

Synthesis and Shape Control of Copper Tin Sulphide Nanocrystals and Formation of Gold–Copper Tin Sulphide Hybrid Nanostructures

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Hexagonal prismatic Cu_3SnS_4 nanoparticles and nanorods were synthesized by a hot-injection procedure. Changing the reaction conditions leads to the formation of different shapes. When oleylamine is used as a solvent, hexagonal prismatic particles are obtained, while a reaction in octadecene results in the formation of nanorods. The growth process of copper tin sulphide starts with the formation of djurleite copper sulphide seeds. Their reaction with Sn^{4+} ions leads to the formation of Cu_3SnS_4 . These Cu_3SnS_4 nanocrystals form Au– Cu_3SnS_4 hybrid nanostructures by reaction with gold seeds.

Key words: Copper Tin Sulphide; Shape Control; Nanorods; Colloidal Synthesis; Semiconductor–Metal Hybrid Nanoparticles.

1. Introduction

Copper-based chalcogenide nanocrystals have attracted much interest as light absorbing materials in photovoltaic devices, due to their electrical and optical properties as well as the environmental compatibility and relatively low toxicity [1–4]. For example, thin film solar cells fabricated with $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ nanocrystals have achieved an efficiency over 20% [5] but their production can be limited due to the high price and scarcity of indium. An alternative material could be copper tin sulphide (Cu_3SnS_4), which is a p-type semiconductor with a band gap between 1.2–1.6 eV, depending on the crystallographic structure, and an absorption coefficient of 10^4 cm^{-1} in the visible range. Due to its suitable band gap, copper tin sulphide (CTS) can be potentially used as a relatively cheap light absorbing material in solar cells.

In spite of their high application potential, CTS nanocrystals are not well studied so far, and there are not many reports about the synthesis and shape control of this material yet. Up until now, zero- and two-dimensional CTS nanostructures have been reported [6–10], however no examples of uniform one-dimensional nanocrystals or metal–semiconductor hybrid nanoparticles based on CTS were shown.

Here, we describe the synthesis of monodisperse CTS nanocrystals with hexagonal prismatic and nanorod shape by a simple and fast hot-injection method. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-Vis absorption spectroscopy were applied to investigate the shape, the structure, and the optical properties of the CTS nanocrystals. Furthermore, we evaluated the possibility to generate semiconductor–metal hybrid nanoparticles based on our CTS nanocrystals, which could further extend their application potential. We could synthesize Au–CTS heterostructured nanocrystals by reaction of the CTS particles with gold seeds.

2. Experimental

2.1. Materials

Copper(II) acetylacetonate (CuAcac_2 , $\geq 99.99\%$ trace metals basis), tin(IV) acetate (SnAc_4 , $\geq 99.99\%$ trace metal basis), 1-dodecanethiol (1-DDT, 98+%), *tert*-dodecanethiol (*t*-DDT, 98.5%, mixture of isomers), gold(III) chloride (AuCl_3 , 98%) and dodecyldimethylammonium bromide (DDAB, 98%) were purchased from Aldrich. Oleylamine (OLAM) and dodecylamine (DDA) were delivered from Acros Organics and trioctylphosphine oxide (TOPO, 98%) from

Alfa Aesar. All chemical were used without any further purification.

2.2. Synthesis of CTS Nanocrystals

1 mmol of CuAcac₂, 0.3 mmol of SnAc₄, and 3.8 mmol of TOPO were dissolved in 10 ml of OLAM under vacuum at room temperature. After 30 min, the reaction mixture was purged with nitrogen and heated to 200 °C. Subsequently, 2 ml of a mixture of 1-DDT and *t*-DDT, with the volume ratio 1 : 7, was quickly injected and the reaction temperature was increased to 240 °C. The growth of the nanocrystals was finished after 1 h. In the meantime aliquots were taken at reaction times between 1 and 15 min, to capture different growth stages of the particles. The final nanocrystals were cooled to room temperature, precipitated with ethanol, and redissolved in hexane for further investigations.

2.3. Preparation of Nanorod Shaped CTS Nanoparticles

1 mmol of CuAcac₂, 0.3 mmol of SnAc₄, and 3.8 mmol of TOPO were mixed and subsequently dissolved in 10 ml of ODE in a three neck flask. The reaction mixture was stirred under vacuum condition at room temperature. After 30 min, the reaction solution was purged with nitrogen and heated to 200 °C. Then, 7.5 ml of *t*-DDT was quickly injected and the reaction temperature was increased to 240 °C and maintained for 1 h. Aliquots were taken from the reaction solution at different times to monitor the growth process. The resulting nanocrystals were washed with ethanol and redissolved in hexane for the further investigations.

