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Growth and Transformation Mechanism of Ternary CuAgSe Dendrites from Binary Ag_2Se Dendrites

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For the first time, ternary CuAgSe dendrites on a Ag foil substrate have been synthesized at room temperature by inheriting the dendritic structures of Ag_2Se nanocrystals, and Cu nanoparticles and Se powders were used to feed the growth in aqueous ammonia solution. The new nano approach for the fabrication of CuAgSe dendrites can be regarded as a successful chemical alternative to the recently developed technique for electrochemical atomic layer epitaxy deposition for chalcogenides. The transformation process and mechanism from the binary Ag_2Se phase to the ternary CuAgSe phase are discussed along with analysis their of thermodynamic, kinetic, and crystallographic properties.

Introduction

In current nanomaterial studies, researchers have recognized that crystalline semiconductors with different morphologies exhibit different physical and chemical properties even if their chemical compositions are the same.[1,2] In some examples in electrochemical devices, 2D or 3D nanostructures or nanowebs are more attractive than 1D nanorods or nanowires because they can transport holes or electrons more effectively through interconnected networks in the 2D and 3D scaffolds.[3] Nanodendrites are such network materials and their 3D dendritic nanostructures can provide both electrical links and a high surface/volume ratio. To date, some binary metal chalcogenide dendrites have been synthesized. For example, well defined hierarchical cadmium sulfide nanodendrites have been synthesized by hydrothermal treatment with $CdCl_2$ and thiourea as reagents and poly(ethyleneglycol) as a capping agent.[4] Recently, copper sulfide dendrites have been prepared in high yields by a concentration-controlled reaction of ethylenediamine and tributylphosphite.[5] We have previously demonstrated an in situ reaction strategy for the fabrication of both Ag_2Se and $Cu_{2-x}Se$ dendrites.[6,7] Despite the considerable fabrication of binary metal chalcogenides with dendritic structures, to the best of our knowledge, ternary dendrite compounds have not been reported to date.

CuAgSe, an important ternary selenide, has some similar properties and applications to silver and copper selenides. For example, CuAgSe is a superionic conductor due to the mobility of both the Cu^+ and Ag^+ ions, and can be used in electrochemical devices.[8–10] However, unlike most of the silver and copper selenides, CuAgSe is rarely studied due to the difficulty of its synthesis. The synthesis of ternary chalcogenides, including CuAgSe, from an aqueous solution of the component elements by hydrazine reduction has been proven by Kulify.[11] CuAgSe can be thermochemically prepared by heating a mixture of Ag, Cu, and Se to over 1000 K, with several heating and cooling processes.[12,13] The present interest in the synthesis of CuAgSe has been provoked by the report that a CuAgSe polycrystalline membrane has been commercialized for Cu^{2+} ion-selective electrodes with a lifetime as long as ten years.[14] Recently, CuAgSe films have been electrochemically synthesized by a technique for electrochemical atomic layer epitaxy deposition for chalcogenides[15,16] first proposed by Stickney.[17]

In this paper, we report the design of a new nano approach to grow ternary CuAgSe dendrites at room temperature by inheriting the initial dendritic structures of Ag_2Se reagents, and Cu nanoparticles and Se powders are used to feed the growth in aqueous ammonia solution. The reaction design adopts the electrochemical behavior studied by Neshkova et al.[15] that the ternary CuAgSe phase appears at potentials close to or coincident with those that lead to the deposition of binary compounds, Ag_2Se and Cu_2Se. Thus, it is believed that both Ag_2Se and Cu_2Se are prerequisites for CuAgSe growth at room temperature. The design further adopts the behavior of Cu_2Se formation when elemental Se and Cu are in contact.[18] The two design concepts led to our new nano approach using Cu nanoparticles and Se powders for the growth of dendritic CuAgSe nanocrystals by inheriting the initial dendritic structures of the Ag_2Se reagents. In this work, the dendritic Ag_2Se reagents were prepared on Ag foil substrate (Ag_2Se/Ag) so that the as synthesized CuAgSe dendrites on Ag foil substrate (CuAgSe/Ag) can be easily separated from the unreacted Cu nanoparticles and Se powders. The resulting CuAgSe den-

