Supplementary Data

A Facile Chemical Route to Semiconductor Metal Sulfide Nanocrystal Superlattices

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***Experimental details**:* In a typical synthesis of PbS NCSs, a warm solution (~90 °C) of 5 mL $C_{12}H_{25}SH$ including 0.4 mmol of thioacetamide (TAA) was added into a hot solution (e.g. 100 °C) of 10 mL of $C_{12}H_{25}SH$ containing 0.5 mmol $Pb(OAc)_2{\cdot}3H_2O$. After mixing, the yellowish Pb-thiolate complexes solution rapidly changed to brown black. After aging at 100 °C for 90 min, the resulting colloidal solution was treated with 40 mL of ethanol to cause the PbS nanocrystals to be precipitated. The precipitate was collected by centrifugation and washed with ethanol several times to remove the excess $C_{12}H_{25}SH$. For the synthesis of Cu_2S (or Ag_2S) NCSs, 1 mmol of CuCl (or $AgNO_3$) was used instead of the lead salt. Moreover, the reaction temperatures were increased to 120 °C, and the aging period was elongated to 5 h. X-ray diffraction (XRD) analysis was performed using a Philip X' Pert PRO SUPER γA rotation anode with Ni-filtered Cu Kα radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were taken with a Hitachi Model H-800 instrument at an acceleration voltage of 200 kV. High-resolution TEM (HRTEM) images and SAED patterns were obtained on a JEOL-2010 transmission electron microscopy at an acceleration voltage of 200 kV. SEM images were taken with a field emission scanning electron microscope (FESEM, JEOL-6300F, 15 kV). Thermogravimetric analysis (TGA) (Shimadzu TGA-50) was carried out at a heating rate of 2 $^{o}C{\cdot}min^{-1}$ in an inert atmosphere (nitrogen, 50 $mL{\cdot}min^{-1}$).

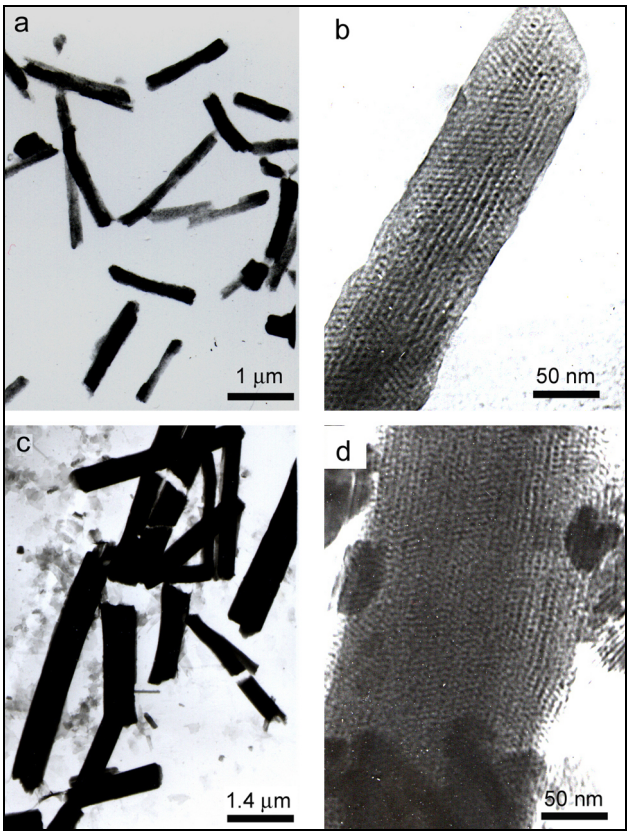

Fig. S1 (a, c) Low-magnification TEM images of PbS and Cu_2S NCSs, respectively. (b, d) high-magnification TEM images of PbS and Cu_2S NCSs, respectively.

