

Supporting Information

Shape Dependent Confinement in Ultrasmall Zero, One, and Two Dimensional PbS Nanostructures

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Synthesis and Experimental Methods:

All syntheses were carried out at or below 100°C in an oil bath with nitrogen purging in a one step bench-top procedure. In all cases, the ligand trioctylamine (TOA) (Aldrich, 98%) was placed in a test tube at 60 °C and held for 10 minutes at this temperature before adding lead xanthate salt. For the synthesis of spherical particles, 0.07g of lead ethylxanthate was added in one shot to the 3 ml of TOA at 60 °C with continuous stirring followed by annealing for 4 hours at the same temperature. The annealing was stopped when a dark yellow color appeared. For 1D rods, 0.065g lead hexadecylxanthate was added in one shot to 1.6 ml of trioctylamine at 65°C with continuous stirring under N₂. A grayish-milky color appeared after 5 minutes and then the temperature was increased to 80°C. Annealing was carried for 40 min at this temperature. For 2D sheets, 0.075 g of lead ethylxanthate were added to TOA at 60 °C and annealed for 10 min, while no color change has been observed. The temperature was then increased to 100 °C where a dark red wine color appeared after 5 minutes and annealing was carried out for 90 minutes. In each case, the PbS particles were collected at 60°C by flocculating the sample with a mixture of methanol and dichloromethane (4:1 by volume) and centrifuging three times at 2500 rpm for 3 min. All samples were then dried in air and redispersed in dichloromethane for various measurements. No additional post synthesis stages were carried out for the size and shape selectivity of these ultra-narrow structures. Materials were characterized using TEM (JEOL JEM-2100F field emission transmission electron microscope), and confocal Raman measurements were carried out in JOBIN YVON T64000 spectrophotometer with 514 and 644 nm laser lines.

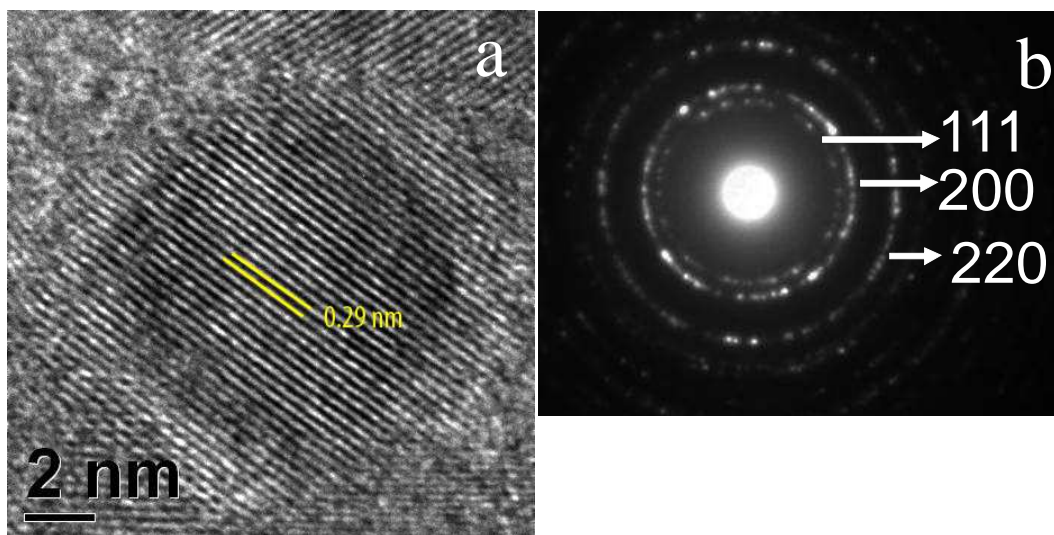


Fig. S1. (a) HRTEM image of PbS dots showing well resolved lattice planes of 0.29 nm spacing corresponding to PbS rock salt structure. (b) The selected area electron diffraction (SAED) pattern obtained from the PbS dots shows the rock salt cubic structure with 111, 200 and 220 diffraction rings, in line with the inter-planer distances of 0.342 nm, 0.297 and 2.099 of PbS bulk rock salt structure (JCPDS #05-0592).

