

## Supporting Information

# Surface Chemistry Exchange of Alloyed Germanium Nanocrystals: A Pathway Toward Conductive Group IV Nanocrystal Films

*Daniel A. Ruddy,<sup>a,\*</sup> Peter T. Erslev,<sup>b</sup> Susan E. Habas,<sup>b</sup> Jason A. Seabold,<sup>a</sup> and Nathan R. Neale<sup>a,\*</sup>*

<sup>a</sup>Chemical and Materials Science Center and <sup>b</sup>National Center for Photovoltaics, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401

## Experimental Details

**General.** Germanium diiodide (>97%, Gelest GEG5200), germanium tetraiodide (>97%, Gelest GEG5800), aluminum triiodide (99.999%, Aldrich 409324), phosphorus triiodide (99%, Aldrich 241555), gallium triiodide (99.99%, Aldrich 399116), arsenic triiodide (Aldrich 401145), indium triiodide (99.998%, Aldrich 413666), tin diiodide (>95%, Gelest SNT7945), antimony triiodide (98%, Aldrich 401188), and *n*-butyllithium in hexanes (1.6 M, Aldrich) were stored under nitrogen inert atmosphere in a Vacuum Atmospheres glovebox and used as received. 1-Octadecene (ODE, 90%, Aldrich) was distilled under vacuum from molten sodium prior to storage and use in the glovebox. Oleylamine (OA, 90%, Aldrich) was degassed and dehydrated under vacuum ( $5 \times 10^{-3}$  torr) at 120 °C prior to storage and use in the glovebox.

Common solvents (i.e., toluene, methanol, acetone) used in the nanocrystal purifications were used as received (Aldrich or Fisher, ACS grade) under ambient conditions. Small molecule reagents (i.e., methylamine, ethylenediamine, ethanedithiol) and triethyloxonium tetrafluoroborate used in film exchange experiments were used as received (Aldrich or Fisher, ACS grade) in the glovebox. Polyethylenimine (PEI) was purchased from Aldrich and used as received. Tetrachloroethylene and acetonitrile were dried over  $P_2O_5$  and distilled under nitrogen prior to storage and use in the glovebox. Hexanes were dried through an alumina column prior to use in TEM sample preparation.

**Synthesis of 1 mol% nominal  $Ge_{1-x}E_x$  NCs.** In a glovebox, a quartz 50-mL three-neck round-bottom flask fitted with a reflux condenser was charged with  $GeI_2$  (98 mg,  $3.0 \times 10^{-4}$  mol),  $GeI_4$  (174 mg,  $3.0 \times 10^{-4}$  mol), and 2.9 g of OA. The other two inlets of the reaction flask were capped with septa. Also in the glovebox, BuLi (1.1 equiv versus total iodide, 1.25 mL, 2.0 mmol) was diluted with 3 mL of ODE and sealed in a gastight syringe for transfer to the fume hood. Separately in the glovebox, a 0.050 M solution of  $EI_n$  in OA was prepared via dissolution of the iodide at 50–70 °C with stirring. A small portion (120  $\mu$ L) of this solution ( $6.0 \times 10^{-6}$  mol, 1 mol% versus total Ge) was sealed in a gastight syringe and transported to the fume hood. The reaction flask was connected to an inert gas-vacuum (Schlenk) manifold and heated under nitrogen to 200 °C at 5 °C min<sup>-1</sup>. At 150 °C, the  $EI_n$ /OA solution was injected, with minimal temperature change. At 200 °C, the BuLi/ODE solution was rapidly injected (<3 s), and the temperature decreased to ca. 150 °C. After 5 min, the temperature had recovered to 200 °C, and was then increased to 300 °C (ramp rate  $\sim 2.5$  °C min<sup>-1</sup>) and held for 1 h. The reaction undergoes characteristic color changes from yellow to orange to brown associated with the formation of Ge NCs. After 1 h at 300 °C, the dark brown reaction solution was cooled to 100 °C, transferred to a

centrifuge tube, and dissolved in 10 mL of toluene. The nanocrystals were precipitated by adding 30 mL of methanol/ethanol solution (5:1, v/v), and separated by centrifugation (10k–12k  $\times$  g). After removal of the supernatant, the suspension-precipitation-centrifugation step was repeated twice using 10 mL toluene and 30 mL (5:1, v/v) methanol/ethanol as non-solvent. The brown solid product was isolated by evaporating residual solvent under nitrogen flow and stored in the glovebox.