2.4. Growth of Au on the CTS Surface

The formation of Au–CTS hybrid nanoparticles was achieved using a procedure developed by Mokari et al. [11]. In the first step, a gold seeds solution was prepared as follows: 0.0116 g of AuCl₃, 0.0515 g of DDAB, and 0.0913 g of DDA were dissolved and stirred in toluene (4 ml). Next, the gold seeds solution was stepwise injected (within 15 min) to a solution of 15 mg CTS nanocrystals in 2 ml toluene. The reaction took place under inter gas atmosphere at room temperature and was completed after 15 min.

2.5. Characterization

The morphology of the nanocrystals was investigated by TEM using a Zeiss EM902A microscope with an acceleration voltage of 80 kV. High resolution TEM images were taken on a JEOL JEM2100F. All samples were prepared by dropping a diluted solution of the nanocrystals onto carbon-coated TEM grids. UV-Vis absorption spectra were measured with a Varian Carry 100 Scan spectrophotometer. XRD patterns were measured with a PANalyticalX'Pert PROMPD diffractometer operating with copper *K*α radiation and Bragg–Brentano $\theta - 2\theta$ geometry.

3. Results and Discussion

CTS nanocrystals were prepared using copper acetylacetonate and tin acetate as copper and tin precursors, respectively. Oleylamine was used as solvent, and the formation of the particles was induced by the injection of a mixture of 1-DDT and *t*-DDT at high temperature. *t*-DDT is a suitable sulphur source for the growth of metal sulphide particles [12–14]. It can also play a role of a stabilizer in the beginning of the reaction; however, it decomposes relatively fast at high temperature, therefore, addition of other compounds is necessary to provide sufficient stabilization of the growing particles. CTS is a ternary semiconductor build up of two cations with different chemical properties: Cu⁺ is a soft Lewis acid, Sn⁴⁺ a hard one. Therefore, we use two additional ligands: 1-DDT and TOPO. 1-DDT, which is a soft Lewis base reacts preferentially with Cu⁺ ions and controls their activity in solution, furthermore it can bind to the copper atoms on the surface of the nanocrystals. TOPO, which is a hard Lewis base is used as coordinating reagent that controls the activity of the tin ions and passivates the tin surface atoms.

Figure 1a shows a typical overview TEM image of CTS nanocrystals obtained with this method. The particles are hexagonal prisms. We can see them in two different orientations in the TEM image, as hexagons and rectangles. Furthermore, some larger particles of irregular shapes can be found in the sample. The uniform hexagonal prismatic particles show a pronounced tendency to self-organization into two-dimensional superstructures, as can be seen in Figure 1b.

UV-Vis absorption spectroscopy was used to investigate the optical properties of the hexagonal prismatic nanocrystals. A typical absorption spectrum of

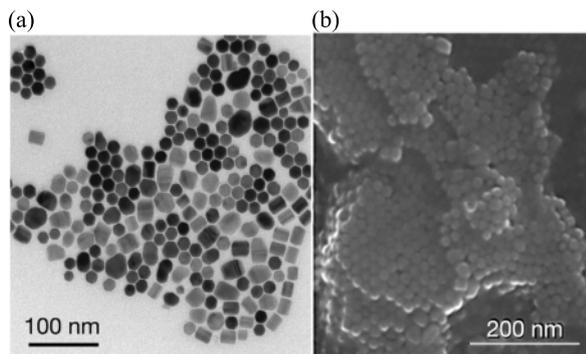


Fig. 1. Transmission electron microscope (a) and scanning electron microscopy (b) images of CTS nanocrystals.

the nanocrystals is shown in Figure 2. The nanocrystals absorb light in the visible range; therefore, their solution appears dark brown. The featureless absorption spectrum is typical for an indirect semiconductor. The optical energy gap E_g of a semiconductor material can be estimated based on the following equation:

$$\alpha\hbar\nu = A(\hbar\nu - E_g)^n,$$

where α is the absorption coefficient, \hbar the Planck constant, ν the photon frequency, A a constant, and n an index related to the optical absorption process ($n = 1/2$ for a direct allowed transition, $n = 3/2$ for a direct forbidden transition, $n = 2$ for an indirect allowed transition). The plot of $(\alpha\hbar\nu)^{1/2}$ versus $\hbar\nu$ shows linear behavior, corresponding to an indirect allowed transition. The value of the optical band gap calculated from this plot is 1.46 eV. Thus, the absorption onset is red-shifted, compared with orthorhombic Cu_3SnS_4 (bandgap 1.55 eV). This might be due to the presence of other phases, most likely, other modifications

