Electronic Supporting Information for *Chemical Communications*

Synthesis of Germanium Nanocrystals from Solid-State Disproportionation of a Chloride-Derived Germania Glass

*Yujie Wang,[a] Utkarsh Ramesh,[a] Charles K. A. Nyamekye,[bc] Bradley J. Ryan,[a] Rainie D. Nelson,[a] Abdulla M. Alebri,[a] Umar H. Hamdeh,[a] Atefe Hadi,[a] Emily A. Smith,[bc] Matthew G. Panthani *[a]*

[a] Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States of America

[b] Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States of America

[c] Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011-3111, United States of America

I. Experimental Procedures

Materials: $GeCl_2 \cdot$dioxane was purchased from Gelest. Ethanol was purchased from Fisher (200 proof). Chloroform (99.8%), anhydrous ethanol (≤0.003% water), anhydrous toluene (99.8%), anhydrous isopropanol (99.5%), and hydrofluoric acid (HF, 48%) were obtained from Sigma Aldrich. 1-octadecene (98%) was purchased from Acros Organics. Deionized water was obtained using Milli-Q® Advantage A10 water purification system with a resistivity of 18.2 MΩ•cm.

Hydrolysis of $GeCl_2$: In a typical process, 100 mL of degassed deionized water was added to 25 g of $GeCl_2 \cdot$dioxane in a N_2-filled glovebox, yielding a yellow turbid suspension immediately. The suspension was then centrifuged to obtain a yellow centrifugate with a colorless supernatant. The centrifugate was transferred into a three-neck round-bottom flask, sealed, brought out of the glovebox, and connected to a Schlenk line. The centrifugate was dried in the flask under vacuum on a hotplate set at 130 °C for ~15 h. A final yellow powder was obtained for the hydrolyzed and dried $GeCl_2$ sample.

Synthesis of Oxide-Embedded Ge NCs: The hydrolyzed and dried $GeCl_2$ was ground manually with a ceramic mortar and pestle to a fine powder; ~1 g of the fine powder was placed in an alumina boat, and loaded into a tube furnace (MTI Corporation, model: GSL-1500X). The tube furnace was sealed and then purged with N_2 for 3 h with a flow rate around 1 bubble per second to remove air in the tube. The samples were heated at a rate of 10 °C/min under flowing N_2 to 250 °C and held at this temperature for 2 h for dehydration. Further heating of the samples to peak processing temperatures between 300 and 450 °C was performed in 25 °C increments; the peak temperature was held and held at those temperatures for 1 h before cooling down to room temperature naturally.

Hydrogermylation of Ge NCs: Oxide-embedded Ge NCs (0.25 g) were finely ground with a ceramic mortar and pestle. The powder was suspended in 10 mL deionized water and stirred on a hotplate set to 60 °C for 1 h before allowing it to cool down to room temperature. 8 mL hydrofluoric acid (HF) was added to the suspension (*Caution! HF must be handled with extreme care and in accordance with local regulations*) and after stirring for 30 min, the mixture was centrifuged at 8000 rpm for 5 min. The centrifugate was suspended in ~12.5 mL 200 proof ethanol and precipitated out by centrifugation (twice), then suspended in ~7.5 mL chloroform before finally being suspended in 30 mL 1-octadecene. The suspension was transferred to a 100 mL three-neck round-bottom flask attached to a Schlenk line, followed by exposing to three freeze-pump-thaw cycles to remove dissolved gases. The N_2 filled flask was heated to 200 °C while stirring at 500 rpm for 20 h. The mixture was cooled down to room temperature and transferred into a N_2 filled glovebox. The suspension was centrifuged at 7830 rpm for 10 min, to remove poorly-capped NCs. The brown, optically clear supernatant was observed and retained. 10 mL anhydrous ethanol and 5 mL anhydrous isopropanol were added to the obtained supernatant and centrifuged at 7830 rpm for 10 min. There were two phases after centrifugation; the upper phase was clear and colorless which was discarded, while 10 mL anhydrous isopropanol was added to the brown bottom phase. The mixture was centrifuged at 7830 rpm for 20 min, followed by removal of the clear and colorless supernatant. Anhydrous toluene (3 mL) was added to the centrifugate to obtain a uniform dispersion. Anhydrous ethanol (5 mL) was added to the dispersion and the mixture was centrifuged at 7830 rpm for 15 min. The preceding antisolvent precipitation/redispersion process was carried out nine more times to remove excess 1-octadecene with 2 mL anhydrous toluene as solvent and 3 mL anhydrous ethanol as antisolvent.

Characterization

Powder X-ray diffraction (XRD) patterns were collected with a Bruker DaVinci D8 Advance diffractometer with a Cu Kα radiation source.

Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2-F20 instrument operated at 200 kV. For a typical TEM sample preparation, 0.03 g of the oxide-embedded Ge NCs was ground in a ceramic mortar and pestle and suspended in 1.5 mL deionized water. The dispersion was heated to 60 °C while stirring at 500 rpm for 1.5 h before diluting and depositing onto an ultra-thin carbon-coated Cu TEM grid. TEM of 1-octadecene-passivated Ge NCs was prepared by drop-casting a dilute toluene dispersion onto an ultra-thin carbon-coated Cu TEM grid.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Physical Electronics PHI ESCA 5500 unit. The sample was irradiated with 250 W unmonochromated Al K-alpha X-rays. The pass energy was set to 24 eV for high resolution scans. CasaXPS Version 2.3.19PR 1.0 was used to process raw data files. Binding energies were calibrated using the C 1s peak as a reference (284.6 eV) and a Shirley background model was applied during peak fitting. Peak contributions from Ge^{4+}, Ge^{2+} and Ge^0 were fitted using a 30% Gaussian/70% Lorentzian profile centered at 33.2, 31.2 and 30.2 eV, respectively.

