



Preparation and Photocatalytic Activity of ZnO/CdS Core/Shell Structure Nanopowders†

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Zinc oxide nanopowders were prepared by a polyacrylamide-gel method, ZnO/ZnS and ZnO/CdS core/shell structure nanopowders were prepared by ion-exchange method, respectively. The as-prepared samples were characterized by X-ray diffraction, high resolution transmission electron microscopy (HRTEM). The results indicate that the hexagonal phase CdS nanoparticles grow on the surfaces of Wurtzite structure ZnO particles to form core/shell structure. The photocatalytic activities of the ZnO/CdS core/shell structure nanopowders were evaluated by degradation of methyl orange under UV, solar light and solar-simulated light irradiation. The results show that ZnO/CdS core/shell structure nanopowders exhibit an appreciable photocatalytic property, especially under UV and solar light irradiation.

Keywords: ZnO, CdS, Core/shell structure, Photocatalytic activity.

INTRODUCTION

Zinc oxide (ZnO) is deemed to be one of the most important semiconductor photo-catalysts because of its high photosensitivity and stability. However, ZnO itself is a wide bandgap (3.2 eV) semiconductor, which is disadvantageous in regarding to the absorption of radiation in the visible light region of the solar spectrum. Thus, ZnO has been sensitized by incorporation with various narrow band-gap materials. One of the most well-known semiconductor photocatalyst, CdS, is an interesting visible light sensitive photocatalyst material owing to its narrow band gap (2.4 eV). Therefore, several methods have been used to prepare CdS sensitized ZnO composites, such as chemical bath deposition¹, successive ionic layer adsorption and reaction (SILAR)², sol-gel³ and microwave assist method⁴. However, those methods are difficult to form a uniform CdS layer on the ZnO and the contact of CdS quantum dots and ZnO is incompact, which will inhibit the charge transfer easily from CdS to ZnO. In the present work, CdS was used as photosensitizer in ZnO-based composite to enhance visible light photocatalytic efficiency. The ZnO/CdS core/shell structure nanopowders were prepared *via* a two steps ion-exchange method. Moreover, the photocatalytic activities of ZnO/CdS core/shell structure nanopowders were examined.

EXPERIMENTAL

All chemical reagents were analytical grade without further purification. Deionized water was used throughout this experimental study.

Synthesis of ZnO nanopowders: ZnO nanopowders were synthesized by polyacrylamide-gel method. 2.2 g of zinc acetate was dissolved in 50 mL deionized water, then 0.2 g N,N'-methylene diacrylamide and 1 g acrylamide were added to the zinc acetate solutions under constant stirring. The polymerization was promoted by the addition of a small amount of ammonium persulfate as the initiator, subsequently. After heating at 80 °C for 2 h, the mixed solution was converted to gel and then dried at 100 °C for 4 h. The dried gel was annealed at 550 °C for 8 h and slowly cooled to the room temperature to obtain a white powder (A powder).

Synthesis of ZnO/ZnS and ZnO/CdS core/shell structure nanopowders: To prepare the ZnO/ZnS core/shell structure nanopowders, ion-exchange method was used. 0.1 g as-prepared ZnO nanopowders and 5.90 g Na₂S·9H₂O were added into 50 mL deionized water, continuously magnetic stirring for 6 h. The product was then collected by centrifugation, repeatedly washed with water and absolute ethanol and finally dried at 60 °C for 4 h. Thereafter, a white powder was prepared (B powder).

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To prepare ZnO/CdS core/shell structure nanopowders, the metal cation exchange process of ZnS to CdS was initiated by transferring the as-prepared ZnO/ZnS core/shell structure nanopowders into a 50 mM aqueous cadmium nitrate solution for 15 min at 90 °C. Then the sample was washed to obtain a yellow powder (C powder).