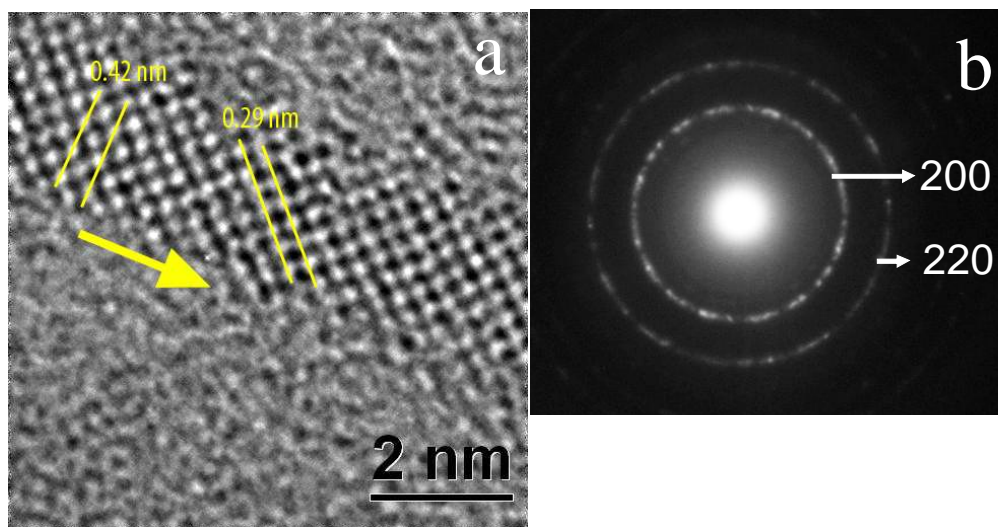


Fig. S2. (a) HRTEM image ultra narrow PbS rods showing core diameter of 1.7 nm with well resolved lattice planes of 0.29 nm and 0.42 nm spacing corresponding to PbS rock salt structure with the arrow indicates the long axis of the rod. (b) SAED pattern from the ultranarrow rods shows the rock salt cubic structure with predominant 200 and 220

diffraction rings, corresponding to the inter-planer distances of 0.297 and 0.210 nm of PbS bulk rock salt structure.

