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One-Pot Synthesis and Optical Property of Copper(I) Sulfide Nanodisks

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Copper(I) sulfide (Cu_2S) nanodisks with controllable size and aspect ratio have been synthesized by using a one-pot colloidal process, in which no pre-prepared organometallic precursors are required. The reaction involves the injection of dodecanethiol into a hot solution containing copper salt, surfactants, and a high boiling-point organic solvent. Copper thiolate forms at the beginning of the reaction which effectively acts as a precursor whose decomposition leads to further nucleation and growth of Cu_2S nanocrystals. The nanocrystals begin as small nanodots in the early stages of the reaction, gradually turning into nanodisks with aspect ratios (average disk diameter divided by thickness) up to 2.0, while the band gap of the nanocrystals decreases accordingly. As the growth of nanocrystals follows the monomer addition mechanism, the diameter, thickness, aspect ratio, and optical property of the Cu_2S nanodisks can be tuned systematically by changing the reaction time, the amount of surfactants, and the concentration of the precursors. This synthesis provides a simple and highly reproducible method for the preparation of Cu_2S nanocrystals that may find potential applications in the fabrication of photovoltaic devices.

Introduction

Semiconductor nanocrystals have attracted broad attention because of their unique structure-, size-, and shape-dependent physical and chemical properties.[1−7] After more than two decades of continuous development, understanding of the nucleation and growth of nanocrystals in solution phase has greatly improved. Many strategies are now available to effectively control the size and shape of colloidal nanocrystals, making it possible to produce high quality nanomaterials with not only uniform sizes, but also a large variety of shapes including spheres, wires, rods, pyramids, belts, disks, and plates. Typically regarded as an indirect semiconductor with a bulk band gap of 1.21 eV,[8−10] copper(I) sulfide (Cu_2S), when prepared in the form of well-defined nanoscale structures, shows great potential in applications such as solar cells,[11] cold cathodes,[12] and nanoscale electric switches.[13]

Conventionally, Cu_2S nanostructures are prepared through the thermal decomposition of a single-source organometallic precursor that contains Cu species.[14−24] For example, copper

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alkythiolate prepared by a phase transfer reaction among copper nitrate, sodium octanoate, and dodecanethiol, has been used as a precursor to prepare Cu_2S nanodisks, nanorods, and nanoplatelets.[15] A solventless thermolysis process was also reported to synthesize uniform Cu_2S nanodisks with a constant thickness (~12 nm) and tunable diameters (21.7−27.5 nm) through the decomposition of the precursor $[Cu(SC_{12}H_{25})_2]$.[16] Hyeon et al. recently reported a general and relatively simple synthesis for copper(I) sulfide via the thermal decomposition of pre-synthesized copper oleate complexes in a solution of alkanethiol.[7] To simplify the synthesis by eliminating the additional steps for preparing the special copper precursors, Li and co-workers developed a solvothermal reaction which directly uses a mixture of copper salts and dodecanethiol to prepare monodisperse Cu_2S nanocrystals with shape and size controllable by introducing additional salts and acid.[14] Alivisatos et al. also prepared monodisperse hexagonal-faceted nanocrystals of Cu_2S by directly injecting a copper salt into a hot mixture of dodecanethiol, oleic acid, and ammonium diethyldithiocarbamate, although no shape control was demonstrated.[11]

In this paper, we report the development of a one-pot high temperature reaction (160−220 °C) for the synthesis of Cu_2S nanodisks with excellent control of both size and aspect ratio. The process was designed by following the classic injection-based thermolysis methods: the nanocrystals were prepared by injecting dodecanethiol into a hot solution containing copper salt, surfactant, and a high boiling-point organic solvent.[25] An intermediate compound $[Cu(SC_{12}H_{25})]$ was produced at the elevated reaction temperature which then directly decomposed to form Cu_2S species, eventually leading to the nucleation and growth of nanocrystals. As no extra steps are required for preparing special copper precursors, it represents a highly reproducible process suitable for large scale production of high quality Cu_2S disk shaped nanocrystals. Unlike the aggregation-based growth mechanism proposed previously reports,[16] the nanodisks grow through the classic monomer addition route which ensures a progressive increase in the overall size of the products. As a result, the diameter and thickness (and therefore the aspect ratio) of the nanodisks can be conveniently tailored by tuning the reaction time and temperature, the amount of surfactants, and the concentration of precursors. Their band gap can be tuned in the range of ~1.36−1.53 eV, which makes such Cu_2S nanocrystals candidate materials for the fabrication of photovoltaic devices with optimal energy utilization.

Experimental Section

Synthesis of Cu_2S Nanocrystals. Cuprous acetate (CuOAc, 0.0488 g, 97%, Aldrich), tri-*n*-octylphosphine oxide (TOPO, 1 g, 99%, Fisher), and 1-octadecene (ODE, 30 mL, 90%, Aldrich) were mixed in a three-neck flask and then degassed under argon flow for 30 min. Upon heating the solution up to 160 °C, 1-dodecanethiol (1 mL, > 98%, Aldrich) was injected quickly into the flask under vigorous stirring. The resulting mixture was further heated to a target temperature (e.g., 160, 180, 185, 190, 200, 220 °C) and then reacted for a fixed time, producing a black precipitate containing Cu_2S nanocrystals. The product was purified by three repeated actions of dissolving the precipitate in toluene and then reprecipitating the particles out by adding an excess amount of methanol. Finally, the Cu_2S nanocrystals were dispersed in toluene.

