Anhydrous solution synthesis of germanium nanocrystals from the germanium(II) precursor Ge[N(SiMe₃)₂]₂†

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A convenient, simple, single-source solution synthesis of Ge nanocrystals *via* thermal reduction of Ge(II) precursor Ge[N(SiMe₃)₂]₂ in a non-coordinating solvent at 300 °C and 1 atm Ar is described.

Crystalline semiconductor nanocrystals (NCs) have been extensively researched for their potential applications in optoelectronics,[1] photovoltaics,[2] and biological imaging.[3] These applications are dependant upon the quantum confinement effect, which gives rise to the size-dependent electronic and optical properties found in these NCs.[4] To date, much attention has been given to the development of convenient, large-scale solution synthesis of crystalline semiconductor NCs such as CdSe,[5] InP,[6] and AgBr.[7] These semiconductor NCs have been produced with a narrow size distribution and definitive morphological control in order to "tune" their properties.[8] In contrast, research in Group IV NCs (*e.g.*, Si and Ge) has been less vigorous since these materials possess an indirect bandgap; however, interest has increased due to the discovery of luminescence in porous Si[9] and the development of synthetic routes to Si NCs.[10] A recent report demonstrates stimulated emission and light amplification from Si NCs embedded in a layer of SiO₂ upon single-pass transmission of 390 nm excitation with a net material gain comparable to III–V quantum dots.[11]

In comparison to Si NCs, Ge NCs have a larger exciton Bohr radius, which imparts a strong quantum confinement independent of the relatively large NC radius.[12] Even though bulk Ge is an indirect bandgap material, Ge NCs have been found to behave as a direct bandgap material.[13] This transformation opens up the possibility of using Ge NCs as light-emitting or power-generating elements. In addition, modification of the Ge surface with organic layers could bring Ge NCs into further use as chemical sensors.[14]

Previously reported Ge NC syntheses rely on direct reduction of Ge(IV) precursors to Ge(0) by utilizing Na/K as a reducing agent,[15] Zintl salt as a precursor,[16] reduction of GeCl₄[17] or GeI₄[18] using LiAlH₄ as reducing agent, high-pressure reduction,[19] high temperature supercritical fluid,[20] and laser illumination.[21] However, the presence of reducing agents or salt by-products in the reaction makes the separation and purification processes, as well as control over Ge NC surface, more difficult. Herein, we demonstrate a simple, single source solution synthesis route of Ge NCs *via* thermal reduction of a Ge(II) precursor to Ge(0). The reasoning is based on the reduction potentials of Ge(II) and Ge(IV), where a Ge(II) precursor, compared to a Ge(IV) precursor, will

decompose under milder conditions without the need for additional reducing agents. The reduction potential of Ge(II) to Ge(0) is +0.247 V, whereas that of Ge(IV) to Ge(0) is +0.124 V.[22] A similar approach has been developed successfully for the solution-based synthesis of Cu, Ag, and Au NCs.[23]

For the Ge(II) precursor, we chose the amido based Ge[N(SiMe₃)₂]₂ which can be prepared at room temperature and pressure following previously reported synthetic methods.[24] The selection of Ge[N(SiMe₃)₂]₂ is also based on the ease of synthesis, the absence of potential halide contamination, and the labile amido ligand sets. Full details of the Ge NC syntheses are supplied in the experimental section.‡[25] As shown by Fourier transform infrared (FTIR) data (*vide infra*), oleylamine encapsulates the surface of Ge NCs to prevent agglomeration in an ~89% yield.

