Electronic Supplementary Material (ESI) for CrystEngComm.

# Seed-Mediated Phase-Selected Growth of $Cu_2GeS_3$ Hollow Nanoparticles with Huge Cavities

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**Figure S1.** (a) TEM image, (b) XRD pattern, (c) XPS Cu 2p spectrum, and (d) XPS S 2p spectrum of cubic $Cu_{2-x}S$ NPs obtained by the thermal decomposition of 1 mmol of $(Et_2NCS_2)_2Cu$ in OLA at 280 °C under $N_2$ atmosphere. The two peaks in the Cu spectrum at 952.1 eV and 932.2 eV with a peak spitting of 19.9 eV correspond to Cu $2p_{1/2}$ and $2p_{3/2}$ peaks, indicating monovalent copper Cu(I). The two peaks at 162.5 and 161.5 eV with a peak spitting of 1.0 eV in the S spectrum correspond to S $2p_{1/2}$ and $2p_{3/2}$ peaks, which is the characteristic of $S^{2-}$ in multinary sulfides.

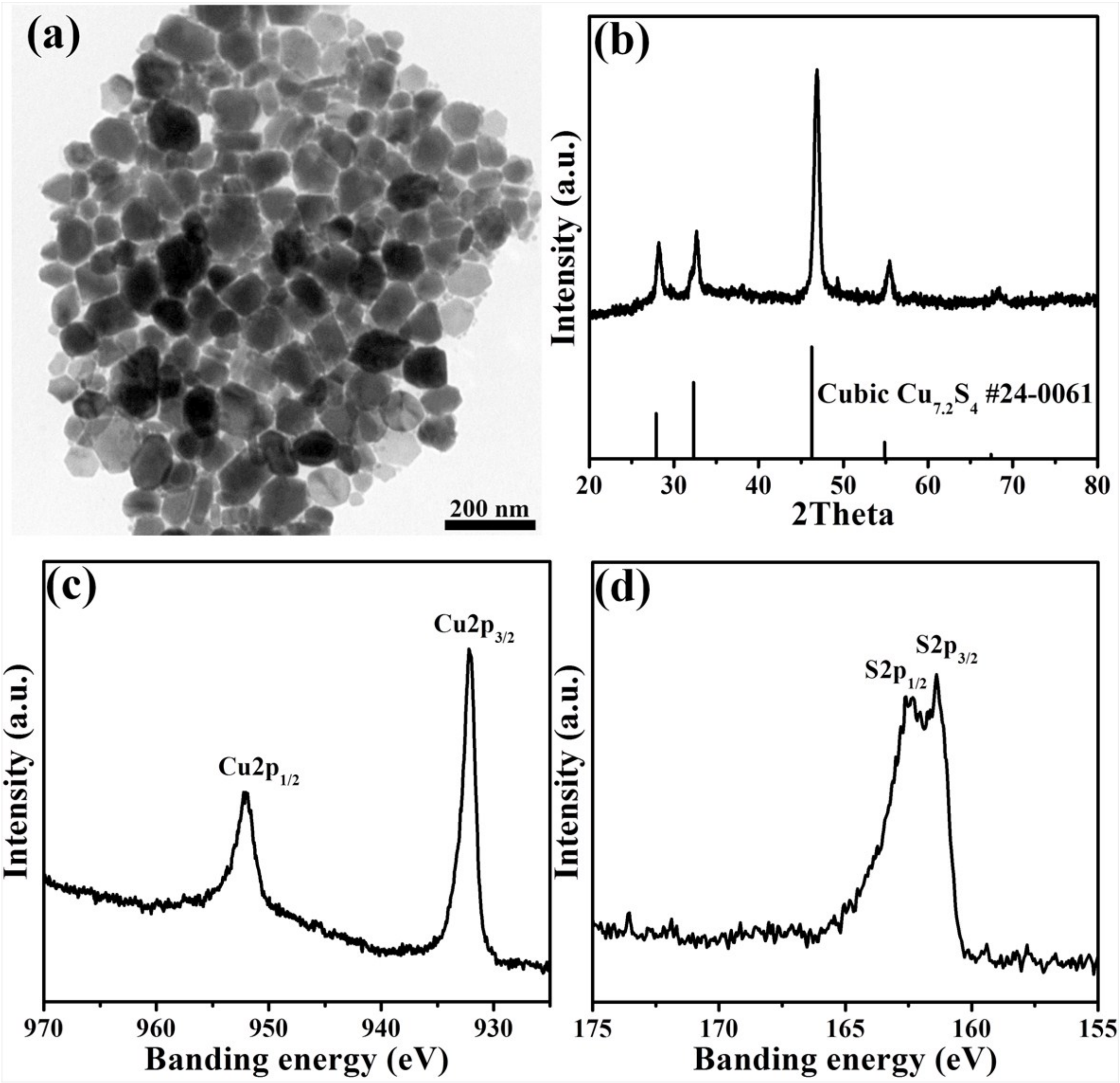


**Figure S2.** TEM image of cubic large $Cu_2GeS_3$ HNPs prepared after the injection of Ge-TGA complex for 1 min.

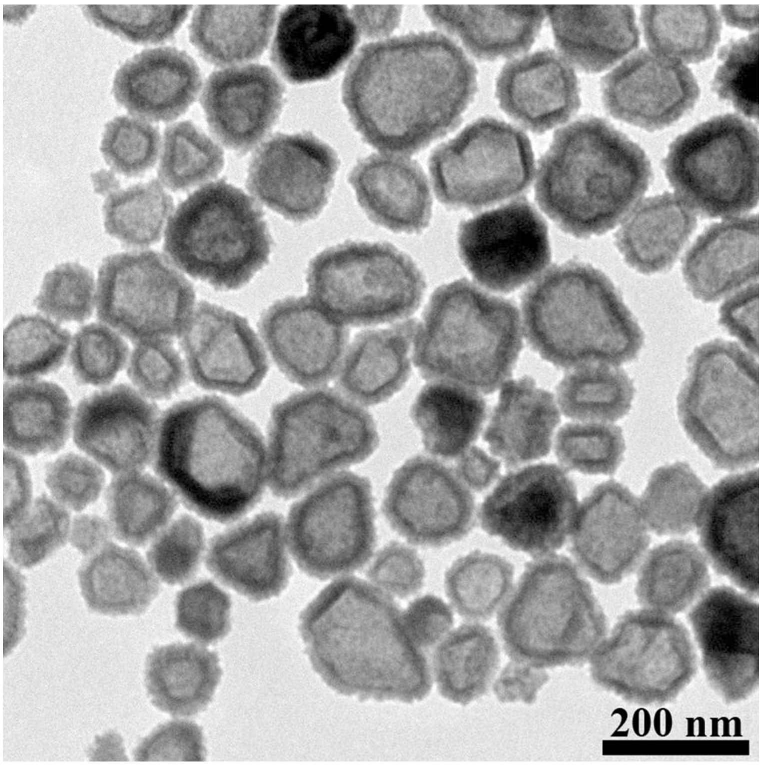


**Figure S3.** XPS (a) Cu 2p, (b) Ge 3d, and (c) S 2p spectrum of large $Cu_2GeS_3$ HNPs.

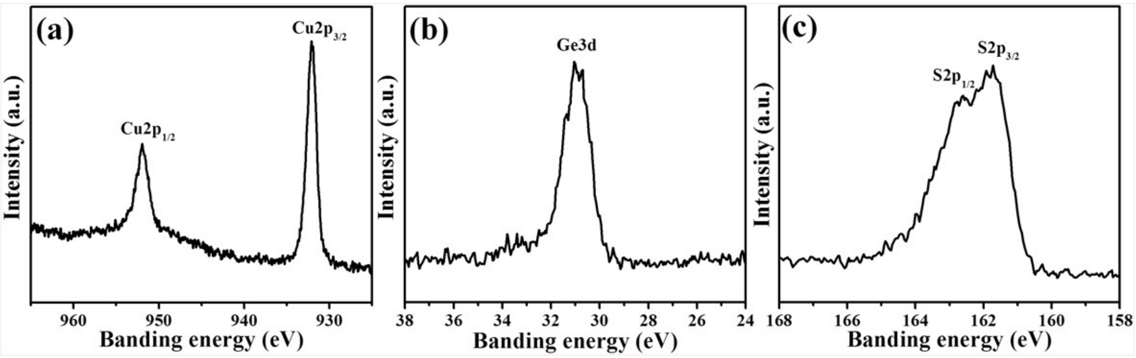


**Figure S4.** (a) TEM image, (b) XRD pattern, (c) XPS Cu 2p spectrum, and XPS (d) S 2p spectrum of monoclinic $Cu_{2-x}S$ NPs obtained by heating the OLA solution containing 0.6 mmol of CuCl and 0.1 ml of TGA to 240 °C. The two peaks in the Cu spectrum at 952.0 eV and 932.2 eV with a peak spitting of 19.8 eV correspond to Cu $2p_{1/2}$ and $2p_{3/2}$ peaks, indicating monovalent copper Cu(I). The two peaks at 162.5 and 161.5 eV with a peak spitting of 1.0 eV in the S spectrum belonging to S $2p_{1/2}$ and $2p_{3/2}$ peaks prove the existence of $S^{2-}$ in multinary sulfides. (e) TEM image and (f) XRD pattern of wurtzite $Cu_2GeS_3$ NPs synthesized by injecting Ge-TGA complex (0.3 mmol) in OLA into the solution of monoclinic $Cu_{2-x}S$ NPs at 240 °C and then rising to 300 °C under $N_2$ atmosphere.