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drites display highly symmetric corolitic morphology, similar to that of the initial Ag_2Se template reagents. This paper describes the transformation process and mechanism from dendritic Ag_2Se nanocrystals to crystalline CuAgSe dendrites. The new nano approach for the fabrication of CuAgSe can be regarded as a successful chemical alternative to the electrochemical atomic layer epitaxy deposition technique for chalcogenides, and could be applied to the fabrication of other ternary semiconductors with specific, desirable morphology.

Results and Discussion

The Synthesis and Characterization of CuAgSe Dendrites

Ternary CuAgSe dendrites on a Ag foil substrate (CuAgSe/Ag) were fabricated by inheriting the dendritic structure of Ag_2Se nanocrystals on a Ag foil substrate (Ag_2Se/Ag). The reaction design adopts the electrochemical behavior of the admixture of Cu_2Se and Ag_2Se that immediately transforms structurally into the ternary CuAgSe phase at room temperature.[15] In our experiment, the dendritic Ag_2Se/Ag was first immersed in a Se powder suspension in water to adsorb Se powders on the surface of Ag_2Se dendrites (Se–Ag_2Se/Ag). In the second step, the Se–Ag_2Se/Ag foil was immersed in a freshly prepared Cu nanoparticle suspension in an aqueous ammonia solution. In the two stage process, the residual Se powders on the surface of the Ag_2Se dendrites were treated with the freshly prepared Cu nanoparticles to form residual Cu_2Se on the surface of the Ag_2Se dendrites (Cu_2Se–Ag_2Se/Ag). As growth proceeds, the dendritic Ag_2Se reagents reacted with the residual Cu_2Se to form CuAgSe dendrites at room temperature. It is worth noting that the Ag substrate in the dendritic Ag_2Se/Ag reagent is a necessary element to separate the products from the suspension of Se powder and Cu nanoparticles in the two stage process.

Figure 1 shows the SEM morphologies of the dendritic Ag_2Se reagents and the as obtained CuAgSe dendrites. As shown in Figure 1 (a), the Ag_2Se dendrites display highly symmetrical, hierarchical, corolitic morphology with a branch diameter of about 700 nm. After the conversion process, the CuAgSe products keep the well defined dendritic morphology, in which the dimensions, including diameter and thickness, are similar to those of the initial Ag_2Se template reagents (Figure 1, b).

XRD patterns of the dendritic Ag_2Se/Ag reagents and the dendritic CuAgSe/Ag product are shown in Figure 2. Figure 2 (a) shows the representative diffraction pattern of dendritic Ag_2Se/Ag, indicating that the Ag_2Se dendrite is in the orthorhombic Ag_2Se phase with cell constants of a = 4.333 Å, b = 7.062 Å, c = 7.764 Å, and Z = 4 (JCPDS card, no. 24-1041), which we have discussed previously.[6] Figure 2 (b) shows the XRD pattern of dendritic CuAgSe/Ag. The diffraction peaks at 2θ = 28.30, 30.99, 34.20, 36.18, 42.46, 43.20, 44.18, 44.51, 48.80, 51.99, 53.60, 58.30, and 63.32° can be indexed to the (002), (110), (111), (012), (112), (003), (200), (020), (103), (211), (113), (212), and (203) planes of orthorhombic CuAgSe, and the cell constants are calculated to be a = 4.112 Å, b = 4.082 Å, c = 6.322 Å, and Z = 2, which agree well with literature data (JCPDS card, no. 25-1180). In these XRD patterns, the diffraction peaks labeled with ♣ originate from the Ag substrate (JCPDS card, no. 87-720) as the dendrites are all present on a Ag foil substrate.

