Facile Synthesis of Nanocrystalline Wurtzite ZnO and its Application for Photodegradation Activity

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ABSTRACT

Nanocrystalline wurtzite ZnO was successfully prepared by a facile low-temperature co-precipitation method. The crystalline phase of synthesized sample was characterized by X-ray diffraction (XRD). The absorption spectra and optical band gap were determined by Diffused Reflectance UV-visible Spectroscopy. The morphology and microstructure were characterized by Scanning Electron Microscope and Transmission Electron Microscopy. XRD result of as-prepared ZnO photocatalyst are corresponded to hexagonal wurtzite structure. This evidence can confirm that a facile co-precipitation is successfully and reproducibility. The specific surface area of ZnO sample was significantly higher than commercial ZnO. The photocatalytic degradation of methyl orange and methomyl were investigated over ZnO aqueous solution under UV light irradiation. Methomyl was degraded 54.27% in 60 min.

INTRODUCTION

Zinc oxide (ZnO) is a promising semiconductor which has been found broad application in many fields, such as dye-sensitized solar cell [1], biosensor [3], and photocatalyst [5], because of its low cost and chemical stability, large band gap energy (3.37 eV). In the past decades, various methods have been developed for the preparation of high crystalline nanostructured ZnO [6]. Compared to hydrothermal [9] and sol-gel method [10], co-precipitation route is very effective for the synthesis of ZnO due to the much lower cost together with easy equipment, low temperature, environmental compatibility, solvent-free and surfactant useless process [11]. Moreover, the ZnO nanostructures prepared by a facile co-precipitation method at low thermal process at only 80 °C can obtain high quality crystal structure and high specific surface area (S\text{BET}). In the present work, ZnO nanocatalyst synthesized by a facile low-temperature method was investigated for the photocatalytic degradation of methomyl (MT) in aqueous solution under UV light irradiation.

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MATERIALS AND METHODS

Nanocatalyst Preparation

All Chemicals used in this work are analytical grade and without further purification. ZnO nanocatalyst was synthesized by low-temperature co-precipitation method. The molar ratio of Zn/OH was kept at 1:4. Firstly, Zn(CH₃COO)₂.2H₂O was dissolved in 100 mL of deionized water (0.2 M) and vigorously stirred at 40°C until a clear solution was obtained. Then, 0.8 M NaOH was slowly dropped into the above solution with constant stir. Then, the pH of the solution was adjusted to 10. Secondly, the mixture was heated at 70°C for 2 h. The obtained suspension was then centrifuged and dried in at 60°C for 24h.

Sample Characterization

The phase crystallinity was characterized by PANalytical X'Pert PRO XRD diffractometer (Cu–Kα radiation and λ = 0.15401). The morphology were performed by using a Phillipse S-4800 Field Emission Scanning Electron Microscopy with energy-dispersive X-ray spectroscopy analysis (SEM-EDX,) and JEM-2010 Transmission Electron microscope (TEM). Diffused reflectance spectrum were analyzed by a Shimazu UV-3101PC. The S_BET was determined by a Micromeritics Tristar 3000 surface area analyzer (BET method).

Photocatalytic Experiments

The photocatalytic degradation performance of methomyl (MT) was studied using aqueous ZnO solution under UV illumination (8 Watt UV lamp). The photolysis activity of the commercial ZnO (S_BET15.0 m²/g) was also investigated for comparison. Prior irradiation, a 1.0 g/L of ZnO catalyst dissolving in 20 ppm of MT was constantly stirred for 30 min in the dark condition until the adsorption equilibrium was obtained. After the light on, a 4 mL of suspension was withdrawn, filtered by a 0.22 µm Millipore filter, and the amount of MT was determined by using a PG instrument T92 UV-vis spectrophotometer at ~234 nm.

