

Supporting Information

Ultra Narrow PbS Nanorods with Intense Fluorescence

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Experimental Section:

For the synthesis of 1.7 nm rods, Leadhexadecylxanthate (0.065g) was added in one shot to 1.6 ml of trioctylamine (Aldrich, 98%) at 65°C with continuous stirring under N₂. A grayish-milky color appeared after 5 minutes. The temperature was then increased to 80°C. Annealing was carried for 40 min at this temperature. Finally the temperature was reduced to 70°C and the rods were collected by washing two times with methanol (centrifuged at 3000 rpm for 3 min) and finally with mixture of dichloromethane and methanol (5:40 by volume) to remove excess surfactants.

The BF and DF TEM measurements were carried out in JEOL JEM-2100F field emission electron microscope. The optical spectra were measured using JASCO V570 for UV-vis and Fluorolog 3, Jobin Yvon for PL. For, confocal microscopy, the images were taken with 672 mS CCD integration time with NIKON confocal microscope (Eclipse TE2000-U). The image was taken with 330-380 nm excitation and 400-420 nm emission collection. For spin cast samples, we have put 7 drops ($7 \times 10 \mu\text{L}$) of 10^{-1} to 10^{-6} M suspension on different substrates rotating at different rotation per minutes (rpm, 300-3000/min). Confocal Raman measurements were carried out in JOBIN YVON T64000 with 514 and 644 nm laser lines.

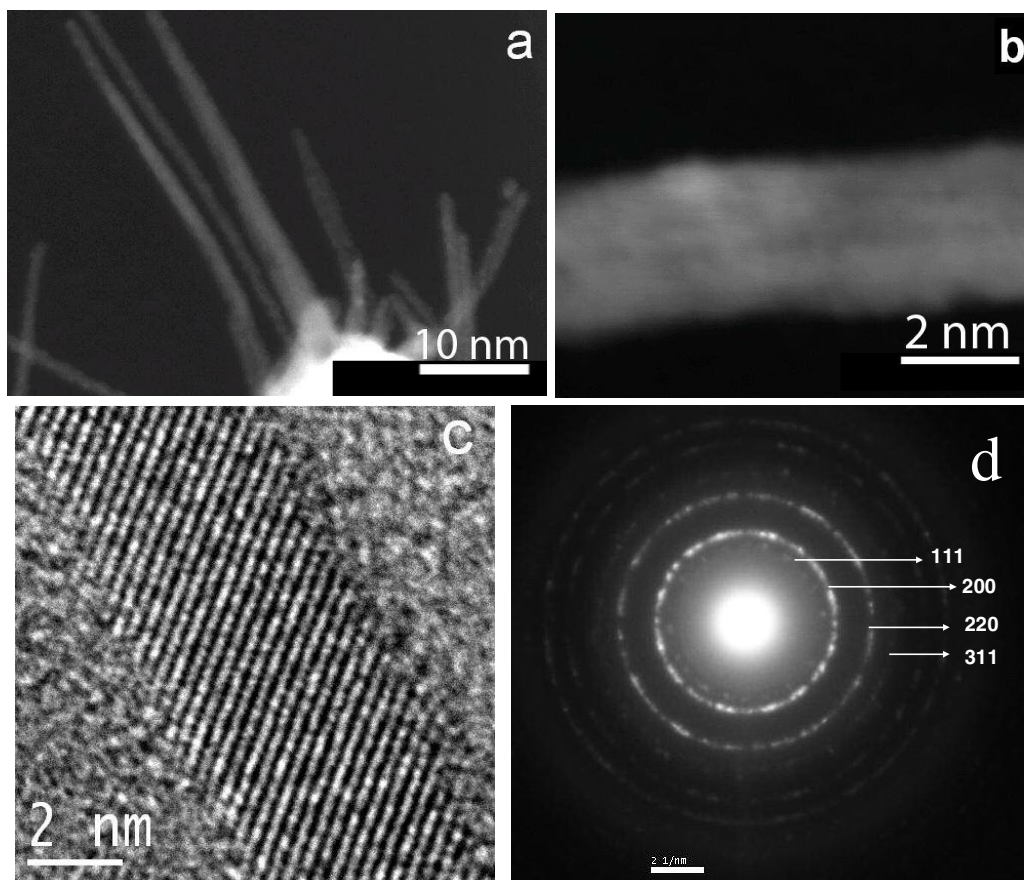
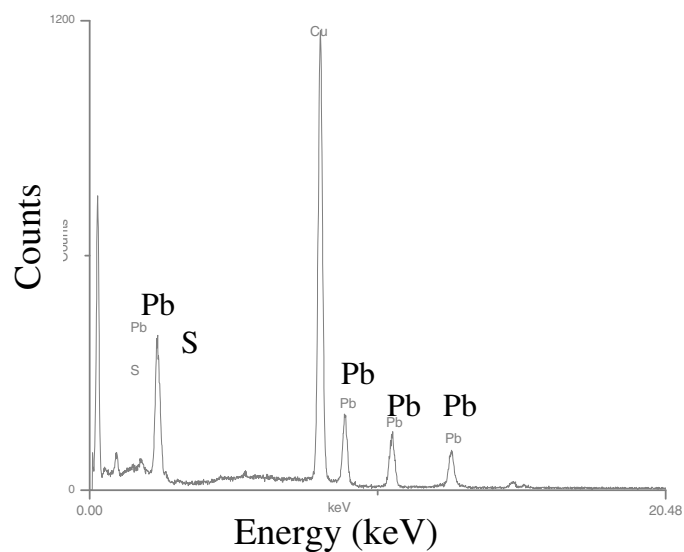


Fig. S1. We have controlled the sizes (aspect ratio) of the nanorods in a relatively straightforward way using the same amount of precursor injected at relatively higher temperature (90°C). For, 2.5 nm rods, the same amount (0.065g) of precursor was injected at 90°C. The color turned red immediately and annealing was carried out for 15 minutes. Finally the temperature was reduced to 70°C and the rods were collected by washing two times with methanol (centrifuged at 3000 rpm for 3 min) and finally with mixture of dichloromethane and methanol (5:40 by volume) to remove excess surfactants.

