Growing Cu_2S Nanoparticles on CdS/ITO Substrates for Photocatalytic Degradation of Methylene Blue

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Abstract. CdS thin films were deposited on indium–tin-oxide (ITO) coated glass substrates by a chemical bath deposition method. Then the CdS/ITO slides were immersed in the solution containing 1.6 mM $CuCl_2$ and 1.4 mM cetyltrimethylamonium chloride at 37°C for 3 h to growth Cu_2S nanoparticles on the CdS/ITO slides. The scanning electron microscopy (SEM) and X-ray diffraction analysis demonstrated the presence of Cu_2S on the surface of CdS/ITO slides. The electrochemical behavior of the Cu_2S-CdS/ITO slide was studied using voltammetric scanning method. The Cu_2S-CdS/ITO slides exhibited an enhanced photocatalytic efficiency towards the degradation of methylene blue dye under irradiation with a Xenon lamp.

Introduction

Cu_2S is an important semiconductor with a bulk band gap of 1.21 eV and has been extensively investigated and used in a wide variety of fields such as photocatalysts, solar cells and oxygen evolution reaction[1-6]. The availability of Cu_2S nanostructures with well-defined morphologies and dimensions should enable new types of applications and/or enhance the performance of currently existing photoelectric devices because of the quantum-size effects.

Recent efforts have focused on the development of new synthetic methodologies for fabricating Cu_2S nanocrystals with controlled shape, size, and assembled structure. Du et al report a facile approach to fabricate hexagonal Cu_2S nanocrystals through thermolysis of a copper dithiolate precursor in dodecanethiol[7]. Xie et al. developed a template- and surfactant-free method to synthesize double-fold snowflake Cu_2S dendrites[8]. Jiang et al. prepared hierarchically assembled ITO@Cu_2S nanowire arrays with conductive single-crystalline ITO cores and Cu_2S nanocrystal shells for solar cell. These arrays not only provided an efficient three-dimensional charge transport network but also allowed for the effective deposition of more Cu_2S nanocrystals as active sites to catalyze the electrolyte reaction[9]. Also, copper alkanethiolates have been used as organometallic precursors to form Cu_2S nanodisks upon thermal decomposition. This method provides new insights into the use of liquid crystalline phases as templates for nanocrystal synthesis and as a potential route for achieving highly anisotropic inorganic nanostructures[10]. A liquid-state transformation process from hexagonal-phase CuS nanoparticles was employed to fabricate the cubic-phase Cu_2S nanoparticles. The CuS nanoparticles were converted into Cu_2S nanoparticles but maintained the morphology. The Cu_2S nanoparticles exhibit better oxygen evolution reaction activity than CuS nanoparticles[11].

Here we report a simple method to growth Cu_2S nanoparticles onto CdS/ITO substrates. Scanning electron microscopy (SEM), UV-vis absorption spectra, cyclic voltammetry (CV) and X-ray diffraction (XRD) analyses were carried out to investigate Cu_2S and CdS nanoparticles. We also studied the photocatalytic efficiency of the Cu_2S-CdS/ITO slides towards the degradation of methylene blue (MB).

Experimental Section

Materials. $CdCl_2$ and Na_3-citrate were purchased from Longxi chemical (Shantou, China). Thiourea was obtained from Dahao Fine Chemicals (Guangdong, China). Ammonia was from Ailian chemical (Guangdong, China). $CuCl_2$, methylene blue (MB), and cetyltrimethylamonium chloride (CTAC) were obtained from Sinopharm Chemical Reagent (Beijing, China). Other reagents were of analytical grade. Ultrapure water (resistivity>18 MΩ cm) was obtained from a WP-UP-IV-30 purification system (Woter, China) and used in the all experiments.

Deposition of CdS thin films. CdS thin films were deposited on indium–tin-oxide (ITO) coated glass substrates by chemical bath deposition technique. Films of CdS were deposited from stirred aqueous solutions containing 15 mL of 5 mM $CdCl_2$, 4 mL of 0.05 M thiourea, 8 mL of ammonia (2.5%, w/w), 5 mL of 0.05 M Na_3-citrate, and 18 mL ultrapure water. Before the deposition, the ITO substrates were ultrasonically cleaned subsequently in ethanol, acetone, and water, followed by drying in air. The cleaned substrates were immersed in the deposition solution at 83 ^oC for 3 h. Then the substrates were removed from the deposition bath, rinsed with ultrapure water, dried in air. After the deposition, yellowish and adherent CdS thin films were observed (hereafter abbreviated as CdS/ITO).

Growth of Cu_2S on CdS/ITO slides. To a 15-mL beaker were sequentially added with 9.85 mL ultrapure water, 80 μL of 0.2 M $CuCl_2$, 70 μL of 0.2 M CTAC, the total volume of the growth solution being increased to 10 mL by the addition of ultrapure water. Then the solution was heated to 37^oC and the CdS/ITO slides were immersed in the solution for 3 h. The slides were then taken out, rinsed with ultrapure water, and dried in air.

