General synthesis of I–III–VI_2 ternary semiconductor nanocrystals

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Metastable orthorhombic phase of $AgInS_2$ nanocrystals with various shapes, including particles, rods, and worms, have been obtained to demonstrate a facile and effective one-pot chemical route for the synthesis of high quality I–III–VI_2 ternary semiconductor nanocrystals ($AgInS_2$, $CuInS_2$, $AgInSe_2$) with controllable shape and size.

In recent years, the controllable synthesis of nanostructural materials has remained of great interest due to their unique chemical and physical properties, which are different from those of their bulk counterparts, and potential applications in various areas.[1–4] I–III–VI_2-type chalcogenides, as ternary semiconductors which offer alternatives for appropriate band-gap energies, have been the focus of much recent research because of their excellent optical and electrical properties and important applications in linear and nonlinear optical devices and photovoltaic solar cells.[5–10] For example, $AgInS_2$ with a tetragonal or orthorhombic ordered phase is a direct semiconductor displaying a twofold optical structure close to the fundamental edge and thus has promising applications in photovoltaic and optoelectronic fields.[11,12] Chalcopyrite semiconductor $CuInS_2$ has also attracted much attention as an ideal candidate for use in thin-film solar cells owing to its high absorption coefficient and optimal band gap energy of 1.45 eV, which is well matched to the solar spectrum.[13,14] $AgInSe_2$, a semiconductor with a band gap of 1.19 eV, is one of the most useful materials for NIR application as well as for the preparation of Schottky diodes and solar cells.[15,16]

There have been many methods for the synthesis of I–III–VI_2 ternary compounds, such as molecular beam deposition, chemical vapor deposition, hydrothermal or solvothermal technique, single-source precursor route, *etc.*[17–23] In the past decades, $CuInS_2$ and $AgInSe_2$ nanocrystals with various morphologies, including nanoparticles, nanorods, nanowires and nanotubes, have been successfully synthesized.[24–29] In 2006, Shapiro and co-workers reported the production of ultrafine $CuInS_2$ nanoparticles with ~2 nm diameter from the photolytic decomposition of a molecular single source precursor.[28] Orthorhombic $AgInSe_2$ nanorods were also obtained at 185 °C in mixed thiol and amine solution by the Vittal group.[29] However, the synthesis of good quality $AgInS_2$ nanocrystals with desired shape and size has seldom been achieved. Only recently, monodisperse $AgInS_2$ nanoparticles were successfully obtained by direct thermal decomposition of the single-source precursor $[(Ph_3P)_2Ag(\mu\text{-}SC\{O\}PhS)_2In(SC\{O\}Ph)_2]$ in a bisurfactant system.[30] In 2007, the same group synthesized polyhedral shaped $AgInS_2$ nanocrystals from dual-source precursors.[31] Monodisperse rectangular $AgInS_2$ nanocrystals were also prepared through a convenient and improved solvothermal process that uses hexadecylamine as a capping reagent by Qian and co-workers.[32] Therefore, developing a facile, general and inexpensive method to prepare ternary semiconductors with controlled shape and size still remains a great challenge, which is of interest and importance for their further applications.

Herein, a simple wet chemical route was presented to synthesize the I–III–VI_2 nanocrystalline compounds. Using $AgNO_3$, $In(NO_3)_3$ and sulfur powder as the reactants and octadecylamine as the solvent, we have obtained $AgInS_2$ nanocrystals. Their morphologies, including particles, rods and worms, can be controlled by adjusting the reaction conditions. If we use CuCl or Se instead of $AgNO_3$ or S, respectively, we can also obtain $CuInS_2$ or $AgInSe_2$ nanocrystals. This type of one-pot synthesis strategy offers us an effective route for the general preparation of ternary semiconductor nanocrystals.

In a typical synthesis of $AgInS_2$ nanorods, analytical grade $AgNO_3$ (0.04 g), $In(NO_3)_3$ (0.1 g) and sulfur powder (0.05 g) were put into a warm solvent of octadecylamine (10 ml) at 120 °C. After 10 min of magnetic stirring, they were maintained at this temperature for further growth and crystallization. Then, excess ethanol was added to wash the dark red solid collected at the bottom of the beaker. Finally, we can disperse the as-obtained products in a non-polar solvent, such as cyclohexane. Similarly, $AgInS_2$ nanoparticles were prepared under the same conditions, except that the dosage of sulfur powder was only 0.01 g. We can also obtain worm-like $AgInS_2$ nanocrystals if the growth and crystallization temperature was maintained at 200 °C.

The composition and crystal phase of the as-synthesized products were examined by powder X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of $AgInS_2$ nanocrystals with different morphologies, from which we can see that the three samples present similar profiles and all the diffraction peaks can be assigned to the orthorhombic-phase $AgInS_2$ (JCPDS 25-1328; a = 7.001 Å, b = 8.278 Å, c = 6.698 Å). No characteristic peaks of other impurities such Ag_2S or In_2S_3 were observed. As we all know, the orthorhombic $AgInS_2$ is a high-temperature phase which is stable above 620 °C, while the low-temperature phase, tetragonal $AgInS_2$ is stable below 620 °C.[11,33] However, in our present work, we have obtained the metastable orthorhombic $AgInS_2$ nanocrystals at even 120 °C. The reason might be that the solvent octadecylamine has changed the chemical growth environment, leading to the phase reversion temporarily.

