Journal of Colloid and Interface Science 377 (2012) 13–17

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Controllable synthesis of MnS nanocrystals from a single-source precursor

Long Peng [a,b], Shuling Shen [b], Yejun Zhang [b], Huarui Xu [a,*], Qiangbin Wang [b,*]

[a] School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China
[b] Division of Nanobiomedicine and i-Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

ARTICLE INFO

Article history:
Received 5 October 2011
Accepted 19 March 2012
Available online 4 April 2012

Keywords:
Controllable synthesis
MnS nanocrystals
Single-source precursor
Morphology
Crystal structure

ABSTRACT

A facile single-source precursor method has been applied for the selective synthesis of MnS nanocrystals (NCs) with well-defined shapes and crystal structures such as hexapod, octahedral, hexagonal shaped α-MnS NCs, and pencil-shaped γ-MnS NCs. The effects of the composition of precursor, reaction temperature, and the heating rate on the morphologies, and crystal structures of MnS NCs were systematically studied for the first time.

1. Introduction

Colloidal semiconductor nanocrystals (NCs) have received considerable attention owing to their potential applications in photodetectors, light-emitting devices, solar cells, biological labeling, medical diagnostics, *etc.* [1–7]. These applications originate from the unique optical and electronic properties of semiconductor nanocrystals which not only depend on the size but also on the shape and crystal phase [8–11]. Therefore, fabrication of semiconductor nanocrystals with well-defined shape and desired crystal structure in a controlled manner is of key importance in rational designing and tailoring the properties of semiconductor nanocrystals.

As a p-type semiconductor with wide band energy (3.7 eV) and varied crystal structures (rock-salt structure α-MnS, zinc blende structure β-MnS, and wurtzite structure γ-MnS), MnS own promising optoelectronic properties and then have great potential applications in optoelectronic devices [12–14]. Moreover, MnS is an important diluted magnetic semiconductor, the outstanding magneto-optical properties of MnS has been extensively studied [15,16]. These novel properties of MnS NCs have been found closely depend on their size, shape, and crystal phase. Up to date, some synthetic routes have been developed for controlled synthesis of single-phase MnS NCs [17–19]. For example, Hyeon reported the synthesis of hexagonal MnS with wurtzite structure by heating a mixture of $MnCl_2$ and sulfur in oleyamine at 280 °C [17]. Octahedral α-MnS was synthesized by decomposing manganese oleate and elemental sulfur in octadecene at high temperature (250–320 °C) [18]. More recently, by a similar way, Hu and his coworkers synthesized star-shaped α-MnS nanocrystals, which show a high blocking temperature (275 K) and a large coercive field (1573 Oe) [19]. However, it is difficult to achieve size, shape and crystal structure control simultaneously by these methods.

Single-source precursor method is considered as a facile and reproducible route for fabrication of semiconductor nanocrystals with well-defined shape and crystal structure [20–22]. Various shapes of α-, β-, and γ-MnS nanocrystals including cubes, spheres, monowires, and branched wires were prepared by the thermal decomposition of a single-molecular precursor, $Mn(S_2CNEt_2)_2$, in a hexadecylamine (HDA) monosurfactant system through varying the growth temperature and the reaction time [23]. In addition to the reaction temperature and time, we have reported that the composition of precursor, the sorts of solvents, and the heating rate play crucial roles in determining the size, shape, and composition of metal sulfide nanocrystals synthesized from a single-source precursor method [24–29]. However, to our best knowledge, how these factors affect the morphology and crystal structure of MnS NCs has not been reported yet.

Herein, we report the synthesis of MnS NCs with well-defined shapes and crystal structures by using Mn-diethyldithiocarbamate ($Mn(DDTC)_2$) or $Mn(DDTC)_2(Phen)$ (Phen = 1,10-Phenanthroline) as the single-source precursor and thermo-decomposing in the solvents of oleic acid (OA)/oleylamine (OM)/1-octadecene (ODE). The effects of the composition of precursor, reaction temperature, and the heating rate on the morphology and crystal structure of MnS NCs were comprehensively studied for the first time. Hexapod,

* Corresponding authors. Fax: +86 512 62872620 (Q. Wang).
E-mail addresses: huaruixu@guet.edu.cn (H. Xu), qbwang2008@sinano.ac.cn (Q. Wang).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.03.052

octahedral, quasi-sphere shaped α-MnS NCs, and pencil-shaped γ-MnS NCs can be selectively synthesized by tuning the synthetic conditions.

2. Experimental section

2.1. Chemicals

Manganese chloride ($MnCl_2{\cdot}4H_2O$, 99%), diethyldithiocarbamate trihydrate (Na(DDTC)·$3H_2O$, 99%), 1,10-Phenanthroline ((Phen)·H_2O, 99%) were purchased by Sinopharm Chemical Reagent Company. Oleic acid (OA; 90%, Aldrich), Oleylamine (OM; 80–90%, Aladdin), 1-Octadecane (ODE; 90%, Aldrich), absolute ethanol, and cyclohexane were analytical grade and used without further purification.

2.2. Synthesis of $Mn(DDTC)_2$

In a typical experiment, a solution of Na(DDTC)·$3H_2O$ (10 mmol in 30 mL of water) was added into an aqueous solution of $MnCl_2{\cdot}4H_2O$ (5 mmol in 80 mL of water) under vigorous stirring. After continuous stirring for 0.5 h, the reaction solution was kept stationary under the ambient condition for 3 h. The resulting precipitate was filtered, washed several times with distilled water and then dried in air at 60 °C overnight and the $Mn(DDTC)_2$ powders were obtained.