Characterization. Crystal structure of the Cu_2S nanocrystals was measured using a Bruker D8 Advance X-ray Diffractometer with Cu Kα radiation (λ = 1.5418 Å). Fourier transform infrared (FT-IR) spectra were collected with a Bruker Equinox 55 spectrophotometer scanning from 400 to 4000 cm^{-1}. The morphology of the nanostructures was investigated using a Philips Tecnai 12 transmission electron microscope (TEM) with an acceleration voltage of 120 keV. UV−vis absorption spectra measurements of the nanocrystal solution were carried out using a Varian Cary 50 spectrophotometer. High-resolution TEM (HRTEM) images and selected-area electron diffraction (SAED) patterns were obtained on a JEOL/JEM2100F transmission electron microscope at an acceleration voltage of 200 kV.

Results and Discussion

Synthesis of Cu_2S Nanostructures. Cu_2S nanocrystals were synthesized by injecting dodecanethiol into a hot mixture of CuOAc, TOPO, and ODE. In this case, dodecanethiol and CuOAc are precursors which react at high temperature to produce the final product of Cu_2S nanocrystals. Both dodecanethiol and TOPO serve as surfactants which direct the growth of the nanocrystals and prevent interparticle aggregation. ODE acts as a solvent which allows the reaction to be performed at temperatures up to its boiling point of ~315 °C. The reaction of CuOAc and dodecanethiol at an elevated temperature leads to the formation of $[Cu(SC_{12}H_{25})]$, as suggested by the change from turbid suspension to a clear pale yellow solution within ~2 min of injection. If the system was kept at a relatively low temperature (160 °C), the reaction solution gradually changed from pale yellow to red within 15 min, and further turned to dark gray within another 10 min. At higher temperatures, the color change was greatly accelerated, suggesting higher reaction rates. For a typical synthesis performed at 190 °C, it only took ~10 min to change from pale yellow to red and another ~5 min from red to dark gray. Nucleation occurred during the red-to-dark gray transition, followed by a continuous growth period lasting several hours. The nanocrystalline products formed small aggregates during the growth, probably because of the formation of polar side products such as acetic acid, and eventually precipitated out of the solution when the magnetic stirring was stopped at the end of the reaction. The precipitates can be separated from the reaction mixture by centrifugation, and then re-dispersed in nonpolar solvents.

The intermediate before the red-to-dark gray transition can be collected by precipitation with methanol. X-ray diffraction (XRD) measurement shows sharp diffraction peaks, confirming a layered structure which can be attributed to the formation of $[Cu(SC_{12}H_{25})]$ (Figure 1a). The sharp diffraction peaks at lower angles correspond to successive (0*k*0) orders of diffractions from a periodic layered structure of copper thiolate which has been observed previously by Wu et al.[16,26] The sharp diffraction peaks with large interlayer spacing can be attributed to stacked layers of Cu and S atoms separated by two layers of dodecane chains. Estimation using Bragg's law suggests an average interlayer spacing of 34.726 Å, matching the double-layer stacked structure proposed by Pradeep et al. as the alkane chain length of dodecanethiol is ~1.6 nm.[26,27]

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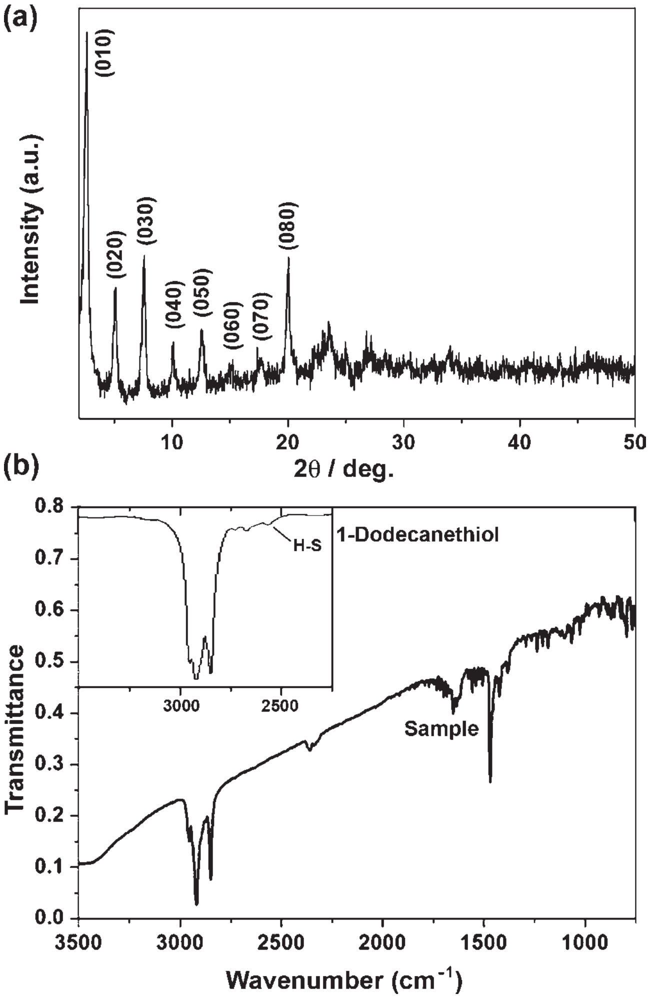

Figure 1. (a) XRD pattern and (b) FTIR spectra of the intermediate collected at the early stage (5 min) of reaction between dodecanethiol and CuOAc at 190 °C. The inset in (b) is the IR spectrum of pure 1-dodecanethiol obtained from the Spectral Database for Organic Compounds provided by National Institute of Advanced Industrial Science and Technology, Japan, SDBS No.10643).

