Preparation and Enhanced Photocatalytic Performance of One-dimensional ZnO Nanorods

Jiilin Lin, Dongfang Wang, Da Chen, Qisheng Ge, Guangxing Ping, Meiqiang Fan, Laishun Qin, and Kangying Shu

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One dimensional (1D) ZnO nanorods were successfully synthesized via a facile solution route by refluxing borate/acetate precursors in diethylene glycol medium at 160 °C. The as-prepared ZnO nanorods were characterized by field emission scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. Experimental results demonstrated that the resultant products showed a 1D rod-like hexagonal wurtzite crystal structure with diameters of about 5 nm and lengths of up to 100–200 nm. A possible growth mechanism of ZnO nanorods was tentatively proposed. Photocatalytic measurements demonstrated that the as-prepared ZnO nanorods showed higher photocatalytic activities than the commercial photocatalyst TiO2 P25 nanoparticles. In addition, the effect of solution pH values and initial solution concentrations on the photocatalytic activities of as-prepared ZnO nanorods was also evaluated. © 2014 American Institute of Chemical Engineers Environ Prog, 34: 74–80, 2015

Keywords: ZnO nanorods, reflux process, growth mechanism, photocatalysis

INTRODUCTION

Over the past few years, the degradation of organic pollutants in wastewater has been a serious concern throughout the world. For example, methylene blue (MB), as one of the most commonly used dye pigments in the textile industry, has become one of the most common pollutants in the industrial sewage. It has high toxicity and carcinogenic character, which can result in considerable damages and threats to the ecosystem in water and human health. Because of its high stability and solubility in water, however, it is not easy to remove MB from wastewater by adsorption, chemical oxidation with strong oxidants, or biological oxidation [1–3]. Recently, metal oxide semiconductor mediated photocatalysis has emerged as an attractive route toward the mitigation of environmental pollution due to its high efficacy to degrade/mineralize a wide range of organic, inorganic, and microbial pollutants [4–9]. When an appropriate light source illuminates metal oxide semiconductor with energy equal to or greater than band-gap energy, the valence band electrons can be excited to the conduction band, leaving a positive hole in the valence band. The electron/hole pairs are thus produced. The produced electron/hole pairs can induce a complex series of reactions that might lead to the complete degradation of the organic pollutants adsorbed on the semiconductor surface.

As an important II–VI semiconductor with a wide bandgap of 3.37 eV [10], zinc oxide (ZnO) has attracted extensive attention as a promising candidate for applications in photocatalysis [11–14], light emitting diodes (LED) [15], nanogenerators [16], dye-sensitized solar cells (DSSCs) [17–19], etc. Among these applications, ZnO is being increasingly used as photocatalysts to inactivate bacteria and viruses and for the degradation of environmental pollutants such as dyes, pesticides, and volatile organic compounds under appropriate light irradiation [20–23]. As already known, the photocatalytic properties of ZnO depend on their size, morphology, and dimensionality. Therefore, development of morphologically controllable synthesis of ZnO nano- or microstructures is urgently important to answer the demand for exploring the potentials of ZnO in photocatalysis [24,25].

Until now, different shapes of ZnO nanocrystallites including wires, tubes, rods, needles, and flower-like structures have been prepared by using different synthesis methods, such as thermal evaporation, chemical vapor deposition, sol–gel method, hydrothermal synthesis, template synthesis, and so on [11,26–30]. However, most of the aforementioned methods for ZnO synthesis need the rigorous experimental conditions, high energy consumption, sophisticated equipment, and complicated process. Thus, the shape-controlled synthesis of ZnO nanocrystals, especially regarding control over the morphological structure, still remains a remarkable challenge.

It’s well conceived that the chemical solution synthesis, by thermal treatment of the reactant in different solvents, may be one of the simplest and most effective ways to prepare sufficiently crystallized materials with superior uniformity at relatively low temperatures, compared to the high temperature preparation methods such as high temperature sputtering, molecular beam epitaxy, and chemical vapor deposition. Different from the other techniques, chemical solution process has some major advantages such as preparing the powders directly from solution, ability to control the shape and the size of structures, being highly reactive and not needing calcination and milling process [31]. Thus, chemical solution process provides an easy and convenient method for preparing ZnO nanostructures with high abilities in controlling their physicochemical properties.
This work highlights the possibility of chemical solution synthesis of ZnO nanorods with enhanced photocatalytic activities for the degradation of organic dyes. In this case, ZnO nanorods were prepared via a facile chemical solution route by refluxing their acetate precursors in diethylene glycol (DEG, HO–CH₂–CH₂–O–CH₂–CH₂–OH) at a relatively low temperature. The as-prepared ZnO nanorods were characterized by using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The reaction mechanism was also investigated. In addition, the photocatalytic activities of as-prepared ZnO nanorods were also evaluated by the photodegradation of MB as a probe reaction.