Raman spectroscopy was performed on the Ge NCs at each annealing temperature between 250 to 450 °C and the precursor $GeCl_2$·dioxane complex using a commercially available XploRA Plus Raman confocal upright microscope (HORIBA Scientific, Edison, New Jersey) equipped with an Olympus objective (10X magnification, 0.25 numerical aperture). Raman spectra were collected in the epi-direction using a 300 μm confocal pinhole. A 600 grooves/millimeter grating

(1400 cm^{-1} center wavelength) was used to collect the spectrum of $GeCl_2$·dioxane precursor and a 2400 grooves/millimeter grating (350 cm^{-1} center wavelength) was used to collect the spectra of annealed samples. The Ge NCs were placed onto a glass slide and irradiated with a 7.3×10^4 W cm^{-2} solid-state 532-nm diode laser producing a 16.8 ± 0.3 μm laser spot size at the sample. The acquisition time was 10 s with five accumulations. The data were plotted using IGOR Pro (WaveMetrics, Inc., Portland, OR).

Fourier transform infrared (FTIR) spectroscopy measurements were collected using a Bruker Tensor 37 spectrometer. Sample pellets were obtained by mixing a small amount of a sample with KBr powder and the mixture was pressed by a hydraulic jack. The pellet was then placed inside a sample compartment in the FTIR spectrometer, from which transmission data were obtained through single beam measurements. Empty KBr pellet was prepared the same way and measured as background. An average of 16 scans was used for each sample. FTIR data were processed using the OPUS software package, which allowed for subtraction of atmospheric features (water and carbon dioxide) and baseline corrections.

Thermogravimetric Analysis and Digital Scanning Calorimetry (TGA/DSC) measurement was collected using Netzsch Jupiter STA449 F1. The data was collected with hydrolyzed and dried $GeCl_2$·dioxane in an alumina (Al_2O_3) crucible, with a flow rate of 20 mL/min of N_2 (and 20 mL N_2 as protective gas) and a ramp rate of 10 °C/min.

II. Supporting Figures

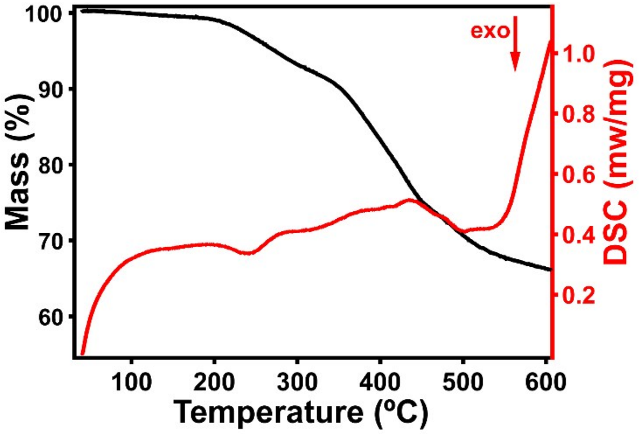

Figure S1. TGA/DSC plots of hydrolyzed $GeCl_2$·dioxane as a function of temperature.

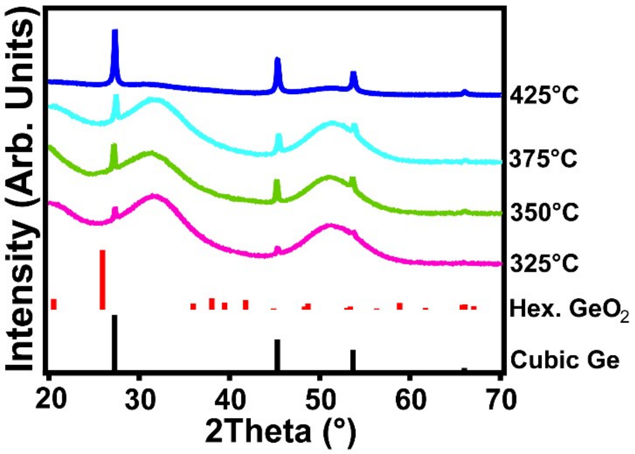

Figure S2. XRD patterns of annealed samples at different temperatures taken when the humidity was low (RH ≤ 20%). Cubic Ge reference: PDF # 00-004-0545, hexagonal GeO_2 reference: PDF# 00-036-1463.

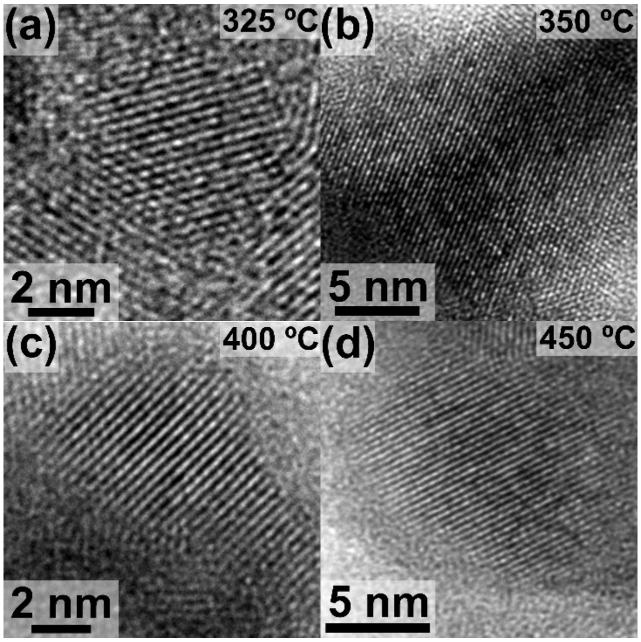

Figure S3. TEM images of nanocrystals obtained from hydrolyzed $GeCl_2$·dioxane annealed at (a) 325 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C.

