

Supporting Information for

Temperature-Dependent Hall and Field-effect Mobility in Strongly Coupled All-Inorganic Nanocrystal Arrays

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Chemicals and substrates. Indium(III) chloride (InCl_3 , anhydrous, powder, 99.999%, Aldrich), indium(III) selenide (In_2Se_3 , powder, 99.99%, Alfa Aesar), selenium (powder, 99.99%, Alfa Aesar), copper(I) sulfide (Cu_2S , 99.99%, anhydrous, Aldrich), and sulfur (powder, 99.998%, Aldrich) were used as purchased. Tris(trimethylsilyl)arsine ($(\text{TMS})_3\text{As}$) was prepared as detailed in the literature.¹ Hydrazine (98%, anhydrous, Aldrich) was purified by distillation, then stored and handled inside a nitrogen-filled glovebox. Glass substrates (Fisherbrand®, thickness = 1 mm) were purchased from Fisher Scientific and cleaned with an aqueous detergent solution, acetone, and iso-propanol. The substrates were then blown with N_2 before use. $\langle 100 \rangle$ -oriented, n -doped silicon (Si) wafers (resistivity = 0.001–0.005 Ωcm , thickness = 525 ± 25 μm , and $C_i = 10.0$ nF/cm^2) coated with 300 nm of thermal oxide (SiO_2) growth were purchased from Silicon Inc. These were cleaned with a piranha treatment, rinsed with DI water, and blown with N_2 before use.

Synthesis of InAs colloidal nanocrystals. 2g of TOP was heated to 300°C under N_2 while being vigorously stirred magnetically. One mL stock solution of InCl_3 and $(\text{TMS})_3\text{As}$ in TOP (see below) was swiftly injected to promote NC growth and the temperature was maintained at 260°C. To monitor NC growth, we measured the absorption spectra of the aliquots extracted from the reaction solution. Growing large InAs NCs required an additional solution injection. The reaction was stopped and cooled to room temperature once the desired size was reached. Then the

solution was transferred into a glovebox and anhydrous toluene was added to the reaction solution. Adding methanol to the solution isolated the InAs NCs. The solution was then put through a centrifuge and re-dissolved into toluene. A typical reaction usually has a size distribution of approximately $\pm 15\%$. Monodisperse InAs NCs were obtained by using size selective precipitation with toluene (solvent) and methanol (nonsolvent).

Stock solution for InAs NC synthesis. 3.5g of InCl_3 was dissolved into 10g of TOP under N_2 at 260°C while being stirred. The solution was cooled down to room temperature and transferred into a glovebox. The stock solution was prepared by mixing InCl_3 -TOP solution and $(\text{TMS})_3\text{As}$ with In:As in a molar ratio of 3:2.

Calculation of NC size. The diameter (d) of a synthesized InAs NC was calculated based on the first excitonic peak position (x) using the following equation:²

$$d = 0.00000196x^{2.08} = 5.3 \text{ nm} \quad (\text{S1})$$

Composition of a $(\text{N}_2\text{H}_5)\text{Cu}_7\text{S}_4$ MCC ligand. It is known that copper sulfide can form multiple anionic chalcogenidometallate compounds³ and the actual composition of this MCC ligand can vary (e.g., between $(\text{N}_2\text{H}_5)\text{Cu}_7\text{S}_4$ and $(\text{N}_2\text{H}_5)_2\text{Cu}_6\text{S}_4$).^{4,5}

