

Synthesis of Uniform Cu₂S Nanowires from Copper–Thiolate Polymer Precursors by a Solventless Thermolytic Method

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One-dimensional (1D) nanostructures have become the focus of considerable research because of their unique applications in mesoscopic physics and fabrication of optical, electronic, and magnetic nanosize devices.^{1,2} One-dimensional nanostructures not only have potential technological advantages over quantum dots and wells but also provide good systems for testing theoretical predictions on dimensionality effects, especially since extremely thin nanowires with large aspect ratios are likely to find a range of applications.^{3–5} Diverse synthesis methods have been developed to achieve 1D morphologies, such as nanolithography techniques, template-directed syntheses, vapor-phase methods, vapor–liquid–solid (VLS), solution–liquid–solid (SLS), and solvothermal methods, and so forth.⁶ For example, solution synthetic approaches based on capping reagents show high degrees of success owing greatly to the ability of the capping ligands to provide steric stabilization and to change the surface energies and the kinetics of growth.^{6i,j} Recently, the solventless thermolysis of thiolate solid precursors has been successfully applied to synthesize Cu₂S⁷ and Ni₂S⁸ nanoparticles. Compared to the solution condition, this novel approach has striking advantages in which interparticle collisions rarely occur, with the undesired aggregation of the nanoproducts being hindered by the presence of capping ligands. Thiols are well-known coordination ligands for transition metals, and the diversity of the metal–thiolate coordination chemistry is prominent. So far, the reported structures include from mono- up to tetradecanuclear discrete clusters, 1D chains, and 2D layers.⁹ These hint that control of the polymerization and coordination modes of the thiolate precursors is likely to affect the size and shape of the final nanoproduct in a solventless thermolysis method. A positive answer will definitely open a great opportunity to join the traditional coordination chemistry and the increasing nanosyntheses based on chemistry methods.

Cu₂S is an interesting material for its semiconduction and photovoltaic capabilities.¹⁰ Monoclinic Cu₂S nanowire arrays with 10–100 nm diameters were grown on Cu foil substrates with the aid of H₂S gas.¹¹ Cu₂S nanorods could be made by a solventless method with 4 nm diameters and 12 nm lengths.^{7a} When we prepared the copper–thiolate precursor according to this solventless method,⁷ it was found that the viscosity of the as-synthesized Cu–thiolate colloid (η_{VAC})¹² decreased with an increase of stirring speed and stirring time during the process of coordination of Cu ions to thiols. In general, a higher viscosity indicates a higher degree of the polymerization of the precursor. Here, we report the discovery that the use of highly polymerized Cu–thiolate as a precursor generates uniform Cu₂S nanowires with 2–6 nm diameters and lengths of 0.1 to several μm after precipitation and firing. The morphology of our as-synthesized Cu₂S nanowires is totally

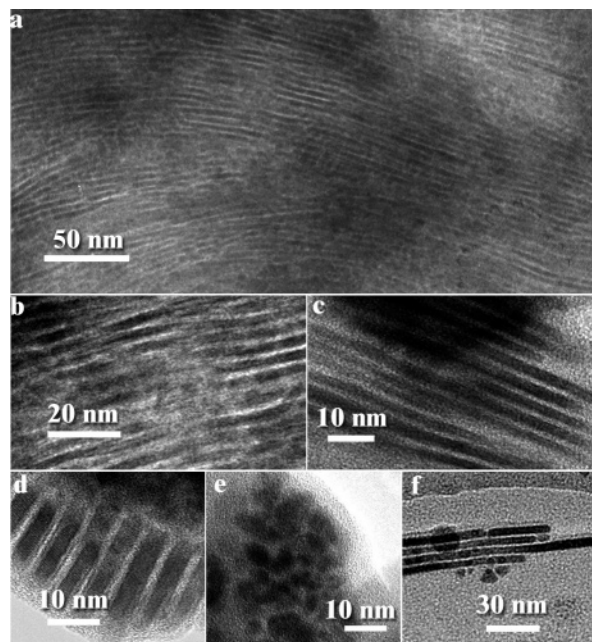


Figure 1. TEM images of Cu₂S nanowires produced at: (a–c) 155 °C for 120 min ($\eta_{\text{VAC}} = 93.5$ mPa/s); (d) 155 °C for 120 min ($\eta_{\text{VAC}} = 13.2$ mPa/s); (e) 155 °C for 120 min ($\eta_{\text{VAC}} < 10$ mPa/s); and (f) 180 °C for 30 min ($\eta_{\text{VAC}} = 93.5$ mPa/s).

different from that of the Cu₂S nanorods in ref 7. The evolution of these nanowires with the polymerization and heating temperature is reported, as well. This new approach is expected to be adaptable to the preparation of nanowires of numerous materials.

The Cu–thiolate precursor is synthesized with a phase-transfer method similar to that in a previous report,⁷ but with very gentle stirring while adding thiol to the copper-containing organic solution to ensure a high degree of the polymerization of the Cu–thiolate fragments (full synthetic details in the Supporting Information). Adjustment of stirring speed and time at this coordination step can easily govern the viscosity of the as-synthesized colloid.¹² The η_{VAC} value increases 7-fold with this decrease of stirring speed. Normally, the thiolate precursor is made at room temperature in this report. Temperatures over 30 °C are disadvantageous for high polymerization of the thiolate colloid. The yield for the final nanowire following pyrolysis at 155 °C and reprecipitation from CHCl₃/EtOH is usually 10–20%.

