

Supporting information for

## **Synergistic synthesis of quasi-monocrystal CdS nanoboxes with high-energy facets**

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## I. Experimental and Calculation Section

**Synthesis of 15.6 nm-sized PbS nanocubes (NCs).** The 15.6-nm-sized PbS NCs was synthesized via a hot-injection method. The procedures were mainly same as previously reported in the literature with only slight modifications<sup>1</sup>. 0.56 g of PbCl<sub>2</sub> was placed into a 500 mL three-neck flask with 10 mL of oleylamine at room temperature. The resulted solution was then stirred with a magnetic stirring bar for 15 min at 220 °C. 54 mg of sulfur powder was ultrasonically dissolved in 5 mL of oleylamine at room temperature, and the resulting sulfur solution was injected into the Pb-oleylamine complex solution at 220 °C. The mixture was aged for 1h at 220 °C, resulting in a black colloidal solution. After cooling down, the black solution was centrifugated at 12,000 rpm for 15 min and the supernatant was removed. The black deposit was washed with ethanol several times and finally dried in a vacuum desiccator at 60 °C for 6 h.

**Synthesis of 50 nm-sized PbS NCs.** The 50 nm-sized PbS NCs were synthesized via a solvothermal route in a Teflon-lined autoclave. A S-containing precursor (0.1 M) was prepared by dissolving sulfur powder (0.320 g, 10 mmol) in 100 mL of 1-octadecene (ODE) in a 250 mL Erlenmeyer flask at 100 °C for 2 h. 0.893g (0.4 mmol) of PbO powder was directly added to a 50 mL of Teflon-lined stainless steel autoclave containing a mixture of 10 mL of oleic acid (OA), 2 mL of oleyamine (OAm) and 14 mL of ODE at room temperature. 2 mL of ODE-dissolved sulfur was mixed with the Pb-containing precursor in the autoclave and then heated to 200 °C and kept at this temperature for 2 h. When the reaction was completed, the autoclave was quenched with cold water to room temperature. The further treatment of this product was same as that previously described for the smaller PbS NCs (15.6 nm).

**Synthesis of PbS nanooctahedra.** PbS nanooctahedra was synthesized as follows. 0.7586g (2 mmol) lead acetate trihydrate and 0.064 g (2 mmol) sulfur powder were dissolved in 20 mL OA by stirring at 100 °C for 15 min, respectively. They were mixed together and the mixture solution was directly added to a 50 mL of the Teflon-lined stainless steel autoclave. The autoclave was placed in a furnace at 200 °C and kept at this temperature for 2 h. The subsequent treatment of the products was the same as the preparation of the 15.6-nm PbS NCs.

**Synthesis of CdS nanoboxes.** First, 0.2658 g of PbS NCs with the size of 15.6 nm was dispersed in 100 mL of OA, to obtain a suspension. Then, 3 mL of the suspension was mixed with 15 mL of 0.5 M OA-dissolved cadmium acetate. The mixture was loaded into a three-neck flask (100 mL and equipped with a magnetic stirring bar) and kept at 180 °C. After the reaction proceeded for a given period of time (2 min ~ 35 min), the mixture was momentarily cooled down to room temperature and centrifugated to separate the deposit. Finally, the product was washed with ethanol several times prior to further characterization. When 50-nm-sized PbS NCs were used as templates, the process was same except that the cadmium acetate concentration was 0.05 M instead of 0.5 M.

**Synthesis of PbS@CdS core/shell nanocubes.** PbS@CdS core/shell nanocubes were synthesized following the procedures previously reported for the preparation of PbTe@CdTe core/shell NPs<sup>2</sup>. In more detail, 11.7 mmol of Cd(Ac)<sub>2</sub>·3H<sub>2</sub>O was dissolved in a mixed solvent (9 mL of OA and 6 mL of ODE) and heated at 100°C during 1h. The solution was injected to a 100-mL three-neck flask (equipped with a magnetic stirring bar) with 3 mL of ODE suspension of 15.6-nm-sized PbS NCs (2.658 g/L). The obtained mixture reacted for 10 min at 250 °C under Ar flow. The black precipitate was retrieved by centrifugation and washed with ethanol twice.

**Synthesis of Co<sub>9</sub>S<sub>8</sub> and Cu<sub>7.2</sub>S<sub>4</sub> SCHNOs.** The processes were same as described above for the preparation of CdS nanoboxes except for that Co (II) acetate tetrahydrate and Cu (II) acetate monohydrate were used instead of Cd acetate trihydrate and the reaction temperatures were set at 300 °C and 150 °C, respectively.