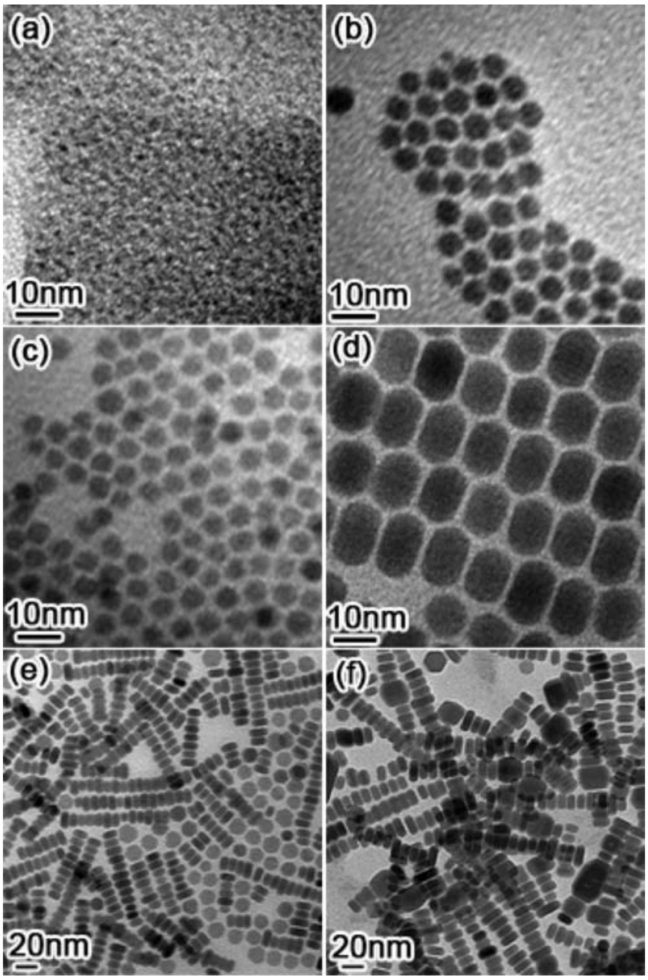

Figure 2. TEM images of Cu_2S nanocrystals obtained at different reaction temperatures: (a) 160 °C; (b) 180 °C; (c) 185 °C; (d) 190 °C; (e) 200 °C; and (f) 220 °C.

The composition of the intermediate was characterized by FTIR, and the spectrum was compared to the standard data from pure dodecanethiol. As shown in the inset in Figure 1b, pure dodecanethiol exhibits sharp bands at 2921 cm^{-1} and 2850 cm^{-1} due to asymmetric methyl stretching vibration and the asymmetric and symmetric methylene stretching vibration. In the spectrum of the intermediate sample, these two bands were also clearly present, whereas the band at 2579 cm^{-1} due to the S−H vibrations of dodecanethiol was not observed, suggesting the deprotonation of dodecanethiol (Figure 1b). It has been also suggested that the intensity ratio of the two peaks at 2921 cm^{-1} and 2850 cm^{-1} can be taken as a measure of disorder, with a higher degree of conformational order at a small ratio.[26,28] The intermediate product shows a relatively small ratio between these two peaks, suggesting a reasonably good order. In addition, the small shoulder at 2350 cm^{-1} can be assigned to COO^- groups which may be attributed to the byproduct of acid, while the band at 1638 cm^{-1} may be due to the existence of C=C from ODE.

Temperature Dependence. Figure 2 shows the TEM images of Cu_2S nanocrystals prepared after reacting for 210 min at different temperatures, while all other reaction conditions were kept the same. As shown in Figure 2a, very small (< 3 nm) particles were obtained at 160 °C because of the low reaction rate and incomplete conversion of the precursors. As the temperature was raised to 180 and 185 °C, the average diameter of the particles increased to ~5 nm and then ~5.7 nm. The particles display a narrow size distribution and an overall spherical shape. When the reaction was performed at 190 °C, the products were disk shaped, with an average diameter of 13.1 ± 0.9 nm and thickness of 9.0 ± 0.7 nm (Figure 2d). Consistent with the prior observations,[14,15,23] the disk shaped nanocrystals tended to stack together into extended chains. The face-to-face packing is believed to be a preferred means of self-assembly for minimizing the surface energy and stabilizing the nanodisks, as driven by the strong capillary force that appears during the drying process. As a result, they stood on their edges on a solid substrate such as the carbon film of the TEM grids,

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enabling convenient measurement of their diameter and thickness directly from their TEM images. Upon further raising the temperature to 200 and 220 °C, the diameter of the nanodisks increased to 14.5 ± 1.3 nm and 16.9 ± 2.3 nm, respectively, while the thickness was barely changed. While the nanodisks produced at 200 °C were still highly uniform, a small amount of larger particles started to appear in the samples synthesized at 220 °C, probably because of interparticle aggregation (Figure 2f). Although it is possible to further increase the disk size by carrying out the reaction at even higher temperatures, aggregation became a severe problem and made it difficult to control the size distribution.

