Facile Synthesis and Assembly of Cu_2S Nanodisks to Corncoblike Nanostructures

Xu-Sheng Du,[†,‡] Zhong-Zhen Yu,[†] Aravind Dasari,[†]
Jun Ma,[†] Yue-Zhong Meng,[‡] and Yiu-Wing Mai*,[†]

Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical, and Mechatronic Engineering J07, The University of Sydney, Sydney, NSW 2006, Australia, State Key Laboratory of Optoelectronic Materials and Technologies/Institute of Optoelectronic and Functional Composite Materials, Sun Yat-Sen University, Guangzhou 510275, P. R. China

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In the past decades, colloidal nanocrystals have attracted broad attention from researchers in various disciplines because of their structure-, size-, and shape-dependent characteristics and novel electronic, magnetic, optical, chemical, and mechanical properties that cannot be obtained in their bulk counterparts.[1] Among various kinds of nanomaterials, nanoplates and nanoprisms are studied widely because they are superior to spherical nanoparticles as building blocks for constructing nanodevices with crystal orientation controlled by a "bottom-up" method because of their anisotropic structures.[2] Cu_2S (chalcocite) is an important semiconductor with a bulk band gap of 1.21 eV and has been extensively investigated and used in solar cells.[3] The availability of Cu_2S nanostructures with well-defined morphologies and dimensions should enable new types of applications and/or enhance the performance of currently existing photoelectric devices because of the quantum-size effects. Recent efforts have focused on the development of new synthetic methodologies for fabricating Cu_2S nanocrystals with controlled shape, size, and assembled structure. Cu_2S nanoparticles were successfully produced in microemulsions.[4] Nanowire arrays of monoclinic Cu_2S were grown on Cu foil substrates with the aid of H_2S at room temperature.[5] Various copper sulfide assembly nanostructures such as nanowire, nanotube, and nanovesicle were prepared by an organic amine-assisted hydrothermal method.[6] Liu et al. synthesized chalcocite Cu_2S nanocrystals via the reaction between copper thiolate and thioacetamide.[7] They also prepared Cu_2S nanowires by thermal decomposition of CuS_2CNEt_2 in a binary surfactant solvent of dodecanethiol and oleic acid.[8] Also, the digenite copper sulfide spherical nanoparticles were prepared by decomposition of $Cu(S_2CNEt)_2$ in a TOP/TOPO/TOPS solution.[9] Three-dimensional (3D) superlattice assembly by hexagonal Cu_2S nanoplates was obtained through the reaction between copper salt and sulfur in oleylamine.[10] The approach of solventless thermolysis of the copper thiolate precursor was first applied to prepare the hexagonal Cu_2S nanoplatelets by Korgel et al.,[11] and Wu et al. further used the method to prepare Cu_2S nanowires.[12] In the present work, we report a facile approach to fabricate hexagonal Cu_2S nanocrystals through thermolysis of a copper dithiolate precursor in dodecanethiol and their novel self-assembly structures.

In a typical synthesis procedure, 0.5 mL of 1,6-hexanedithiol (Aldrich 96%) was added slowly to a 25 mL ethanol solution containing 1.2 g of $CuCl_2$. During the dithiol addition, the system becomes a slurry because of dithiolate precipitation. After being stirred slowly for 1 h, the metal dithiolates were separated by filtration and washed several times with ethanol. It was then dried under vacuum at 50 °C for 12 h. We obtained 0.9 g of yellow powder. The reaction yield was close to 100% because of the very low dithiolate solubility in the alcoholic medium. The copper precursor was added to dodecanethiol (Aldrich 98%) and heated at 185 °C for 1.5 h. After reaction, the bottle was cooled to room temperature. The resulting brown solid product was collected, washed with absolute alcohol several times to remove the byproducts and the excess dodecanethiol, and redispersed in ethanol for the measurements.

Images a and b of Figure 1 are the TEM images of the product. It is seen that the product consists of self-assembled monodisperse nanodisks. The nanodisks are fairly uniform in size and tend to stack together as extended chains. Moreover, the chains are well aligned along their longitudinal direction, forming a corncoblike nanostructure. The model of the self-assembly structure is shown in panels c and d of Figure 1. However, from Figure 1a, it is also evident that there is still disorder among the stacks. That is, the disks in

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* Corresponding author: Fax: 61-20-93513760. E-mail: mai@aeromech.usyd.edu.au.
[†] The University of Sydney.
[‡] Sun Yat-Sen University.

