Morphology and Composition-Controls of Cu_xS Nanocrystals Using Alkyl-Amine Ligands

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Nearly monodispersed-size Cu_xS nanocrystals (NCs) were obtained by sulfuration of Cu(II) -alkyl-amine complexes using dodecanethiol-solvated sulfur at 363 K. The morphology and chemical composition of Cu_xS NCs can be controlled by using appropriate alkyl-amine ligands. NCs of Cu -deficient sulfides, $\text{Cu}_{1.8}\text{S}$ (digenite) or a $\text{Cu}_{1.8}\text{S}$ - Cu_2S mixture, were obtained using octylamine or di-octylamine, while stoichiometric Cu_2S NCs using tri-octylamine and oleylamine ligands. [doi:10.2320/matertrans.47.1953]

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1. Introduction

Semiconductor nanostructured materials have been extensively studied to develop novel properties different from the bulk counterparts. Copper sulfide NCs with anomalous optical properties are expected to be a efficient third-order nonlinear optical materials¹⁾ and hetero-junction solar cell materials,²⁾ while a Cu_2S thin film is applicable for an electrolyte-capacitated quantum atom switch.³⁾

Such a copper sulfide group (Cu_xS) involves various compounds, Cu_2S (chalcocite), $\text{Cu}_{1.96}\text{S}$ (djurleite), $\text{Cu}_{1.8}\text{S}$ (digenite) and CuS (covellite). The electronic structures depend on their stoichiometries, i.e., the copper deficiency. $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.8}\text{S}$ and CuS are of a direct band gap type, while Cu_2S is of an indirect band gap type. The energy band gap varies from 1.2 eV for $x = 2$ and 1.5 eV for $x = 1.8$ to 2 eV for $x = 1$.⁴⁾ Since their optical properties also depend on the size and shape of NCs, it is important to control their morphology and composition for application to optoelectrical devices. However, there have been a few reports on detailed controls of morphology and composition of copper sulfide NCs.

The solution phase synthesis of copper sulfide NCs have been based upon a sulfur oleylamine system^{5,6)} or a thermolysis of single-source precursor such as copper thiolat^{7,8)} and $\text{Cu}(\text{S}_2\text{CNET}_2)_2$.⁹⁾ Recently, Korgel *et al.* reported the composition control of copper sulfide NCs by changing the Cu/S source ratio.¹⁰⁾ In these methods, however expensive and toxic high-boiling-temperature solvents such as TOPO, TOP, dichlorobenzene or octylether are requisite for the high temperature reaction processes ($> \sim 473$ K). In this paper, we report a synthesis of nearly monodispersed-size copper sulfide NCs at low temperature ($< \sim 363$ K). The reaction temperature of sulfuration is effectively lowered using mixtures of alkyl-amines and 1-dodecanthiol (DT, HSR; $\text{R} = \text{CH}_3(\text{CH}_2)_{11}$). The morphology and composition of Cu_xS NCs are also controlled using an appropriate alkyl-amine.

2. Experimental Procedures

2.1 Synthesis process

All reagents used were as received. 74.9 mg of copper(II) acetate dehydrate ($\text{Cu}(\text{ace})_2$) was mixed with $1.88 \times 10^{-6} \text{ m}^3$ oleylamine (OLA, C_{18}NH_2) and $20 \times 10^{-6} \text{ m}^3$ of toluene in a round-bottom flask, which was degassed by Ar gas flushing for 2.4 ks. After flushing, it was heated up to 363 K and toluene was refluxed using a condenser. Then, $2.46 \times 10^{-6} \text{ m}^3$ of S/DT solution, in which 13.1 mg of sulfur powder was dissolved, was injected into the solution and annealed at 363 K for 1.8 ks.

2.2 Purification process

When ethanol was mixed with the colloidal solution at ambient temperature, the brown precipitates were obtained. They were separated by centrifugation to remove excess reaction agents and then redispersed in hexane. This precipitate-redispersion procedure was repeated two times for purification.

2.3 Characterizations

A drop of the colloidal solution was placed on a carbon-coated micro-grid and examined with a field emission transmission electron microscope (TEM) (Hitachi, HF-2000) operating at 200 kV with a point-to-point resolution of 0.23 nm. The crystal structures of copper sulfide were identified by X-ray diffraction (XRD) (Mac Science, M18XCE). UV-visible absorption spectra were observed between 200 and 1700 nm (JASCO, V-570).

3. Results

$\text{Cu}(\text{ace})_2$ reacts with OLA to form an $(\text{ace})_2\text{Cu}(\text{NH}_2\text{R})_n$ complex, which exhibits a transparent blue color in toluene. When S/DT solution was injected into this Cu-complex solution, its color turned to reddish dark brown, indicating the formation of copper sulfide NCs. This facile process can provide monodispersed spherical particles with the average diameter of 4.4 nm and the standard deviation (σ) less than 10% (see Fig. 1). The XRD pattern in Fig. 2 indicates that

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Fig. 1 A TEM image of Cu_xS NCs prepared with OLA. The average diameter is about 4.4 nm.

Fig. 2 An XRD pattern of Cu_xS NCs prepared with OLA. Vertical bars indicate the diffraction lines for a Cu_2S chalcocite.

copper sulfide NCs have a Cu_2S “chalcocite” structure with a hexagonal symmetry. These results indicate that di-valent copper is reduced to mono-valent ones by DT or OLA.

