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One-Pot Synthesis of Copper−Indium Sulfide Nanocrystal Heterostructures with Acorn, Bottle, and Larva Shapes

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Nanocrystalline materials have attracted a great deal of attention from researchers in various fields for both their fundamental size-dependent properties and their many important technological applications.[1] Among the various nanocrystals, transition metal chalcogenide nanocrystals have been investigated for many applications, including biological labeling, light emitting diodes, and photovoltaic devices.[2] Over the past several years, several groups reported the synthesis of many metal sulfide nanocrystals using various synthetic routes, including thermolysis of single-source precursors, solvent-less thermolysis of metal−thiolate precursors, and thermal decomposition of metal−surfactant complexes.[3] There are several reports on the fabrication of heterostructured nanocrystals in the last two years.[4] Banin and co-workers fabricated a gold nanoparticle attached on CdSe nanorods and tetrapods.[4a,b] Teranish and co-workers synthesized CoPd sulfide nanoacorns.[4c] Dumbbell-like Au−Fe_3O_4 nanoparticles were synthesized by Sun and co-workers.[4d] Heterostructures of semiconductor and magnetic nanocrystals, including CdS−FePt,[4e] CdSe−Co,[4f] and γ-Fe_2O_3−metal sulfides,[4g] were also fabricated. Recently, our group reported ultra-large-scale synthesis of uniform-sized nanocrystals of various transition metal oxides from the thermal decomposition of metal−oleate complexes.[5] As a continuation of the development of the designed synthesis of uniform-sized and -shaped nanocrystals, herein we report on the synthesis of copper−indium sulfide heterostructured nanocrystals with acorn, bottle, and larva shapes from the thermolysis of a mixture composed of Cu−oleate and In−oleate complexes in alkanethiol.

The metal−oleate complexes were prepared by the reaction of metal chlorides and sodium oleate.[5] In a typical synthesis, 0.1 g (0.16 mmol) of Cu−oleate complex and 0.2 g (0.21 mmol) of In−oleate complex were dissolved in a mixture containing 5 mL of oleylamine (OA, 15.2 mmol) and 5 mL of dodecanethiol ($C_{12}H_{25}$-SH, 20.9 mmol) at room temperature and heated to 230−250 °C under argon flow and kept at this temperature for 10 min to 1 h. The solution gradually changed to a deep brown colloidal solution. The solution was then cooled to room temperature, and excess ethanol was added to yield a deep brown precipitate, which was separated by centrifugation. The resulting precipitate was easily dispersible in nonpolar solvents, such as hexane or toluene.

The shape of Cu−In sulfide nanocrystals could be varied by changing the reaction temperature and time (Figure 1). Figure 1a shows a low-magnification TEM image of acorn-shaped nanocrystals (nanoacorns) with dimensions of 30 nm (thickness in the border) × 48 nm (length) synthesized at 230 °C for 10 min. The high-resolution TEM (HRTEM) image of a nanoacorn showed that the dark region is copper-rich with a (102) interplanar distance of 0.240 nm, and the bright region is indium-rich with a (109) interplanar distance of 0.325 nm. The fast Fourier transform (FFT) pattern of the border region (inset of Figure 1b) showed both a (102) lattice plane from Cu_2S and a (109) lattice plane from In_2S_3.

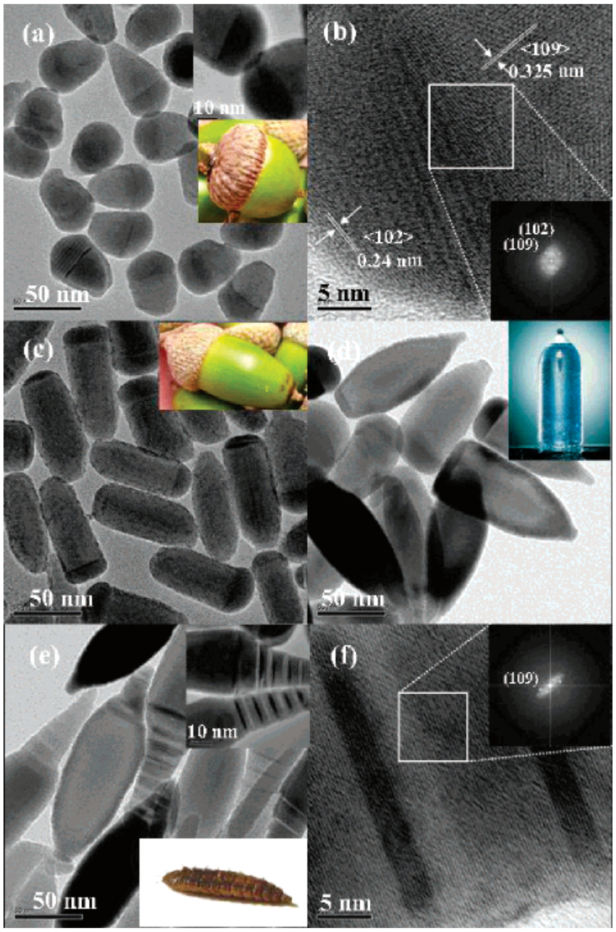

Figure 1. (a) TEM image of short nanoacorns (inset, enlarged image). (b) HRTEM image of short nanoacorns (inset, FFT). (c) TEM image of long nanoacorns. (d) TEM image of nanobottles. (e) TEM image of nanolarvas. (f) HRTEM image (inset, FFT) of nanolarvas.