EXPERIMENTAL

Synthesis of ZnO Nanorods

ZnO nanorods were prepared by refluxing zinc acetate dihydrate (ZnAc) in DEG medium. Typically, 0.05 mol ZnAc precursors and 10 mL of deionized water were added to 500 mL DEG. This solution was heated under reflux with stirring at 160°C for 1 h. White ZnO precipitates were observed shortly after reaching the reaction temperature. Then, the resulting products were collected by centrifugation, rinsed by deionized water several times, and dried in an oven at 100°C.

Characterizations

Scanning electron microscopy (SEM) images and corresponding energy-dispersive spectroscopy (EDS) were taken with a FESEM (JEOLJSM-6700F, Japan). The crystal phase identification of samples was performed on a XRD (Bruker AXS D2 PHASER, Germany) with Cu Kα radiation (λ = 0.15406 nm). The 2θ range used in the measurements was from 20° to 80° at room temperature. Specific surface areas were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (Shimadzu, Micromeritics ASAP 2010 Instrument). The UV–vis spectroscopy was determined by a UV–vis spectrophotometer (Puxi, TU–tuometer (Bruker Tensor 27, Germany). The UV–vis spectra were also measured by a UV–vis spectrometer (Shimazu Co. UV3600, Japan) equipped with integrating sphere accessory.

Photocatalytic Measurements

The aqueous suspensions of MB (5 × 10⁻³ M) was used as a model dye for the measurement of photocatalytic degradation. A paste of as-prepared ZnO nanorods or commercial TiO₂ P25 nanoparticles for the fabrication of photoelectrodes was obtained by mixing ethanol and the ZnO or P25 powder homogeneously (100 mg/mL). The obtained paste was spread on the F-doping SnO₂ (FTO) conducting glass (15 Ω/square) with a glass rod, using adhesive tapes as spacers. After the films were dried under ambient conditions, they were sintered in air at 500°C for 2 h. The film thickness measured with a profilometer was about 5 μm. For the photodegradation of MB, aqueous MB suspensions (5 × 10⁻⁵ M) and the sintered photoelectrodes (ZnO nanorods or P25 nanoparticles) were placed in a 3-mL quartz-glass vessel, and it was allowed to equilibrate for 30 min in the darkness. The photoreaction vessel was then exposed to UV–vis irradiation under ambient conditions with an average intensity of 35 mW/cm² produced by a 300-W Xenon lamp (XinGuang Technology Co., Ltd., Jiangsu, China), which was positioned horizontally 25 cm away from the vessel. The irradiance intensity was measured by a radiometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University, China). At given time intervals, the absorbance of MB solution was analyzed with a 722 visible spectrophotometer (Cany Precision Instruments Co., Ltd., Shanghai, China) by recording variations of the absorption band maximum (662 nm) in the UV–vis spectrum of MB. To study the effect of pH on the photocatalytic degradation of MB, the experiments were carried out at 5 × 10⁻³ M dye concentration with different initial pH values. The initial pH value ranging from 2 to 11 was controlled by the addition of required amounts of 0.1 M HCl or 0.1 M NaOH solution.

RESULTS AND DISCUSSION

Synthesis of ZnO Nanorods

The morphology and structure of as-prepared ZnO nanorods were studied by using SEM measurements. Low-magnification FESEM image (Figure 1a) shows the overall morphology of as-prepared ZnO nanorods, indicating that as-prepared ZnO consisted of nearly uniform nanorods. The enlarged FESEM image of ZnO nanorods (Figure 1b) shows that the as-prepared ZnO nanospheres were uniform with diameters of about 5 μm and lengths of up to 100–200 nm. As shown in the EDS pattern (Figure 1c), no other elements except Zn and O were found in the products, and the quantitative data reveal that the nanorods were made of Zn and O with atomic ratio about 1:1, indicating the high purity of obtained products.