The temperature increase enhances the reaction rate in multiple ways. First, increasing the temperature greatly decreases the stability of the intermediate complexes formed in solution, thus providing more monomer species to the growing nanocrystals.[7,15] It is generally accepted that higher monomer concentrations enhance the rates of both nucleation and growth. Second, a higher temperature promotes nanocrystal growth by increasing the mass transfer rate of the monomers to the surface of nanocrystals. The binding of the surfactants to the nanocrystal surface may also weaken at high temperatures, thus quickening the nanocrystal growth. Lastly, the precipitation reaction between the copper cations and the sulfur species may also accelerate at increased temperature.

Because a TEM image is a two-dimensional projection of three-dimensional objects, disk shaped nanocrystals were sometimes misinterpreted as nanorods when they stacked to each other and stood on substrates vertically. This has occurred not only with Cu_2S, but also Co nanostructures.[17,29,30] Korgel et al. have performed tilting experiments which unambiguously confirmed the disk morphology of Cu_2S nanocrystals.[15] In fact, for nanodisks with high aspect ratios as shown in Figures 2e and 2f, one can clearly discern the disk morphology by carefully observing the overlap of disks in some chains that are standing tilted with respect to the substrate.

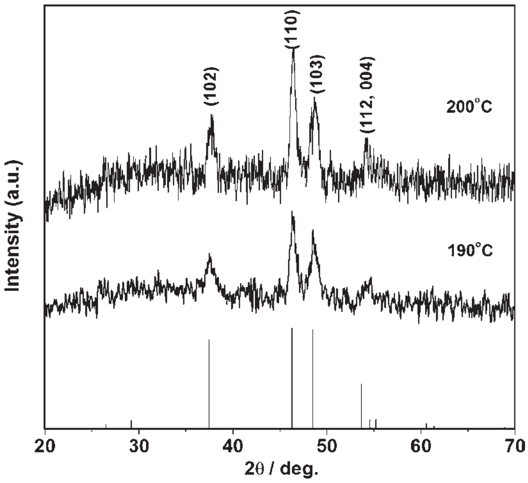

Figure 3. XRD patterns of Cu_2S nanodisks after heating at 190 °C (bottom) and 200 °C (top).

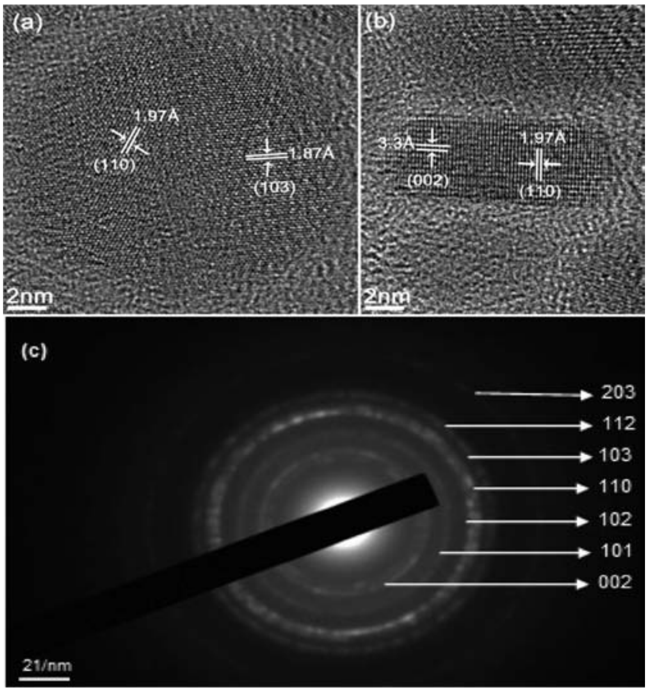

Figure 4. (a) HRTEM image of a nanodisk lying flat on the substrate; (b) HRTEM image of a nanodisk standing on its edge; (c) SAED pattern of the Cu_2S nanodisks.

Previous studies have suggested that the disk morphology is the result of the preferential growth of high energy {100} and {110} facets with respect to the {001} planes.[15] The preferred growth along the flat axis of the disks has been further confirmed by XRD measurements. Figure 3 shows the XRD patterns of Cu_2S nanodisks obtained at 190 and 200 °C, which are consistent with the standard pattern of hexagonal Cu_2S (JCPDS No. 26-1116). In the standard pattern that was measured from bulk samples the three major peaks of (102), (110), and (103) show similar intensities. Prior reports on Cu_2S nanocrystals with the same crystal structure displayed a relatively weaker (110) peak in comparison to the (103) peak.[11] For the as synthesized nanodisk samples, however, the intensity of the (110) peak was significantly enhanced, suggesting that the preferred growth of the nanocrystals is in the ⟨110⟩ direction of the hexagonal lattice. In addition, the sample prepared at 200 °C displayed an even stronger (110) peak than the 190 °C sample, which was in agreement with the above TEM observation of more extensive growth along the diameter than the thickness at higher temperatures.