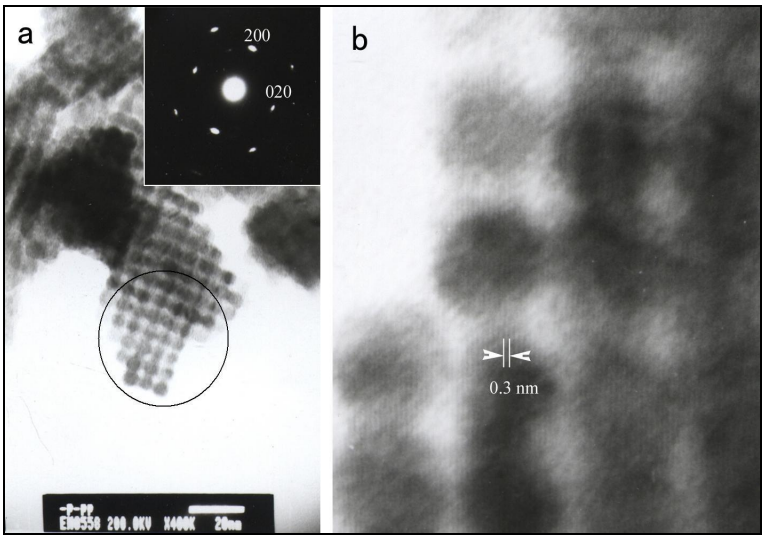

Fig. S2 (a) High-magnification TEM image of PbS nanocrystals, which was obtained by redissolving PbS NCSs sample into toluene; inset is a SAED pattern recorded from the circle region in Fig. S2a, showing diffraction spots of cubic rock-salt PbS. (b) Corresponding high-resolution TEM image of PbS nanocrystals, in which 0.3 nm of lattice spacing is consistent with the separation of {200} planes of cubic rock-salt PbS.

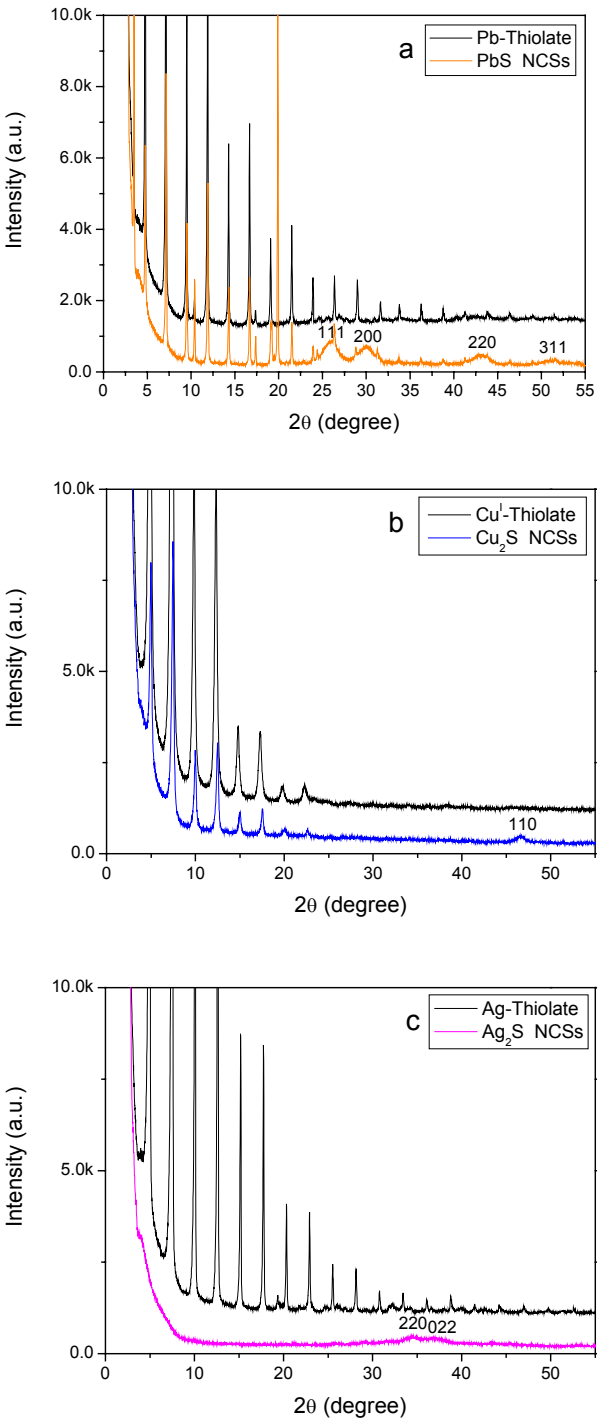

Fig. S3 XRD patterns of crystalline metal thiolate and the corresponding metal sulfide NCSs prepared with 0.4 mmol of TAA: (a) Pb-thiolate and PbS NCSs; (b) Cu^{I}-thiolate and Cu_2S NCSs; and (c) Ag-thiolate and Ag_2S NCSs. These metal-thiolate compounds were prepared by a direct precipitation process through the addition of ethanol into a hot metal-thiolate solution.

