

Supporting Information.

Facile Thermolysis Synthesis of CuInS₂ Nanocrystals with Tunable Anisotropic Shape and Structure

Ningzhong Bao,^{a*} Xinmin Qiu,^a Yu-Hsiang A. Wang,^b Ziyu Zhou,^b Xiaohua Lu,^a Craig A. Grimes,^a and Arunava Gupta^{*b}

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Experimental:

All the chemicals, including absolute ethanol, hexane, oleic acid (OA), oleylamine(OLA), 1-octadecene (90 %)(ODE), elemental sulphur, dodecanethiol (>98 %), sodium oleate (95+ %), CuCl₂(99+ %), and InCl₃•4H₂O(99+ %) were purchased from Fisher Scientific.

The mixed metal (Cu²⁺In³⁺)-oleate complexes were prepared by reaction of sodium oleate and the respective metal chlorides (Cu²⁺ and In³⁺). For the synthesis of Cu²⁺In³⁺(C₁₈H₃₃O₂)₅⁻, 2 mmol CuCl₂, 2 mmol InCl₃•4H₂O, 10 mmol sodium oleate (C₁₈H₃₃NaO₂), 10 ml H₂O, 15 ml ethanol and 30 ml hexane were mixed and refluxed at 60 °C for 4 h. The mixed Cu²⁺In³⁺-oleate complex (CuIn(C₁₈H₃₃O₂)₅) was obtained by separation of the water phase and subsequent evaporation of the residual ethanol and hexane at 70 °C, and water at 110°C.

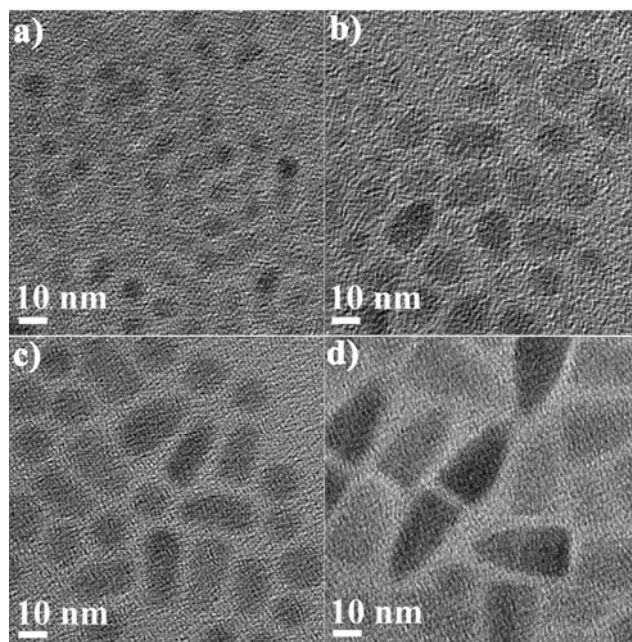
All the reactions involving nanocrystal synthesis were performed in a fume hood, under inert conditions. In a typical synthesis of triangular-pyramid-shaped CIS nanocrystals (nanopyramid), 2 g Cu-In-oleate complexes was dissolved in 2 ml OLA at 150 °C. Separately, 30 ml OLA and 5 ml dodecanethiol were mixed and then heated to 290 °C. 0.4 ml of the Cu-In-oleate complexes dissolved in OLA was rapidly injected under nitrogen atmosphere into the dodecanethiol dissolved in OLA at 290 °C and continually stirred, during which the solution colour rapidly changed from colourless to light green, brown, red, and final black. After aging for a fixed time, the reaction mixture was cooled to room temperature and then transferred to a 50 ml centrifuge tube together with 10 ml mixture of ethanol and hexane with a volume ratio of 1:3. A black precipitate was obtained by centrifugation at 8000 rpm for 15 minutes. The morphology and structure of the products were characterized using transmission electron microscopy (TEM) coupled with high-resolution (HR) (Tecnai F-20). Phase identification and the degree of crystallinity of the products was carried out using powder x-ray diffraction (Bruker D8). The optical absorption spectra were measured using UV–Vis diffuse reflectance spectra (UV-Vis-NIR, Varian Cary 5G). The fluorescence emission spectra were measured using a Cary Eclipse fluorometer (Varian).

