Synthesis and Characterization of Water-soluble Sb_2S_3 Quantum Dots

Na PI [a], Yan HUANG [b, *], Pingping YAO [c], Qinmei WEI [d], Yicheng LIU [e], and Yuxiang YANG [f, *]
School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China
[a]1176908808@qq.com, [b]huangyan@ecust.edu.cn, [c]yaoping@ecust.edu.cn, [d]878307970@qq.com, [e]liuyicheng143@163.com, [f]yxyang@ecust.edu.cn

Abstract. Taking thioacetamide (TAA) as sulfur source and mercaptoacetic acid as capping agent, water-soluble Sb_2S_3 quantum dots were synthesized in aqueous-phase with precipitation method. The influence of temperature (65 to 85 °C) and reaction time (3 to 7 h) on morphological characteristics of the products was studied. The as-prepared Sb_2S_3 quantum dots were characterized with X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet-visible spectrophotometry (UV-vis) and photoluminescence (PL), which suggested the Sb_2S_3 quantum dots have uniform size distribution and excellent optical properties. Moreover, a formation mechanism of Sb_2S_3 quantum dots was also proposed.

1. Introduction

Sb_2S_3 belongs to the group of metal chalcogenides that form an important class of inorganic semiconductors with extensive applications in industrial catalysis, photo-catalysis, adsorption and photosensitive cell materials [1]. For superior optical absorption and photoluminescence, wide band gaps and good electrical properties, Sb_2S_3 quantum dots are also a promising candidate as target materials in electromagnetic devices, television cameras, solar energy conversion, ceramics, chemical or biological sensors and other industrial fields [2].

Owning to the aforementioned extensive application, the preparation of Sb_2S_3 quantum dots has been more attractive [3]. Methods like chemical deposition, successive ionic layer adsorption and reaction thermal treatment of Sb layer in S atmosphere, vacuum evaporation and so on, have been used to prepare Sb_2S_3 quantum dots. Lu [4] and co-workers developed a hydrothermal approach with the assistance of polyvinylpyrrolidone for synthesizing Sb_2S_3 films.

However, the optical properties of Sb_2S_3 quantum dots do also depend on the method of its synthesis [5]. Among these methods, aqueous-phase synthesis has become a potential promising method that can be used widely in the near future due to its simple operation, good repeatability, low cost and low toxicity, relatively easy to use technique in industrial

*Corresponding Author: yxyang@ecust.edu.cn, huangyan@ecust.edu.cn

production.

In the present work, the simple route for the fabrication of Sb_2S_3 quantum dots was made by controlling the reaction conditions in aqueous-phase. SEM, TEM results showed the particles have uniform size distribution, UV absorption spectra and fluorescence spectra showed the products have an excellent optical performance.

2. Experimental

2.1Preparation of Sb2S3 quantum dots

In the present synthesis, 4 mL 0.1mol·L^{-1} $C_4H_2KO_6Sb·1.5H_2O$ and 26 mL 0.2 mol·L^{-1} $C_2H_4O_2S$ were first added into 800 mL deionized water with vigorous stirring for 15 min at room temperature. Afterwards, 40 mL 0.2 mol·L^{-1} C_2H_5NS were added to the mixture, also under constant stirring for another 15min.Then the reaction mixture was rapidly stirred for 5 h at 75 °C. After aging for 10 h, the reaction system was treated with vacuum concentration, washed with acetone, absolute ethanol and distilled water respectively for three times. Finally, the obtained sample was dried in vacuum at 60 °C for 12 h before characterization.

2.2Characterization of Sb2S3 quantum dots

XRD (BDX 3200 with Cu Ka radiation), SEM (Hitachi S-4100), TEM (JEOL 2000EX) and EDS (JEOL JEM-2100) were performed to systematically characterize the as-prepared Sb_2S_3 samples. An UV-visible spectrophotometer (Hitachi U-4100) and photoluminescence spectroscopic technique (Perkin Elmer LS55, He-Ne LASER line) was employed to explore the optical property of Sb_2S_3.