Photocatalytic experiment: Methyl orange was chosen as the model organic dye to evaluate the photoactivity of the prepared ZnO/CdS core/shell structure nanopowders. A 30W UV lamp, a 300W Xe lamp (solar-simulated light) and the solar light (on May 22, 2013, sunny, the highest temperature of 31 °C) were used as the light source. 100 mg the ZnO/CdS core/shell structure nanopowders were added into 50 mL 20 mg/L methyl orange solution to form a mixture. Before the irradiation, the solution was stirred for 15 min to reach adsorption equilibrium. Then the solution was exposed to light irradiation at room temperature. The methyl orange solution was taken 5 mL away at regular intervals to test the transmittance of methyl orange ($\lambda = 460$ nm) during the reaction procedure using 721 spectrophotometer.

Absorbency and degradation rate were calculated by using the following formula:

$$A = -\log T \quad (1)$$

$$D (\%) = \frac{(A_0 - A_t)}{A_0} \times 100 \% \quad (2)$$

where T is transmittance, A is absorbency, A_0 is absorbency of undegraded methyl orange solution, A_t is absorbency of degraded methyl orange solution after the corresponding time, D % is degradation rate of methyl orange solution after the corresponding time.

Analytical methods: Structural characterization of the as-prepared samples was performed by means of XRD (Model Y2000) with $\text{CuK}\alpha$ radiation. Their morphology was observed by HRTEM (JEM-2010).

RESULTS AND DISCUSSION

Characterization of ZnO and core/shell structure ZnO/ZnS nanopowders: Fig. 1 shows the XRD patterns of pure ZnO (A powder) and ZnO/CdS (B powder). The diffraction peaks of the ZnO sample as shown in Fig. 1(a) can be identified to be as same as the literature data in JCPDS No. 36-1451, showing that the Wurtzite (hexagonal) structure ZnO synthesized with a good crystallinity and no impurity phases. The average nanocrystallites size of pure ZnO powders is calculated from full width at half maximum of major XRD peaks using Scherrer's formula and the value is 17 nm. Fig. 1(b) shows the XRD pattern of the ZnO/ZnS powders, in which the diffraction peaks (111), (2 20) and (311) can be well indexed to cubic ZnS (JCPDS No. 05-0566). An obvious broadening of the diffraction peaks is observed, indicating the ZnS formed by small crystalline grains. In addition to ZnS, characteristic diffraction peaks corresponding to hexagonal ZnO is also observed, indicating the ZnS formed on the surface of ZnO. Here, the growth mechanism of ZnS shell on ZnO core is proposed: sodium sulphide hydrolyze and release H_2S in the aqueous solution, which is easy to react with ZnO at the interface of the ZnO particles to produce ZnS nuclei. With