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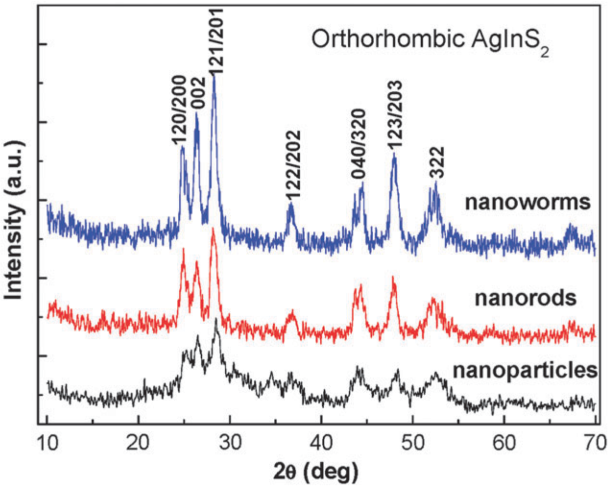

Fig. 1 XRD patterns of $AgInS_2$ nanocrystals.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were used to study the shape and size of $AgInS_2$ nanocrystals. Fig. 2A shows the TEM image of $AgInS_2$ nanoparticles which exhibit irregular shape and have an average size of 10 nm. From their HRTEM image (Fig. 2B), it can be seen that these nanoparticles are well crystallized. The inset of Fig. 2B reveals clear lattice fringes with an interplanar distance of about 0.356 nm which is a characteristic fringe spacing of the orthorhombic $AgInS_2$ crystal phase in the (120) plane. The representative TEM image of $AgInS_2$ nanorods is shown in Fig. 2C. The diameter of these rods is about 10 nm and the length is in the range of 60 to 100 nm. Their corresponding HRTEM image in Fig. 2D indicates that the as-obtained rods are in a single-crystalline structure. The lattice space (Fig. 2D, inset) is also 0.356 nm. Fig. 2E displays the overview image of worm-like $AgInS_2$ nanocrystals with an average diameter of 10 nm and a length of 20 to 60 nm. A typical individual $AgInS_2$ nanoworm is shown in Fig. 2F. The clear lattice fringes reveal that the worms are nanosized single crystals and the measured spacing of the lattice planes (Fig. 2F, inset) is the same as that of $AgInS_2$ nanoparticles and nanorods.

Based on the above experimental results, we can summarize the relationship between the reaction conditions and the shape and size of final products with a schematic diagram (Fig. 3) and analyze the nucleation and growth process of $AgInS_2$ nanocrystals briefly as follows. Generally, there are two critical factors responsible for the shape determination of the nanocrystals. One is the nucleation process and the other is the subsequent growth stage.[34] In the nucleation process, the crystalline phase of the seeds is very important for directing the intrinsic shapes of nanocrystals and is highly dependent on the environment. In our system, the high-temperature phase, orthorhombic $AgInS_2$ is formed owing to the chemical environment of the solvent octadecylamine. In the growth stage, the delicate control of growth conditions can govern the final architecture of the nanocrystals. Particle-, rod- and worm-shaped $AgInS_2$ nanocrystals can be obtained through the change of the growth temperature or the concentration of sulfur powder. Their same diameters (about 10 nm) and lattice spaces (0.356 nm) indicate that the rods and worms are results of oriented growth of anisotropic particles in different conditions. On the other hand, according to the theory proposed by Peng's group,[35,36] the high monomer concentration is in favor of the growth of elongated nanocrystals. In the present system, as the concentration of sulfur powder increases, an environment with a higher chemical potential will be created to accelerate the oriented growth, leading to the formation of 1D nanorods. Additionally, at higher temperature, the system will have sufficient thermal energy. The nuclei move so fast that it is hard to go along straight direction for the anisotropic growth. Thus worm-shaped nanocrystals will form. Certainly, the oriented attachment mechanism could also be responsible