Fig. a-c shows the DF and BF TEM images of the TOA coated rods of 40-50 nm in length and 2.5 ± 0.3 nm in diameter. The HRTEM (Fig. c) of individual rods shows well-resolved lattice planes with an inter-planar distance of 0.29 ± 0.02 nm, consistent with the (200) d-spacing PbS bulk rock salt structure, which is identical to 1.7 nm rods.

The SAED patterns obtained from the 2.5 nm PbS rods (Fig. d) shows the rock salt cubic structure with 111, 200, 220, and 311 diffraction rings, in line with the inter-planer distances of 0.342 nm, 0.2969, 2.099 and 1.790 nm of PbS bulk rock salt structure (JCPDS 05-0592) and similar as 1.7 nm rods. The interplanar distance 0.29 ± 0.03 nm observed in HRTEM corresponds to the (200) plane of PbS rock salt structure. The strongest intensity of the 200 reflection indicates a preferred orientation in which the rods are oriented with the [100] crystallographic axis.

The bigger rods show lesser degree of confinement in comparison to the smaller rods owing to its larger diameter (not reported here). In addition to significant broadening, the slope of the absorption onset steepens with decrease in particle diameter. We attribute the spectral broadening as a result of different degree of confinement in two rod systems as evidenced from the ratio of r/a_B . The comparison of detail spectral properties and differences in other physical properties between these two different sized rods will be reported separately in a follow-up work with detail theoretical explanations.



Elements	1.7 nm rods		2.5 nm rods	
	Pb	S	Pb	S
Atom %	47	53	44	56
Weight %	85	15	82	18

Fig. S2. Energy dispersive spectroscopy (EDS) elemental analysis spectra taken in the TEM of PbS 1.7 nm diameter rods. The 2.5 nm diameter rods also exhibit the same EDS spectrum. The table lists the atom and weight percentage of Pb and S obtained for both types of rods.

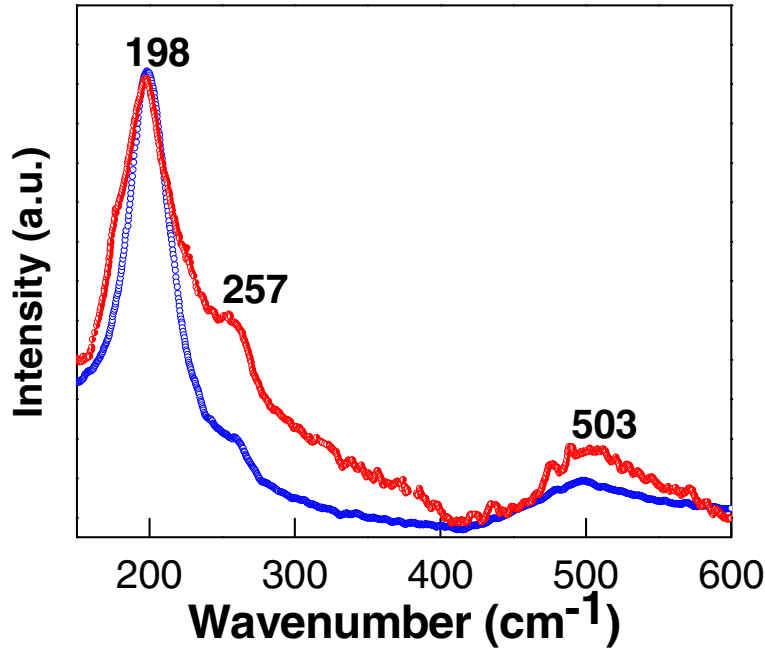


Fig. S3. Raman spectra with 644 nm excitation for powder of 1.7 nm rods (red curve) and 2.5 nm rods (blue curve). The phonon confinement is reflected in size controlled rods in the confocal Raman spectroscopy. The exciton-phonon coupling via Fröhlich interaction of vibrational modes appears at 198 cm^{-1} (angular momentum $lp=0$). Significant narrowing of the 198 cm^{-1} band is observed for the $\sim 2.5\text{ nm}$ rods. The 1.7 nm rods show considerable broadening in comparison to the 2.5 nm rods, as expected for higher degree of confinement with smaller dimension. In addition, the narrow rods has a reproducible shoulder at $\sim 180\text{ cm}^{-1}$ corresponding to fourth-lowest eigen mode with $lp=0$. The shoulder is absent for big rods suggesting lack of surface component modes with $lp \geq 1$ and thus testifying the prediction that the coupled mode frequencies are particle size dependent. Significantly, no spectral shift or photo-destruction has been observed with longer acquisition time ($\sim 3\text{ hour}$), suggesting stability of the rods under laser heating, which is advantageous in applications.