodlike morphology was obtained. This indicates that the interaction between the polar (0001) surface and the polar solvents is strong, which resulted in ZnO crystals grew along the [0001] direction. In lower polarity solvents, such as ethanol and propanol, the disk-like or ellipse-like ZnO was obtained. This is because the interaction between the polar (0001) surface and the polar solvents is weaker, leading to less anisotropic growth rates [26].

3.2 Photoluminescence and photocatalysis

The photoluminescence properties of ZnO thin films are investigated at room temperature, and the results are displayed in figure 4. The PL spectra of ZnO samples exhibit UV emission peak at 379–387 nm and a broad spectral band falling between 500 and 650 nm. It is reported that the UV emission is attributed to the free exciton recombination through free exciton transition process [30], and the broad green emission represents the deep level defects (DLE) resulted from the singly ionized oxygen vacancies and other defects [31–34]. Inset of figure 4 shows the I_{UV}/I_{DLE} ratio of all ZnO thin films. The bigger value of I_{UV}/I_{DLE} indicates the better crystalline quality, while the small value of I_{UV}/I_{DLE} implies the more defects. Therefore, the result demonstrates that ZnO thin film prepared in water solvent exhibits good crystalline quality, and ZnO thin film obtained in ethanol solvent has more defects. The boiling point of the water, ethanol and propanol are 100, 78.5 °C and 97.4 °C, respectively. When the reaction temperature is 80 °C, the ethanol has been boiling while water and propanol has not arrived in the boiling points. ZnO deposition on the Si substrate was not very good under the condition of boiling solvent. Therefore, ZnO thin film prepared in ethanol have more defects than ZnO thin film obtained in water or propanol.

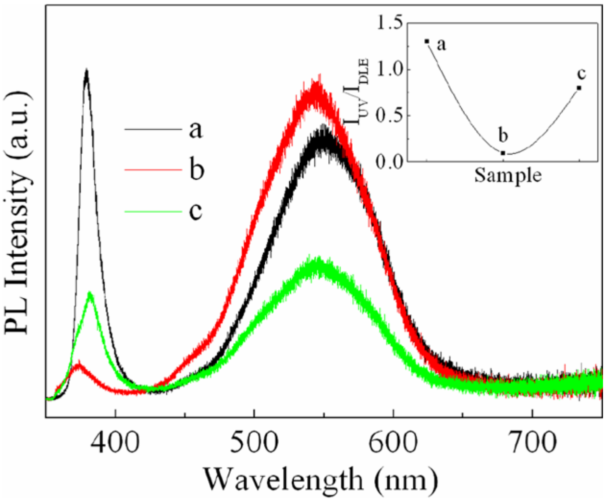

Fig. 4 Room temperature PL spectra of ZnO thin films prepared in different solvents. (a) water, (b) ethanol, and (c) propanol. Inset is the I_{UV}/I_{DLE} ratio.

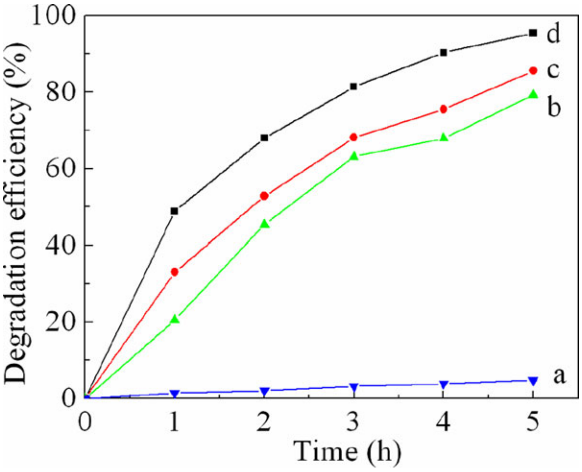

Fig. 5 Photodegradation of RhB under different conditions: (a) without catalyst, (b) microellipses, (c) microdisks, (d) nanorods.

The photocatalytic activities of the as-synthesized ZnO thin films with different morphologies were evaluated in terms of the degradation of RhB dye under UV irradiation and the results shown in figure 5. The blank experiment in the absence of photocatalyst shows that the concentration of RhB slightly decreased, indicating that the photoinduced self-sensitized photolysis of RhB can be neglected. When adding the as-synthesized ZnO thin films photocatalysts in RhB solution, the degradation of RhB obviously increased. The photocatalytic efficiency was 95.4%, 85.5% and 79.2% with using ZnO nanorods, microdisks and microellipses (fungus) as the photocatalysts, respectively. Namely, the photocatalytic activity of ZnO thin films shows the following order: nanorods > microdisks > microellipses. ZnO nanorods exhibit the best photocatalytic activity among all samples because nanorods have more exposed areas of (0001) crystal facet. It is generally accepted that catalyst with more (0001) crystal facet shows better catalytic performance [23, 35]. As we know, (0001) crystal facet has the highest surface energy among all crystals facets of ZnO [26]. In addition, the size of nanorods is smaller than the other two samples. Usually, small size has a beneficial effect on the activity of photocatalysts because smaller particle sizes with higher specific surface area can provide more active sites for photocatalytic reaction [22]. The photocatalytic activity of microdisks shows superior slightly over microellipses not only because the most microdisks have smaller sizes than microellipses but also because the microdisks have more defects than that of microellipses. As reported in the literature, the more defects of materials exhibit the better photocatalytic activity [36].

4 Conclusions

ZnO thin films with different morphologies have been successfully synthesized by the chemical bath deposition (CBD) method by using different solvents. The effect of solvents was investigated in detail and it is found that solvents play a key role in controlling the morphology of ZnO thin films. The photocatalytic results show that the as-prepared ZnO thin films prepared in water solvent showed an excellent photocatalytic ability to degrade RhB, which is expected to be useful in sewage water treatment.

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Key words. ZnO, thin film, solvent, photocatalysis.

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