

A Simple Route to Synthesize $M\text{InS}_2$ ($M = \text{Cu}, \text{Ag}$) Nanorods from Single-Molecule Precursors

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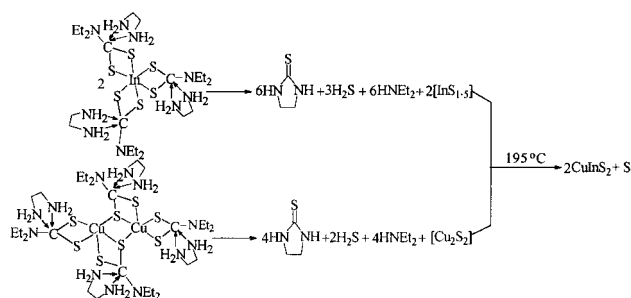
CuInS_2 and AgInS_2 semiconductor nanorods are prepared readily from a stoichiometric mixture of $\text{In}(\text{S}_2\text{CNET}_2)_3$ and $\text{Cu}(\text{S}_2\text{CNET}_2)_2$ or $\text{Ag}(\text{S}_2\text{CNET}_2)$, by remove of the thione groups with ethylenediamine at 195 °C in a solvothermal process.

In the past few years, the synthesis and physical characterization of nanoscale semiconductor crystallites have attracted considerable attention due to their special properties and brilliant application prospects.¹ One-dimensional (1D) nanostructures such as nanotubes and nanorods as building blocks for many novel functional materials are currently the focus of this interest.² Compared with micrometer-diameter 1D structure, they are expected to have remarkable mechanical properties, including electrical, optical, and magnetic properties that are in principle tunable by varying the diameter and chirality.³ The control of nucleation and growth 1D nanostructural material is becoming critical. Although morphological control has recently been demonstrated,⁴ synthetic control of nanocrystalline shape remains a daunting task and is a new challenge to scientists

I-III-VI₂ chalcopyrite structure compounds such as CuInS_2 and AgInS_2 are an interesting class of materials with promise in photovoltaic and optoelectronic applications and have been extensively investigated.⁵ Crystallite compounds of this type can be made in a variety of ways, the most straightforward of which is the combination of the elements at elevated temperature (800–1000 °C).⁶ Such elemental reactions can also be promoted by microwave irradiation.⁷ The traditional homogeneous precipitation method to prepare this type of ternary chalcogenides requires post-annealing at high temperature (~800 °C) to obtain crystalline products.⁸ Recent efforts to develop new methods for chalcopyrites have been focused on the pyrolysis of single-sources organometallic precursors, which was proved to be an effective and convenient technique to generate target products at low temperature.⁹

Dithio- and diselenocarbamate complexes were attractive molecular precursors for the preparation of metal sulfides and selenides, based on which a number of binary metal chalcogenides such as ME ($M = \text{Zn}, \text{Cd}, \text{Pb}, \text{Ga}$ and In ; $E = \text{S}, \text{Se}$), Ga_2S_3 and In_2E_3 have been fabricated.¹⁰ However, reports on metal dichalogenocarbamates for ternary or multielement chalcogenides are rare and only one case involving the preparation of crystalline particles CuInSe_2 from a mixture of $\text{In}(\text{Se}_2\text{CNMenHex})_3$ and $\text{Cu}(\text{Se}_2\text{CNMenHex})_2$, by metal-organic chemical vapor deposition at 450 to 470 °C, is available.¹¹ We are interested in developing novel route to nanoscale chalcogenides¹² and have previously reported the use of cadmium diethylthiocarbamate to prepare quantum-confined CdS nanowires in refluxing ethylenediamine (en).¹³ In this letter, we report on the mixture of $\text{In}(\text{S}_2\text{CNET}_2)_3$ and $\text{Cu}(\text{S}_2\text{CNET}_2)_2$ or $\text{Ag}(\text{S}_2\text{CNET}_2)$ for CuInS_2 and AgInS_2 nanorods through a solvothermal process using en as solvent at 195 °C for 12 h.