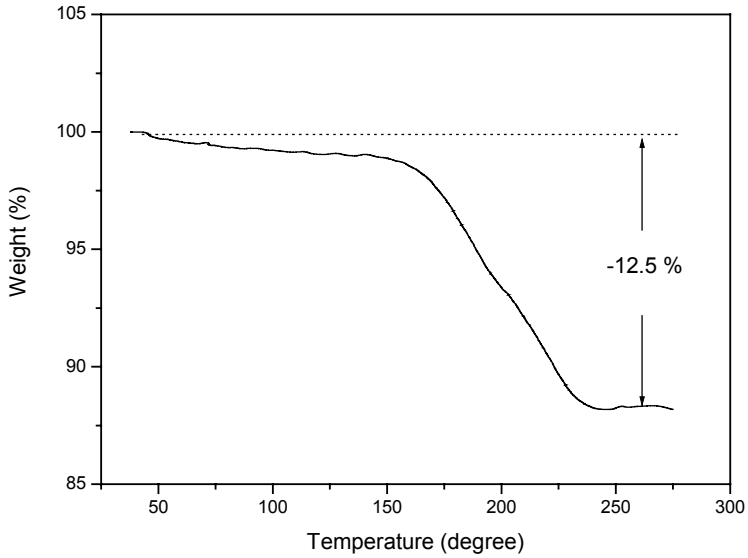

Fig. S4 Thermogravimetric analysis (TGA) for the rodlike PbS NCSs sample prepared with 0.4 mmol of TAA. The TG curve indicates a weight loss of 12.5 % over 40-250ºC, corresponding to the decomposition of the remaining Pb-thiolate.

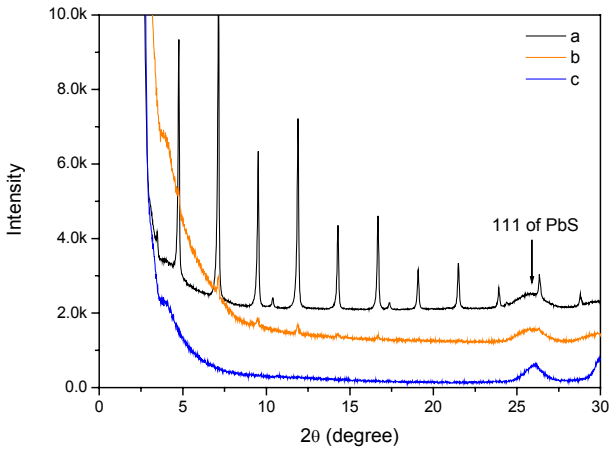

Fig. S5 XRD patterns of PbS NCSs prepared with different amount of TAA: (a) 0.44; (b) 0.48; and (c) 0.5 mmol.

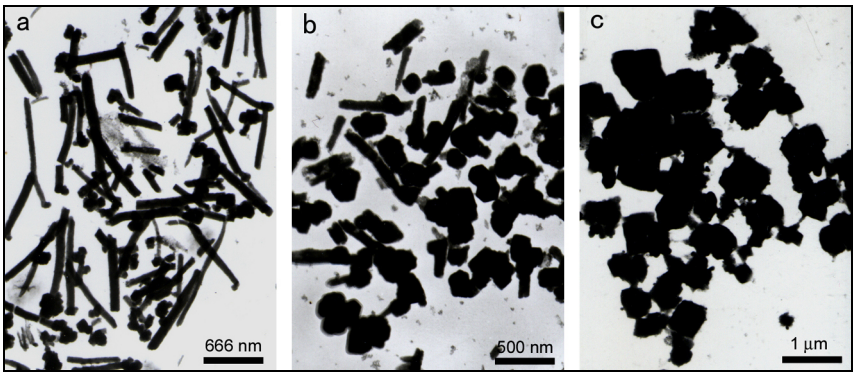

Fig. S6 The corresponding low-magnification TEM images of PbS NCSs prepared with different amount of TAA: (a) 0.44; (b) 0.48; and (c) 0.5 mmol.