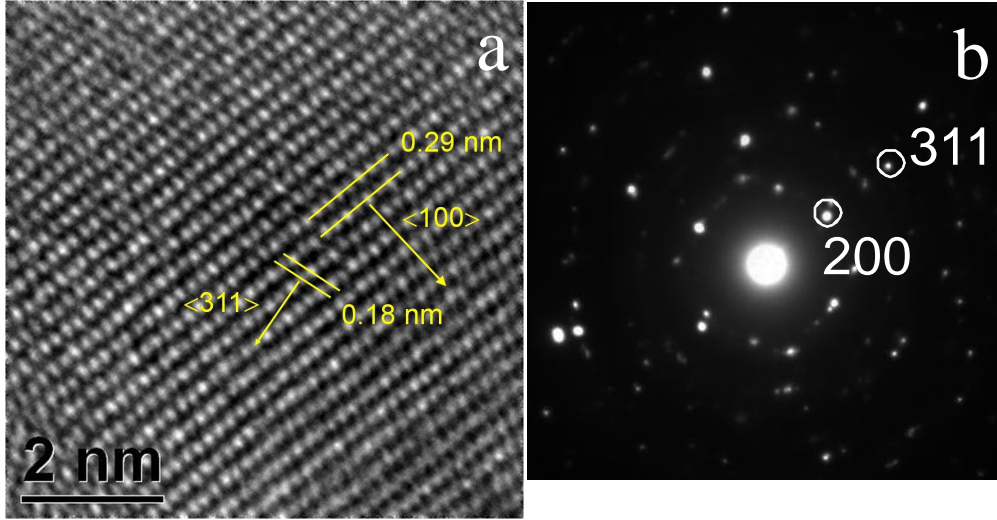
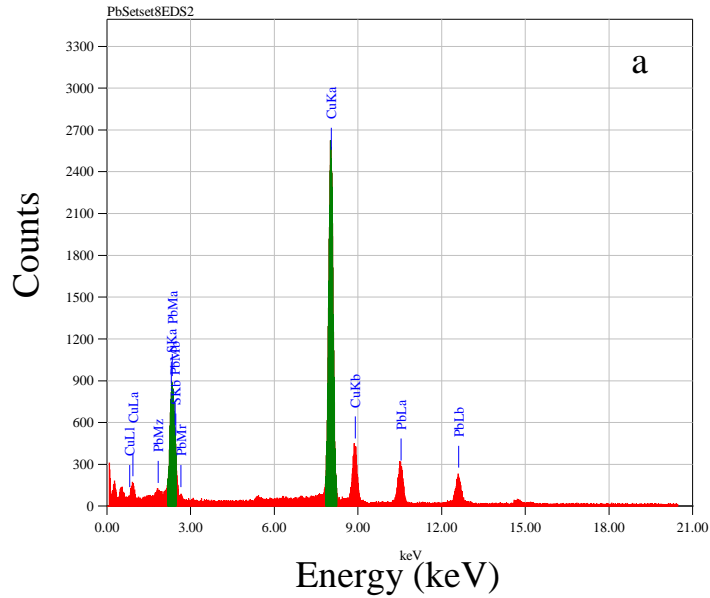
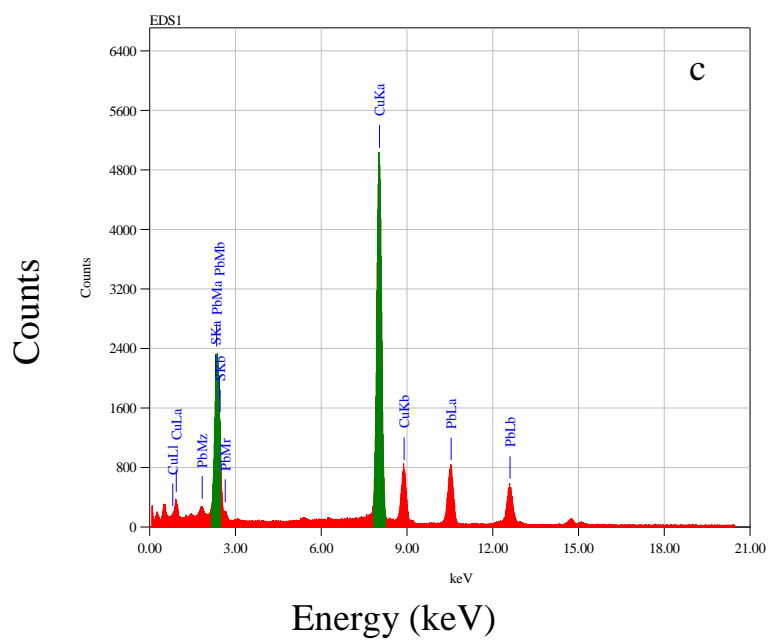
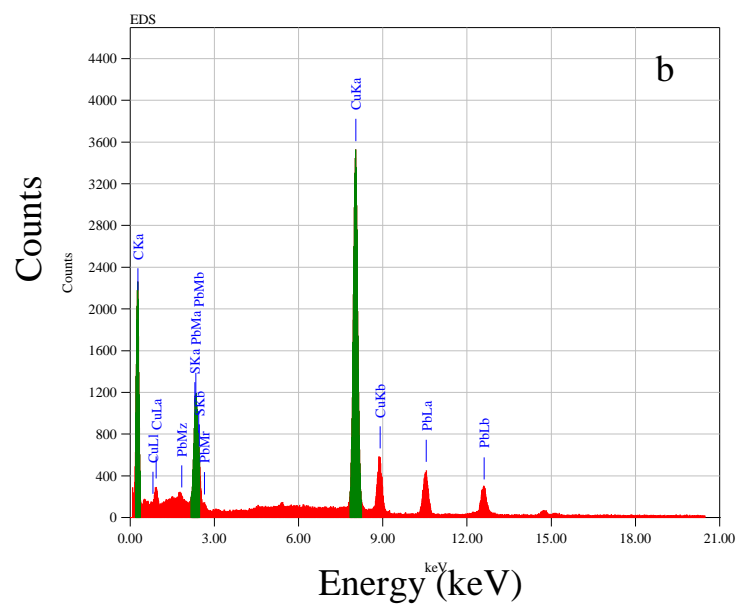


