Synthesis of copper and zinc sulfide nanocrystals via thermolysis of the polymetallic thiolate cage

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Abstract

In this paper report on the synthesis of copper and zinc sulfide nanocrystals (NCs) via the formation of polymetallic thiolate cages. Cu\textsubscript{2}S NCs derived from Cu–dodecanethiol complex formed well-defined spherers, which were sufficiently monodisperse (with a size distribution of \(\leq 10\%\) standard deviation of approximately 4.7 nm diameter on average) to generate ordered self-assemblies. An electron diffraction pattern and UV–vis spectrum of Cu\textsubscript{2}S NCs indicate that this process can provide pure \(\beta\)-chalcocite (Cu\textsubscript{2}S). Nearly monodisperse ZnS NCs with a size ranging from 3 to 7 nm were obtained by thermolysis of the S–Zn–dodecanethiol precursor. The electron diffraction pattern indicates that zinc sulfide NCs are either wurtzite or a mixture of wurtzite and zincblende. TEM observation and UV–vis spectra revealed that the growth rate of ZnS NCs depends strongly on the annealing temperature. UV–vis spectra of 3 nm ZnS NCs show sharp excitonic features and a large blue shift from the bulk material. The photoluminescence spectra exhibit a large red shift from the absorption band edges. These shifts could be attributed to recombination from the surface traps. The narrow size distribution of Cu\textsubscript{2}S and ZnS NCs led to the formation of ordered self-assemblies with various well-defined but nonclosed-packing.

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1. Introduction

Transition-metal chalcogenide nanocrystals (NCs) have been extensively investigated for potential application to catalyst, solar cell, photoluminescence and optical devices [1,2]. Copper sulfide NCs are expected to be a prominent candidate for optical devices because they exhibit a high third-order nonlinear optical susceptibility (which is the largest nonlinear term relating to the polarization function; about \(10^{-7}\) esu\textsuperscript{3}). The chalcocite group (Cu\textsubscript{2−x}S) involves various compounds such as Cu\textsubscript{2}S \(\gamma\)-\(\beta\)-chalcocite), Cu\textsubscript{1.96}S (djurleite) and Cu\textsubscript{1.8}S (digenite) [4], showing stoichiometry-dependent optoelectric properties [3]: Cu\textsubscript{1.96}S, Cu\textsubscript{1.9}S and Cu\textsubscript{1.8}S are the direct band gap materials, while Cu\textsubscript{2}S is the indirect band gap material. Cu\textsubscript{2−x}S is also characterized by an increase in the band gap with the increase of the \(x\) value (from 1.2 eV for Cu\textsubscript{2}S to 1.5 eV for Cu\textsubscript{1.8}S and \(\sim\) 2.0 eV for CuS). This situation encourages the tailoring of single-phase copper sulfide NCs. Copper sulfide NCs have been generally synthesized via the aqueous solution, the inverse micelle [5], the chemical conversion [3] and the solvent-less processes [6]. However, the formation of undesirable by-products such as sub-phase and CuSO\textsubscript{4}·\(n\)H\textsubscript{2}O [6,7] are inevitable in the aqueous or aqueous/organic solution system.

Zinc sulfide is well known to be a photo- and electro-luminescence material, which has a large exciton bond energy (37 meV). Therefore, quantum size effects such as exciton confinement and size dependency of the band gap should be observed in this NCs system. Many reports detailing synthesis of the ZnS thin film ‘quasi 2-dimensional system’ are available. However, to our knowledge, there are few published reports detailing synthesis of the ZnS quantum dot ‘quasi zero dimensional system’.

In the last decade, nonaqueous solution synthesis of monodisperse NCs has been developed to produce
monodisperse semiconductor NCs (such as CdSe, CdS [1], ZnSe [8] and InAs [9]) and transition metals (such as Co [10,11], Fe and Ni [11]). However, these processes require organo-metallic precursors (Cd(CH)₃, alkoxide and metal carbonyl), which are harmful and unstable in ambient atmosphere.

Dance and co-workers revealed the existence of chalcogenide lattice fragments in the [S₄M₁₀(SPh)₁₆]⁴⁻, M=Cd and Zn’ polymetallic thiolate cage [11]. While Herron and co-workers reported that CdS microclusters were derived from the polymetallic thiolate cage by using the chemical control method [12,13]. In this report, polymetallic thiolate cages, which are nontoxic and stable in ambient atmosphere, were annealed in high boiling temperature organic solvent. The annealing process can provide monodisperse Cu₂S NCs [14] with a size ranging from ~2 to 7 nm and monodisperse ZnS NCs with a size ranging from ~3.0 to 7 nm. These monodisperse colloid systems enable us to synthesize the large-scale superlattice.