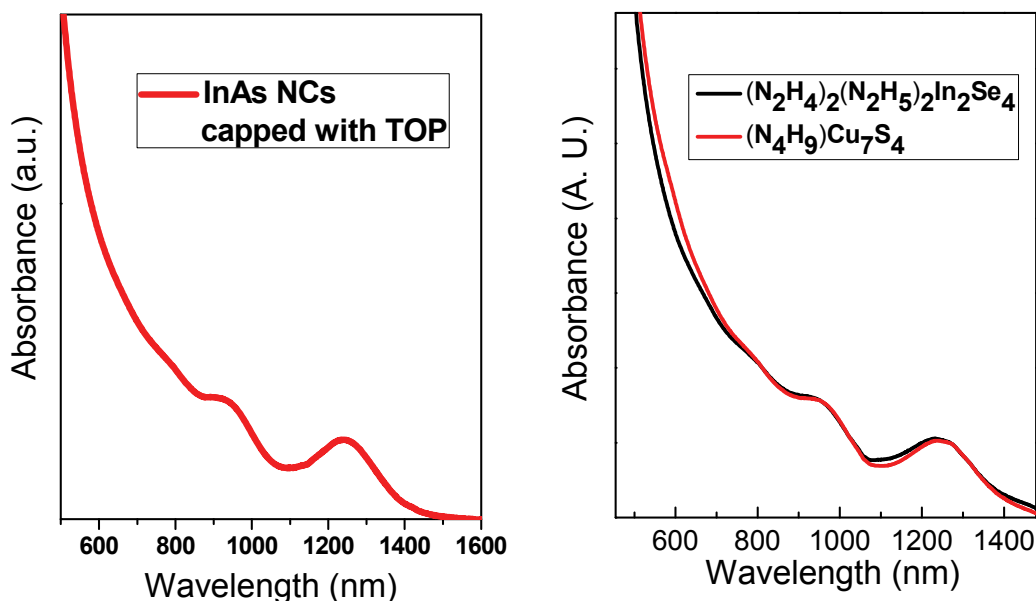


Figure S1. Absorption spectra of InAs NCs capped with TOP in toluene and capped with $(\text{N}_2\text{H}_5)\text{Cu}_7\text{S}_4$ or $(\text{N}_2\text{H}_4)_2(\text{N}_2\text{H}_5)_2\text{In}_2\text{Se}_4$ in hydrazine.

Electrical measurement. All electrical measurements were performed in a physical property measurement system (PPMS, Quantum Design) under He-filled inert atmosphere. Hall and VDP conductivity measurements were performed using a Keithley multimeter (Keithley 2400) controlled by a LabVIEW interface. FET measurements were performed using a Keithley multimeter (Keithley 2636A) controlled by a LabVIEW interface.

Parameter calculation. Hall mobility (μ_H) and concentration (n_H) were calculated from the following equations by fitting experimental data:⁶

$$\mu_H = \frac{h\sigma}{BI} |V_H|, \quad n_H = \frac{BI}{eh} \frac{1}{|V_H|} \quad (S2)$$

where I , B , σ , and h are the applied current, magnetic field, conductivity, and film thickness, respectively. The V_H values, measured from 4 different contact configurations, were averaged to calculate μ_H and n_H .

We have measured several devices with an optimized NC film thickness for each type of surface ligands and those devices showed consistent μ_H and n_H values. We also run consecutive measurements on the same sample stored inside PPMS overnight at zero field and observed excellent reproducibility of measured μ_H and n_H .

The FET mobility (μ_{FET}), extracted in the linear regime, was calculated by fitting the experimental data to the following equation:

$$\mu_{FET} = \frac{L}{WC_i V_D} \frac{dI_D}{dV_G} \quad (S3)$$

where L , W , C_i , V_D , I_D , and V_G are the channel length, channel width, capacitance per unit area, drain voltage, drain current, and gate voltage, respectively.

e^-/NC estimation. e^-/NC values were estimated based on the assumption that an MCC capped InAs NC has a spherical shape and forms *fcc* packing with a center to center distance (a) of 6.3 nm (5.3 nm - InAs core and 1.0 nm - MCC ligands) in thin films. Therefore, e^-/NC in Hall devices could be derived from the following equation with a packing fraction of 0.74:

$$e^-/NC = \frac{nV_{NC}}{0.74} \quad (S4)$$

where V_{NC} denotes the volume of a nanocrystal (i.e., $4/3 \times \pi \times (\frac{a}{2})^3$). For FET devices, we assumed that all injected carriers accumulate in the first monolayer of the NC array. Then this NC array can be regarded as a 2-dimensional hexagonal lattice system with an NC footprint of $(\frac{a}{2})^2 \sqrt{12}$ and e^-/NC in FET devices could be derived from the following equation:

$$e^-/\text{NC} = \frac{\sqrt{3}C_i V_G a^2}{2e} \quad (\text{S5})$$

where e is the elementary charge, $1.6 \times 10^{-19} \text{C}$.

Film conductivity calculation. Film conductivity σ was calculated using the VDP method based on 4-terminal I - V characteristics and film thickness, h . The 4-terminal I - V characteristics shown below were used to extract resistance of the film, R , and the sheet resistance, $R_{\square}$, was calculated using the VDP equation (i.e., $R_{\square} = \pi R / \ln(2)$). Then the conductivity could be derived as: $\sigma = 1/\rho = 1/R_{\square}h$.