SEM, XRD, UV-vis absorption spectra, and electrochemical measurements. The structural properties of the Cu_2S and CdS nanoparticles were studied by scanning electron microscopy (Hitachi FE-SEM S4800, Japan) and XRD (X'pert PRO, Philips, Eindhoven, Netherlands). UV-vis absorption spectra were recorded on a TU-1901 double beam UV-vis Spectrophotometer (Purkinje General, China). CV experiments were carried out on a CHI 660b electrochemical workstation (Ch Instruments, China) with a conventional three-electrode system consisting of a Ag_2S/ZnS/ITO slide as the working electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and a Pt column electrode as the counter electrode.

Results and discussion

SEM and XRD. Fig. 1a and 1b show SEM images before and after the growth of Cu_2S. As can be seen in Fig. 1a, the CdS film consists of densely packed spherical grains with diameters of 70-80 nm. After Growing Cu_2S, it can be seen that large nanoparticles were grown. The size distribution histogram of the nanoparticles (Fig. 1c) is comprised of two groups of populations, one at about 76 nm, and the other at 142 nm. The first one can be attributed to CdS nanoparticles, which is consistent with the average diameter of about 75 nm of the deposited CdS nanoparticles (Fig. 1a). We may reasonably conclude that the second one is attributed to grown Cu_2S nanoparticles. The XRD study supports our conclusion.The XRD pattern in Fig. 1d shows six peaks located at 21.3°, 30.3°, 35.2°, 45.4°, 50.6°, and 60.3°, whose locations and relative intensities are almost the same as those of In_2O_3 with cubic structure (JCPDS 89-4595), except that all peak locations shifted little towards smaller diffraction angles. The shifts of the peak locations should be attributed to the formation of ITO solid solution by doping with Sn^{4+} at In^{3+} site in the In_2O_3. Apart from the diffraction peaks of ITO, the other peaks all correspond to Cu_2S (JCPDS 89-2670). Because the CdS nanoparticles are small and poor crystallinity, we did not observe any discernible peaks of CdS.

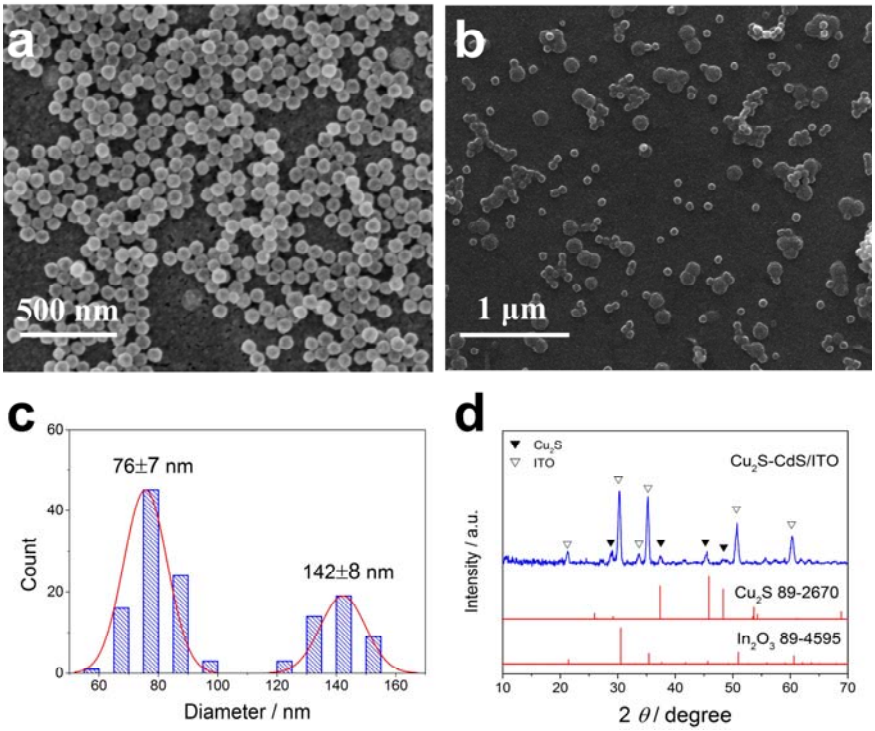

Fig. 1. SEM images of a) before and b) after the growth of Cu_2S onto the CdS/ITO slide. c) the size distribution histogram. d) XRD of the Cu_2S-CdS/ITO slide.

Cyclic voltammogram and photocatalytic degradation of MB. Fig. 2a shows the CV of the Cu_2S-CdS/ITO slide in a solution containing ammonia (13%, w/w) and 0.75 M $(NH_4)_2SO_4$. Two prominent anodic peaks occur. The first one at about -0.5 V could be attributed to the reduction: $Cu_2S \rightarrow CuS + Cu(NH_3)_4^{2+} + 2e^-$. The anodic peak at -0.1 V could be attributed to the reduction: $CuS + 8OH^- \rightarrow Cu(NH_3)_4^{2+} + SO_4^{2-} + 8e^-$. The electrochemical analysis is consistent with the results of SEM and XRD, supporting that Cu_2S nanoparticles are formed.