Table 1: Influence of primary process variable on the morphology and size of CIS nanocrystals.

CuIn(C ₁₈ H ₃₃ O ₂) ₅	Oleylamine (OLA)	Oleic acid (OA)	1-octadecene (ODE)	Products
2 g	30 ml	0	0	nanopyramids (Fig. 1a)
2 g	20 ml	10 ml	0	nanocones (Fig. 1b)
2 g	20 ml	0 ml	10 ml	short nanobullets (SI2 a-c)
2 g	5 ml	0 ml	25 ml	nanobullets (Fig. 1c)
4 g	10 ml	0 ml	50 ml	ultra-long nanobullets (Fig. 1d)

Formation of nanocones:

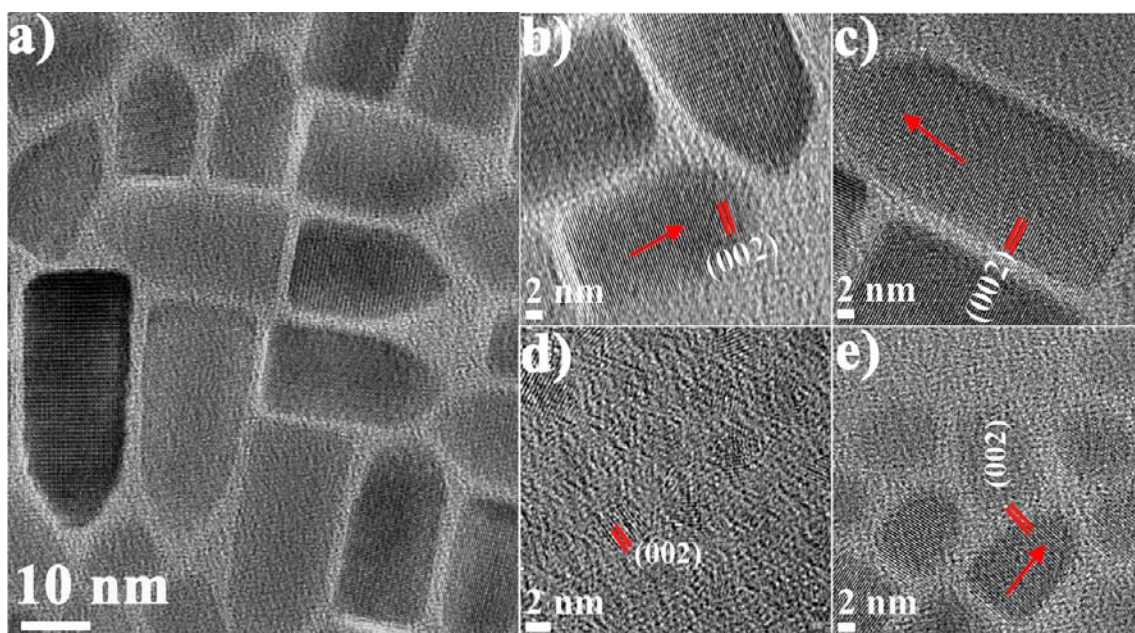
To better understand the formation mechanism of nanocones, we have carried out a detailed TEM study to determine the formation and shape evolution of the nanocrystals as a function of reaction time. For this purpose, a small aliquot of the solution is rapidly withdrawn from the reaction mixture at different aging times during the reaction process for analysis of the solid product. SI1 shows the aging time-dependent shape evolution of the products. Very small monodisperse nuclei, with a uniform size of less than 1 nm, that are not readily observed by TEM, are rapidly formed through homogeneous nucleation immediately following injection of the reactant solution. In less than 10 s, the CIS nuclei grow rapidly to form monodisperse elliptically-shaped nanocrystals with dimensions of about 4.1 nm (average size of major axis) \times 8.6 nm (average size of minor axis) (SI1 a). As the aging time is further prolonged to 30 s, the elliptical nanocrystals continue to grow to form half-ellipse-shaped nanocrystals (one end sharp and the other end flat) with a broad size distribution of the major axis in the range of 4.5-20.6 nm (SI1 b). With further extending the aging time to 1 and 5 min, more and more of the half-ellipse-shaped nanocrystals continue growing to form nanocones with uniform size, but at a reduced growth rate as can be seen by comparing the images in SI1 c and SI1 b. After prolonged aging (25 min), the product transforms almost completely into nanocones with a high yield and uniformly larger size (about 16.4 nm in base diameter and about 30.2 nm in height) (SI1 d). As observed from the products formed at different stages, there is no evidence for the formation of hetero-structured hybrid nanostructures, such as Cu_2S -CIS,^[1,2] during the nucleation and growth of the CIS nanocones.