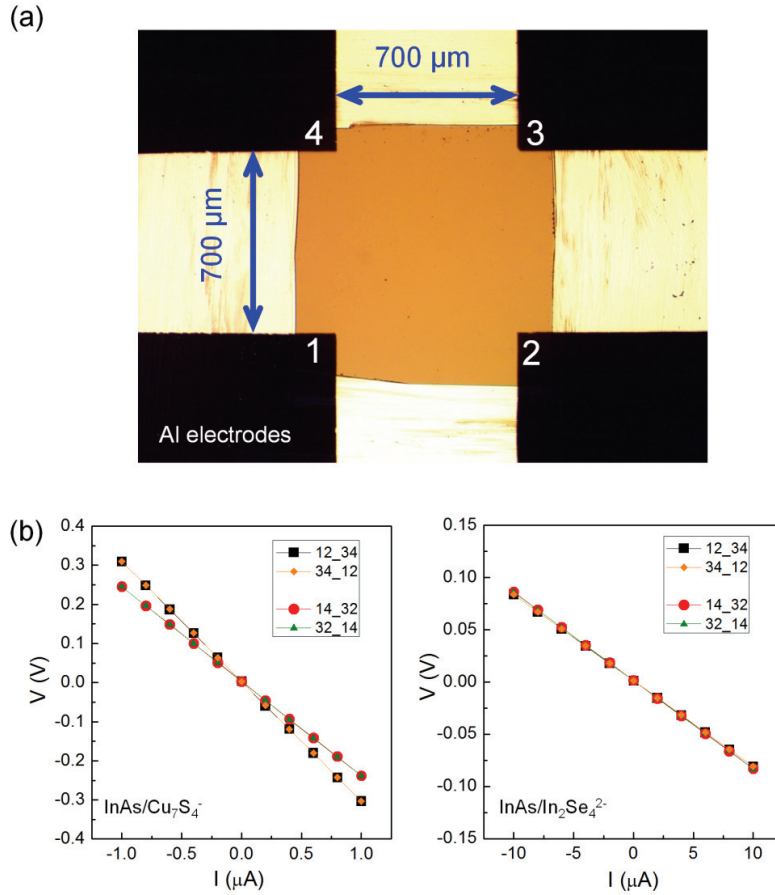


Figure S2. (a) An optical microscope image (transmission mode) of a typical device used for Hall and VDP measurements in this study. (b) 4-terminal I - V characteristics measured using four different VDP configurations for devices of Cu_7S_4^- capped and $\text{In}_2\text{Se}_4^{2-}$ capped InAs NCs ($T = 300\text{K}$), showing ohmic responses. The sequential numbers indicate the number of electrodes used for current injection and voltage measurement, shown in (a). For example, the sequential number 12_34 indicates the use of contacts 1 and 2 for current injection and 3 and 4 for voltage measurement. Almost identical I - V characteristics for pairs of 12_34/34_12 and 15_32/32_15 and a small difference between those pairs suggests good uniformity across NC films and good contact alignment in the devices.

Coulomb charging energy. The charging energy E_c of a spherical NC can be estimated as $E_c = e^2/(4\pi\epsilon_m\epsilon_0d)$ where ϵ_m is the dielectric constant of the surrounding medium and d is the NC diameter. To roughly estimate the dielectric constant of the surrounding medium, we assumed two extreme cases where all the voids in an NC assembly are filled by MCC ligands or are empty (i.e., free space). This system can then be regarded as a mixture of NCs and MCC ligands (or free space) with an effective dielectric constant (ϵ_{eff}) given by the Maxwell-Garnett formula:

$$\epsilon_{eff} = \epsilon_{NC} \frac{2(1 - \delta_{MCC})\epsilon_{NC} + (1 + 2\delta_{MCC})\epsilon_{MCC}}{(2 + \delta_{MCC})\epsilon_{NC} + (1 - \delta_{MCC})\epsilon_{MCC}} \quad (\text{S6})$$

where, δ is the volume fraction which is 0.26 for MCC ligands (or free space) in *fcc* packing. These two extreme cases predict the lower and upper limits of the ϵ_{eff} and we expect that the ϵ_{eff} of our system is between the two limits.

According to reported data,⁷⁻¹⁰ the ϵ_m of InAs, In_2Se_3 , and Cu_2S are about 15.2, 16.7, and 15, respectively. Fitting these values to the above equation gives an ϵ_{eff} of 10.4 ~ 15.6 for $\text{In}_2\text{Se}_4^{2-}$ capped InAs NCs and 10.4 ~ 15.1 for Cu_7S_4^- capped InAs NCs. With these effective dielectric constants, we could obtain $E_c \sim 17\sim 26$ meV for $\text{In}_2\text{Se}_4^{2-}$ capped InAs NCs and 18~26 meV for Cu_7S_4^- capped InAs NCs.