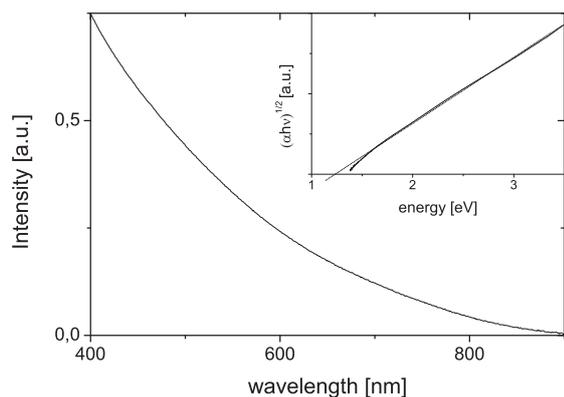


Fig. 2. UV-Vis absorption spectrum of CTS nanocrystals. The inset shows a Tauc plot with $n = 1/2$.

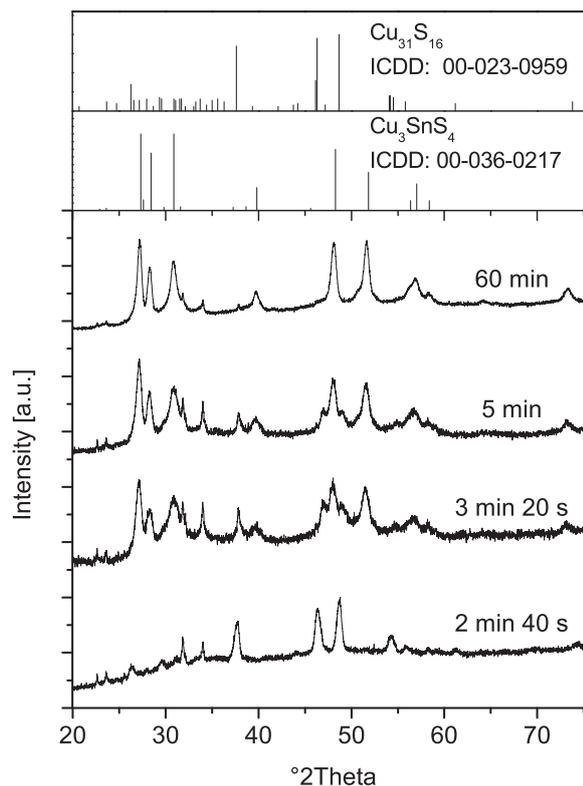


Fig. 3. XRD patterns of samples taken at different times during the growth process of CTS nanocrystals, together with reference data for djurleite copper sulphide, $\text{Cu}_{31}\text{S}_{16}$ and Cu_3SnS_4 .

of CTS, such as the tetragonal Cu_3SnS_4 phase with a bandgap of 1.2 eV [9].

The growth process of Cu_3SnS_4 nanocrystals was investigated by taking aliquots from the reaction solution at different reaction times and analyzing them with XRD. Particles forming in the beginning of the reaction consist of copper sulphide and have djurleite structure (see Fig. 3 bottom). Reflections, which can be assigned to orthorhombic Cu_3SnS_4 appear in the diffraction pattern of the sample that was taken 3 min 20 s after the injection of the thiols. With longer reaction time the copper sulphide phase disappears and the diffraction pattern of the sample taken after 60 min corresponds to Cu_3SnS_4 . The average crystalline domain size of CTS nanocrystals is calculated from the Debye–Scherer formula and is 20 nm. This value is in agreement with size estimated from TEM images.

By changing the reaction conditions, i.e., using a non-coordinating solvent and no strongly binding

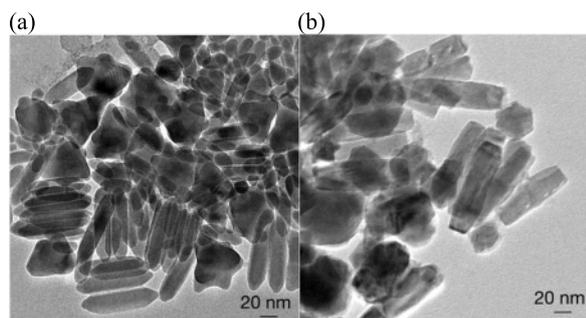


Fig. 4. TEM images of copper sulphide and CTS nanorods.

ligands, we could change the shape of the resulting nanocrystals from hexagonal prismatic to elongate. The nanorods, which were generated in a reaction in octadecene and using *t*-DDT as both sulphur source and stabilizer are shown in Figure 4b. Also this reaction starts with the formation of copper sulphide particles; most of them are rod-shaped, but also some larger particles with irregular shaped can be found in the sample (Fig. 4a). We found a similar shape distribution among the resulting CTS particles: the majority is rod-shaped, however also some larger nanostructures are present. This shows that the shape of the seeds has an influence on the final shape of the CTS particles. The formation of CTS is due to the incorporation of tin ions into copper sulphide particles, which results in an increase of the volume of the particles, but there is no significant change of the shape.