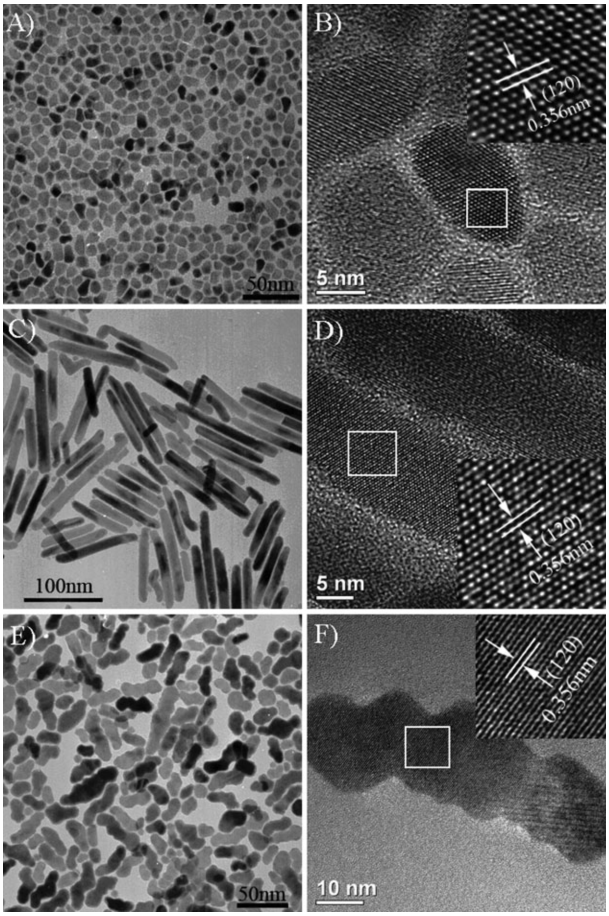

Fig. 2 TEM and HRTEM images of $AgInS_2$ nanocrystals: (A) and (B) $AgInS_2$ nanoparticles; (C) and (D) $AgInS_2$ nanorods; (E) and (F) $AgInS_2$ nanoworms.

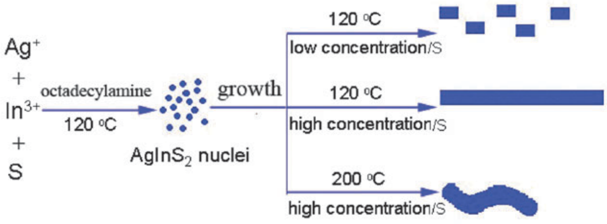

Fig. 3 Schematic diagram of the nucleation and growth process of $AgInS_2$ nanocrystals.

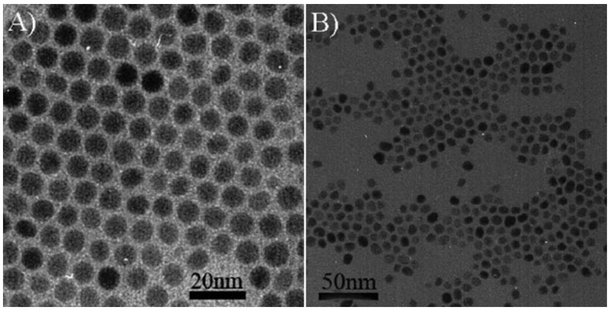

Fig. 4 TEM images of (A) $CuInS_2$ and (B) $AgInSe_2$ nanocrystals.

for different shape formation.[37] Although there is no direct TEM proof that this is happening in the case of 1D $AgInS_2$ synthesis, we can deduce from the results that $AgInS_2$ nanorods and nanoworms are obtained by oriented attachment of collections of nanocrystals that attach and fuse along identical crystal faces, forming oriented chains.

In the above system, other solvents, such as oleylamine, can also be used for the synthesis of $AgInS_2$ nanocrystals. However, octadecylamine is most suitable for 1D $AgInS_2$ formation. Moreover, it is much cheaper than oleylamine. On the other hand, when we used CuCl instead of $AgNO_3$, uniform $CuInS_2$ nanocrystals with diameter of about 7 nm could be synthesized (Fig. 4A); when selenium powder was used instead of sulfur powder, we could obtain $AgInSe_2$ nanoparticles with an average diameter of 6 nm (Fig. 4B). From Fig. 4, it can be seen that $CuInS_2$ nanocrystals show isotropic sphere-morphology with narrower size distribution and can assemble to hexagonal packed arrays on the carbon-covered-copper TEM micro grid, while $AgInSe_2$ nanoparticles are irregular and have a wider size distribution. We can also deduce that $AgInSe_2$ nanoparticles have the trend of oriented growth due to their anisotropic shape. Actually, $AgInSe_2$ nanorods can also be synthesized by changing the experimental parameters. However, for $CuInS_2$, only particle-shaped nanocrystals can be obtained in this system. This is further evidence that the shape of nanocrystals is mainly determined by their inherent crystal structure, that is, the nucleation process under special chemical environment.

In summary, we have developed facile one-pot synthesis to prepare I–III–VI_2 ternary semiconductors. High quality $AgInS_2$ 1D-nanocrystals (nanorods and nanoworms) have been successfully obtained for the first time. $CuInS_2$ and $AgInSe_2$ nanocrystals can also been synthesized through a similar approach. The nucleation and growth process of nanocrystals has been discussed on the basis of experimental data. This method can be readily employed to prepare other ternary chalcogenides. Because the majority of one-pot synthetic efforts are directed to binary semiconductors only, this work would give some elicitations to the controllable synthesis of ternary semiconductor nanocystals.

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