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Diorganyl Dichalcogenides as Surface Capping Ligands for Germanium Nanocrystals

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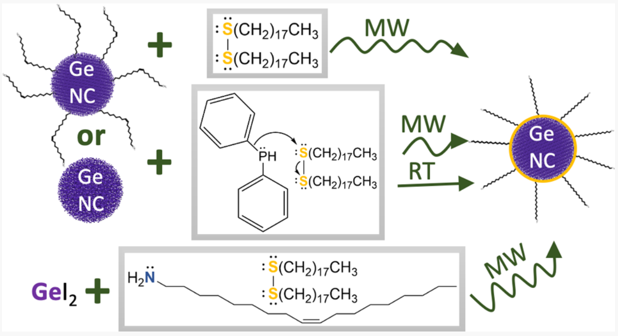

ABSTRACT: Indirect ligand exchange methods have been demonstrated to replace the oleylamine capping with dodecanethiol for germanium nanocrystals (Ge NCs). In these methods, hydrazine is employed to effectively remove the oleylamine ligand before the NCs are passivated by microwave-assisted heating with dodecanethiol. In this work, octadecanethiol passivation is accomplished by the *in situ* reaction of dioctadecyl disulfide with diphenylphosphine. ^{1}H NMR and FTIR are used to characterize the surface ligand capping and the effectiveness of ligand exchange. Thiol passivation is achieved either by an exchange reaction at room temperature or by using microwave-assisted heating. Indirect and direct ligand exchange methods are demonstrated to be effective. The microwave-assisted reaction of GeI_2 with dioctadecyl disulfide also achieves thiol passivation without interfering in the formation of Ge NCs. Additional experiments study the effects of nanoparticle synthesis temperature, solvent, and ligand concentration on the exchange of oleylamine for octadecanethiol ligands.

■ INTRODUCTION

In the solution synthesis of nanomaterials, surface capping ligands moderate growth and help control particle morphology.[1] After synthesis, capping ligands assist solubility and prevent surface oxidation and particle aggregation.[2] Nanoparticles (NPs) have a high surface area to volume ratio; thus, surface defects greatly influence optoelectronic properties. Ligands affect the observed optical properties by influencing nanoparticle band structure and preventing surface trap states that hinder emission.[2,3] Ge and Ge-containing NPs have been synthesized by various colloidal routes to achieve halide, hydride, amine, and alkyl surface passivation.[2] For NPs synthesized with hydride termination, ligand passivation can be achieved by reaction with organic precursors. For example, alkylsilyl termination of Ge NPs was recently achieved via a heteronuclear dehydrocoupling reaction.[4] Direct and indirect ligand exchange methods have also been used to introduce surface functionalities that may otherwise be inaccessible during synthesis. Direct ligand exchange depends on the binding competition between ligands; in one example, oleylamine (OAm) was replaced directly from the surface of $Ge_{1-x}E_x$ NPs by washing with less labile hexylamine.[5,6] For indirect ligand exchange, NPs are chemically treated to remove the original ligand before recapping by heating or stirring in a solution of the new ligand. Indirect ligand exchange methods have been demonstrated to achieve thiol passivation of Ge nanocrystals (NCs).[7,8] Oleylamine was removed from the nanoparticle surface by sonicating with hydrazine before microwave-assisted heating was used to passivate the surface with dodecanethiol or *N*4,*N*4,*N*4′,*N*4′-tetraphenylbiphenyl-4,4′-diamine ligands. An increased optical band gap and resistance to oxidation were observed after recapping; the oxidative signal was lost from cyclic voltammetry, confirming that recapping repairs surface defects.[8] The use of hydrazine, which is acutely toxic, carcinogenic, and has a very low flashpoint (52 °C), requires working in an inert environment and limits the broad applicability of the method. Effective direct ligand exchange methods have been used to passivate other semiconductor, metal, and metal oxide nanocrystal systems with small inorganic molecules while avoiding the use of hydrazine.[9−11] However, hydrazine-free, direct treatment of OAm-capped Ge NCs with dodecanethiol has been shown to result in an incomplete ligand exchange.[7] Hydrazine-free direct ligand exchange may be achievable for Ge NCs with the application of other sulfur-containing molecules as ligands.

Diorganyl dichalcogenide compounds have been used as molecular precursors in the synthesis of a variety of colloidal semiconductor NCs with controlled composition and morphology.[12−15] The relative bond dissociation energies of carbon−chalcogen (C−Q) and chalcogen−chalcogen (Q−Q)

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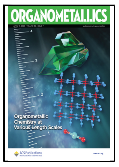

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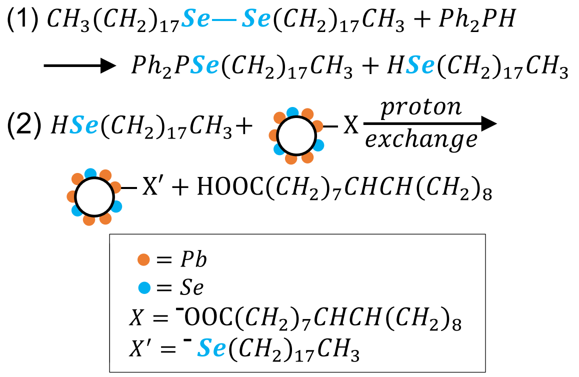
bonds in the diorganyl dichalcogenide reactants have been used to explain the observed compositions and morphologies. A low bond dissociation energy for C−S bonds gives S-rich phases in the Fe_xS_y system.[13] The metastable wurtzite phase $Cu_{2-x}Se$ can be achieved by the reaction of precursors with high bond dissociation energies, while low bond dissociation energies give thermodynamic products.[14] In both cases, alkylamines or other coordinating solvents are important to the formation and reactivity of chalcogenide intermediates. Computational studies by Guo and Alvarado assessed the reactivity of the C−Q and Q−Q bonds and correlated the bond dissociation energies to observed NC morphologies.[15] Anisotropic structures have been observed from the reaction of diethyl disulfide and dimethyl disulfide, which have similar bond dissociation energies for the C−Q and Q−Q bonds. Quantum dots are achieved by the reaction of dibenzyl disulfide, which has a Q−Q bond stronger than a C−Q bond. When it is included in the nanoparticle synthesis reaction, diphenyl disulfide yields phenylthiyl radicals due to a strong C−Q bond and a weak Q−Q bond. The phenylthiyl radical stabilizes small CdS nuclei in solution, yielding no isolatable product.[15]

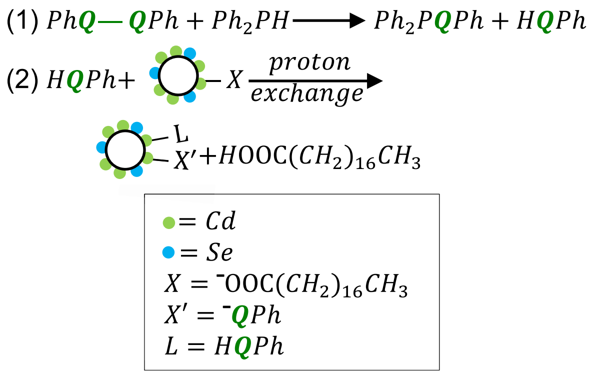
Diorganyl dichalcogenide compounds have also been used as capping ligands for colloidal semiconductor NCs. Hughes reported that the reaction of dioctadecyl diselenide with diphenyphosphine (Ph_2PH) yields octadecylselenol, which replaces oleate ligands on the surface of PbSe via proton transfer for a direct ligand exchange (Scheme 1).[16] A similar direct ligand exchange procedure was also used by Buckley and Couderc to replace the stearate ligand passivation on CdSe NCs. The reduction of diphenyl disulfide, diphenyl diselenide, and diphenyl ditelluride with Ph_2PH gives chalcogenol species, which undergo a direct exchange with the stearate on the nanocrystal surface (Scheme 2).[3]

Scheme 1. Ph_2PH Reduces Dioctadecyl Diselenide, Yielding Octadecaneselenol, Which Replaces the Oleate Ligand via a Proton Exchange Mechanism to Passivate the Surface of PbSe NCs



In this work, the passivation of Ge NCs with octadecanethiol produced by the *in situ* reduction of dioctadecyl disulfide with Ph_2PH is demonstrated. Room-temperature reactions achieve thiol passivation with and without the use of hydrazine to remove the OAm ligand from the Ge NC surface. Microwave-assisted heating is also applied to the indirect and direct ligand exchange procedures. It is further shown that microwave-heated reactions do not require Ph_2PH to achieve ligand exchange. The microwave-assisted reaction of a solution of GeI_2 and dioctadecyl disulfide in OAm is demonstrated to yield Ge NCs with thiol passivation. Additional experiments were performed to determine the effects of nanoparticle synthesis temperature, ligand exchange solvent, and ligand concentration. Proton nuclear magnetic resonance (^1H NMR) and Fourier-transform infrared (FTIR) spectroscopies are used to characterize the nanocrystal surface passivation and the effects of ligand exchange procedures. Diorganyl dichalcogenide compounds are shown to be versatile tools in achieving organic ligand passivation on the surface of Ge NCs.

