

Synthesis and Photocatalytic Property of β - In_2S_3 Nanocrystals

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Tetragonal β - In_2S_3 nanocrystals have been successfully synthesized *via* a simple solvothermal route. The β - In_2S_3 nanorods show good photocatalytic properties under sunlight irradiation.

Key Words: Indium sulfide, Solvothermal, Photocatalyst.

INTRODUCTION

β - In_2S_3 (body-centered tetragonal) is an *n*-type III-VI semiconductor with a band gap of 2.0-2.3 eV, has received increasing attention in recent years¹. β - In_2S_3 is a promising optoelectronic material due to its photoconductive and luminescence properties, which has already inspired applications in the preparation of green and red phosphors in colour televisions, cells and heterojunction for use in photovoltaic electric generators². It can also be used as an effective substitute of toxic CdS in Cu(In, Ga) S_2 -based solar cells³. Furthermore, In_2S_3 nanoparticle bioconjugates can have medical applications, such as cancer diagnosis⁴.

Nanomaterials have attracted a special attention in material science because of their unique chemical, physical and optical properties, which depends not only on its composition and polymorph but also on the morphology and dimensionality. As for synthesis of the β - In_2S_3 nanostructures, several methods have been developed in previous researches². Of course, In_2S_3 nanomaterials with various shapes have been fabricated in the past decades, *e.g.*, nanoparticles⁴, wafer like morphology⁵, urchin-like In_2S_3 microspheres constructed with nanoflakes⁶, hollow nanospheres comprised of small particles⁷, hollow microspheres consisting of nanoflakes¹, halfshells⁸, micropompons composed of randomly oriented flakes⁹, uniform 3D flowerlike architectures of β - In_2S_3 assembled with nanoflakes¹⁰.

In recent years, one of the important goals in materials science is to develop new strategies for tailoring the structure of materials with an unusual and novel form. Hence, more convenient and simpler synthesis route to prepare In_2S_3 nanostructure is desired. In the present work, β - In_2S_3 nanocrystals were synthesized *via* one-step solvothermal

treatment. The syntheses are performed more advantages such as in homogeneous solution, amenable to scaling up, reaction system is relatively simple. Furthermore, obtained β - In_2S_3 nanorods also show good photocatalytic properties under sunlight irradiation.

EXPERIMENTAL

All the analytical reagents were purchased from Shanghai Chemical Reagents Company and used without further purification.

General procedure: In a typical synthesis, 0.065 g (0.20 mmol) of $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ was added into 10 mL pyridine to form a uniform solution. After stirring for 0.5 h, 0.152 mg (2.0 mmol) thiourea was added into the solution and the solution was continuing stirred for 0.5 h. Then the mixture was transferred into a stainless steel autoclave with Teflon liner and 15 mL capacity. The autoclave was maintained at 200 °C for 24 h and cooled to room temperature naturally. The resulting orange precipitate was separated by centrifugation and ultrasonic washed repeatedly with ethanol for several times and dried in air at 60 °C for 2 h.

Detection method: X-Ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (Rigaku D/Max 2200PC) with a graphite monochromator and $\text{CuK}\alpha$ radiation ($\lambda = 0.15148$ nm) in the range of 10-80 °C at room temperature while the tube voltage and electric current were held at 40 kV and 20 mA. The morphology and microstructure of the products were determined by transmission electron microscopy (TEM, JEM-100CXII) with an accelerating voltage of 80 kV and high-resolution TEM (HR-TEM, GEOL-2010) with an accelerating voltage of 200 kV. The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet

5DX-FTIR spectrometer using the KBr pellet method in the range of 4000-400 cm^{-1} .

Photocatalytic property was investigated using RhB aqueous solution and silica beaker as the photoreactor vessel. Under vigorously stirring, 30 mg photocatalyst was added into the aqueous solution of RhB (initial concentration: 1.0×10^{-5} mol/dm^3 , 100 mL) and then the suspension was irradiated by sunlight for various durations. Samples were collected every 0.5 h to measure the RhB degradation by UV-VIS spectra.

RESULTS AND DISCUSSION

Fig. 1a shows the XRD pattern of the product. All the reflections on the XRD pattern could be indexed to the body-centered tetragonal $\beta\text{-In}_2\text{S}_3$ structure ($a = 7.619 \text{ \AA}$, $c = 32.329 \text{ \AA}$, JCPDS: 25-0390). No characteristic peaks were observed for the other impurities such as In_2O_3 , InS or $\text{In}(\text{OH})_3$. TEM image (Fig. 1b) of the sample obtained from pyridine solvothermal route shows that morphology of the nanocrystals are particles with 30-40 nm size.