**Synthesis of CdS debris.** Firstly, PbS@CdS core-shell nanocubes were prepared by only cation exchange in OA under N<sub>2</sub> flow for 35 min at 180°C. The process was same as described above for the preparation of CdS nanoboxes except under N<sub>2</sub> flow instead of in air. Secondly, black precipitate was retrieved by centrifugation and dispersed in 18 mL fresh OA. The black suspension was heated in air for 60 min at 180 °C with magnetic stir. Finally, the yellow suspension containing CdS debris was centrifugated and the supernatant was discarded.

**Synthesis of CdS NPs.** 2 g (7.5 mmol) of cadmium acetate trihydrate and 0.2405 g (7.5 mmol) of sulfur powder were dissolved, each, in 75 mL of OA by stirring at 100 °C for 15 min. The two solutions were mixed together in a 500-mL flask and reacted

for 1 h at 180 °C under magnetic stirring and in Ar flow. The precipitate was retrieved by centrifugation and washed with ethanol and hexane twice.

***Stripping of oleophilic ligands on sample surfaces.*** 10 mg of the sample was first dispersed in 10 mL of chloroform, after which 2.5 mL of ethylenediamine (EDA) and 10 mL of ethanol were added to the solution subsequently under vigorous stirring. The stripping was conducted at 25 °C for 15 min. Then, the mixture was centrifuged and the supernatant was decanted. The deposit was washed with ethanol twice and finally dried in a vacuum desiccator at 60 °C for 6 h.

***Photocatalytic degradation of methylene blue (MB).*** 20 mg of a photocatalyst (CdS SCNBs, NPs, or fragments) was added into 50 mL of MB solution, and the solution was stirred in the dark for 20 min. Then the solution was irradiated for 70 min with a simulated solar light of one sun (AM 1.5, 100 mW/cm<sup>2</sup>). 2 mL of the solution was taken out every 10 min to measure the absorbance at 663 nm in a UV-vis absorption spectrometer and to determine the concentration change of MB.

***Characterization of samples.*** Phase analysis was carried out by means of X-ray diffractometry (XRD, Bruke D8 advance instrument). The product morphology was determined by using transmission electron microscopy (TEM, FEI Technai G2 F20, equipped with a field emission gun operating at 200 kV). Atomic-resolution ADF and ABF images were performed with an Enfina spectrometer on a Hitachi 2700C dedicated STEM. The composition was analyzed with an Oxford INCA energy-dispersive spectroscopy (EDS) module attached to the TEM microscope. TEM samples were prepared by dropping diluted products onto carbon-coated Cu (or Ni) grids and washing with ethanol. A Hitachi S-4800 scanning electron microscope (SEM) was used to analyze the NP shape and surfaces. Fourier transform infrared (FTIR) spectra were recorded in transmission mode on a Bruke Tensor 27 spectrometer. The absorption spectra of the samples were examined using a Hitachi 3010 UV–vis absorption spectrometer. A solar simulator (Sciencetech, SS150) was used as the light source for photocatalysis experiments. Nitrogen sorption measurements were performed at 77K using an autosorb iQ instrument (Quantachrome, US). The total surface area was calculated by using the Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained by using the Density Functional Theory (DFT) method based on the desorption data.

**Aberration-corrected scanning transmission electron microscopy.** A 200 keV aberration-corrected dedicated scanning transmission electron microscopy (Hitachi HD2700C) was used for annular bright-field (ABF) and ultra low-angle annular dark-field (ULAADF) STEM imaging. Imaging condition: probe forming half angle 22 mrad. ABF collection half angles 10-22 mrad. ULAADF collection half angles 24-126 mrad.

**Calculations of the interface formation energies in the PbS-CdS system.** The first-principle calculations of the formation energies of the PbS-CdS interfaces possibly occurring at different facets of the PbS crystal were conducted to evaluate their relative stability. The interfaces with low formation energies were then naturally observed more frequently. The calculations were performed based on the density functional theory (DFT) within the VASP code. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) scheme was adopted for the exchange–correlation potential calculation. The energy cutoff of 350 eV and a  $9 \times 9 \times 3$  k-point mesh were set for slab models. The lattice constants were fixed and the atomic positions were fully relaxed within the convergence criteria of 0.1 meV for energy and 0.01 eV/Å for force. Alternating CdS and PbS slabs were modeled to be infinitely repetitious, while a 10-Å-wide vacuum layer was added to avoid the interactions between neighboring PbS and CdS slabs. The interface formation energy is expressed with the following formula<sup>3</sup>,

$$E_{form-ener} = (E_{total} - m\mu_{Pb} - n\mu_{Cd} - p\mu_S) / A$$

Where  $E_{total}$  is the total energy of the slab supercell;  $m$ ,  $n$  and  $p$  are the numbers of Pb, Cd and S atoms in the supercell, respectively.  $A$  is the interface area between PbS and CdS.  $\mu_{Pb}$ ,  $\mu_{Cd}$ ,  $\mu_S$  are the chemical potentials of Pb, Cd, and S atoms.

