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# Colloidal synthesis and characterization of $\text{Bi}_2\text{S}_3$ nanoparticles for photovoltaic applications

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**Abstract.** Bismuth sulfide is a promising n-type semiconductor for solar energy conversion. We have explored the colloidal synthesis of  $\text{Bi}_2\text{S}_3$  nanocrystals, with the aim of employing them in the fabrication of solution-processable solar cells and to replace toxic heavy metals chalcogenides like PbS or CdS, that are currently employed in such devices. We compare different methods to obtain  $\text{Bi}_2\text{S}_3$  colloidal quantum dots, including the use of environmentally benign reactants, through organometallic synthesis. Different sizes and shapes were obtained according to the synthesis parameters and the growth process has been rationalized by comparing the predicted morphology with systematic physical-chemistry characterization of nanocrystals by X-ray diffraction, FT-IR spectroscopy, Transmission Electron Microscopy (TEM).

## 1. Introduction

Colloidal semiconductor nanocrystals are promising materials for applications in solution-processable optoelectronic devices such as photocatalysts and photovoltaic cells. A wide variety of materials has been used to fabricate semiconductor nanocrystals, but most of them contain heavy metal elements, such as Pb or Cd, which could be dangerous for the health if used on large scale. For this reason, environmentally benign nanocrystals are currently a central topic in materials research. Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) belongs to the class of non-toxic semiconductor materials that can be synthesized in nanocrystalline form by colloidal synthesis; research efforts have been addressed to the fabrication of solution-processed optoelectronic devices, including hybrid bulk nano-heterojunctions for solar energy conversion and sensitized solar cells [1, 2, 4]. The synthesis reported in literature with the best control of nanocrystals size and shape, as well as resulting in the highest conversion efficiencies for solar cells, employ however dangerous chemicals, such hexamethyldisilathiane (HMS), and do not appear sustainable for large scale productions [1, 2]. In this paper we compare several synthesis methods to obtain bismuth sulfide nanoparticles in different shape and morphology, maintaining the same crystallographic phase; particularly, we develop “green” approaches and benchmark them against the well-established techniques extensively reported in literature.



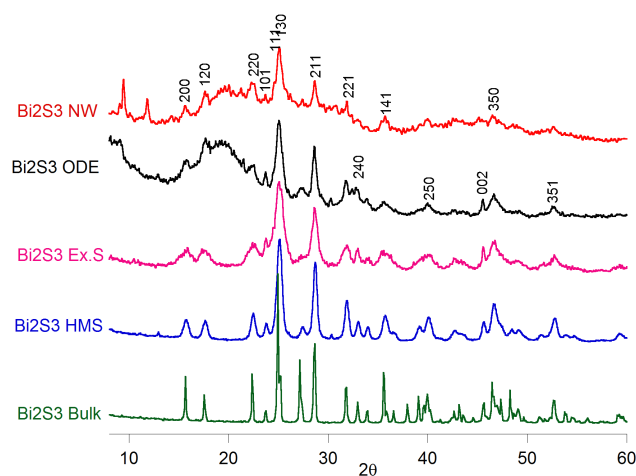
## 2. Synthesis and results

**Bi<sub>2</sub>S<sub>3</sub>-HMS.** The standard route to produce Bi<sub>2</sub>S<sub>3</sub> colloidal nanocrystals presented in literature is an oleic acid-based organometallic synthesis. A mixture of bismuth(III) acetate, oleic acid (OA) and 1-octadecene (ODE) was heated under stirring in argon atmosphere at 90 °C for 16 h and then heated up to 170 °C. A solution of hexamethyldisilathiane (HMS) in ODE was quickly injected into the flask at the same temperature (170°C) or after cooling down at 100°C or at 50°C. The samples were cooled down to room temperature and the nanoparticles were purified by successive dispersion/precipitation and centrifugation steps in toluene/methanol and finally dispersed in anhydrous toluene [1, 2]. These dispersions are colloiddally stable for months. The HMS can easily produce H<sub>2</sub>S, a dangerous, toxic gas. This means that this synthesis is not safe to scale up for large productions. Moreover this synthesis is very sensitive to little variation of its atmosphere and this produces damage on the stability of the colloidal dispersion. For this reason we have tried the following methods, using elemental sulfur as precursor in different solvents.