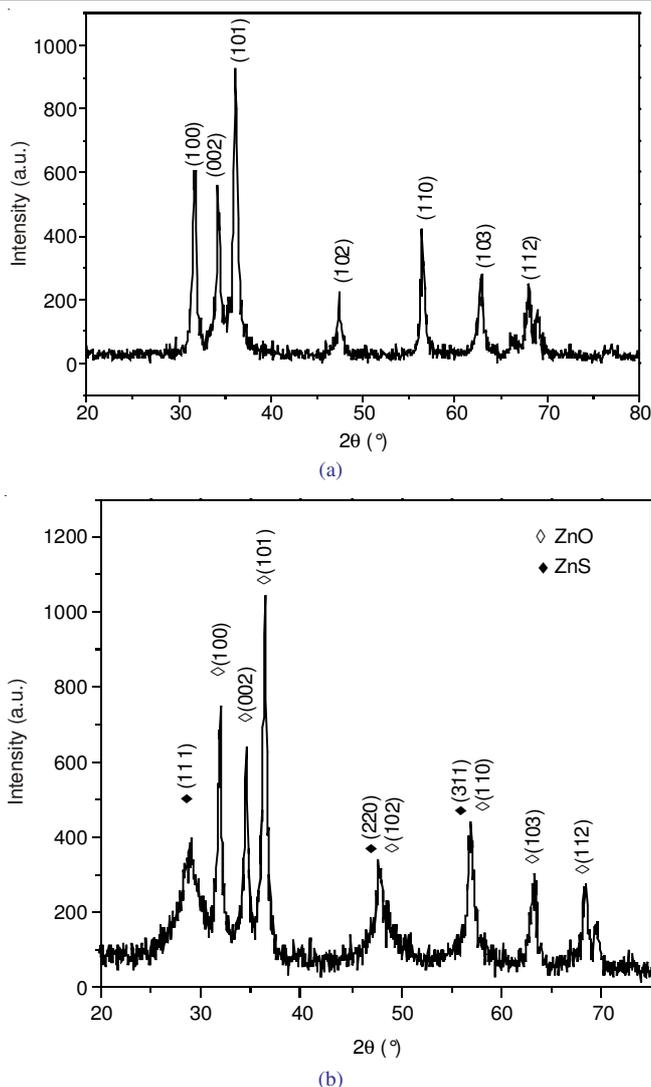


Fig. 1. (a) XRD pattern of the obtained ZnO nanopowders. (b) XRD pattern of the obtained ZnO/ZnS core/shell structure nanopowders

increasing the reaction time, the ZnS nuclei grow larger and larger to form ZnS shells on the ZnO particles for realizing the synthesis of ZnO/ZnS core/shell nanostructure.

Characterization of ZnO/CdS core/shell structure nanopowders: Fig. 2(a) shows the X-ray diffraction (XRD) pattern of the ZnO/CdS powders (C powder). The XRD pattern shows both wurtzite phase ZnO and hexagonal phase CdS (JCPDS No. 41-1049) coexist in the composites, indicating the CdS phase (golden yellow) formed on the surface of ZnO substrate, as shown in Fig. 2(b). Therefore, the ZnO can be transformed into ZnS and further transform into CdS after two steps ion-exchange procedure.

HRTEM images of ZnO/CdS core/shell structure nanopowders are shown in Fig. 2(c) and (d). The apparent contrast between the inner core and the outer shell of the sample is clearly shown in Fig. 2(c). The core part is dark and the shell part is gray, indicating the presence of two different kinds of materials in the core and the shell, in consistence with Chung *et al.* report⁵. It show that some CdS nanoparticles existed and grew on the surfaces of ZnO particles and CdS shell polycrystalline structure is demonstrated by a HRTEM image in Fig. 2(d).

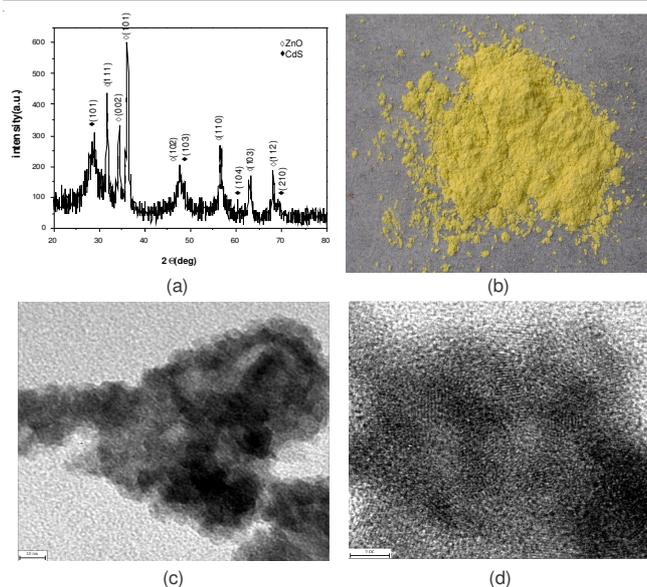


Fig. 2. (a) XRD pattern of the obtained ZnO/CdS Powders. (b) The photo of ZnO/CdS Powders. (c) and (d) HRTEM images of ZnO/CdS powders

A possible mechanism for the formation of ZnO/CdS core/shell nanostructure can be deduced from the solubility difference between ZnS and CdS. When ZnO/ZnS core/shell structure nanopowders are introduced into the cadmium nitrate solution, ZnO/ZnS nanopowders can be *in situ* converted into ZnO/CdS nanopowders, where the solubility difference is the driving force [solubility product constant (K_{sp}) of ZnS is 1.2×10^{-24} , while K_{sp} of CdS is 3.6×10^{-29}]. Compared with ZnS, CdS is more thermodynamically stable due to their lower solubility products. Since Cd^{2+} ions are uniformly distributed in the whole solution, ZnS shells can be transformed into CdS ones due to the fact that the solubility product of $[Cd^{2+}][S^{2-}]$ is smaller than that of $[Zn^{2+}][S^{2-}]$. On the other hand, since the ion-exchange process used here only replaces the Zn^{2+} ions in ZnS with Cd^{2+} ions in solution, the synthesis of ZnO/CdS core/shell nanostructures can be realized.

