

Synthesis of visible light-responsive Cu₂O/ZnO nanocomposite via a facile one-pot route

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A facile one-pot route for synthesizing the visible-light-driven Cu₂O/ZnO nanocomposites has been developed in our work. The as-synthesized samples are characterized by X-ray powder diffraction (XRD). The results show that their phase composition, crystallinity and the crystal size are affected by the reaction temperature, the reaction time and the initial Cu²⁺ concentration. The UV–Vis absorption spectroscopy measurement shows that the optical activity of the as-synthesized Cu₂O/ZnO nanocomposite is changed compared with that of pure ZnO, exhibiting enhanced absorption in the visible light range, which would be hopeful for more practical applications in future photocatalysis.

(Received September 2, 2013; accepted September 11, 2014)

Keywords: Nanocomposites, Cu₂O/ZnO, Visible light-responsive, One-pot route

1. Introduction

The semiconductor photocatalysis technology has attracted extensive attention because of its potential applications in water splitting, water and air purification under light irradiation. As is known to all, ZnO like TiO₂ has been considered to be a desirable material for photocatalytic reaction due to its high photocatalytic activity, low cost and non-toxic, etc. However, ZnO is an n-type semiconductor with a direct band-gap of 3.37 eV, which can only respond to UV light accounting for a small fraction of the solar spectrum, and thus has limitation in the practical applications of photocatalysis using solar energy. Hence various methods such as doping with nonmetals or transition metals, coupling with other semiconductors and depositing noble metal [1-6] have been attempted to extend the photoresponse of the ZnO to the visible region in the last few years. Among these attempts, the coupling of ZnO with narrow-band-gap semiconductors [7, 8] is an interesting approach, which will expand effectively the spectral responsive range to visible light and achieve as highly efficient photocatalytic reactivities as possible under solar light irradiation.

Cu₂O is a typical p-type semiconductor with a narrow band gap of about 2.17 eV and has potential applications in solar-energy conversion, and visible-light-responsive photocatalysis [9–13]. P-Cu₂O coupled with n-ZnO can form a p-n junction between Cu₂O and ZnO, which can efficiently facilitate the separation and transport of charge carriers. Because of the

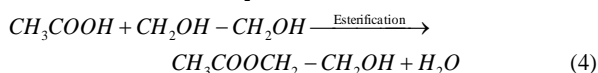
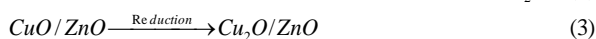
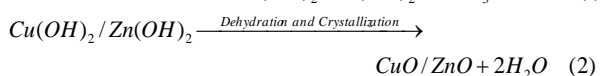
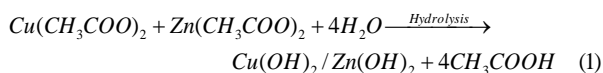
matching of the band structure between Cu₂O and ZnO, photogenerated electrons are transferred from the conduction band (CB) of Cu₂O to the CB of ZnO, and the built-in electric field originated from the Cu₂O/ZnO heterojunction also favors the separation of photogenerated electron–hole. Accordingly, it is expected that Cu₂O/ZnO nanocomposite will achieve the remarkable visible-light photoresponse, the highly efficient photoexcited charge separation and enhanced photocatalytic efficiency [14–18].

Cu₂O/ZnO nanocomposite has been successfully prepared by the previous approaches. However, the typical synthesis processes are generally two or more steps, and are not convenient. A very simple method for synthesis of Cu₂O/ZnO nanocomposite has been developed in our laboratory. Our novel method employs the ethylene glycol as the solvent and the reducing agent through ethylene glycol-mediated solvothermal reduction in the homogeneous hydrolysis processes of Zn(CH₃COO)₂·2H₂O and Cu(CH₃COO)₂·H₂O to get Cu₂O/ZnO nanocomposite. The synthetic process is a facile one-pot way with no additional steps, which is more convenient. In addition, we have investigated the phase composition, the crystallite size and optical activities of the as-synthesized composites.