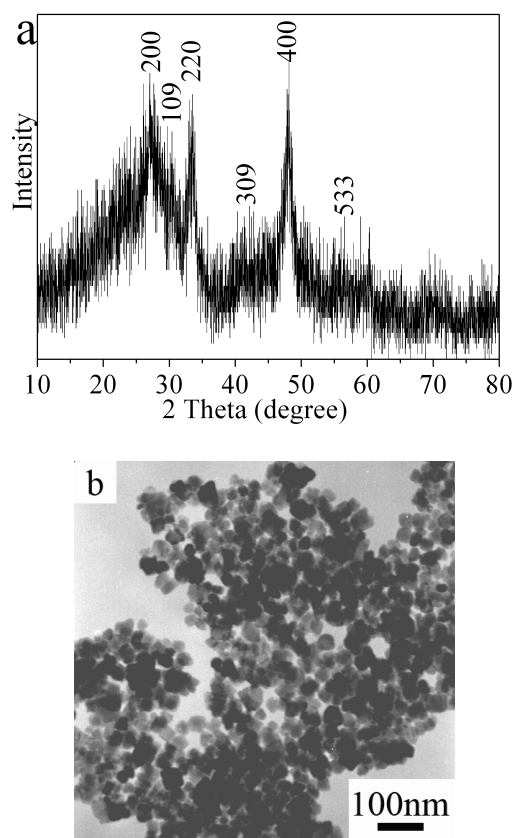


Fig. 1. XRD pattern (a) and TEM image (b) of the product

FT-IR technology are the most useful methods to detect the surface state of the obtained samples. The FT-IR spectra of as prepared $\beta\text{-In}_2\text{S}_3$ nanocrystals (Fig. 2) shows the bands around 2956, 2922 and 2851 cm^{-1} , which can be ascribed to the C-H vibrations¹¹ of pyridine. Obviously, the weak absorptions at 1576 and 1524 cm^{-1} should be attributed to the C=C and C=N vibrations from the pyridine ring¹¹. The result indicates that the surface species of the nanocrystals are mainly pyridine molecules and a few of absorbed water.

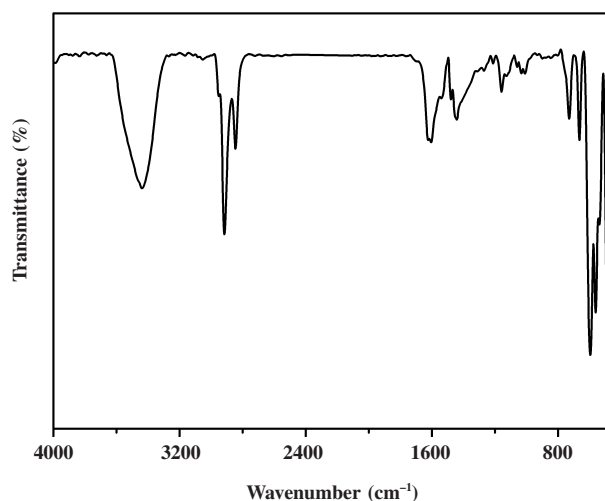


Fig. 2. FT-IR spectra of obtained $\beta\text{-In}_2\text{S}_3$ nanocrystals

As a promising semiconductive material, the UV-VIS absorption of obtained $\beta\text{-In}_2\text{S}_3$ nanocrystals were studied at room temperature. From the UV-VIS absorption spectrum of the nanocrystals shown in Fig. 3A, a strong peak around 264 nm was observed, whose band edge was 510 nm. As well known, the band gap (E_g) in bulk In_2S_3 is reported to be between 2.0 and 2.2 eV with the corresponding UV band from 620-550 nm ⁴. It is obviously revealed the blue shift compared with the bulk In_2S_3 materials which indicated the existence of a weak quantum confinement effect.