2.3. Synthesis of $Mn(DDTC)_2(Phen)$

Typically, 5 mmol of (Phen)·$3H_2O$ were dissolved in 30 mL of boiling water. Then, it was added into 80 mL of $MnCl_2$ (5 mmol) aqueous solution under vigorous stirring. After 10 min, 30 mL of Na(DDTC) (10 mmol) aqueous solution was introduced dropwise into above mixture. After 3 h, the resulting precipitate was collected by vacuum filtration and washed with deionized water. The precipitate was dried at 60 °C overnight and the $Mn(DDTC)_2(Phen)$ powders were obtained.

2.4. Synthesis of hexapod MnS NCs

The synthesis of MnS NCs with various morphologies and crystal structures was accomplished using a single-source method. In a typical procedure for hexapod MnS NCs, 0.1 mmol of $Mn(DDTC)_2$ was added into a mixture of OA, OM, and ODE (10:10:20 mmol) at room temperature. Then, the resulting mixture was heated to 120 °C to remove water and oxygen with vigorous magnetic stirring under vacuum for 30 min in a temperature-controlled electro-mantle. The reaction mixture was then heated to 290 °C at a rate of 15 °C/min under N_2 atmosphere and maintained at 290 °C for 1 h. After cooled down to room temperature naturally, the MnS nanocrystals were purified by precipitation with absolute ethanol. The precipitate was collected by centrifugation and subsequently dispersed in cyclohexane or other nonpolar solvents (hexane, toluene, *etc.*). The morphology and crystal structure of MnS NCs were tuned by changing precursor (using $Mn(DDTC)_2(Phen)$ as precursor), stabilizer (OA,OAM), reaction temperature, time, and heating rate while keeping the other conditions.

2.5. Characterization

The element contents in the presynthesized single-source precursor were determined by elemental analysis on an Elementary Vario EL (Germany) system. Powder X-ray diffraction (PXRD) patterns of the dried powders were recorded on a Bruker D8 Advance powder X-ray diffractometer at a scanning rate of 4° min^{-1}, using Cu Kα radiation (λ = 1.5406 Å). The morphologies and high-resolution TEM (HRTEM) characterization were examined by a Tecnai G2 F20 S-Twin TEM (FEI, USA) operated at 200 kV. Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of nanocrystals dispersed in cyclohexane on amorphous carbon-coated copper grids. The UV–Vis absorption spectra were obtained on a Perkin Elmer/Lambda 25 UV–Vis spectrometer (USA).

3. Results and discussion

3.1. Effect of precursors

The element content of the as-prepared precursors was measured. Table 1 depicted the N, C, H, and S contents in the $Mn(DDTC)_2{\cdot}2H_2O$ and $Mn(DDTC)_2(Phen)$ precursors. The elementary analysis was consistent with the calculated values. FTIR results clearly shown the characteristic peaks of C–S, C–N, and the skeleton vibration of the benzene ring of phen, which belong to $Mn(DDTC)_2$ and $Mn(DDTC)_2(phen)$, respectively (Fig. S1).

The shape and crystal structure of the MnS NCs closely depend on the composition of precursors, solvents, reaction temperature, and heating rate. All the parameters were found to be interdependent, thus resulting in interesting combinations for the shape and crystal structure-selective synthesis of various MnS NCs.

Figs. 1a and S2a show the TEM images of hexapod shaped MnS NCs synthesized from $Mn(DDTC)_2$ in OA/OM/ODE mixture at 290 °C for 1 h. Fig. 1b is a magnification TEM image of single hexapod shaped MnS NC with high symmetry. The length of the pods is about 30 nm. The HRTEM image of the pod section reveals the highly crystalline nature and a lattice plane with interplanar distance of 0.18 nm (Fig. 1c), which belong to (2 2 0) plane of MnS, indicating that the pod growth occurs preferentially on the (2 2 0) planes. This may be due to the growth inhibition of the {1 1 1} planes by the selectively adsorption of OM or OA in the absence of phen in the precursors. Bipods, tripods, and tetrapods MnS NCs have been synthesized by tuning the nucleation and growth temperature and time of single-source precursor [23]. To our best knowledge, it is the first time for hexapod MnS NCs with six highly symmetric arms synthesized by the single-source precursor method.

In our system, 1,10-phenanthroline (phen) was incorporated into the single-source precursor of $Mn(DDTC)_2$ as impurity. It is expected that the incorporation of phen as impurity can provide more means for controllable synthesis of diverse-shaped MnS NCs. When using the mixture of $Mn(DDTC)_2$ and $Mn(DDTC)_2(Phen)$ (with a molar ratio of 1:1) as precursors, octahedral MnS NCs with a diameter of 100–200 nm and rough surface were obtained (Figs. 1d and e and S2b). The SAED pattern on single octahedral MnS NC shown in Fig. 1f demonstrates the high crystalline nature of MnS NCs. The diffraction spots can be clearly indexed to diffraction from (2 2 0) planes of α-MnS. When only $Mn(DDTC)_2(Phen)$ was applied as precursor, hexagonal MnS NCs with rough edges were fabricated (Fig. 1g and h and S2c). The HRTEM image of an edge in a single hexagonal MnS NC shows the lattice spacing of 0.18 nm from (2 2 0) planes (Fig. 1i). It strongly suggests that the bidentate ligands phen can influence the growth of MnS NCs. Impurities such as 1,10-phenanthroline, 2,2′-bipyridine, and methylene blue have significant effect in size and shape control of nanocrystals, which has been observed in many systems [26,30]. In our system, when phen was incorporated into the precursor, it might be competing with OM and OA on surface sites of the nanocrystals inducing the shape evolution from hexapod shaped MnS to octahedral MnS. When increase the reaction temperature, the