The synthetic reaction was carried out in an autoclave and can be represented by Scheme I, with copper complex as an example. In this process, nucleophilic attack by en at the thione carbon atoms of metal diethylthiocarbamates¹⁴ generates inorganic cores $[\text{InS}_{1.5}]$ and $[\text{Cu}_2\text{S}_2]$, and then they combine stoichiometrically with each other producing CuInS_2 grains, which may preferentially grow along a unique direction in en resulting in a 1D structure.



Scheme 1

In a typical procedure, a stoichiometric mixture of $\text{In}(\text{S}_2\text{CNET}_2)_3$ and $\text{Cu}(\text{S}_2\text{CNET}_2)_2$ or $\text{Ag}(\text{S}_2\text{CNET}_2)$, isolated readily from an aqueous solution of metal ions and sodium diethylthiocarbamates, was put into an autoclave of 50 mL capacity that was filled with ethylenediamine up to 80% of the total volume. The autoclave was maintained at 190 °C for 8 h and then cooled to room temperature. The precipitates were collected after being washed with dilute HNO_3 solution, absolute ethanol and distilled water in sequence.

The powder X-ray diffraction (XRD) of as-grown CuInS_2 nanorods depicted in Figure 1(a) revealed that all reflections could be indexed to the pure tetrahedral copper indium disulfide with cell constants $a = 5.512 \text{ \AA}$ and $c = 11.026 \text{ \AA}$, close to literature value in the JCPDS card (27-159). While the XRD pattern shown in Figure 1(b) of AgInS_2 nanorods revealed that this sample is the coexistence of two phases: tetragonal and orthorhombic. The reflections marked with "T" can be indexed to a tetrahedral phase with cell constants $a = 5.884 \text{ \AA}$ and $c = 11.2147 \text{ \AA}$, and other small reflections marked with "O" can be indexed to an orthorhombic phase, with cell constants $a = 6.990 \text{ \AA}$, $b = 8.319 \text{ \AA}$ and $c = 6.706 \text{ \AA}$. Two sets of the cell parameters agree well with the data in JCPDS cards (25-1330 and 25-1328). Further evidence for the formation of CuInS_2 and AgInS_2 can be derived from the X-ray photoelectron spectra (XPS). Three strong peaks for CuInS_2 sample at 444.0, 931.5, and 161.3 eV correspond to $\text{In}(3d)$, $\text{Cu}(2d)$, and $\text{S}(2s)$ binding energy, respectively, and three strong peaks for AgInS_2 sample at 444.0, 367.5, and 161.1 eV correspond to $\text{In}(3d)$, $\text{Ag}(3d)$, and $\text{S}(2s)$ binding energy, respectively. Quantification of the peaks give $\text{Cu}:\text{In}:\text{S}$ molar ratio of 1:1.12:2.23 and $\text{Ag}:\text{In}:\text{S}$ molar ratio of 1:0.92:1.94.

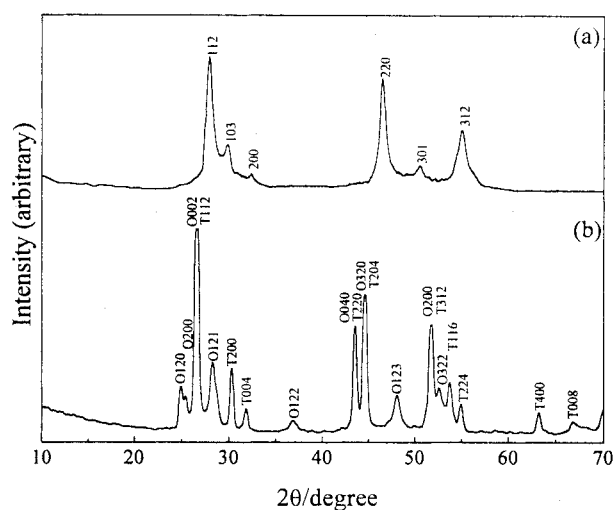


Figure 1. XRD patterns of CuInS_2 (a) and AgInS_2 (b) nanorods.