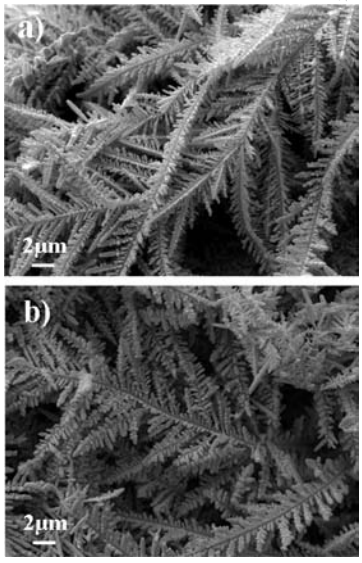


Figure 1. SEM morphologies of (a) dendritic Ag_2Se reagents; (b) as prepared CuAgSe dendrites.

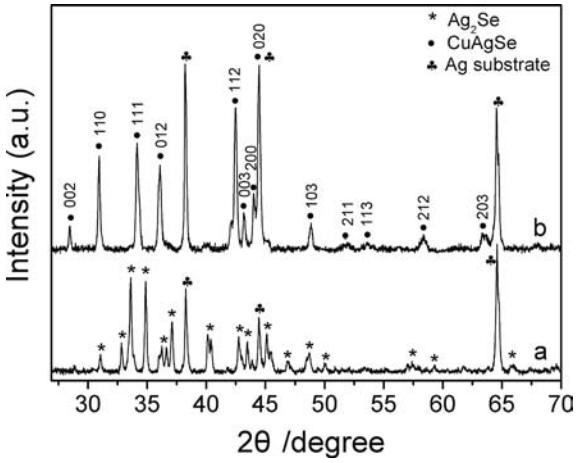


Figure 2. XRD patterns of (a) dendritic Ag_2Se reagents; (b) as prepared CuAgSe dendrites. All samples were present on the Ag foil substrate.

The as obtained CuAgSe dendrites were further studied by TEM. A representative TEM image of an individual dendrite branch is shown in Figure 3 (a). In this image, the diameter of the dendrite branch is about 700 nm. The selected-area electron diffraction (SAED) pattern shown in Figure 3 (b) shows the crystallinity of the dendrite branch and further confirms the nature of the single crystal. The SAED pattern can be indexed to the diffraction spots of orthorhombic CuAgSe. The stoichiometry of CuAgSe dendrite is 1.02:0.99:1.00 for the ratio of Cu:Ag:Se from energy

dispersive X-ray spectroscopy (EDX) data recorded from the boxed area in Figure 3 (a). We did not observed any other crystal phases of CuAgSe with TEM or XRD, indicating that the orthorhombic CuAgSe phase is the most common crystal phase at room temperature.

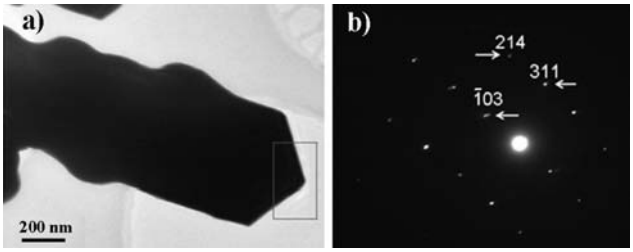


Figure 3. Representative TEM image of (a) an individual dendrite branch of CuAgSe dendrites and (b) the corresponding SAED pattern recorded from the boxed area in (a).

Transformation Process from Binary Ag_2Se Dendrites to the Target CuAgSe Dendrites

Zhang and coworkers have proven that Cu nanoparticles and Se powders with a Cu:Se molar ratio of 1:>2.5 can react to form binary Cu_2Se nanoparticles in aqueous ammonia solution at room temperature.[18] A detailed electrochemical study of CuAgSe electrodeposition by Neshkova revealed that the admixture of Cu_2Se and Ag_2Se can immediately transform structurally into the ternary CuAgSe phase obeying a 1:1:1 molar ratio at room temperature.[15] Therefore, the transformation process from the Ag_2Se phase to the CuAgSe phase can start with the following reaction; see Equations (1) and (2).

$$2Cu + Se \rightarrow Cu_2Se \quad (1)$$

$$Ag_2Se + Cu_2Se \rightarrow 2CuAgSe \quad (2)$$

In our experiments, a trace amount of Se powder and an excess of Cu nanoparticles were used to ensure the formation of the pure Cu_2Se phase on the surface of the dendritic Ag_2Se reagents. Consequently, the binary Ag_2Se phase transformed structurally into the target CuAgSe ternary phase by reacting with the pristine Cu_2Se.