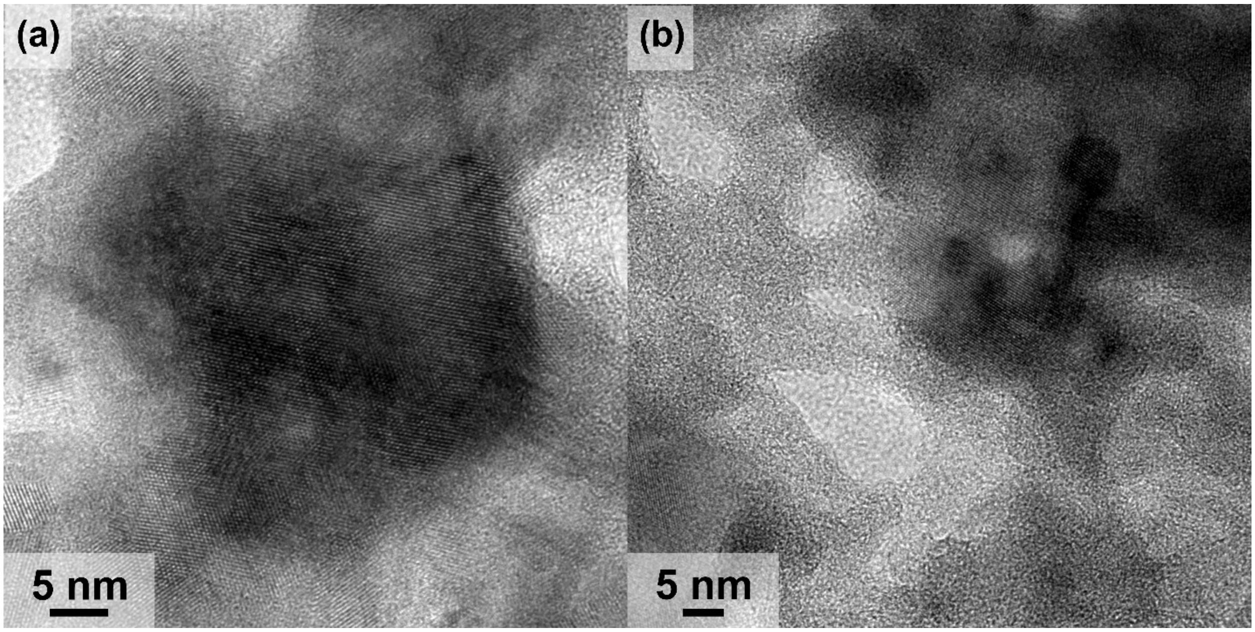

Figure S4. TEM of hydrolyzed $GeCl_2$·dioxane annealed at 450 °C.

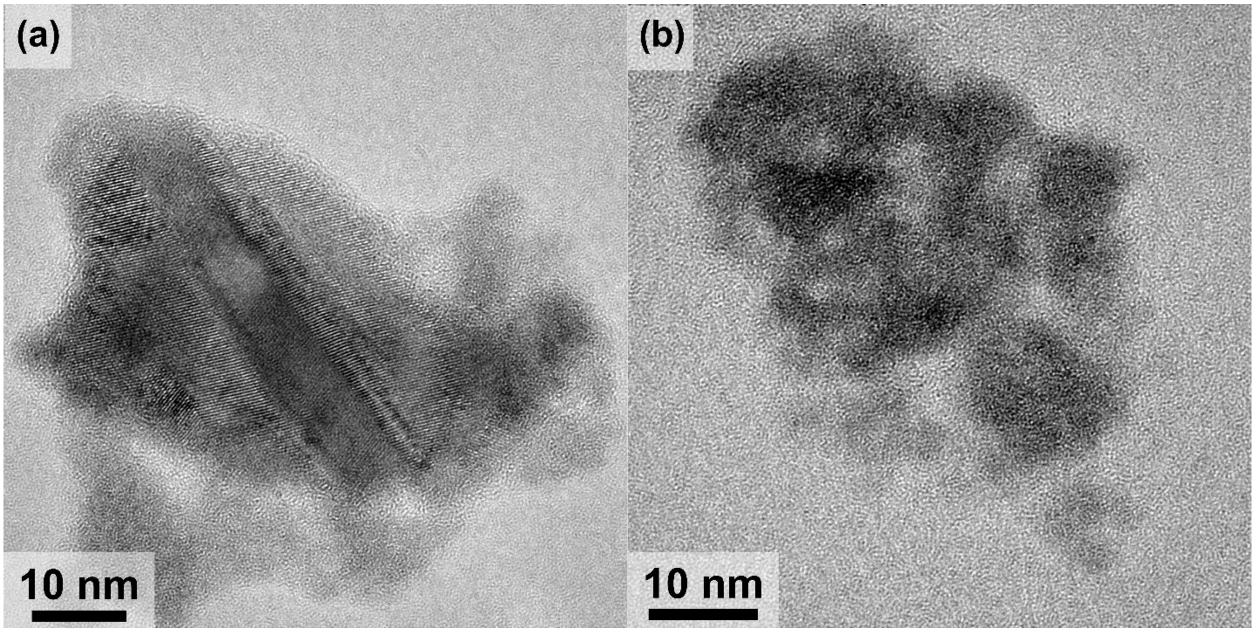

Figure S5. TEM of hydrolyzed $GeCl_2$·dioxane annealed at 425 °C.