Transmission electron microscopy (TEM) is used to characterize the shape, size, and crystallinity of the synthesized Ge NCs. A TEM image of typical Ge NCs is shown in Fig. 1. The crystallinity of the particles is shown by the selected area electron diffraction (SAED) pattern in Fig. 1a. The diffraction pattern shows *d*-spacings of 3.26, 2.00, 1.70, and 1.41 Å, which matches the *d*-spacings of bulk Ge (111), (220), (311), and (400) cubic phase reflections. A high-resolution TEM image of one of the particles in Fig. 1b shows the cubic lattice structure of the Ge NCs. The FTIR and TEM characterizations do not reveal the presence of GeO₂ on
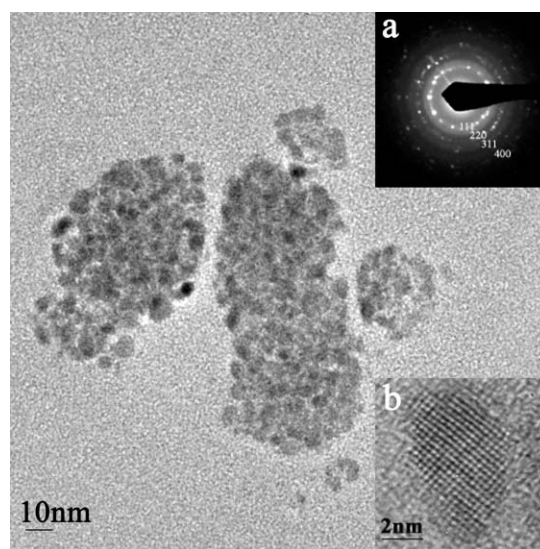

Fig. 1 TEM images of Ge NCs. (a) Selected area electron diffraction (SAED) of Ge NCs with *d*-spacings of 3.26, 2.00, 1.70, and 1.41 Å corresponding to Ge (111), (220), (311), and (400), respectively. (b) High-resolution image of the Ge NCs with a *d*-spacing of 3.26 Å for Ge (111).

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the particles. The average particle size, shown in Fig. 2, is 7 ± 4 nm over 119 particles and measured from the longest dimension of the particle. Cumulative data show that $\sim 95\%$ of the particles are less than 8 nm.

As an indirect measure of amine surface passivation, we compare the FTIR spectrum of pure oleylamine (Fig. 3a) with that of Ge NCs, taken with respect to the Ar ambient background (Fig. 3b). Prior to sampling, the Ge NCs are washed‡ to remove excess surfactants and by-products. The presence of oleylamine group on Ge NCs (Fig. 3b) is indicated by the N–H wagging mode from 650–900 cm^{-1}; NH$_2$ bending modes at 909, 964, and 993 cm^{-1}; and NH$_2$ scissor mode at 1568 cm^{-1}.[26] The spectrum shown in Fig. 3b also reveals the characteristic peak of the C–N stretch at 1042 cm^{-1} which suggests that the C–N bonds in amine groups, and therefore oleylamine ligands, remain intact, encapsulating the Ge NCs. The peak at 1468 cm^{-1} is associated with the
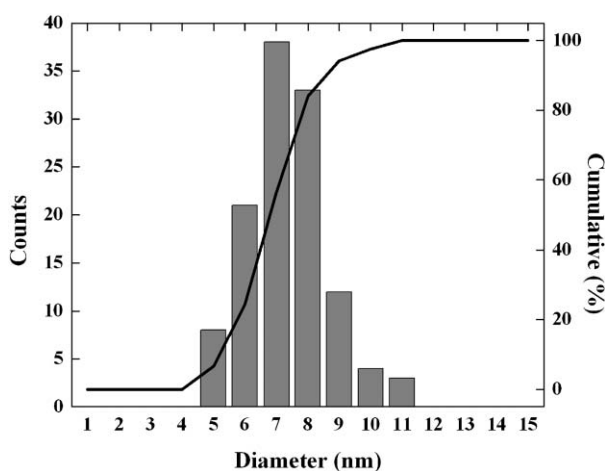