The powder XRD patterns in Figure 4 demonstrate the transformation process from the Ag_2Se phase to the CuAgSe phase. Initially, only the orthorhombic Ag_2Se reagents contribute to the patterns, except for some diffraction peaks originating from the Ag substrate (Figure 4, a). After repeating the two stage process three times, a mixture of the orthorhombic Ag_2Se reagents and the orthorhombic CuAgSe products is formed (Figure 4, b). Repeating the two stage process six times leads to the domination of CuAgSe over Ag_2Se (Figure 4, c). After repeating the two stage process ten times, only diffraction peaks of the orthorhombic CuAgSe phase were observed, except for the diffraction peaks of the Ag substrate (Figure 4, d), which indicates the total transformation of the orthorhombic Ag_2Se phase into the orthorhombic CuAgSe phase. On the whole, no unreacted Cu_2Se phase was observed in these XRD patterns. In fact, the unreacted Cu_2Se phase was found in the final Cu nanoparticle suspension, and proved to be the monoclinic Cu_2Se phase with cell constants a = 14.087 Å, b = 20.481 Å, c = 4.145 Å, β = 90.38°, and Z = 24 (Figure 5).

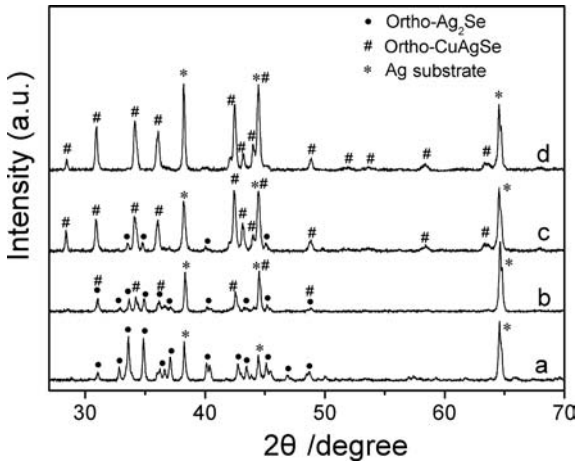


Figure 4. XRD patterns of (a) dendritic Ag_2Se reagents; the reaction mixture obtained from the two stage process repeated (b) three times and (c) six times; (d) the as prepared CuAgSe dendrites obtained from the two stage process repeated ten times. All the samples are present on the Ag foil substrate.

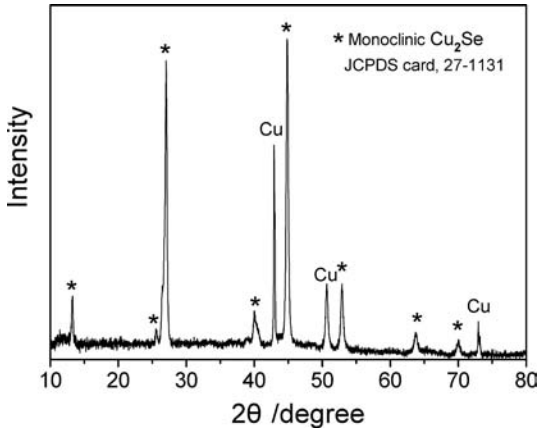


Figure 5. XRD patterns of the monoclinic phase of Cu_2Se obtained from the final Cu nanoparticle suspension.