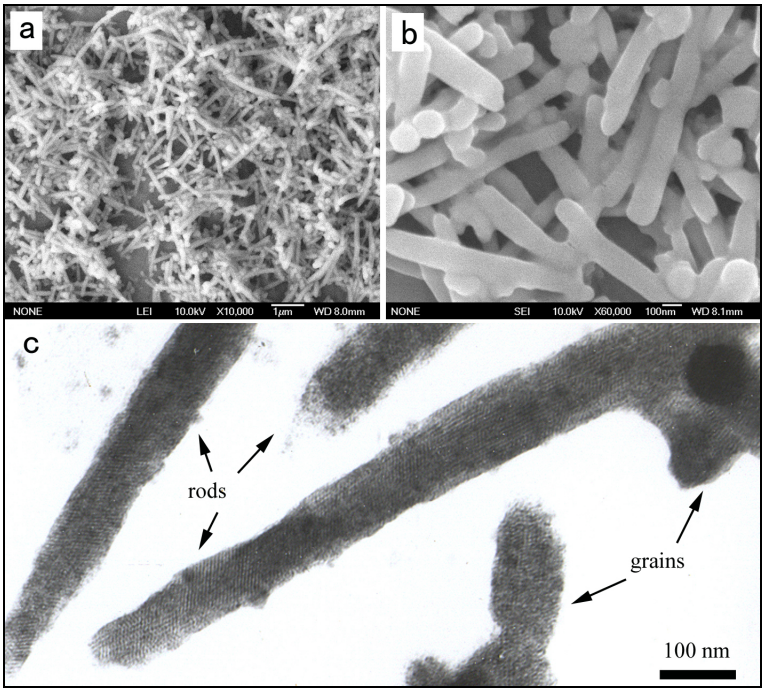

Fig. S7 (a, b) Low- and high-magnification FESEM images of PbS NCSs sample prepared with 0.44 mmol of TAA, showing that the rods account for about 85 % of the total particles. (c) High-magnification TEM image of this sample reveals that both the rods and the grains are composed of highly ordered nanocrystals.

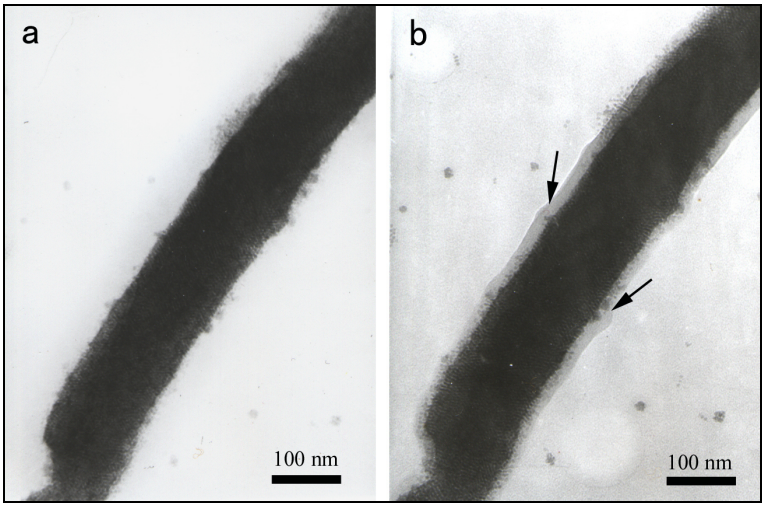

Fig. S8 High-magnification TEM images of a rodlike PbS NCSs under the electron beam irradiation for different periods of time: (a) within 1 min, (b) about 5 min. A layer of contamination with thickness of about 10 nm (indicated by arrows) can be clearly seen in Figure S8b, suggesting that the crystalline Pb-thiolate is unstable under a long time of electron beam irradiation.