

Supporting Information

Highly Conductive Copper Selenide Nanocrystal Thin-Films for Advanced Electronics

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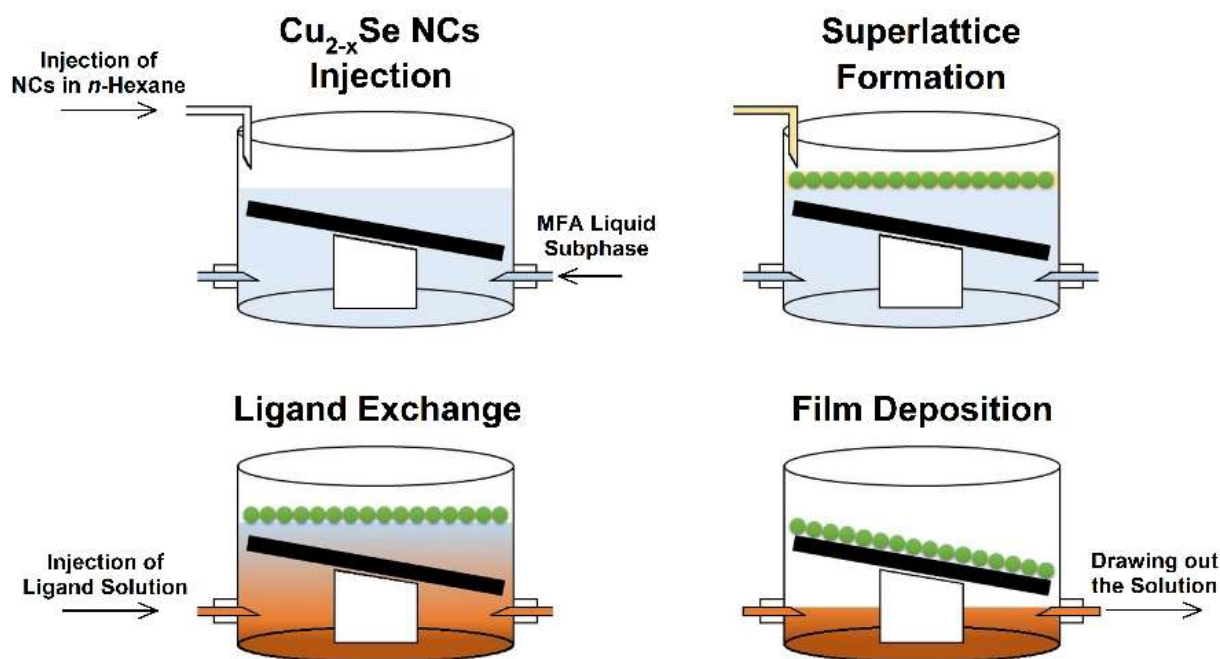


Figure S1. Scheme of the fabrication process of Cu_{2-x}Se NC superlattice thin-films by a Langmuir-type assembly at the liquid/air interface.

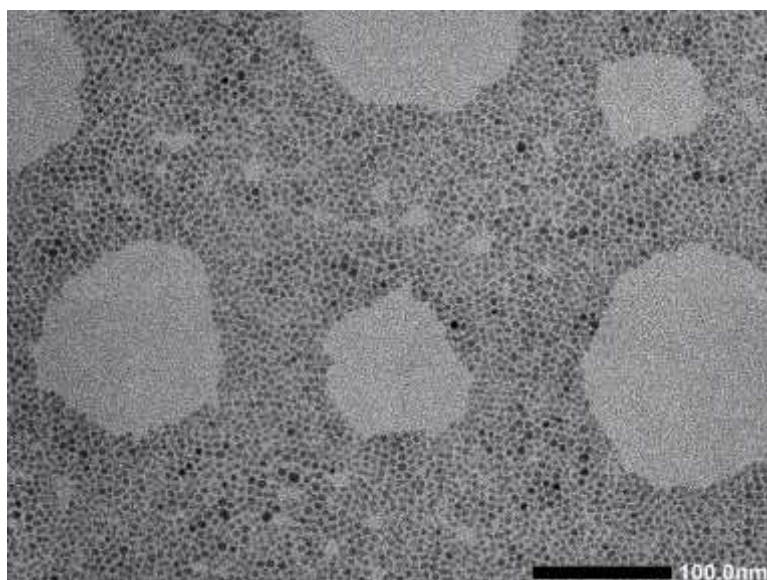


Figure S2. TEM image of as-synthesized Cu_{2-x}Se NCs (the samples were prepared by diluting the NC dispersion and drop-casting onto a carbon-coated copper grid with subsequent evaporation of the solvent).