In order to explore the factors affecting the growth of dendritic CuAgSe nanocrystals, several control experiments at different concentrations of Se powders were performed and revealed a few interesting morphology changes as shown in Figure 6. Typically, the well defined dendritic CuAgSe nanocrystals were prepared by the two stage process repeated ten times with a Se concentration of 100 mg L^{-1}. When the Se concentration was increased to 200 mg L^{-1}, the pure CuAgSe dendrites were obtained by the two stage process repeated six times, however, a few CuAgSe agglomerates occurred (Figure 6, a). Further increasing the Se concentration to 500 or 700 mg L^{-1}, repeating the two stage process three or four times led to pure CuAgSe products with rough dendritic branches (Figure 6, b and c). If the Se concentration was increased to 1.0 g L^{-1}, repeating the two

stage process twice led to pure CuAgSe products in which the dendritic morphology was destroyed (Figure 6, d). From these results, it can be concluded that the rate of formation of the Cu_2Se precursor plays an important role on the fabrication of the CuAgSe dendrites, which can be explained as follows: with a low Se concentration, which is a key factor in inheriting the initial dendritic structures, the dendritic Ag_2Se/Se reagents obtained in first step have little residual Se that would be transformed into Cu_2Se in the second step. Therefore, the rate of growth of the CuAgSe is limited due to the small amount of Cu_2Se used to feed the growth. With the appropriate Se concentration and treatment with the two stage process, well defined dendritic CuAgSe crystals were obtained (see Figure 1, b).

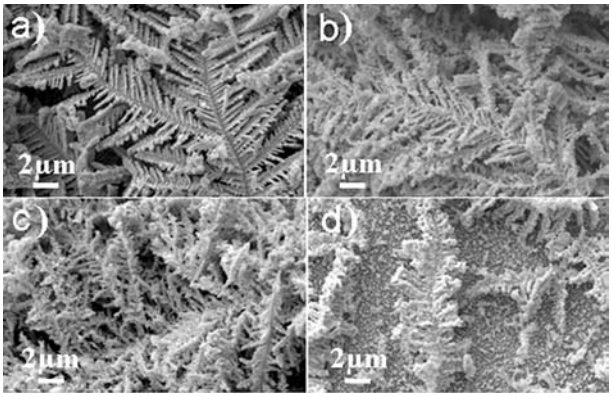


Figure 6. SEM morphologies of the as obtained CuAgSe products of (a) the two stage process repeated six times at a Se concentration of 200 mg L^{-1}; (b) the two stage process repeated four times at a Se concentration of 500 mg L^{-1}; (c) the two stage process repeated three times at a Se concentration of 700 mg L^{-1}; (d) the two stage process repeated twice at a Se concentration of 1.0 g L^{-1}.

Transformation Mechanism from the Ag_2Se Phase to the CuAgSe Phase

To probe into the formation mechanism from the Ag_2Se phase to the CuAgSe phase, several control experiments were designed and performed in the same solvent system at room temperature by selecting different reaction precursors.

As above, the orthorhombic CuAgSe phase was prepared by reacting Ag_2Se/Se composite with fresh Cu nanoparticles. Conversely, the orthorhombic CuAgSe phase was also obtained by reacting the Cu_2Se/Se composite with fresh Ag nanoparticles. However, no CuAgSe phase was produced if the pure orthorhombic Ag_2Se was used to react with fresh Cu nanoparticles or Cu^{2+} ions (such as $CuSO_4$). This suggests that Ag^+ ions in Ag_2Se phase cannot be replaced by elemental Cu or Cu^{2+} ions. Moreover, when the orthorhombic Ag_2Se phase was mixed with a hexagonal CuSe phase or a tetragonal Cu_3Se_2[18] no reaction occurred. Interestingly, if the pure orthorhombic Ag_2Se reacted with Cu^+ ions (such as CuCl) in the aqueous ammonia solution, pure orthorhombic $Cu_{0.5}Ag_{1.5}Se$ was obtained (Figure 7), which indicates that Ag^+ ions in the Ag_2Se phase can be partially replaced only by Cu^+ ions at room temperature. Significantly, when the orthorhombic Ag_2Se was used to react with the monoclinic Cu_2Se in aqueous ammonia solution, the orthorhombic CuAgSe phase was produced. This result supports the electrochemical behavior described by Neshkova[15] and indicates that both the monoclinic Cu_2Se phase and orthorhombic Ag_2Se phase can be adopted for the growth of the orthorhombic CuAgSe phase.