To further investigate their crystal structures, we have measured the HRTEM images and the SAED pattern of the as-prepared Cu_2S nanodisks. Figure 4a and 4b are two HRTEM images recorded for nanodisks with flat surfaces oriented parallel or perpendicular to the substrate. For a typical nanodisk lying flat on the substrate (Figure 4a), we can observe lattice fringes with interplanar spacing of ~1.97 and 1.87 Å corresponding to (110) and (103) planes of a hexagonal Cu_2S phase, respectively. For a nanodisk oriented perpendicular to the substrate shown in Figure 4b, lattice fringes with interplanar spacing of 3.3 and 1.97 Å can be assigned to the (002) and (110) planes of the hexagonal

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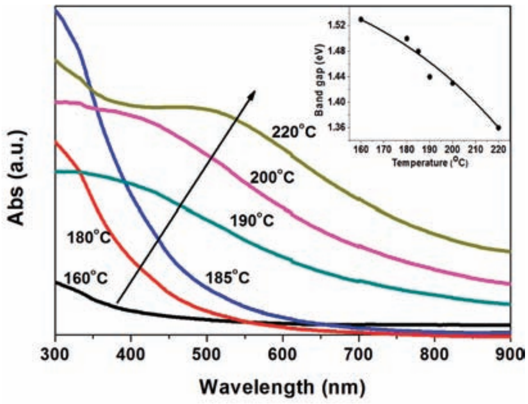

Figure 5. UV−vis−NIR absorption spectra of Cu_2S nanocrystals obtained at different reaction temperatures; the inset shows variation of band gap as a function of reaction temperature.

Cu_2S phase, respectively. As the (110) planes are perpendicular to the flat disk surface, it again confirms the preferred side-wise growth of the nanocrystals along the ⟨110⟩ direction of the hexagonal lattice. On the other hand, the growth along the *c*-axis of the hexagonal lattice is limited, as evidenced by the appearance of (002) planes that are parallel to the flat surface of the disks. In consistent with the XRD measurements, the SAED pattern of a number of nanodisks displays characteristic diffraction rings that can be indexed to the hexagonal phase of Cu_2S crystals (Figure 4c).

UV−vis absorption spectra of Cu_2S nanocrystals obtained at different temperatures were recorded to investigate their band gap properties (Figure 5). The absorption spectra of spherical Cu_2S nanoparticles (< 6 nm) obtained at 160, 180, and 185 °C present similar shapes lacking peaks or shoulders, which is consistent with the observations reported in the literature.[16] Shoulders appeared in the absorption spectra of products when the reaction temperature was raised above 190 °C, and a broad absorption peak can be clearly observed at 220 °C. The absorption peak shifted toward longer wavelength as the reaction temperature increased because of the larger particle size.[31]

As Cu_2S is a crystalline semiconductor of indirect transition, the band gap of the nanostructures can be estimated from the plot of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$,[32] where α is the absorption coefficient, $h\nu$ is the photon energy, and λ is the wavelength in nanometers. As shown in the inset in Figure 5, the band gap of the products plotted as a function of reaction temperature shows a gradual decrease from 1.53 to 1.36 eV with increasing temperature. The decrease of the band gap is ascribed to the increased size of Cu_2S nanocrystals at higher reaction temperatures. Compared to the value for bulk Cu_2S (1.21 eV), the band gap of all as-synthesized Cu_2S nanostructures increases because of the quantum confinement effect.

Shape Evolution over Time. The growth of Cu_2S nanocrystals has been monitored by characterizing samples collected at different reaction times by using TEM and UV−vis absorption spectroscopy. We first looked at the reaction performed at 190 °C. Soon after the injection of dodecanethiol, the solution turned pale yellow because of the formation of $[Cu(SC_{12}H_{25})]$ through the reaction between CuOAc and dodecanethiol. Adding methanol to the system at this stage caused precipitation of a small amount of gel-like polymeric substance, as shown in the TEM image in Figure 6a, which might be attributed to the intermediate compound $[Cu(SC_{12}H_{25})]$.[17] It is believed that the transition from pale yellow to deep red was due to the accumulation of active monomer species that eventually led to nucleation of nanocrystals upon supersaturation. After nucleation, the remaining monomer species were deposited onto the surface of Cu_2S nuclei, promoting the progressive growth of nanocrystals. This classic nucleation and growth model, which has been extensively studied in the case of CdSe quantum dots,[25] was found to control the formation Cu_2S nanostructures. As can be seen in Figure 6b, nanoparticles with an average diameter of ~2.3 nm appeared, accompanied by a decreased amount of $[Cu(SC_{12}H_{25})]$ complex. After 60 min of continuous heating at 190 °C, the large amorphous aggregates disappeared as the $[Cu(SC_{12}H_{25})]$ complex was partially consumed, producing a uniform population of nanocrystals with an increased diameter of ~3.1 nm. Further prolonging the reaction time to 120 min allowed the nanocrystals to grow larger to ~4.9 nm. Careful inspection of the sample obtained at 180 min suggests

