

Water-free Solution Synthesis of Monodisperse Cu_2S Nanocrystals

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We report a novel water-free processing of monodisperse and pure Cu_2S nanocrystals (NCs) by thermolysis of copper-decanethiol complex. The narrow size distribution led to the formation of ordered self-assemblies with various well-defined structures. However, unclose-packing structure was observed as a predominant phase.

Transition-metal chalcogenide nanocrystals (NCs) have been extensively investigated for the potential applications 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 (about 10^{-7} esu).³ This chalcocite group (Cu_{2-x}S) involves various compounds such as Cu_2S (γ, β -chalcocite), $\text{Cu}_{1.96}\text{S}$ (djurleite), and $\text{Cu}_{1.8}\text{S}$ (digenite),⁴ showing stoichiometry-dependent optoelectric properties.³ $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.9}\text{S}$, and $\text{Cu}_{1.8}\text{S}$ are the direct band gap materials, while Cu_2S is the indirect band gap one. This situation encourages tailoring the single-phase copper sulfide NCs. Copper sulfide NCs have been generally synthesized via the aqueous solution, the inverse micelle,⁵ the chemical conversion³ and the solventless processes.⁶ However, the formation of undesirable by-products such as subphase and $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$ ^{6,7} is inevitable in aqueous or aqueous/organic solution system.

Here, we report a new water-free-solution process of pure copper sulfide NCs in a high boiling-temperature organic solvent. It is based on the hot-soap process, which has been developed to produce monodisperse NCs of chalcogenide semiconductors^{1,2} and transition metals.^{8,9} In the present method, an alkane thiol plays multiple roles to produce copper sulfide NCs, serving as the sulfur source, reducing and stabilizing agents. The synthesized NCs are a single-phase Cu_2S and sufficiently monodisperse to generate ordered self-assemblies.

The following is a typical experimental procedure for synthesis of copper sulfide NCs. All reagents were used as received. 0.10 g of copper(II) acetylacetone ($\text{Cu}(\text{acac})_2$) was mixed with 20 cm³ of octyl ether in a flask, 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 up to 500 K. The solution turned to yellowish transparent at around 400 K and then to orange. It immediately changed to black colloidal solution at around 490 K. After it was cooled down to room temperature, 200 cm³ of ethanol was mixed. The dark brown precipitates 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. It was focused to control the size distribution of NCs (size-selective process). To prepare a sample for transmis-

sion electron microscope (TEM) observation, a drop of hexane solution of NCs was placed on a carbon-coated TEM grid. The grids were then examined with a Hitachi HF-2000 field emission TEM operating at 200 kV.

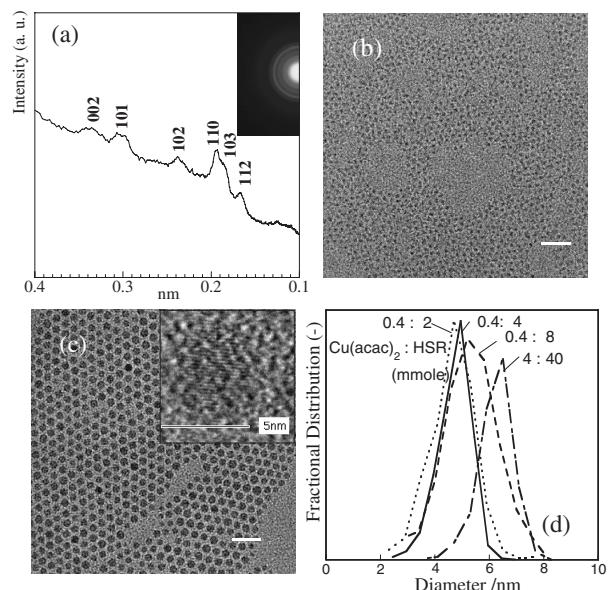


Figure 1. Electron-diffraction pattern and profile of the dark brown precipitates (a), Cu_2S NCs with average diameter of ≈ 2.0 nm (duration time 13 min) (b) and ≈ 4.7 nm (duration time 30 min) (c), high-resolution TEM image of 4.7 nm NCs (inset in (c)) and size distribution of Cu_2S NCs (d). (bar = 20 nm)

