Research Article

Nanosheet-Assembled ZnO Microflower Photocatalysts

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Large scale ZnO microflowers assembled by numerous nanosheets are synthesized through a facile and effective hydrothermal route. The structure and morphology of the resultant products are characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Photocatalytic properties of the as-synthesized products are also investigated. The results demonstrate that eosin red aqueous solution can be degraded over 97% after 110 min under UV light irradiation. In addition, methyl orange (MO) and Congo red (CR) aqueous solution degradation experiments also are conducted in the same condition, respectively. It showed that nanosheet-assembled ZnO microflowers represent high photocatalytic activities with a degradation efficiency of 91% for CR with 90 min of irradiation and 90% for MO with 60 min of irradiation. The reported ZnO products may be promising candidates as the photocatalysts in waste water treatment.

1. Introduction

In recent years, a variety of ZnO micro/nanostructures have been reported, such as nanowires, nanobelts, nanospring, nanotubes, and hierarchical structures [1–5]. It was believed that these structures may possess unique physical and chemical properties different from their bulk counterpart to meet specific device fabrication demand [6, 7]. Among the ZnO nanostructures reported previously, two-dimensional (2D) nanostructures (such as nanosheets and nanowalls) have attracted more interests due to their unique spatial architecture and large aspect ratio, demonstrating some potential applications in photocatalyst and supercapacitor [8–10]. In literature, Lei et al. synthesized ZnO nanosheets on the zinc substrate by a hydrothermal method and studied their optical properties [5]. Qiu et al. reported porous ZnO nanoplate electrodes for dye sensitized solar cells [11]. Kim and coworkers successfully fabricated ZnO nanowall networks on GaN/sapphire substrate and investigated their optical properties [12]. Synthesis of porous ZnO nanoplates by a facile microwave approach has also been reported, as discussed by Jing and Zhan [13].

At present, environment pollution is one of the most serious problems people facing. Therefore it is an urgent task to eliminate the pollutants from water and air. As

an important wide bandgap semiconductor material, ZnO nanostructures may become excellent photocatalyst candidate for photodegradation of the organic dyes molecules due to their low cost, nontoxicity, and high photoactivity [14–16]. The photocatalytic properties of hierarchical ZnO microflowers and $\text{Ag}_2\text{O}/\text{ZnO}$ microflowers have been investigated, as discussed elsewhere [17–19]. In this paper, we used a facile hydrothermal route to synthesize ZnO nanosheets at mild temperature. The photocatalytic efficiencies of the synthesized product were evaluated by photodegradation of methyl orange, eosin red, and Congo red under UV irradiation, showing that the as-synthesized ZnO nanosheets possess high photocatalytic activity in the degradation of organic dyes.

2. Experimental Details

In this experiment, all reagents were of analytical grade and used without further purification. A typical experiment procedure is described as follows: 1.32 g $\text{Zn}(\text{CH}_3\text{COO})_2$ and 1.68 g NaHCO_3 were added into 20 mL distilled water, respectively. Then 0.1 g sodium dodecyl sulfate (SDS) was added into the $\text{Zn}(\text{CH}_3\text{COO})_2$ mixture solution. Then the above solution was added to NaHCO_3 solution under vigorous

FIGURE 1: Morphologies of the as-synthesized ZnO microflowers. (a) Low magnification SEM images. (b) High magnification SEM images.

stirring. After stirring for 1 h, the suspension was transferred into a PTFE-line autoclave with a volume of 100 mL. The autoclave was sealed and kept at 140°C for 12 h. After that, the solution was cooled down to room temperature. The precipitate was then washed several times with deionized water and ethanol, respectively. Finally the product was dried in a chamber at 60°C for 12 h and annealed in a muffle kiln at 280°C for 2 h.

The obtained product was characterized by scanning electron microscope (SEM, Hitachi-4800). The phases of the as-obtained products were identified by means of X-ray powder diffraction (XRD, Rigaku Dmax-2600/pc, Cu K α radiation, λ = 0.1542 nm, 40 KV, 100 mA). The photocatalytic degradation efficiency was analyzed by monitoring dye decolorization at the maximum absorption wavelength, using a UV/Vis Spectrometer (Shimadzu UV-2550).