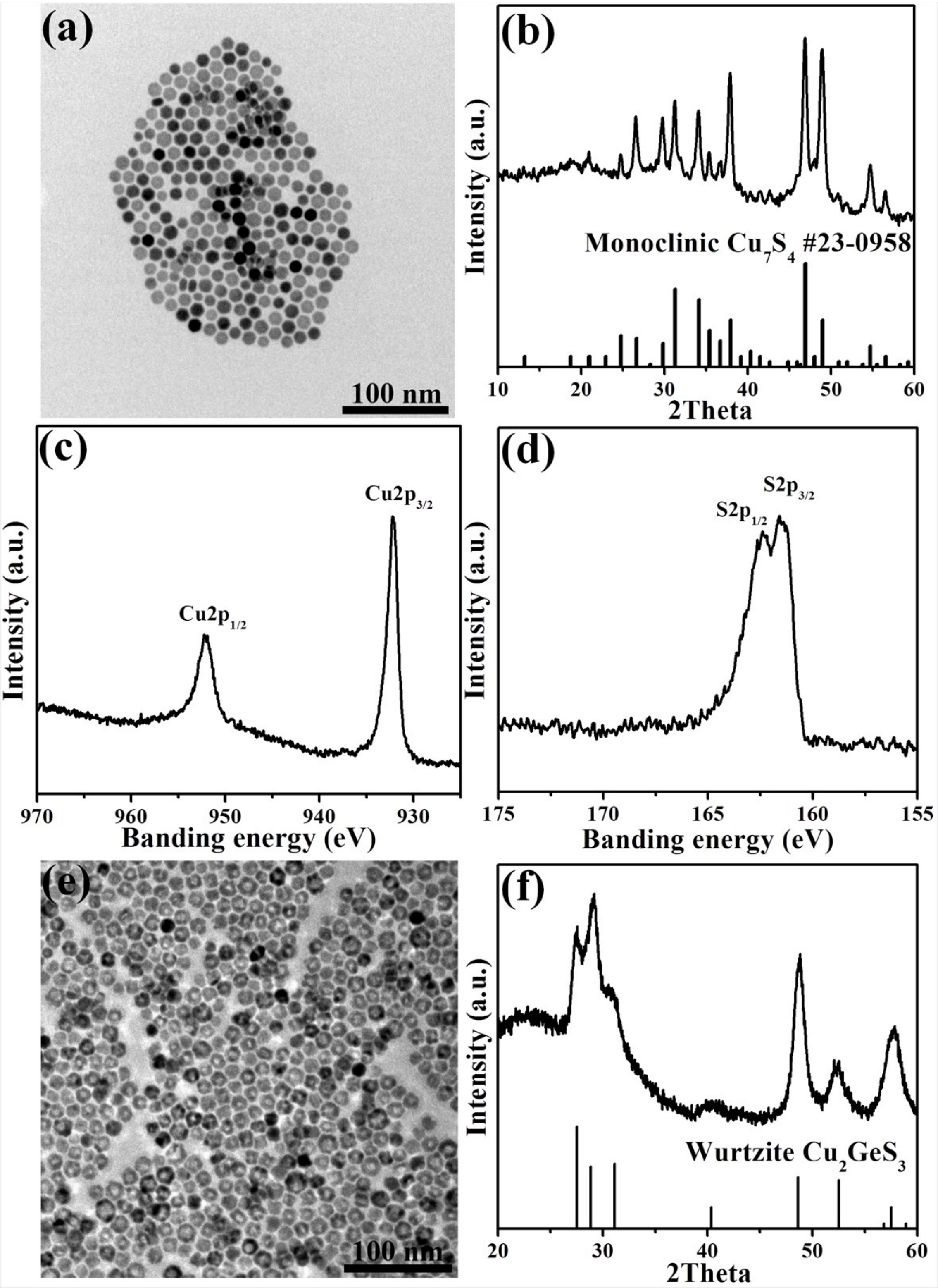

(a)
100 nm
(b)
Intensity (a.u.)
Monoclinic $Cu_7S_4$ #23-0958
10
20
30
40
50
60
2Theta
(c)
Cu2p$_{3/2}$
Cu2p$_{1/2}$
Intensity (a.u.)
970
960
950
940
930
Banding energy (eV)
(d)
S2p$_{3/2}$
S2p$_{1/2}$
Intensity (a.u.)
175
170
165
160
155
Banding energy (eV)
(e)
100 nm
(f)
Intensity (a.u.)
Wurtzite $Cu_2GeS_3$
20
30
40
50
60
2Theta

**Figure S5.** (a) TEM image and (b) XRD pattern of $Cu_2GeS_3$ NPs synthesized by heating elemental sulfur (0.9 mmol), CuCl (0.6 mmol), and Ge-TGA (0.3 mmol of $GeO_2$ in a mixture of 0.2 ml of TGA and 0.4 ml of $NH_3 \cdot H_2O$) in OLA at 300 $^oC$ for 30 min under $N_2$ atmosphere after removing the water.