Scheme 2. Ph_2PH Reduces Diphenyl Dichalcogenide, Yielding Phenyl Chalcogenol, Which Replaces the Stearate Ligand via a Proton Exchange Mechanism to Passivate the Surface of CdSe NCs



■ EXPERIMENTAL SECTION

Chemicals. Germanium(II) iodide (GeI_2) was purchased from Professor Richard Blair's laboratory at the University of Central Florida.[17] Oleylamine ($CH_3(CH_2)_7CHCH(CH_2)_8NH_2$, ≥98%, Sigma-Aldrich) and 1-dodecene ($CH_3(CH_2)_9CHCH_2$, 95%, Sigma-Aldrich) were dried over 3 Å molecular sieves for several days and degassed by heating to 150 °C under vacuum for 2 h before use. Hydrazine (N_2H_4, anhydrous, 98%, Sigma-Aldrich), diphenylphosphine (Ph_2PH, 98%, Sigma-Aldrich), ethanol (CH_3CH_2OH anhydrous, ≥99.5%, Sigma-Aldrich), methanol (CH_3OH anhydrous, ≥99.5%, Sigma-Aldrich), dioctadecyl disulfide ($CH_3(CH_2)_{17}SS(CH_2)_{17}CH_3$, 98%, Alfa Aesar), deuterated benzene (C_6D_6) (99.5 atom % D, Cambridge Isotope Laboratories), and deuterated chloroform ($CDCl_3$) (99.8 atom % D, Cambridge Isotope Laboratories) were used as received. Toluene, hexane, and acetonitrile (HPLC grade, Sigma-Aldrich) were passed through a solvent still prior to use. All chemicals, except deuterated solvents, were stored in an argon glovebox.

Microwave Synthesis. In an argon-filled glovebox, 6 mL of OAm was added to 0.4 mmol of GeI_2 in a 35 mL CEM microwave tube with a stir bar and sealed with a Teflon cap. The mixture was sonicated outside the glovebox to form a transparent yellow solution. The solution was heated at 230 or 250 °C for 30 min in dynamic heating mode using a CEM Discover microwave equipped with a CEM Explorer autosampler. The reaction produced a dark brown suspension. In an argon-filled glovebox, the suspension was transferred to a centrifuge tube using 4 mL of toluene, and 15 mL of ethanol and 10 mL of methanol were added as an antisolvent. The mixture was centrifuged at 8500 rpm for 10 min, yielding a colorless solution and dark precipitate. In an argon-filled glovebox, the supernatant was decanted, and the Ge NC precipitate was dispersed in 5 mL of hexane or toluene. All samples were stored in an argon-filled glovebox.

Ligand Exchange. *Hydrazine Treatment.* A ligand exchange procedure was performed on 1 mL aliquots of OAm-capped Ge NCs in hexane. In an argon-filled glovebox, 2 mL of toluene and 3 mL of 5 M hydrazine in acetonitrile were added to 1 mL of Ge NC solution.

Outside the glovebox, the mixture was sonicated for 90 min and then centrifuged at 8500 rpm for 10 min to separate the uncapped Ge NCs from the solvent. The colorless liquid phase was decanted, and a dark brown precipitate was collected. The precipitate was briefly sonicated with 5 mL of acetonitrile and then centrifuged at 8500 rpm for 5 min. After the colorless supernatant was removed, the particles were resuspended in 5 mL of hexane and separated without centrifugation. After separation, the supernatant was decanted, and the precipitate was retained. The precipitate was washed with hexane a total of three times using this procedure. The precipitate was stored under 3 mL of hexane in an argon-filled glovebox.

Hydrazine-Assisted Exchange. Uncapped Ge NCs were treated with dioctadecyl disulfide to achieve thiol surface passivation. In an argon-filled glovebox, 0.1 or 0.2 mmol of dioctadecyl disulfide was dissolved in 2 mL of toluene or 1-dodecene and added to a 3 mL suspension of uncapped Ge NCs. After the recapping mixture was stirred for 5 min, 0.17 mmol (30 μL) of Ph_2PH was added to it. The mixture was stirred in an argon-filled glovebox without heating for 3 days or was transferred to a 35 mL microwave tube with a stir bar, sealed with a Teflon cap, and heated at 150 °C for 60 min in dynamic heating mode in the microwave reactor. Following the recapping reaction, the NC solutions were transferred into an argon-filled glovebox and transferred to a centrifuge tube with 4 mL of hexane. A 20 mL portion of anhydrous ethanol was added as an antisolvent, and the mixture was centrifuged at 8500 rpm for 10 min, yielding a clear, colorless solution. In an argon-filled glovebox, the supernatant was discarded. In the PXRD pattern, the ligand gives low-angle peaks that are narrow in comparison with the peaks from the Ge NCs. The samples were resuspended in 30 mL of toluene, precipitated with 3−6 mL of acetonitrile, and centrifuged at 8500 rpm for 5 min. This process was repeated three times until all ligand peaks were removed from the PXRD pattern. The thiol-passivated Ge NC precipitate was suspended in 2 mL of hexane.

Direct Exchange. The above procedure was repeated using OAm-capped Ge NCs that were not treated with hydrazine. In an argon-filled glovebox, 0.1 mmol of dioctadecyl disulfide was dissolved in 2 mL of toluene and added to a 3 mL suspension of OAm-capped Ge NCs. After the recapping mixture was stirred for 5 min, 0.17 mmol (30 μL) of Ph_2PH was added to it, and this mixture was stirred in an argon-filled glovebox without heating for 3 days or was transferred to a 35 mL microwave tube with a stir bar, sealed with a Teflon cap, and heated at 150 °C for 60 min in dynamic heating mode in the microwave reactor. Following the recapping reaction, the NC solutions were transferred into an argon-filled glovebox and washed using the procedure given above. The thiol-passivated Ge NCs were then suspended in 2 mL of hexane.

Exchange without Diphenylphosphine. To test the need for a catalyst and the effects of nanocrystal synthesis temperature, solvent, and dioctadecyl disulfide concentration, these parameters were varied for some exchanges. Toluene dispersions of OAm-capped Ge NCs synthesized at 230 or 250 °C were sonicated with 5 M hydrazine, washed with acetonitrile and hexane, and then heated in the microwave at 150 °C for 1 h with 0.1 or 0.2 mmol of dioctadecyl disulfide in 1-dodecene or toluene. In these experiments, Ph_2PH was excluded from the reaction. The NCs were isolated from solution and washed using the procedure given above. All products were stored in an argon-filled glovebox.

Nanocrystal Synthesis with Dioctadecyl Disulfide. Ge NCs were synthesized with dioctadecyl disulfide in the reaction mixture to see if thiol passivation could be accomplished without use of a ligand exchange procedure. In an argon-filled glovebox, 0.4 mmol of GeI_2 and 0.1 mmol of dioctadecyl disulfide were added to 6 mL of OAm in a capped CEM microwave tube. After dissolution by sonication, the solution was heated in the microwave reactor at 250 °C for 30 min, resulting in a dark brown suspension. In an argon-filled glovebox, the Ge NC precipitate was washed with 4 mL of toluene and 15 mL of anhydrous methanol. Following centrifugation at 8500 rpm for 10 min, the mixture was returned to the glovebox and the colorless supernatant was decanted. The samples were resuspended in toluene and precipitated with acetonitrile. This process was repeated multiple times until all ligand peaks were removed from the PXRD pattern. The dark precipitate was then dispersed in 6 mL of toluene and stored in an argon-filled glovebox.