2. Experimental

All solvents and reagents used in this study were of analytical grade quality. In a typical procedure, a given amount of Zn(CH₃COO)₂·2H₂O and Cu(CH₃COO)₂·H₂O

were firstly dissolved in 80ml ethylene glycol under vigorously stirring, and the resulting solution was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. Subsequently, the sealed autoclave was heated at a given temperature for a certain time, and naturally cooled to room temperature. Finally, the as-synthesized products were isolated by centrifugation, washed with ethanol for several times, dried in vacuum at 80 °C for 6 h and stored in a desiccator. The proposed synthetic route for the formation of the product was represented by the following chemical equations:



The crystal phase composition and the crystallite size of the synthesized samples were determined by the X-ray powder diffractometer (A Bruker D8 ADVANCE) using Cu K α radiation ($\lambda = 0.15406$ nm), at 40 kV and 40 mA over the 2θ range 20–80°. The UV–Vis diffuse reflectance spectra of the samples were obtained on a UV–Vis spectrophotometer (TU-1901, Beijing Purkinje General Instrumental Co., China).

3. Results and discussion

The X-ray powder diffraction patterns of the samples synthesized in different initial Cu^{2+} concentration are showed in Fig. 1. It is obviously seen that all the diffraction peaks of the as-synthesized samples are well assigned to the crystal planes of hexagonal phase ZnO (JCPDS Card No. 36-1451) with lattice constant of $a = b = 3.25$ Å and $c = 5.207$ Å and cubic phase Cu_2O (JCPDS Card No. 05-0667) with lattice constants of $a = b = c = 4.27$ Å. Furthermore, no characteristic peaks of impurities are observed. It reveals that the as-prepared samples are pure $\text{Cu}_2\text{O}/\text{ZnO}$ composites, and CuO can be efficiently reduced by ethylene glycol to Cu_2O . In Fig. 1, we also see that the intensities of diffraction peaks of ZnO decrease with increasing of the initial Cu^{2+} concentration, while those of Cu_2O increase. In addition, the mean crystallite sizes of Cu_2O and ZnO are separately calculated from the Scherrer equation, with ca. 26.2, 21.5, 17.3 and 13.1 nm for Cu_2O , ca. 18.7, 16.5, 15.3 and 14.2 nm for ZnO corresponding to the initial Cu^{2+} concentrations of 0.05, 0.1, 0.2 and 0.3 mol/L, respectively, showing decrease with increasing the initial Cu^{2+} concentration. The results can be explained as

follows: With increasing the initial concentration of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, the nucleation rate is greater than the growth rate during the hydrolysis reaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. At the same time, the increase of Cu_2O content restrains the crystallite growth of ZnO.

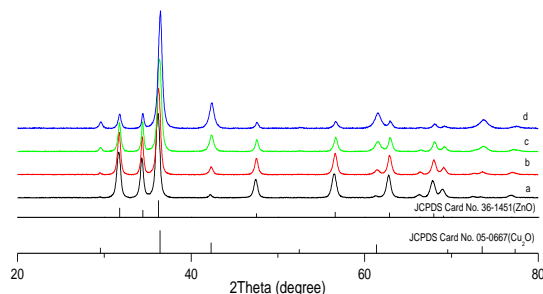


Fig. 1. XRD patterns of the samples synthesized at 160 °C for 10 h with different initial Cu^{2+} concentration: (a) 0.05 mol/L, (b) 0.1 mol/L, (c) 0.2 mol/L and (d) 0.3 mol/L.

Fig. 2 displays the XRD patterns of the samples synthesized at different reaction temperatures for 10 h with the initial concentrations of 0.5 mol/L $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ and 0.05 mol/L $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. It can be seen that the crystallization degrees of ZnO and Cu_2O increase significantly as the reaction temperature rises. Moreover, the mean crystallite sizes of Cu_2O and ZnO calculated according to the Scherrer equation also show the increasing trends at elevated temperatures, that is, the mean crystallite sizes of Cu_2O increase from 16.7 to 26.2 nm and ZnO from 11.3 to 18.7 nm corresponding to the reaction temperatures of 130 up to 160 °C. Besides, we find that the diffraction peaks of metallic copper (Cu) appear in the XRD patterns of the samples synthesized at the temperature above 170°C, indicating that part Cu_2O is further reduced to Cu.

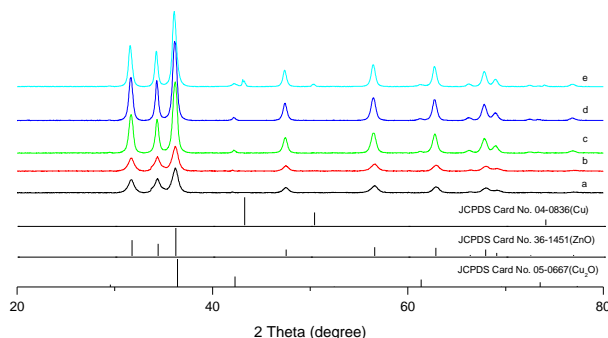


Fig. 2. XRD patterns of the samples synthesized at different reaction temperature: (a) 130 °C, (b) 140 °C, (c) 150 °C, (d) 160 °C and (e) 170 °C.