When the reaction time was increased to 1 h and the temperature kept at 230 °C, elongated nanoacorns with dimensions of 30 nm × 82 nm were produced (Figure 1c). When the reaction was performed at the higher temperature of 250 °C at 10 min, bottle-shaped nanocrystals (nanobottles) with dimensions of 40 nm × 110 nm were generated (Figure 1d). When the reaction was performed at the longer time of 1 h at 250 °C, the *Fannia canicularis* larva-shaped nanocrystals (nanolarvas) of 45 nm × 185 nm were produced (Figure 1e). The HRTEM image (Figure 1f) of a nanolarva showed that the nanolarvas are highly crystalline, and the (109) lattice plane of In_2S_3 was clearly observed in the FFT pattern (inset).

The X-ray diffraction (XRD) patterns of Cu−In sulfide nanostructures with shapes of acorn (blue curve), bottle (red curve), and larva (black curve), shown in Figure 2, were nearly identical,

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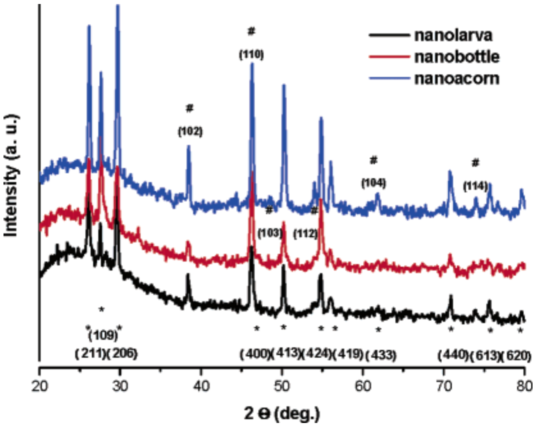

Figure 2. XRD patterns of nanoacorns (blue), nanobottles (red), and nanolarvas (black curve). Asterisks (∗) and number signs (#) indicate the peaks from In_2S_3 (JCPDS * 73-1366) and Cu2S (JCPDS # 84-0206), respectively.

and they revealed that the nanocrystals are composed of hexagonal chalcocite-structured Cu_2S and tetragonal-structured In_2S_3, rather than the formation of the solid solution of copper sulfide and indium sulfide. The elemental analysis results showed that the compositions of the short nanoacorns and nanolarvas were $CuIn_{1.05}S_{1.65}$ and $CuIn_{1.30}S_{1.24}$, respectively.

The GC−MS spectrum of the byproducts from the thermal decomposition of the Cu−oleate complex in dodecanethiol showed two peaks corresponding to oleic acid and 1-dodecene, demonstrating that the following reaction seems to be responsible for the production of Cu_2S nanocrystals: $C_{12}H_{25}SH + 2\ Cu{-}(OC({=}O)\text{-}C_{17}H_{33} \rightarrow Cu_2S + 2\ C_{17}H_{33}C({=}O)OH + C_{12}H_{24}$. The energy-dispersive X-ray spectroscopic (EDX) results of the nanoacorns showed that Cu_2S was richer in the head part and In_2S_3 was richer in the body of nanoacorns. The EDX results and TEM images collected at the various stages of the thermolysis reaction (see Figures S1 and S2) demonstrated that Cu_2S seeds seemed to generate first, and subsequent growth of indium sulfide (In_2S_3) occurred on these seeds via a so-called seed-mediated growth mechanism, which is similar to the formation of other heterostructured nanocrystals, such as Co−Pd nanoacorns.[4,6] On the other hand, the EDX results of the nanolarvas revealed that the atomic composition was nearly constant all over the nanolarva, demonstrating that the initially formed polydisperse Cu_2S nanoparticles were aggregated via a process similar to the oriented attachment mechanism, and subsequent incorporation of In_2S_3 species generated larva-shaped nanostructures with a constant Cu/In atomic ratio (see Figure S1).

In conclusion, we synthesized Cu−In sulfide heterostructured nanocrystals from the thermal decomposition of a mixture of Cu−oleate and In−oleate complexes in dodecanethiol. By varying the reaction temperature and time, we were able to synthesize Cu−In sulfide nanocrystals with acorn, bottle, and larva shapes. We are working on the generalization of the current synthetic method to synthesize many other heterostructured nanocrystals.

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Supporting Information Available: EDX and TEM of CuIn sulfide nanocrystals. TEM at various stages of the reaction. TEM of CuIn sulfide nanocrystals at 215 °C. TEM of Cu_2S and In_2S_3 nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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