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation (40 kV, 40 mA). The colloidal solution was deposited on a silica zero-background holder and dried before data collection. Data were collected in air in the 2θ range of 10−80° with a step size of 0.02°. The crystallite diameter was determined from the (220) reflection using a Scherrer analysis in MDI Jade 5.0 software.[18] Patterns were compared to reference powder diffraction files (PDFs) from the International Center for Diffraction Data (ICDD).

Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM). An ultrathin carbon film on a lacey carbon support film on 400 mesh copper grids (Ted Pella Inc.) or an ultrathin carbon film on a holey carbon support film on 300 mesh copper grids (Structure Probe Inc.) were used for TEM and STEM imaging. Dispersions of NCs in toluene were drop-cast on the grid and dried overnight under an incandescent lamp for TEM imaging or in a 120 °C vacuum oven for STEM imaging. TEM imaging was performed on a JEOL-JEM 2500 SE transmission electron microscope (JEOL Ltd. Tokyo, Japan), which was operated at 200 keV and was equipped with a Schottky field emission gun (FEG) and a retractable 1k × 1k Gatan Multiscan CCD camera (Gatan Inc., Model 794). STEM imaging was performed on an aberration-corrected JEOL JEM-2100AC transmission electron microscope equipped with a Gatan annular dark field (ADF) detector. Particles were imaged in high-angle annular dark field (HAADF) and bright field STEM imaging modes with camera lengths of 10 or 12 cm. TEM and STEM images were collected using Digital Micrograph software. ImageJ software was used to measure particle diameters of approximately 200−350 unique NCs on each specimen grid.[19] Using TEM images, particle diameters were determined from intensity line profiles taken across individual particles in one consistent direction. Using STEM images, particle diameters were determined as the geometric mean of the minimum and maximum Feret diameters.

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). ^{1}H NMR spectra were collected at room temperature using a 400 MHz Bruker Nanobay AVIIIHD spectrometer. To prepare samples for NMR, 0.5 mL of NC solution was heated to dryness in a vacuum oven at 100 °C for 3 h. In an argon-filled glovebox the dry NC samples were redispersed in 0.5 mL of *d*-chloroform or *d*-benzene and transferred to an NMR tube. Spectral analysis was performed using MestReNova Version 10.0.2-15465 software.[20]

Fourier-Transform Infrared (FTIR) Spectroscopy. FTIR spectra were collected on a Bruker Alpha-P spectrometer from 4500 to 375 cm^{-1}. NC dispersions were deposited on the instrument's attenuated total reflectance (ATR) chip and allowed to dry before data collection.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Samples for SEM-EDS were prepared by drop-casting concentrated dispersions of Ge NCs in toluene on a 1 × 1 cm^2 silicon substrate. The samples were dried at room temperature under vacuum overnight. SEM images and EDS maps were collected on an FEI Scios dual-beam scanning electron microscope with a 20 kV acceleration voltage. Oxford AZtec software was used to collect EDS maps and spectra.[21]

■ RESULTS AND DISCUSSION

Synthesis and Characterization of OAm-Capped Ge NCs. Following an adapted literature procedure, Ge nanocrystals (NCs) were synthesized by the microwave-assisted reduction of GeI_2 in OAm at 230 or 250 °C.[22] Oleylamine acts as the solvent, reducing agent, and capping ligand for the synthesis reaction. The resulting OAm-capped Ge NCs were precipitated and dispersed in hexane for characterization. The powder X-ray diffraction patterns of the Ge NCs are consistent with cubic Ge (Figure 1). By Scherrer analysis of the (220) reflection, the crystallite sizes are determined to be 3.12(9) and

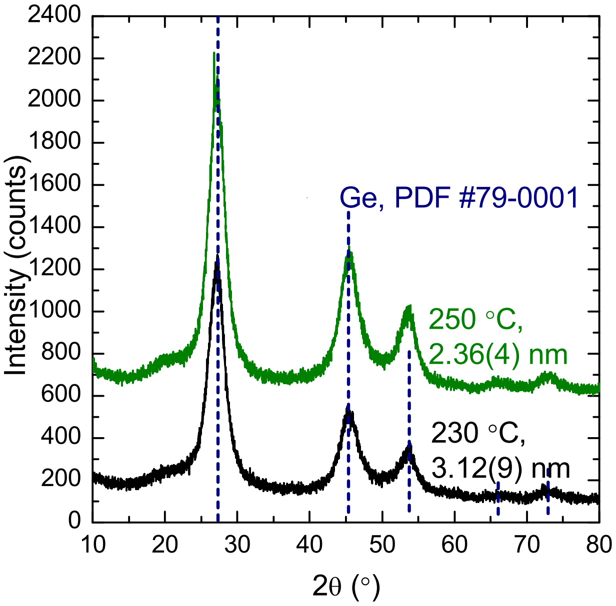


Figure 1. PXRD pattern of OAm-capped Ge NCs synthesized at 230 and 250 °C compared to the reference pattern of cubic Ge (ICDD PDF #79-0001, dark blue dashed lines).

2.36(4) nm for Ge NCs synthesized at 230 and 250 °C, respectively. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) imaging were used to characterize particle size and morphology for the Ge NCs synthesized at 230 and 250 °C. From TEM images, the particle diameter was determined from intensity line profiles across individual particles (Figure 2 and Figure S1 in the Supporting Information). Particles are observed to be quasi-spherical in shape with average diameters of 4.1 ± 0.7 and 4.7 ± 0.6 nm for the 230 and 250 °C syntheses, respectively. Bright field and high-angle annular dark field (HAADF) STEM images of Ge NCs synthesized at 250 °C are available in Figure S2 in the Supporting Information, with the corresponding particle size distribution histograms.

The surface of the OAm-capped Ge NCs was characterized by ^{1}H NMR, and the spectra were compared to that of unbound OAm (Figure 3 and Figure S3 and Table S1 in the Supporting Information). Peaks corresponding to vinylic and allylic protons are observed at 5.33 and 1.96 ppm, respectively, and are characteristic of the C=C double bond in OAm. The peak near 2.89 ppm is attributed to the α protons, which are deshielded by the terminal amine group, causing the peak to shift from the expected position at 2.6 ppm.[7,23] Peaks for the alkyl chain and terminal methyl groups are found at 1.24 and 0.85 ppm, respectively, and are broadened relative to those of the free ligand. Peak shifting and broadening indicate a ligand–surface interaction and have been attributed to poor solvation of the ligand shell, slow rotation of bound ligands, and heterogeneous particle size.[24−26] In free OAm, the chemical shift from the amine proton is found at 1.05 ppm, but it is not observed for OAm-capped Ge NCs; this is consistent with previous observations for amine ligands on the surface of Ge and ZnO NCs and may be attributed to rapid exchange of the acidic proton or broadening due to close proximity to the NC surface.[24,25,27,28] Peaks at 2.33 and 1.52 ppm are attributed to toluene and water impurities in the NMR solvent, respectively.[29]