**Bi<sub>2</sub>S<sub>3</sub>-ODE.** This synthesis is equal to the Bi<sub>2</sub>S<sub>3</sub>-HMS except for the use of S precursor, that now is a solution of elemental S heated at 100°C for 20 min and then at 180°C for 1 h in ODE [2, 3]. This method needs a temperature growth of 170°C to produce a crystalline sample.

**Bi<sub>2</sub>S<sub>3</sub>-OAm.** In this case the sulfur precursor was a sulfur/oleylamine solution, produced by vigorous stirring at room temperature of the sulfur powder in oleylamine (OAm), to obtain a red clear appearance. The same mixture of bismuth acetate, oleic acid and 1-octadecene was heated under stirring at 90°C in vacuum for 1 h, and then heated up at 170°C in argon atmosphere. The solution was quickly injected into the flask. After 10 min, 30 min or 6 h, the reaction was quenched with ethanol and purified by dispersion/precipitation and centrifugation steps with toluene/ethanol. At the end, the sample was collected in toluene [4]. This method was tested in excess (ExS), in defect (DfS) of sulfur or with Bi/S stoichiometric ratio (StS).

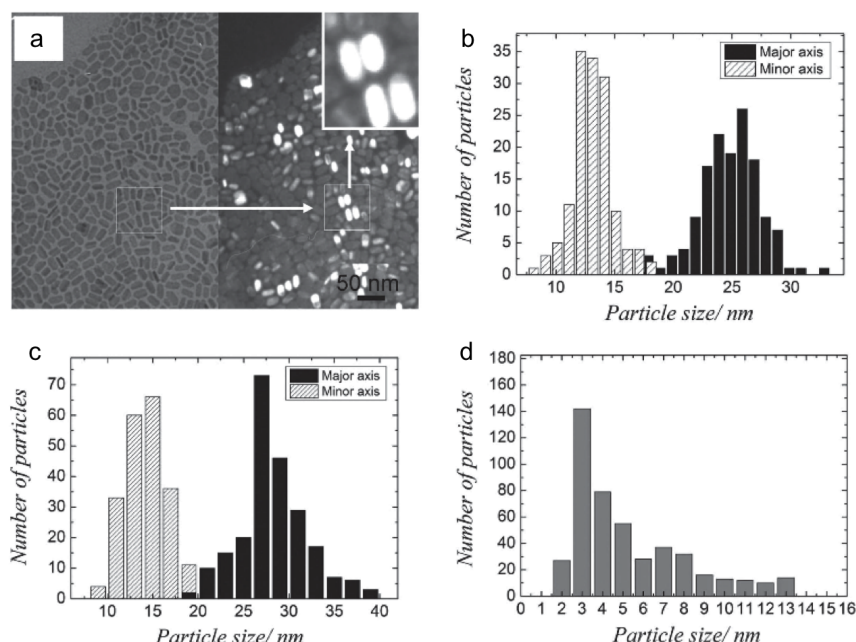
**Bi<sub>2</sub>S<sub>3</sub>-NW.** This synthesis is similar to the Bi<sub>2</sub>S<sub>3</sub>-OAm except for the fact that the ODE and OA mixture was replaced by pure oleylamine. A mixture of bismuth acetate and OAm was stirred and heated to 130°C over the course of 30 min and then kept at the same temperature for 30 min, under Ar atmosphere. The solution of S/OAm was quickly injected in the flask. After 30 min at 100°C the reaction was quenched with cold toluene. Unsolubilized materials were removed by centrifugation, and acetone was added to the supernatant until it became turbid. The mixture was centrifuged, the supernatant discarded and the precipitated nanocrystals redispersed in toluene [5].