**Table S1.** Interface formation energies for three different interface types.

Interface type	Atoms number (S, Cd, Pb)	Interface area (Å <sup>2</sup> )	Interface-energy (eV/Å <sup>2</sup> )
(100)-(100)	22, 10, 14	5.88×5.88	-4.5588
(110)-(110)	18, 9, 9	5.88×4.16	-5.0883
(111)-(111)	13, 7, 6	4.16×3.60	-5.7931

**Calculations of apparent reaction rate constant per unit surface area.** The apparent rate constant of degradation (k) can be calculated using pseudo first-order reaction, i.e.  $\ln(C_0/C) = kt$ , where  $C_0$  and C are initial concentration and concentration at time t (min), respectively. Then, the specific surface area per gram (SBET) of photocatalysts is estimated from the Brunauer, Emmett and Teller (BET) measurement. Finally, the apparent rate constants per unit surface area ( $k_s$ ) are estimated from the equation,  $k_s = k/(m \cdot \text{SBET})$ , where m is the mass of photocatalysts. The obtained results are summarized in Table S2.” The obtained results are summarized in Table S2.

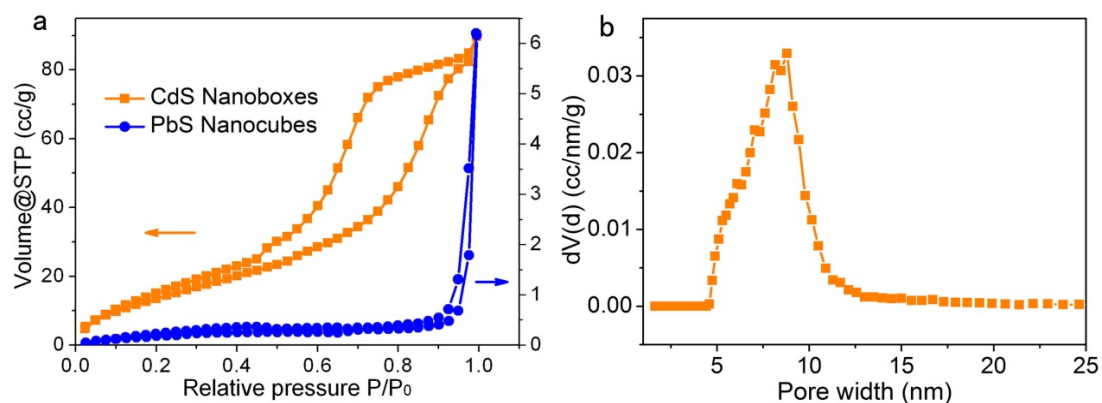
**Table S2.** Specific surface area, apparent rate constant (k) and apparent rate constant per unit surface area ( $k_s$ ) of photocatalysts.

CdS catalysts	Specific surface area	k (min <sup>-1</sup> )	$k_s$ (min <sup>-1</sup> m <sup>-2</sup> )
Debris	49.663	0.01±0.00024831	0.010068
Nanoparticles	77.09	0.0114±0.00131	0.007394
QMNBs	63	0.04638±0.00612	0.03681