2. Experimental procedure

2.1. Synthesis process

In the case of copper sulfide NCs synthesis, all reagents were used as received. 0.10 g of copper(II) acetylacetonate (Cu(acac)₂) was mixed with 20 cm³ of octyl ether in a flask (details of the experimental apparatus are shown in Fig. 1), which was then degassed by Ar gas flushing for 2 h. 0.83 g of 1-dodecanethiol (HSR) was injected into the mixture solution and heated to 500 K. The solution turned to a transparent yellow at around 400 K, then to orange, and then immediately changed to a black colloidal solution at around 490 K.

All reagents were then used again as received for the synthesis of zinc sulfide NCs. Zinc(II) chloride/methanol solution and sulfur/1-dodecanethiol solution were mixed with 20 ml of octyl ether in a flask, which was degassed by Ar gas flushing for 7.2 ks, at 333 K (conditioning). If the reaction temperature was higher than 473 K, the mixture solution was heated at 473 K for 30 min to eliminate hydrated water (dehydration). Then, 1.88 cm³ of oleylamine was injected into the mixture solution and heated to the set temperature (annealing).

2.2. Purification process

After the mixture solution was cooled to room temperature, 200 cm³ of ethanol was mixed. The precipitates (dark brown: Cu₂S, white: ZnS) were separated by centrifuging the colloidal solution to remove excess reaction agents and then redispersed in hexane. This precipitate—redispersion procedure was repeated several times to purify the precipitates.

2.3. Characterizations

To prepare a sample for transmission electron microscope (TEM) observation, a drop of the hexane solution of NCs was placed on a carbon-coated micro grid for TEM observation. The grids were then examined with field emission TEM (Hitachi, HF-2000) operating at 200 kV with a point-to-point resolution of 0.23 nm. Matrix Assisted Laser Desorption/Ionization—Time of Flight Mass Spectroscopy (MALDI-TOF MS) was performed on a TOF mass instrument (BRUKER DALTONICS, autoflex) using anthracene as the matrix. Nanocrystals were dispersed in hexane, which contained the matrix and deposited onto a stainless steel target plate. Desorption and ionization of ZnS and Cu₂S NCs were achieved by irradiation of the N₂ laser (337 nm).

3. Results and discussion

3.1. Synthesis of Cu₂S NCs

The respective ring was indexed as shown in Fig. 2 and the obtained d-spacing values, which were also given in the fingerprint of Fig. 2, were identified with those of bulk Cu₂S with hexagonal symmetry. Thiolate molecules react with copper ions to form poly-nuclear complexes ([Cu₄(SR)₆]²⁻; e.g. [Cu₄(SR)₆]²⁻; R' = methyl, ethyl, phenyl) [11]. These complexes have Cu–S bonds, which form a CuₙSₘ core at the center of the complex. Laser-TOF-MS measurements indicated that the Cu–dodecanethiol complexes (extracted from yellowish gel) were decomposed to (Cu₂₋₃S)ₙ clusters (n ~ 10, ~1500 Da.) via the UV-induced cleavage of alkyl-mercapto (C–S) bond [15]. Therefore, CuₙSₘ core exists in the Cu–dodecanethiol complex, which serves as a single source precursor of
copper sulfide NCs. The reaction is considered to proceed via formation and decomposition of the Cu–dodecanethiol complex, in which Cu(II) is reduced to monovalent Cu(I) by dodecanethiol.

A synthesis of copper sulfide NCs via a phenylthiol precursor was also examined. The phenylthiol precursor is slightly soluble in octylether without using a co-surfactant, because this precursor has hydrophilic sites. Decomposition of such a precursor was not observed below 560 K. Meanwhile, the dodecanethiol precursor is well dissolved in octylether above 400 K. The melting point and pyrolysis temperature of the dodecanethiol precursor are lower than those of the phenylthiol precursor. Therefore, we chose the dodecanethiol precursor to prepare copper sulfide NCs.

Fig. 3(a) and (b) shows TEM micrographs of Cu$_2$S NC without the size-selection process. A shorter duration time of crystal growth provides smaller NCs (as shown in Fig. 3(a)). They grew uniformly with time. Fig. 3(b) indicates NCs with an average diameter of 4.7 nm and a standard deviation ($\sigma$) of about 10%. The inset lattice image ($d \approx 0.19$ nm, (1 0 3)) indicates the precipitation of single-crystal particles. The narrow size distribution led to the formation of a self-assembly monolayer with a hexagonal closed packing (hcp) structure (as shown in Fig. 3(b)). The isolation of individual particles indicates that they were isolated from the neighboring NCs by dodecanethiol shells. UV–Vis spectrum of dodecanethiol capped Cu$_2$S NCs redispersed in hexane are shown in Fig. 3(c). This absorption spectrum exhibits no excitonic peaks.

