Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2015

Supporting Information

Facet-Controlled Facilitation of PbS Nanoarchitectures by Understanding Nanocrystal Growth

Welley Siu Loc,[†,¤] Zewei Quan,[†,¤,▼] Cuikun Lin,[§] Jinfong Pan,[‡] Yuxuan Wang,[‡] Kaikun Yang,[‖] Wen-Bin Jian,[⊥] Bo Zhao,[§] Howard Wang[‖] and Jiye Fang*[,†,‡]

[†]Department of Chemistry, [‡]Materials Science and Engineering Program, and [‖]Department of Mechanical Engineering, State University of New York at Binghamton, Binghamton, New York 13902, United States

[§]Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States

[⊥]Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan, ROC

[▼] Present Address: Department of Chemistry, South University of Science and Technology of China, Shenzhen, Guangdong 518055, P. R. China.

*Corresponding author: jfang@binghamton.edu

¤ W.S.L. and Z.Q. contributed equally

Experimental Section

Chemicals.

Oleylamine (OAm, 70%), trioctylphosphine (TOP, 90%), oleic acid (OA, 90%) and 1,2-dichloroethane (DCE, 99.8%) were purchased from Sigma-Aldrich. Lead oxide (PbO, 99.99%) and diphenyl ether (DPE, 99%) were obtained from Alfa Aesar. Toluene (99.5%) and anhydrous hexane were received from BDH. Sublimed sulphur (S) powder and ethyl alcohol (200 proof) were products from J. T. Baker and AAPER, respectively. All chemicals were used as received without further purification.

Precursor Preparation.

Sulphur-oleylamine (S-OAm) stock solution (1M) was prepared by dissolving 50 mmol of sublimed sulphur powder into 50 mL of OAm at 100°C on a hot plate. Sulphur-trioctylphosphine (S-TOP) solution (1M) was prepared in a glovebox by dissolving 50 mmol of the sublimed sulphur powder into 50 mL of TOP. The lead precursor, Pb-oleate (0.15 M), was prepared under argon (Ar) atmosphere (Airgas, 99.999%) by dissolving 3 mmol of PbO in a mixture containing 14 mL of DPE and 6 mL of OA. This mixture was heated to 150°C and remained for 1 h to form a transparent yellow solution which was stored in a flask with purged Ar at room temperature for further use.

Synthesis of PbS 1D NWs.

A standard air-free Schlenk line system was used to conduct the synthesis in the presence of argon stream. To prepare PbS NWs, 20 mL of Pb-oleate was transferred into a three-neck round-bottom flask in the presence of 3 mL of OAm and 15 mL of DPE. When the mixture was heated to 180°C, 3 mL of S-TOP (1 M) was injected into the flask. After 5.0 min, the heating source was removed and the flask was immediately immersed into a cold water bath. The resultant PbS NCbs in black suspensions were collected at 50-60°C, washed with an equal volume of ethyl alcohol, isolated by centrifugation, and re-dispersed in hexane for two cycles in order to remove the supernatants.

Synthesis of PbS 2D NSs.

Similarly, synthesis of PbS NSs was carried out at a relatively low temperature (150 °C) using S-TOP. Furthermore, 10 sec after the addition of the S-TOP solution (1 M), 3 mL of DCE was subsequently injected into the system, and the growth was allowed to proceed for 7.5 min. PbS NSs were isolated and cleaned for 2 cycles according to above-mentioned procedure in which hexane was replaced by toluene.

Synthesis of PbS 0D NPs.

PbS NCbs were prepared using a similar recipe, in which S-OAm (1 M, 3 mL) was utilized in place of the S-TOP precursor. A similar reaction at 200°C was held for 7.5 min, followed by the same sample collection/cleaning procedures with 1D NWs. To prepare PbS NCOs, all procedures are identical except an immediate addition of 3 mL DCE after the injection of S-OAm solution.

Characterizations.

XRD patterns were collected from a PANalytical X'Pert X-ray diffractometer equipped with a copper ($CuK_{\alpha1}$) radiation source of 1.5406 Å. Scanning electron microscopy (SEM) images were obtained from a Carl Zeiss Supra 55VP operating at 65 kV. A Hitachi 7000 transmission electron microscope (TEM) operating at an accelerating voltage of 75 kV was primarily used to evaluate the average size and shape of the PbS products at low magnification. An FEI Tecnai Spirit TEM operating at 120 kV and a JEOL-2100F TEM operating at 200 kV were utilized for high-resolution TEM (HRTEM) imaging. Atomic force microscopy (AFM) images were taken on a Digital Instruments Multimode/Nanoscope V scanning probe microscope in the tapping mode under ambient environment.