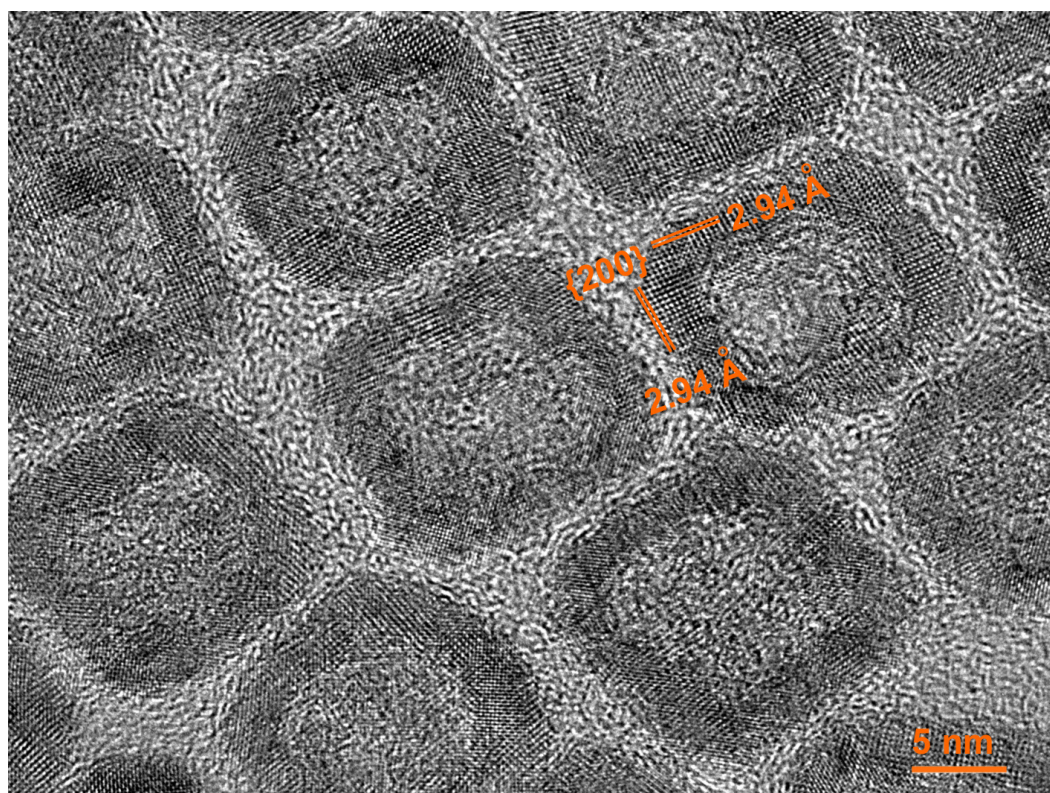
### References:

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- 3 B. Sadtler, D. O. Demchenko, H. Zheng, S. M. Hughes, M. G. Merkle, U. Dahmen, L.-W. Wang and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2009, **131**, 5285-5293.

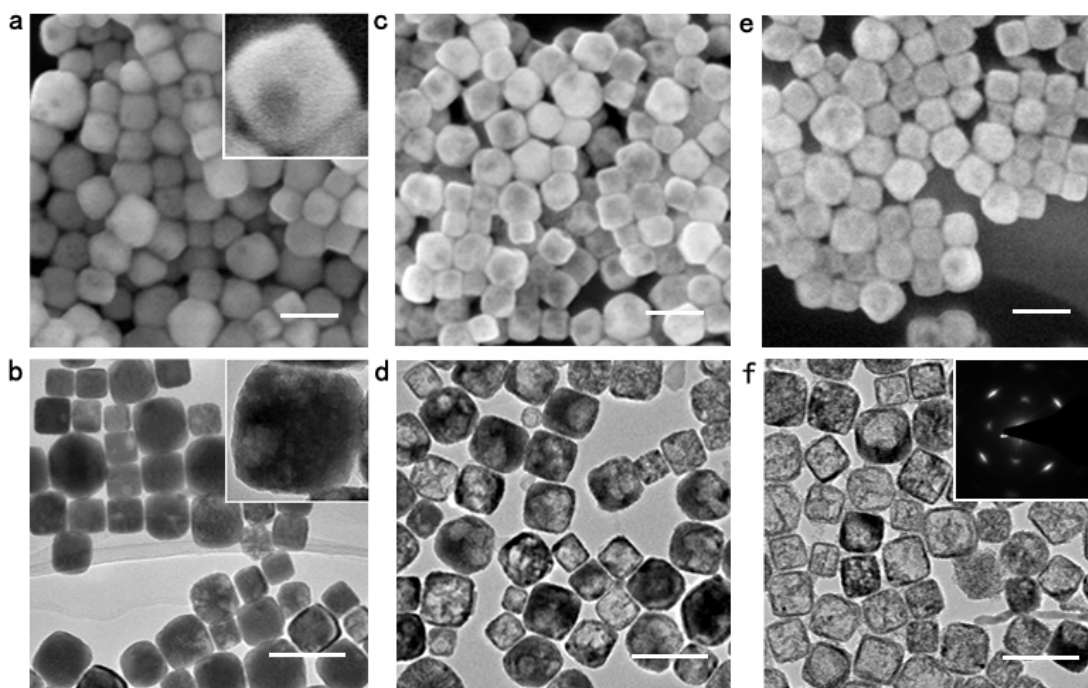
## II. Supplementary Results



**Fig. S1**(a)  $N_2$  adsorption/desorption isotherms of CdS QMNBS and PbS NCs. (b) Pore-size distribution curve for CdS nanoboxes. The specific surface areas of the CdS SCNBs and PbS NCs are determined as  $63$  and  $0.76 \text{ m}^2 \text{ g}^{-1}$ , respectively, while the pore size of SCNBs is evaluated to be about  $8.8 \text{ nm}$ .