An electron-diffraction pattern of the dark brown precipitates is shown in Figure 1a. The ring pattern corresponding to Cu_2S "chalcocite" with a hexagonal symmetry was identified. The absorption spectrum (not shown) exhibits no excitonic peaks corresponding to $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.9}\text{S}$, and $\text{Cu}_{1.8}\text{S}$. Thiolate molecules react with copper ions to form polynuclear complexes ($[(\text{solvent})\text{Cu}_n(\text{SR}')_m]^{k-}$: e.g. $[\text{Cu}_4(\text{SR}')_6]^{2-}$; R' = methyl, ethyl, phenyl).¹⁰ These complexes have the Cu-S bonds, which form Cu_nS_m core at the center of the complex.¹⁰ Laser-TOFMS measurements indicated that the Cu-dodecanethiol complexes (extracted from yellowish gel) were decomposed to $(\text{Cu}_{2-x}\text{S})_n$ clusters ($n = \approx 10$, ≈ 1500 Da.) via the UV-induced cleavage of alkyl-mercapto (C-S) bond.¹¹ Therefore, Cu_nS_m 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 Cu-dodecanethiol complex, in which Cu(II) is reduced to monovalent Cu(I) by dodecanethiol. A synthesis of copper sulfide NCs via

a benzenethiol precursor was also examined. The benzenethiol precursor is slightly soluble in octyl ether 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 octyl ether above 400 K. The melting point and pyrolysis temperature of the dodecanethiol precursor are lower than those of the benzenethiol precursor. Therefore, we choose dodecanethiol precursor to prepare copper sulfide NCs.

Other chalcocite group compounds (such as $\text{Cu}_{1.96}\text{S}$ (djurleite) and $\text{Cu}_{1.8}\text{S}$ (digenite)) and copper sulfate were not identified in the dark brown precipitates as indicated in Figure 1. Water-free synthesis provides unhydratable Cu-dodecanethiol complexes. Therefore, the oxidation of copper sulfide and formation of copper sulfate may be excluded in this water-free processing.

Figures 1b and c show TEM micrographs of Cu_2S NC before the size-selective process. Shorter duration time of crystal growth provides smaller NCs (as shown in Figure 1b). They grew uniformly with time. Figure 1c indicates NCs with the average diameter of 4.7 nm and the standard deviation (σ) of about 10%. The inset lattice image indicates the precipitation of single-crystal particles. The individual particles were isolated by 1-dodecanethiol shell from neighboring NCs. The narrow size distribution led to the formation of a self-assembly monolayer with a hexagonal close-packing (hcp) structure (as shown in Figure 1c). The synthesis of copper sulfide NCs was examined with various [HSR]/[Cu] ratio and precursor concentration. Shown in Figure 1d are the size distributions of copper sulfide NCs. The standard deviation in the size increased with increasing [HSR]/Cu ratio. However, there was a slight increase in the average diameter of NCs. The average size of NCs increased with increasing precursor concentration.

The colloidal solution drops were dispersed on a carbon-coated grid (substrate) to prepare Cu_2S NC superlattice (multi-layer). The TEM images are demonstrated in Figures 2a-c. Figure 2a indicates that 4.7 nm NCs form micrometer-order multi-domain superlattices over the entire area. As shown in Figures 2b and c, stripe arrays were mainly observed in 2 nm (Figure 2b) and 4.7 nm (Figure 2c) Cu_2S NCs assemblies. Dodecanethiol-capped Cu_2S 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 counterbalance between van der Waals attraction and short-range steric repulsion of alkyl chain. This stripe array may be attributed to a surface dipole-dipole interaction between $\text{R}-\text{S}^--\text{Cu}^+$ dipoles¹² or the crystal habit of Cu_2S NCs.¹³ The packing structure of these NCs is currently under investigation.

In conclusion, monodisperse and stoichiometrically well-defined copper sulfide NCs was successfully tailored with water-free solution processing. It may be easily develop to create the superlattice for optical devices in larger scale with dropping cast technique.

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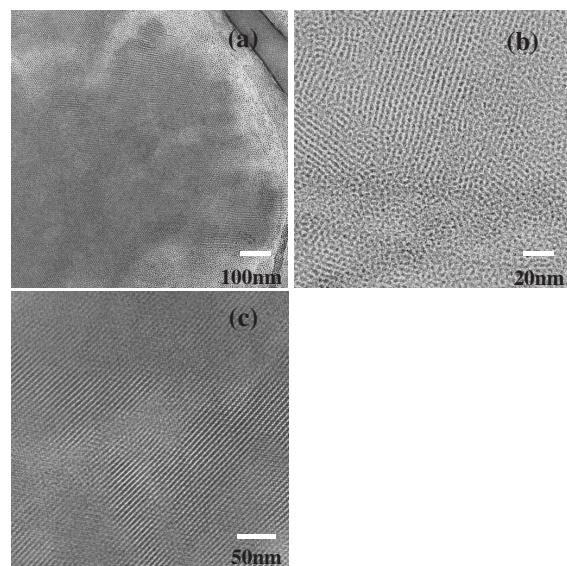


Figure 2. Transmission electron micrographs of Cu_2S superlattice. Superlattice of 4.7 nm Cu_2S NCs (low resolution) (a), Typical packing structure, Superlattice of ≈ 2 nm Cu_2S NCs (b), 4.7 nm Cu_2S NCs (c).

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