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Acetic Acid-Assisted Solution Process for Growth of Complex Copper Sulfide Microtubes Constructed by Hexagonal Nanoflakes

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Semiconductoring transition metal chalcogenides are a family of most important nanomaterials as a result of their interesting properties which are different from those of bulk substances.[1] Particularly, shape-controlled synthesis of low-dimension nanocrystals has been an interesting research topic because of their distinguished electronic and optical properties. The fabrication of technologically useful nanomaterials and their applications depend not only on the quality of the nanoparticles (e.g., size and shape) but also on their spatial orientation and arrangement.[2] In recent years, one of the important goals in materials science is to develop new strategies for tailoring the structure of materials with an unusual and novel form.[3]

Copper chalcogenides are of particular interest as a result of their variations on stoichiometric composition, which are widely used as p-type semiconductors in solar cells, as optical filters, and as surperionic materials.[4] Different approaches such as solid-state reaction,[5] hydrothermal microemulsions,[6] and solvothermal and chemical vapor deposition methods were usually applied for the assembly of nanoparticles into well-defined superstructures. Previous efforts focus on the synthesis of organized two-dimensional or three-dimensional arrays of copper sulfide nanoparticles such as shrub-like,[7] urchin-like, hollow sphere,[8] and macroporous sphere.[9] A few reports have appeared on the synthesis of one-dimensional copper sulfide including Cu_2S nanowires[10] or nanorod,[11] digenite phase nanowires and djurleite phase nanotubes.[12]

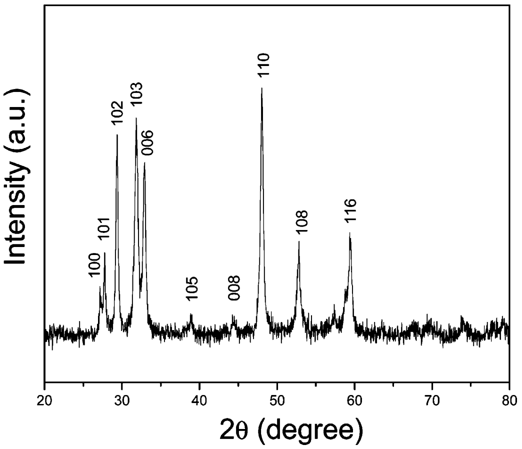

Figure 1. XRD pattern of hexagonal CuS phase obtained at 80 °C for 8 h. $[CuCl_2] = 0.033$ M, $[TAA] = 0.066$ M, $[HAc] = 0.04$ M, and pH 1.45.

In this communication, we report a facile one-pot solution approach for growth of unusual copper sulfide microtubes based on an acetic acid-assisted solution process at 80 °C using acetic acid as an additive and controlling the molar ratio of reactants ($CuCl_2 \cdot 2H_2O$) and thioacetamide (TAA).

All chemicals are analytical grade and used as received without further purification. In a typical experiment, 10 mL of $CuCl_2 \cdot 2H_2O$ (1 mmol) solution and 20 μL of CH_3COOH (HAc; 99.5%, w/w) were added into 15 mL of TAA (2 mmol) solution drop by drop under vigorous stirring, resulting in the formation of a milky-like dispersion. Such solution was transferred into a conical bottle with a capacity of 35 mL, which was sealed and maintained at 80 °C for 8 h. After the reaction, the glass bottle was cooled naturally. All of the blue-black precipitate with higher yield (>95%) was collected and washed with distilled water and ethanol several times, respectively, and then dried in a vacuum at 50 °C for 3 h.