**Figure 1.** XRD patterns of NW, ODE, OAm ExS, HMS samples compared with the Bi<sub>2</sub>S<sub>3</sub> bulk pattern.

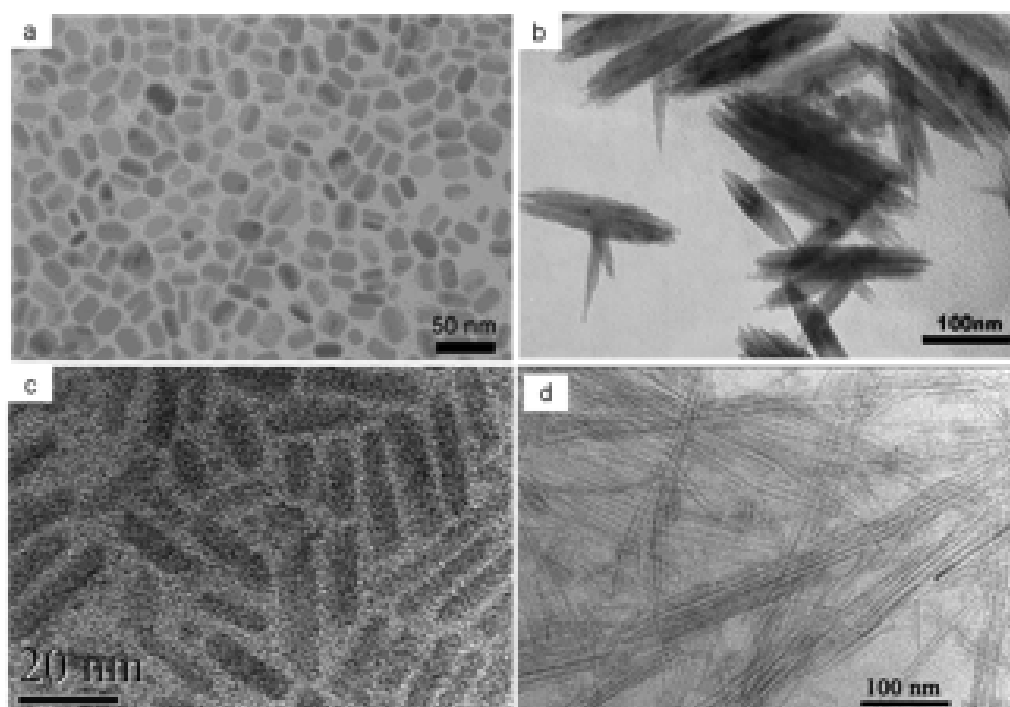
X-ray diffraction (XRD) pattern of the most representative  $\text{Bi}_2\text{S}_3$ -HMS sample obtained under stoichiometric conditions after 6 h of growth, is reported in Figure 1, compared with the XRD patterns of the other samples and bulk bismuth sulfide. Bragg reflections indicate the presence of  $\text{Bi}_2\text{S}_3$  with orthorhombic structure as the unique phase in the sample. All the other synthesis methods we employed produce bismuth sulfide in orthorhombic phase, like the  $\text{Bi}_2\text{S}_3$ -HMS, but with a different morphology.

TEM bright and dark field images of the  $\text{Bi}_2\text{S}_3$ -HMS sample at temperature of growth ( $T_g$ ) of  $170^\circ\text{C}$ , reported in Figure 2, show the formation of rod shaped nanoparticles of average length of 25 nm (10% polydispersity) and width of 13 nm (13% polydispersity). The brightness of the nanorods in the dark field image is evidence that most of them are single crystals. Changing the temperature of growth, is possible to control size and shape of the nanocrystals. With lower temperature, in fact, the nanoparticles change from rod shape to quasi-spherical shape with a size of 4 nm.

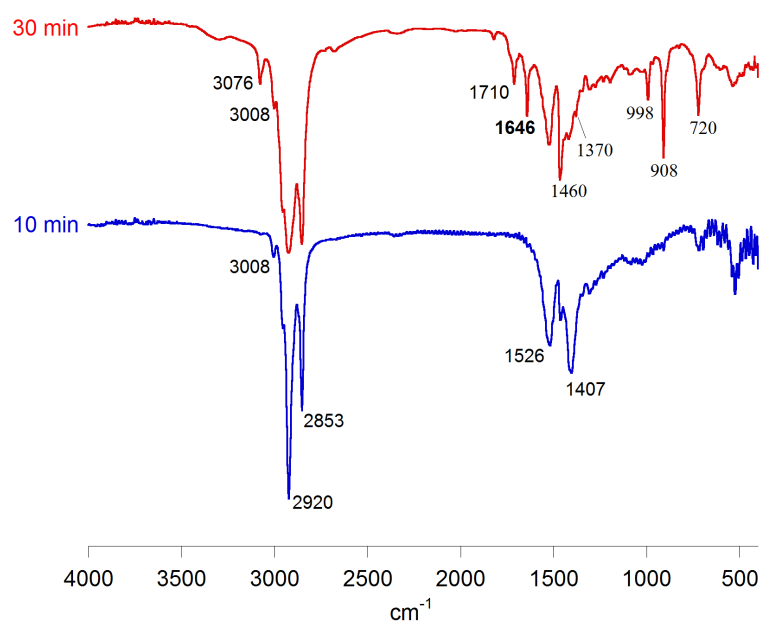


**Figure 2.** (a) TEM bright and dark field images of  $T_g = 170^\circ\text{C}$   $\text{Bi}_2\text{S}_3$ -HMS sample and is (b) particle size distributions calculated by bright field images. (c) Particle size distributions of  $T_g = 100^\circ\text{C}$  sample. (d) Particle size distributions of  $T_g = 50^\circ\text{C}$  sample [1].

