2D molecular precursor for a one-pot synthesis of semiconducting metal sulphide nanocrystals

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MS received 19 March 2018; accepted 1 May 2018; published online 6 September 2018

Abstract. 2D molecular materials, namely, metal alkyl thiolates, have been used as a single-source precursor for the synthesis of semiconducting metal sulphide nanocrystals (NCs) by thermal decomposition. These 2D molecular precursors have all the ingredients required for metal sulphide synthesis (metal source, sulphur source and protecting ligand). In this study, we demonstrate a simple and general ‘solvothermal decomposition’ approach for the synthesis of high-quality Cu₂S, PbS, CdS, MnS and ZnS NCs. The size of the NC can also be controlled by changing the decomposition temperature. Furthermore, the optical properties of the NCs have also been studied.

Keywords. Single-source precursor; nanocrystal; thermal decomposition; optical properties.

1. Introduction

Over the past few decades, there has been great interest in the utilization of semiconducting nanocrystals (NCs) for biomedical [1–3], electronic [4–6] and alternative-energy applications [7–9]. This interest stems from their optical properties, which can be tuned by particle size via quantum confinement or changing the composition. Even a slight change of size, morphology or composition of NCs has a considerable effect on the optical properties, including the energies of the absorption onset, fluorescence emission and surface plasmons [10]. Thus, the synthesis of monodisperse, single-crystalline metal sulphide NCs is highly desired. While there are many ways to synthesize NCs, solution-based colloidal synthesis often yields the high-quality materials, with desired monodispersity displaying uniform properties [10]. Over the past several years, several groups have reported the synthesis of metal sulphide NCs using various synthesis routes, including the thermolysis of single-source precursors [11–13], solvent-less synthesis [14], thermolysis of metal–oleylamine complexes [15] and a simple organic-amine-assisted hydrothermal process [16].

In this communication, a general ‘solvothermal decomposition’ approach has been carried out for synthesizing metal sulphide NCs. It is a direct-heating approach without any subsequent reagent injection. Both the ‘direct-heating’ and ‘hot-injection’ processes are very convenient

and are suitable for large-scale synthesis. However, to obtain high-quality NCs, the hot-injection method poses some drawbacks as the reagents used are characterized with high reactivity [17]. Therefore, modulating size via this ‘hot-injection’ process becomes tricky for many systems. On the other hand, the 2D molecular precursors (metal alkyl thiolates) that we propose here have ideal reactivity and have all the ingredients required for metal sulphide synthesis (metal source, sulphur source and protecting ligand). Because of their low reactivity below a certain temperature (i.e., the reaction temperature) a short nucleation process can be achieved simply by direct heating of these metal thiolates at or above the decomposition temperature. Thus, at these high temperatures, the decomposition of thiols leads to the formation of metal sulphides and at the termination of the reaction, the particles get *in-situ* capped with a layer of intact thiols. Furthermore, metal thiolates of different metals are easy to prepare in large scale by a simple solvent-less process, which are highly stable in air below the decomposition temperature. Accordingly, we show in this work that by the decomposition of a suitable metal thiolate in a high boiling solvent like 1-octadecene a series of metal sulphide NCs, such as Cu₂S, PbS, ZnS, MnS and CdS, can be successfully synthesized. Interestingly their size also can be controlled by varying the decomposition temperature. This method avoids injecting a second reagent during the reaction and uses air-free manipulation, which is very suitable for large-scale synthesis.

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12034-018-1639-6>) contains supplementary material, which is available to authorized users.

Scheme 1. Schematic representation of the metal thiolate synthesis.

2. Experimental

2.1 General procedure for metal sulphide NCs

A quantity of 200 mg of metal thiolates powder was taken along with 15 ml of 1-ODE in a 100 ml RB flask. First, the reaction mixture was heated at mild temperature (130–140°C); the homogeneous clear solution formed was then further heated at high temperature (200–240°C) for 30 min. This reaction mixture was precipitated and washed with methanol to obtain pure metal sulphide NCs. These products were re-dispersed into toluene or tetrachloroethylene and characterized by PXRD and UV–vis absorption, fluorescence spectra and transmission electron microscopy (TEM).

3. Results and discussion

A series of 2D molecular precursors (metal thiolates of different metals like Cu, Pb, Cd, Mn and Zn) were

synthesized following our previously reported protocol [18].

Briefly, metal precursors (such as metal acetate or metal iodide) were taken in a glass vial and alkyl thiol (octane thiol) was added into this (the generic procedure for metal thiolate synthesis is shown in scheme 1). This immediately led to a colour change due to M–S co-ordination (synthesis and cleaning of materials are explained in detail in the Experimental section in supplementary information). These metal alkyl thiolates are coordination compounds and exist as lamellae or stacked sheets in the solid state [18]. The PXRD patterns of different metal thiolates are shown in figure 1a, which shows periodically spaced (00 l) reflections. SEM images (shown in figure 1b–f) of these metal thiolates also clearly indicate that all of the metal thiolates are featured with layer-like structures and justify the sheet-like (2D) morphology. It is confirmed by energy-dispersive X-ray analysis (see supplementary figure S1) that the stoichiometry of metal thiolates is $\text{M}_n(\text{SR})_n$ (where M = Cu, Pb, Cd, Mn and Zn and n = oxidation state of metal). This simple and generic solvent-less synthesis of 2D single-source precursors is scalable and the resulting materials are also highly stable in air [18].