To conduct the electrical measurement of the PbS NWs, a wafer substrate was taken as a back gate electrode. Before the dispersion of the NWs on the Si substrate, a SiO_2 layer was capped on the substrate by thermal oxidation to prevent the on-chip devices from any current leakages through the substrate. Afterward, micrometer-scale connection lines, markers, and sub-millimeter electrode pads for electrical probing were patterned on the substrate by photo-lithography and thermal evaporation of Ti/Au thin films. The suspensions of PbS NWs in toluene were then drop-cast to disperse the NWs on the patterned substrate. Prior to metallization procedure, the substrate with bare PbS NWs was pre-heated in a high vacuum at 150 ^{o}C for 12 h to remove any contaminations such as surface-capped organic ligands. The position of these NWs was determined using SEM. Subsequently, a standard electron-beam lithography and thermal evaporation were adopted to make two Ti/Au current leads (~20/100 nm in thickness) on an individual NW, connecting to the large pattern (micrometer-scale electrodes). The separation distance between two (source and drain) electrodes on the selected PbS NW was maintained as a constant of ~600 nm. To improve the contact, these NW devices fabricated were heated again in a high vacuum up to 400 ^{o}C with an increasing rate of 10 ^{o}C/min, annealed for 1 min, and cooled to room temperature. The typical configuration of a NW device is illustrated in Figure 5b.

Current-voltage (I_{ds}-V_{ds}) curves, having current and voltage resolutions of 10 pA and 1 mV, respectively, were measured using an electrometer (Keithley K6430) and programmed by the LabVIEW software. The values of device resistances were calculated through a linear least square fit to the I_{ds}-V_{ds} curves near the zero bias at the back-gate voltage of 0 V and their standard deviation was evaluated to be less than 0.1 %. For acquiring temperature dependence of electrical properties, the NW devices were loaded into a cryostat (Variable Temperature Inert Cryostat, CRYO Industries of America Inc.) in 1 atm helium (99.99%). The temperature was precisely monitored within the range from 300 to 80 K using a LakeShore 340 temperature controller. On the other hand, the NW devices were also placed in a vacuum chamber for characterizing light- and gas- responses.

Table S1 Synthesis Conditions for PbS 1D NWs, 2D NSs and 0D NPs (including NCbs and NCOs)

	1D NWs	**2D NSs**	**0D NCbs**	**0D NCOs**
DPE	15 mL	15 mL	15 mL	15 mL
Pb-oleate	20 mL	20 mL	20 mL	20 mL
OAm	3 mL	3 mL	3 mL	3 mL
S-OAm/S-TOP	0/3 mL	0/3 mL	3/0 mL	3/0 mL
DCE	0	3 mL	0	3 mL
Temperature	180 °C	150 °C	200 °C	200 °C
Reaction Time	5.0 min	7.5 min	7.5 min	7.5 min

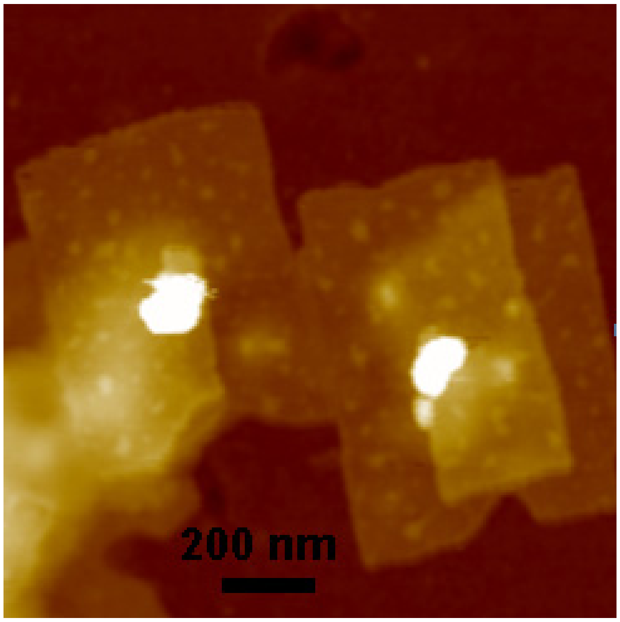

Figure S1. AFM image of PbS NSs spin-coated onto a crystalline Si substrate using a non-contact mode, showing a thickness of 5-7 nm.