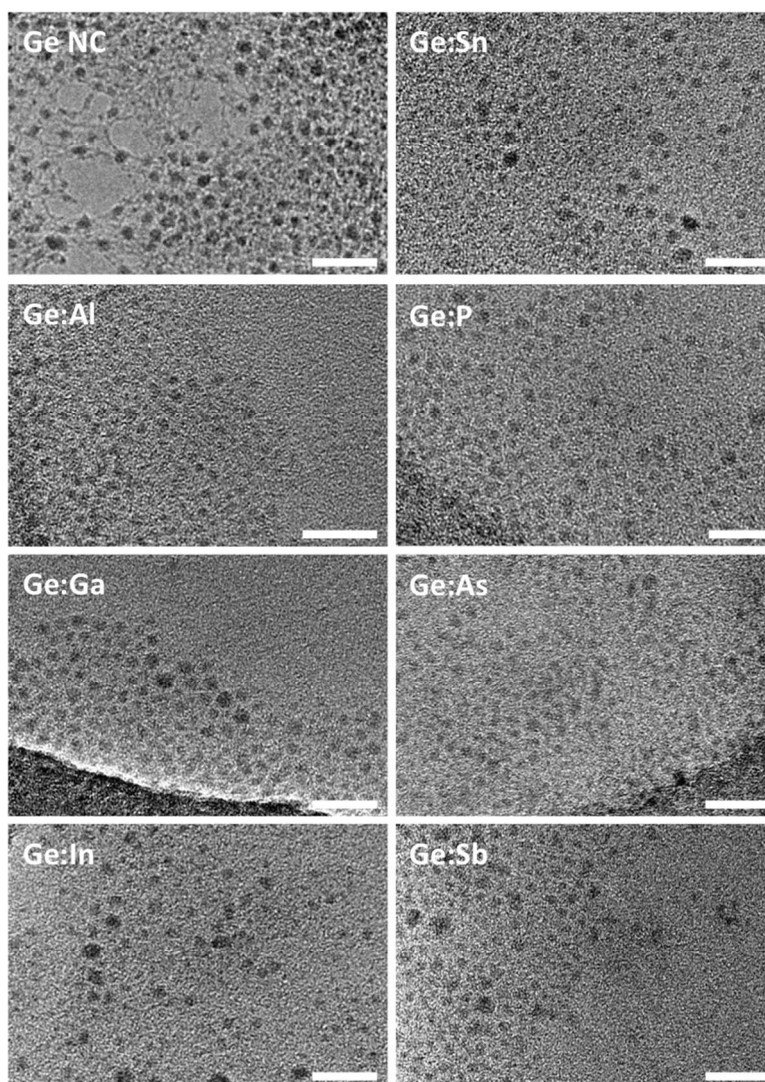
Notably, samples of  $\text{Ge}_{1-x}\text{E}_x$  NCs ( $\text{E} = \text{In}, \text{Sb}$ ) were collected following each of five washes during purification, and XRF analyses confirmed that the alloying level in the  $\text{Ge}_{1-x}\text{E}_x$  NCs (1.0 mol% E) did not change after successive washing. For instance, for  $\text{Ge}_{0.989}\text{In}_{0.011}$  samples, XRF data on NCs following the first purification wash gave a 1.04 mol% In content, whereas for the fifth wash 1.02 mol% In was found. These experiments suggest that the main group elements are strongly bound either within or at the surface of the NCs, and that loosely associated dopants or potential impurities (small amounts of incompletely reduced  $\text{EI}_n$ ,  $\text{E}_x\text{O}_y$  or metallic E) at the surface of  $\text{Ge}_{1-x}\text{E}_x$  NCs are not present.