3. Results and Discussion

3.1Structural analysis of Sb2S3 quantum dots

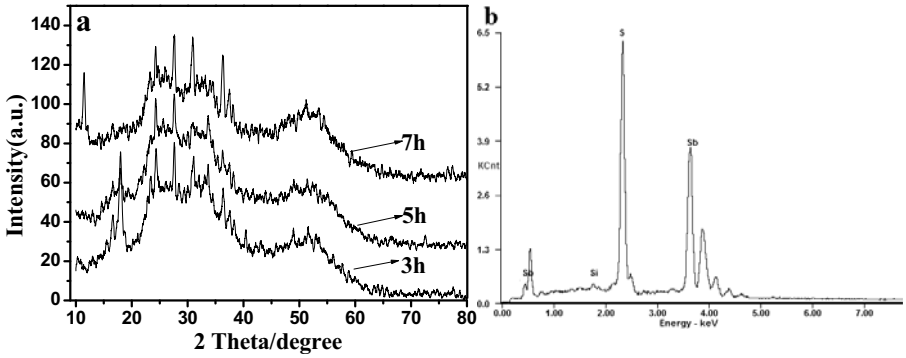

Fig. 1: XRD patterns and EDS of the Sb_2S_3 quantum dots (a) XRD; (b) EDS

XRD patterns of products could be seen from Fig. 1a, which shows that with increasing of reaction time, the crystallinity was not obviously increased, indicating that the obtained products have the same composition and crystal forms. All defined peaks can be well

indexed to the orthorhombic phase of the Sb_2S_3 (JCPDS: File No. 06-474) with the lattice constants of a=11.22 Å，b=11.31 Å，c=3.839 Å, confirming the reactants have formed Sb_2S_3 quantum dots.

The sample composition was studied by energy dispersive X-ray spectroscopy (EDS) analysis in Fig. 1b. The EDS spectrum represented two sharp peaks of antimony and sulfur (the Si signal comes from the substrate), confirming the composition of antimony and sulfur in Sb_2S_3 quantum dots. Quantification of the EDS peaks gives the molar ratio of Sb:S from the peak areas is 1:1.45, which is consistent with the stoichiometric composition of Sb_2S_3. It also can be found that no peaks of other elements are observed in the EDS spectrum, indicating high purity of the Sb_2S_3 quantum dots.

3.2Morphological analysis

The morphological characteristics of the products have been studied by SEM and TEM. A series of contrastive experiments have illustrated that temperature and reaction time play an important role in the synthesis of Sb_2S_3 quantum dots with different morphologies.

3.3TEM analysis of Sb2S3 quantum dots

As shown in Fig. 2a, samples collected at 3 h are consisted of different size and nonuniform distribution of the quasi-spherical particles in the diameter region of 400 nm ~1.5 μm. With the extension of reaction time, the spherical-particles become much larger and rounder. When the reaction time comes to 5 h, the quantum dots presented spherical completely within the size of about 500~700 nm as shown in Fig. 2b and Fig. 2c, and small particles disappeared. When the reaction time lasted for 7 h, the particles continue to grow with an average size of 1.2 μm (Fig. 2d). Meanwhile, the partial aggregation also took place due to the Ostwald ripening. By comparison, we found that the obtained samples at 5 h are more uniform and regular.

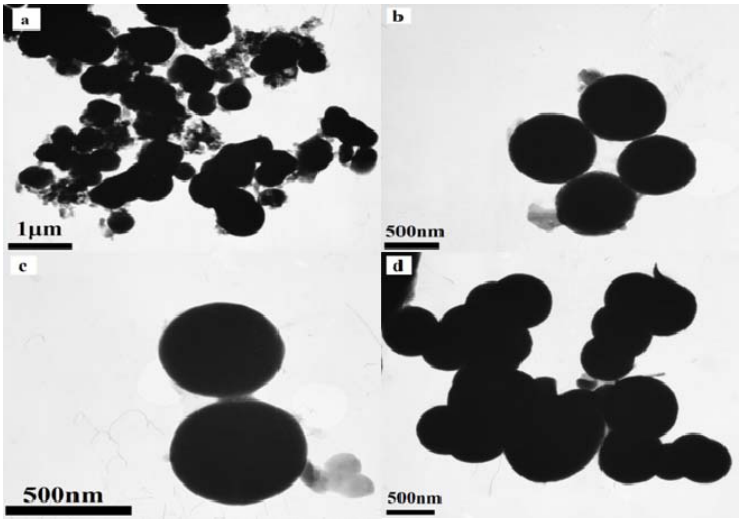

Fig. 2: TEM images of the Sb_2S_3 sub-microspheres by aqueous synthesis in a reaction of (a) 3h; (b,c) 5h; (d) 7h; respectively

