

Research Article

Preparation of ZnO-Zn₂TiO₄ Sol Composite Films and Its Photocatalytic Activities

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Received 16 April 2013; Accepted 8 September 2013

Academic Editor: Tifeng Jiao

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Ti-doped ZnO sol-composite films were prepared on the glass substrate by the two-step sol-gel technique. X-ray diffraction, Uv-Vis spectrophotometer, and FS spectrum of composite films were used to help make structure characterization and optical performance testing. The results showed that the composite was a mixture of ZnO + Zn₂TiO₄. Because of synergistic effect of both semiconductor oxides, composite films had a wide range of spectral response in the visible region, and the absorption band edge was about 510 nm, and the Green Belt of composite films luminous significantly enhanced. Photocatalytic oxidation experiments showed that using the composite films treatment (16.5 ml, 10 mg/L methyl orange aqueous solution)/cm², the decolorization rate of methyl-orange was 90% after 3 hours irradiation.

1. Introduction

Due to low energy consumption, strong oxidation ability, mild reaction conditions, and no secondary pollution, semiconductor photocatalytic oxidation technique potential applications in the field of environmental protection attract widespread interest of many scholars. TiO₂ and ZnO are ideal semiconductor oxide materials and have a broad application prospects in respect of wastewater treatment and air purification. ZnO has aroused much attention because it has high photocatalytic activity in some organic photodegradation reactions [1, 2]. It has also been found that both quantum efficiency and catalytic efficiency of powdered ZnO are higher than those of TiO₂ [2]. Most of the studies related to photodegradation reactions have been carried out using suspensions of powdered ZnO in aqueous solutions [3]. Although suspension/slurry reactors are generally found to be more efficient, their effective applications are hindered by some serious disadvantages, namely, difficulties of the separation and recovery of catalyst and easiness to aggregate. In recent years, there are fewer reports on photocatalytic properties of ZnO nanocomposite materials including nanocomposite

powder [4–8] and films [9–17]. Some investigators have prepared ZnO/TiO₂ composite films and ZnO/TiO₂ multi-layer films [14–19]. ZnO and TiO₂ have similar band gap ($E_g = 3.2$ eV) and staggered band position. Using different semiconductor conduction band and valence band energy level difference, they are both mixed on the molecular level, so the photoexcited carriers can separate. It is helpful to reduce the recombination probability of photoinduced electron/hole pairs, improving quantum efficiency, and this is very important to the design and preparation of the photocatalyst. In general, the details of the surface morphology, crystal structure, and chemical composition critically influence the photocatalytic performance of the photocatalysts. Therefore, nanocomposite films prepared by different composite techniques can have different photocatalytic activity for those films composed of ZnO and TiO₂.

In this paper, Titanium ion-doped ZnO sol nanocomposite films were prepared by using a two-step sol-gel process. The photocatalytic activity of the composite films prepared by different methods was compared. And the micromechanism of the composite films photocatalytic efficiency was explored.

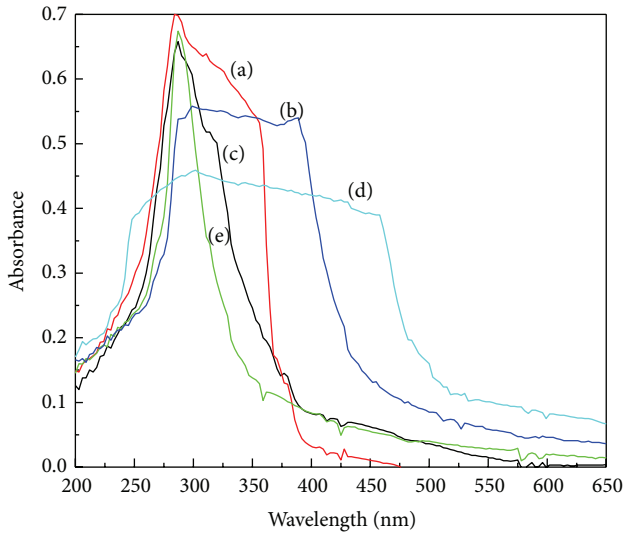


FIGURE 1: UV-vis absorbance curves of films (a) multilayer films, (b) doping films, (c) ZnO, (d) sol composite films, and (e) TiO₂.