The properties of nanomaterials can be further modified by combining two different materials within one nanostructure, e. g., a semiconductor and a metal. This class of materials exhibits interesting new properties, due to the presence of a direct contact between two materials at the nanometer scale [15–17]. For instance, the combination of a metal and a semiconductor material can facilitate charge separation of the photogenerated charge carriers, which is interesting from the point of view of applications such as photovoltaics or photocatalysis.

CTS nanocrystals obtained by our method were further used to synthesize hybrid metal–semiconductor nanostructures by reaction with a solution of gold seeds. Figure 5a presents an overview TEM image showing the hybrid nanocrystals composed of gold with the average size of 3 nm on CTS nanocrystals. The gold nanodots form on the surface of the semiconductor particles without changing the shape of the original CTS nanoparticles. The gold islands do not

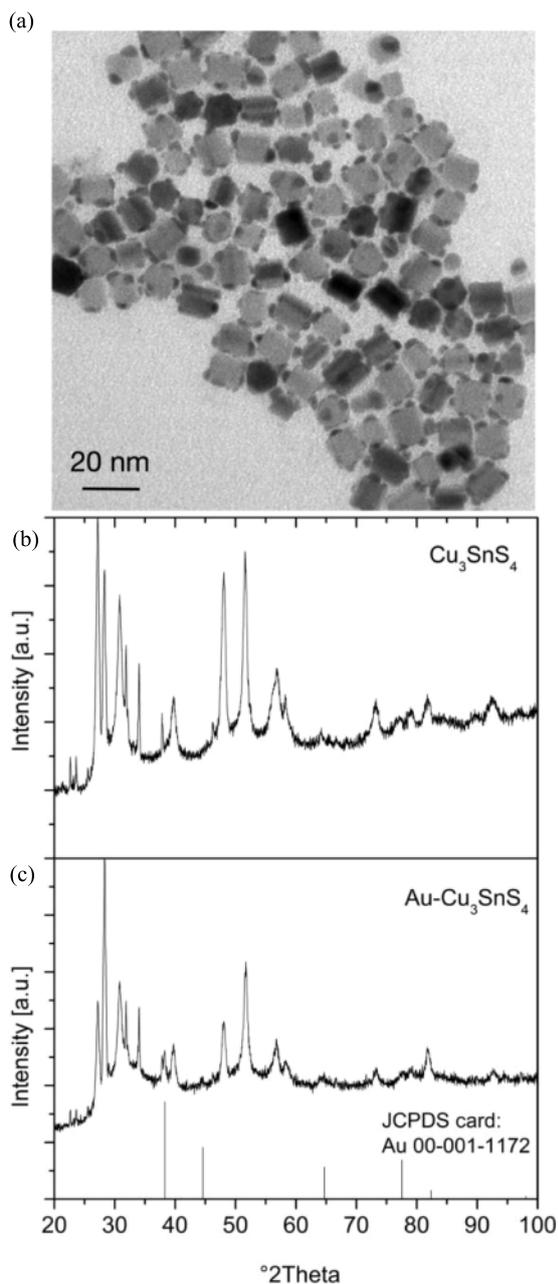


Fig. 5. An overview TEM image of Au–CTS hybrid nanocrystals (a) and the XRD patterns of CTS particles before and after the reaction with gold seeds.

form at any specific positions on the surface or edges of the hexagonal pyramids and seem to be randomly distributed. Probably the nucleation process preferentially starts on surface defects, similar to the growth process observed for CdS or CuInS_2 nanorods [18, 19].