X-ray powder diffraction patterns (XRD) of the products were obtained on a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.541\,78$ Å). Transmission electron microscopy (TEM) photographs were taken on a Hitachi model H-800 transmission electron microscope at an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) photographs and selected area electron diffraction patterns were performed on a JEOL-2010 transmission electron microscope. Element analysis was conducted by energy-dispersive spectroscopy on a JEOL JSM 6700 scanning electron microscope. Fourier transform infrared (FTIR) spectra were measured on a Bruker Vector-22 FTIR spectrometer at room temperature. UV−vis spectra were recorded on a Shimadzu UV-240 spectrophotometer

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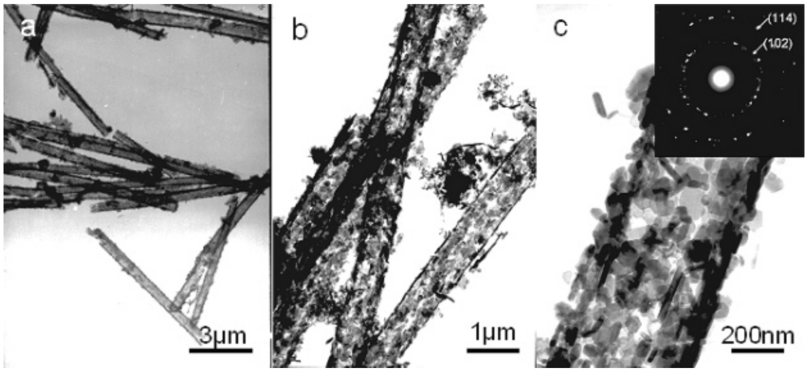

Figure 2. (a, b) TEM images of CuS microtubes obtained at 80 °C in 0.04 M HAc solution. $[CuCl_2] = 0.033$ M, $[TAA] = 0.066$ M, and pH 1.45. (c) An enlarged TEM image and selected diffraction pattern taken on the tube.

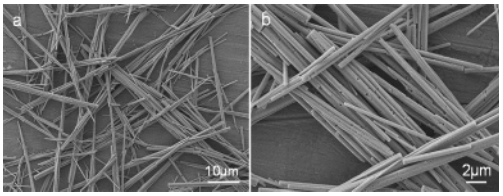

Figure 3. SEM images of the microrods of the $[Cu-(TAA)_2]Cl_2$ complex precipitated from the initial solution containing $[CuCl_2] = 0.033$ M and $[TAA] = 0.066$ M in 0.04 M HAc solution before heating up.

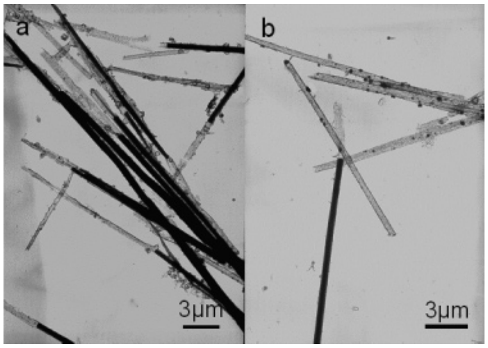

Figure 4. TEM images of the products prepared with $[CuCl_2] = 0.033$ M and $[TAA] = 0.066$ M in 0.04 M HAc solution at 80 °C for different reaction times: (a) 2 h and (b) 4 h, respectively.

at room temperature. X-ray fluorescence (XRF) was performed on XRF-1800 X-ray fluorescence spectrometer at room temperature. Thermogravimetric analysis (TGA) was carried out on a TGA-50 thermal analyzer (Shimadzu Corporation) with a heating rate of 10 °C min^{-1} in flowing N_2.

The XRD pattern confirmed that all the diffraction peaks can be indexed as the corresponding hexagonal CuS phase with the calculated cell parameters $a = 3.75$ Å and $c = 16.58$ Å, which is in good agreement with the literature values (JCPDS no. 78-2121; Figure 1). A series of samples were also synthesized under different reaction conditions (Supporting Information, Figure S1). TEM images of the samples show that the particles are microtubes with an average width of 800 nm and length of 16 μm (Figure 2a,b). A magnified TEM image of a typical microtube (Figure 2c) clearly showed that these microtubes are constructed by nanoflakes with an average size of 130 nm. The fraction of the microtubes is about 80%, and the remnant consists of individual nanoflakes. The observed electron diffraction pattern taken on a single tube (inset in Figure 2c) shows a polycrystalline nature with a lattice spacing of 0.304 and 0.173 nm, corresponding to the (102) and (114) planes of the hexagonal CuS phase, respectively.

