

Electronic Supplementary Information (ESI†)

Synthesis and Metallic Probe Induced Conductance of Au Tipped Ultranarrow PbS Rods

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Experimental Details

Chemicals: Hexadecanol, carbondisulfide, lead nitrate, trioctylamine (TOA) and hydrogen tetrachloroaurate(III) (HAuCl₄) were purchased from Aldrich and used without further purification. All the solvents used in this work were purged with dry nitrogen for few minutes before starting a reaction.

PbS rod synthesis: For the synthesis of 1.7 nm diameter PbS rods, lead hexadecylxanthate was prepared using hexadecanol and carbondisulfide and added (0.065g) in one shot to 1.6 ml of TOA 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 minutes at 80°C. Finally the temperature was reduced to 50°C and the rods were collected by washing two times with methanol (centrifuge at 3000 rpm for 3 min) and finally with mixture of dichloromethane and methanol (5:40 by volume) to remove excess TOA.

Au-PbS rod synthesis: The ultra narrow PbS rods prepared by above mentioned route was dried in ambient conditions and a stock suspension of 1mg/ml was prepared in toluene. In a separate test tube, HAuCl₄ of 1.2 mM in methanol was prepared in ice bath. Both PbS suspension in toluene and HAuCl₄ in methanol was kept in ice bath before mixing. Then, 3 ml PbS nanorod suspension was added to the 0.6 ml of HAuCl₄ in a separate test tube in ice bath with medium stirring. The stirring was continued for 90 minutes for metal deposition. The bright field and dark field TEM measurements were carried out in JEOL JEM-2100F field emission electron microscope.

Theoretical calculations

The electronic structure of isolated PbS nanorod cluster, Au cluster and Au-PbS-Au heterostructure are calculated using density functional theory (DFT) as implemented in Gaussian 03 software.¹ The hybrid functional B3LYP is used along with 6-31⁺⁺G** basis-set for S atoms and Lanl2DZ² basis-set with effective core potential is used for Au and Pb atoms.^{3,4} The hybrid functional B3LYP has been widely used for systems containing metal atoms and is known to give results which match well with experimental data.^{5,6} The nature and the energies of the frontier molecular orbitals, especially the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their energy difference (HOMO-LUMO gap) are analyzed to understand the electronic transport pathways.

To model the electronic transport, the nanorod is covalently connected to two gold electrodes forming a stable symmetric two-probe junction. This system closely resembles the experimentally synthesized PbS nanorods with two gold deposited tips.

The structure of the model nanorod ($\text{Pb}_{32}\text{S}_{32}$) for theoretical calculations is taken according to the experimentally obtained nanorod lattice parameters without relaxation. We have also theoretically studied a smaller sized $\text{Pb}_{20}\text{S}_{20}$ nanorod which gives very similar electronic structure and transport results. The electronic transport through the nanorod in a Au-PbS-Au based two probe molecular junction is calculated using ATK software,⁷ which combines non-equilibrium Green's Function (NEGF) formalism and DFT. The DFT implementation uses numerical atomic basis set to solve the Kohn-Sham equations.⁸⁻¹⁰ For the two-probe study, double zeta polarized basis-set is used for PbS and single zeta polarized basis-set for electrode gold atoms with GGA-PBE functional for the exchange correlation method. The transport studies consists of two $(111)_{\text{Au}}$ electrodes on both sides, with $\text{Pb}_{32}\text{S}_{32}$ connected in between. The interaction region consists of $\text{Pb}_{32}\text{S}_{32}$ along with a portion of the electrodes containing six 3×3 layers of gold atoms so that screening approximations hold good. The sulfur atoms of PbS form covalent bonds with the Au electrodes with Au-S distance of 2.5 Å, thus creating two identical junctions at the two ends of the nanorod. The transmission spectrum is obtained from the equation,

$T(E,V) = \text{Tr}[\Gamma_L(E,V)G(E,V)\Gamma_R(E,V)G^+(E,V)]$ where $\Gamma_{L(R)}$ stands for the coupling matrix between the left and right electrodes and the scattering region. $G(E,V)$ is the retarded Green's function of scattering region. The current through the junction can be obtained from

$$I(V) = \frac{2e}{h} \int T(E,V) [f(E - \mu_L) - f(E - \mu_R)] dE, \text{ where } f(E - \mu_{L(R)}) \text{ is the}$$