3.4SEM analysis of Sb2S3 quantum dots

As illustrated in Fig. 3, the products obtained at different time are all spherical particles. As the reaction proceeded for 3 h, we can see only a small part of products are spherical particles in Fig. 3a and Fig. 3b. When the reaction lasted for 5 h, spherical particles are completely formed, and the as-prepared particles show more regular and uniform than that of 3 h with diameter of about 700 nm in Fig.3c and Fig. 3d. As shown in Fig.3e and Fig. 3f, Sb_2S_3 quantum dots obtained at 7 h became much larger because of serious aggregation of particles, generating a large class of clusters.

The effects of temperature on Sb_2S_3 can be seen in Fig. 4a and Fig. 4b, which revealed that the growth of Sb_2S_3 quantum dots follows the rules of Ostwald growth [6]. The higher the temperature accelerates the TAA hydrolysis, the more easily to achieve supersaturation generation of small nuclear. When the temperature is 65 °C, we cannot obtain the spherical particles, but with further increase of temperature to 85 °C, the aggregated products can be obtained with the diameter of 1.5 μm, which is much larger than that of 75 °C. Therefore, the optimum reaction temperature is 75 °C.

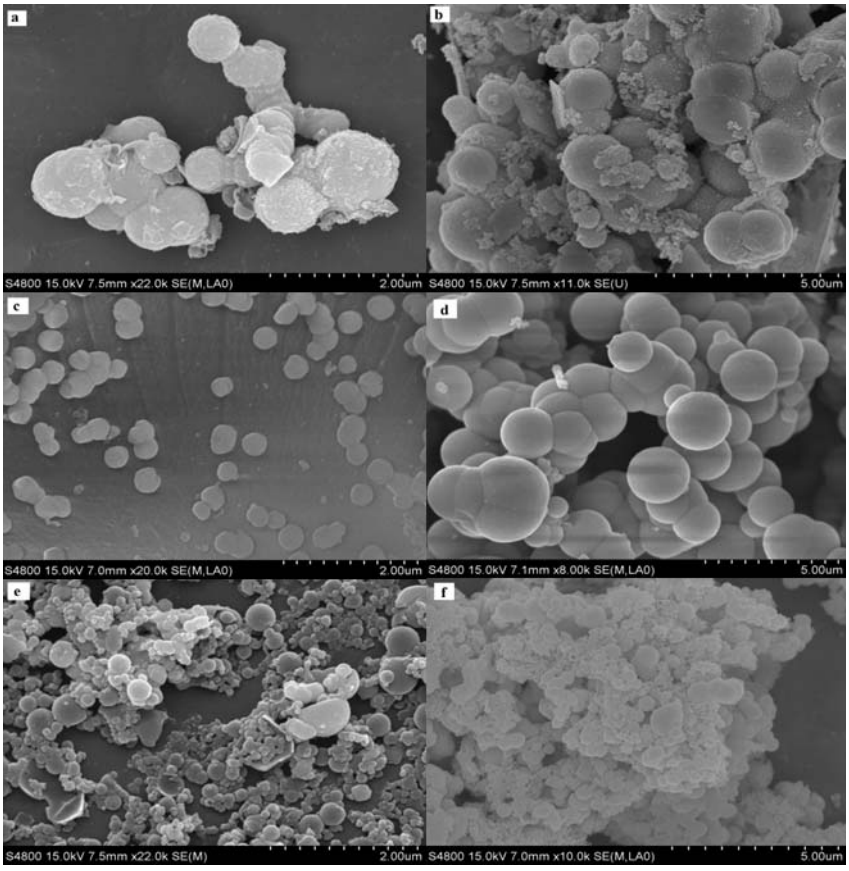

Fig. 3: SEM images of as-prepared Sb_2S_3 quantum dots by aqueous synthesis in a reaction of (a,b) 3h; (c,d) 5h; (e,f) 7h; respectively