RESULTS AND DISCUSSION

XRD Analysis

XRD diffraction pattern of ZnO sample is shown in Fig. 1. The 2θ of as-prepared ZnO sample at 31.7°, 34.4°, 36.3°, 47.5°, 56.6° and 62.9° were corresponded to (101), (002), (100), (102), (110), (103), and (112) indexing to wurtzite structure (JCPDS 36-1451) [13]. The narrow and sharp of diffraction peaks indicated the well crystallite of the ZnO particles and also confirmed the success and reproducibility of a facile method in present work [14]. In addition, the average crystallite size of ZnO are calculated using Scherrer’s equation as Equation (1) below,

\[ L = \frac{k\lambda}{\beta \cos \theta} \] (1)
where $k$ is 0.89, $\lambda$ is X-ray wavelength (1.541 nm), $\beta$ is full width half maximum intensity (FWHM) in radian and $\theta$ is the half diffraction angle in degree [15]. The calculated crystallite size of ZnO was 44.23 nm. $S_{BET}$ of ZnO sample was 29.35 m$^2$/g. The high value of $S_{BET}$ of ZnO might be the main factor to explain the more adsorption of the organic pollutants on ZnO surface, leading to the enhanced photocatalysis efficiency [16].

![XRD pattern of prepared ZnO](image1)

**Figure 1.** XRD pattern of prepared ZnO.

**Optical Response**

![Kubelka-Munk absorbance spectra of prepared ZnO, commercial ZnO](image2)

**Figure 2.** Kubelka-Munk absorbance spectra of prepared ZnO, commercial ZnO and the inset band gap energies of samples.

Diffuse reflectance spectra (DR-UV-vis) of commercial ZnO, and prepared ZnO are shown in Fig. 2. The absorption spectra were examined by calculating the reflectance measurement with Kubelka-Munk emission function Equation (2) and the band gap of the sample is obtained by Equation (3) as below,

$$F(R_\infty) = [1 - (R_\infty)]^2/2R_\infty$$  \hspace{1cm} (2)

$$E_g = 1241/\lambda \text{ and } [F(R_\infty)h\nu]^{1/2}$$  \hspace{1cm} (3)
where $E_g$ is band gap energy, $h$ is Planck’s constant, and $\nu$ is frequency of vibration, respectively [18]. As shown in Fig. 3, the absorption edge of $\sim 386$ nm whereas commercial ZnO reveals the absorption onset of $\sim 380$ nm. From Equation 3 and the inset of Fig. 3, the optical band gap energy of prepared ZnO and commercial ZnO were $\sim 3.14$ and $\sim 3.21$ eV, respectively.

Morphology

The SEM images of ZnO presented an aggregated rod structure with different rod sizes in the range of 100-200 nm (Fig. 3(a,b)). EDS spectra showed the presence of Zn and O elements in the sample (Fig. 3(c)). The primary particle size of ZnO exhibited uncertain rod shape of nanoparticles with the size of 40-50 nm. In addition, particle size values from TEM (Fig. 3(d)) are nearby to the crystallite size calculated by Scherrer equation from XRD result. The selected area electron diffraction pattern (SAED) inset in Figure 3d showed separated diffraction rings, indicating that the ZnO sample is polycrystalline [17].

Photocatalytic Activity Study

Photoactivity of the prepared ZnO was evaluated by testing the photocatalytic degradation of MT under UV irradiation. The absorption changes of MT during the photocatalysis is shown in Fig. 4(a). The absorption peaks of MT decreased consequently under UV light illumination. The photocatalytic degradation over commercial ZnO and direct photolysis were also investigated for comparison purpose. As seen from Fig. 4(b), only 18.72% and 23.85% mineralized over direct photolysis and commercial ZnO, respectively. On the other hand, the prepared ZnO showed significant higher degradation performance than commercial ZnO. The photocatalytic degradation efficiency increased to 54.27% with the use of prepared ZnO within 60 min. This is possibly due to high crystallinity of ZnO, regular shape, higher $S_{BET}$ as evidence results [20]. In addition, it can be implied that the adsorbed MT molecules on respectively.
CONCLUSIONS

The wurtzite ZnO nanostructure was successfully synthesized by a low-temperature co-precipitation route. The high crystallite crystal nanorod and high $S_{\text{BET}}$ can confirmed the reproducibility of this method. The high photocatalytic degradation efficiencies of MT over prepared ZnO nanocrystalline semiconductor reveals that this method are can be utilized for preparing high quality ZnO photocatalyst.

![Figure 4.](image)

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