**Preparation of  $\text{Ge}_{1-x}\text{E}_x$ –OA NCs and exchange into PEI.** The amounts of reagents are identical to that for the octadecyl-capped NCs detailed above, with the exception that ODE was not added to the BuLi solution. After injection and heating to 300 °C (ramp rate  $\sim 2.5$  °C  $\text{min}^{-1}$ ), the reaction was held for 1 min at 300 °C. The dark brown reaction solution was cooled to 100 °C, transferred to a centrifuge tube, and dissolved in 10 mL of toluene. The NCs were precipitated by adding 30 mL of methanol/ethanol solution (5:1, v/v), and separated by centrifugation (10k–12k  $\times$  g). After removal of the supernatant, the suspension-precipitation-centrifugation step was repeated twice dissolving in 10 mL toluene with 0.1 mL OA, and

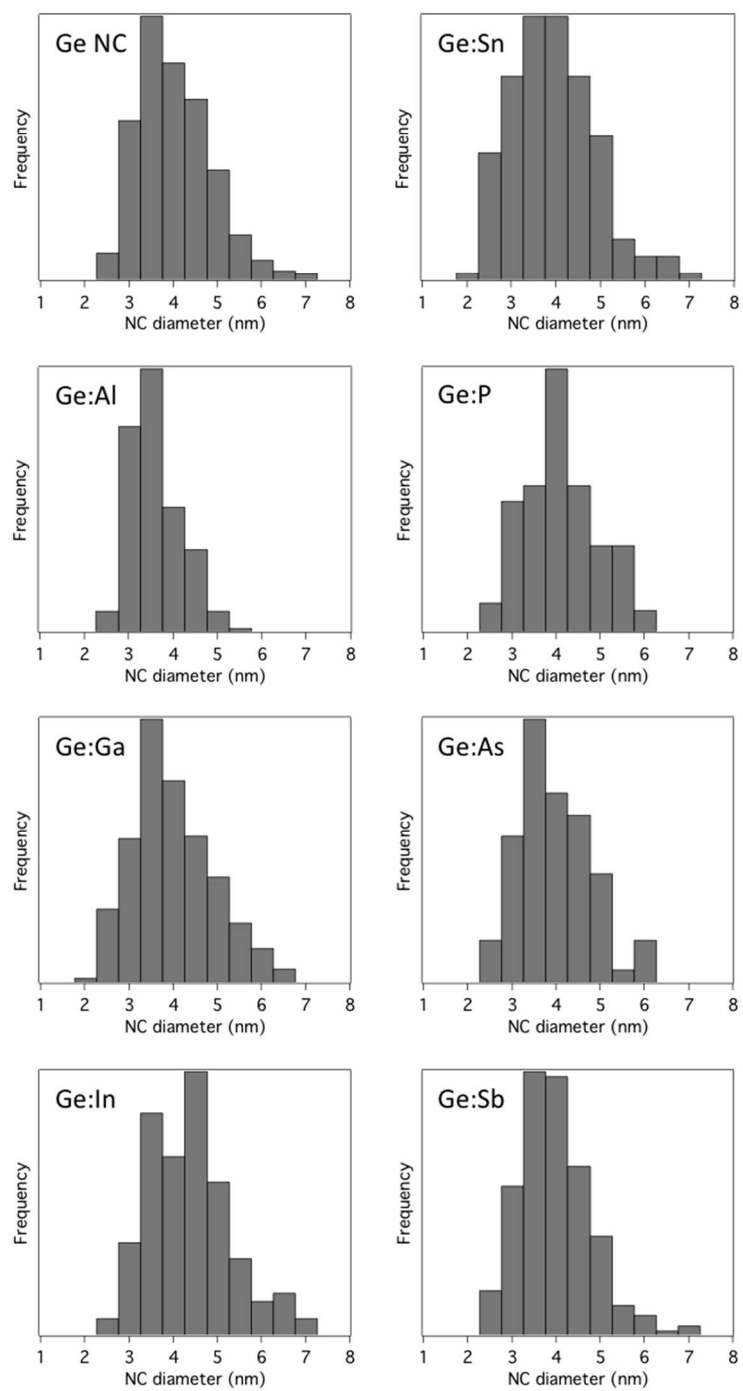
precipitating with 30 mL (5:1, v/v) methanol/ethanol as non-solvent. A solution of PEI in chloroform (0.25 g in 10 mL) was then added to the dark brown solid, and the solution was sonicated at low power for 10 min to disperse the NCs into the polymer. The NCs were precipitated with 30 mL hexanes, and separated by centrifugation (10k–12k  $\times g$ ). This suspension-precipitation-centrifugation step was repeated once using 5–10 mL chloroform and precipitating with 30 mL hexanes. The dense, sticky, dark brown solid was isolated by evaporating residual solvent under nitrogen flow and stored in the glovebox.