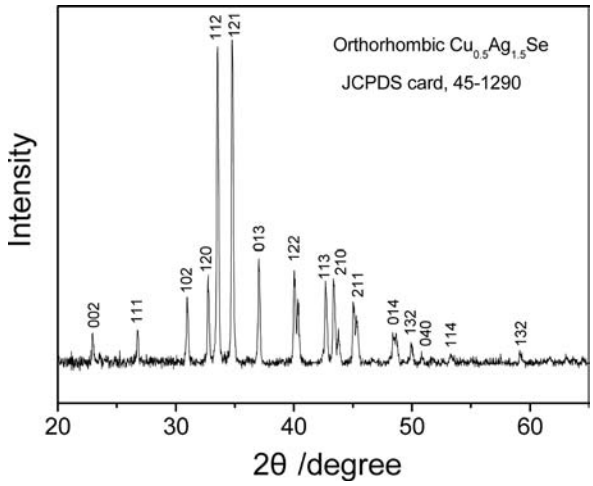
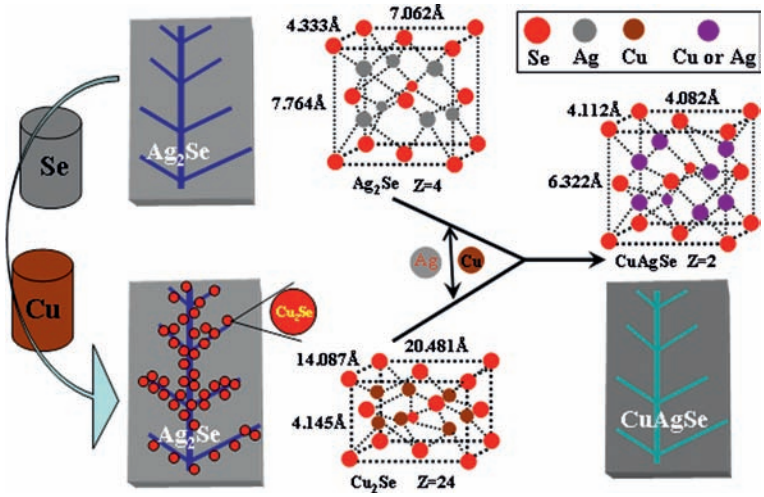


Figure 7. XRD pattern of the pure orthorhombic $Cu_{0.5}Ag_{1.5}Se$ obtained by reacting Ag_2Se with CuCl in aqueous ammonia solution.

From a structural perspective, it is worth noting that ternary CuAgSe can be represented formally as 1/2[Ag_2Se]·1/2[Cu_2Se]. Hence, formation of the CuAgSe phase is believed to relate to the assimilation between the monoclinic Cu_2Se phase and the orthorhombic Ag_2Se phase. Crystallographically, the crystal systems of the reactants (Ag_2Se and Cu_2Se) and the product (CuAgSe) are all alike, namely, an orthorhombic phase for Ag_2Se and CuAgSe and a monoclinic phase for Cu_2Se with only β = 90.38° near to 90°, which is beneficial for the structural translation from the Ag_2Se/Cu_2Se phases to the CuAgSe phase. In fact, the structural translation from the Ag_2Se/Cu_2Se phases to the CuAgSe phase is only related to the slight variation at the bond angle and bond lengths of Cu–Se and Ag–Se. Thermodynamically, the structural translation process from the Ag_2Se/Cu_2Se phases to the CuAgSe phase can take place spontaneously according to the calculated $\Delta G_{(298)}$ (–35.5 kJ mol^{-1}), which is calculated as follows: consulting the literature,[15,19] the Gibbs free energies $G_{(298)}$ for Ag_2Se, Cu_2Se, and CuAgSe are –49.4, –73.4, and –96.9 kJ mol^{-1}, respectively. Therefore, the free energy changes for the formation of CuAgSe are calculated to be $\Delta G_{(298)}$ = –35.5 kJ mol^{-1}, according to the equation 0.5Ag_2Se + 0.5Cu_2Se → CuAgSe.