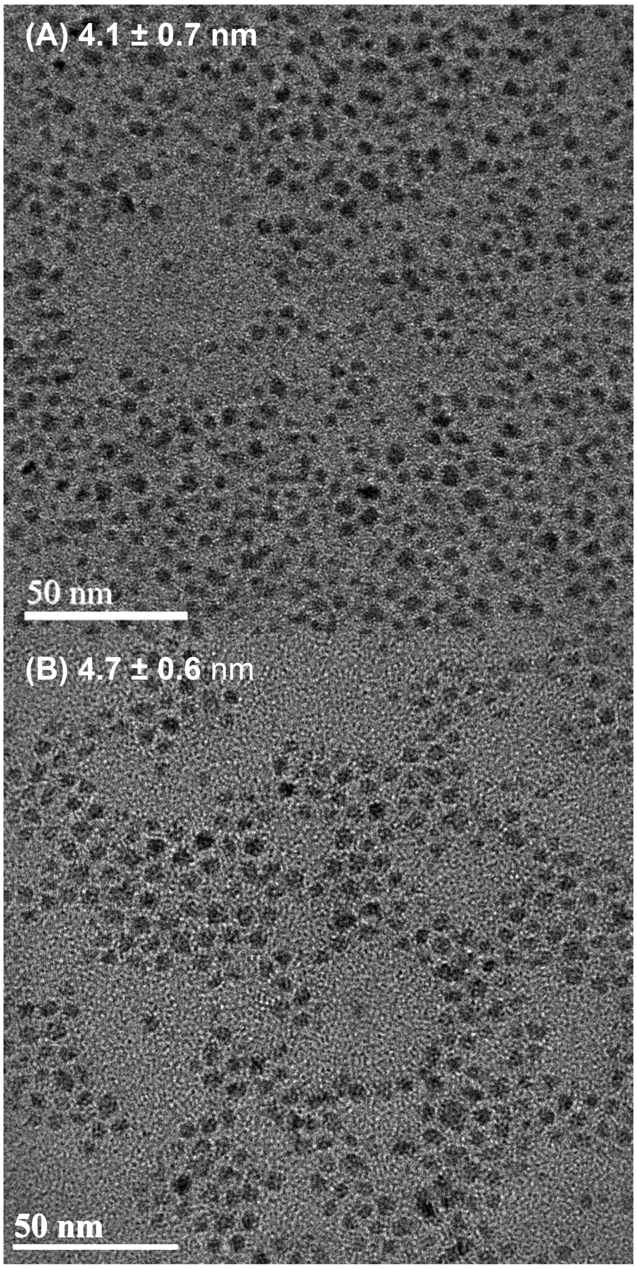


Figure 2. TEM images of OAm-capped Ge NCs synthesized at (A) 230 and (B) 250 °C.

FTIR spectroscopy was used to further characterize the NC surface capping prior to ligand exchange (Figure 4). The FTIR spectrum shows a vinylic C–H stretch at 3005 cm^{-1}, a C=C stretch at 1645 cm^{-1}, and an NH$_2$ bend at 1558 cm^{-1}, which are consistent with OAm passivation. The secondary amine N–H stretch is observed as a broad peak near 3300 cm^{-1}. The small peak near 965 cm^{-1} suggests that some of the ligand converts from the *cis* to the *trans* isomer during the reaction.[30,31] A peak for the Ge–N stretch, expected between 600 and 800 cm^{-1}, is not explicitly observed.[32] Oxidation may occur during the time in which a spectrum is collected; broad peaks from 650 to 900 cm^{-1} may include contributions from Ge–OH, Ge–O, Ge–O–Ge, and Ge–N stretches.[22,33−35]

Hydrazine-Assisted Ligand Exchange to Achieve Octadecanethiol Passivation. Thiol passivation has been demonstrated to give changes in band gap and improved

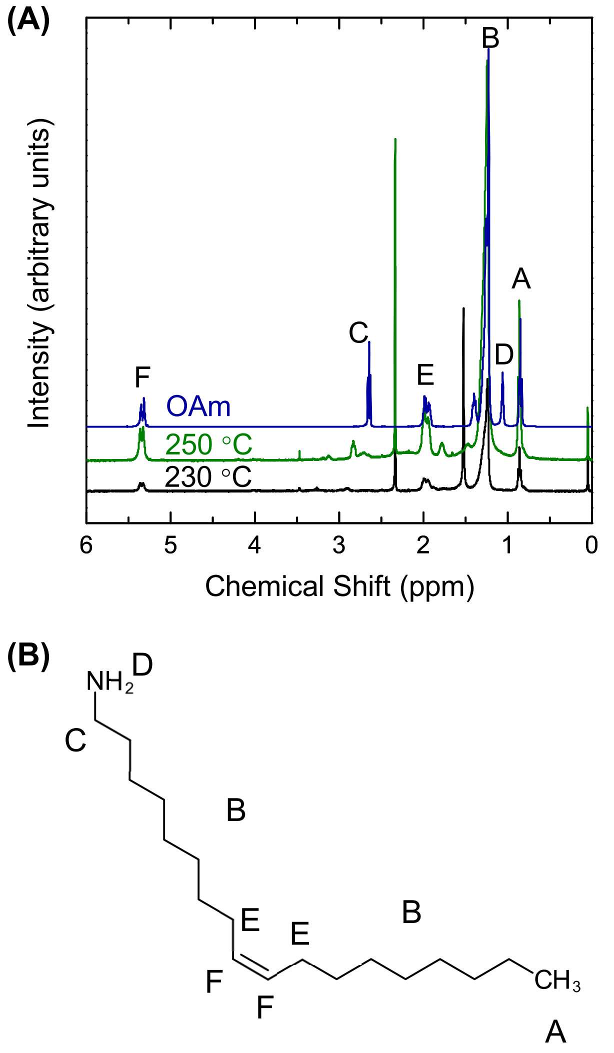


Figure 3. (A) ^{1}H NMR spectra of free OAm and OAm-capped Ge NCs synthesized at 230 and 250 °C and (B) the line structure of OAm with corresponding labels.

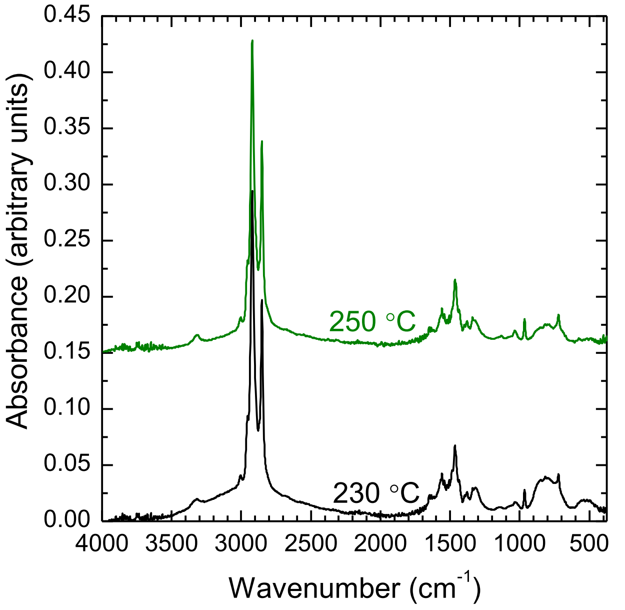
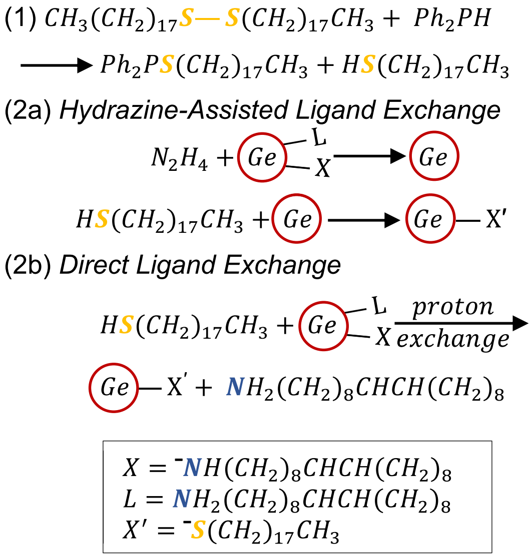


Figure 4. FTIR spectra of OAm-capped Ge NCs synthesized at 230 and 250 °C.

Scheme 3. Ph$_2$PH Reduces Dioctadecyl Disulfide, Yielding Octadecanethiol, Which Passivates the Surface of Ge NCs by a Hydrazine-Assisted Method or a Direct Ligand Exchange Method



protection from oxidation for Ge NCs. Although thiol passivation has been achieved by ligand exchange methods, there is interest in expanding the toolbox of ligand exchange chemistry and achieving chalcogenol passivation from other precursors. Thiols are malodorous irritants, and chalogenols, especially selenols and tellurols, are unstable in air and moisture. Dichalcogenides, however, are stable in air and moisture, lending ease of handling. Thus, this work demonstrates that thiol passivation can be achieved by the reaction of diphenylphosphine (Ph$_2$PH) and a diorganyl disulfide precursor. In the presence of Ge NCs, dioctadecyl disulfide is reduced by Ph$_2$PH, breaking the disulfide bond to yield octadecanethiol (Scheme 3). Octadecanethiol can then passivate the NC surface through Ge−S bonding.