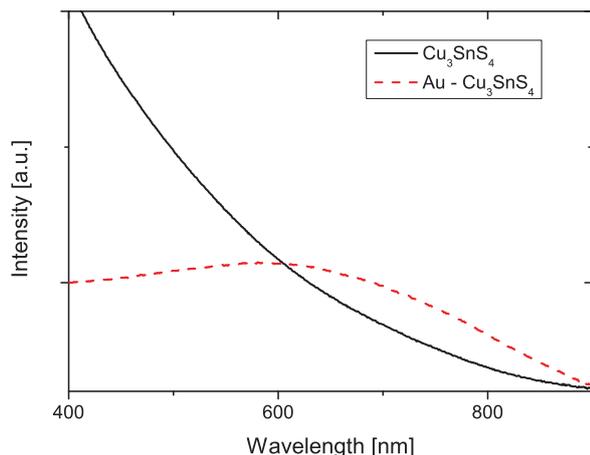


Fig. 6 (colour online). UV-Vis absorption spectra of CTS particles before and after the reaction with gold seeds.

The crystallographic structure of Au-CTS hybrid nanocrystals was studied by XRD (Fig. 5c). New reflections, which can be assigned to the cubic gold phase appeared in the diffraction pattern. These reflections are strongly broadened, which is in accordance with the relatively small size of the gold nanocrystals. The UV-Vis absorption spectrum of the hybrid structure is shown in Figure 6 together with the spectrum of the original CTS particles. The shape of the absorption spectrum changes due to the formation of the hybrid nanostructure. The broad shoulder,

which appears around 600 nm could be due to the plasmon resonance of the gold particles. It is red shifted, compared with the typical plasmon absorption of spherical gold nanocrystals. A red shift can originate from the interaction between the gold nanoparticles on the surface of the CTS nanoparticles with one another, or with the semiconductor material.

4. Conclusions

Uniform Cu_3SnS_4 nanoparticles could be synthesized by a simple and fast hot-injection method. Their growth process starts with the formation of djurleite copper sulphide seeds, which gradually disappear during the further growth process of the CTS particles. These nanocrystals can be used to generate semiconductor-metal hybrid nanostructures, exhibiting new optical properties. These Au-CTS heterostructured nanocrystals could be interesting candidates for application in solar energy conversion or photocatalysis.

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- [1] Y. Zhao and C. Burda, *Energy Environ. Sci.* **5**, 5564 (2012).
- [2] D. Aldakov, A. Lefrançois, and P. Reiss, *J. Mater. Chem. C* **1**, 3756 (2013).
- [3] J. Kolny-Olesiak and H. Weller, *ACS Appl. Mater. Interfaces* **5**, 12221 (2013).
- [4] E. Witt and J. Kolny-Olesiak, *Chem. A Eur. J.* **19**, 9746 (2013).
- [5] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, *Prog. Photovoltaics Res. Appl.* **21**, 1 (2013).
- [6] X. Lin, A. Steigert, M. C. Lux-Steiner, and A. Ennaoui, *RSC Adv.* **2**, 9798 (2012).
- [7] B. Li, Y. Xie, J. Huang, and Y. Qian, *J. Solid State Chem.* **153**, 170 (2000).
- [8] C. Wu, Z. Hu, C. Wang, H. Sheng, J. Yang, and Y. Xie, *Appl. Phys. Lett.* **91**, 143104 (2007).
- [9] L. Yi, D. Wang, and M. Gao, *Cryst. Eng. Commun.* **14**, 401 (2012).
- [10] Y. Xiong, Y. Xie, G. Du, and H. Su, *Inorg. Chem.* **41**, 2953 (2002).
- [11] T. Mokari, E. Rothenberg, I. Popov, R. Costi, and U. Banin, *Science* **304**, 1787 (2004).
- [12] M. Kruszynska, H. Borchert, J. Parisi, and J. Kolny-Olesiak, *J. Nanoparticle Res.* **13**, 5815 (2011).
- [13] M. Kruszynska, H. Borchert, J. Parisi, and J. Kolny-Olesiak, *J. Am. Chem. Soc.* **132**, 15976 (2010).
- [14] M. Kruszynska, H. Borchert, A. Bachmatiuk, M. H. Rummeli, B. Buechner, J. Parisi, and J. Kolny-Olesiak, *ACS Nano* **6**, 5889 (2012).
- [15] L. Carbone and P. D. Cozzoli, *Nano Today* **5**, 449 (2010).
- [16] P. D. Cozzoli, T. Pellegrino, and L. Manna, *Chem. Soc. Rev.* **35**, 1195 (2006).
- [17] R. Costi, A. E. Saunders, and U. Banin, *Angew. Chemie Int. Ed.* **49**, 4878 (2010).
- [18] A. E. Saunders, I. Popov, and U. Banin, *J. Phys. Chem. B* **110**, 25421 (2006).
- [19] E. Witt, J. Parisi, and J. Kolny-Olesiak, *Z. Naturforsch.* **68a**, 398 (2013).