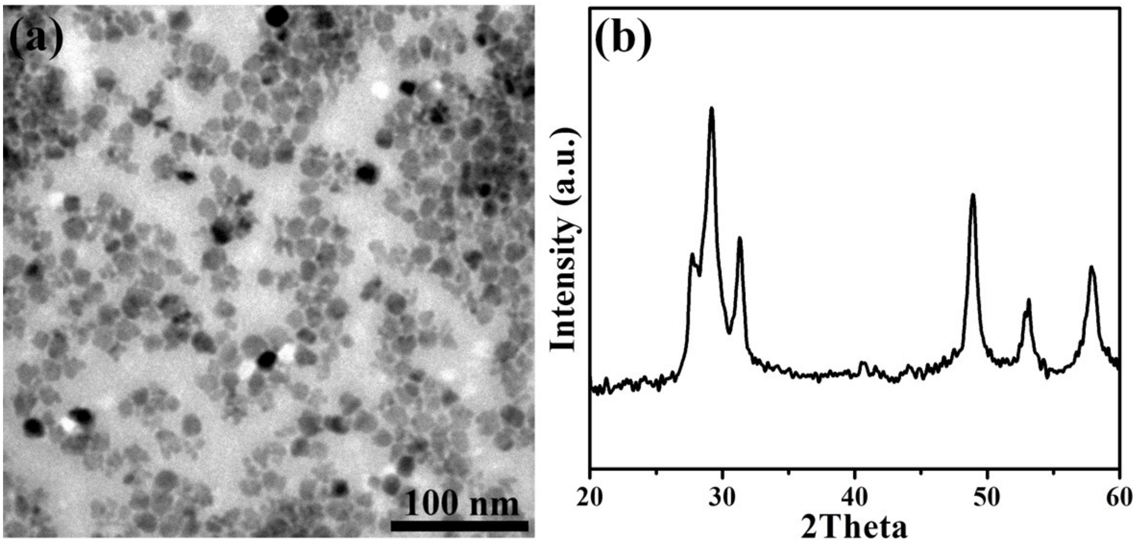


**Figure S6.** (a) TEM image and (b) XRD pattern of $Cu_2GeS_3$ NPs synthesized by heating $(Et_2NCS_2)_2Cu$ (0.6 mmol) and Ge-TGA (0.3 mmol of $GeO_2$ in a mixture of 0.2 ml of TGA and 0.4 ml of $NH_3·H_2O$) in OLA at 300 °C for 30 min under $N_2$ atmosphere after removing the water.

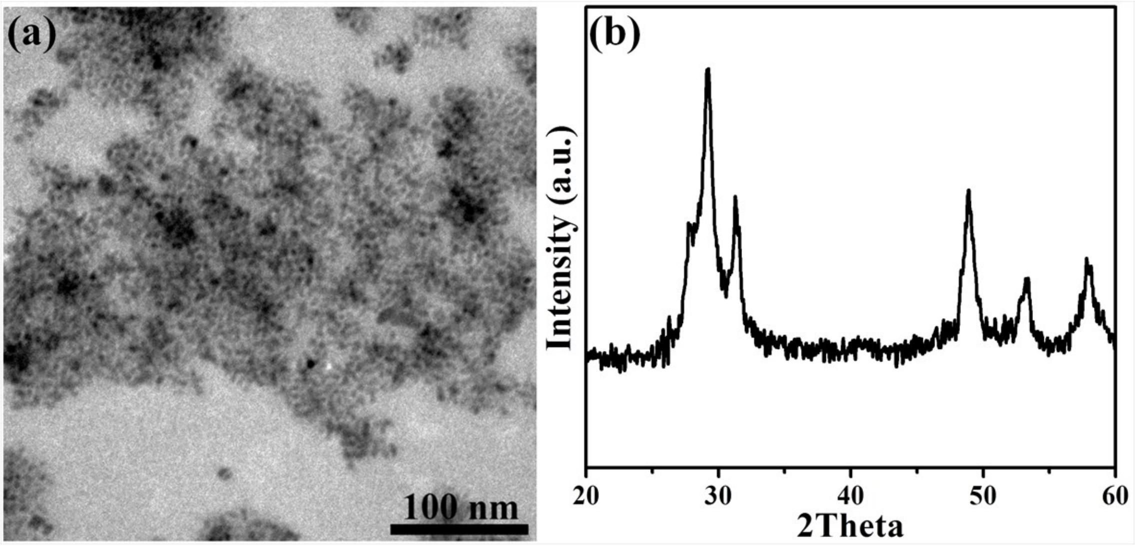


**Figure S7.** XPS (a) Cu 2p, (b) Ge 3d, and (c) S 2p spectrum of small $Cu_2GeS_3$ HNPs. The two peaks in the Cu spectrum at 951.9 eV and 932.0 eV with a peak spitting of 19.9 eV correspond to Cu $2p_{1/2}$ and $2p_{3/2}$ peaks, indicating monovalent copper Cu(I). The single peak at 30.7 eV belonging to the Ge 3d in the Ge spectrum proves the existence of germanium(IV) sulfide other than germanium(IV) oxide. The two peaks at 162.6 and 161.6 eV with a peak spitting of 1.0 eV in the S spectrum correspond to S $2p_{1/2}$ and $2p_{3/2}$ peaks, which is the characteristic of $S^{2-}$ in multinary sulfides.