Fig. 2 Size distribution of Ge NCs showing an average of 7 ± 4 nm from 119 particles, with $\sim 95\%$ less than 8 nm.
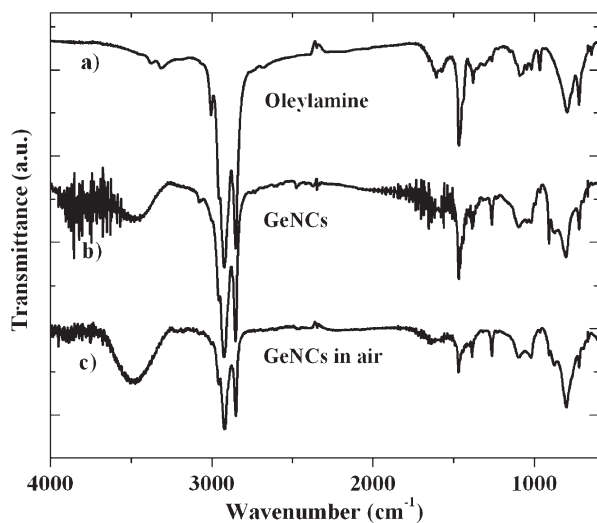

Fig. 3 FTIR spectrum of (a) oleylamine, (b) Ge NCs after being washed (time = 0), and (c) air exposed Ge NCs (time = 5 months). The characteristic vibrational modes of NH$_2$ indicate that oleylamine encapsulates Ge NCs.

C–H bending mode and the three peaks at 2850, 2922, and 2955 cm^{-1} represent the C–H stretching modes of the oleylamine carbon chain. The large peak at 3500 cm^{-1} has been assigned to the MeOH used in the separation step. The presence of various N–H peaks suggests that amines are bound to the surface of the Ge NCs. Upon exposure to air for an extended period of 5 months, no substantial change is observed in the FTIR spectrum (Fig. 3c). The Ge–O stretch (800–1000 cm^{-1}) cannot be resolved from the spectra due to its overlap with the N–H wagging mode.[27] However, no appreciable increase in the Ge–O stretching mode at 850 cm^{-1} is observed, even after 5 months of exposure in air. This result suggests that formation of GeO$_2$ is minimal, presumably due to the encapsulation of the Ge NC surface by the oleylamine ligands.

Based on the FTIR data, we deduce the following reaction mechanism. Upon injection of Ge[N(SiMe$_3$)$_2$]$_2$ and oleylamine into hot octadecene solution, the Ge–N bond is cleaved by the oleylamine group and Ge is subsequently reduced. The reported Ge–N and Si–N bond strengths are 55 and 78 kcal mol^{-1}, respectively, which indicate that Ge–N is more susceptible than Si–N to cleavage.[28] Furthermore, primary amines do not dissociate in the presence of Ge, but upon absorption on Si, primary amines will undergo N–H dissociation, resulting in the formation of a Si–H bond with a characteristic IR stretching mode at 2066 cm^{-1}.[26] The absence of a Si–H peak in these spectra indicates that no detectable Si is present on the sample. The absence of Si in the Ge NCs is confirmed through energy dispersive X-ray spectroscopy (EDS) investigations (shown in Fig. 4).

The photoluminescence (PL) of Ge NCs in a toluene solution is conducted at 1 atm of Ar to confirm the quantum confinement effect and shown in Fig. 5. UV-visible (UV-vis) spectroscopy shows continuous absorption across the spectrum with increasing absorption near the UV region. The NCs are excited with 325 and 442 nm HeCd laser lines to excite NCs of different sizes. The full width at half maximum (FWHM) of the excitation from the two laser sources is 2 nm. Since the particles are polydispersed, different emission wavelengths are observed. The emission spectra exhibit strong luminescence at 375 and 500 nm, corresponding to different
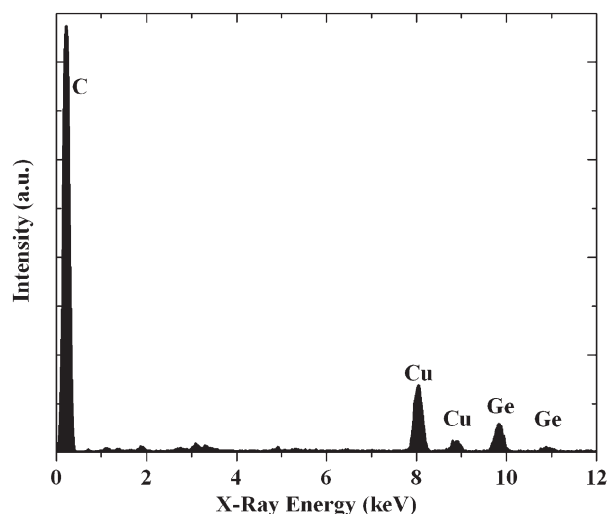