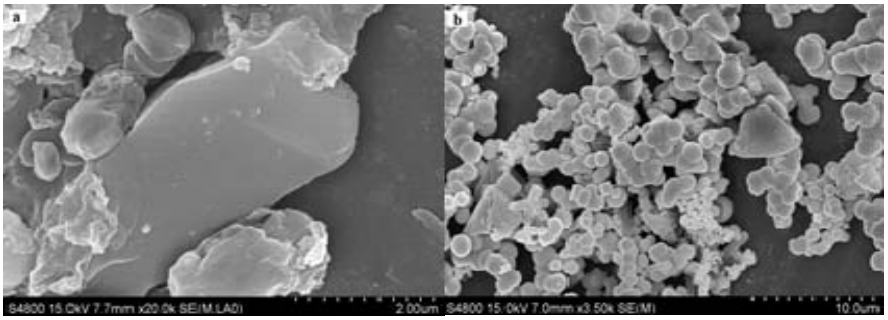

Fig. 4: SEM images of as-prepared Sb_2S_3 quantum dots by aqueous synthesis in a reaction of (a) 65 °C; (b) 85 °C

3.5UV absorption spectra and fluorescence spectra of Sb2S3

In order to explore the optical property of Sb_2S_3 quantum dots, UV absorption spectra and fluorescence spectra of Sb_2S_3 quantum dots are observed in Fig. 5a and Fig. 5b, respectively. Fig. 5a shows the UV-visible reflection spectrum taken on Sb_2S_3 quantum dots prepared under different reacting time. When the size of quantum dots becomes larger, red shift can be seen in absorption spectrum. With the reaction time prolonging, all the UV-visible absorption spectrum exhibits an extinction peak, but its position with the increasing time gradually moved from 525 nm to 576 nm. Besides, UV-visible absorption spectra of absorption edge showed a similar result. This may be related to particles growing up with reaction time, which is consistent with the results of TEM and SEM.

Optical absorption spectroscopy of Sb_2S_3 quantum dots is well known and widely reported in literatures for semiconductor nano-crystals. The photoluminescence spectra of Sb_2S_3 quantum dots was showed in Fig.5b, it can be observed that there is one obvious characteristic peak of Sb_2S_3 quantum dots at 358 nm corresponding to the calculated band gap of 3.47 eV, which is in agreement with the results of UV-visible reflection spectrum. In view of the above, Sb_2S_3 quantum dots with its luminescence properties, is suitable for optoelectronic applications.

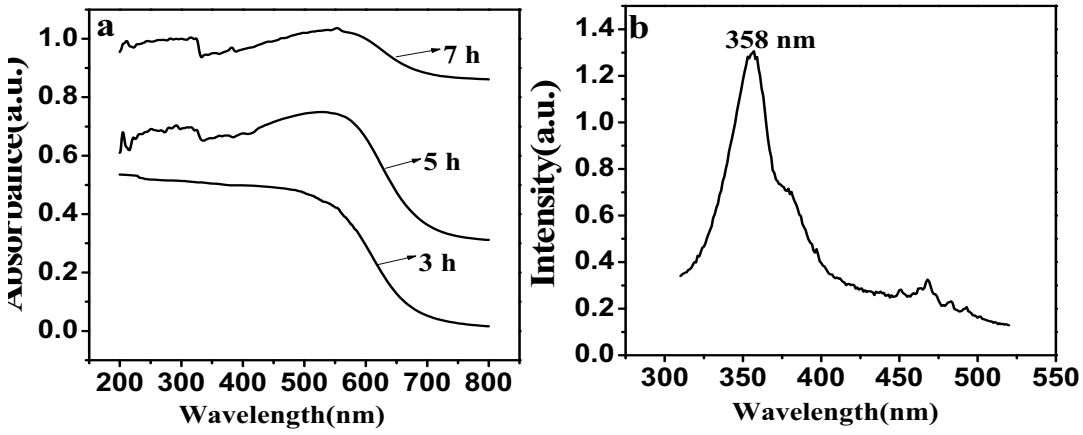

Fig. 5: UV absorption spectra and fluorescence spectra of Sb_2S_3 (a) UV-vis spectra of Sb_2S_3 in a reaction of 3h, 5h and 7h, respectively; (b) PL spectra of Sb_2S_3

