# Mapping Charge Distribution in Single PbS Core – CdS Arm Nano-Multipod Heterostructures by Off-Axis Electron

# Holography

Rajesh Chalasani<sup>†,|</sup>, Alexander Pekin<sup>‡,§</sup>, Alexander Rabkin<sup>‡,§</sup>, Ran E. Abutbul<sup>‡,§</sup>, Oswaldo Diéguez<sup>†,†</sup>, Yaron Kauffmann<sup>⊥</sup>, Yuval Golan<sup>\*,‡,§</sup> and Amit Kohn<sup>\*,†,I</sup>

<sup>†</sup>Department of Materials Science and Engineering, Tel Aviv University, Ramat Aviv, Tel Aviv 6997801, Israel.

<sup>1</sup>Research Center for Nanoscience and Nanotechnology, Tel Aviv University, Ramat Aviv, Tel Aviv 6997801, Israel.

<sup>\*</sup>The Raymond and Beverly Sackler Center for Computational Molecular and Materials Science, Tel Aviv University, Ramat Aviv, Tel Aviv 6997801, Israel

<sup>\*</sup>Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

<sup>§</sup>Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

<sup>1</sup>Department of Materials Science and Engineering, Technion - Israel Institute of Technology, Haifa 32000, Israel.

#### **Corresponding Authors**

\*E-mail: ygolan@bgu.ac.il, akohn@tauex.tau.ac.il

# **Supporting Information**

#### Materials and methods:

*Materials:* Octadecyl amine (ODA) (Aldrich, 99%), potassium ethyl xanthogenate (Fluka, 98%), cadmium perchlorate hydrate (Aldrich) and lead perchlorate trihydrate (Aldrich, 98%) were used as received. ODA was stored under argon and sealed with parafilm to prevent reaction with CO<sub>2</sub>. Methanol (Bio-lab, absolute) and chloroform (Bio-lab, stabilized with amylene) were used as received without any further purification. Deionized water (resistivity 18.2 M $\Omega$ ·cm) was obtained from a Millipore filter system.

*Metal Ethylxanthate Synthesis:* Cadmium ethylxanthate and lead ethylxanthate were prepared separately by dissolving 3.00 g potassium ethyl xanthogenate in 400 ml of water and the metal perchlorate hydrate (2.913 g of cadmium perchlorate hydrate for Cd-ethylxanthate, 4.305 g of lead perchlorate trihydrate for lead-ethylxanthate) in 100 ml of water. Both the solutions were mixed together and metal xanthate salt precipitated out. The precipitate was washed 5 times with water, filtered and dried in air.

*PbS–CdS NMHs synthesis:* NMHs were prepared in a simple glass test tube placed in silicone oil bath. Cadmium-ethylxanthate (0.046 g) and lead-ethylxanthate (0.059 g) were added to 1.53 g of molten octadecyl amine at 70°C and the reaction mixture was allowed to stir for 30 minutes. The PbS–CdS NMHs were purified by centrifuging with methanol and chloroform mixture.



Figure S1. TEM images of NMHs synthesized at (a) 70° C and (b) 120° C



**Figure S2**. (a) Aligned TEM images series of PbS-CdS NMH and (b) power spectrum corresponding to one of the images in series. (c) Parameters used for exit-wave reconstruction. Rectangular in (a) denotes area of interest and white circle in (b) indicates objective aperture in reciprocal space.



**Figure S3**. (a) The phase of the exit wave reconstructed from a focal series of aberration corrected HRTEM images of a PbS–CdS core-arm NMH. (b) Power spectrum calculated from the area shown schematically by the red square in (a). (c) Reconstructed image using the frequencies of the reflections marked by red circles in (b). (d) Image intensity variations in (c) along the direction denoted by the red arrow in the region of the blue rectangle from which interplanar distances are extracted.