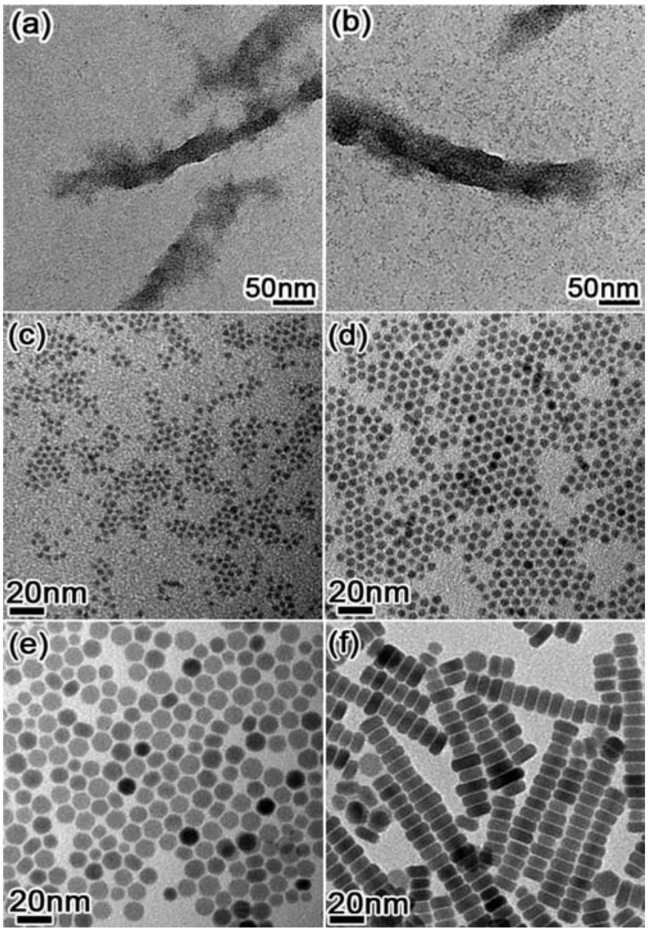

Figure 6. TEM images of Cu_2S nanocrystals formed after prolonging reaction times at 190 °C: (a) 5 min and (b) 15 min, (c) 60 min; (d) 120 min; (e) 180 min; and (f) 540 min.

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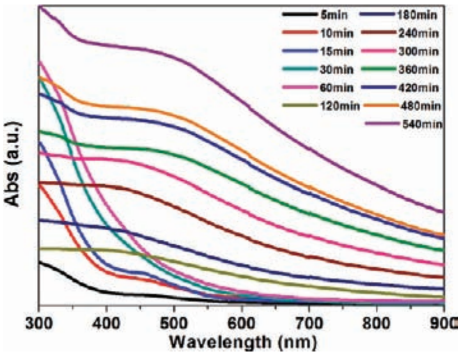

Figure 7. Temporal evolution of UV−vis−NIR absorption spectrum of Cu_2S nanocrystals obtained at 190 °C.

that these nanocrystals already possessed an hexagonal disk shape, with a diameter of ∼11 nm and a thickness of ∼7.1 nm. Because of the low aspect ratio, only a small amount of nanodisks stood on their edges while the rest laid on their faces. As the majority of the precursor has been consumed at this stage, continuous heating only slightly increased the size of the nanodisks, for example, to ∼13 nm in diameter and ∼7.9 nm in thickness for samples collected at 540 min (Figure 6f). Because no quantized increase in nanocrystal size has been observed, we can rule out the aggregation and coalescence mechanism that was proposed in the previously reported solventless synthesis procedures.[16] Instead, the nanodisks grow through the classic monomer addition route which ensures a progressive increase in the overall size of the products.

UV−vis spectroscopy was again used to monitor the change in the optical property of the nanocrystals during their size/shape evolution. Figure 7 reveals an increase of absorbance in the UV range (300−470 nm) at the early stage (5−60 min) of crystal growth, which may be attributed to the dominant presence of $[Cu(SC_{12}H_{25})]$ complex. As the system after 5 min of reaction just turned to transparent yellow, $Cu(SC_{12}H_{25})$ is believed to be the major intermediate product that contributed to the absorption. The concentration of $Cu(SC_{12}H_{25})$ increased initially, but finally dropped when it was consumed to produce Cu_2S nanocrystals. Broad and weak peaks around 450−500 nm were apparent for the sample collected before 15 min of reaction, suggesting the formation of an intermediate substance associated with the formation of monomer species. After the relatively fast nucleation at around 15 min, the slow growth of Cu_2S nanocrystals gradually strengthened the absorption of the nanocrystals, leading to a red shift of the peak as the reaction proceeds. The relatively fast nucleation and slow growth processes are believed to contribute to the high uniformity of the nanocrystals.[25] One can notice slight broadening in size for samples heated for a long time (e.g., 540 min) because of the Ostwald ripening process (Figure 6f). The final product after 540 min of reaction shows a very broad absorption spanning from UV to near IR which may make this material a good candidate for photovoltaic devices.

Because the disk shape is more distinct at higher temperatures, we studied the control of nanodisk growth over time in more detail for samples prepared at 200 °C. As shown in Figure 8, the diameter/thickness of Cu_2S disks changed from 13/7.5 nm to 18.2/9.6 nm gradually when the reaction time extended from 60 to 300 min. Both the diameter and the thickness increased almost linearly over time, but the change in diameter appeared faster than that of the thickness. The overall change in aspect ratio (diameter/thickness) was small, although from the inset in Figure 8e one can observe the relatively fast increase in aspect ratio in the early stage of the disk growth. Because of the large aspect ratio, the as-made disks tended to assemble preferentially face-to-face into extended chains.