Transmission electron microscopy (TEM) reveals the product to consist of crystalline Cu₂S (chalcocite) nanowires (Figures 1 and 2, and Figures S1 and S2 of the Supporting Information). The nanowires produced at 155 °C for 120 min are approximately 2–6 nm in diameter and 0.1 to several μm in length, with relatively uniform diameters, very large aspect ratios, and monodisperse

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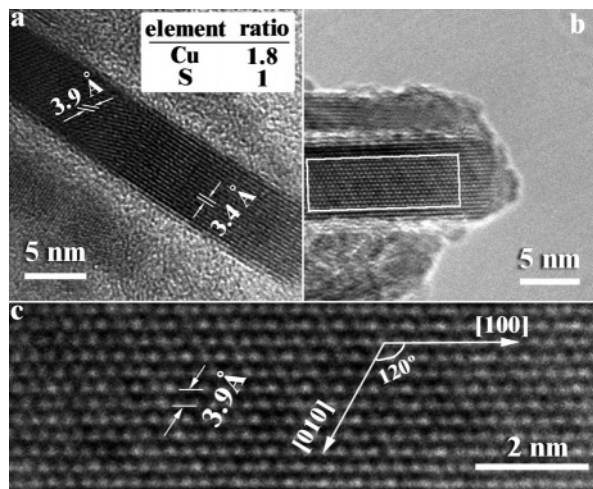


Figure 2. HRTEM images of Cu_2S nanowires (a–b). The inset in (a) shows the EDX result of the nanowire on a Mo grid.¹⁵ (c) An enlarged image of the selected part in (b). The hexagonally arranged spots are 3.9 Å apart, and the angle between [100] and [010] is measured to be 120° , corresponding to the parameters of high chalcocite Cu_2S . The long direction of the nanowire is perpendicular to [001].

morphology. Increased annealing temperature simply appears to increase the diameter of the nanowire, as shown in Figure 1c versus 1f. The nanowires presented in the latter have diameters of 8–10 nm.

The polymerization of the Cu–thiolate precursor seems to play an important role in determining the shape of the final nanoproducts in this solventless thermolytic approach. Higher degrees of polymerization favor nanowires ($\eta_{\text{VAC}} = 93.5$ mPa/s, Figure 1a–c), whereas lower polymerization produces nanorods ($\eta_{\text{VAC}} = 13.2$ mPa/s, Figure 1d) or spherical nanoparticles ($\eta_{\text{VAC}} < 10$ mPa/s, Figure 1e), the latter being similar to previous reports.⁷ In the preparation of the Cu–thiolate precursor, the reactions of copper ions with thiols result in formation of copper (I)–thiolate polymers, as expected for the silver (I)–thiolate process in which the polymers consist of alternating Ag and S six-ring fragments.¹³ We infer that the Cu–thiolate precursors with high viscosities exhibit higher associations of the Cu/S fragments encapsulated by thiol ligands, and this polymer serves as the template to produce the Cu_2S nanowires on firing.

The HRTEM image of the Cu_2S nanowire (looking down [001] zone axis) in Figure 2c clearly shows hexagonally arranged spots that are 3.9 Å apart, and the angle between [100] and [010] is measured to be 120° , corresponding to the parameters of high chalcocite Cu_2S ¹⁴ ($P6_3/mmc$, $a = 3.89$ Å, $c = 6.88$ Å). The long direction of the nanowires is perpendicular to [001], in agreement with previous reports for Cu_2S nanorods.⁷ Some defects in the array are noticeable in Figure 2c. The growth orientation changes in some nanowires are visible, as indicated in Figure 2a. The lower-right part has a 3.4 Å spacing, corresponding to that between either {100} or {002} lattice planes, whereas the orientation of the upper-left part, which is consistent with that in Figure 2c, is noticeably rotated. The driving force for the wire growth may come from the high polymerization of precursor and the dipole–dipole interactions suggested by Korgel.⁷

The thermal desorption of the solid Cu–dodecanethiolate precursor has been examined with the aid of a TDS Gerstel system.¹⁶ Only two organic molecules are desorbed from the precursor in range of 60–220 °C: 1-dodecene and octanoic acid ($\text{CH}_3(\text{CH}_2)_6\text{COOH}$) from the Cu complexant. These suggest that, thermolyti-

cally, octanoate ions are stable before and after the heating, only serving as a surfactant to hinder the interparticle collisions, whereas the dodecanethiol undergoes cleavage of a C–S bond to serve as a sulfur source for the Cu_2S ; no further decomposition of the organic chain occurs under the conditions used.

In conclusion, the viscosity of colloidal thiolate indicates the degree of polymerization of the precursor, which governs the morphology of the final nanoparticle in the solventless thermolysis method. Uniform Cu_2S nanowires with large aspect ratios are synthesized from highly polymerized thiolate precursors. The parameters controlling the viscosity of the colloid precursor mainly include stirring speed, time, and temperature during which the chemical coordination between Cu ions and thiols occurs. This new approach based on the viscosity control in the solventless thermolysis method is expected to be applicable to a wide variety of materials, and the explorations with other Se-, P-, or N-containing ligands and metals are ongoing.

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Supporting Information Available: Full synthetic details, EDX results, additional TEM images, and the TDS results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) The viscosity of precursor is measured with the aid of an NDJ-9S viscometer (ShangPing) at room temperature with a rotor (diameter = 19 mm) speed at 60 r/min. The viscosity of each sample was read after the rotor had been in the sample for 10 min.
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- (15) Elemental analysis performed by EDX of nanocrystals on a Mo grid with the aid of a JEOL 2010F TEM equipped with an Oxford INCA spectrometer showed that the Cu:S atomic ratio is 1.8:1.
- (16) The thermal desorption measurements were performed on TDS Gerstel (thermodesorption system), Agilent 6890N, GC, and Agilent 5973N MS.

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