2. Materials and Methods

2.1. Film Catalyst Preparation. Reagents used in the experiment are of analytical grade.

The preparation of TiO₂ sol. According to the ratio of 6:2:1:0.3 (volume ratio), anhydrous ethanol, acetic acid, tetrabutyl titanate, and ethanolamine were sequentially placed in a beaker, which magnetic stirring for 0.5 h, getting a solution A. Ethanol and distilled water were prepared to a solution B with a ratio of 36:1. The solution B was slowly added dropwise (9 mL/min) to the solution A, and then it was obtained a uniform and transparent yellowish solution after stirring for 1.5 h. The solution was aged for 20 h.

The preparation of ZnO sol. Zinc nitrate hexahydrate, ethanol, and citric acid, respectively, were used as a solute, solvent, complexing agent. Zinc nitrate and citric acid were mixed with a molar ratio of 1:1 and prepared to Zn²⁺ concentration of 0.5 mol/L solution by the water bath temperature of 60°C and magnetically stirred 2 h. The solution was aged for 20 h.

The preparation of Zn-doped TiO₂ composite sol. Its steps were basically the same as TiO₂ sol preparation steps, just a certain amount of Zn(NO₃)₂·6H₂O (with 20% ZnO/TiO₂ molar ratio) was dissolved in solution B, and slowly dropped into the solution A after full dissolution.

The preparation of Ti-doped ZnO composite sol with two-step method. ZnO sol was slowly poured into TiO₂ sol with different molar ratios. Stirring mixed sol under room temperature for 0.5 h and Aging the solution for 20 h.

In this study, Ti-doped ZnO composite films (hereinafter referred to as sol composite film) were prepared on glass substrate by sol-gel dip-coating technique. As a comparison, single component ZnO and TiO₂ films, ZnO/TiO₂ alternating multilayer film, and Zn-doped TiO₂ composite film (hereinafter referred to as doped composite film) were also prepared under optimized conditions, respectively.

Glass substrates were dipped in the starting solution for 20 s and were drawn at a rate of 4 cm/min using the TL 0.01 vertical pulling machine (Shenyang Scientific Precision Instrument Factory). The deposited layers were then dried in air at 70°C for 30 min after each dipping. The crystallization of the films was finally performed by thermal annealing in air at temperature of 500°C for 1.5 h after several coating cycles, cooling along with the furnace. The film thickness was measured using XP-2TM surface Talysurf (Shenyang Science Precision Instruments Factory).

2.2. Sample Performance Testing. X-ray diffraction (XRD) measurements were performed by a D/Max-2500/PC diffractometer with Cu K α line for an angle range of $2\theta = 20\text{--}70^\circ$ (Rigaku). Optical absorption properties and photoluminescence spectra of the samples were carried out employing an UV-2550 ultraviolet-visible spectrum (Shimadzu) and FL-1039 fluorescence spectrum using an excitation wavelength of 325 nm (France Jobin Yvon).

3. Results and Discussion

3.1. Optical Absorption Properties of Films. Optical absorption behavior of Ti-doped ZnO sol composite films with different molar ratio prepared by the two-step sol-gel method was first studied. The results showed that all composite films exhibit a wide range of spectral response in the UV-visible region. Among them, the sol composite film with 15% of Ti content appears as the widest absorption band and has a better absorption within the 245 nm–460 nm wavelength range. Absorption band edge is near 510 nm. The extension of the spectral response range of sol composite films may be resulted from the formation of a moderate amount of Zn_xTi_yO_{2y+x} composite oxide in the film.