3.6Formation mechanisms of Sb2S3 quantum dots

The formation process of Sb_2S_3 can be inferred in Fig. 6, that the growth of the seeds will be turned into kinetic control. This leads to very tiny nanoparticles formation at initial time with TAA as S source and precipitator, with an increase of reaction time, Ostwald ripening occurred, and very tiny particles gradually disappeared to complete raw materials which eventually formed larger size of the quantum dots [7]. This is because the surface of very tiny particles is large, there is a tendency for more particles filling on the surface of the seeds to keep the system relatively stable [8].

The formation process of Sb_2S_3 quantum dots can be illustrated as follows:

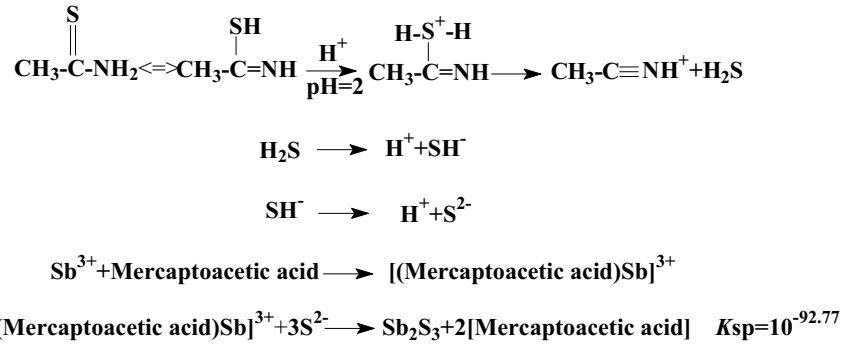

Fig. 6: Reaction mechanism and growth process of Sb_2S_3 quantum dots

4. Summary

In summary, spherical Sb_2S_3 quantum dots with diameters of about 500~700 nm were successfully prepared by aqueous-phase arrested precipitation using mercaptoacetic acid as capping agent and thioacetamide (TAA) as sulfur source. The study described the evolution of the morphology, structural and optical properties of the particles with good correlation among them, which revealed that, these water-soluble Sb_2S_3 are suitable for further optoelectronic and biological applications.

References

1. HL Zhang, CG Hu, Y Dong and Y Lin, Synthesis of 1D Sb_2S_3 nanostructures and its application in visible-light-driven photodegradation for MO, Journal of Alloys and Compounds. 625 (2015) 90-94.
2. A. N. Kulkarni, M. B. Rajendra Prasad, R. V. Ingle and et al. Structural and optical properties of nanocrystalline Sb_2S_3 films deposited by chemical solution deposition, Optical Materials. 46 (2015) 536-541.
3. GQ Zhu, P Liu, HY Miao and et al, Large-scale synthesis of ultralong Sb_2S_3 sub-microwires via a hydrothermal process, Materials Research Bulletin. 43 (2008) 2636-2642.
4. QF Lu, HB Zeng, ZY Wang and et al, Design of Sb_2S_3 nanorod-bundles: imperfect oriented attachment, Nanotechnology. 17 (2006) 2098-2104.
5. F. Aousgi, W. Dimassi, B. Bessais and et al. Effect of substrate temperature on the

structural, morphological, and optical properties of Sb_2S_3 thin films, Applied Surface Science. 350 (2015) 19-24.

6. S. B. Simonsen, I. Chorkendorff, S. Dahl and et al, Ostwald ripening in a Pt/SiO_2 model catalyst studied by in situ TEM, Journal of Catalysis. 281 (2011) 147-155.
7. XL Yu, CB Cao, HS Zhu, Synthesis and photoluminescence properties of Sb_2S_3 nanowires via surfactant micelle-template inducing reaction, Solid State Communications. 134 (2005) 239-243.
8. H Zhang, Z Zhou and B Yang, The influence of carboxyl groups on the photoluminescence of mercaptocarboxylic acid-stabilized CdTe nanoparticles, J. Phys. Chem. B. 107 (2003) 8-13.