



Photo-degradation of organic dye by zinc oxide nanosystems with special defect structure: Effect of the morphology and annealing temperature

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ABSTRACT

The fabrication of strong photocatalysts applied to the degradation of organic pollutants is necessary in environmental applications. In a single-stage method, acetate precursor and poly vinyl pyrrolidone are used to produce ZnO nanostructures with various morphologies in annealing temperatures ranging from 300 to 900 °C. The physical properties of the prepared nanostructures were characterized by SEM, TEM, XRD, BET, DRS, CHN analysis and PL spectroscopy. The SEM images exhibit a variety of the as-prepared hexagonal zinc oxides including wires, rods, particles and porous network of welded particles of ZnO nanoparticles. The results of the photocatalytic degradation of methylene blue as an organic dye in aqueous suspension showed that the morphology of ZnO nanostructures influences on the photocatalytic efficiency of ZnO nanostructures, greatly. For the best result, the highest MB degradation occurs by ZnO nanowires within 16 min and in others samples, degradation of higher than 95% occurs within 20 min. The XRD and PL spectroscopy revealed neither V_{Zn} nor O_i are in all of samples but only V_O^- , V_O^{2-} and Zn_i exist in ZnO nanostructures.

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1. Introduction

Oxide semiconductors such as titanium dioxide (TiO_2) [1–3] and zinc oxide (ZnO) [4,5] are very influential photocatalysts in degradation of organic pollutants dissolved in water and other solvents. Although they both have a band gap of about 3.3 eV, their electronic structure is quite different. This difference offers ZnO some advantages over TiO_2 . For instance, ZnO has higher exciton energy binding about 60 meV and consequently longer lifetime at room temperature. Longer lifetime for excitons enhances the yield of photocatalysis by postponing the of recombination of electron–hole. ZnO absorbs a larger fraction of UV spectrum and absorbs more light than TiO_2 [6,7]. In the photo-degradation of organic compounds under UV-light illumination, ZnO is more efficient than TiO_2 and it generates H_2O_2 more efficiently [8]. Also, it has higher mineralization rates [9] and has more active sites per surface area [5]. In the spite of these advantages, the major disadvantage of ZnO is that surface defects in ZnO lead to the rapid electron–hole recombination. Therefore, to achieve benefits of ZnO, the modification of ZnO surface is important. It is clear that the shape, crystalline structure, and size of semiconductors

are among the important factors in determining their physical and chemical properties. In terms of structural properties, ZnO is a polar crystal with a number of alternating planes, which are composed of tetrahedral coordinated O^{2-} and Zn^{2+} ions, alternately stacked along the *c*-axis. Thus, a ZnO crystal consists of a positively charged plane (0 0 0 1) terminated with zinc, a negatively charged plane (0 0 0 $\bar{1}$) terminated with oxygen, and a nonpolar plane (0 1 $\bar{1}$ 0) with C_{6v} symmetry [10]. Studies show that ZnO (0 0 0 1) planes are chemically active whereas (0 0 0 $\bar{1}$) planes are inert [11,12]. The amount of these planes are different in varied morphologies of ZnO nanostructures. For example, the exposed crystal faces of oriented ZnO rods and flowers are mainly composed of (0 0 0 1) planes [13,14].

The photocatalytic activity of ZnO nanocrystals is not only sensitive to crystal size but also to morphology. Photocatalytic reaction occurs at the contact points between catalyst surface and organic pollutants and the morphology of the photocatalyst affects surface atomic arrangements and coordination number. Because of the effects of morphology, it can play an important role in photocatalytic process [15–17]. Based on the argument above, some research groups have tried to explore the relationship between ZnO crystals morphology and their photocatalytic activity [18,19].

In this article, a simple and single-stage route has been used to prepare ZnO photocatalysts with various morphologies through altering only annealing temperature. The photocatalytic activity of

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the prepared ZnO nanostructure photocatalyst was evaluated by the degradation of methylene blue (MB) in the presence of UV light. Afterwards, special optical, and structural properties of these ZnO samples were investigated by XRD, PL spectroscopy and CHN analysis. It was shown that only some surface defects play a role in photocatalytic activity.

2. Experiment

2.1. Preparation of ZnO photocatalyst

All reagents (including zinc acetate dihydrate, poly vinyl pyrrolidone and methylene blue) used in these experiments were of an analytical grade (purchased from Merck Co., Ltd.) and were used without further purification. The method mentioned in Ref. [20] was used with major modification. First, 5 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as precursor and 0.5 g PVP as stabilizing material were dissolved in 50 ml DI water with a 10 to 1 ratio ($\text{Zn}^{2+}/\text{PVP}$). The solution was then placed on a hot plate and stirred at 70 °C until one-tenth of the initial solution remained in the form of a yellow gel-like substance including zinc acetate and PVP in plate. Then the gel-like substance was dried at 110 °C in an oven for 12 h. The dried gel-like substance was annealed at temperatures ranging from 300 °C to 900 °C for 2 h and the last sample was prepared at 900 °C for 24 h. Upon increasing the annealing temperatures, the resulted samples take on various morphologies – wire, rod, spherical particle, porous network of welded particles – depended on the annealing temperature.