Another approach for taking into account the dielectric properties of the ligands around a NC is based on the assumption that a metal sphere is embedded in a metallic shell with an insulating gap of thickness, l , and an NC radius, r :¹¹

$$E_C = \frac{e^2}{4\pi\epsilon_m\epsilon_0 d} \times \frac{l}{(r+l)} \quad (S7)$$

Assuming that the inter NC surface-to-surface distance (l) is 1.0 nm, the predicted E_C is about ~ 4.5 meV for $\text{In}_2\text{Se}_4^{2-}$ capped InAs NCs and ~ 5.0 meV for Cu_7S_4^- capped InAs NCs. Both approaches suggest that the Coulomb charging energy of $\text{In}_2\text{Se}_4^{2-}$ capped InAs NCs is higher than the smallest E_a value (~ 2 meV) of $\text{In}_2\text{Se}_4^{2-}$ capped InAs NC arrays, observed in Hall devices.

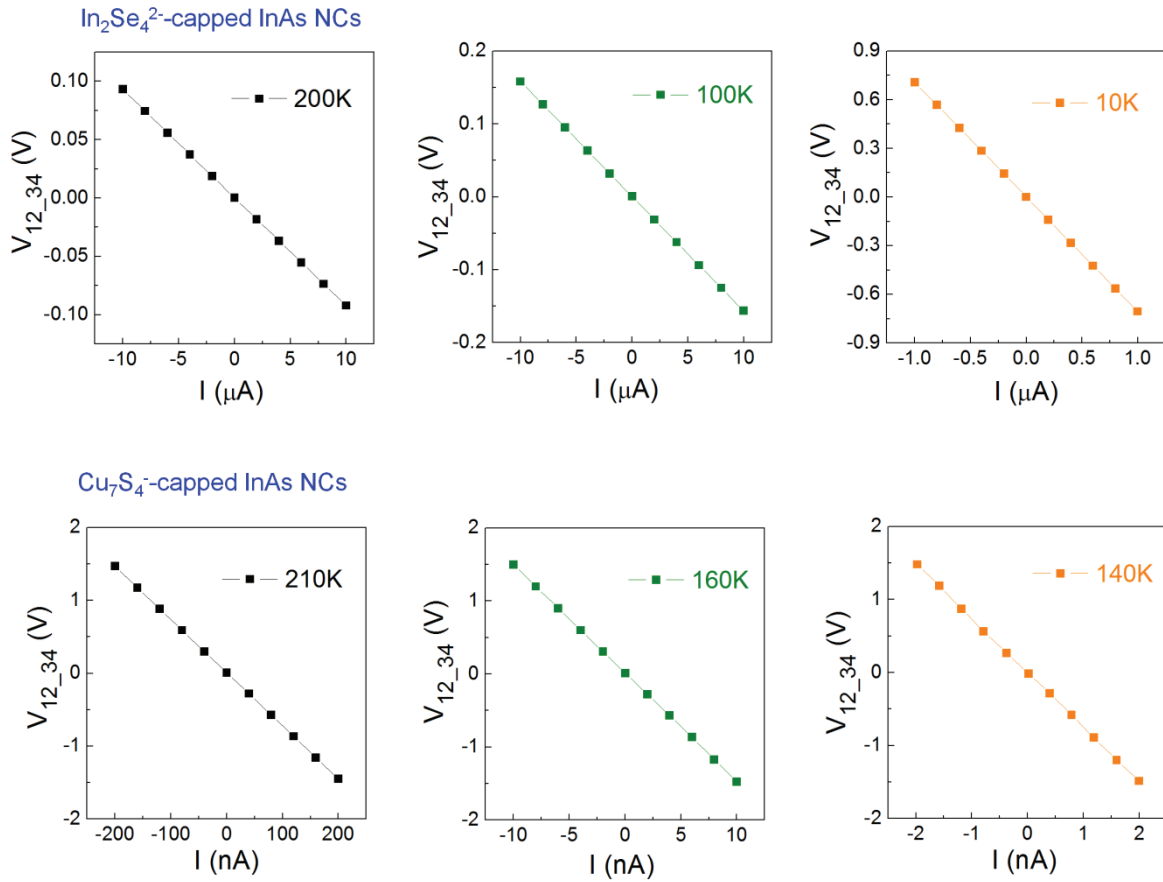


Figure S3. 4-terminal I - V characteristics measured using a VDP configuration for devices of Cu_7S_4^- capped and $\text{In}_2\text{Se}_4^{2-}$ capped InAs NCs at various temperatures. Only the input current range that showed the ohmic response was used to calculate the film's conductivity. For Cu_7S_4^- capped NC devices, we could not obtain an ohmic I - V response at temperatures lower than 140K, thus measurements stopped at 140K. As the temperature decreased and thereby conductivity decreased, the background voltage and noise during the Hall measurement also increased. The input current was correspondingly adjusted to minimize the noise. The adjusted input current was within the ohmic response range, as determined from the VDP measurements.

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