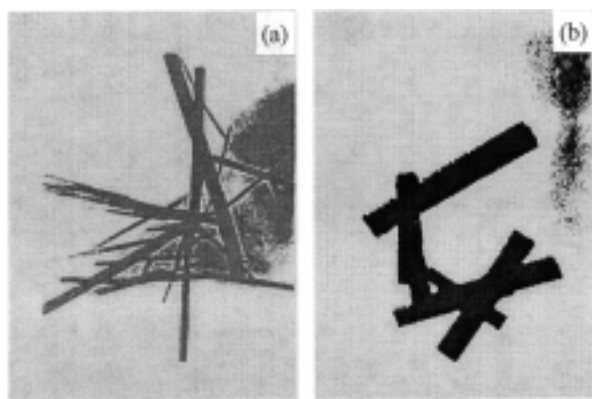


Figure 2. TEM images of CuInS_2 (a) and AgInS_2 (b) nanorods

The morphologies and sizes of as-prepared CuInS_2 and AgInS_2 nanorods were studied by transmission electron microscopy (TEM). Figure 2(a) shows a typical area of the as-prepared CuInS_2 nanorods. It clearly shows that the diameters vary from 3 to 20 nm and the length from 80 to 450 nm. For the AgInS_2 nanorods shown in Figure 2(b), the diameters range from 20 to 50 nm, while the lengths range from 140 to 300 nm.

It was a key factor that en was selected as the solvent in the growth of MInS_2 nanorods. En, a bidentate solvent, was chosen because of its strong *N*-chelation ability and basicity. It can be used as nucleophiles to attack and cut off the thione groups of metal diethyldithiocarbamates, generating the intermediates $[\text{InS}_{1.5}]$ and $[\text{Cu}_2\text{S}_2]$ (Scheme I), which then interacted with each other in 2:1 molar ratio yielding CuInS_2 grains. In this process, en may have ordered the $[\text{InS}_{1.5}]$ and $[\text{Cu}_2\text{S}_2]$ cores forcing the CuInS_2 grains to grow in one dimension, and therefore may have controlled the nucleation of CuInS_2 grains finally resulting in a nanorod. It is noteworthy that the resulting organic product in Scheme 1 has been well characterized in organic chemistry.¹⁵ This mechanism is somewhat similar to the nanowire growth mechanism of VLS (vapor-liquid-solid).¹⁶ Other nucleophiles such as pyridine and diethylamine, both of which have weaker *N*-chelation properties but form no chelate structure as en does, were

also tested to remove the thione carbon groups, however, non-rod like products were obtained. The purity of the product was low and the CuInS_2 particles were spherical. Using benzene as the solvent, which has no *N*-chelation or base properties, no CuInS_2 peaks appeared in the XRD pattern of the product. Similar observations were made for preparing AgInS_2 . These results further supported the possible growth mechanism of MInS_2 nanorods.

Optimum conditions for preparing the nanorods were at 180–220 °C for 10–15 h in the autoclave. Lower temperatures or shorter times led to incomplete reaction with decreased yield and crystallinity. High temperature was beneficial to the product's crystallinity and crystal growth, but the product was contaminated by carbonization of the ligand and solvent. Further prolongation of the time will lead to larger size of the products. In summary, a novel strategy of utilizing nucleophilic attack to cut off the undesired parts of single-molecular precursors has been successfully developed for the synthesis of CuInS_2 and AgInS_2 nanorods at low temperature. This method can be easily controlled and is expected to be applicable to fabricate other ternary chalcogenides and even quaternary chalcogenides.

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