Fig. 3 shows the XRD patterns of the samples synthesized at 150°C for a certain time with the initial concentrations of 0.5 mol·L⁻¹ $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ and

0.05 mol·L⁻¹ Cu(CH₃COO)₂·H₂O. We can see that the intensities of the diffraction peaks of the as-synthesized samples slightly increase with the increasing of reaction time. Similarly, the mean crystallite sizes of the Cu₂O and ZnO gradually increase with the increasing of reaction time, with ca. 19.8, 23.6, 24.3 nm for Cu₂O and ca. 16.4, 17.3, 18.1 nm for ZnO corresponding to the reaction times of 10, 16 and 24 h, respectively. The results demonstrate that the crystal growths of ZnO and Cu₂O in as-synthesized composites are controlled by the prolongation of reaction time.

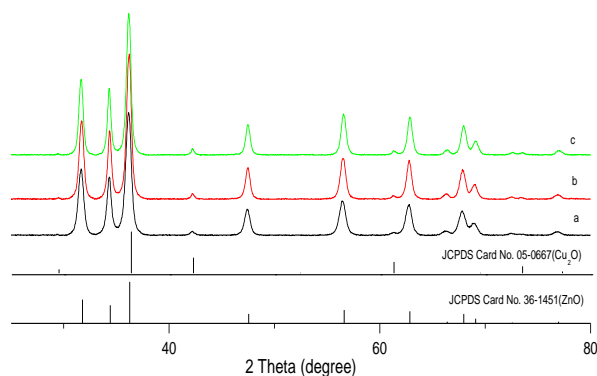


Fig. 3. XRD patterns of the samples synthesized with different reaction time: (a)10h, (b)16h and (c)24h.

Expecting to offer enhanced optical absorption properties, we have investigated the optical properties of the synthesized samples. The UV-Vis absorption spectrum of Cu₂O/ZnO sample synthesized at 160 °C for 10 h with the initial Zn²⁺ concentration of 0.5 mol/L and the initial Cu²⁺ concentrations of 0.2 mol/L is given in Fig. 4. For comparison purposes, those of ZnO and Cu₂O samples are also given in Fig. 4. In Fig. 4, the absorption spectra show that the Cu₂O/ZnO nanocomposite can absorb not only ultraviolet light like pure ZnO but also the considerable amounts of visible light (>400 nm) like the traditional pure Cu₂O. Moreover, the Cu₂O/ZnO nanocomposite has stronger absorption than Cu₂O in ultraviolet light area and ZnO in visible light area, suggesting its enhanced activity for more practical applications in photocatalysis.

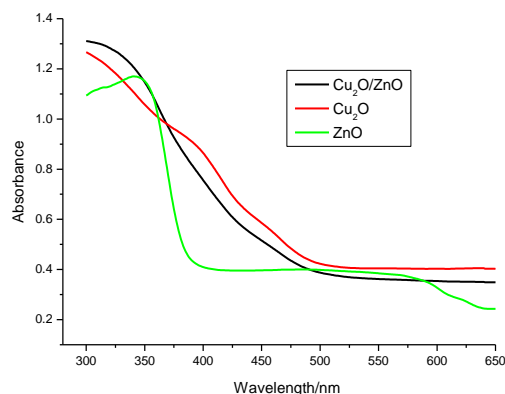


Fig. 4. UV-Vis absorbance spectra of different samples.

4. Conclusions

In this work, the visible-light-driven Cu₂O/ZnO nanocomposites have been successfully synthesized via a simple one-pot method. The phase composition, crystallinity and the crystallite size of as-synthesized composites have been investigated. The results show that the composition and crystallite sizes are controlled by the initial concentrations of Cu²⁺, the reaction temperature and the reaction time. In addition, the initial concentrations of Cu²⁺ have an effect on the crystallinity of ZnO, that is, the crystallinity of ZnO decreases with increasing the concentration of Cu²⁺. UV-Vis diffuse reflectance analysis exhibits that the visible light absorption of the as-synthesized Cu₂O/ZnO nanocomposites greatly improves.

Acknowledgments

This work is financially supported by Anhui Provincial Natural Science Foundation (No. 1208085MB30), Natural Science Foundation of Anhui Provincial Department of Education (Nos. KJ2013A231, KJ2014A230, and KJ2010A302).

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