The Ge NCs were synthesized with an OAm capping ligand. It was previously demonstrated that treatment with hydrazine (hydrazine-assisted exchange) to remove the OAm capping ligand prior to addition of the new passivation results in a complete ligand exchange.[7] Direct exchange, without hydrazine treatment, was shown to achieve only a partial exchange. In 2014, He demonstrated the synthesis of monodisperse In, Ga, Bi, Sb, and Sn NCs by the reaction of OAm with *n*-butyllithium and metal chlorides.[23] The surface ligand capping was characterized to consist of a mixture of weaker L-type oleylamine ligands and stronger X-type oleylamide ligands. It was recently demonstrated that OAm binds to the surface of Ge NCs as an X-type oleylamide ligand (Ge−NHR bonding), but physiosorbed OAm may also be present.[26] Upon introduction of undecenethiol to the OAm-capped Ge NCs, thiol binding as an X-type thiolate ligand was observed. There was no observed loss of OAm; thus, it was concluded that the thiol occupies uncoordinated surface sites rather than displaces OAm. A high kinetic barrier to exchange necessitates the use of hydrazine to remove the X-type oleylamide capping ligand to achieve a complete ligand exchange.

Following a modified literature procedure, Ge NCs were sonicated with hydrazine to remove the OAm ligand from the surface.[7] A solution of dioctadecyl disulfide and Ph_2PH in toluene was added to a solution of uncapped Ge NCs, and the solution was heated by microwave-assisted methods at 150 °C for 1 h or stirred at room temperature for 72 h in an argon-filled glovebox. After the reaction, the octadecanethiol-capped Ge NCs were isolated by washing with anhydrous ethanol, acetonitrile, and hexane and then dispersed in hexane for characterization.

The surface passivation of the octadecanethiol-capped Ge NCs was characterized by ^1H NMR spectroscopy (Figure 5 and Figure S4 in the Supporting Information). The ^1H NMR spectra of octadecanethiol-capped Ge NCs were compared to those of unbound dioctadecyl disulfide (Figure S5 and Table S2 in the Supporting Information). The chemical shifts of the octadecanethiol ligand are expected to be broadened and shifted downfield from those of unbound dioctadecyl disulfide and to have different integrations. For both the microwave-heated and the room-temperature reactions, protons β to the thiol and the thiol proton are observed at 1.76 and 1.66 ppm, respectively. The α proton, expected at 2.66 ppm, was not observed, likely due to broadening into the background. Peaks consistent with the alkyl chain and terminal methyl group are observed at 1.36 and 0.98 ppm, respectively. Very weak intensities are observed at 5.52 ppm, consistent with the vinylic group of oleylamine, but the allylic protons expected near 2.0 ppm are not observed.

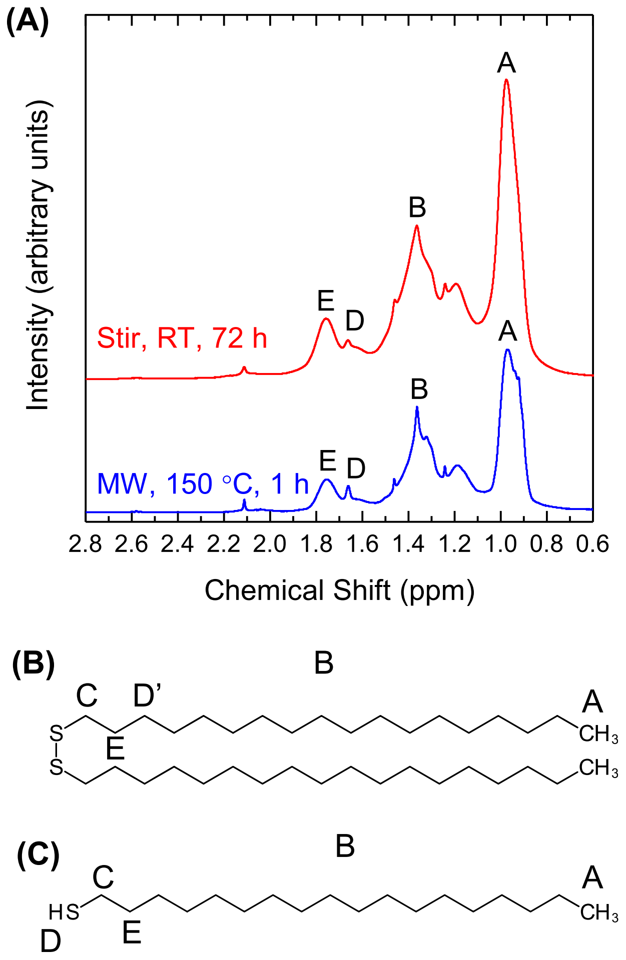


Figure 5. (A) ^1H NMR spectra of Ge NCs recapped with dioctadecyl disulfide by a hydrazine-assisted ligand exchange procedure with microwave-assisted heating at 150 °C for 1 h or stirring at room temperature for 72 h and the line structures of (B) dioctadecyl disulfide and (C) 1-octadecanethiol with corresponding labels.

The FTIR spectra provide further support for thiol passivation and loss of OAm at the particle surface. Peaks consistent with an alkyl chain are observed at 2853, 2922, and 2952 cm^{-1} (Figure 6).[36] The S–H and C–S stretches, expected at 2550–2600 and 720 cm^{-1}, respectively, are not observed, likely due to overall low intensities.[7,8,37] The alkenyl peak expected at 3005 cm^{-1} for OAm is not observed, consistent with removal of the OAm ligand. The Ge–S stretching mode is expected at 375 cm^{-1}, which is near the limit of the instrument's collection range and is not observed. Oxidation peaks are observed below 900 cm^{-1}.

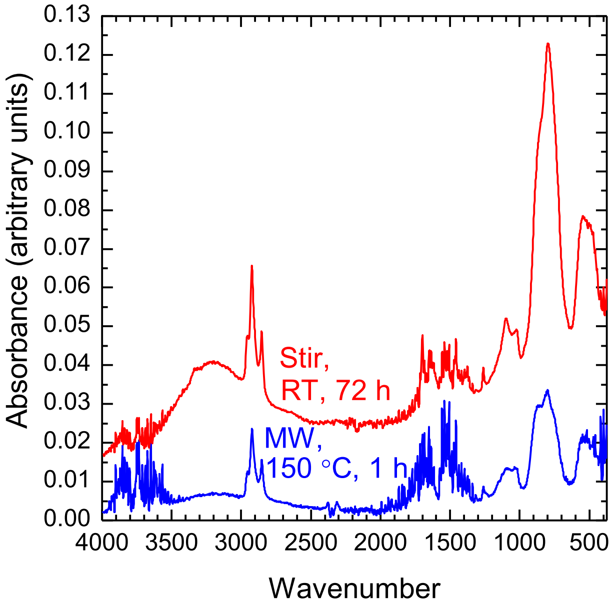


Figure 6. FTIR spectra of Ge NCs recapped with dioctadecyl disulfide by a hydrazine-assisted ligand exchange procedure with microwave-assisted heating at 150 °C for 1 h or stirring at room temperature for 72 h.

Direct Ligand Exchange to Achieve Octadecanethiol Passivation. In the literature, it was shown that treatment of OAm-capped Ge NCs with dodecanethiol results in an incomplete ligand exchange and that a complete ligand exchange could only be achieved by using hydrazine to remove the OAm ligand before passivation with dodecanethiol. Hydrazine is acutely toxic and carcinogenic and has a very low flashpoint (52 °C). Ligand exchange methods that avoid the use of hydrazine are safer. Direct methods, which avoid the use of hydrazine, have been used to achieve complete ligand exchange by the reaction of octadecyl diselenide and diphenylphosphine on the surface of PbSe. To determine the effectiveness of hydrazine-free direct ligand exchange methods, dioctadecyl disulfide and Ph_2PH were reacted in the presence of OAm-capped Ge NCs, which had not been previously treated with hydrazine. The reaction mixture was heated by microwave-assisted methods at 150 °C for 1 h or was stirred at room temperature for 72 h in an argon-filled glovebox. Following ligand exchange, the octadecanethiol-capped Ge NCs were washed with hexane, anhydrous ethanol, and acetonitrile and were dispersed in hexane. The ^1H NMR spectra are consistent with those of Ge NCs passivated with octadecanethiol following hydrazine treatment shown in Figure 7 (Figure 7 and Figure S6 in the Supporting Information).