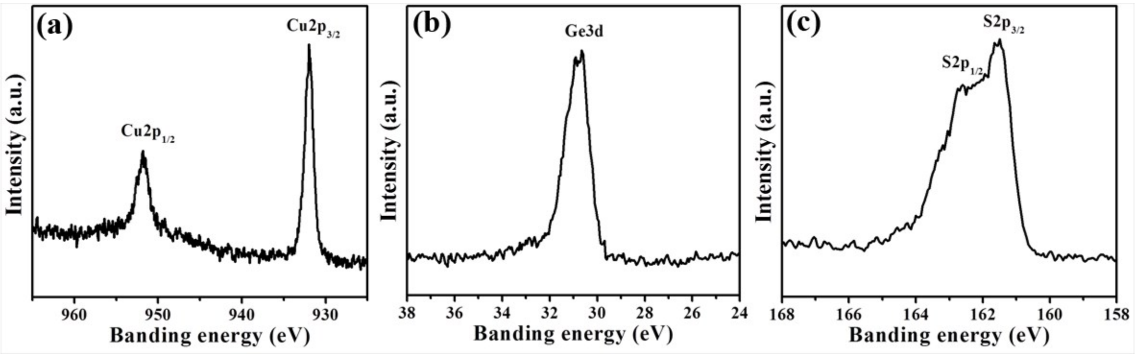
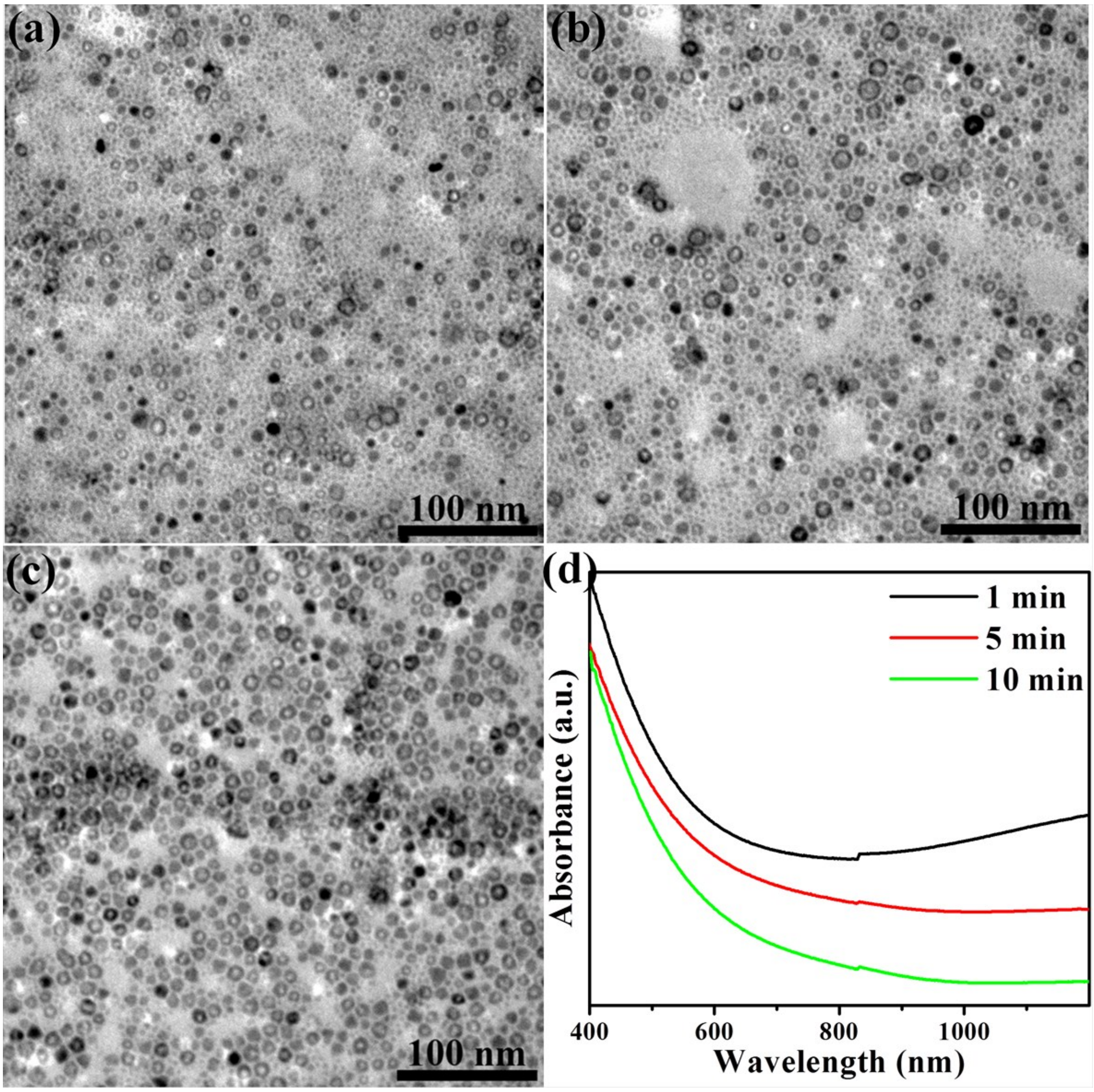


