

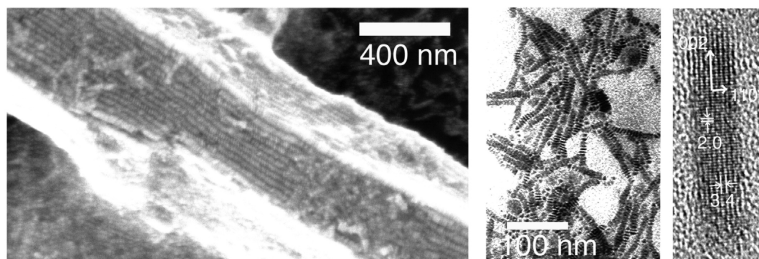
Communication

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Solventless Synthesis of Copper Sulfide Nanorods by Thermolysis of a Single Source Thiolate-Derived Precursor

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Arrested precipitation has proven to be a powerful method for synthesizing various metal and semiconductor nanocrystals and nanorods.^{1–3} Organic “capping” ligands are central to this approach: bifunctional stabilizer molecules with a “reactive” binding group provide a bulky steric layer to the particle surface to prevent undesired aggregation.⁴ The capping ligands control particle nucleation and growth.⁵ Nanocrystal growth by coagulation leads to very broad size distributions, whereas growth by condensation leads to narrow size distributions.⁶ Therefore, ligands must provide a strong steric barrier to aggregation with reversible binding that enables monomer addition to the particle surface. As these syntheses are generally carried out in solution, both molecular and particle diffusion are fast, and it is in practice impossible to completely eliminate coagulative growth. Here we demonstrate a new *solventless* synthesis of size- and shape-monodisperse Cu₂S nanorods by copper thiolate thermolysis. A copper thiolate complex serves as the molecular precursor and provides the capping ligand to control particle growth. In the solventless reaction environment, interparticle collisions rarely occur, and particle growth proceeds primarily by monomer addition to the particle surface leading to monodisperse size and shape distributions.⁷

The copper precursor is made by combining an aqueous Cu(NO₃)₂ solution (0.21 g in 36 mL) with 24.5 mL of chloroform, and then adding sodium octanoate (0.18 g, Aldrich, 98%) as a phase transfer catalyst to solubilize the copper cations in the organic phase. After the blue copper octanoate complex transfers into the organic phase, the aqueous phase is discarded. Dodecanethiol (240 μL, Aldrich, 98%) is added to the organic solution, which changes color from blue to green as dodecanethiol displaces octanoate bound to the copper species. The green color results from the mixture of copper complexed with thiol (which produces a yellow color) and carboxylated ligands. Evaporation of the organic solvent leaves a waxy residue consisting of the copper precursor species. The solid residue is heated to 148 °C for 140 min to produce a brown solid material. This material redisperses in chloroform for precipitation with ethanol to remove unreacted surfactant and byproducts. A typical preparation yields 10–20 mg of purified nanorods (yield = 10–20%).

Transmission electron microscopy (TEM), X-ray diffraction, and elemental analysis⁸ reveal the product to consist of crystalline Cu₂S (chalcocite) nanorods (Figures 1a–d, 2, and Supporting Information). The nanorods produced at 148 °C (140 min reaction time) are approximately 4 nm in diameter and 12 nm long with relatively narrow size and shape distributions. Temperatures lower than 140 °C did not produce any solid product. Reaction temperatures greater than 198 °C promoted isotropic spherical growth, as shown in Figure 1e and 1f. In this solventless system, it appears that rods and spheres form simultaneously, as opposed to the rod-to-sphere transformation process that has been observed in other nanorod/nanocrystal systems.³ Lower temperature favors rod formation,