Figure 1 gives UV-visible optical absorption curves of all kinds of films (8 layers). As can be seen, order of the spectral response range is Ti-doped ZnO sol composite films, Zn-doped TiO₂ doped composite films, ZnO/TiO₂ alternating multilayer film, ZnO film, and TiO₂ film. Obviously, the spectral response ranges of the composite films are wider than that of the single component film. And absorption band edge of the composite films occur red shift, which is consistent with the result reported in the literature [12, 17, 20]. The spectral response range of Ti-doped ZnO sol composite film is the widest in the three composite films. Absorption band edge of Ti-doped ZnO sol composite film lie 510 nm, approximate red shift 50 nm comparing with Zn-doped TiO₂ doped composite film. According to the relationship of the optical absorption threshold and band gap of the semiconductor [20], the band gap of the Ti-doped ZnO sol composite film (film thickness of 400 nm) is near 2.44 eV:

$$\lambda_g \text{ (nm)} = \frac{1240}{E_g \text{ (eV)}}. \quad (1)$$

3.2. Sol Composite Film Structure. X-ray diffraction pattern of 15% Ti-doped ZnO sol composite film prepared by the two-step sol-gel method was shown in Figure 2. We can see that the main phase is still the hexagonal wurtzite structure

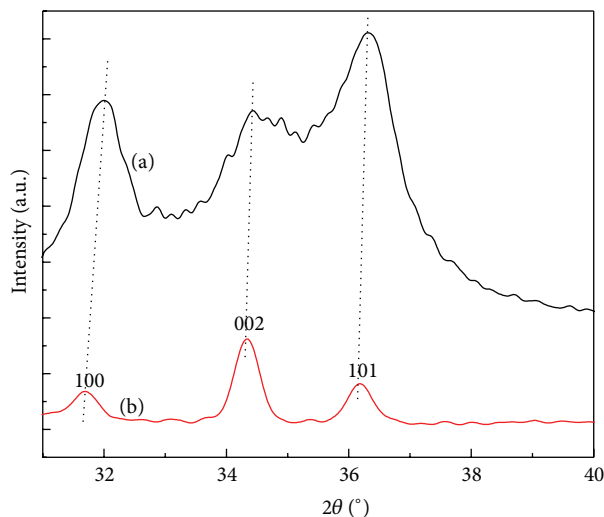


FIGURE 2: XRD pattern of samples. (a) ZnO + Zn₂TiO₄ sol composite films and (b) ZnO film.

for ZnO (JCPDS 36-1451), but it can be clearly observed that there is several weak diffraction peaks except ZnO main phase in the X-ray diffraction spectrum labeled as “a” of sol composite film. After careful comparison with the JCPDS card. The weak diffraction peaks in the curve labeled as “a” of sol composite film are characteristic peak of No. 26-1500 ZnTiO₃ and No. 25-1164 Zn₂TiO₄ (mostly), no TiO₂ characteristic peaks are found, suggesting the doped-Ti formation of solid solution with ZnO. On the basis of the XRD profiles, the average grain sizes of the products were calculated according to the Debye-Scherrer Equation, being 54 nm and 46 nm for Ti-doped ZnO sol composite film and single component ZnO film, respectively, indicating that the dopant Ti improves the crystallinity of ZnO. When ZnO react with TiO₂, the composition of titanate depends on the ratio between ZnO and TiO₂. When the ZnO is excess, reacted product is mainly Zn₂TiO₄ [21]. As shown in Figure 2, nanocomposite film exhibits a slightly higher angle shift from that of single ZnO film, indicating a lattice distortion due to the introduction of other elements. Just because of the formation of the new phase, structure of the sol composite film changed.

3.3. Photocatalytic Properties of Ti-Doped ZnO Sol Composite Films. Photocatalytic degraded 10 mg/L methyl orange aqueous solution, which served as a model organic pollutant, was carried out under UV light irradiation. The glass sample coated with sol composite films was cut into 35 mm × 26 mm rectangular. And then it was suspended into the vessel which contained 150 mL methyl orange solution, and the mixture was continuously stirred for 30 min in dark to reach an adsorption-desorption equilibrium. After that, they were irradiated from top using a UV lamp (Philips 125 W, 360 nm). The distance between vessel and lamp was 30 cm. At regular intervals, 5 mL of the aliquot samples were withdrawn from the reaction mixture. The used solution was returned to the vessel and degraded again after measure absorbance