To understand the formation mechanism of such CuS microtubes, the detailed growth process of the microtubes was carefully followed by time-dependent experiments. Before heating up, the initial white precipitate from the solution is composed of microrods with a diameter of about 700 nm and the length of about 30∼50 μm as shown in Figure 3. This microrod-like precursor formed at room temperature should be a complex from the strong coordination interaction between Cu^{2+} and TAA. The XRF spectra of this precursor reveal that the complex contains Cu, S, N, and C. The quantitive analysis indicated that the molar ratio of Cu, S, and N is about 1:1.7:2.1. (Supporting Information, Figure S2). In fact, there are lone pair electrons on nitrogen and sulfur atoms of each TAA, which provides the possibility that TAA can combine with the Cu^{2+} ions to form a $Cu^{2+}-$TAA complex as in the case of the transition metal ions M^{2+} (M = Cu, Cd, Zn, Ni, etc.).[13,14] It can be inferred that the complex possibly has a composition of $[Cu-(TAA)_2]Cl_2$. The thermal stability of the complex was examined by TGA. The result showed that the complex will decompose at 160 °C and gives a weight loss of about 56.1 wt %, which is lower than the calculated value 66.3 wt % for $[Cu-(TAA)_2]Cl_2$ (Supporting Information, Figure S3). The reason for this difference is still not clear, and the detailed structural characterization needs to be done in the future.

The FTIR spectrum of the proposed $[Cu-(TAA)_2]Cl_2$ complex is similar to that of pure TAA, but there are two changes presented (Supporting Information, Figure S4): (i) the stretching vibration of C═S is weakened, and the stretching vibration of C—N is remarkably widened and weakened; (ii) the vibration peaks of C═S and N—H shift to lower wavenumbers. Because the electronegativity of nitrogen and sulfur atoms on the TAA molecule is weakened via the partial donation of the lone pair electrons to the vacant *d* orbital of the Cu^{2+} ions, which results in decreasing in the vibration constant and the bonding energy of the N—H and C═S, it is reasonable that vibrations of the N—H and C═S shift to lower wavenumbers.[15] The CuS phase formation in the present system happened at 80 °C, which is much lower than the thermal decomposition temperature for the complex,

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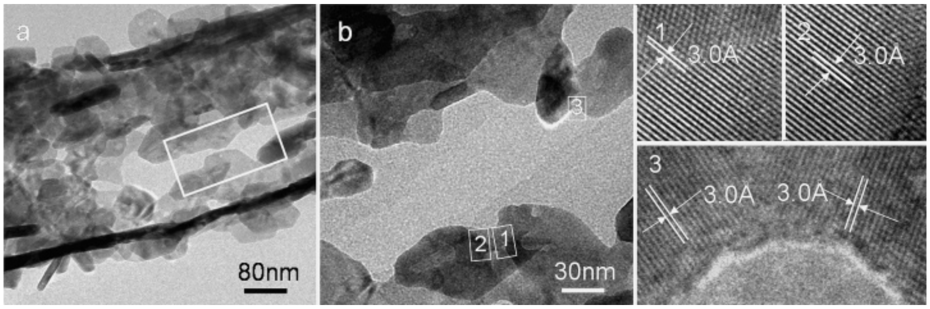

Figure 5. HRTEM images of the intermediate product prepared at 80 °C for 4 h. [$CuCl_2$] = 0.033 M, [TAA] = 0.066 M, [HAc] = 0.04 M, and pH 1.45 solution after reaction. (a) A typical intermediate tube and (b) a magnified image from the marked area in part a. Note: images 1−3 are the HRTEM images taken in the areas marked in part b.

implying that the formation of CuS in the present reaction system is not through the thermal decomposition route but through the dissociation of the complex and the reaction of Cu^{2+} ions with S^{2-} anions.