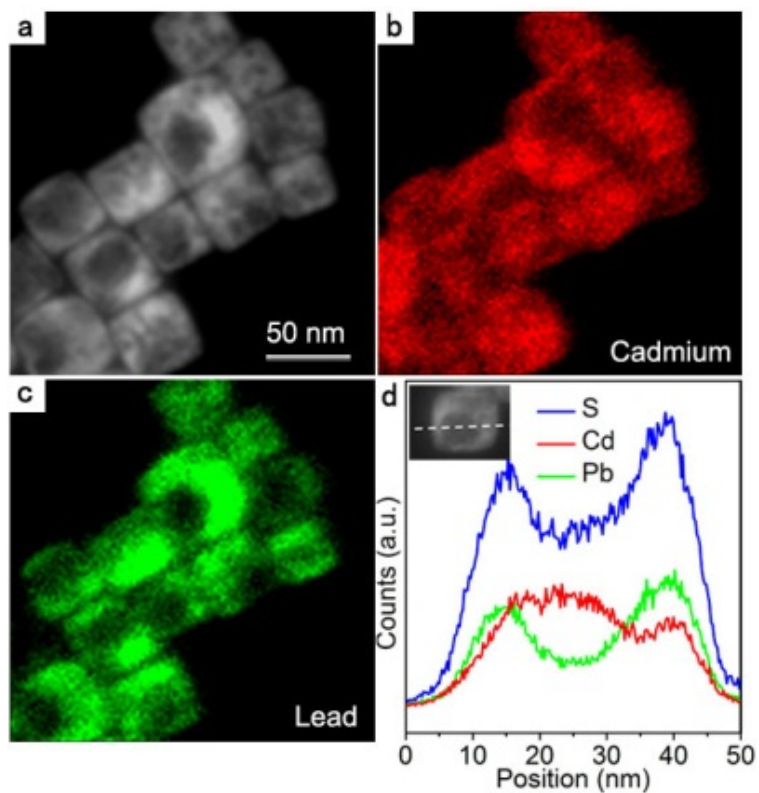


**Fig.S2** High resolution TEM image of QMNBS: Each nanobox exhibits a quasi-monocrystal structure and  $\{100\}$  exposed facets.