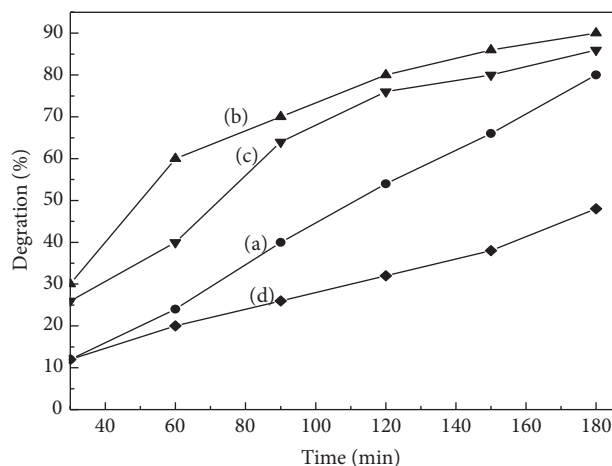


FIGURE 3: Effect of the thickness of sol composite films on the decolorization rate. (a) 275 nm, (b) 380 nm, (c) 490 nm, and (d) ZnO-390 nm.

($\lambda_{\max} = 465$ nm) every time. Decolorization rate of methyl orange solution was used to estimate the photocatalytic activity of the film [7]:

$$\eta = \frac{(A_0 - A)}{A_0} \times 100\%, \quad (2)$$

where A_0 and A are the absorbance of methyl orange solution before and after irradiation. In general, increasing the film thickness can enhance photocatalytic activities of the film, but this increase is limited. Effect of sol composite film thickness on photocatalytic activities was studied. The results are shown in Figure 3. We notice that the photocatalytic activities of the sol composite film increase with the increasing of a film thickness in a 300–400 nm range. When the film thickness is greater than 400 nm, the photocatalytic activities of the film reduces. Thus, the maximum decolorization rate of methylorange solution reaches 90% after degradation for 180 min in a suitable film thickness of 400 nm or so, while the maximum decolorization rate of pure ZnO films is only 48% (curve labeled as “d” in Figure 3). The photocatalytic activities of the sol composite film vary with film thickness. The main reason is that the load volume of film increases with the increase of the film thickness, then photo-generated electrons/holes concentration and hydroxyl content relatively increase, which enhance the photocatalytic activities of the sol composite film. Nevertheless, when the film is too thick, the diffusion speed of the reaction solution reaching composite film interior and the resultant reaching composite film surface reduced. And the enlarging of migration distance of the photoexcited electrons and holes hindered diffusion of the carrier. Furthermore, part of the grains grew up and became agglomerate during the course of film thickness increase via layer by layer, which decreased the specific surface area of the film and reduced the adsorption properties of the film. So the photocatalytic activities of too thick films are decreased.

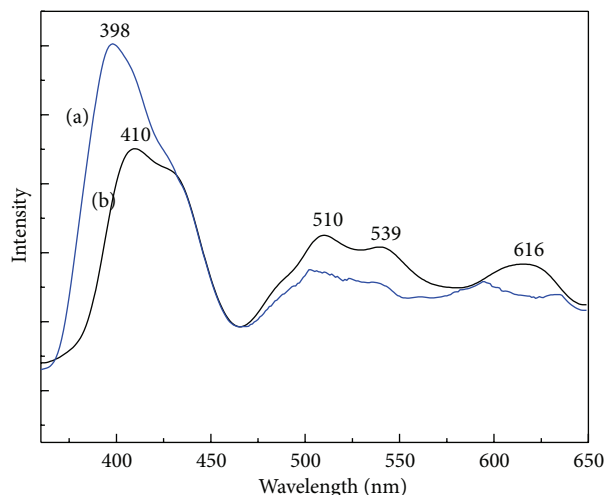


FIGURE 4: PL spectra of the films. (a) ZnO and (b) ZnO + Zn₂TiO₄.