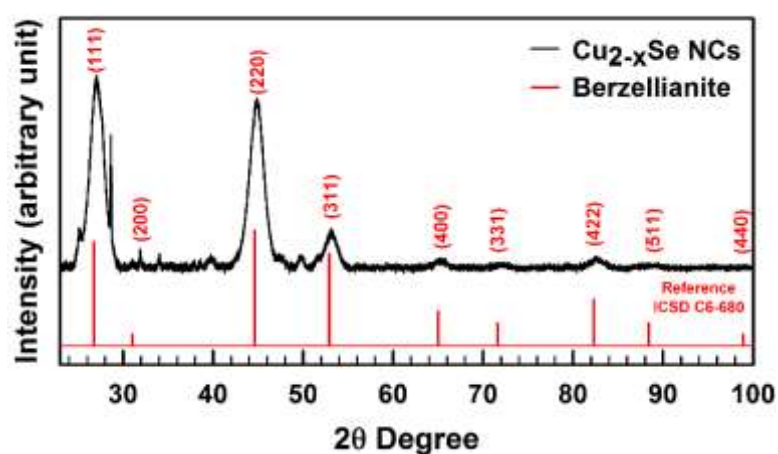


Figure S3. XRD pattern of Cu_{2-x}Se NCs confirms the cubic berzelianite phase compared to the reference pattern ICSD C6-680.

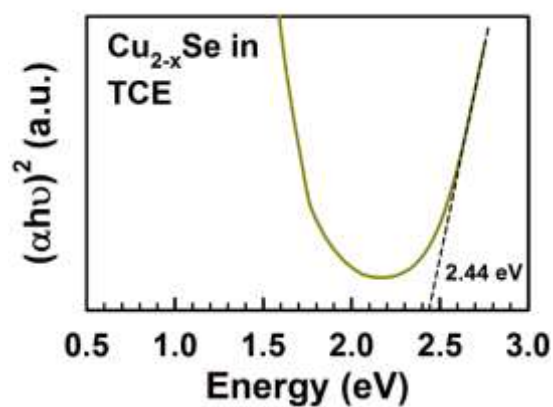


Figure S4. $(\alpha h\nu)^2$ versus energy plot to extract the optical bandgap of Cu_{2-x}Se NCs dispersed in TCE.

Synthesis of Cu_{2-x}Se Nanocrystals

In a three neck round-bottom flask a mixture of 262 mg of Cu(acac)₂ (1 mmol) in 9.5 mL OlAm and 3 mL DDT was degassed under vacuum and vigorous stirring at 60 °C for 1 h. After refilling the flask with argon, the mixture was heated to 170 °C within a short time resulting in a yellow-orange clear solution. Subsequently, 0.666 mL of a Se-precursor stock solution (0.67 mmol), previously prepared by dissolving 790 mg Se powder (10 mmol) in 5 mL of DDT and 5 mL of OlAm under vacuum at 50 °C for 1 h, and 1.5 mL of DDT (previously degassed under vacuum) was rapidly injected from a syringe resulting in a greenish-brown solution. The temperature was maintained for 30 s with subsequent cooling to room temperature. The Cu_{2-x}Se NCs were purified by the precipitation with methanol and redispersion in hexane once.

Characterization

The XRD measurements were performed on a Bruker D2 Phaser using a Cu source operating at 30 kV and 10 mA. For the analysis of the XRD pattern, the WinXPow software with references of the Inorganic Crystal Structure Database was used.