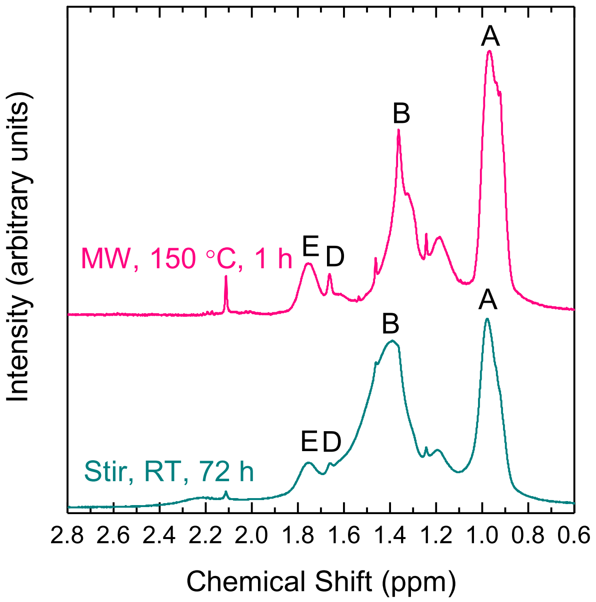


Figure 7. ^{1}H NMR spectrum of Ge NCs recapped with dioctadecyl disulfide by a direct ligand exchange procedure with microwave-assisted heating at 150 °C for 1 h or stirring at room temperature for 72 h.

Peaks consistent with alkanethiol passivation are observed, including the thiol proton at 1.66 ppm. The vinylic protons, indicative of OAm, are observed at 5.61 ppm after recapping by stirring at room temperature. The allylic protons, indicative of OAm, are not observed in either sample. FTIR spectra include alkyl stretches at 2853, 2922, and 2952 cm^{-1}, and S−H and C−S stretches are observed at 2680 and 720 cm^{-1}, respectively, following recapping at room temperature (Figure 8).[7,8,36,37] Weak alkenyl peaks, expected at 3005 and 1645 cm^{-1} for OAm, are also observed. Oxidation peaks are observed from 650 to 900 cm^{-1} following recapping at 150 °C and to a lesser degree following recapping at room temperature. The results indicate that octadecanethiol can directly displace OAm from the Ge NC surface without pretreatment with hydrazine, but some residual OAm remains.

Role of Diphenylphosphine in Microwave-Assisted Ligand Exchange. Diorganyl dichalcogenides have been used as synthons for binary metal−chalcogenide NCs without the use of Ph_2PH to reduce the dichalcogenide bond. Rather, the reactions use heat or light to induce cleavage of the dichalcogenide bond, generating chalcogenyl radicals, which undergo further reaction to form nanomaterials. It was hypothesized that microwave-assisted heating may break the dichalcogenide bond without the use of Ph_2PH, giving octadecanethyl radicals which could passivate the surface of uncapped Ge NCs. OAm-capped Ge NCs were synthesized at 230 °C and treated with hydrazine to remove the surface ligand capping. The uncapped Ge NCs were then heated in the microwave at 150 °C with 0.2 mmol of dioctadecyl disulfide in dodecene without Ph_2PH. ^{1}H NMR spectra were collected after a single washing step and after multiple washings (Figure 9 and Figure S7 in the Supporting Information). The spectra are consistent with octadecanethiol passivation. Peaks consistent with the β protons, alkyl chain, and terminal methyl groups are observed shifted downfield from their expected positions at 1.65, 1.23, and 0.86 ppm, respectively. Peak shifting is greater following multiple washes in comparison to that following a single wash, suggesting excess ligand is removed with additional washes (Figure S7 in the Supporting Information). Following multiple washes, a peak is observed at 1.55 ppm and may be assigned as the thiol proton shifted from its expected position near 1.3 ppm. A small peak, consistent with the vinylic proton of OAm, is observed at 5.3 ppm, indicating that some OAm remains after ligand exchange. The peak at 0.4 ppm is attributed to a water impurity in the NMR solvent. These results indicate that, at elevated temperatures,

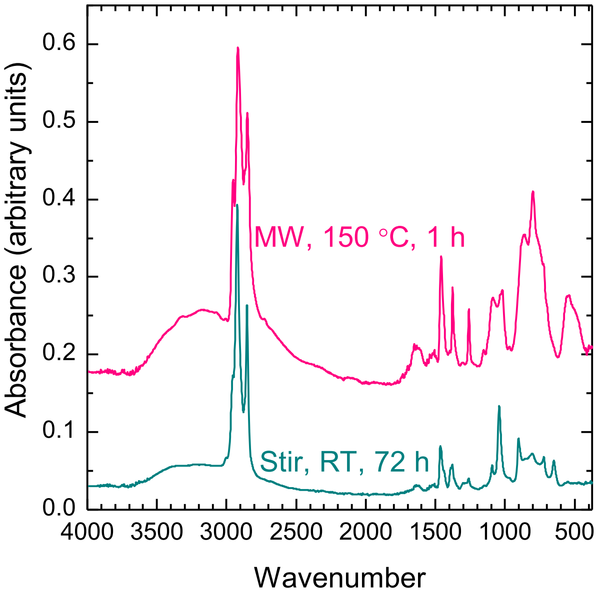


Figure 8. FTIR spectrum of Ge NCs recapped with dioctadecyl disulfide by a direct ligand exchange procedure with microwave-assisted heating at 150 °C for 1 h or stirring at room temperature for 72 h.

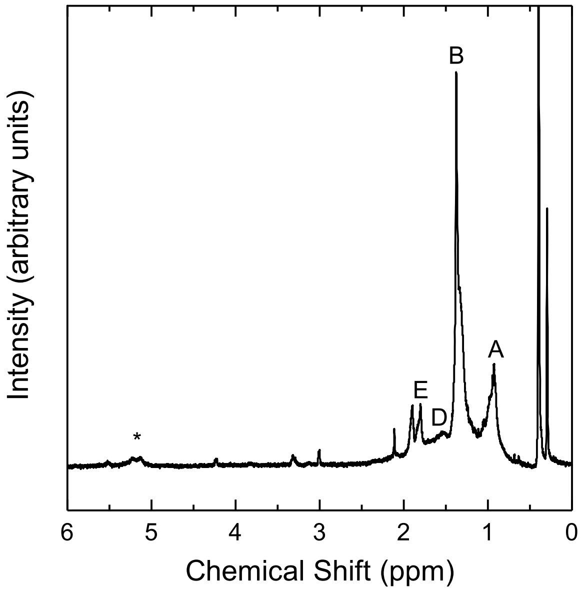


Figure 9. ^{1}H NMR spectrum after multiple washes of Ge NCs synthesized at 230 °C and recapped with dioctadecyl disulfide without Ph_2PH. The asterisk indicates a resonance consistent with residual OAm.

the dioctadecyl disulfide will react to yield thiol passivating ligands without the use of Ph_2PH.

Effect of Concentration, Solvent, and Synthesis Temperature on Ligand Exchange. Ge NCs synthesized at 250 °C were recapped with 0.1 or 0.2 mmol of dioctadecyl disulfide in toluene to determine the effect of ligand precursor concentration. After the recapped Ge-NCs were isolated, the nanocrystal surface was characterized with ^1H NMR. When the ligand concentration was varied, the ^1H NMR spectra of Ge NCs synthesized at 250 °C showed peaks consistent with octadecanethiol capping (Figure 10). A strong peak at 1.54 ppm may include contributions from the β and thiol protons. A peak for the α proton, expected at 2.66 ppm, is not observed. Weak shifts are observed at 5.3 and 2.0 ppm and are consistent with the vinylic and allylic protons peaks from OAm, suggesting that residual OAm is present after ligand exchange. No difference is observed on the basis of the concentration of the ligand precursor.