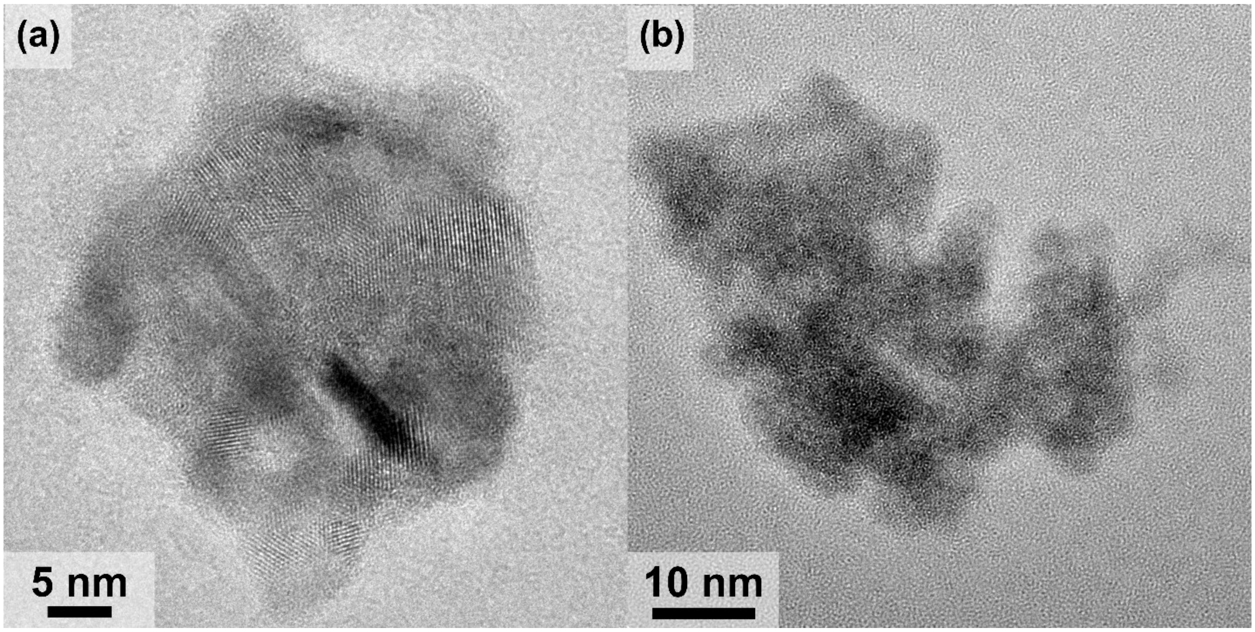

Figure S6. TEM of hydrolyzed $GeCl_2 \cdot$dioxane annealed at 400 °C.

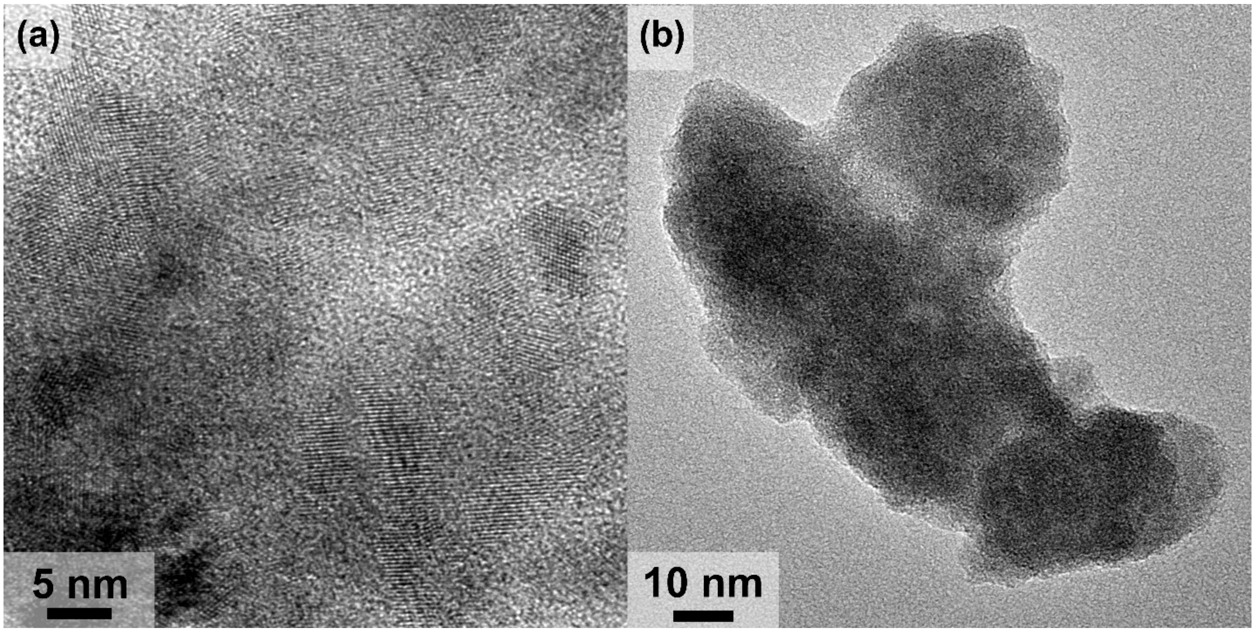

Figure S7. TEM of hydrolyzed $GeCl_2 \cdot$dioxane annealed at 375 °C.