Figure 2 shows the typical XRD pattern of the as-prepared ZnO nanorods. Clearly, all diffraction peaks were well indexed as the hexagonal wurtzite structure phase of ZnO with lattice constants of a = 3.249 Å, c = 5.206 Å (JCPDS No. 36-1451) [32], and no diffraction peaks of other impurities were detected. In addition, FTIR spectrum is an effective method to reveal the composition of the products. As shown in the FTIR spectrum of as-prepared ZnO nanorods (Figure 3), the strong absorption at about 502 cm⁻¹ was attributed to the stretching vibration of Zn=O of ZnO [33]. The two peaks at 3430 and 1642 cm⁻¹ could be attributed to O–H stretching vibration and H–O–H bending vibration, which were assigned to small amount of H₂O existing in the as-prepared ZnO nanorods. Besides, a series of weak peaks at low frequency (about 1400 cm⁻¹, 1073 cm⁻¹, 902 cm⁻¹, 658 cm⁻¹) were also found in the spectrum, which could be ascribed to the different group frequencies (the C=H bending, C–O–C stretching, O–H (out of plane) bending, and the O–C=O stretching vibration) of solvent (DEG) and the reaction byproducts (water and acetic acid) absorbed in the ZnO nanorods [34].

On the basis of the information that we have gathered from the FESEM, XRD, and FTIR studies, a possible mechanism for the formation of ZnO nanorods could be proposed. According to literature reports, the growth unit for the formation of ZnO nanorods by the alcoholysis of Zn⁴⁺ was the [Zn(OH)₄]²⁻ ion [35,36], which further underwent dehydrogenation according to the following equations (Eqs. (1–4)) to produce ZnO:

\[ \text{CH₃COOH} + \text{H}_2\text{O} \rightarrow \text{CH₃COO}^- + \text{OH}^- \] (1)
\[ 2\text{CH₃COOH} + \text{HO}^+ \rightarrow \text{CH₃COO}^- + \text{H}_2\text{O} + \text{CH₂COOH} \] (2)
\[ 4\text{OH}^- + \text{Zn}^{2+} \rightarrow \text{Zn(OH)}_{4}^{2-} \] (3)
\[ \text{Zn(OH)}_{4}^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \] (4)

In an early stage, as this dehydration reaction progressed, more and more ZnO clusters were formed in the solution. When the supersaturation state was attained in the reaction medium, nucleation started and the ZnO clusters were self-assembled to aggregate into thermodynamically stable (lower surface energy) quasi rod-shaped ZnO seeds (ZnO...
intermediates). Furthermore, as soon as the primary nanocrystallites (seeds) were formed, they rapidly assembled to give larger, more-stable secondary aggregates during a ripening process. In our case, these secondary aggregates of ZnO finally formed ZnO nanorods.

Photocatalytic Activities

The photocatalytic activities of the as-prepared ZnO nanorods and P25 TiO₂ nanoparticles were evaluated by measuring the decomposition of MB as a model reaction, and the results are given in Figure 4. The UV–visible absorption spectrum (Figure 4a) provided the spectral changes accompanying the photodegradation of MB over the as-prepared ZnO nanorods. The MB dye initially showed a major absorption peak at 662 nm, which decreased gradually with the temporal evolution of light irradiation, and the absorbance peak completely disappeared after 120 min of irradiation. This course was consistent with the solution color changed from blue to nearly transparent, since the chromophoric structure of the MB was easily destructive. Figure 4b illustrated the temporal concentration changes of MB solution catalyzed by the as-prepared ZnO nanorods and P25 TiO₂ nanoparticles, respectively. Here, \(C/C_0\) was used instead of \(A/A_0\) because the normalized concentration of the solution \((C/C_0)\) was proportional to the normalized maximum absorbance \((A/A_0)\) according to the Beer–Lambert law. A satisfactory fitting was clearly observed in photodegradation processes, confirming the quasi-first-order-type kinetics. It was evidenced by the linear plot of \(\ln(C/C_0)\) versus reaction time, \(-\ln(C/C_0) = Kt\), where \(K\) was the rate constant of the degradation. In this case, \(K\) was calculated to be 0.0346, 0.0261 min⁻¹ for the as-prepared ZnO nanorods and the P25 TiO₂ nanoparticles, respectively. Apparently, the photocatalytic activity of ZnO nanorods was higher than that of P25 TiO₂ nanoparticles.