Fermi function and $\mu_{L(R)}$ is the chemical potential of the left/right electrode. Finally, for all cases, the transmission spectrum with 6×6 k-points is calculated and the zero-bias conductance is obtained from the transmission at Fermi energy. Generally, the transmission peaks in the transmission spectrum can be correlated to the molecular orbitals of the bridge nanorod, which have been modified in presence of electrodes. These modified states are obtained using the Molecular Projected Self-consistent Hamiltonian (MPSH).⁷ Those MPSH energy states which are spatially delocalized throughout the scattering region with significant electron densities on the terminating atoms, and have overlapping with semi-infinite bulk electrodes at the ends, give peaks in the transmission spectrum. Prominent transmission peaks on either side of the electrode

Fermi energy are observed in the transmission spectrum which serves as conduction pathways. When the nanorod is covalently connected to gold electrodes, the nanorod states align with the Fermi energy of gold electrode and thus the energies are reported relative to Au Fermi energy in the transmission spectra.

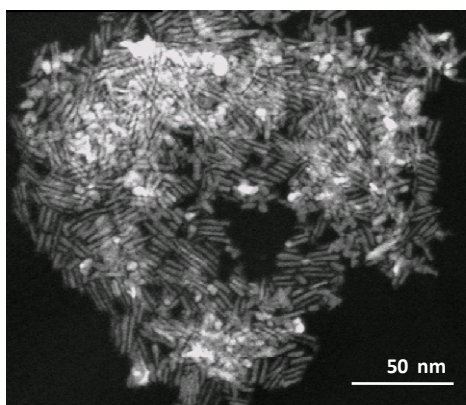


Fig. S1 Dark field TEM images of ultra narrow PbS rods of 1.7 nm diameter and 10-12 nm in length. The size and shape of these initial PbS rods are tightly preserved after Au deposition (Figure 1a of the manuscript).

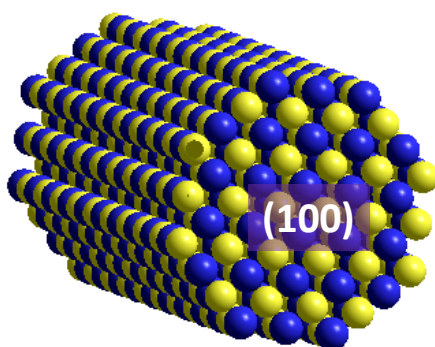


Fig. S2 Reconstructed structure of PbS nanorod with $4 \times 4 \times 10$ unit cells. The blue and yellow balls represent lead and sulfur atoms respectively. The crystallographic

parameters have been extracted from HRTEM with rock-salt structure, showing the $\langle 100 \rangle$ crystallographic axis is along long axis of the rod. This implies that the ends of the nanorods are terminated by mixed $\{100\}$ facets consisting of both Pb and S atoms.

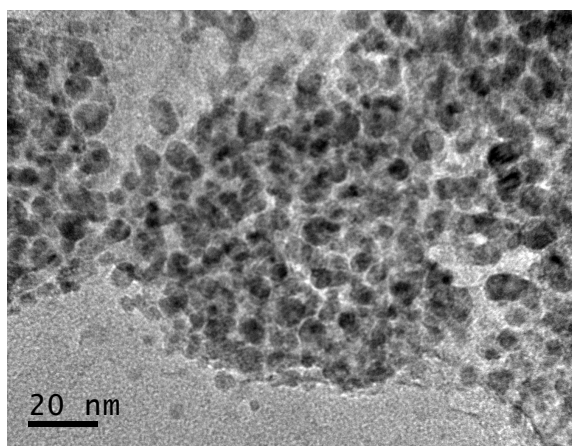


Fig. S3 TEM images of PbS nanorods when attempting to reduce Au^{3+} to Au^0 using strong reducing agent NaBH_4 . A solution mixture of HAuCl_4 and PbS was prepared first using the method described in the manuscript in ice bath. NaBH_4 (1 mM) in methanol was added to this mixture as reducing agent. The TEM image shows that the size and shape of the PbS rods are destroyed after NaBH_4 treatment.

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