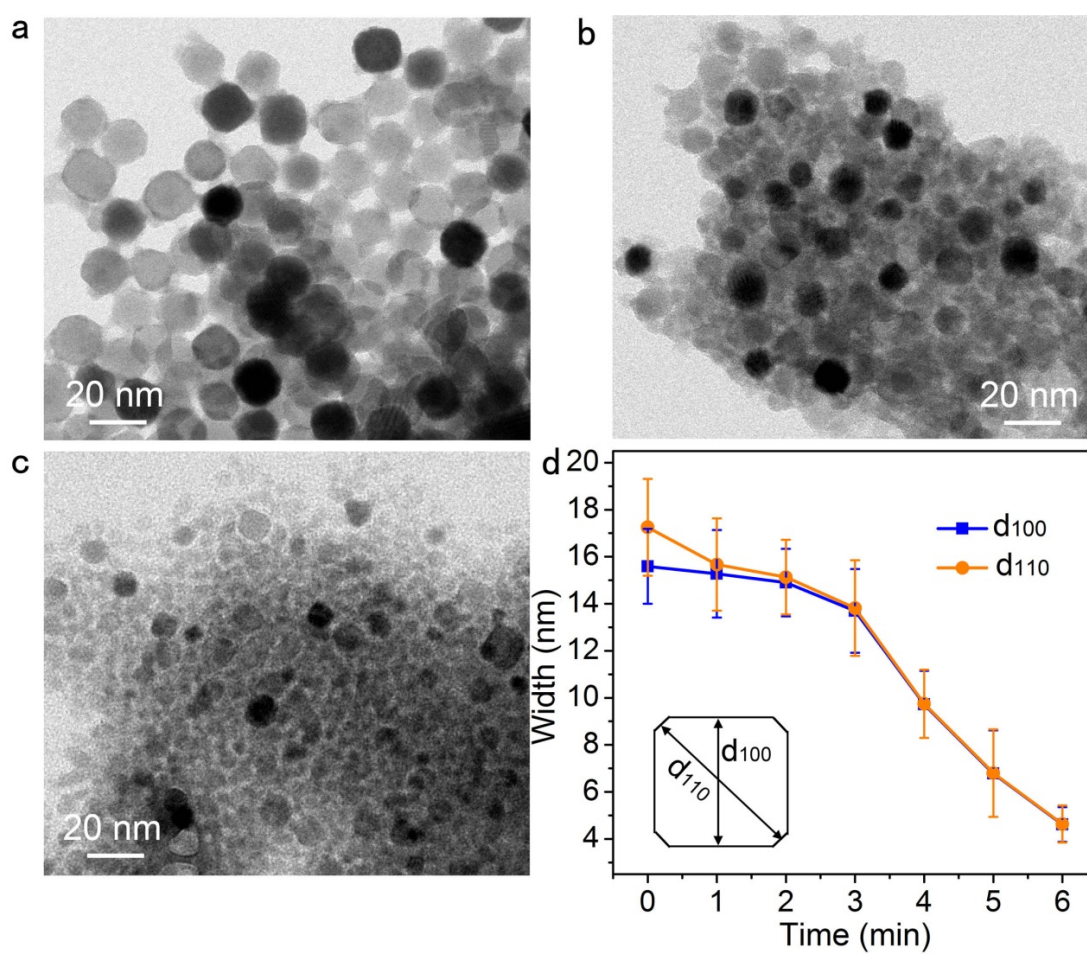


**Fig. S3** Structural evolution with the heating time of 50-nm-sized PbS NCs. SEM and TEM images of the products with OA exposed to air at 180 °C. (a) and (b) 2 min. (c) and (d) 10 min. (e) and (f) 30 min. The insets in (a) and (b) are magnified images of single nanocubes with pin-holes on their surfaces. The scale bar is 50 nm.