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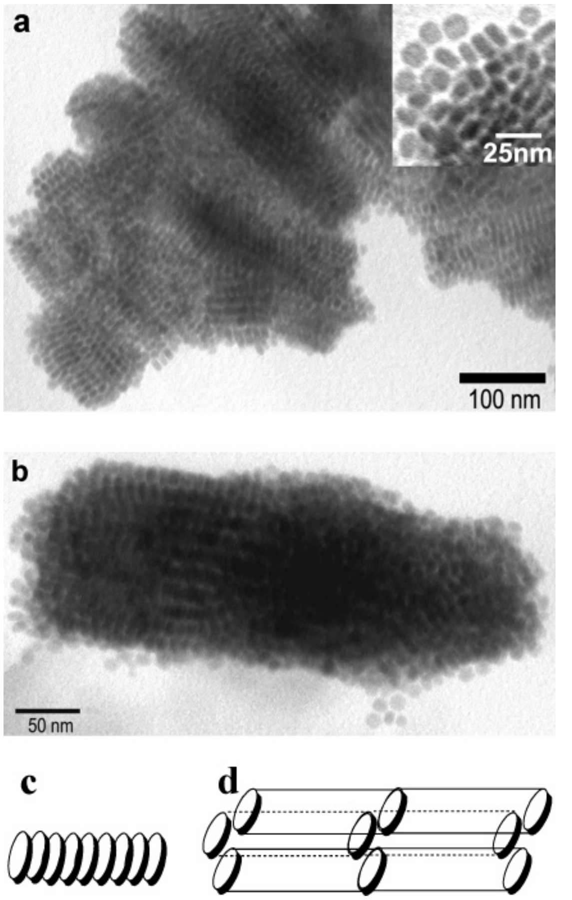

Figure 1. (a,b) TEM images self-assembled Cu_2S nanoplates. (c,d) Proposed model for the nanoplates and their self-assembly.

a stack are tilted relative to other disks in other stacks, suggesting a smectic packing of the disks. Obviously, the differences in contrast among the disks in the stacks in the TEM micrograph suggests that the stack is multilayered. TEM tilting experiments were used to further confirm this assembly nanostructures (see the Supporting Information, Figure S1). Comparing identical locations before and after tilting the sample to 30° (toward the reader; see the Supporting Information, Figure S1a), the disks in the bottom part of the image appear to move closer to the voided region on the copper grid, indicating the multilayer structure. Furthermore, this is confirmed by tilting the sample to 90° (see the Supporting Information, Figure S1b), where the cross-sectional image clearly shows a multilayered structure. Korgel et al. reported one-dimensional chainlike assemblies of rod-shaped chalcocite Cu_2S crystals, which corresponded to the plates that were stacked face-to-face and lying on their edges.[11] The assembly structure of the nanocrystals here is similar to their work, except the chains are further stacked together into a novel ordered stacking structure. It is believed that the long-range 3D ordering observed in the nanoarrays can be attributed to the synergistic effect of the steric repulsions exerted by thiol carbon chains, the asymmetric van der Waals attractive forces, and also the dipole−dipole interactions, because the Cu_2S nanocrystals are ferroelectric.[11] From the disks standing on their edges and lying flat on the substrate in the image, the average diameter and thickness of the nanodisks are estimated to be about 16 and 7 nm, respectively.

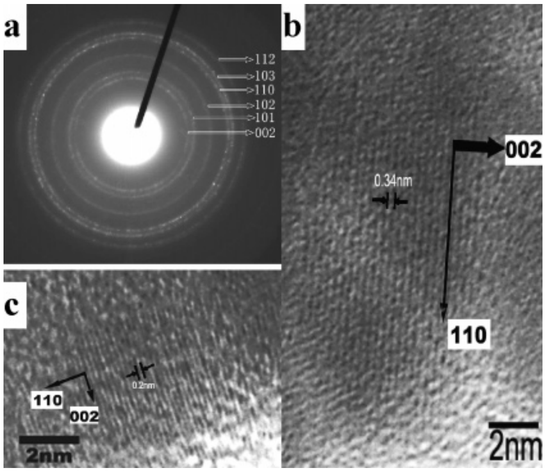

Figure 2. (a) SAED pattern and (b,c) HRTEM image of nanoplates standing on edges perpendicular to the substrate with the electron beam perpendicular to the (001) direction.

The SAED pattern (Figure 2a) was obtained by focusing the electronic beam on the nanodisks. All the respective rings in the pattern can be indexed as hexagonal-phase Cu_2S (chalcocite) reported in the literature (JCPDS card 84-0207), and the pattern is consistent with the X-ray powder diffraction pattern of the product (see the Supporting Information, Figure S2) and with other published results.[8] HRTEM was used to further investigate the crystal structure of the nanodisks. The lattice fringes (images b and c of Figure 2) are evident with the nanodisks standing on their edges. The corresponding lattice in Figure 2b is assigned to the (002) planes with an interplanar distance of 3.4 Å, whereas Figure 2c shows lattice fringes with the interfringe distance measured to be 2.0 Å, which is attributed to the lattice spacing of the (110) planes. The formation of a hexagonal crystal structure of Cu_2S is reasonable because the present synthetic temperature (185 °C) is higher than its phase-transition temperature (103.5 °C), at which γ-Cu_2S (monoclinic) undergoes a phase transition to β-Cu_2S (hexagonal).[5c]