In the Figure 3 are shown the TEM images of the most representative sample obtained with the other methods, compared with the  $\text{Bi}_2\text{S}_3$ -HMS sample. The ODE sample is a petal-like nanoparticle formed by needles of sulfide. The average length is 300 nm and these particles are not stable in organic solvent, so it is not a solution-processable sample. The OAm sample is amorphous if synthesized with stoichiometric ratio, very little in sulphur defect and rod-shaped in sulfur excess. This last one grows after 10 min at the same average length of the HMS sample after 6h of growth, but the width is halved. The time of growth influences the stability of this sample; if this is higher than 1 h, the yield of stable nanoparticles decrease. The  $\text{Bi}_2\text{S}_3$ -NW sample is formed by nanowires with a average width of 3-4 nm and a length over 300 nm. These ones are very stable in toluene. The preferential growth along a single dimension is attributable to the absence of oleic acid, which then has a primary role in the growth in the spherical form of the bismuth sulfide.



**Figure 3.** TEM images of (a)  $\text{Bi}_2\text{S}_3$ -HMS sample, (b)  $\text{Bi}_2\text{S}_3$ -ODE sample and HR-TEM images of (c)  $\text{Bi}_2\text{S}_3$ -OAm ExS and (d)  $\text{Bi}_2\text{S}_3$ -NW.



**Figure 4.** FT-IR spectra of  $\text{Bi}_2\text{S}_3$ -OAm sample after 10 min and 30 min of growth.

The correlation between the time of growth of the particles, after the injection of the sulfur solution, and its stability could be explained with the help of the infrared spectroscopy. The FT-IR spectra of the Bi<sub>2</sub>S<sub>3</sub>-OAm sample, are shown in the Figure 4. The signals at 2922 cm<sup>-1</sup> and 2853 cm<sup>-1</sup> are due to the asymmetric and symmetric CH<sub>2</sub> stretching modes. The peak at 3008 cm<sup>-1</sup> is attributed to a cis HC=CH arrangement, while at 3076 cm<sup>-1</sup> is a trans arrangement [6]. Another proof of the organic capping layer are the signals at 1467, 1370 and 720 cm<sup>-1</sup>, characteristic of a long organic chain, and at 998 and 908 cm<sup>-1</sup>, due to CH<sub>2</sub> bending modes. 1526 cm<sup>-1</sup> and 1407 cm<sup>-1</sup> are attributed at the carboxylate group, and this confirms the presence of oleic acid. The apparition, after 30 min, of the new signals at 1710 cm<sup>-1</sup>, the stretching of a carbonyl group (C=O), and 1646 cm<sup>-1</sup> suggest the presence of an amide [7]. The only way to have it, is a reaction between the oleylamine and the oleic acid. In fact, this signal is not present in the FT-IR spectra of Bi<sub>2</sub>S<sub>3</sub>-HMS and Bi<sub>2</sub>S<sub>3</sub>-NW samples, synthesized in presence of only OA and OAm, respectively. The high steric hindrance of the chains, can cause a multi-layer capping with some functional group facing the apolar solvent, decreasing the stability of the particles.

### 3. Conclusions

In summary, we presented different synthesis methods to produce Bi<sub>2</sub>S<sub>3</sub> in orthorhombic phase with different size and morphologies. The Bi<sub>2</sub>S<sub>3</sub>-HMS method is the standard one and most employed for the production of photovoltaic devices. It allows a variation in size of the particles and so a control on the quantum size effect of the material. The other methods employ less aggressive chemicals and allow to change the morphology going from nanorods to nanowires, a fact that could prove useful to tune the conductive and optical properties. We have investigated the effect of the oleylamine on the growth of the particles and on its stability. Our results may prove useful to develop a dependable and “green” synthesis route for the production of colloidal Bi<sub>2</sub>S<sub>3</sub> nanocrystals.

### Acknowledgments

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