Fig. 4 EDS spectrum of Ge NCs dispersed on a carbon coated TEM copper grid.
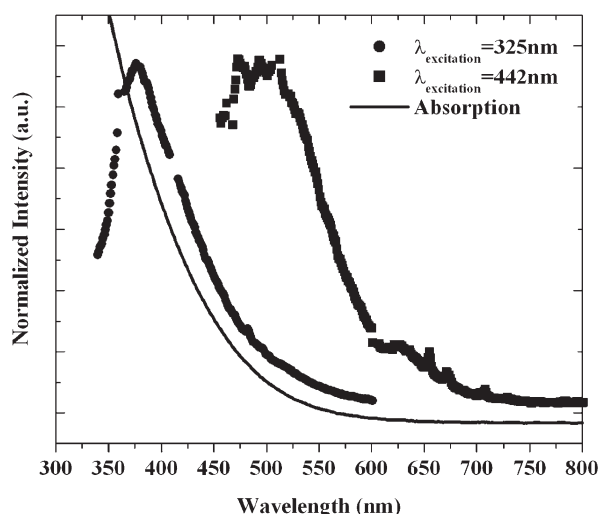
Fig. 5 Photoluminescence (PL) of Ge NCs dispersed in toluene. The UV-vis absorption spectrum shows continuous absorption across the spectrum, with increasing absorption nearing the UV region. Excitation wavelengths are 325 and 442 nm. Due to sample polydispersity, different particle sizes emit at different wavelengths of 375 and 500 nm that indicate quantum confinement effect.

particle sizes. The corresponding particle sizes based on a theoretical calculation of the emission wavelengths[29] are 5 and 7 nm respectively, in agreement with our observation. Consistent with published results, the size-dependence manifests the quantum confinement effect.[30]

In summary, we have demonstrated a simple, convenient, single-source Ge NC synthesis *via* thermolysis of the Ge(II) precursor Ge[N(SiMe$_3$)$_2$]$_2$. This simple reaction is performed at 1 atm without the use of reducing agents and with no salt by-products. Detailed studies are underway to control and improve the Ge NC size and distribution, and morphology through variations in precursor concentration, temperature, reaction time, and surfactants.

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Notes and references

‡ *Experimental*: All reactions are performed under standard air sensitive synthetic methods employing a dual manifold Schlenk-line. To a solution

of 32 mmol octadecene, which is heated to 300 °C, an orange solution of 1.0 mmol Ge[N(SiMe$_3$)$_2$]$_2$ in 12 mmol oleylamine is rapidly injected, whereupon the mixture turns dark brownish-red. The solution is held at 285 °C for 5 min and then allowed to cool to room temperature. After completion, toluene or chloroform is added, and the solution is extracted twice with methanol. Excess acetone is used to precipitate the Ge NCs. The precipitate is separated by centrifugation (33000 rpm for 25 min) and then re-dispersed in toluene, hexane, or chloroform. The resulting colloid is stable at room temperature under inert conditions. TEM samples are prepared in an Ar-filled glovebox by placing a drop of Ge NCs dispersed in toluene onto a 30-mesh carbon coated copper TEM grid and transported to the TEM instrument (JEOL 2010) under an atmosphere of Ar. An EDS spectrum is also collected on the same TEM sample. IR spectra of oleylamine or Ge NC particles in KBr pellet are obtained with 2 cm^{-1} resolution and 32 scans. Samples for UV-vis and PL (He–Cd laser, CVI DK 480 monochromator, cooled GaAs photomultiplier) are prepared by diluting Ge NCs in toluene, hexane or chloroform solution under Ar.