3.4. The Photoluminescence Spectra of Ti-Doped ZnO Sol Composite Film. In order to investigate the micromechanism of significantly enhanced photocatalytic activity for the ZnO + Zn₂TiO₄ sol composite film prepared by the two-step sol-gel method, the photoluminescence spectra of sol composite film were measured (excitation wavelength of 330 nm), as shown in Figure 4. As we can observe from Figure 4, luminescent peak in the spectrum of sample ZnO + Zn₂TiO₄ sol composite film (curve labeled as “b”) located in the UV-violet range present weak and redshift comparing with the pure ZnO film (curve labeled as “a”), which is consistent with the above conclusion obtained from optical absorption curve in Figure 1. At the same time we also notice that the green band emission in the visible region (510–530 nm) is significantly enhanced. It is well known that there are two kinds of emission bands of near band edge (NBE) excitonic UV emission and defect-related deep-level emission (DLE) in the visible region in ZnO crystals [20, 22]. Although the exact mechanisms for UV-violet and visible emissions are not yet clear, the UV emission is believed to originate from the excitonic recombination corresponding to the band edge emission of ZnO, while the origin of the green luminescence is associated with the intrinsic defect centers, such as oxygen vacancy (V_O), zinc vacancy (V_{Zn}), or antisite oxygen (O_{Zn}) [20]. Formation of Zn₂TiO₄ in the sol composite film made the surface state of the film different, resulting in an increase of content of oxygen vacancy (V_O), therefore, sol composite film exhibits a strong emission in the green region. In general, during the photocatalytic oxidation reaction process, oxygen vacancy defect in ZnO crystallinity can act as the active centers to capture photoinduced electrons, thereby the recombination of photoinduced electrons and holes can be effectively inhibited, so that the photocatalytic activity can be greatly improved. And the existence of oxygen vacancy also promotes the adsorption of the sample on the oxygen. Moreover, there is a strong interaction between photoexcited electron shackled or captured by oxygen vacancies and its adsorbed oxygen. This implies that oxygen vacancy

shackle of the photoexcited electron may be conducive to capture of adsorbed oxygen on photoexcited electron, which alleviated the bottleneck factors of photocatalytic oxidation technology to some extent, that is, transmission slow of photoexcited electron to adsorbed oxygen [23]. Meanwhile, activated species peroxy radical $\cdot\text{O}_2$ was further generated, accelerating oxidation of organic matter [12]. Hence, the oxygen vacancy can enhance photocatalytic activity of film.

In addition, we also observe that there is an obvious orange luminescent peak at the 616 nm in the spectrum of the sol composite film. The emission peak is rarely reported in the previous literature. This may be a new defect in ZnO crystallinity introduced by the generation of a new phase in the sol composite film, and the light-emitting mechanism still needs to do further in-depth study.

4. Conclusions

Ti-doped ZnO sol-composite films were prepared on glass substrate by the two-step sol-gel technique. X-ray diffraction test results show that the composite film composed of a mixture of ZnO + Zn₂TiO₄. When Ti doping ratio was 15%, sol composite film had the widest spectral response range and exhibited high photocatalytic efficiency. According to the processing (16.5 mL, 10 mg/L of methyl orange solution)/cm² composite film calculation, decolorization rate of methyl orange was 90% after degraded 3 hours. Obvious improvement of sol composite film photocatalytic efficiency results from formation of the appropriate amount Zn₂TiO₄ in composite film, due to both phases of ZnO and Zn₂TiO₄ coexisting in the film, and it is probable that the coupling of both semiconductor oxides promote the charge separation, which decreases the photoexcited electron-hole recombination. Moreover, formation of the new phase caused surface state of the composite film to change, which led to the increase of the oxygen vacancy concentration of the film. So when quantum efficiency of the sol composite film was improved, its photocatalytic activity was greatly enhanced.

Acknowledgments

The authors are grateful for the financial support from the Natural Science Foundation of Hebei Province (no. B2012203070) and support from education department of Hebei province on “key projects of natural science research” for institution of higher learning (no. ZD20131010).

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