The evolution process of such microtubes from the precursor microrods at elevated temperature was presented in Figure 4. After 2 h, the nanoflakes begin to form and tend to aggregate on the backbone of the precursor microrods. With the reaction prolonged for 4 h, more microtubes formed gradually and longer microtubes appear (Figure 4b). To understand the formation process of the microrods, the intermediate product of the samples was examined by the HRTEM. The selected area HRTEM images (Figure 5) taken on the backbone of a typical microtube demonstrated that perfect parallel fringes with a spacing of 3.0 Å corresponding to that for (102) planes are observed. However, the (102) lattice fringes observed in the selected areas of joint parts of two flakes can take both the perfect orientation and misorientation, suggesting that the nanoflakes both aggregated by so-called oriented attachment[16,17] and randomly branched aggregation. At the growth temperature, there was a thermodynamic driving force for aggregated growth because the surface energy is reduced substantially when the interface is eliminated.[18,19]

In the present systems, the acetic acid played a key role in the formation of the unusual CuS microtubes. It is known that acetic acid is a rather weak electrolyte with a low degree of dissociation, so here HAc is a good buffer, which can keep a stable pH range in this reaction system. The suitable pH value could effectively control the dissociation speed of the [$Cu-(TAA)_2$]Cl_2 complex and the hydrolysis rate of TAA to release S^{2-} in the initial reaction stage and, thus, kinetically control the growth rate of CuS nanoflakes and their assembly into microtubes. In addition, different carboxylic acids such as formic acid and butyric acid were also tested. Similar microtubes can even be synthesized by addition of formic acid and butyric acid (Supporting Information, Figure S5). In contrast, rod-shaped CuS crystals consisting of spheres were the predominant product if there was no acetic acid present in the solution (Supporting Information, Figure S6).

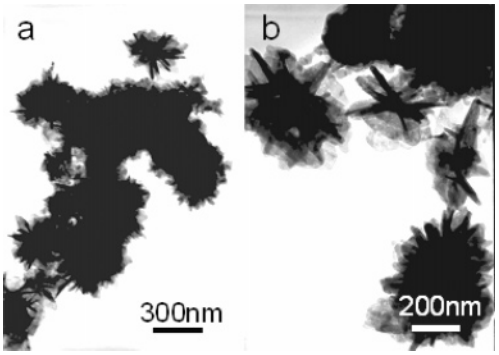

Figure 6. TEM images of nanosphere-like CuS obtained at 80 °C in the 0.02 M HAc solution.

The concentration of HAc also influences the morphology of the CuS crystals significantly. It was found that well-defined microtube-like CuS particles can be obtained at a suitable concentration of HAc between 0.04 and 0.1 M, and too high of a HAc concentration was not favorable for the formation of microtubes (Supporting Information, Figure S7). With a suitable concentration of HAc (0.04 M), the fraction of the microtubes can reach up to about 85%. When the HAc concentration was decreased to 0.02 M, the product was a mixture of spherical aggregates constructed by nanoflakes and individual nanoflakes, and no microtube-like CuS particles formed (Figure 6).

In addition, the molar ratio of [TAA]/[$CuCl_2$] also showed a significant effect on the shape of CuS particles even in the presence of acetate acid. The results suggested that the molar ratio [TAA]/[$CuCl_2$] = 2:1 is suitable for the formation of microtube-like CuS particles (Figure 7a). If the ratio increased to 3:1, the fraction of the microtubes is estimated to be only about 50% and the remnant particles are individual nanoflakes (Figure 7b). If the ratio was increased up to 4:1, the microtubes cannot form and most particles are discrete nanoflakes (Figure 7c).

On the basis of the above analysis, the formation process of the CuS microtubes in the presence of HAc can be proposed as the following: At the beginning, the [$Cu-(TAA)_2$]Cl_2 complex microrods formed, then the CuS nucleated on those microrods at the cost of them by continuing dissolution, accompanying their preferential growth into hexagonal flakes. During the growth process of hexagonal CuS nanoflakes, these hexagonal particles tend to self-assemble and aggregate under the present special solution

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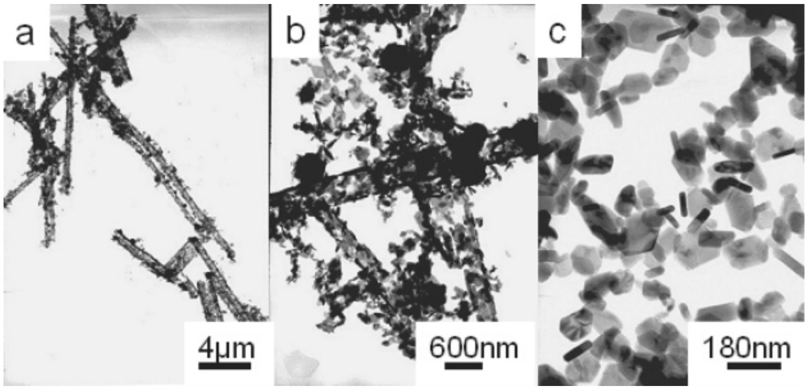