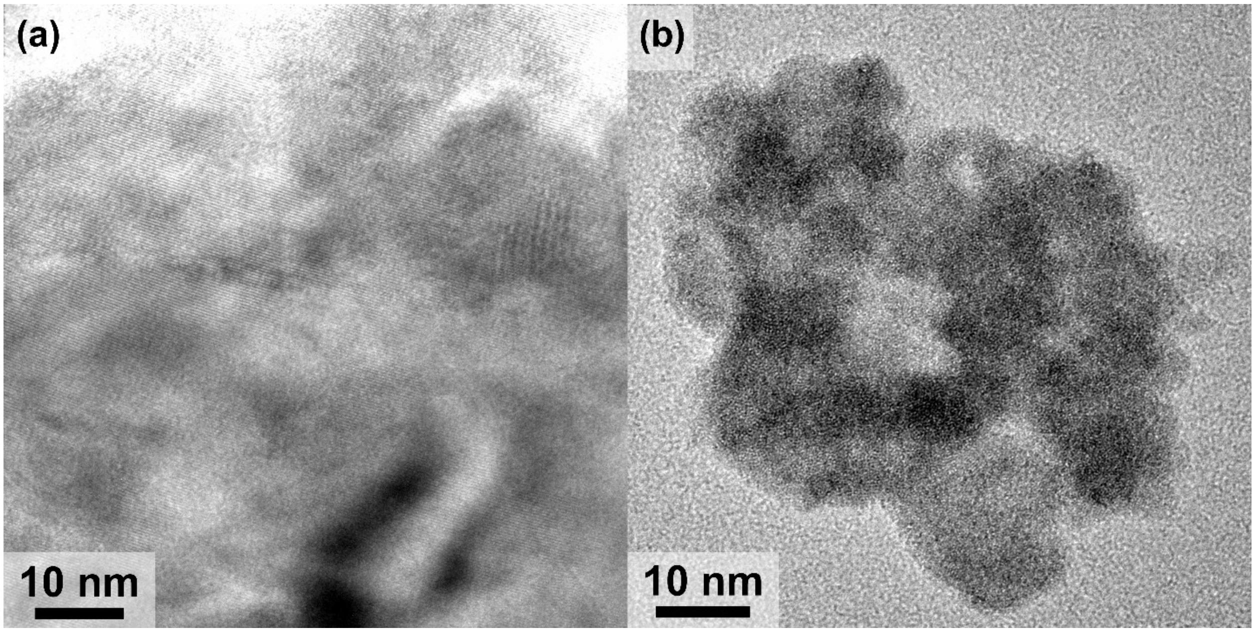

Figure S8. TEM of hydrolyzed $GeCl_2$·dioxane annealed at 350 °C.

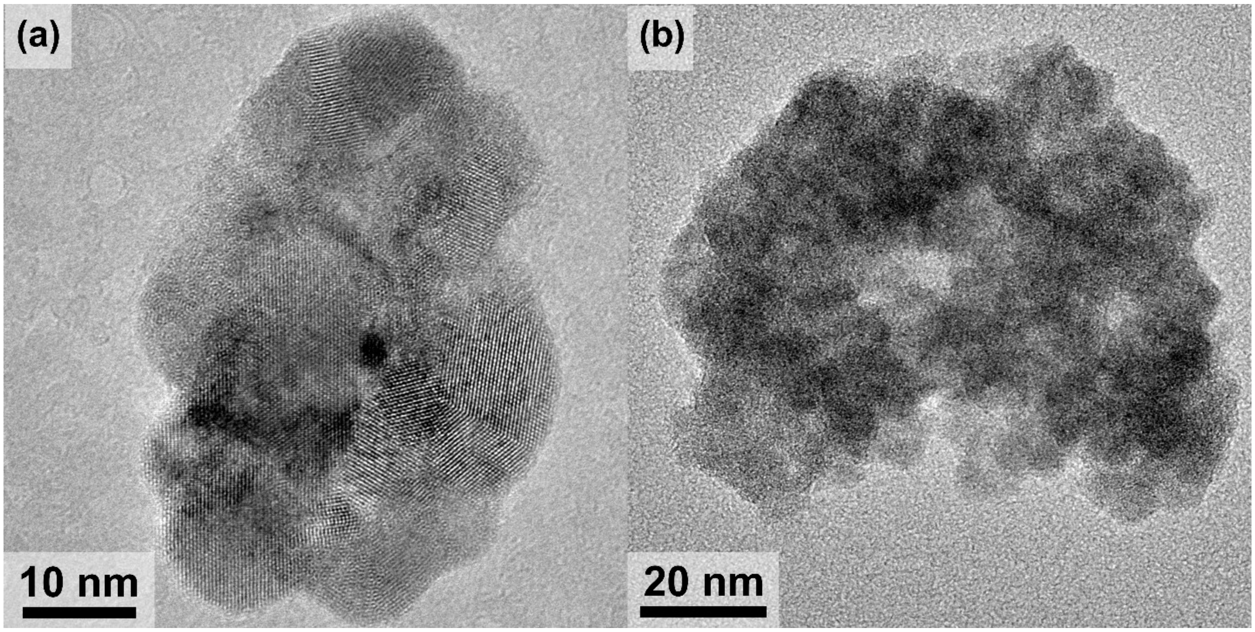

Figure S9. TEM of hydrolyzed $GeCl_2$·dioxane annealed at 325 °C.