2.2. Characterization

Field emission scanning electron microscopy (FE–SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), Photoluminescence spectroscopy (PL, He–Cd Laser, 325 nm, 3 mW), Brunauer–Emmett–Teller (BET) instrument, diffuse reflectance spectra (DRS) and CHN analysis were used to characterize the crystal structure, morphologies, impurities and optical properties of ZnO nanostructures.

2.3. Photocatalytic activity measurements

The photocatalytic activity measurements were carried out as follows: The absorption mode of UV–vis spectroscopy was used to measure the absorbance of various MB concentration to plot the diagram of absorbance at 664 nm (in a.u.) vs concentration (in ppm). The reaction system containing 20 mL methylene blue (MB) aqueous solution (four-times distilled, DI, 18 M Ω water) with 10 ppm concentration and 0.001 g ZnO photocatalyst was stirred magnetically in darkness at pH 7, for 30 min. To ensure a well dispersing and de-agglomeration of ZnO nanopowder suspended in aqueous solution, a 400 W ultrasonic bath was used for 4 min. Before the irradiation, 3 ml of solution were taken out for adsorption analysis. The stirring was performed to reach the adsorption equilibrium of the MB before exposure to UV irradiation from a 300 W high-pressure Hg lamp (centered at 365 nm). The distance between the lamp and reaction system was 30 cm and the temperature was set on 25 °C. First, some experiments were done in two cases: (a) in the presence of ZnO photocatalyst and without any UV irradiation to identify the catalysis's mechanism and (b) under only UV radiation to probe degradation of MB solution. For recording the first results without any light source, we put the prepared dispersed solution in a dark and cool place under vagarious stirring for 30 min. For measuring the absorbance of dark time sample, we centrifuged it on 7000 rpm for 10 min, and then the upper part of solution was analyzed by UV–vis spectroscopy. After beginning irradiation process, the same amount of solution was taken out for each quantitative analysis, at an interval of 10-min. Every sampled solution was centrifuged at a

spin rate of 7000 rpm. A Hitachi U-2000 UV–vis spectrophotometer was used to monitor the residue concentration of methylene blue. All the photocatalytic experiments were repeated three times and data is presented with error bars $\pm 5\%$ values.

3. Result and discussion

3.1. Morphology and structure of ZnO photocatalysts

Fig. 1 shows the FE–SEM images of ZnO samples of different morphologies. All samples of various morphologies resulted from one procedure and material but they underwent different annealing temperatures and times such as 300 °C/2 h, 450 °C/2 h, 600 °C/2 h, 750 °C/2 h, 900 °C/2 h and 900 °C/24 h. As shown in Fig. 1a, the ZnO nanowires with the diameter of 50–80 nm and the length of 1 μm were produced. These nanowires were produced while being annealed in air at 300 °C in 2 h. Fig. 1b. shows the FE–SEM image of ZnO nanorods developed by increasing annealing temperature to 450 °C for 2 h; at a diameter ranging from 70 to 110 nm, with the ratio of length to diameter being less than five. The ZnO nanoparticles were produced by an incremental annealing temperature up to 600 °C and remained at this temperature for 2 h. The morphology feature of nanoparticles is shown in Fig. 1c.

The ZnO nanoparticles with a spherical shape have an average diameter of 70 nm and size distributions between 60 and 110 nm. Fig. 1d exhibits the morphology of the sample produced, annealed at 750 °C.

In the preparation method, no reductive agent was used and morphology changed only through annealing temperature. The SEM images related to morphologies of the porous-like ZnO structures annealed in 900 °C, 2 h and 900 °C, 24 h are shown in Fig. 1e and f, respectively.

Fig. 2a shows the XRD patterns of as-synthesized samples. All of the XRD patterns of ZnO nanostructures can be indexed as to the pure hexagonal wurtzite ZnO structure (JCPDS, card no. 36-1451). Furthermore, no peaks are detected from any other crystalline impurities.

This indicates that zinc precursors have been decomposed entirely into pure nanostructured ZnO, through the synthesis. However, all of peaks have been shifted gradually to the right and the diffraction peaks in XRD pattern of all samples were broadened. In Fig. 2b, the first three peaks are shown. As it is shown, upon increasing the annealing temperatures, the width and maximum size of the peaks have shifted. These irregularities may be related to the strain and some kinds of defects in ZnO lattice.

In the sample annealed at 300 °C with nanowire morphology d-spacing value related to the third peak is 2.4722 Å that is similar to the bulk ZnO with 2.4759 Å, and in the other annealing temperature and time, the corresponding d-spacing values are shown in Table 1. The reduction of d-spacing may be related to the high strain created by annealing in lattice.

One useful factor is the ratio of (002) polar plane (second peak in XRD pattern) to (100) nonpolar plane (first peak in XRD pattern) that it can be related to the photocatalytic activity. It is found that the polar planes of ZnO are important for the activity, because they favor forming more oxygen vacancies [21]. This factor is given in Table 1. The samples have the following order: sample 1 > sample 3 > sample 2 > sample 4 ~ sample 5 > sample 6.

Findings show that the growth of ZnO in an aqueous solution is influenced by external conditions such as temperature, solution pH and the concentration of additional solution components. As to the present case, the only difference among the samples is the annealing temperature. With regard to the point that there is no reductive agent in the preparation process, the role of PVP is to confine zinc precursor so as to prevent the growth of small ZnO

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