**Figure S8.** TEM images of the small $Cu_2GeS_3$ HNPs at different reaction time: (a) 1 min, (b) 5 min, and (c) 10 min. (e) UV-vis sbsorption spectra of the small $Cu_2GeS_3$ HNPs at different reaction time.



In order to investigate the reaction mechanism, the reaction process is monitored by taking aliquots of reaction mixtures from the flask at different time after the injection. TEM images of the NPs taken at 1 min, 5 min, and 10 min are shown in Figure S8a-c. In the initial stage, only a small part of hollow NPs are formed, many small NPs with the size less than 2 nm can be seen in the TEM image (Figure S8a). With increasing the reaction time, the number of the small NPs decreased while the hollow NPs increased (Figure S8b). When the reaction time reaches 10 min, the small NPs disappear completely (Figure S8c). UV-vis absorption spectra are also used for characterization. As shown in Figure S8d, the NPs taken at 1 min exhibit the strong absorption in the infrared region (800-1200 nm) belonging to the indirect band gap adsorption of $Cu_{2-x}S$ NPs, indicating the existence of $Cu_{2-x}S$ in the products. As for the NPs taken at 5 min and 10 min, no absorption is observed in the infrared region, which illuminates $Cu_{2-x}S$ has disappeared completely. However, there are still many small NPs can be seen in Figure S8b. Thus, it can be conclude that the small NPs should be $GeS_2$ NPs produced by the decomposition of Ge-TGA complex at high temperature before the injection of $(Et_2NCS_2)_2Cu$.

Based on the results above, we speculate that the formation mechanism of the small cubic $Cu_2GeS_3$ HNPs is still based on the nucleation of cubic $Cu_{2-x}S$ seeds and the following unequal diffusion between $Cu^+$ inside the seeds and $Ge^{4+}$ dissolved from $GeS_2$ NPs. Although the small $GeS_2$ NPs have been formed in the solution beforehand, the copper precursor ($(Et_2NCS_2)_2Cu$) has much higher activity and easily decomposes to form cubic $Cu_{2-x}S$ NPs at high temperature (>250 $^oC$). After the nucleation of $Cu_{2-x}S$ seeds, $Ge^{4+}$ could dissociate from small $GeS_2$ NPs, and then diffuse into $Cu_{2-x}S$ NPs through the Kirkendall effect. This is consistent with the decrease of the number of $GeS_2$ NPs as shown in Figure S6a-c.