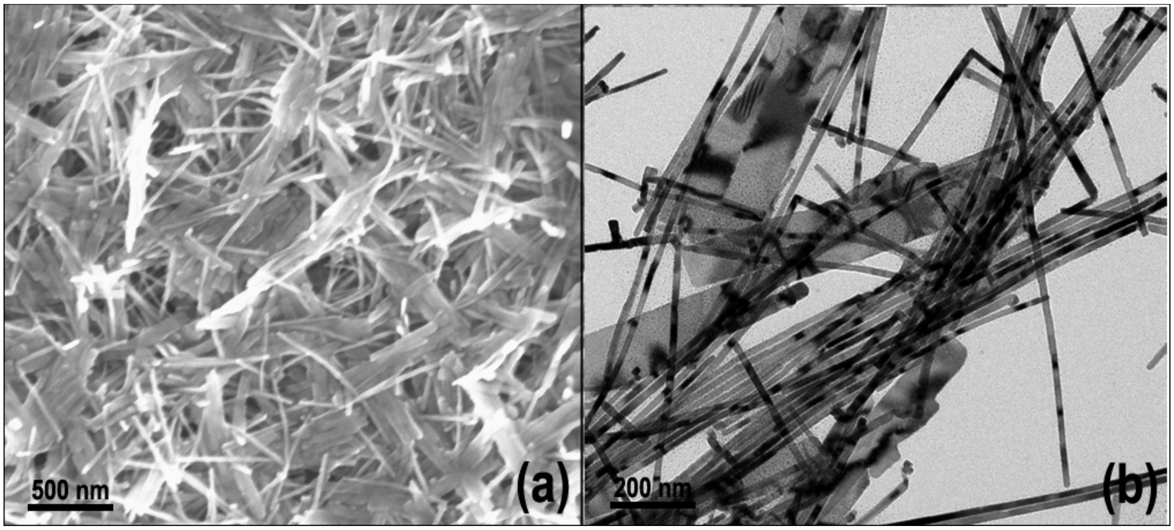

Figure S2. (a) SEM image of NWs synthesized without OAm; (b) TEM image of NWs together with some NSs synthesized with 0.3 mL of OAm.

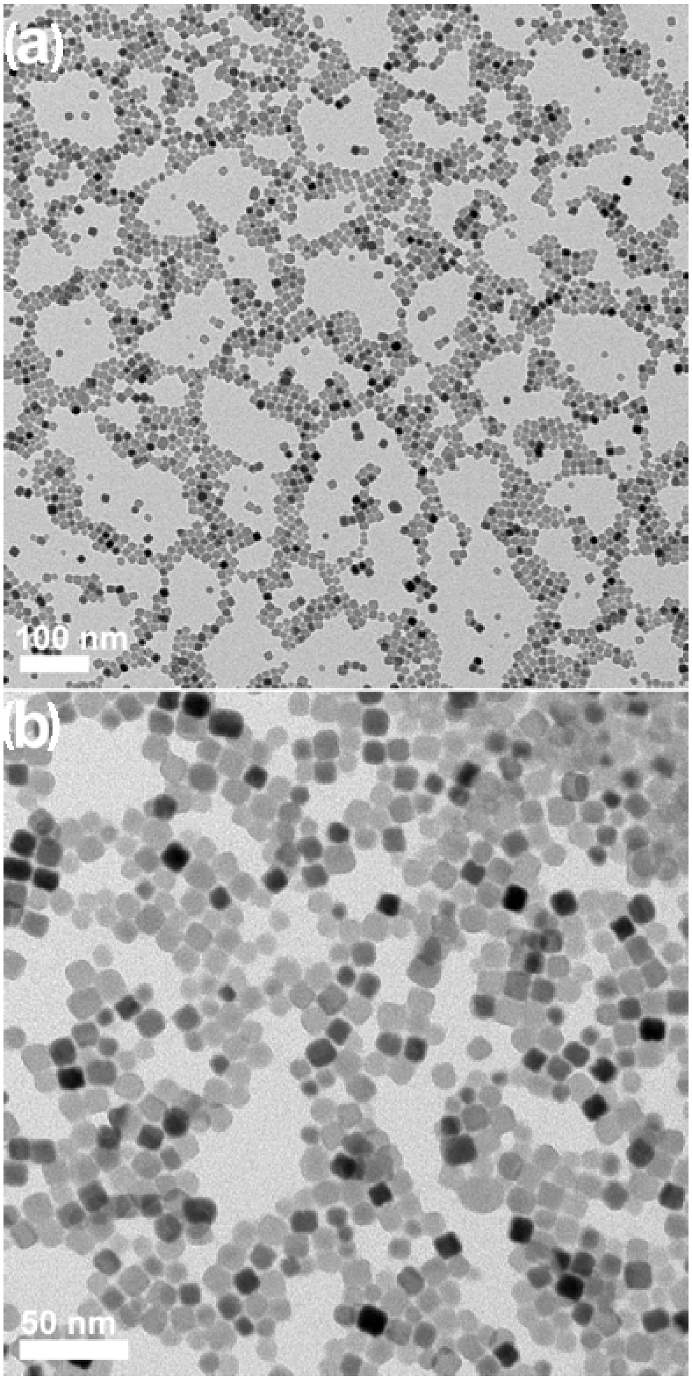

Figure S3. TEM images at different magnifications of PbS truncated NCbs grown for 7.5 min at 180 °C.