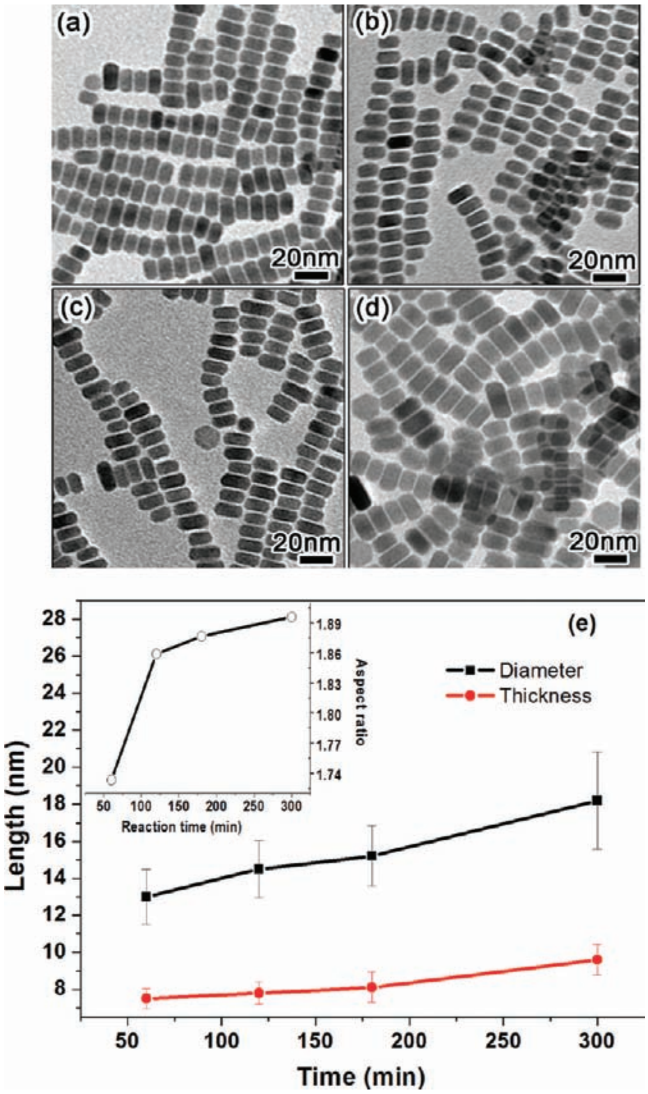

Figure 8. (a−d) TEM images of Cu_2S nanocrystals formed after different reaction times at 200 °C: (a) 60 min; (b) 120 min; (c) 180 min; (d) 300 min. (e) The dependence of diameter and thickness on reaction time, the inset shows aspect ratio as a function of reaction time.

Role of Surfactants. TOPO and dodecanethiol are both surfactants that direct the anisotropic growth of Cu_2S nanodisks. Similar to the surfactants in many other nanocrystal syntheses, TOPO may selectively adsorb onto (001) crystal facets, and dodecanethiol may preferentially stabilize (110) and (100) facets. TOPO binds more strongly to the nanocrystal facets than dodecanethiol does, thus facilitating the anisotropic growth of nanocrystals and producing stable disk morphologies. This assumption is supported by the fact that when TOPO is absent in

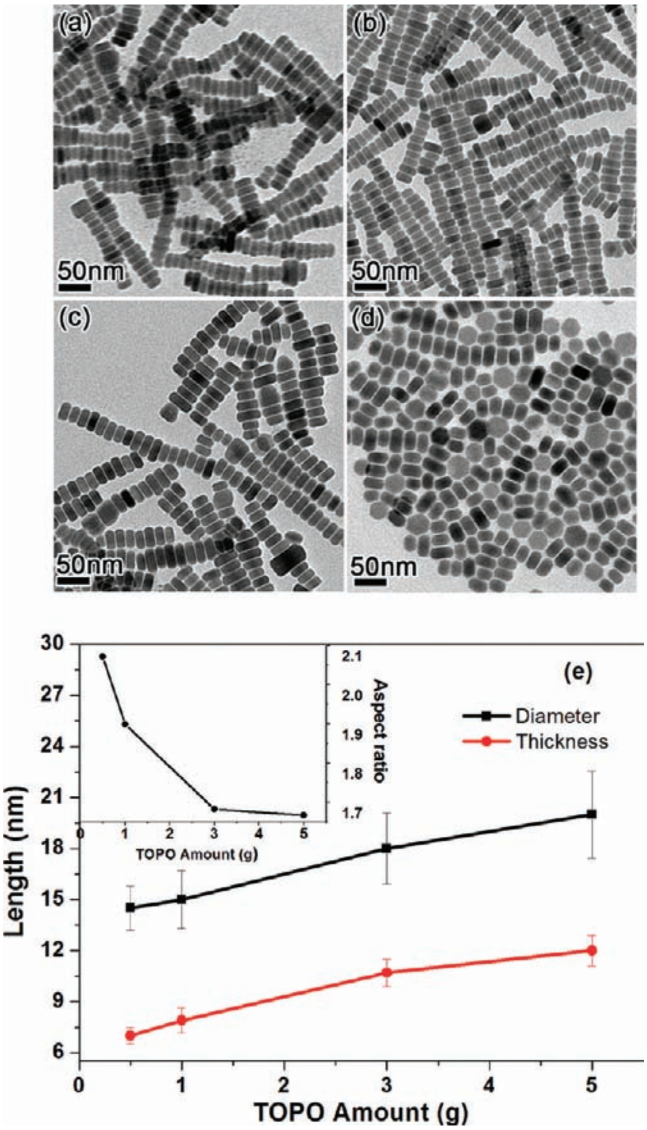

Figure 9. (a−d) TEM images of Cu_2S nanocrystals prepared using different amounts of TOPO: (a) 0.5 g; (b) 1 g; (c) 3 g; and (d) 5 g. (e) The dependence of diameter and thickness on TOPO amount, the inset shows aspect ratio as a function of TOPO amount.

the reaction, no Cu_2S nanodisks can form and only irregular shaped particles are obtained. The relatively weak binding of dodecanethiol to Cu_2S has also been described in prior works.[15]

We have systematically changed the concentration of TOPO to determine its contribution to the particle shape evolution. As the amount of TOPO was increased from 0.5 to 5 g, the average diameter of nanodisks increased almost linearly from ~14.5 nm to ~20 nm, and the thickness from ~7 to ~12 nm (Figure 9). Accordingly, the aspect ratio of the Cu_2S nanodisks decreased from 2 to 1.6. Such a concentration effect is different from the general case in which increasing the concentration of surfactants limits the growth of nanocrystals and produces smaller particles. Interestingly, a similar phenomenon has been observed previously in the synthesis of Co nanodisks when using TOPO and oleic acid as surfactants.[29] At a fixed oleic acid concentration, the diameter of the nanodisks was found to be directly proportional to the concentration of TOPO. It has been pointed out that TOPO can promote atom exchange between particles, thus increasing the average size of the final samples. We suspect a similar mechanism may occur in the current case.