**Characterization.** Samples for transmission electron microscopy (TEM) were prepared in a glovebox by drop-casting a solution of NCs in dry hexanes onto lacey-carbon-coated copper grids (Ted Pella, part # 01824). Imaging was performed on a Philips CM-200 electron microscope operating at 200 kV and energy dispersive X-ray spectroscopy (EDS) was recorded in-situ with an EDAX detector. High-resolution imaging was performed on an FEI Tecnai T30 electron microscope operating at 300 kV. Average particle diameters and standard deviations were calculated by counting at least 150 particles for each preparation. Samples of the  $\text{Ge}_{1-x}\text{E}_x\text{-C}_{18}\text{H}_{37}$  and  $\text{Ge}_{1-x}\text{E}_x\text{-OA}$  NCs for absorption and PL emission spectroscopies were prepared as dilute solutions in dry tetrachloroethylene, whereas those of  $\text{Ge}_{1-x}\text{E}_x\text{-PEI}$  NCs were prepared as dilute solutions in dry chloroform (absorbance  $\sim 1.0$  at 400 nm with 1.0 cm path length). Absorption spectra were recorded using a Shimadzu UV-3600 spectrophotometer. Absorption onsets in Tauc plots were determined from best fits to the linear region in each plot, from  $\sim 0.15$  to  $\sim 0.050$  absorbance units. The absolute PL quantum yield was measured as previously reported.<sup>1</sup> Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN) using inductively coupled plasma optical emission spectroscopy (ICP-OES). Samples for X-ray fluorescence (XRF) spectroscopy were drop-cast from anhydrous, oxygen-free toluene solutions