Subsequently, the semiconducting metal sulphide NCs were synthesized using these 2D molecular precursors as a starting material (the generic procedure for metal sulphide synthesis is shown in scheme 2). The main advantage is that the 2D metal thiolates used here are single-source precursors,

Figure 1. (a) PXRD of metal thiolates; PXRD of manganese octanethiolate (MnC_8S) is in black, cadmium octanethiolate (CdC_8S) in blue, lead octanethiolate (PbC_8S) in red, copper octanethiolate (CuC_8S) in green and zinc octanethiolate (ZnC_8S) in pink. SEM images of metal thiolates: (b) CuC_8S , (c) CdC_8S , (d) PbC_8S , (e) ZnC_8S and (f) MnC_8S .

Scheme 2. Method for generic metal sulphide NCs synthesis.

Thermal decomposition of metal thiolates

Scheme 3. Proposed reaction mechanism for thermal decomposition of metal thiolates to metal sulphide NCs (following Ref. [19]). The equation has not been balanced.

where all the ingredients required for metal sulphide NCs are inbuilt in their structure (metal source, sulphur source and capping agent). These metal thiolates are highly stable and are dispersible at mild temperatures (120–140°C) in a high boiling solvent like 1-octadecene. After or at a certain temperature (decomposition temperature) the uniform dispersion of metal thiolates (which have been shown to exist as individual sheet-like structures in solution) [18] can decompose into metal sulphide and an alkene [19] and some of the undecomposed alkyl thiol passivate the surface of the NCs to control the growth (proposed reaction mechanism is shown in scheme 3, according to Choi *et al* [19]). In the following, the synthesis procedure is explained in detail through the synthesis of cadmium sulphide NCs as an example. First, 200 mg of the Cd-octanethiolate 2D molecular complex was taken along with a solvent (1-octadecene) and the temperature was raised to 130°C to get a homogeneous clear solution. The temperature was then raised to 200–240°C in argon flow and the reaction was kept at this temperature for 30 min. The colourless solution became pale yellow, indicating formation of CdS. The heating was stopped immediately after the colour change and the system was allowed to naturally cool to room temperature (which took ~45 min). The product of this reaction was collected by precipitating it with acetone/ethanol addition, and after washing it two times with acetone/ethanol (centrifuged at 5000 rpm for 3 min) the precipitate was dried in argon flow. The precipitate was re-dispersed into tetrachloroethylene or toluene for various measurements. The PXRD pattern of the purified materials clearly matched those of the CdS cubic phases (for PXRD pattern of these samples, see supplementary figure S2), which corresponds to JCPDS card No#43-1469. Figure 2 shows the UV–vis absorption spectra of CdS NCs synthesized between 200 and

Figure 2. Absorption (solid line) and emission (dotted line) spectra of CdS NCs synthesized at different temperatures (200–240°C).

240°C. As can be noticed, all spectra exhibit sharp bandgap absorption features, indicating the formation of nearly monodisperse CdS NCs. It may be noticed that the samples display a well-defined excitonic peak and the peak position varied gradually from 370 to 385 to 405 nm as the reaction temperature was varied to 200 to 220 to 240°C (figure 2). The absorption peak also becomes narrow and the peak shifts towards red (figure 2). The photoluminescence (PL) of CdS NCs (figure 2) shows both a sharp bandgap emission as well as trap state emission centred around 450–700 nm. The trap state emission is significantly depressed on increasing reaction temperature and bandgap emission dominates the fluorescence of CdS NCs for synthesis temperatures over 200°C (figure 2).

TEM images show near-spherical NCs with average size of ~3 nm and the size of CdS NCs can be tuned between ~3 and 5 nm, with longer reaction times and higher reaction temperatures favouring the formation of larger NCs (figure 3a–c).

Similar to the synthesis of CdS NCs, nearly monodisperse sub-13 nm PbS NCs can be synthesized by heating Pb-octanethiolate precursor in ODE solution at 200°C. The PXRD pattern of the purified materials clearly matched that of the PbS with rock salt structure (see supplementary figure S2), which corresponds to JCPDS card No#05-0592. TEM images showed NCs with nearly spherical shape and average size of 13 nm (figure 3d). As in the case of CdS and PbS NCs, monodisperse ~sub-3 nm ZnS and MnS can also be synthesized by thermal decomposition of zinc octanethiolate and Mn-octanethiolate, respectively, in ODE at 240°C. The PXRD pattern of the purified materials shows zinc blende ZnS phase (supplementary figure S2; JCPDF no-75-1546), and the average size of NCs in both these cases was found to be ~3.5 nm (see figure 3e for TEM image of ZnS NCs and figure 3f for TEM image of MnS NCs).