#### **Density Functional Theory-Methodology**

We used the Perdew-Burke-Ernzerhof exchange-correlation functional adapted to solids (PBEsol).<sup>S-1</sup> Our basis set contained plane waves with a kinetic energy cutoff of 500 eV. We imposed periodic boundary conditions in all simulation cells, built using at least 6 pairs of metal-sulfur layers of CdS and/or PbS stacked along the (0001)/(000-1) direction of wurtzite and the (111) direction of rocksalt; the in-plane lattice vectors joined first and second nearest-neighbor metals, respectively. For calculations in reciprocal space we used a 8×4×1 Mohkhorst-Pack<sup>S-2</sup> grid. The ionic cores were handled using the projector-augmented wave method,<sup>S-3</sup> solving for the 3s and 3p electrons of S; the 4d and 5s electrons of Cd; and the 5d, 6s, and 6p electrons of Pb. When optimizing crystal structures, relaxations were carried out until the forces on the atoms were below 0.03 eV/Å. In order to simulate the PbS–CdS interface, we used a periodic supercell with 8 double layers of CdS on top of 8 double layers of PbS (64 atoms), surrounded by around 10 Å of vacuum (adding more vacuum did not change our results). The in-plane lattice parameters were fixed to reproduce bulk PbS, so that the CdS is epitaxially constrained on it.

#### **TEM-EDS analysis of PbS-CdS NMH**

The Cd to S ratio in the nanostructure arm was evaluated by energy dispersive X-ray spectroscopy (EDS) in a scanning TEM (STEM).<sup>S-4</sup> Spectrum images (SI) of several nanostructures were acquired to measure the Cd L<sub> $\alpha$ </sub> and S K<sub> $\alpha$ </sub> X-ray photons with high spatial resolution. EDS measurements were carried using FEI Super-X detectors with a combined area of 120mm<sup>2</sup>, at 80 kV with a probe size of approximately 0.1nm and an overall dwell time of around 0.3msec per pixel

Due to low count statistics, spectra were added from several CdS arms. Assuming that the composition within and between CdS arms are homogeneous the spectra were combined as shown in Figure S4. The background signal at these energies was removed by a linear approximation, and Gaussian peaks were fitted to the characteristic X-ray peaks (Figure S5). The integral intensities of these peaks were applied to the Cliff-Lorimer equation using K ratios supplied by the manufacturer of the detectors in order to calculate the Cd:S atomic ratio, which was determined at 55.2: 44.8 with an error of 2.4% (Table S1).



Figure S4. (a)-(c) EDS spectrum imaging (SI) of PbS-CdS NMHs.



Figure S5. EDS spectrum of CdS arms obtained by adding spectra measured from different arms.

**Table S1.** Relative atomic% composition of Cd and S in the CdS arm calculated from energy dispersive spectra.

Characteristic X- rays	Energy (keV)	Integral counts	Error %	Atom %
S Κα	2.307	860	2.4	44.8
Cd La	3.133	1057	2.2	55.2





**Figure S6-S8.** (a) Reconstructed phase of the electron wave from a hologram of a PbS-CdS NMH. (b) Averaged reconstructed phase values and relative thickness from 10 holograms following correction for sample drift. Arrow in (a) shows direction of the phase profile from the region marked schematically by the white rectangle. (c) Conversion of phase variation to potential with respect to vacuum for the region marked between blue dashed lines in (b). (d) Potential variations after subtracting the MIP measured from individual PbS and CdS particles from their corresponding regions in (c).

	Built-in potential	Potential drop	Electric field due to potential drop
Particle 1	500 mV	1.6 V	1.7 MV/cm
Particle 2	400 mV	1.2 V	1.0 MV/cm
Particle 3	500 mV	1.3 V	1.4 MV/cm

Table S2. Built-in potential values of PbS-CdS NMHs



**Figure S9.** (a) Reconstructed phase of the electron wave from a hologram of a PbS-CdS NMH. (b) Phase change values near the particle on the ultrathin amorphous carbon supporting film. The arrow in (a) shows the direction of the phase profile obtained from the region marked by the blue rectangle.



**Figure S10**. (a) and (b) are reconstructed phase of the electron wave for NMH when the sample is tilted to  $0^{\circ}$  and  $10^{\circ}$ , respectively. (c) Phase profile across the NMH at  $0^{\circ}$  and  $10^{\circ}$  tilt angles. The arrows in (b) and (c) show the direction of phase profile from CdS arm to PbS core from the region marked schematically by the red rectangle.