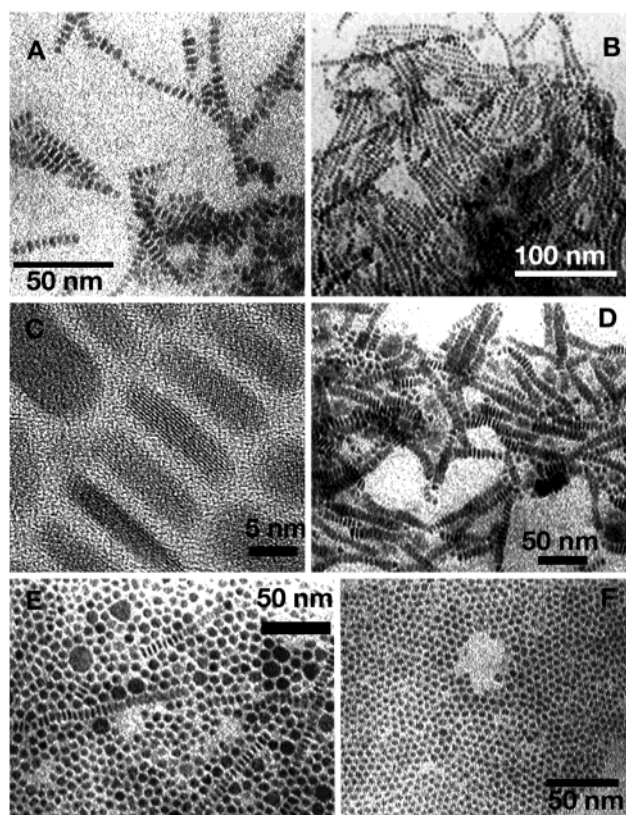


Figure 1. TEM images of Cu₂S nanorods and nanocrystals produced at 148 °C (140 min) (a–c); 190 °C (60 min) (d); 198 °C (120 min) (e); 218 °C (60 min) (f).

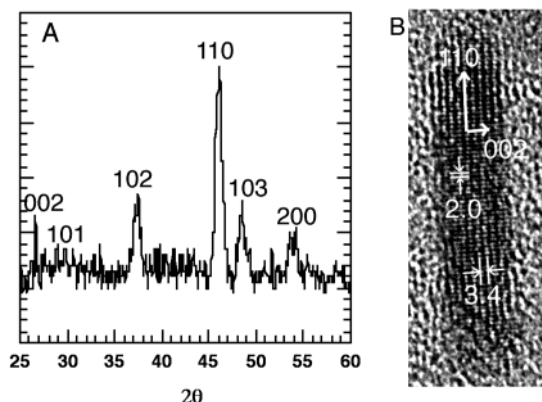


Figure 2. XRD (a) and TEM (b) of Cu₂S nanorods. Both XRD and TEM reveal nanorod growth primarily in the [110] direction of the hexagonal lattice.

whereas higher temperatures produce spherical nanocrystals—crystallization kinetics become isotropic at high temperatures,



Figure 3. HRSEM image of Cu_2S nanorods self-assembled into a colloidal crystal.

overcoming the energetic barrier favoring asymmetric nanorod growth. Increased reaction time simply appears to increase the size and shape distribution in the sample to yield poor results—heating over 4 h generally produced no recoverable product.

Cu_2S forms by homolytic cleavage of the thiol and alkyl groups—the sulfur consequently incorporates into the hexagonal close-packed lattice, while the Cu cations inhabit the interstitial space. The thiols (and perhaps the carboxyl ligands) also contribute to the reduction of Cu(II) to Cu(I). The remaining excess thiol controls the nanorod/particle growth process. The carboxyl ligands most likely also participate in this role.

Cu_2S undergoes a phase transition from the low-temperature monoclinic crystal structure to the high-temperature hexagonal phase at 103 °C.⁹ Because of the relatively high synthesis temperature, Cu_2S forms with the hexagonal crystal structure. This anisotropic structure promotes nanorod formation. However, unlike the majority of hcp nanorods, like CdSe,⁵ GaP,¹⁰ and Co,³ the Cu_2S preferentially grows in the [110] direction with the *c*-axis perpendicular to the long axis, as Figure 2 reveals. Upon cooling below the monoclinic-hexagonal transition temperature, the nanorods retain the hexagonal structure.

Figure 3 shows a high-resolution scanning electron microscope (HRSEM) image of a colloidal crystal of Cu_2S nanorods formed by drop-casting a concentrated dispersion in chloroform onto a glass carbon substrate. The size- and shape-monodisperse nanorods arrange into the thermodynamically most favorable structure on the time scale allowed by the evaporating solvent.^{11,12} It is worth noting that these nanorods organize into relatively thick structures as compared to silver or gold nanocrystals that tend to spread onto the substrate surface as opposed to crystallizing into three-dimensional superlattices when drop-cast from a good solvent.¹³ TEM images also reveal that the interparticle attractions are anisotropic and relatively large, leading to the formation of long linear strands of nanorods that extend typically 15–30 particles in length (approximately 75–150 nm long). Although one would expect one-dimensional ordering of this type for magnetic particles with strong magnetic dipole–dipole interactions,³ asymmetric van

der Waals forces—although directional—are not expected to give rise to these structures. Both hexagonal and monoclinic forms of Cu_2S are ferroelectric,¹⁴ and apparently dipole–dipole interactions are responsible for these long strands of nanorods. The potential ferroelectric properties of these nanorods are currently under investigation.

The solventless approach to nanocrystal and nanorod synthesis provides a reaction environment that under the appropriate conditions eliminates coagulative particle growth. This leads to very size- and shape-monodisperse products. The use of metal thiolates as precursors should also apply to a variety of other metal chalcogenides, such as CoS and NiS. By identifying the appropriate molecular precursors and capping ligands, the solventless approach to nanocrystal and nanorod synthesis should be generally applicable to a wide variety of materials.

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Supporting Information Available: A complete set of XRD and additional TEM images (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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