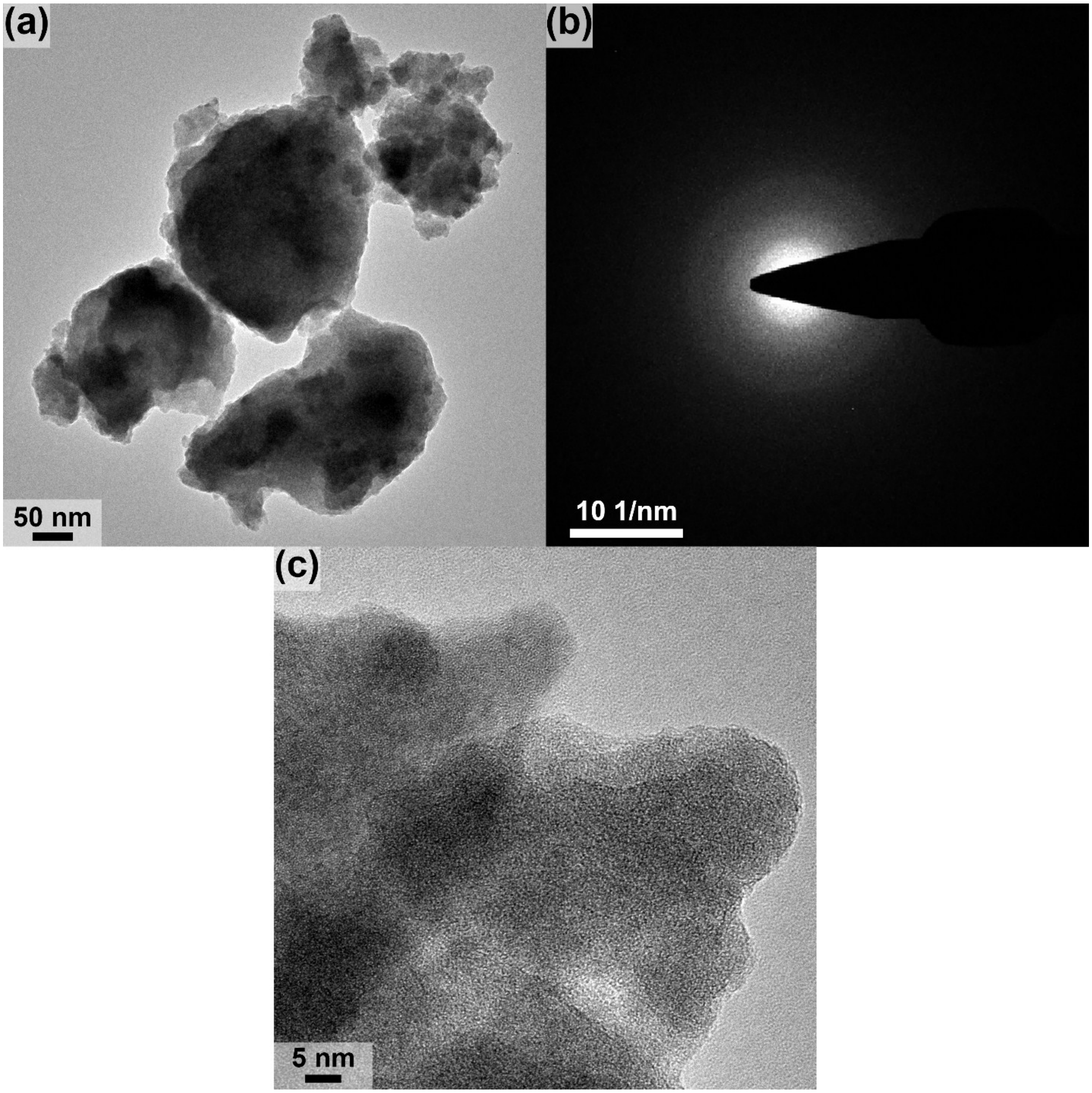

Figure S10. TEM of hydrolyzed GeCl$_2$·dioxane annealed at 250 °C (a) with low magnification, and (c) with high magnification. (b) shows the corresponding SAED in (a). There is no lattice fringe in HRTEM and SAED shows the absence of diffraction pattern, confirming the amorphous nature of this sample.

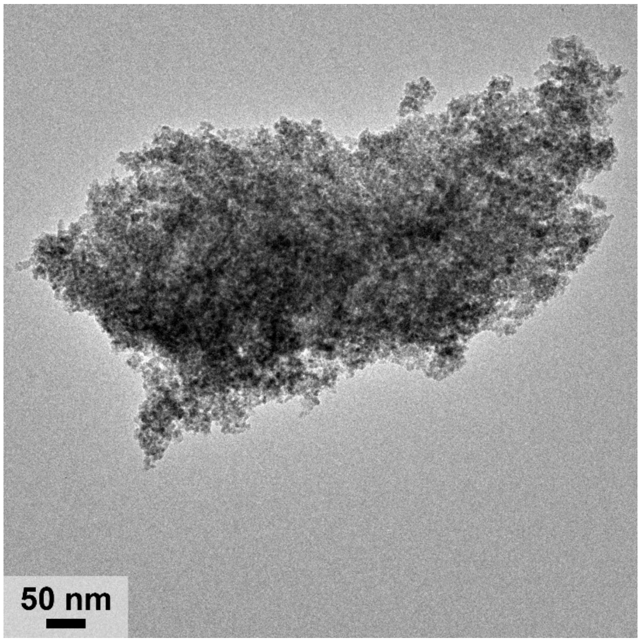

Figure S11. TEM of hydrolyzed $GeCl_2$·dioxane annealed at 425 °C with low magnification. It is representative for annealing temperature at or higher than 325 °C.

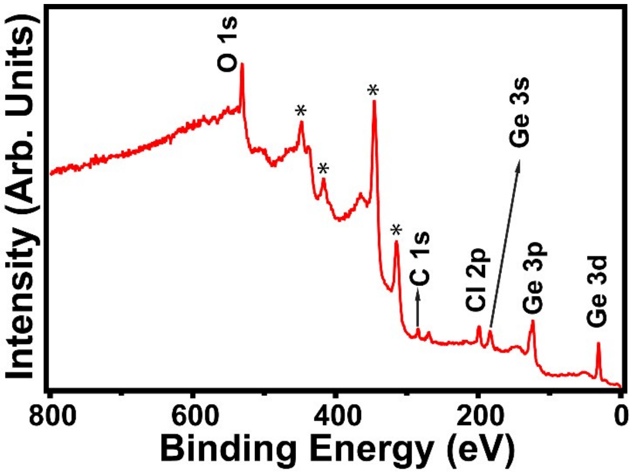

Figure S12. Survey XP spectrum of hydrolyzed $GeCl_2$·dioxane without annealing. The spectrum shows Ge, C, O and Cl. Signals assigned by an '*' are related to Ge LMM. Ratio between O and Cl was determined to be 2 : 1.