A factor contributing to the enhanced photocatalytic activity of as-prepared ZnO nanorods was its higher specific surface (127 m²/g, calculated from BET results), compared to 53 m²/g of the P25 TiO₂ nanoparticles. The higher specific
surface area would be responsible for providing the higher adsorption ability of the catalytic surface toward target molecules and the higher ability of generating photoinduced electron–hole pairs of active sites. The enhanced photocatalytic activity of as-prepared ZnO nanorods could be further ascribed to the enhanced optical absorption spectral response range in the UV–visible region, which arises from the optical bandgap of the semiconductor photocatalyst. It is known that the optical band-gaps of semiconductor nanoparticles can be calculated from the DRS measurement by plotting the square of the Kubelka–Munk function ($F(R)^2$) vs. energy in electron volts. In the present work, according to the plot of $F(R)^2$ vs. $hv$ shown in Figure 5, the band-gap energy of as-prepared ZnO nanorods was calculated to be $3.32 \text{ eV}$, which was less than that of P25 TiO$_2$ nanoparticles (3.42 eV) [37]. This indicated that ZnO nanorods could possess enhanced optical absorption spectral response range in the UV–vis region compared to P25 TiO$_2$ nanoparticles, which might lead to the enhancement of the photocatalytic activity. Moreover, the enhancement in photocatalytic activities could be also ascribed to the unique one-dimensional (1D) structure of ZnO nanorods, which could improve the electron transport and reduce the recombination of photogenerated electron–hole pairs.

In addition, the effect of the solution pH values on the photodegradation of MB was investigated. It is known that the solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic reactions [38,39]. The effect of pH on MB photodegradation was studied by keeping all other experimental conditions constant and changing the initial pH value of the MB solution from 2.8 to 11.5, and the results are illustrated in Figure 6a and Table 1. As can be seen, the degradation rate constant ($K$) increased with the increase of the solution pH value from 2.8 to 6.3 and then decreased. Since the isoelectric point value of ZnO is about 9.5 [40], the surface of the photocatalyst is positive below pH 9.5. Again the given pKa for MB is 0 to 1 [41]; therefore MB is negatively charged above pH 1 that might result in electrostatic attraction between the ZnO photocatalyst and MB. This will increase both the dye adsorption and the degree of photodegradation. Unfortunately, the mere electrostatic argument is unable to exhaustively account for the relative photocatalytic behavior as a function of pH. Other concomitant effect can come into play. For example, ZnO can undergo photo-corrosion through self-oxidation (Eq. 5). In particular, ZnO powders exhibit tendency to dissolve with decreasing the pH (Eq. 6).

$$\text{ZnO} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O} \quad (6)$$

In a strongly alkaline environment, ZnO can undergo dissolution according to the following reaction [42]:

$$\text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \quad (7)$$

Therefore, the reduction of photocatalytic activity of ZnO at exceedingly low and high pH values can originate from either acidic/photochemical corrosion of the catalyst (Eqs. 5 and 6), from alkaline dissolution (Eq. 7). In addition, reactions 5 and 7 can compete with the formation of hydroxyl radicals by decreasing the availability of holes for water or surface OH$^-$ oxidation.

Moreover, the effect of various initial MB concentrations on the photocatalytic degradation of MB was also investigated. The results are shown in Figure 6b, and summarized

**Figure 4.** (a) UV–visible absorption spectral changes of MB aqueous solution over the as-prepared ZnO nanorods as a function of irradiation time (curves from top to bottom represent different irradiation times: 0 min, 10 min, 30 min, 60 min, 120 min, respectively). (b) Absorption changes ($\lambda = 662 \text{ nm}$) plot for the photocatalytic degradation of MB with ZnO nanorods and P25 TiO$_2$ nanoparticles. ($C/C_0$ is the normalized concentration of the solution).

**Figure 5.** UV–vis DRS of as-prepared ZnO nanorods (inset: the plot of $F(R)^2$ vs. $hv$ obtained from reflectance).
As can be seen, the degradation rate constant \( K \) decreased with the increase of the MB concentration from \( 2 \times 10^{-5} \) M to \( 1 \times 10^{-4} \) M in 120 min of UV irradiation, indicating the decrease of dye degradation with the increase of the dye concentration. This might be closely related to the attachment of dye molecules on the surface of the photocatalyst. With increasing dye concentration, more organic substances would be covering the active sites of ZnO. As the intensity of light and irradiation time are constant, so there will be less number of photons reaching the catalyst surface. Less \( \cdot OH \) radicals will be formed and subsequently the relative number of \( \cdot OH \) radicals that attack the compound also decreases. Thus, an inhibitive effect in photodegradation is anticipated. Another possible cause for such results is the UV-screening effect of the dye itself. A significant amount of UV may be absorbed at a high dye concentration by the dye molecules rather than the ZnO particles, which can further reduce the efficiency of the catalytic reaction.