3. Results and Discussion

Morphologies of the as-synthesized product were observed first by SEM. Figure 1(a) represents a typical low magnification SEM image, demonstrating large quantities of flower-like structures. Further observation finds that these microflowers consisted of numerous porous sheets with an average thickness of about tens of nanometers, as shown in Figure 1(b). XRD pattern of the as-obtained products was shown in Figure 2. All of the diffraction peaks can be straightforwardly indexed to hexagonal wurtzite ZnO structure, which are in accordance with the standard PDF card (JCPDS: 36-1451). No peaks of other phases were detected, indicating high purity of the as-synthesized product.

To investigate the effect of the growth parameters on the morphology of ZnO nanosheets, a series of comparison experiments was conducted. First, Figures 3(a) and 3(b) show SEM images of the product before calcination, finding that no pores appear and showing that the annealing treatment plays a very important role in the formation of pores. Subsequently, we will use Na₂CO₃ instead of NaHCO₃; it is obvious that the sheet-like ZnO nanostructures become coarse, as shown in Figures 3(c) and 3(d). Based on the above experimental

FIGURE 2: XRD pattern of the as-synthesized samples.

results, a possible growth mechanism can be proposed as follows:

In the initial stage, Zn²⁺ and CO₃²⁻ react with each other to form ZnCO₃ small particles. These particles have a tendency to aggregate due to large surface energy [20]. Surface energy is substantially reduced when the neighboring nanoparticles are grown. With the crystal growth continuing, each nanoparticle in the aggregates or nanosheet acts as a nucleus for further growth. These growth processes are not only related to the anisotropic ZnO crystal structure, but also related to the involved reaction conditions. The growth habit

FIGURE 3: (a) and (b) SEM images of the product before calcination. (c) and (d) SEM images of the product using Na_2CO_3 instead of NaHCO_3 .

FIGURE 4: Growth schematic of the as-synthesized ZnO microflowers.

FIGURE 5: Variations of adsorption spectra of aqueous (a) MO, (b) eosin red, and (c) CR solution in the presence of porous ZnO nanosheets; (d) degradation rate curves from different dyes at the same time, respectively.

of ZnO crystals can control the ZnO crystals to grow into the nanosheets. SDS serves as a surfactant to induce ZnCO_3 nanoparticles into the nanosheets. The ZnCO_3 nanosheets precursor is then calcined at 280°C in air for 2 h. It is found clearly that the as-synthesized product still keeps nanosheets structure, and the nanosheets possess porous structures, which may be attributed to the overflowing of SDS and CO_2 during the calcination process, which is consistent with the previous report [21, 22]. Figure 4 shows a possible growth schematic of the as-synthesized porous ZnO nanosheets.

In order to study the photocatalytic activities of ZnO nanostructures with different dye molecules, the photocatalytic degradation experiments of MO, eosin red, and CR were conducted. Figure 5(a) shows the adsorption spectra of MO solution in the presence of porous ZnO nanosheets under UV light at different time interval. The main absorption peak of MO centered at 465 nm. When the illumination time was extended to 90 min, the absorption peak diminished gradually and the photodegradation ratios of MO were up to 90%. Figure 5(b) shows UV adsorption spectra of eosin red with the absorption peak of 517 nm; nearly 97% of eosin red molecules were decomposed in 110 min. Figure 5(c) shows the absorption spectra of CR solution in the presence of ZnO microflowers under UV light; the main absorption peak of CR centered at 495 nm. When the light was turned on, the main peaks decreased continuously with increased irradiation time, indicating that the CR solution was decomposed in the present system. When the illumination time was extended to 60 min, the color of the CR solution almost disappeared, and the absorption peak corresponding to CR at 495 nm diminished tremendously with the photocatalytic degradation rate of CR of 91%. Porous ZnO nanosheets are the optimal catalysts to degrade CR than the other two dyes. In order to illustrate to which type of dye molecule ZnO nanosheets are highly selective, we take the same 60 min to compare the degradation efficiency of different dyes. The results show the order of degradation rate is eosin red (73%) < MO (75%) < CR (91%). It indicates that CR degradation efficiency is better than MO and eosin red as shown in Figure 5(d).

4. Conclusion

Nanosheet-assembled ZnO microflowers with high yield have been successfully obtained by a simple hydrothermal approach. The possible growth mechanism of the ZnO microflowers is proposed based on the experimental results. The photocatalytic degradation experiments showed that ZnO microflowers possess a high photocatalytic activity for the degradation of Congo red dyes with the degradation rate being 97% in 60 min. It is expected that such ZnO microflowers may have applications in eliminating organic pollutant in waste water.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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