XPS measurements were carried out using a spectrometer equipped with a monochromatized X-ray source (Al K_α, 1486.61 eV) and a Scienta 200 analyzer. The pressure in the analyzer chamber was maintained below 5×10^{-10} mbar during the measurements. All survey spectra, scans of 1100 eV, were taken at an analyzer pass energy of 200 eV. High-resolution scans were performed at the pass energy of 50 eV and steps of 0.05 eV. The binding energies were corrected for electrical charge effects by referencing to C 1s sp³ peak, which was assumed to have a binding energy of 284.8 eV. The photoelectrons were detected at a takeoff angle of $\Phi = 0^\circ$ with respect to the surface normal. Acquisition and storage of data were accomplished using SES software version 1.2.6. Data fitting was performed using Gauss-Lorentz profiles. The background was calculated and subtracted using the Shirley method. The Cu:Se ratio was calculated by taking the photoionization cross sections¹ of 8.66, 16.73, 0.934, and 1.36 for Cu 2p_{1/2}, Cu 2p_{3/2}, Se 3d_{3/2}, and Se 3d_{5/2}, respectively; using the ratio of the Cu 2p to Se 3d peak area.

Electrical measurements on the NC arrays were performed using a Keithley 2634B dual source-meter unit. The free-floating ligand-exchanged Cu_{2-x}Se superlattices were deposited on a commercially available bottom-gate, bottom-contact transistor substrate (Fraunhofer Institute for Photonic Microsystems, Dresden, Germany) with interdigitated Au electrodes of 10 mm width and 2.5, 5, 10, and 20 μm channel length (distance between Au electrodes). Substrates were contacted using a miniprober enclosed in a nitrogen-filled glovebox. The sheet resistance is calculated as $R_s = R w / l$, where R is the measured resistance and l and w are the length and the width of the channel between two gold electrodes, respectively.

For investigating the *vapor sensing properties*, NC superlattices were deposited on commercially available glass substrates with interdigitated gold electrode structure (180 finger pairs, 5 μm microelectrode gap, and 5 μm and 150 nm microelectrode width and height, respectively; ED-IDE3-Au micrux Technologies). The sensitivity of the films was characterized by dosing them with vapors of 4-methyl-2-pentanone (4M2P), toluene, isopropanol, and water while monitoring their resistances at 0.1 V. The relative differential resistance was used to express the sensor responses. It was calculated by measuring the change in the resistance, ΔR , divided by the baseline resistance, R_0 . All vapor sensing experiments were carried out at room temperature (ca. 25 $^{\circ}\text{C}$) with dried purified air as a carrier gas using the previously reported commercial instrumentation.² Due to the integrated mass flow controllers in the system $\sim 3\times$ to $\sim 1000\times$ dilution of saturated test vapors was possible. With the vapor pressures of the analyses (21, 29, 20, and 23 mbar at 20 $^{\circ}\text{C}$, respectively³) concentrations between 50 and 5000 ppm were accessible. As all the mentioned test vapors had comparable vapor pressures, their interaction with the samples was expected to mainly arise from their chemical nature (polarity and structural features) and not from the differences in vapor pressure.

References

- (1) Scofield, J. H. Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487eV. *J. Electron. Spectrosc.* **1976**, *8*, 129-137.
- (2) Joseph, Y.; Besnard, I.; Rosenberger, M.; Guse, B.; Nothofer, H. G.; Wessels, J. M.; Wild, U.; Knop-Gericke, A.; Su, D. S.; Schlogl, R.; Yasuda, A.; Vossmeier, T. Self-Assembled Gold Nanoparticle/Alkanedithiol Films: Preparation, Electron Microscopy, XPS-Analysis, Charge Transport, and Vapor-Sensing properties. *J. Phys. Chem. B* **2003**, *107*, 7406-7413.
- (3) Joseph, Y.; Peić, A.; Chen, X.; Michl, J.; Vossmeier, T.; Yasuda, A. Vapor Sensitivity of Networked Gold Nanoparticle Chemiresistors: Importance of Flexibility and Resistivity of the Interlinkage. *J. Phys. Chem. C* **2007**, *111*, 12855-12859.