The PL of ZnS NCs (figure 4a) shows a sharp bandgap emission at ~410 nm. The PXRD pattern of MnS NCs (supplementary figure S2) is broad in nature, which we ascribe

Figure 3. TEM images of different metal sulphide quantum dots synthesized using their corresponding thiols as precursors. CdS at different temperatures: (a) 200, (b) 220 and (c) 240°C. (d) PbS at 200°C, (e) ZnS at 200°C and (f) MnS at 200°C. In all images, the scale bar corresponds to 20 nm.

Figure 4. Optical spectra of ZnS and MnS NCs. (a) Absorption (red line) and emission (black line) spectra of ZnS NCs. (b) Emission spectra of MnS NCs synthesized at different temperatures.

to the small-sized particles (2.5–3 nm). The PL of MnS NCs, synthesized at different reaction temperatures, shows a sharp bandgap emission range of 470–490 nm (figure 4b). The TEM image of the MnS NCs synthesized at 200°C (figure 3f) reveals the presence of small spherical-shaped NCs.

Similar to the synthesis of different NCs described earlier, monodisperse NCs of ~6–10 nm Cu_2S were also synthesized

by the thermal decomposition of copper octanethiolate in ODE at 200–240°C. For this, first, 200 mg of the Cu-octanethiolate (prepared using copper acetate as Cu source) 2D molecular complex was taken in a solvent (1-octadecene) and the temperature was raised to 130°C to get a homogeneous clear solution. The temperature was then raised to 200°C in argon flow and the reaction was kept at this

Figure 5. TEM images of Cu_2S prepared by thermolysis from Cu-octanethiolate ($\text{Cu}(\text{ac})_2$ as metal precursor) at (a) 200 and (b) 240°C. (c, d) Effect of iodide in thermolysis of Cu-octanethiolate (CuI as metal precursor); mixed shape of particles formed (like plates, sheets as well as spherical particles are present).

temperature for 30 min. The pale yellow coloured solution became brownish black, indicating formation of Cu_2S . The heating was stopped immediately after the colour change; the system was allowed to naturally cool to room temperature (which took ~ 45 min) and later the material was purified, similar to the CdS NCs synthesis. The PXRD pattern of the purified materials clearly matched with the chalcocite Cu_2S structure (for PXRD pattern of these samples, see supplementary figure S2), which corresponds to JCPDS 84-0206. TEM images (figure 5a) reveal that the NCs are almost uniform in size and spherical in shape with a particle diameter of ~ 6 nm. One of the notable features of this synthesis procedure is the tunability of NCs size by changing the reaction temperature. For instance, when the Cu-thiolate clear

solution (obtained by heating the Cu-thiolate in 1-octadecene to 130°C) was heated to 240°C for 30 min, ~ 10 -nm-sized spherical Cu_2S NCs were obtained (TEM images shown in figure 5b).

Interestingly, not only the size of Cu_2S NCs but also the shape (morphology) can be controlled by changing the metal source during synthesis of metal thiolate preparation. For instance, we found that the high-temperature decomposition of Cu-octanethiolate prepared from CuI at 240°C in 1-ODE resulted in the formation of plate-like Cu_2S NCs (with very few spherical NCs, see figure 5c and d). This is in agreement with the results of Wu *et al* [20], where they reported that introduction of halide ions slows down the growth kinetics and therefore the Cu_2S NCs with plate-like morphology

are more favoured. In our case as the Cu-octanethiolate was prepared from CuI, some iodide ions were found to be left behind as confirmed from the EDS results (see supplementary figures S3 and S4) of the Cu-octanethiolate sample. We strongly believe that these iodide ions act as shape-directing agents, resulting in the formation of Cu₂S plates, similar to the previous studies [20].

We believe that the simple process described here can be easily extended to prepare heterostructure of different metal sulphides like CdS–ZnS, CdS–MnS and ZnS–MnS; Cd_xZn_{1–x}S, Zn_xCd_{1–x}S, etc. by simply heating the corresponding metal thiolates (in a proper ratio) in a high boiling solvent. It is well known that the afore-mentioned heterostructure NCs show high quantum yield; hence these type of heterostructures are expected to be highly useful in LED (optoelectronic devices) applications. Similarly, synthesis of doped NCs like Mn:CdS and Mn:ZnS could also be attempted by heating manganese thiolates (taken in a proper ratio) with cadmium or zinc thiolates in a high boiling solvent.

4. Conclusion

In conclusion, a simple and general direct-heating solvothermal decomposition synthesis method using 2D molecular precursor (metal thiolates as single-source precursor) has been developed for the synthesis of different metal sulphide NCs like Cu₂S, PbS, CdS, MnS and ZnS. The synthesis of starting material (metal thiolate 2D sheets) is also very simple and scalable. We also showed that the size and shape of the NCs could be controlled by changing the reaction temperature and changing the metal precursor (used for metal thiolate preparation).

Acknowledgements

AB thanks UGC, New Delhi, for research fellowship. We thank the Council of Scientific and Industrial Research

(CSIR), New Delhi, for financial assistance through the 12th Five-Year Plan Project (CSC 0134).

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