Supplementary Information

$Cu_{1.94}S$ nanocrystal seed mediated solution-phase growth of unique Cu_2S-PbS heteronanostructures

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Experimental Section

Materials. The chemicals sodium diethyldithiocarbamate ($Na(S_2CNEt_2)$), $Pb(NO_3)_2$, copper(II) acetylacetonate ($Cu(acac)_2$) and dodecanethiol (DDT) were purchased from the Shanghai Reagent Company (P. R. China).

Synthesis of $Pb(S_2CNEt_2)_2$ ($Pb(dedc)_2$). In a typical synthesis of lead diethyldithiocarbamate, NaS_2CNEt_2(2 mmol) and $Pb(NO_3)_2$(1 mmol) were dissolved in ionized water (50 ml), respectively. Then, $Pb(NO_3)_2$ aqueous solution was dropwise added to NaS_2CNEt_2 solution, washed at least 3 times with ionized water and ethanol followed by drying.

Synthesis of $Cu_{1.94}S$ nanocrystals. The synthesis of the copper sulfide nanocrystals was based on previously published procedures.[1] In a typical procedure, 0.25 mmol (0.065 g) $Cu(acac)_2$ was dissolved by 15 ml dodecanethiol (DDT) in a three-neck flask with magnetic stirring under the protection of nitrogen gas and heated at 200 □ for 20 min. with the increase of temperature, the reaction mixture changed from turbid yellow (~25 □) to turbid white (~110 □), transparent yellow (~150 □) and turbid brown (200 □, 10 min) lastly. After reaction, the flask was naturally cooled to room temperature. The resulting $Cu_{1.94}S$ nanoparticles were collected by centrifugation, washed with ethanol and hexane to remove the unreacted precursors and DDT.

Synthesis of Cu_2S-PbS heteronanostructures. In a typical synthesis, $Cu_{1.94}S$ nanocrystals were first prepared as described above, 0.25 mmol (0.129 g) $Pb(dedc)_2$ was then swiftly added under vigorously stirring for about 10-30 min at this temperature. The mixture solution turned black at once, indicating the formation of PbS. The two-component nanocrystals were washed and precipitated using ethanol and hexane.

Synthesis of PbS nanocrystals. The synthesis of lead sulfide nanocrystals was accomplished by directly

heating a dodecanethiol (15 ml) solution of $Pb(dedc)_2$ (0.25 mmol, 0.129 g) with magnetic stirring under the protection of nitrogen gas at 200 □ for 30 min.

Laster irradiation and temperature measurement. To better investigate the photothermal conversion properties of the as-obtained $Cu_{1.94}S$ and Cu_2S-PbS heterostructure nanocrystals, 0.5 mg ml^{-1} nanocrystals n-hexane solution was ready for subsequent measurement. An 808 nm continuous-wave NIR laster (MDL-808-2W) with a laser spot size of 8×5 mm was used to measure photothermal conversion effect. A thermocouple was immersed in the suspension to measure the increase in temperature.

Characterization. The samples were characterized by powder X-ray power diffraction (XRD), using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromaticized Cu Kα radiation (λ = 1.54056 Å). The operation voltage and current were kept at 40 kV and 400 mA, respectively. TEM and HRTEM were performed on Hitachi H-7650 and JEOL-F2010 with an acceleration voltage of 200 KV. HAADF-STEM and STEM EDS element mapping was carried out on Oxford Inca equipped on JEOL-F2010. Optical absorption spectra of nanocrystals dispersed in hexane were measured at room temperature using a DUV—3700 UV-vis-NIR spectrometer. Photothermal conversion effect was measured with an 808 nm continuous-wave NIR laser (MDL-808-2W) with the power density of 2 W cm^{-2} and the laser spot size of 8×5 mm.