In addition, the reaction temperature and time both affect the morphology of the Cu_2S nanocrystals. Figure 3a shows the TEM image of the copper dithiolate precursor. The filmlike morphology indicates that the precursor has a layered structure, which is similar to the layered structure of the copper thiolate polymers.[13] In Figure 3b−d, TEM images of Cu_2S nanocrystals synthesized at 185 °C reveal the shape evolution from small spherical particles into flat disks with increased reaction time. After 0.25 h (Figure 3b), small spheres started to form; and after 0.75 h (Figure 3c), the nanocrystals became disklike and parts of the disks began to stand on their edges for the self-assembly. At a longer reaction time (1.5 h), the plates stacked together into extended chains and self-assembled to a corncoblike structure (Figure 3d). When the reaction time was longer than 4 h, the products were mainly spherical particles with a broad size distribution (Figure 3e), indicating an Ostwald ripening process. However, when the temperature was increased to 200 °C, the well-formed hexagon platelets became the main product (Figure 3f). Obviously, the size of the hexagon

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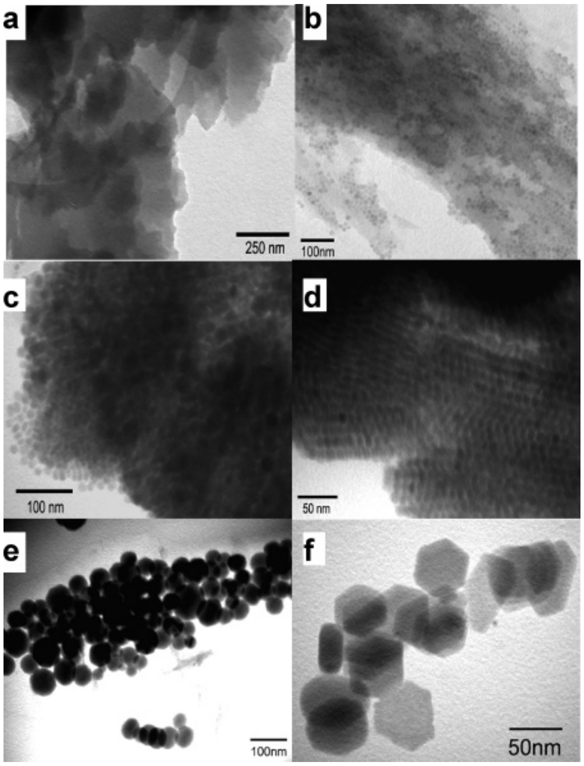

Figure 3. TEM images of (a) the copper thiolate precursor, Cu_2S nanocrystals and nanoplatelets formed at 185 °C after reaction times of (b) 0.25, (c) 0.75, (d)1.5, and (e) 4.5 h; and those formed at 200 °C for (f) 4.5 h.

nanoplates is much larger than the ones prepared through reaction between copper salt and sulfur,[10] where the hexagon nanoplate has an edge length about 9 nm.

The use of functional molecules as capping ligands to control the shape, size, and also the assembly structure of nanocrystallites in the solution-phase synthesis has been extensively studied recently.[14] To gain further insights into the growth mechanism of the Cu_2S nanoplates, we conducted some control experiments. When the solvent was replaced with *N*-methyl-pyrrolidone, the resulting product was spherical nanoparticles with sizes of several nanometers. In this case, no nanodisks could be obtained, even if many other synthetic parameters were adjusted. When thermolysis of the dithiolate-derived precursor occurred at 185 °C in a vacuum for 1.5 h, no nanodisk was obtained. These results indicate that the use of dodecanethiol does induce the growth of Cu_2S nanodisks. In the reports of Korgel et al. and Wu et al. on the syntheses of Cu_2S nanoplates and nanowires by the solventless thermolysis method, it was suggested that, between the two surfactants (octanoate and dodecanethiol) used, only octanoate served as the capping ligand that stabilized particle sizes and shapes and also controlled the anisotropic growth.[11,12] In our synthesis, however, dodecanethiol was obviously used both as a solvent and a capping reagent to determine the nanodisk shape. Although the formation mechanism of ordered Cu_2S nanostructure needs to be further investigated, it is reasonable that the dithiol in the system may play an important role in forming the 3D nanostructure. This is because organothiol is a well-known strong ligand to many metals, and alkyl-dithiols (such as 1,9-nonanedithiol) have been widely used to cap and link metal nanoparticles into some ordered structure (normally linear or spherical aggregation).[15]

In summary, we have demonstrated a facile and effective solution-phase approach to synthesizing hexagonal-phase Cu_2S with different morphologies. Such a solution-phase route using the sole surfactants as the solvent may represent a promising method for the synthesis of controlled morphology of Cu_2S nanocrystals. By carefully adjusting the synthetic parameters, we could selectively control the resulting Cu_2S nanocrystals to be disks and hexagonal and spherical particles with various sizes. In addition, a new ordered Cu_2S nanoarray can be obtained under certain experimental conditions.

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Supporting Information Available: TEM images of the assembly of Cu_2S nanostructures tilted by different degrees, and X-ray powder diffraction pattern of synthesized Cu_2S nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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