SI1. TEM images of the intermediate shapes formed at 290 °C after aging for a) 10 s, b) 30 s, c) 1 min, and d) 25 min during the formation of the circular conical CIS nanocrystals in a solvent mixture of OLA and OA.

Size control of the nanobullets:

The size of the nanobullets can be tuned by simply adjusting the ratio of OLA to ODE. Instead of the nanobullets shown in Fig. 1c, shorter nanobullets (SI2a) can be prepared by replacing a smaller amount of OLA (10 ml) with ODE. The nanobullets exhibit an aging-time-dependent anisotropic shape evolution that is similar to that of nanocones (SI1). In less than 10 s, the CIS nuclei grow rapidly to form monodisperse elliptical nanocrystals with sizes of about 3-5 nm (SI2 d). As the aging time is further prolonged to 30 s, the ellipse-shaped nanocrystals continue to grow to form nanobullets with one sharp end (SI2 e). The lattice fringes vertical to the long axis of typical nanocrystals, formed after aging at 290 °C for 10 s, 30 s, and 60 min (SI2 b-d), show spacing distances close to 0.322 nm, corresponding to the (002) planes of the wurtzite structure of CIS. This indicates the preference for [001] growth of anisotropic-shaped CIS, which is also observed for the growth of one dimensional wurtzite nanorods of ZnO³ and CdSe⁴. The formation of one sharp end is likely a result of oriented nucleation of CIS onto one side of the nanobullets, as well as the (001) face terminated with Cu, In cations. Such preferential growth on the cationic (001) face has previously been noted for the growth of tadpole-shaped wurtzite CdSe nanocrystals.⁴ It should be noted that all the intermediates (SI2 b-e) and final product (SI2 a) exhibit consistently uniform and continuous lattice fringes, independent of the growth stage of nanocrystals. This clearly indicates that the structure and composition of the as-grown nanocrystals are homogeneous. This is different from the previously observed segregation of Cu₂S/In₂S₃, or formation of CIS by converting intermediates of Cu₂S-CIS hybrid nanostructures.^{1,2}



SI 2: (a) TEM and (b-e) HRTEM images of the products formed at 290 °C after aging for a-c) 60 min, d) 10 s, and e) 30 s during the formation of shorter CIS nanobullets. The arrows indicate the *c*-axis (001) of the wurtzite structure aligned along the long axis of the crystals.

All the HRTEM results indicate preference for [001] growth of anisotropic-shaped CIS with homogeneous nucleation and growth of single phase materials, and no evidence for the formation of hetero-structured hybrid nanostructures, such as Cu₂S-CIS, during the nucleation and growth of the CIS nanocrystals. The Cu : In : S ratio measured by EDS is 25.49 : 25.21 : 49.3, very close to the stoichiometric ratio of 1 : 1 : 2.

References:

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