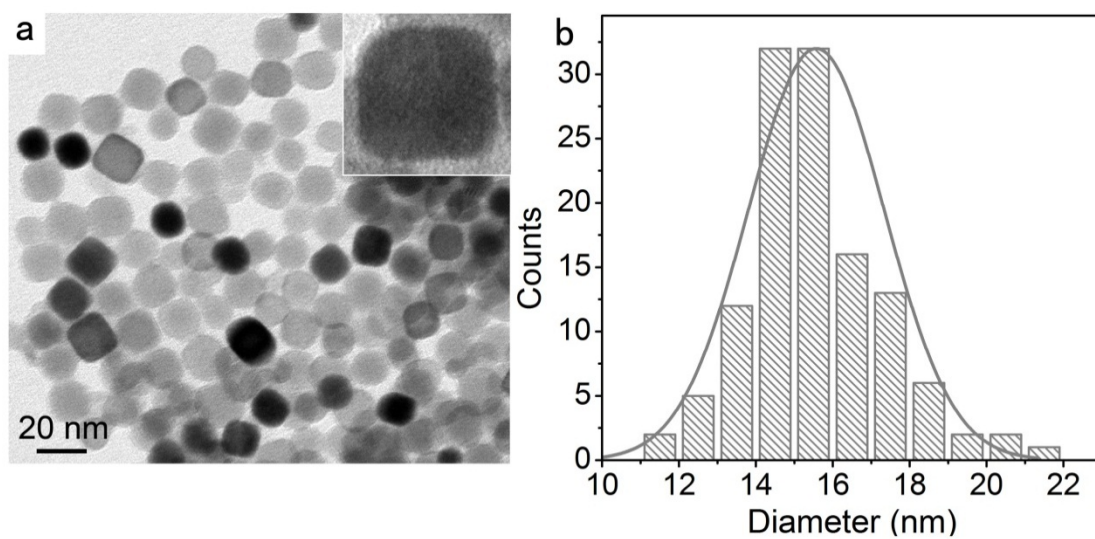




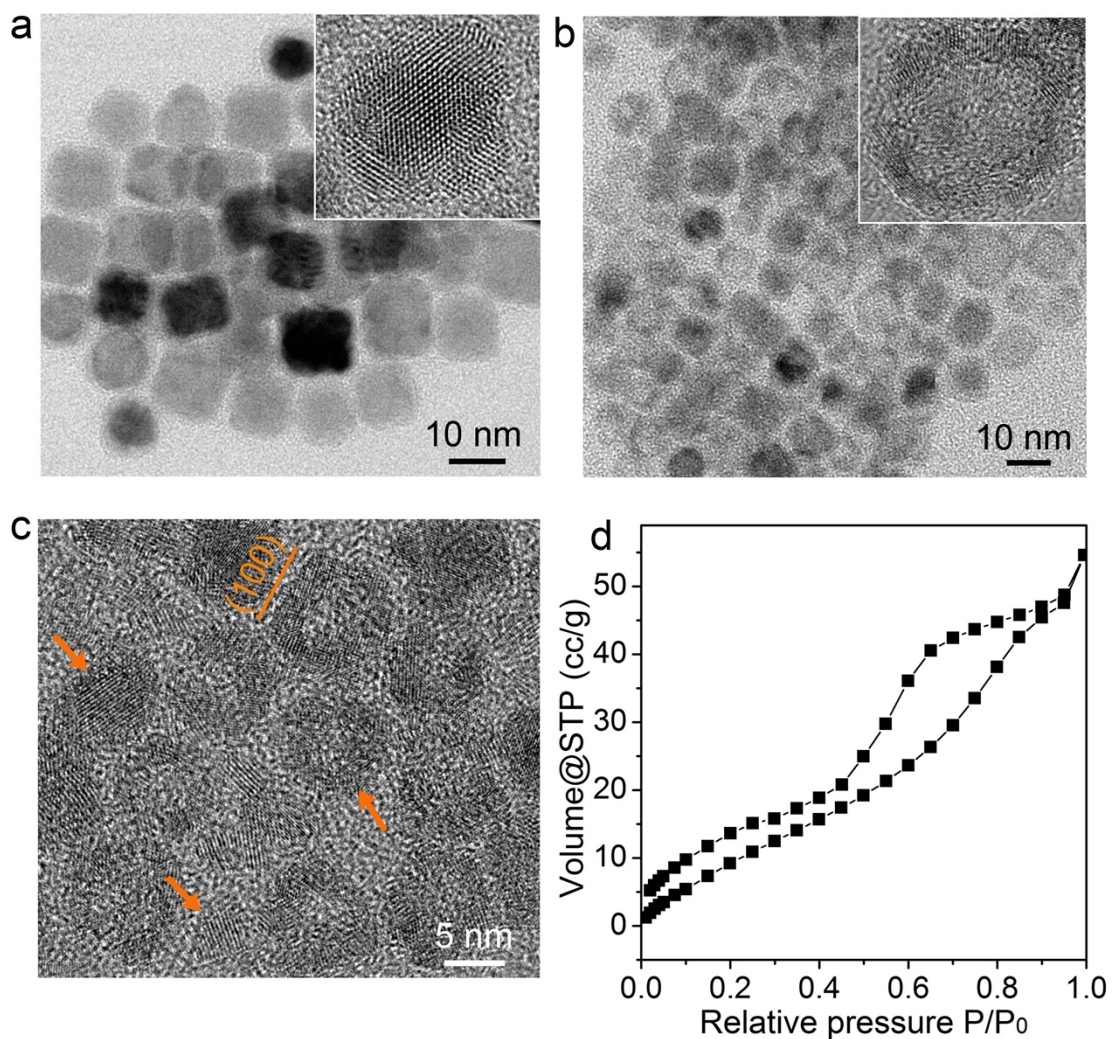
**Fig. S4** Characterizations of the product obtained by heating 50-nm-sized PbS nanocubes at 180 °C for 10 min. (a) STEM image. (b) Cadmium mapping. (c) Lead mapping. (d) EDS line-scanning profile of an individual particle.



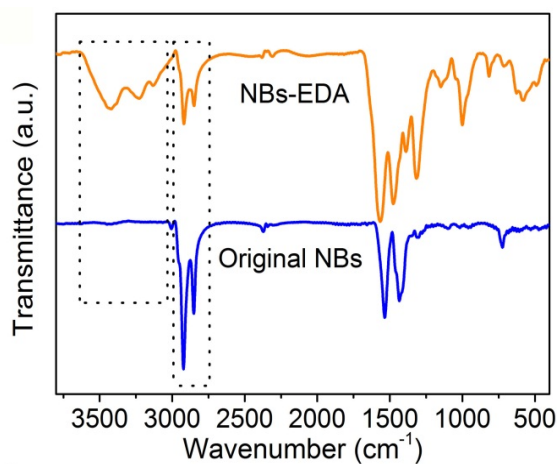
**Fig. S5** Morphological and size evolution with heating time of PbS NCs with OA exposed to air at 180 °C. (a) 2 min, (b) 4 min and (c) 5 min. (d) Size change in  $\langle 100 \rangle$  and  $\langle 110 \rangle$  orientations.



**Fig. S6** PbS NCs heated with OA in N<sub>2</sub> flow at 180°C for 35 min. (a) Low magnification TEM image, inset is the high magnification image of a single nanocube. (b) Size-distribution histogram.