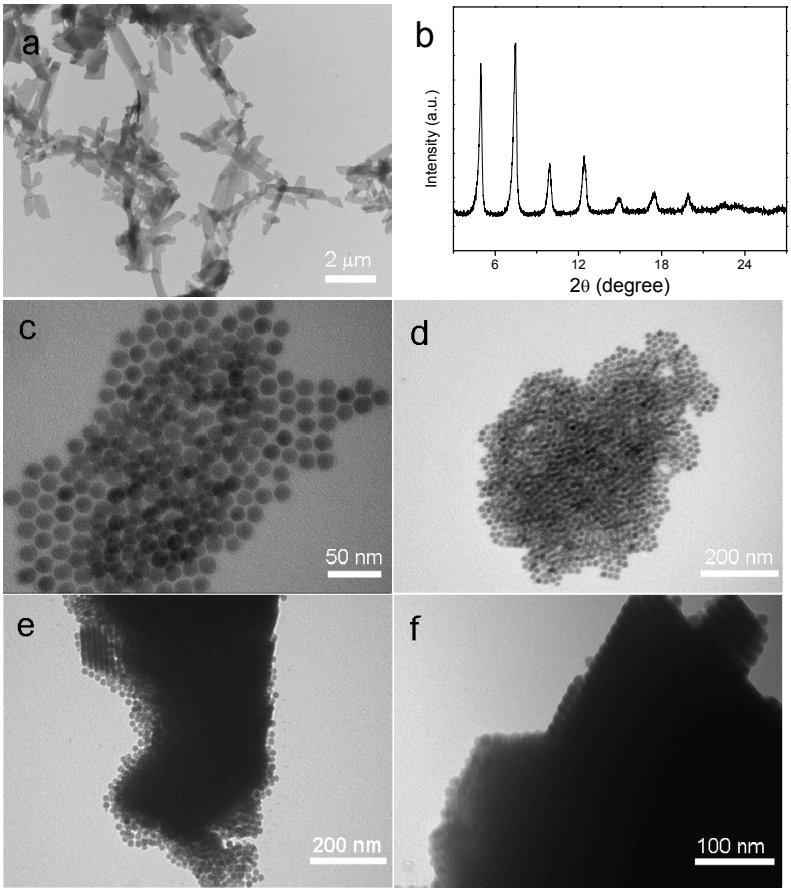

Fig. S1 Typical TEM images of the nanocrystals obtained by pyrolysis of 0.25 mmol $Cu(acac)_2$ in 15 ml DDT when reaction temperature was raised to (c) 210 ^oC,(d) 230 ^oC, (e) 250 ^oC for 20 min, and at 200 ^oC for (a) 0 min, (f) 90 min. (b) XRD pattern of the sample shown in (a).

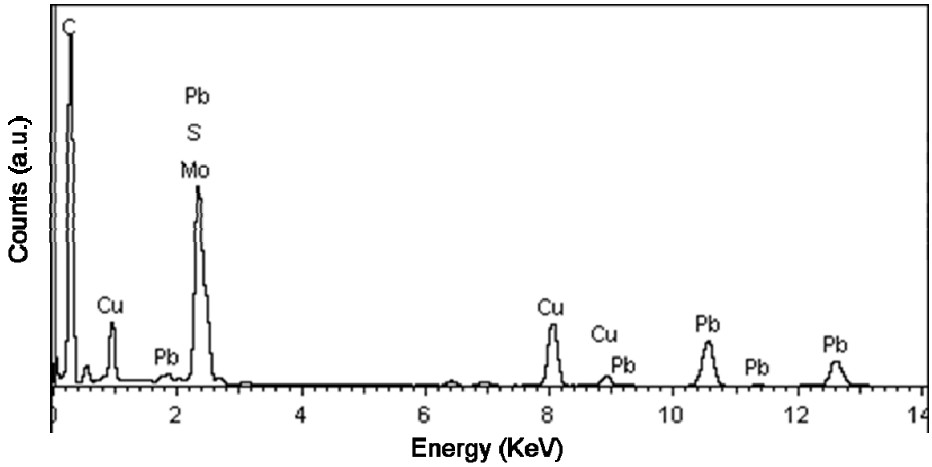

Fig. S2 EDS spectrum of Cu_2S-PbS heteronanostructures. The Mo and C elements are attributed to molybdenum grid and carbon film, respectively.