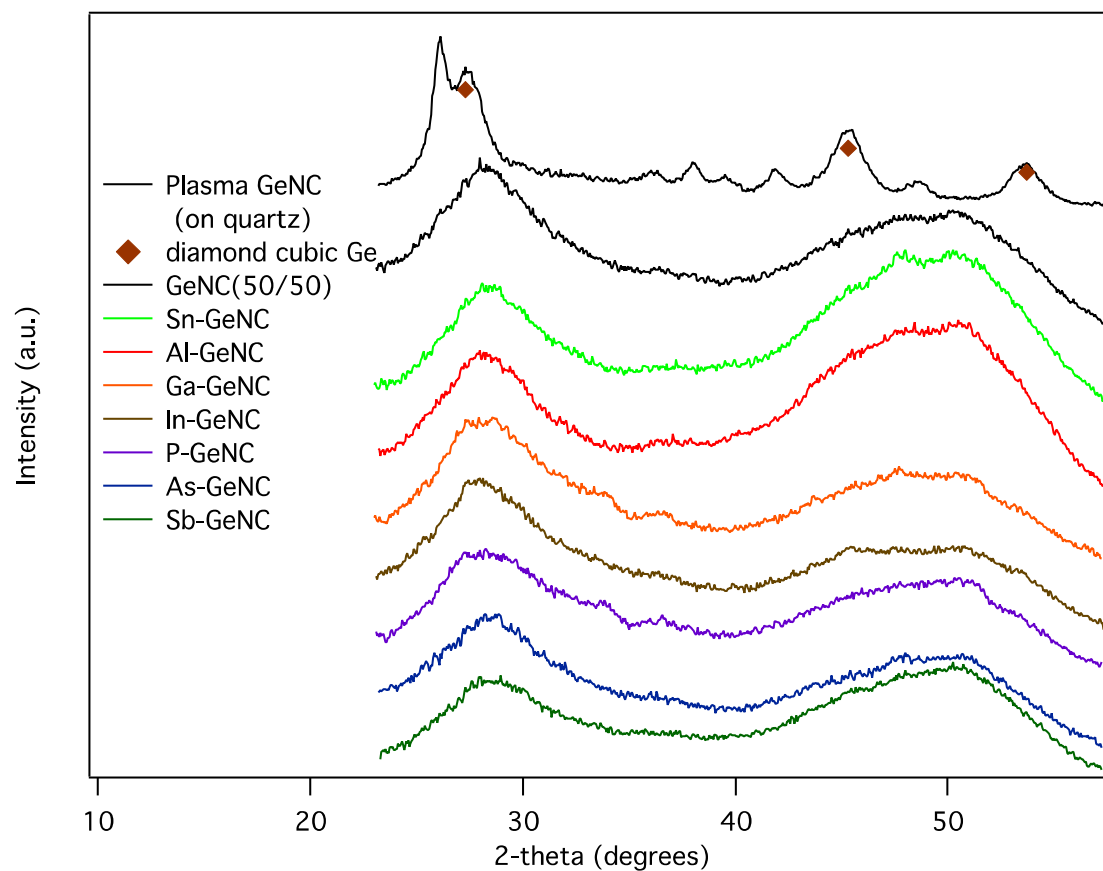
onto a c-Si wafer in the glovebox. XRF spectra were recorded on at least three areas of the drop-cast film ( $\sim 50$  mg/mL) using a Maxxi5 PIN spectrometer with a W K $\alpha$  X-ray source and an aperture diameter of 800  $\mu\text{m}$ , and elemental compositions were determined via calibration to standards of each element. Samples for FTIR spectroscopy were drop-cast from anhydrous, oxygen-free toluene solutions ( $\sim 50$  mg/mL) onto a c-Si wafer in the glovebox. Small molecule exchange reactions were conducted by submersing the film in a 1.0 M ethanol solution of the reagent for 1 h, followed by evaporative drying in the glovebox. Meerwein's salt exchange reaction was conducted by immersing the film in 50 mM Et<sub>3</sub>OBf<sub>4</sub> in acetonitrile for 12 h. FTIR spectra were recorded using a Nicolet 510 G spectrometer with a DTGS detector operating at 8  $\text{cm}^{-1}$  resolution. NMR experiments were performed using a Varian Inova 400 MHz spectrometer, with chloroform-*d* as the solvent. Current-voltage measurements were performed on films of Ge<sub>1-x</sub>E<sub>x</sub> NCs prepared by drop-casting concentrated NC solutions ( $\sim 50$  mg/mL) in either dry toluene (for Ge<sub>1-x</sub>E<sub>x</sub>-C<sub>18</sub>H<sub>37</sub> or Ge<sub>1-x</sub>E<sub>x</sub>-OA NCs) or dry chloroform (for Ge<sub>1-x</sub>E<sub>x</sub>-PEI NCs) onto Si/SiO<sub>2</sub> substrates with coplanar Au contacts (2 mm length, 25  $\mu\text{m}$  spacing). Film thicknesses were typically 25-35 microns with just 1 drop of solution, which filled the very shallow channel formed by the 40 nm high Au contacts. After drop-casting, films were heated under inert atmosphere to 75 °C for 10 minutes to remove any remaining solvent. While still under inert atmosphere, the dried films were transferred to a sealed stage (custom Linkam Instruments LTS350), which was continuously purged with dinitrogen gas after removal from the glove box to protect from air during current-voltage testing.



**Figure S1.** Representative TEM images of Ge<sub>1-x</sub>E<sub>x</sub> NCs. The scale bar in each image corresponds to 20 nm.