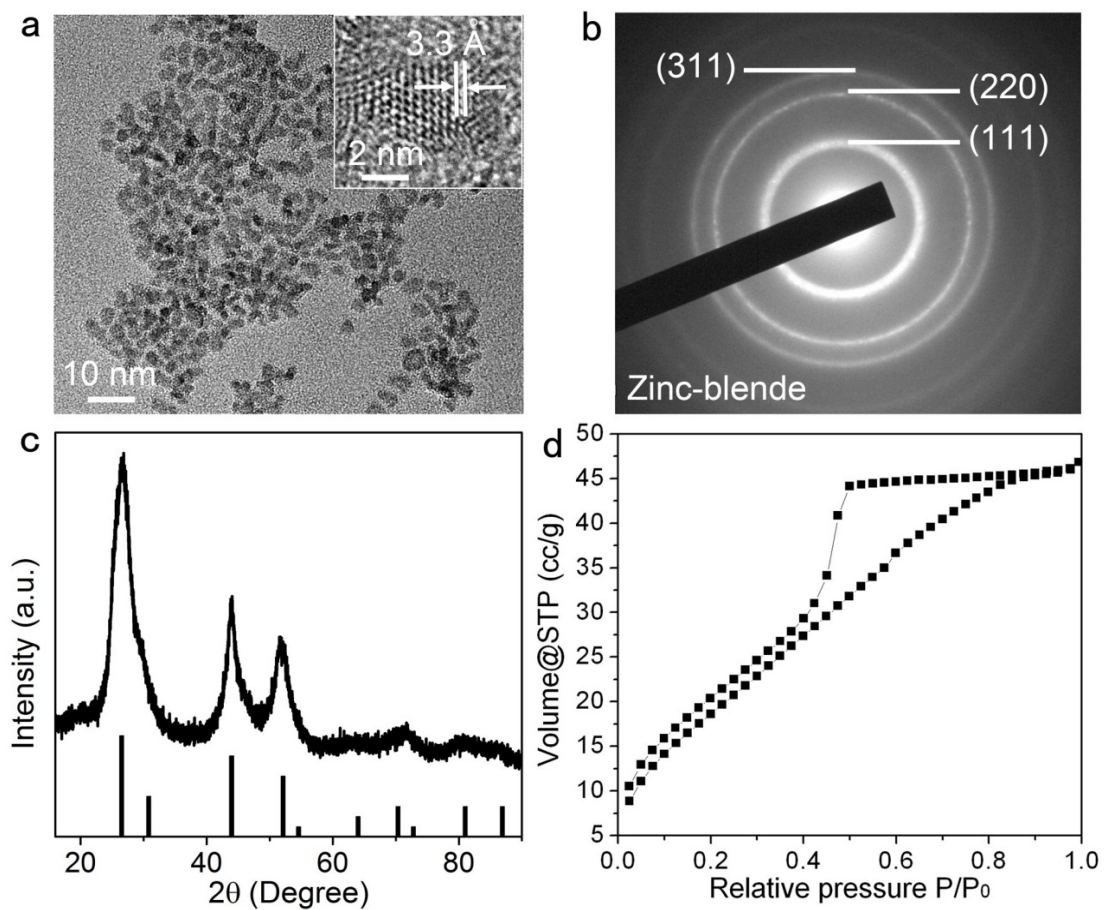


**Fig. S7** Products obtained by other synthetic routes. (a) PbS@CdS core-shell nanocubes by cation exchange in OA under N<sub>2</sub> flow for 35 min at 180°C. (b) CdS debris obtained when the product in panel (a) was then etched in OA saturated with air (as a next step) for 60 min. (c) HRTEM image and (d) N<sub>2</sub> adsorption/desorption isotherm of CdS debris. The specific surface area is determined as 49.663 m<sup>2</sup> g<sup>-1</sup> by BET measurement.



**Fig.S8** FTIR spectra of as-prepared and EDA-treated CdS QMNBs. The spectrum of nanoboxes exhibited an intensity reduction of the C–H stretching vibration (2800–3000 cm<sup>-1</sup>) and the appearance of N–H stretching between 3000 and 3650 cm<sup>-1</sup>, demonstrating successful substitution of OA with EDA.





**Fig. S9** Characterization of CdS NPs. (a) TEM image, the inset is a high-resolution TEM image of a single nanoparticle. (b) SAED pattern, (c) XRD pattern, (d) N<sub>2</sub> adsorption/desorption isotherm of CdS NPs. The specific surface area is determined as 77.09 m<sup>2</sup> g<sup>-1</sup> by BET measurement.