**Figure S9.** Photograph of the small and large $Cu_2GeS_3$ HNPs solution by using hexane as the solvent.

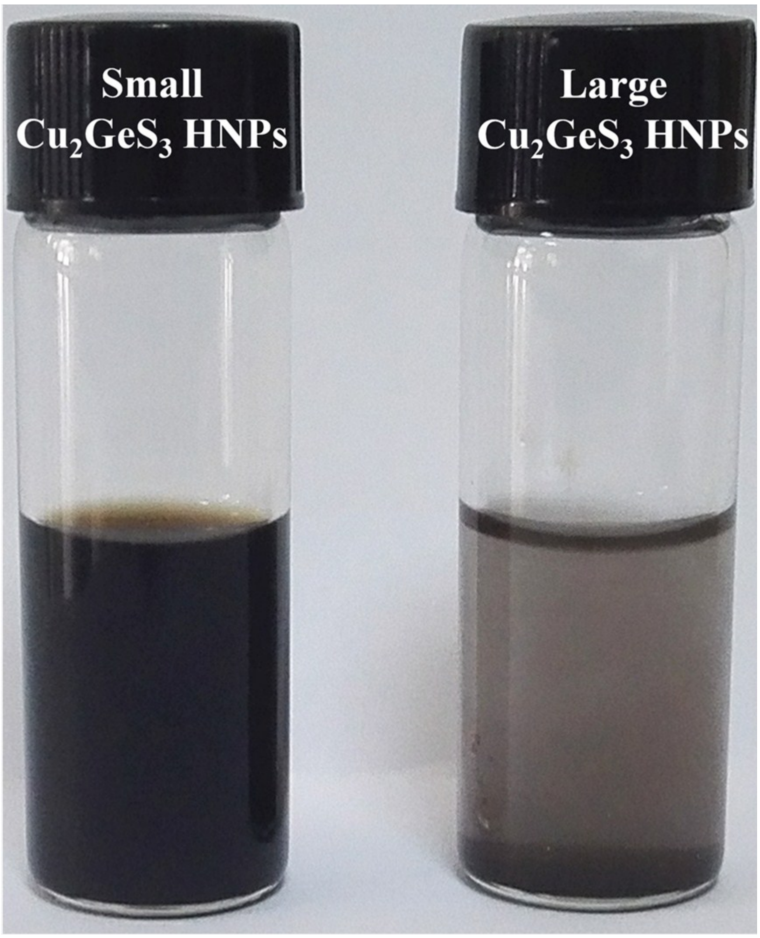


**Figure S10.** Top view SEM image of original large $Cu_2GeS_3$ HNPs without annealing.

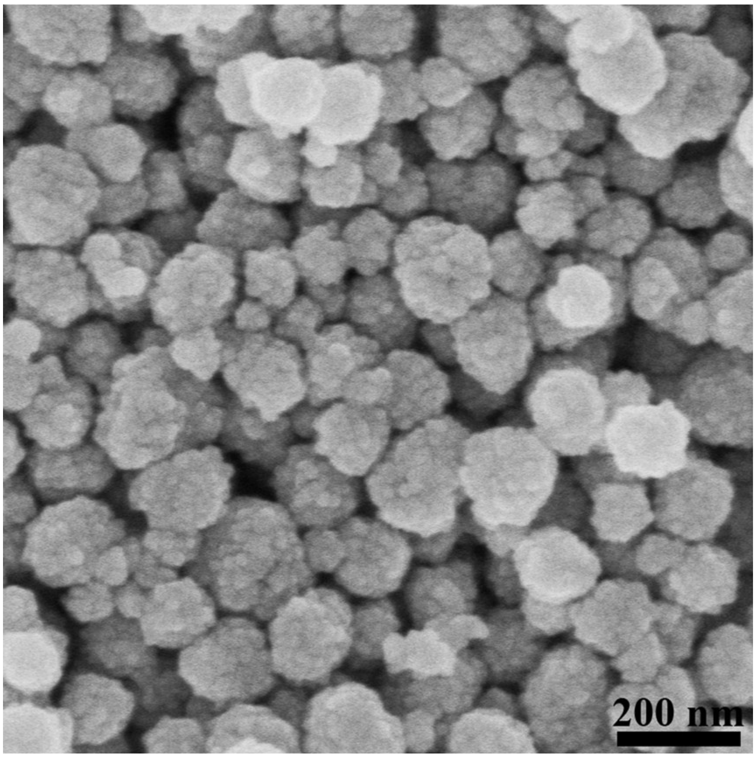


**Figure S11.** Mott–Schottky plots of the three photoelectrodes. The ac amplitude is 10 mV and the frequenciey is 1000 Hz.