Fig. S3. (a) HRTEM image of PbS sheets showing well resolved lattice planes of 0.29 nm and 0.18 nm spacing corresponding to the (200) and (311) plane of PbS rock salt structure. (b) The SAED pattern with corresponding diffraction spots of predominant 200 and 311 diffraction, corresponding to the inter-planer distances of 0.29 and 0.18 nm of PbS bulk rock salt structure. The HRTEM image depicts two different d-spacings along <100> and <311> crystallographic directions, as indicated by the arrows.





Elements	0D Dots		1D Rods		2D Sheets	
	Pb	S	Pb	S	Pb	S
Atom %	42	58	47	53	46	54
Weight %	81	19	85	15	84	16

Fig. S4. Energy dispersive spectroscopy (EDS) elemental analysis spectra taken in the TEM for PbS a) 0D dots b) 1D rods and c) 2D sheets. The table lists the atom and weight percentage of Pb and S obtained for different structures.

Excitation 644 nm	1LO (cm^{-1})	2LO (cm^{-1})	3LO (cm^{-1})	4LO (cm^{-1})
Sheet	179	310	427	600
Rod	195	381	537	670
Dot	202	395	600	-

Excitation 514 nm	1LO (cm^{-1})	2LO (cm^{-1})	3LO (cm^{-1})	4LO (cm^{-1})
Sheet	178	290	430	600
Rod	195	383	552	-
Dot	202	425	600	-

Fig. S5. A tabular form of the peak positions with different excitation wavelength for 0D dots, 1D rods and 2D sheets.

Excitation Wavelengths→	644 nm	514 nm
2D Sheets	0.49 ± 0.03	0.70 ± 0.05
1D Rods	0.26 ± 0.05	0.55 ± 0.03
0D Dots	0.10 ± 0.05	0.34 ± 0.06

Fig. S6. A tabular form of experimental determination of Huang-Rhys parameter in the adiabatic approximation calculated from the intensity ratios of the first overtone to the fundamental frequency (2LO/1LO) for different nanoshapes after baseline correction.

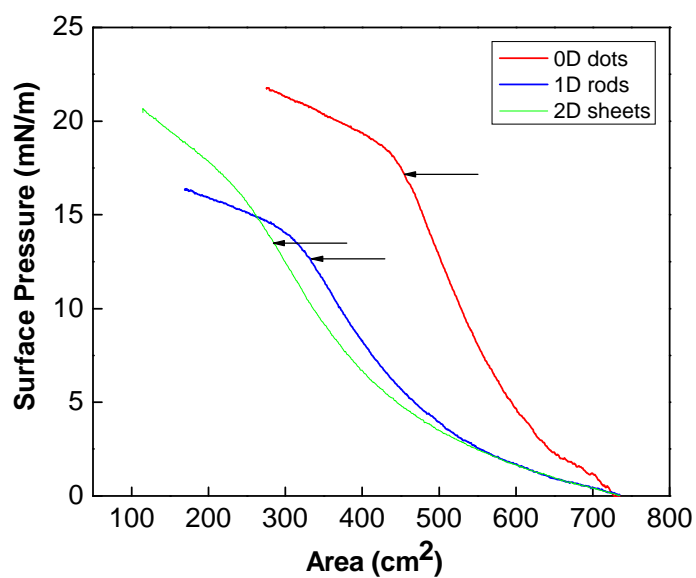


Fig. S7. Surface pressure versus area isotherms of PbS dots (red curve), rods (blue curve) and sheets (green curve) at temperature 21°C dispersed from dichloromethane. The arrows indicate the corresponding surface pressure of Z-type LB lifting.