**Figure S11**. (a) Elastic, zero energy-loss filtered bright-field TEM image of PbS–CdS corearm NMH and (b) the corresponding relative thickness map. (c) Relative thickness values of the NMH. The arrow in (b) shows schematically the direction of thickness values from the CdS arm to the PbS core in the region denoted by the blue rectangle.

#### **COMSOL** calculations:

The materials in the model are defined by their characteristic properties such as dielectric constant, band gap, electron affinity, and density of states.

In the first step, the "Semiconductor" module calculated the electrostatic potential by solving Poisson's equation for an unbiased NMH. We defined a boundary condition in which the bottom side of the particle is grounded representing the electrical conductivity of the supporting ultrathin carbon film of the TEM grid.

In the second step, three-dimensional simulations of electrostatic potentials around the particle, namely the formation of fringing fields, were calculated by solving Poisson's equation applied to dielectric materials in the "AC/DC module". The electrostatic potential around the particle was calculated in a vacuum region of  $100 \times 100 \times 75$  nm<sup>3</sup>. The boundary conditions included zero charge boundary condition, used for treating the insulating surface of the particle. All sides of the

cube representing vacuum around the particle are grounded to indicate zero fringing fields far from the particle. The electrostatic potential obtained from the previous Semiconductor model was used as source for the calculation of fringing fields.

### **Bethe-Bloch equation:**

The magnitude of charge carrier generation rates for electrons  $(G_n)$  and holes  $(G_p)$  were estimated by the Bethe-Bloch equation, which determines the energy loss, E, of the fast electron as a function of the penetration depth, *x*, into the material.<sup>S-5,S-6</sup>

$$-\frac{dE}{dx} = Kx \frac{\rho Z}{A} \frac{1}{\beta^2} \left( \frac{1}{2} \ln \frac{2m_e c^2 \beta^2 \gamma^2 E}{I^2} - \beta^2 - \frac{\delta}{2} \right)$$
(1)

Where Z is the atomic number, A is the atomic weight,  $\rho$  is the density of the material, c is the speed of light,  $m_e$  is the electron mass, E is accelerating voltage of the electrons, I is the electronhole pair creation energy,  $\beta$  is velocity of the incident particle divided by c,  $\gamma = E/m_0c^2$ ,  $\delta/2$  is the mass density correction for high particle energies.<sup>8-7</sup> The value of K is a constant given by

$$K = 2\pi N_A r_e^2 m_e c^2 = 0.1535 \left[ \frac{MeV \cdot cm^2}{g} \right]$$
(2)

Where  $N_A$  is the Avagadro Number and  $r_e$  is the classical radius of an electron:

$$r_e = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{m_e c^2} \qquad (3)$$

For an electron beam current density  $j_{BC}$  (1.2 pA/cm<sup>2</sup>) and sample thickness *t* (thickness of PbS and CdS are 13 nm and 5.5 nm, respectively), the electron hole pair generation rate can be calculated by:

$$G_n = G_p = \frac{j_{BC} \left| \frac{dE}{dx} \right|}{eI} \qquad (4)$$

The above equation is based on the assumption that all the energy goes to electron hole generation without competing mechanisms, for example plasmons. Since CdS and PbS are direct band gap semiconductors, we assume that the majority of the energy loss is due to electron hole generation.

## **References:**

- S-1. Perdew, J. P.; Ruzsinszky, A. Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.;
  Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* 2008, 100, 136406 1-4.
- S-2. Monkhorst, H. J.; Pack, J. D. Phys. Rev. B 1976, 13, 5188-5192.
- S-3. Blöchl, P. E.; *Phys. Rev. B* **1994**, *50*, 17953-17979.
- S-4. Kovács, A.; Schierholz, R.; Tillmann, K. *Journal of large-scale research facilities*2016, 2, A43 1-4.
- S-5. Houben, L.; Luysberg, M.; Brammer, T. Phys. Rev. B 2004, 70, 165313 1-8.
- S-6. Metcalfe, J.; Mejia, I.; Murphy, J.; Quevedo, M.; Smith, L.; Alvarado, J.;
  Gnade, B.; Takai, H. *arXiv preprint*, **2014**, arXiv:1411.1794.
- S-7. Sternheimer, R. M. Atomic data and nuclear data tables, 1984, 30,261-271.