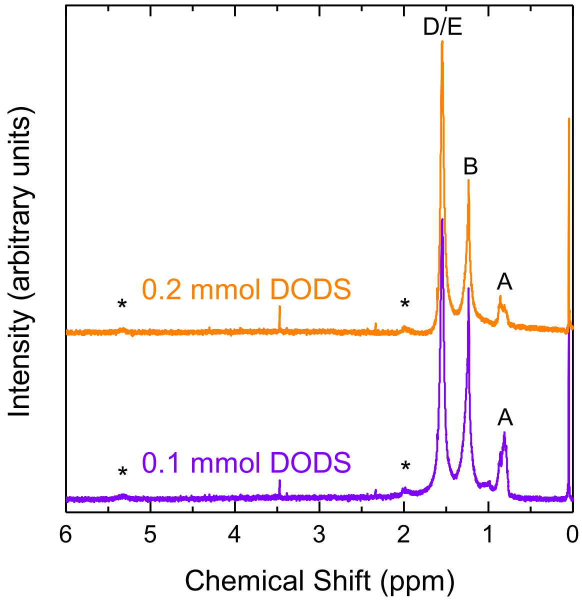


Figure 10. ^1H NMR spectra of Ge NCs synthesized at 250 °C and recapped with 0.1 or 0.2 mmol of dioctadecyl disulfide in toluene. The asterisks indicate resonances consistent with residual OAm.

Ge NCs synthesized at 250 °C were recapped with 0.1 mmol of dioctadecyl disulfide in toluene or 1-dodecene to determine the effect of solvent. The ^1H NMR spectra show peaks consistent with octadecanethiol passivation and residual OAm, independent of solvent (Figure 11). In the FTIR spectra, the alkenyl peak for OAm is not observed at 3005 cm^{-1}, but an additional peak is observed at 3080 cm^{-1} and is consistent with residual 1-dodecene. This peak is not observed for the reaction in toluene, suggesting that additional washing steps are required to fully remove the 1-dodecene solvent.

The ^1H NMR spectrum (Figure 12) of Ge NCs synthesized at 250 °C and recapped with 0.2 mmol of dioctadecyl disulfide in dodecene was compared to the spectrum shown in Figure 9 of Ge NCs synthesized at 230 °C. Both ^1H NMR spectra after ligand exchange are consistent with octadecanethiol passivation. For Ge NCs synthesized at 250 °C, a strong peak is observed at 1.54 ppm and is attributed to the β and thiol protons, but a peak for the α proton, expected at 2.66 ppm, is not observed. Chemical shifts consistent with the vinylic and allylic proton peaks from residual OAm are observed at 5.3 and 2.0 ppm for the 250 °C synthesis. These results suggest that, at higher synthesis temperatures, the OAm passivation is more robust, and harsher reaction conditions may be required to achieve a complete ligand exchange.

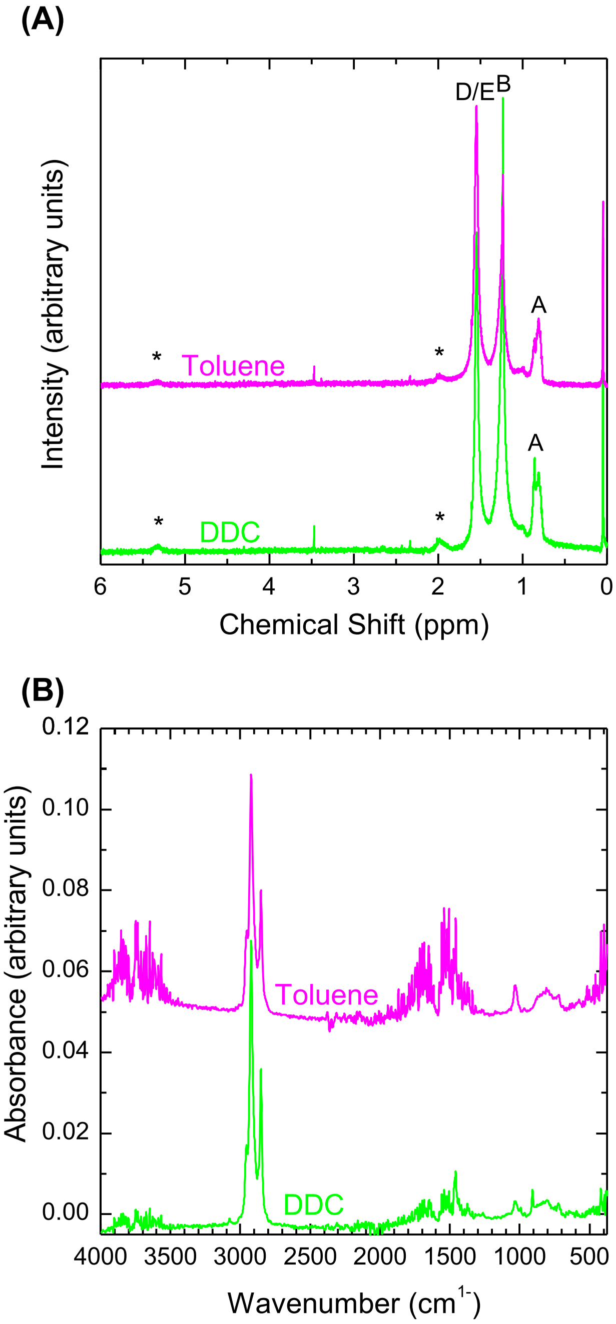


Figure 11. (A) ^1H NMR and (B) FTIR spectra of Ge NCs synthesized at 250 °C and recapped with 0.1 mmol of dioctadecyl disulfide in toluene or 1-dodecene. The asterisks in (A) indicate resonances consistent with residual OAm.

Synthesis of Ge NCs with Dioctadecyl Disulfide. In a previous study, addition of dodecene to the microwave-assisted reaction of GeI_2 in OAm resulted in mixed ligand passivation. While the nanoparticle size generally increased with dodecene concentration, low concentrations of dodecene (5−40%) produced amorphous nanoparticles.[28] In a similar experiment, 0.1 mmol of dioctadecyl disulfide was included in the

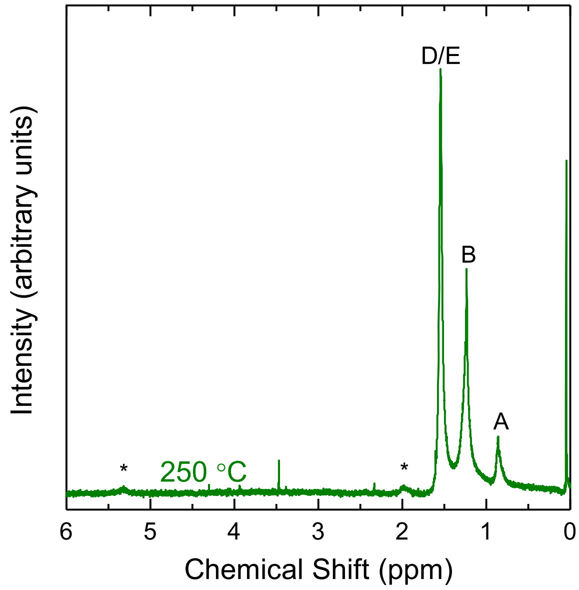


Figure 12. ^{1}H NMR spectrum of Ge NCs synthesized at 250 °C and recapped with dioctadecyl disulfide. The asterisks indicate resonances consistent with residual OAm.

microwave-assisted reaction of 0.4 mmol of GeI_2 and 6 mL of OAm at 250 °C to study the effects of in situ thiol passivation. The resulting octadecanethiol-capped Ge NCs were precipitated and dispersed in hexane for characterization. The PXRD pattern of the precipitate is consistent with crystalline cubic Ge (Figure 13). Peaks consistent with a GeS structure are not observed. The crystallite size was determined to be 3.2(1) nm by a Scherrer analysis of the (220) reflection. STEM images show quasi-spherical particles with an average diameter of 5.7 ± 1.0 nm (Figure 14). The corresponding HAADF image and particle size distribution histograms are given in Figure S8 in the Supporting Information.