Ring patterns of other chalcocite group compounds (such as (1 0 3) of Cu$_{1.96}$S ($d = 0.274$ nm, JCPDS 29-0578) (djurleite) and (1 0 10) of Cu$_{1.8}$S ($d = 0.278$ nm, JCPDS 47-1748) (digenite)) and copper sulfate were not identified in the electron diffraction pattern (Fig. 2). Also, the Cu$_{2-x}$S ‘direct-band gap semiconductor’ NCs exhibit prominent absorption peaks, which are centered at $\sim 1.86$ eV (for Cu$_{1.96}$S and Cu$_{1.9}$S) and $\sim 2.2$ eV (for Cu$_{1.8}$S). However, Cu$_{2-x}$S ‘indirect-band gap semiconductor’ NCs do not show any peaks in the absorption spectrum [16]. Therefore, the dark brown precipitates were estimated to be pure Cu$_2$S NCs. Water-free synthesis provides un-hydratable Cu–dodecanethiol complexes. Therefore, the oxidation of copper sulfide and formation of copper sulfate may be excluded in this water-free processing.

The synthesis of copper sulfide NCs was examined based on various [HSR]/[Cu] ratios and precursor concentrations. The size distributions of copper sulfide NCs are shown in Fig. 3(d). The standard deviation of copper sulfide NCs increased together with an increase in the [HSR]/Cu ratio. However, there was a slight increase in the average diameter of the NCs, which increased with increasing precursor concentration.

Co-surfactant plays an important role in controlling the morphology and size distribution of NCs. An addition of oleylamine leads to the morphological change of Cu$_2$S NCs. Fig. 4(a) reveals the formation of coinage NCs. The highly magnified TEM image of coinage NCs perpendicular to the minor axis is shown in Fig. 4(b). The (0 0 2) lattice image with a spacing of 0.34 nm indicates that the minor axis is parallel to the [001] direction of $\beta$-chalcochalcoite. Hexagonal Cu$_3$S crystals should exhibit higher surface energies on the (1 0 1) and (1 0 0) lattice phases.
The large (0 0 1) crystal facets lead to reducing the total surface free energy of Cu$_2$S NC. However, reduction of the surface free energy of the NCs alone cannot explain the role of oleylamine.

3.2. Synthesis of ZnS NCs

A synthesis of zinc sulfide NCs via a thiol precursor was examined. The TEM image of white precipitates obtained by thermolysis of the Zn–dodecanethiol precursors is shown in Fig. 5(a) and (b). These figures reveal that the thermolysis of Zn–dodecanethiol leads to the formation of irregular shaped NCs.

The S–Zn–thiol precursors, which are so-called ‘Herron’s or Dance’s cluster compounds’ [11–13], were also examined. Dodecanethiol reduced elemental sulfur to $S^{2−}$ ions, which react with Zn–dodecanethiol complexes to form $S/Zn_{m}(SR)_{n}$ cluster compounds. This precursor was then annealed in octyl ether at 503–560 K.

When the annealing temperature exceeded 400 K, the mixture solution slowly became cloudy, and immediately changed to become colorless, as soon as 1.88 cm$^3$ of...
oleylamine was injected into it at 463 K. When oleic acid was injected into the mixture solution the color change occurred at a higher temperature (∼553 K). Annealing without co-surfactant provided aggregates of small sized NCs (not shown). Fig. 5(c) and (d) reveal that these co-surfactants play an important role in producing a monodisperse ZnS NCs. However, oleylamine is more effective for producing monodisperse NCs, because the amine group adsorbs...
the Zn site of the NC’s surface more strongly than the carboxylic group.