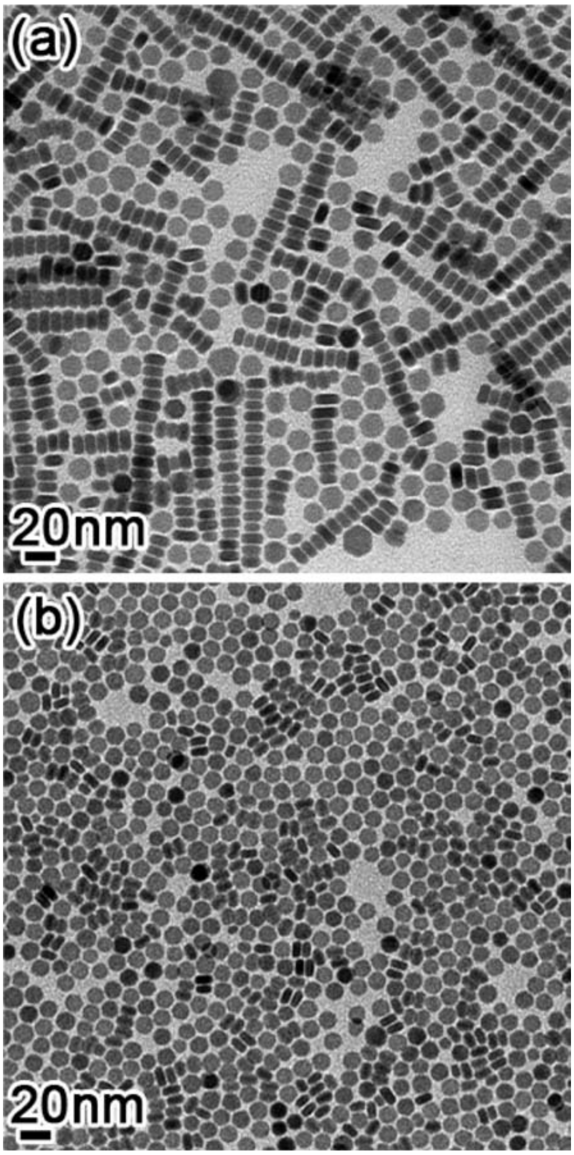

Figure 10. TEM images of Cu_2S nanocrytstals obtained with different precursor concentrations: (a) 0.4 mmol CuOAc/1 mL dodecanethiol; (b) 1.6 mmol CuOAc/4 mL dodecanethiol.

Concentration of Precursors. The initial precursor concentration affects the size of nanocrystals because it determines the kinetics of nucleation and growth. We have compared the Cu_2S nanocrystals prepared at two different concentrations of CuOAc and dodecanethiol at 200 °C while controlling other experimental conditions. The ratio of CuOAc to dodecanethiol was also kept at 2/5 mmol/mL in these experiments. As shown in Figure 10, at a low precursor concentration (0.4 mmol CuOAc/1 mL dodecanethiol), highly uniform Cu_2S nanodisks with a diameter of 14.8 ± 1.4 nm and a thickness of 7.9 ± 0.8 nm can be obtained. Increasing the concentration of the precursors to 1.6 mmol CuOAc/4 mL dodecanethiol also led to monodisperse samples, but with reduced dimensions (10.2 ± 0.9 nm in diameter and 5.5 ± 0.5 nm in thickness).

The size reduction at higher precursor concentrations is consistent with the classic LaMer model which describes the nucleation and growth of colloidal particles.[33] It is generally accepted that a high concentration of monomer species is preferred for the synthesis of uniform nanocrystals as it promotes nucleation events and produces a large amount of nuclei. In this case, the increased precursor concentration resulted in the rapid formation of many more nuclei, and eventually led to the reduction of the overall size of the nanodisks. Because the nucleation rate was enhanced, the nanocrystals still retained a narrow size distribution.

Conclusion

In summary, high quality Cu_2S nanostructures with both dot and disk morphologies have been successfully synthesized through a one-pot process that does not require the use of a pre-prepared single source precursor. Copper thiolate forms at the early stage of reaction which effectively acts as a precursor whose decomposition leads to further nucleation and growth of Cu_2S nanocrystals. During this process, very small Cu_2S dots (3−6 nm) gradually transform into nanodisks with increasing reaction temperature or prolonged reaction time. The diameter, thickness, and aspect ratio of the nanodisks can be tuned by simply changing the experimental parameters such as reaction temperature, reaction time, amount of surfactants, and the concentration of precursors. The band gap of as-synthesized Cu_2S nanodisks can be tuned in the range of ~1.36−1.53 eV, thus moving the absorption spectrum to the visible/NIR spectrum range. The nanodisks show a broad absorption peak, making them good candidates for applications in photovoltaic devices.

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