Photocatalytic activity: Fig. 3 shows the photocatalytic efficiencies of the ZnO/CdS core/shell structure nanopowders under the various light source. It can be clearly observed that methyl oranges have underwent a significant degradation and the as-samples exhibit higher photoactivity under UV light and solar light irradiation. It is clear that 86.8 % (under UV light) and 78.0 % (under solar light) methyl orange can be degraded by ZnO/CdS core/shell structure nanopowders for a 2 h exposure period and 69.6 % (under solar-simulated light) methyl orange can be degraded by ZnO/CdS nanopowders for a 9 h exposure period. Although the degradation rate of methyl orange under solar-simulated light irradiation is lower

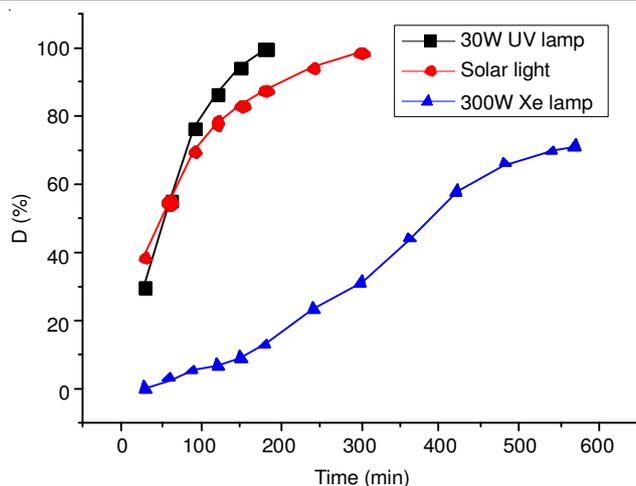


Fig. 3. Photocatalytic efficiencies of the ZnO/CdS nanopowders under the various light source

than that of methyl orange under UV and solar light irradiation, ZnO/CdS core/shell structure nanopowders show the photocatalytic ability for methyl orange dye decomposition under both UV and visible light irradiation as shown in Fig. 3.

Conclusion

The ZnO/CdS core-shell structure nano-powders were synthesized by two steps ion-exchange procedure. During the synthesis process, ZnO nanopowders were used as precursor for producing ZnO/ZnS core/shell structure powders, cation exchange between ZnS precursor and Cd^{2+} resulted in the deposition of CdS nanoparticles on ZnS surface. Samples were characterized by XRD and HRTEM techniques. The photocatalytic activities of the ZnO/CdS core/shell structure nanopowders were examined by measuring the photodegradation rate of methyl orange under UV light, solar light and solar-simulated light irradiation. Results show that the methyl orange dye can be photocatalytically degraded by ZnO/CdS nanopowders and the degradation rates under UV and solar light irradiation are higher than the degradation rate under solar-simulated light irradiation.

REFERENCES

1. G. Wang, X. Yang, F. Qian, J.Z. Zhang and Y. Li, *Nano Lett.*, **10**, 1088 (2010).
2. M. Zirak, O. Moradlou, M.R. Bayati, Y.T. Nien and A.Z. Moshfegh, *Appl. Surf. Sci.*, **273**, 391 (2013).
3. S.K. Panda, S. Chakrabarti, B. Satpati, P.V. Satyam and S. Chaudhuri, *J. Phys. D; Appl. Phys.*, **37**, 628 (2004).
4. S. Mingwang, L. Qing, X. Bo, W. Ji and Q. Yitai, *Mater. Chem. Phys.*, **78**, 288 (2002).
5. J. Chung, J. Myoung, J. Oh and S. Lim, *J. Phys. Chem. C*, **114**, 21360 (2010).