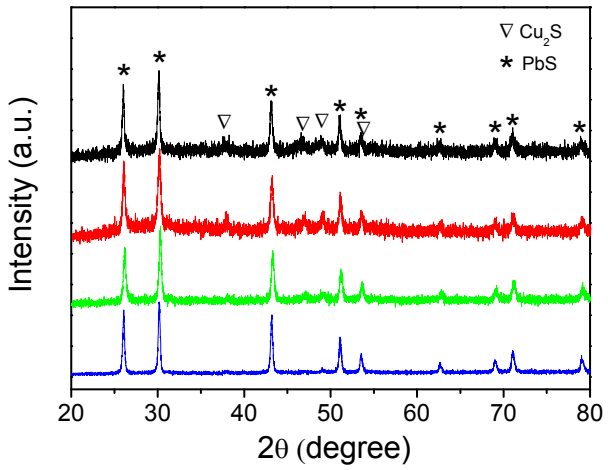

Fig. S3 XRD patterns of the samples obtained after reaction for 10 min with different molar ratio of Cu/Pb: black (1/0. 5), red (1/1), green (1/1.5) and blue (1/2).

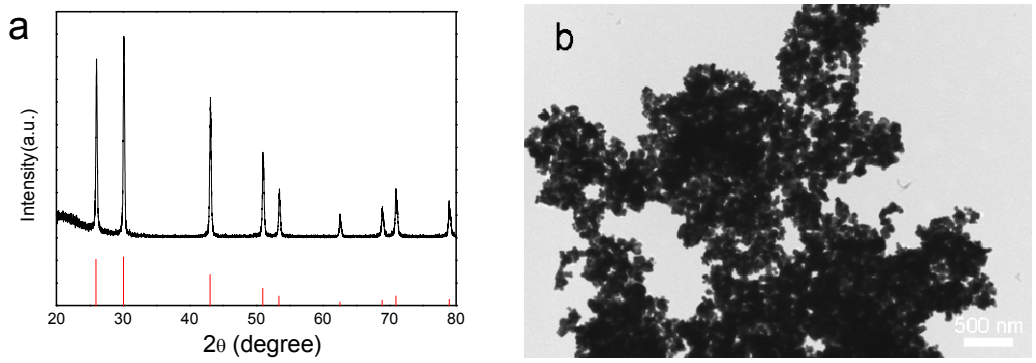

Fig. S4 (a) XRD pattern and (b) TEM image of irregularly shaped PbS nanocrystals obtained by pyrolysis of $Pb(dedc)_2$ in DDT without $Cu_{1.94}S$ nanocrystals. Note: red lines in (a) is PbS Standard data (JCPDS No. 78-1901).

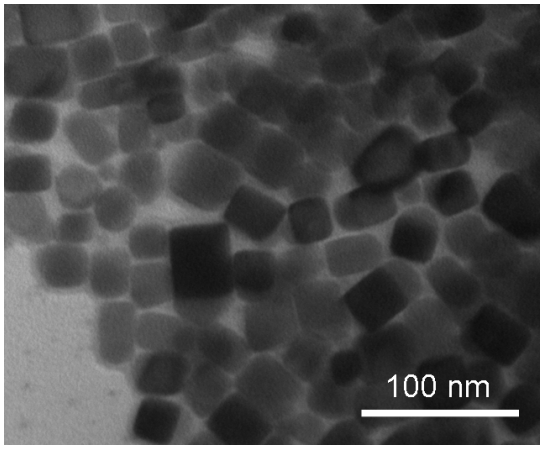

Fig. S5 TEM image of as-prepared heteronanostructures after reaction for 10 min with the molar ratio of Cu/Pb (1/2).