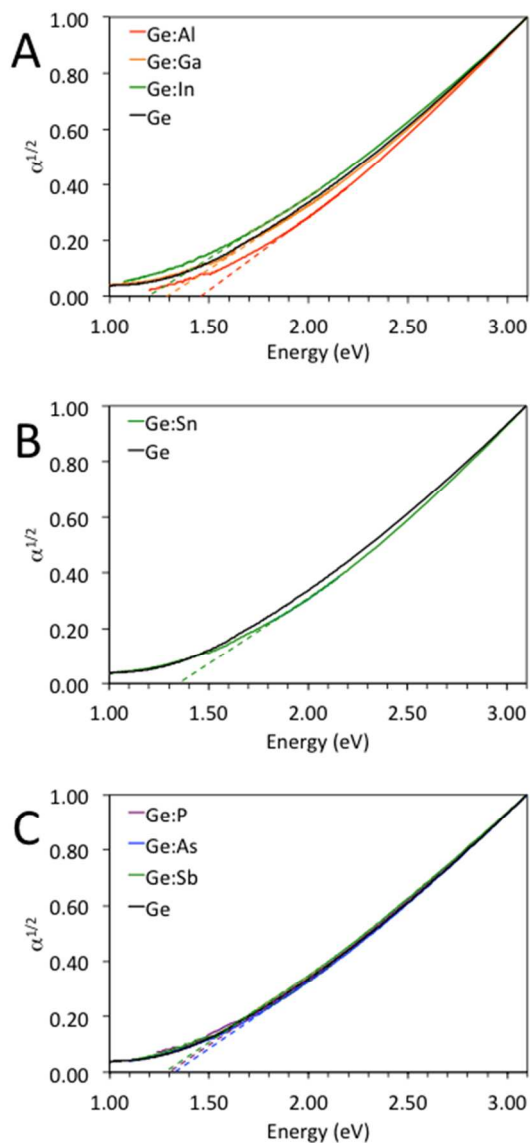


**Figure S2.** Size histograms for  $\text{Ge}_{1-x}\text{E}_x$  NCs.

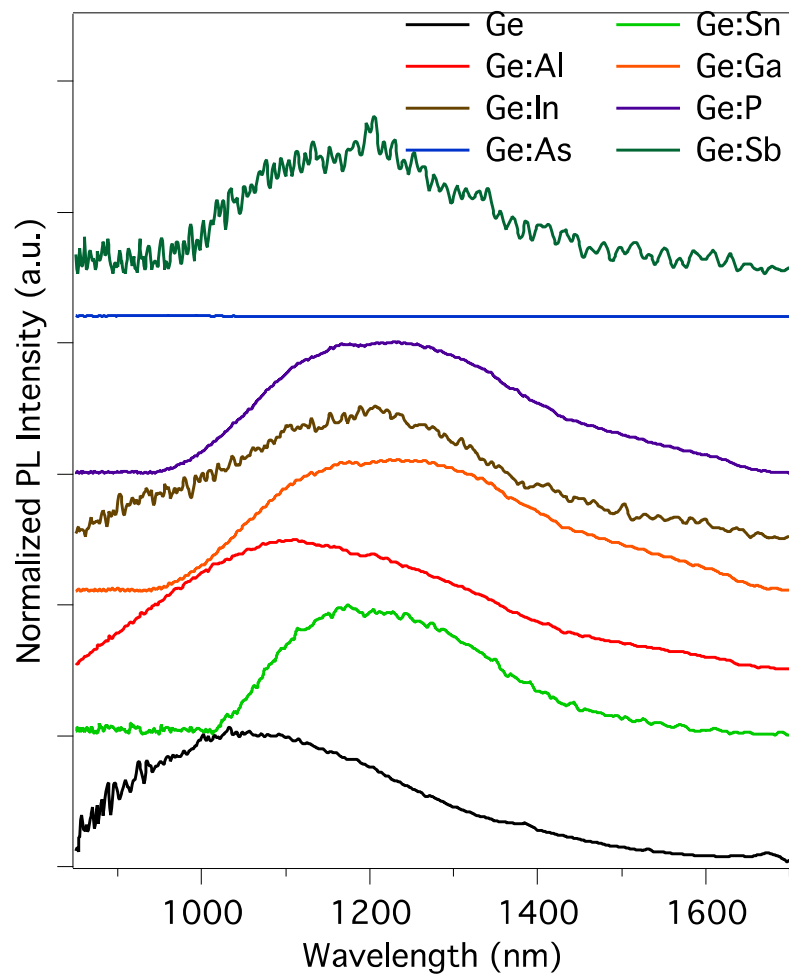


**Figure S3.** X-ray diffraction patterns for RF plasma-synthesized Ge NCs on quartz, Ge NC, and  $\text{Ge}_{1-x}\text{E}_x$  NCs. Unlabeled peaks in the plasma-prepared Ge NCs are due to the quartz substrate. Plasma-generated Ge NCs were provided by U. Kortshagen (Univ. of Minnesota).<sup>2</sup>