LDI–TOF mass spectra and UV–Vis spectra revealed that the growth rate depends considerably on the annealing temperature and S/Zn ratio. In this section, ZnS NCs with various sizes were synthesized. The TEM images of ZnS NCs are shown in Fig. 6(a) and (c). The average size, which was estimated by mass spectrum and TEM image, is about 3.0 nm for NCs annealed at 503 K, 6.2 nm for S/Zn = 1.0/1.0 at 553 K and 7.0 nm for S/Zn = 0.4/1.0 at 553 K. The HRTEM image indicates that the morphology of NCs exhibits an ellipsoidal shape with an aspect ratio of about 1.2. The standard deviations of 6.2 and 7 nm NC were estimated by image analysis to be about 15% of the average diameter. The formation of relatively well-defined NC lattice as shown in Fig. 6(a) indicates that standard deviation of 3 nm NCs is smaller than the average diameter by 10%. We can almost synthesize monodisperse ZnS NCs with sizes ranging from 3 to 7 nm. Fig. 6(d) shows the SAED pattern of 7 nm ZnS NCs. A ring pattern corresponding to h (1 0 3) and weak ring pattern corresponding to h (1 0 2), which are identified with wurtzite (hexagonal symmetry), are observed. Therefore, these precipitates are wurtzite or a mixture of wurtzite and zincblende.

The UV–Vis spectra of ZnS NCs shown in Fig. 7(a) reveal the quantum effect such as the size dependency of band gap energy. The absorption edges are shifted to higher energies from the bulk band gap of ZnS with a decrease in the average size of the NCs. The UV–Vis spectrum of 3 nm ZnS NCs exhibits a sharp absorption peak centered at 294 nm, which also indicates the formation of monodisperse NCs. The lowest excited state energy of semiconductor NCs is expressed in the following equation [18].

\[
dE = \pi^2/4R^2 + A_1/R + A_2
\]

Where \( R = r/a_B \), \( r \) is the radius of NCs, \( a_B \) is the Bohr radius of the bulk exciton (\( = 3.5 \text{ nm} \)), \( A_1 \) and \( A_2 \) are the coefficients related to \( \varepsilon_1/\varepsilon_2 \) (\( \varepsilon_1 \) and \( \varepsilon_2 \) are dielectric constants of NCs and surfactant layer (or medium)). To our knowledge, there are no data regarding the dielectric constant of dodecanethiol.

Fig. 7. UV–vis spectra and photoluminescence of ZnS NCs with size ranging from \( \sim 3–7 \) nm.

Fig. 8. Transmission electron micrographs of Cu2S superlattice. Superlattice of 4.7 nm Cu2S NCs (low resolution) (a), typical packing structure, superlattice of \( \sim 3 \) nm Cu2S NCs (b), 4.7 nm Cu2S NCs (c) and \( \sim 3 \) nm ZnS NCs (d).
and oleylamine. Therefore, the dielectric constant of AOT was assigned to $\varepsilon_z (\varepsilon_1 = 8.3)$. A1 and A2, which were derived from these constants and relationship, are $-2.593$ and $-0.4818$. The calculated results indicate that the absorption peaks of 3.0, 6.2 and 7.0 nm ZnS NCs are blue-shifted by 0.80, 0.15 and 0.11 (eV) from the band edge of the bulk material. The band edge of 3.0, 6.2 and 7.0 nm–ZnS NCs were estimated to be 274.8, 321.9 and 325.3 nm. The predictions of 6.2 and 7.0 nm–ZnS NCs are in good agreement with the experimental results. The photoluminescence spectra are shown in Fig. 7(b). These spectra exhibit a large red shift from the absorption band edges, which is attributed to electron–hole recombination from the surface traps.

3.3. Synthesis of the superlattice

Colloidal solution drops were dispersed on a carbon-coated grid (substrate) in order to prepare Cu$_2$S and ZnS NC superlattices (multilayer). The TEM images are demonstrated in Fig. 8(a) and (c). Fig. 8(a) indicates that 4.7 nm Cu$_2$S NCs form micrometer order multi-domain superlattices over the entire area. As shown in Fig. 8(b) and (c), stripe arrays were mainly observed in about 3 nm (Fig. 8(b)) and 4.7 nm (Fig. 8(c)) Cu$_2$S and 3.0 nm ZnS NC assemblies. Capped Cu$_2$S and ZnS NCs tend to occupy two-fold saddle sites of a monolayered hcp lattice. However, they are energetically less favorable than that of three-fold hollow sites under the interactions between van der Waals attraction and the short-range steric repulsion of alkylchain. This stripe array may be attributed to a surface dipole–dipole interaction between R–S$^-$–M$^+$ dipoles [19] or the crystal habit of NCs [20]. The packing structure of these NCs is currently under investigation.

4. Conclusion

In conclusion, monodisperse and stoichiometrically well-defined copper sulfide and zinc sulfide NCs were successfully tailored with the thermolysis of transition metal–thiol precursor. This may be extended to create a superlattice for larger scale optical devices using the dropping cast technique.

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