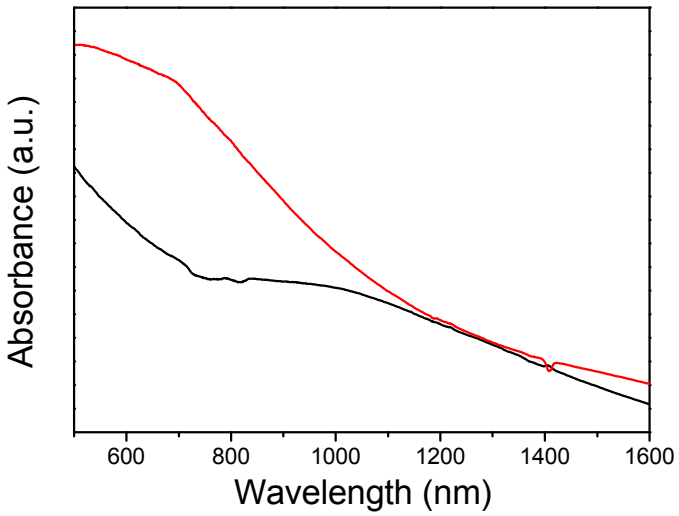

Fig. S6 Absorption spectra of $Cu_{1.94}S$ (black), and Cu_2S-PbS (red) heteronanostructures dispersed in n-hexane, the weak peak at ~1400 nm is related to the absorption of n-hexane.

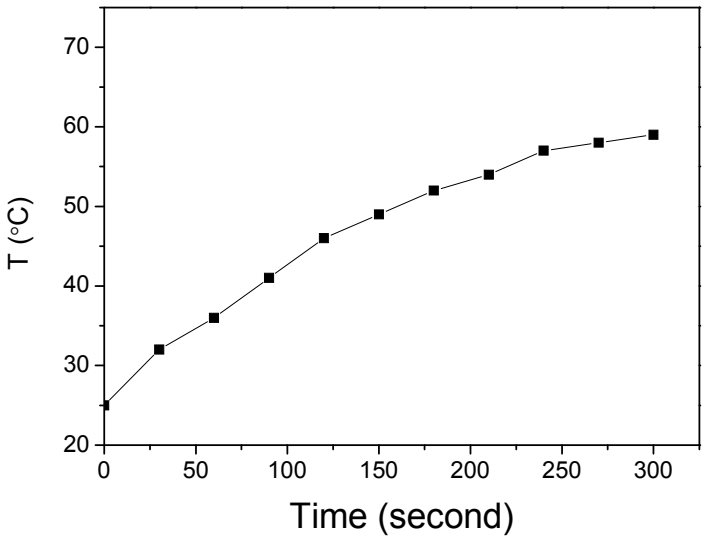

Fig. S7 The photothermal response of PbS nanocrystals with a concentration of 0.5 mg ml^{-1} by NIR light.

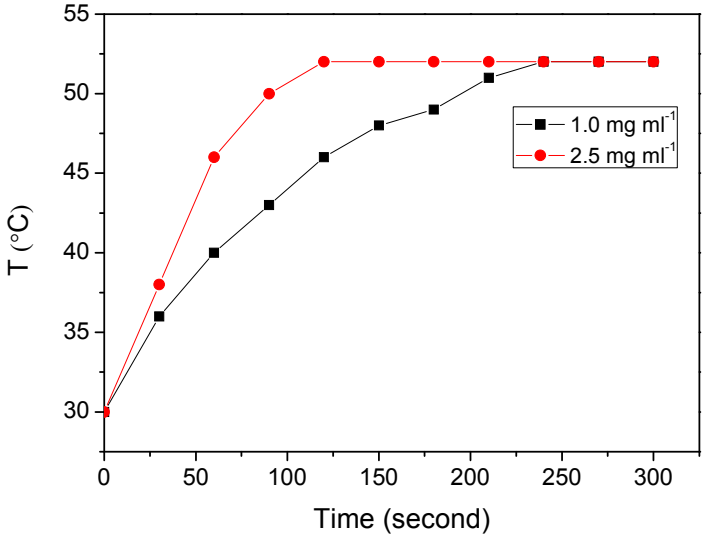

Fig. S8 The photothermal response of $Cu_{1.94}S$ nanocrystals with different concentration by NIR light.

Reference

S1. W. Han, L. Yi, N. Zhao, A. Tang, M. Gao and Z. Tang, *J. Am. Chem. Soc.*, 2008, **130**, 13152-13161.