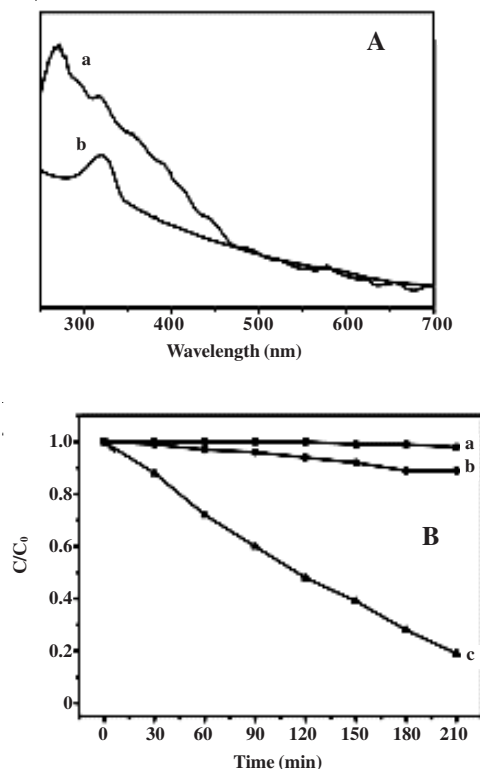


Fig. 3. (A) UV-VIS absorption spectrum (a) In_2S_3 nanocrystals, (b) P25. (B) Photodegradation of rhodamine-B under different photocatalysts under sunlight (a) without catalyst, (b) P25 nanoparticles, (c) In_2S_3 nanoparticles obtained when thiol replaced by thiourea

The indium sulfides with strong absorption from the visible region to UV region may be good candidates for photocatalytic organic pollutants (Fig. 3A). Thus, the experiments of the photocatalytic degradation of rhodamine-B with the as-prepared In_2S_3 nanocrystals as photocatalysts were carried out. Under vigorously stirring, 30 mg photocatalyst was added into the aqueous solution of rhodamine-B and then the suspension was irradiated by sunlight for various durations, respectively. The characteristic absorption of rhodamine-B at 553 nm was chosen as the parameter to be monitored for the photocatalytic degradation process. The absorption peaks corresponding to rhodamine-B diminished gradually as the exposure time was extended when In_2S_3 nanocrystals as photocatalyst. After irradiation by sunlight 210 min, the characteristic absorption of rhodamine-B nearly disappeared. The rhodamine-B hardly decomposes after irradiated by the sunlight without catalyst. The commercial Degussa P25 was used as the reference catalyst under the same conditions. Furthermore, to demonstrate the excellent photocatalytic efficiency, we studied the degradation process of rhodamine-B with the commercial P25. From the above experiments, it can be seen that the In_2S_3 nanocrystals show much better photocatalytic activities than commercial P25. Further experiments show that as photocatalyst, β - In_2S_3 nanocrystals are stable and can be repeatedly used for many times. The higher photo-catalytic activity of In_2S_3 nanocrystals comparing to commercial Degussa P25 might relate to their wider UV-VIS absorptions region (Fig. 3A) and several deep trap states or defects in their structure⁹.

Conclusion

In summary, β - In_2S_3 nanocrystals were synthesized *via* one-step solvothermal treatment. A strong absorption peak

around 264 nm, which blue shift compared with the bulk In_2S_3 materials, indicates the strong quantum confinement effect. The higher photocatalytic activity of In_2S_3 nanocrystals comparing to commercial Degussa P25 might relate to their wider UV-VIS absorptions region and defects in their structure.

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REFERENCES

1. Y. Liu, H.Y. Xu and Y.T. Qian, *Crystal Growth Design*, **6**, 1304 (2006).
2. S. Avivi, O. Palchik, V. Palchik, M.A. Slifkin, A.M. Weiss and A. Gedanken, *Chem. Mater.*, **13**, 2195 (2001).
3. J. Sterner, J. Malmstrom and L. Stolt, *Prog. Photovol.*, **13**, 179 (2005).
4. D.K. Nagesha, X.R. Liang, A.A. Mamedov, G. Gainer, M.A. Eastman, M. Giersig, J.J. Song, T. Ni and N.A. Kotov, *J. Phys. Chem. B*, **105**, 7490 (2001).
5. J. Tabernor, P. Christian and P. O'Brien, *J. Mater. Chem.*, **16**, 2082 (2006).
6. X.Y. Chen, Z.J. Zhang, X.F. Zhang, J.W. Liu and Y.T. Qian, *Chem. Phys. Lett.*, **407**, 482 (2005).
7. X.B. Cao, L. Gu, L.J. Zhuge, W.H. Qian, C. Zhao, X.M. Lan, W.J. Sheng and D. Yao, *Colloids Surf. A*, **297**, 183 (2007).
8. P. Gao, Y. Xie, S.W. Chen and M.Z. Zhou, *Nanotechnology*, **17**, 320 (2006).
9. A. Datta, S.K. Panda, D. Ganguli, P. Mishra and S. Chaudhuri, *Crystal Growth Design*, **7**, 163 (2007).
10. L.Y. Chen, Z.D. Zhang and W.Z. Wang, *J. Phys. Chem. C*, **112**, 4117 (2008).
11. X. Xing, S. Chen and S. Me, *The Workable Index of IR Spectra*, Tianjin Science & Technology Press, Tianjin (1992) (in Chinese).