**CONCLUSIONS**

In this work, ZnO nanorods were successfully prepared through a facile refluxing method at a relatively low temperature. Experimental results showed that the as-prepared ZnO nanorods had a 1D rod-like hexagonal wurtzite crystal structure with diameters of about 5 nm and lengths of up to 100–200 nm. A possible growth mechanism of ZnO nanorods was tentatively proposed. In addition, the photocatalytic activity of the as-prepared ZnO nanorods was also investigated. It was demonstrated that the photocatalytic activity of ZnO nanorods was significantly higher than that of commercial photocatalyst P25 TiO \(_2\) nanoparticles. This enhancement could be ascribed to, on the one hand, an increase of the surface area, which could enhance the light harvest and the ability of generating photoinduced electron–hole pairs of active sites and, on the other hand, the decreased band-gap energy and the favorable electron-transfer properties of the as-prepared 1D ZnO nanorods. The effect of the solution pH values and initial MB solution concentrations on the photocatalytic activities of ZnO nanorods was also presented. It was found that the photocatalytic activities of ZnO nanorods increased with the increase of the solution pH value from 2.8 to 6.3 and then decreased, and decreased with the increase of the MB concentration from \( 2 \times 10^{-5} \) M to \( 1 \times 10^{-4} \) M in 120 min of UV irradiation.

**Table 1.** Summary on the effect of the solution pH values on the photodegradation of MB.

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution pH value</th>
<th>Initial MB concentration, ( C_0 ) (mol/L)</th>
<th>Final MB concentration, ( C_t ) (mol/L)</th>
<th>Removal of MB (%)</th>
<th>Degradation rate constant, ( K ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.8</td>
<td>( 5 \times 10^{-5} )</td>
<td>( 1.79 \times 10^{-6} )</td>
<td>96.42</td>
<td>0.0281</td>
</tr>
<tr>
<td>2</td>
<td>5.2</td>
<td>( 5 \times 10^{-5} )</td>
<td>( 8.88 \times 10^{-7} )</td>
<td>98.22</td>
<td>0.0343</td>
</tr>
<tr>
<td>3</td>
<td>6.3</td>
<td>( 5 \times 10^{-5} )</td>
<td>( 6.58 \times 10^{-7} )</td>
<td>98.68</td>
<td>0.03529</td>
</tr>
<tr>
<td>4</td>
<td>8.6</td>
<td>( 5 \times 10^{-5} )</td>
<td>( 2.16 \times 10^{-6} )</td>
<td>95.68</td>
<td>0.02698</td>
</tr>
<tr>
<td>5</td>
<td>11.5</td>
<td>( 5 \times 10^{-5} )</td>
<td>( 4.94 \times 10^{-6} )</td>
<td>90.11</td>
<td>0.02032</td>
</tr>
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</table>

**Table 2.** Summary on the effect of initial MB concentrations on the photocatalytic degradation of MB.

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial MB concentration, ( C_0 ) (mol/L)</th>
<th>Final MB concentration, ( C_t ) (mol/L)</th>
<th>Removal of MB (%)</th>
<th>Degradation rate constant, ( K ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 2 \times 10^{-5} )</td>
<td>( 1.948 \times 10^{-7} )</td>
<td>99.03</td>
<td>0.03629</td>
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<tr>
<td>2</td>
<td>( 5 \times 10^{-5} )</td>
<td>( 8.03 \times 10^{-7} )</td>
<td>98.39</td>
<td>0.03463</td>
</tr>
<tr>
<td>3</td>
<td>( 8 \times 10^{-5} )</td>
<td>( 1.92 \times 10^{-6} )</td>
<td>97.6</td>
<td>0.03223</td>
</tr>
<tr>
<td>4</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 6.11 \times 10^{-6} )</td>
<td>93.89</td>
<td>0.02464</td>
</tr>
</tbody>
</table>
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LITERATURE CITED