Our former results,¹¹⁾ moreover, revealed that the morphology and Cu/S composition of NCs depends upon DT/OLA ratio in a mixture solution. Alkyl-amine, which has a bulky hydrophobic group, exhibits a strong steric repulsion between N and metal atoms. Therefore, the number (primary (RNH_2), secondary (R_2NH) and tertiary (R_3N); alkyl-chain) and the length of alkyl-chains affect the stability of Cu-amine complexes, leading to an alternative way to control the sulfuration reaction. In order to investigate the role of amine-ligand, we synthesized copper sulfide NCs, using octylamine (primary amine: OCA, C_8NH_2), dioctylamine (secondary amine: DOCA, $(\text{C}_8)_2\text{NH}$) and trioctylamine

(tertiary amine: TOCA, $(\text{C}_8)_3\text{N}$). When copper sulfide NCs were prepared with OCA, DOCA and TOCA systems, the greenish dark brown precipitates (OCA and DOCA) and reddish dark brown precipitates (from TOCA system) were obtained. TEM images of NCs obtained with OCA, DOCA and TOCA are shown in Figs. 3(a), (b) and (c), respectively. TEM images indicate that their sizes depend on the amine-ligand: they decrease with increase in the number of alkyl-chains.

The XRD patterns Figs. 4(a) and (b) indicate that NCs prepared with OCA and DOCA are rhombohedral digenite $\text{Cu}_{1.8}\text{S}$ or Cu_2S - $\text{Cu}_{1.8}\text{S}$ mixtures. While the XRD pattern of copper sulfide NCs prepared with TOCA exhibits a relatively strong peak at around 37 degree, being attributed to Cu_2S . UV-vis spectra of Cu_xS NCs in Fig. 5 exhibits a broad absorption peak in the near IR region, which is attributed to Cu-deficients. These spectra reveal that the Cu-deficients decrease with increase in the number of alkyl-chains because the peak intensity is proportional to the amount of Cu-deficients.¹²⁻¹⁵⁾ In the spectrum of copper sulfide NCs prepared with TOCA, no near IR absorption peak was observed, indicating that the brown precipitate is nearly pure Cu_2S . These results are consistent with the XRD results shown in Fig. 4.

4. Discussion

In the present experimental procedures, we suppose that sulfur is reduced by DT and form S^{2-} , being solvated with DT molecules, while Cu(II) ions, which are also solvated with alkyl-amine, react with S^{2-} to form copper sulfide NCs as follows.^{14,16)}

The ligand mixtures play important roles to control the stability and sulfuration speed of copper sulfide(Cu_nS_m) NCs. Actually, the sulfuration reaction without alkyl-amine proceeds very slowly and gives rise to irregular shape Cu_2S NCs. Alkyl-amine reacts with DT to form a DT-alkyl-amine ($\text{R-NH}_2\text{HS-R'}$) association and serve as a de-proton agent for H_2S . Since it suppresses the masking effect of DT and enhances the sulfuration speed, we can synthesize mono-dispersed-size Cu_2S NCs at low temperature.

Above mentioned results also reveal that alkyl-amine species affect the size and chemical composition of copper sulfide NCs. Alkyl-amine, which has bulky hydrophobic group, serves as weak ligands for copper ions and sulfur species. Therefore, the sulfuration speed of Cu-amine complex may increase with the number of alkyl-chains. This enhancement of sulfuration reaction may lead to decrease in the size of copper sulfide NCs.

It is worth to emphasize that the chemical composition of copper sulfide NCs is controlled by suitable selection of alkyl-amine. $\text{Cu}_{1.8}\text{S}$ and Cu_2S NCs can be synthesized using the primary, secondary and tertiary-amine. The Cu-deficient NCs formation is not attributed to the Cu oxidation because the characteristic peak of a Cu(II) oxidation state could not be

Fig. 3 TEM images of Cu_xS NCs prepared with (a) octylamine, (b) dioctylamine and (c) trioctylamine respectively.

Fig. 4 XRD patterns of Cu_xS NCs prepared with (a) octylamine, (b) dioctylamine and (c) trioctylamine respectively. Vertical bars indicate diffraction lines of Cu_2S chalcocite, and $\text{Cu}_{1.8}\text{S}$ digenite, respectively.

Fig. 5 UV-vis spectrum of Cu_xS NCs prepared with octylamine(OCA), dioctylamine(DOCA) and trioctylamine(TOCA) respectively.

detected in the XPS spectra of Cu-deficient sulfides (Cu_xS ; $x = 1, 1.8$). However, the XPS S-2p spectra indicates presence of S-S bonding,^{11,17,18)} which is attributed to S_n^{2-} or S_n^0 species formed from alkyl-amine and DT mixtures. The present results suggest that the Cu-deficiency concentration increases with decrease in the number of alkyl-chains because the reduction ability of alkyl-amines is proportional to the number and the length of alkyl-chains ($\text{RSH} \sim \text{C}_{18}\text{NH}_2 \sim (\text{C}_8)_3\text{N} > (\text{C}_8)_2\text{NH} > \text{C}_8\text{NH}_2$).¹⁹⁾

5. Conclusion

Copper sulfide NCs have been successfully synthesized with sulfuration of Cu-alkyl-amine complexes using S/DT solution. NCs obtained from OLA system is monodispersed-size Cu_2S NCs with a spherical shape. The morphology and chemical composition of copper sulfide NCs depend on alkyl-amine species. Those prepared with OCA and DOCA are $\text{Cu}_{1.8}\text{S}$ or $\text{Cu}_{1.8}\text{S}$ - Cu_2S mixture, while that prepared with TOCA, which has the bulkiest hydrophobic group, is Cu_2S and smallest.

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