Fig. 2a show the UV–vis absorption spectra of an aqueous solution of 0.025 mM MB with a Cu_2S-CdS/ITO slide after irradiation with a 300-W Xenon lamp for different durations of time. The characteristic absorption peak of MB at 664 nm is monitored as a function of the light exposure time. It can be seen that the absorption peak at 664 nm diminishes sharply after 10 min of irradiation and almost completely disappears after 40 min of irradiation. No new absorption peaks appear in the UV–vis region, which clearly indicates the complete photocatalytic degradation of MB. It must be pointed out here that an adsorption of MB onto the Cu_2S-CdS/ITO slide in dark prior to light exposure did not result in any significant change in the absorption spectrum of MB.

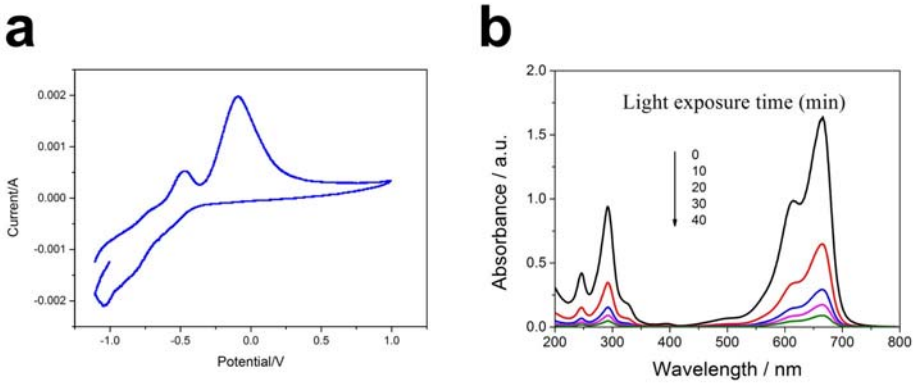

Fig. 2 a) CV of CV of the Cu_2S-CdS/ITO slide in a solution containing ammonia (13%, w/w) and 0.75 M $(NH_4)_2SO_4$. b) UV–vis absorption spectra showing temporal evolution of photocatalytic degradation of MB upon irradiation with a 300-W Xenon lamp.

Conclusions

In this study, we have synthesized Cu_2S-CdS nanoparticles on the ITO slides by using a facile wet chemical method. The structural, electrochemical, and photocatalytic properties of Cu_2S-CdS/ITO slides have been investigated. The CdS film consists of densely packed spherical grains with diameters of 70-80 nm. After the CdS/ITO slides were immersed into a solution containing $CuCl_2$ and CTAC, large Cu_2S nanoparticles (about 140 nm in diameter) were grown near the CdS nanoparticles. The electrochemical behavior of the Cu_2S-CdS/ITO slide was studied using voltammetric scanning method. The Cu_2S-CdS/ITO slides exhibited an enhanced photocatalytic efficiency towards the degradation of methylene blue dye under irradiation with a Xenon lamp.

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References

[1] S.C. Riha, R.D. Schaller, D.J. Gosztola, G.P. Wiederrecht, A.B.F. Martinson: J. Phys. Chem. Lett., Vol. 5 (2014), p. 4055
[2] Y. Jiang, X. Zhang, Q. Ge, B.-B. Yu, Y. Zou, W. Jiang, W. Song, L. Wan, J. Hu: Nano Lett., Vol. 14 (2014), p. 365
[3] S.C. Riha, S. Jin, S.V. Baryshev, E. Thimsen, G.P. Wiederrecht, A.B.F. Martinson: ACS Appl. Mater. Inter., Vol. 5 (2013), p. 10302
[4] Z. Zhuang, Q. Peng, B. Zhang, Y. Li: J. Am. Chem. Soc., Vol. 130 (2008), p. 10482
[5] J.-F. Zhu, Y.-J. Zhu, M.-G. Ma, L.-X. Yang, L. Gao: J. Phys. Chem. C, Vol. 111 (2007), p. 3920
[6] Z. Liu, D. Xu, J. Liang, J. Shen, S. Zhang, Y. Qian: J. Phys. Chem. B, Vol. 109 (2005), p. 10699
[7] X. Du, Z. Yu, A. Dasari, J. Ma, Y. Meng, Y. Mai: Chem. Mater., Vol. 18 (2006), p. 5156
[8] Z. Wu, C. Pan, Z. Yao, Q. Zhao, Y. Xie: Cryst. Growth Des., Vol. 6 (2006), p. 1717
[9] Y. Jiang, B.-B. Yu, J. Liu, Z.-H. Li, J.-K. Sun, X.-H. Zhong, J.-S. Hu, W.-G. Song, L.-J. Wan: Nano Lett., Vol. 15 (2015), p. 3088
[10] W. Bryks, M. Wette, N. Velez, S.-W. Hsu, A.R. Tao: J. Am. Chem. Soc., Vol. 136 (2014), p. 6175
[11] L. An, P. Zhou, J. Yin, H. Liu, F. Chen, H. Liu, Y. Du, P. Xi: Inorg. Chem., Vol. 54 (2015), p. 3281