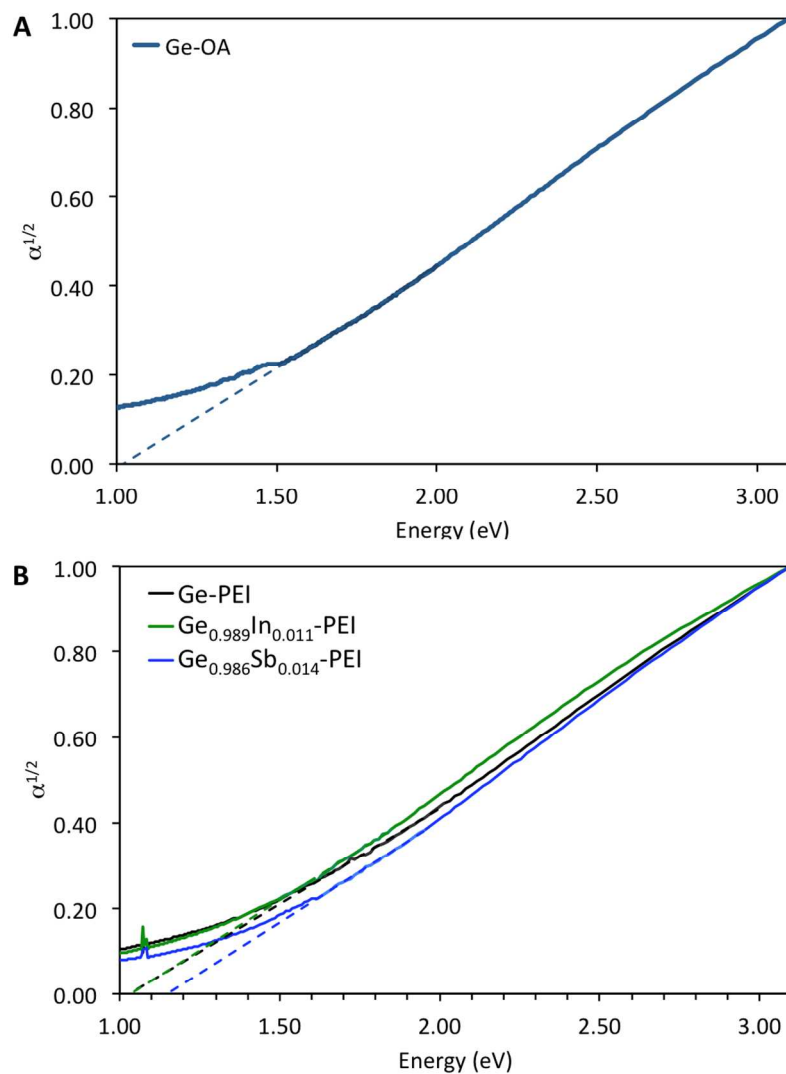




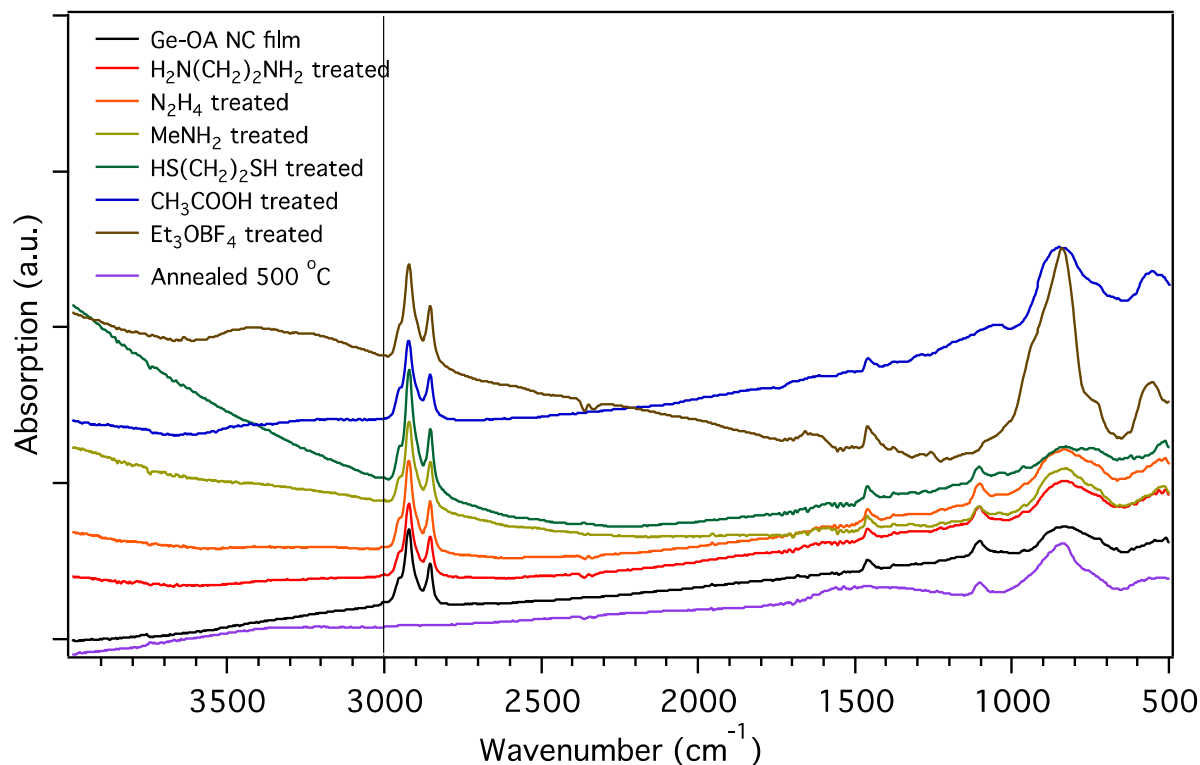
**Figure S4.** Tauc plots of the UV-vis-NIR absorbance spectra of tetrachlorethylene solutions of (A) Group III  $\text{Ge}_{1-x}\text{E}_x$  NCs, (B) Group IV  $\text{Ge}_{1-x}\text{E}_x$  NCs, and (C) Group V  $\text{Ge}_{1-x}\text{E}_x$  NCs. The black trace in all panels is the absorbance spectrum for native Ge NC. Dashed lines represent linear fits to the data used to determine the absorption onset. No linear relationship was observed in plots of  $\alpha^2$  vs. energy consistent with the indirect bandgap nature of germanium.



**Figure S5.** Photoluminescence spectra for Ge<sub>1-x</sub>E<sub>x</sub> NCs in tetrachloroethylene solution. The excitation wavelength was 550 nm.



**Figure S6.** Tauc plots of the UV-vis-NIR absorbance spectra of (A) tetrachlorethylene solution of Ge-OA NCs (B) chloroform solution of Ge<sub>1-x</sub>E<sub>x</sub>-PEI NCs. Dashed lines represent linear fits to the data used to determine the absorption onset.



**Figure S7.** FTIR spectra of Ge–OA NC films treated with various small molecules. The vertical line at  $3005\text{ cm}^{-1}$  highlights the low intensity alkenyl C–H stretch, indicative of OA. The minimal differences in the spectra suggest that these treatments did not effectively remove the OA capping groups. Further, characteristic peaks associated with the various small molecules are not observed (e.g., S–H, C=O,  $\text{BF}_4^-$ ).

### References

1. Semonin, O. E.; Johnson, J. C.; Luther, J. M.; Midgett, A. G.; Nozik, A. J.; Beard, M. C. Absolute Photoluminescence Quantum Yields of IR-26 Dye, PbS, and PbSe Quantum Dots. *J. Phys. Chem. Lett.* **2010**, *1*, 2445-2450.
2. Holman, Z. C.; Kortshagen, U. R. A flexible method for depositing dense nanocrystal thin films: impaction of germanium nanocrystals. *Nanotechnology* **2010**, *21*, 335302.