1 V. I. Klimov and M. G. Bawendi, *MRS Bull.*, 2001, **26**, 998.
2 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425.
3 M. Bruchez, M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science*, 1998, **281**, 2013.
4 A. P. Alivisatos, *Science*, 1996, **271**, 933.
5 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
6 O. I. Micic, J. R. Sprague, C. J. Curtis, K. M. Jones, J. L. Machol, A. J. Nozik, H. Giessen, B. Fluegel, G. Mohs and N. Peyghambarian, *J. Phys. Chem.*, 1995, **99**, 7754.
7 W. Chen, G. Mclendon, A. Marchetti, J. M. Rehm, M. I. Freedhoff and C. Myers, *J. Am. Chem. Soc.*, 1994, **116**, 1585.
8 X. G. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343; S. D. Bunge, K. M. Krueger, T. J. Boyle, M. A. Rodriguez, T. J. Headley and V. L. Colvin, *J. Mater. Chem.*, 2003, **13**, 1705.
9 A. G. Cullis and L. T. Canham, *Nature*, 1991, **353**, 335.
10 J. Heath, *Science*, 1992, **258**, 1131.
11 L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo and F. Priolo, *Nature*, 2000, **408**, 440.
12 A. L. Efros and M. Rosen, *Annu. Rev. Mater. Sci.*, 2000, **30**, 475.
13 Y. Kanemitsu, H. Uto, Y. Masumoto and Y. Maeda, *Appl. Phys. Lett.*, 1992, **61**, 2187.
14 S. Bent, *Surf. Sci.*, 2002, **500**, 879.
15 J. Heath, J. Shiang and A. Alivisatos, *J. Chem. Phys.*, 1994, **101**, 1607.
16 B. R. Taylor, S. M. Kauzlarich, H. W. H. Lee and G. R. Delgado, *Chem. Mater.*, 1998, **10**, 22.
17 J. P. Wilcoxon, P. P. Provencio and G. A. Samara, *Phys. Rev. B*, 2001, **64**, 35417.
18 E. Fok, M. L. Shih, A. Meldrum and J. G. C. Veinot, *Chem. Commun.*, 2004, 386.
19 D. Gerion, N. Zaitseva, C. Saw, M. F. Casula, S. Fakra, T. Van Buuren and G. Galli, *Nano Lett.*, 2004, **4**, 597.
20 X. M. Lu, K. J. Ziegler, A. Ghezelbash, K. P. Johnston and B. A. Korgel, *Nano Lett.*, 2004, **4**, 969.
21 A. Kornowski, M. Giersig, R. Vogel, A. Chemseddine and H. Weller, *Adv. Mater.*, 1993, **5**, 634.
22 A. J. Bard, R. Parsons and J. Jordan, *Standard Potentials in Aqueous Solutions*, IUPAC (Marcel Dekker), New York, 1985.
23 S. D. Bunge, T. J. Boyle and T. J. Headley, *Nano Lett.*, 2003, **3**, 901.
24 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
25 D. Battaglia and X. G. Peng, *Nano Lett.*, 2002, **2**, 1027.
26 C. Mui, J. Han, G. Wang, C. Musgrave and S. Bent, *J. Am. Chem. Soc.*, 2002, **124**, 4027.
27 F. L. Galeener, A. J. Leadbetter and M. W. Stringfellow, *Phys. Rev. B*, 1983, **27**, 1052.
28 J. C. Baldwin, M. F. Lappert, J. B. Pedley and J. S. Poland, *J. Chem. Soc., Dalton Trans.*, 1972, **18**, 1943.
29 Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu and Y. Masumoto, *Appl. Phys. Lett.*, 1991, **59**, 3168.
30 N. Myung, X. M. Lu, K. P. Johnston and A. J. Bard, *Nano Lett.*, 2004, **4**, 183; B. Taylor, G. Fox, L. Hope-Weeks, R. Maxwell, S. Kauzlarich and H. Lee, *Mater. Sci. Eng., B*, 2002, **96**, 90; B. R. Taylor, S. M. Kauzlarich, G. R. Delgado and H. W. H. Lee, *Chem. Mater.*, 1999, **11**, 2493.