We speculate that assimilation between the Cu_2Se phase and the Ag_2Se phase may be due to ion exchange between the Cu^+ and Ag^+ ions. It is well known that Ag_2Se, Cu_2Se, and CuAgSe are superionic conductors with a high mobility of Cu^+/Ag^+ ions. Kinetically, cation exchange between Ag_2Se and Cu_2Se can easily take place due to the high mobility of Cu^+ and Ag^+ ions. The control experiment for the formation of $Cu_{0.5}Ag_{1.5}Se$ provides some support



Scheme 1. The formation mechanism of the Ag_2Se phase to the CuAgSe phase. The unit cells with cell constants are placed beside the corresponding products.

for the cation exchange mechanism. On the basis of the experimental results and speculations, the formation mechanism from the Ag_2Se phase to the CuAgSe phase is illustrated in Scheme 1.

Conclusions

In this paper, we demonstrate a new nano approach for the fabrication of ternary CuAgSe nanodendrites from dendritic Ag_2Se nanocrystals assisted by copper nanoparticles and selenium powder. The resulting CuAgSe dendrites display highly symmetric, corolitic morphology, which is similar to that of the initial Ag_2Se reagent, including diameter and thickness. We found that the monoclinic Cu_2Se could react with the orthorhombic Ag_2Se to form orthorhombic CuAgSe in ammonia solution at room temperature. These new findings can be regarded as a successful chemical alternative of the electrochemical atomic layer epitaxy deposition technique for preparing chalcogenides. It was found that low Se concentration is a key factor for inheriting the initial dendritic structure of Ag_2Se nanocrystals. This work demonstrates the availability of in situ template conversion routes in the field of duplicating nanostructures, especially for some particular morphologies. It is worth noting that the nanosized CuAgSe particles were also obtained in ammonia solution without any substrate using the new nano approach. We advocate the new nano approach as a practical method for the synthesis of CuAgSe nanoparticles, especially those with particular morphologies.

Experimental Section

General: All the reagents are of analytical grade and were used in experiments without further purification. Ag_2Se dendrites on a Ag foil substrate (Ag_2Se/Ag) were prepared as we described previously.[6] Typically, the synthesis of CuAgSe dendrites on a Ag foil substrate (CuAgSe/Ag) was performed at room temperature as follows: in the first step, the dendritic Ag_2Se/Ag (2×0.3 cm, Ag_2Se thickness 0.05 mm) was immersed in a Se powder suspension in water (Se concentration: 100 mg L^{-1}) for 5–10 min to adsorb the Se powders on the surface of the Ag_2Se dendrites (Se–Ag_2Se/Ag). In the second step, the Se–Ag_2Se/Ag foil was immersed for 10–15 min in a suspension of Cu nanoparticles (0.1 mol L^{-1}, 50 mL) in aqueous ammonia solution that had been freshly prepared as reported.[18] In this process, the residual Se powders on the surface of the Ag_2Se dendrites were treated with freshly prepared Cu nanoparticles to form residual Cu_2Se on the surface of the Ag_2Se dendrites (Cu_2Se–Ag_2Se/Ag). As the growth proceeds, the freshly prepared Cu_2Se was treated with dendritic Ag_2Se reagents to form CuAgSe dendrites (CuAgSe/Ag). The two stage process was repeated several times to deplete the Ag_2Se reagents. Finally, the CuAgSe dendrites on the Ag foil substrate (CuAgSe/Ag) were obtained by washing the product several times with water.

X-ray diffraction (XRD) patterns were recorded with a Philips MPD 18801 diffractometer using Cu-K_α radiation (λ = 1.54178 Å). Scanning electron micrographs were taken using a JSM-5600 scanning electron microscope. TEM images and SAED patterns were obtained with a JEOL JEM 2100 high-resolution transmission electron microscope operated at 200 kV equipped with an Oxford INCA EDX, which was used to collect EDX data.

Acknowledgments

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