Figure 7. TEM images of the products prepared at 80 °C in 0.04 M HAc solution employing various ratios of [TAA]/[$CuCl_2$] = (a) 2:1, (b) 3:1, and (c) 4:1.

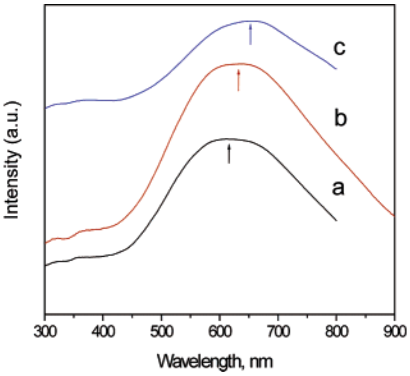

Figure 8. UV−vis absorption spectra of the copper sulfide samples obtained at 80 °C: (a) nanoflake-like CuS particles, (b) spherical-like CuS particles, and (c) microtube-like CuS particles.

environment, resulting in the formation of microtubes with hollow interiors in the final stage. The formation of CuS is based on the reactions among $CuCl_2$, TAA, HAc, and H_2O, which could be described as follows:

$$CuCl_2 + 2TAA \xrightarrow{298K} [Cu-(TAA)_2]Cl_2 \quad (1)$$

$$[Cu-(TAA)_2]Cl_2 \Leftrightarrow Cu^{2+} + 2TAA + 2Cl^- \quad (2)$$

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COO^- + NH_4^+ + H_2S\uparrow \quad (3)$$

$$[Cu-(TAA)_2]Cl_2 + 2H_2O \xrightarrow{HAc,353K} CuS + 2HCl + CH_3COONH_4 \quad (4)$$

UV−vis spectroscopy was used to characterize the optical properties of the obtained samples. Figure 8a shows that there is a wide absorption peak centered at about 617 nm for the discrete CuS nanoflakes. However, the UV−vis absorption spectra of the copper sulfide spheres and microtubes reveal that the absorption edge red-shifts toward long wavelengths at about 633 and 654 nm, respectively. It indicates clearly that there is a slight red shift compared with the results in the literature.[20] It is possible that the red shift of the absorption maximum may be associated with the formation of aggregated spheres and microtube-like structures made of individual nanoflakes in the present experimental system as reported previously for the aggregated noble metal particles.[21]

In summary, a simple acetic acid-assisted hydrothermal process can selectively synthesize CuS microtubes, CuS spheres, and discrete hexagonal CuS nanoflakes. The formation process of complex microtube-like structures suggested that one-dimensional microrods of the initial precursor [Cu−(TAA)$_2$]Cl_2 complex acted as a sacrificial template for the self-aggregation and oriented growth of CuS nanoflakes on its backbone. The presence of acetic acid, its concentration, and an appropriate molar ratio of [TAA]/[$CuCl_2$] played crucial roles for the formation of the unusual CuS microtubes. This one-pot solution approach represents an example for the construction of complex microstructures based on a self-assembly mechanism through a mild solution approach, which also could be further extended as a facile and promising synthetic route to access other inorganic nanomaterials with interesting and complex form.

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Supporting Information Available: XRD patterns of hexagonal phase CuS, XRF pattern of the [Cu−(TAA)$_2$]Cl_2 complex and the quantitive results, TGA curve of the [Cu−(TAA)$_2$]Cl_2 complex, FTIR spectrum of pure TAA, FTIR spectrum of the [Cu−(TAA)$_2$]Cl_2 complex obtained in CH_3CSNH_2 solution, TEM images of the products prepared with different acids, SEM images of the product prepared without addition of HAc, TEM image of the rod prepared without addition of HAc, and TEM images of the products prepared with addition of different concentrations of HAc (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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