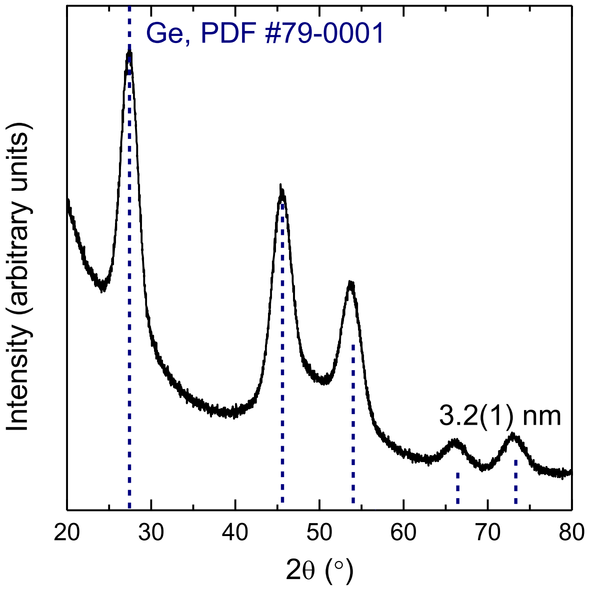


Figure 13. PXRD pattern of Ge NCs synthesized with dioctadecyl disulfide in the reaction mixture compared to the reference pattern of cubic Ge (ICDD PDF #79-0001, dark blue dashed lines).

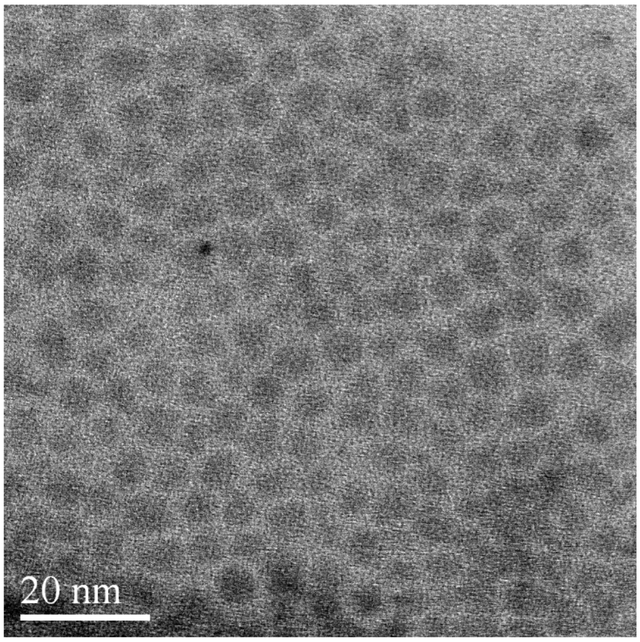


Figure 14. Bright field STEM image of Ge NCs synthesized with dioctadecyl disulfide in the reaction mixture.

The NMR spectrum is consistent with alkanethiol passivation (Figure 15). Peaks consistent with the terminal methyl group, alkyl chain, and α protons are observed shifted downfield from their expected positions at 0.86, 1.23, and 2.66 ppm, respectively. The alkyl peak is significantly broadened and may contain contributions from the thiol proton, which is not otherwise observed. Peaks are also observed at 2.2 and 5.5 ppm, which are consistent with allylic and vinylic protons and indicate that OAm is also present. The FTIR spectrum of the Ge NCs synthesized with dioctadecyl disulfide in the reaction further supports the presence of OAm and octadecanethiol on the NC surface (Figure 16). A very weak vinylic C−H stretch is observed near 3005 cm^{-1}, and a broad C═C stretch is

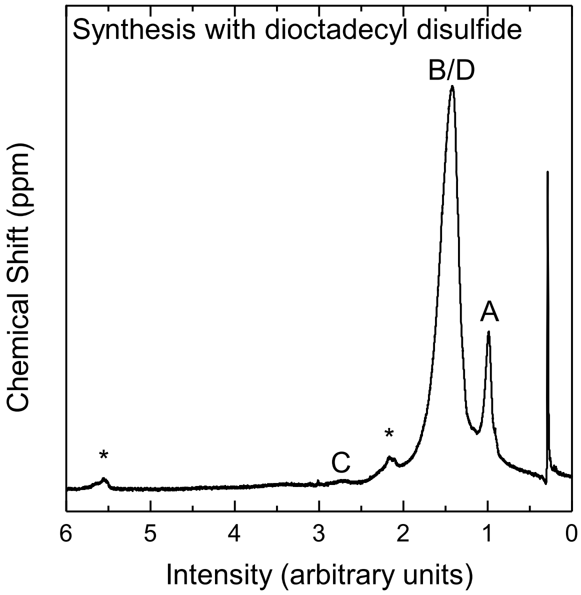


Figure 15. ^{1}H NMR spectrum of Ge NCs synthesized with dioctadecyl disulfide in the reaction mixture.

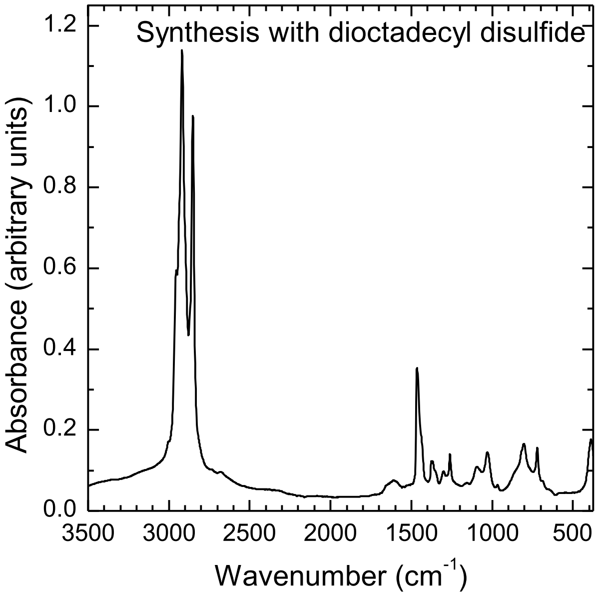


Figure 16. FTIR spectrum of Ge NCs synthesized with dioctadecyl disulfide in the reaction mixture.

observed near 1620 cm^{-1}. An additional broad peak from 600 to 900 cm^{-1} may include contributions from Ge—OH, Ge—O, Ge—O—Ge, and Ge—N stretches.[7,8,22,33−35,37] A weak peak is observed at 2680 cm^{-1} and can be attributed to an S—H stretch. The strong peak observed at 720 cm^{-1} is consistent with a C—S stretch but is also consistent with CH_2 rocking. The Ge—S stretching mode is observed just below 400 cm^{-1}, near the limit of the instrument's collection range.

To confirm the presence of sulfur at the NC surface, scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) were used (Figure S9 in the Supporting Information). EDS maps were collected of a NC sample that was washed several times to ensure the removal of all excess or unbound ligand. Elemental mapping shows a homogeneous distribution of Ge and S throughout the sample area. In the EDS spectrum, the signal at 2.3 keV is attributed to S and confirms the presence of octadecanethiol as a bound ligand at the NC surface. A peak for Si is observed at 1.7 keV and is attributed to the sample substrate. A peak for O is observed at 0.5 keV and is attributed to oxidation of the Ge NCs during preparation of the SEM sample. From the spectrum average elemental compositions of 79.6 and 20.4 atom % are obtained for Ge and S, respectively.

■ SUMMARY

Achieving new surface functionality by means of ligand exchange remains an active area of study to overcome existing inconsistencies between particle size and observed photophysical properties.[2] It is demonstrated that thiol ligand capping of Ge NCs from dioctadecyl disulfide can be accomplished by direct and indirect ligand exchange methods. Ph_2PH reduces octadecyl disulfide to give octadecanethiol ligands in both room-temperature and microwave-heated reactions. However, it is also shown that, with the application of microwave-assisted heating, Ph_2PH is not required for a complete ligand exchange. It is also shown that including dioctadecyl disulfide in the Ge NC synthesis does not interfere with the formation of the Ge NCs and results in octadecanethiol passivation of the nanocrystal surface. These results demonstrate disulfide compounds to be an effective tool for the passivation of semiconducting nanomaterials and that substitution with selenium- and tellurium-containing ligands may also be possible.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00749.

> STEM images and size analysis of OAm-capped Ge NCs, NMR spectrum of OAm and table of corresponding chemical shifts, full NMR spectra of octadecanethiol-capped Ge NCs, reduced range NMR spectra of octadecanethiol-capped Ge NCs, NMR spectrum of dioctadecyl disulfide and table of corresponding chemical shifts, HAADF STEM image and size analysis of octadecanethiol-capped Ge NCs, and SEM-EDS map and spectrum of octadecanethiol-capped Ge NCs (PDF)

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Notes

The authors declare no competing financial interest.

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