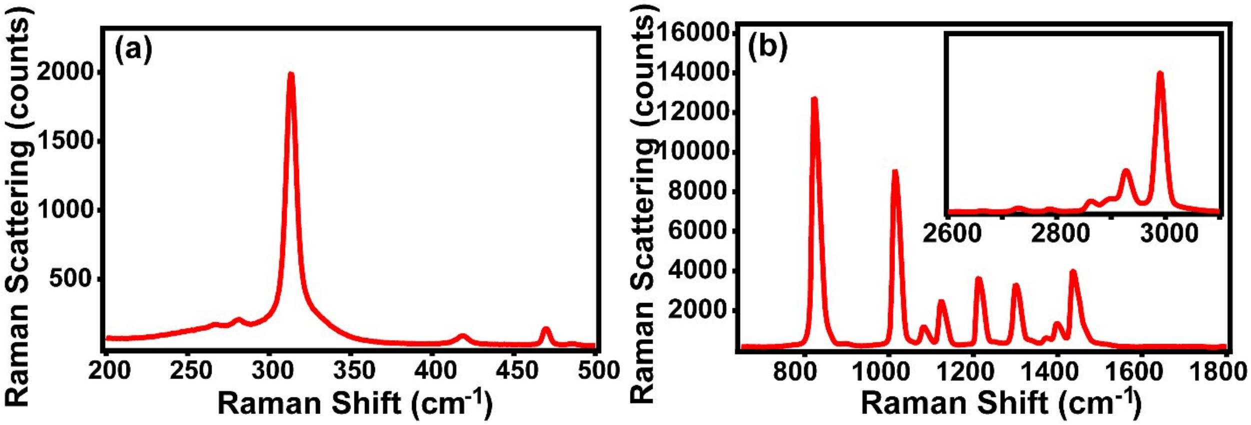

Figure S13. Raman spectra of $GeCl_2$·dioxane acquired with (a) 2400 grooves/mm and (b) 600 grooves/mm gratings. The spectra were acquired for 10 s with a 3.60 mW 532 nm excitation laser. The Raman peak assignments and vibrational modes can be found in Table S1.

Table S1. Raman peak assignments and vibrational modes of $GeCl_2 \cdot$dioxane complex.

Raman Shift (cm^{-1})	Assignment / Vibrational Modes [d]
282	Amorphous Ge
314	Ge phonon mode of Ge-Cl stretch
420	Symmetric stretching of GeO_2 Terminal Ge-Cl stretching mode
470	O-C-C deformation mode of dioxane
485	Ge-Cl stretch
821	C-O-C symmetric stretch
1014	C-C stretch
1083	C-C stretch and
1124	H-C-C bend
1214	C-O-C antisymmetric stretch
1299	CH_2 bend
1373	
1398	
1438	
2728	C-H stretch
2786	
2863	asymmetric/symmetric C-H stretch
2929	
2992	

[d] References for the indicated peak assignments and vibrational modes can be found as references 1-5 in the References section.

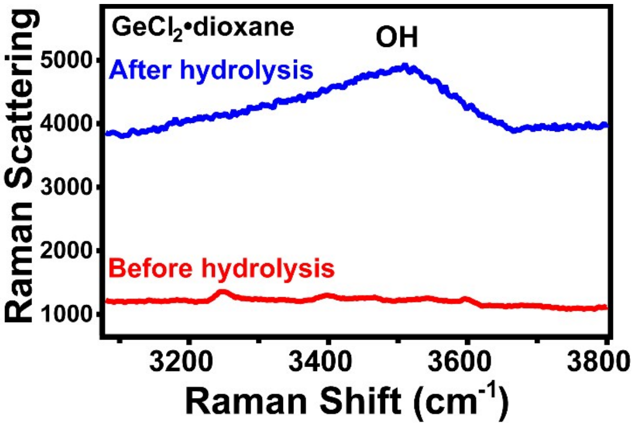

Figure S14. Raman spectra of $GeCl_2 \cdot$dioxane before and after hydrolysis. The OH stretching vibrational mode is shown at 3510 cm^{-1}. The spectrum was collected for 10 s with a 3.60 mW 532 nm excitation laser.

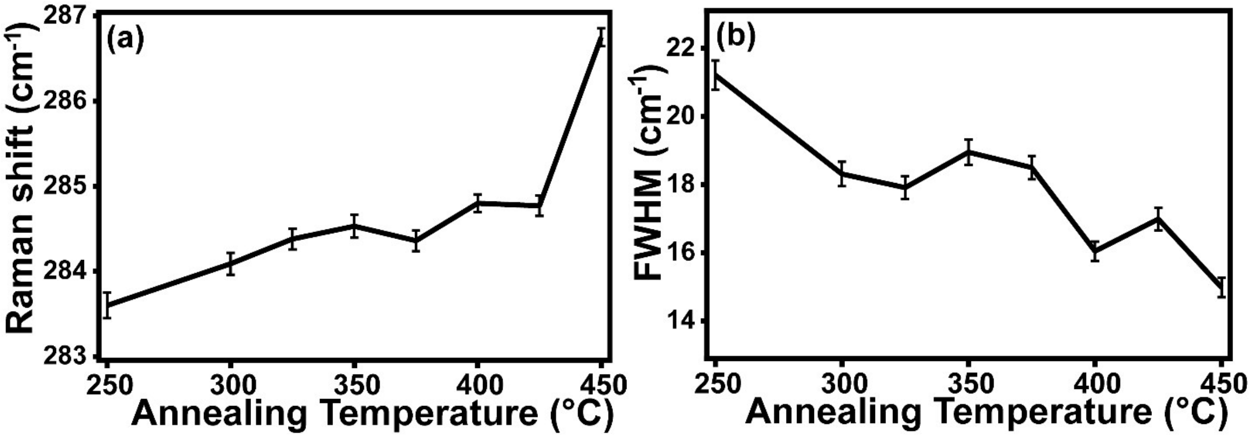

Figure S15. (a) Annealing temperature dependence of Ge-Ge LO phonon (a) Raman peak position and (b) full width at half maximum (FWHM). As the annealing temperature increases, the Ge LO phonon peak is shifted to higher wavenumbers and the FWHM decreases. The patterns are consistent with quantum confined excitons in nanocrystals of increasing size.[6] The uncertainties represent standard deviations from five spectra collected at each annealing temperature.

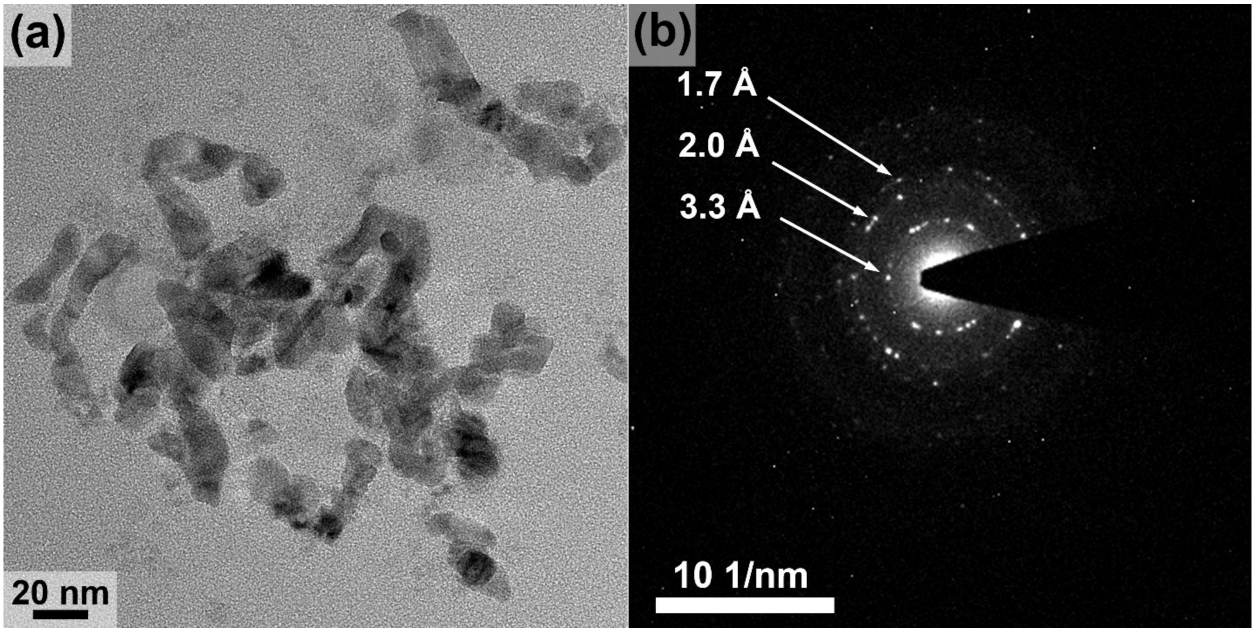

Figure S16. (a)TEM of octadecene-passivated Ge NCs from annealing hydrolyzed $GeCl_2$·dioxane at 425 °C. (b) Selected area electron diffraction (SAED) pattern of the area in (a).

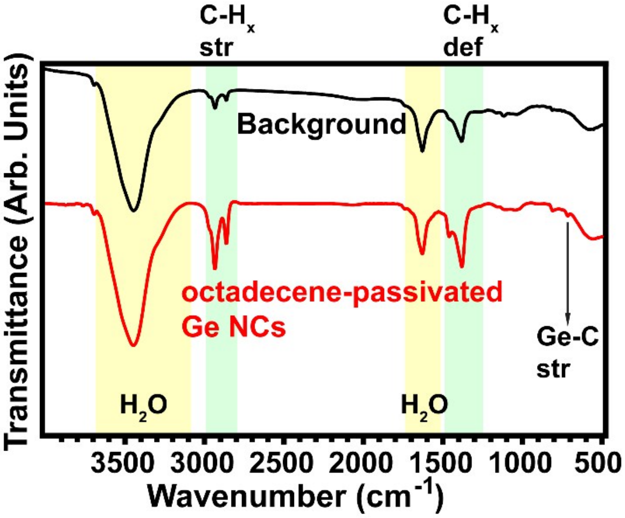

Figure S17. Normalized FTIR spectrum of background and octadecene-passivated Ge NCs from annealing hydrolyzed $GeCl_2$·dioxane at 425 °C.

(1) P. Borowski, W. Gac, P. Pulay and K. Woliński, *New Journal of Chemistry*, 2016, **40**, 7663–7670.

(2) E. R. Lippincott, P. Mercier and M. C. Tobin, *The Journal of Physical Chemistry*, 1953, **57**, 939–942.

(3) F. E. Malherbe and H. J. Bernstein, *Journal of the American Chemical Society*, 1952, **74**, 4408–4410.

(4) G. A. Ozin and A. V. Voet, *J. Chem. Phys.*, 1972, **56**, 4768–4775

(5) R. Wada and M. Kato, *Chemical Physics Letters*, 2015, **641**, 74–79

(6) E. J. Henderson, C. M. Hessel and J. G. C. Veinot, *J. Am. Chem. Soc.*, 2008, **130**, 3624–3632.

III. References: