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Preparation of alkyl-surface functionalized germanium quantum dots *via* thermally initiated hydrogermylation†

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Received (in Purdue, IN, USA) 18th November 2003, Accepted 23rd December 2003
First published as an Advance Article on the web 23rd January 2004

A new, thermally initiated hydrogermylation-based method for the synthesis and surface functionalization of air- and moisture-stable germanium quantum dots is reported.

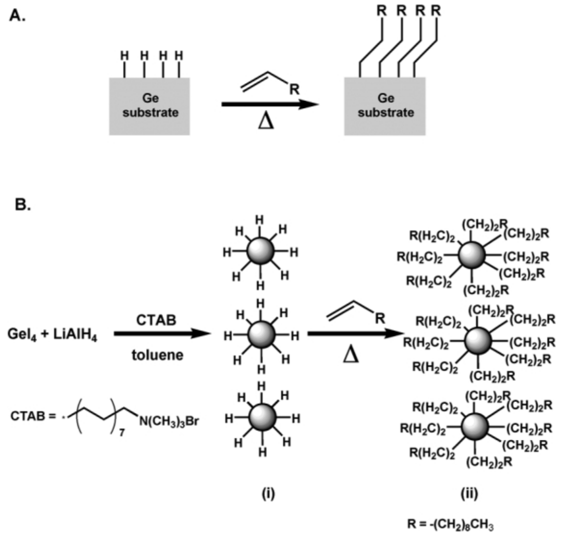
The study of nanoparticles, or clusters composed of ~10–1000 atoms, lies at an interface between traditional chemistry and solid-state physics.[1] Although important fundamental questions remain, much current research is driven by an interest in new materials with specific properties for technological applications. Semiconductor nanoparticles, or quantum dots, demonstrate size-dependent optical absorption and photoluminescence.[1b] These properties arise from the confinement of charge carriers (quantum confinement) within nanoparticles whose dimensions are smaller than the Bohr radius of an electrostatically bound electron–hole pair (exciton) in the bulk material.[1b] Compound semiconductor quantum dots such as CdSe, CdS, InP and GaAs have been prepared with well-defined size, shape, and surface chemistry.[2] Quantum confinement in these *direct bandgap* semiconductor quantum dots is well understood[1,3] and their device applications include light-emitting diodes,[4a] single electron transistors,[4b] liquid crystals,[4c] and solar cells.[4d] Although no operational lifetime data has been presented for these devices, it is expected that their practical utility may be hampered by the inherent electrochemical instability of II–VI and III–V semiconductors.

Unlike the II–VI and III–V materials, Si and Ge are *indirect bandgap* semiconductors and they are electrochemically stable.[5] Due to the relatively narrow bandgap (0.66 eV at 291 K) and large Bohr exciton radius of germanium (>20 nm) it is possible to tune the photoluminescence of Ge quantum dots throughout the visible spectrum, with only relatively small changes in particle dimension.[6] These properties make Ge quantum dots particularly appealing for a many of the optoelectronic applications noted above. Solution-based synthetic procedures are among the most attractive methods for quantum dot preparation because they offer simultaneous control of particle size/shape[7f] and surface chemistry. Established solution-based strategies for the synthesis of crystalline Ge quantum dots include, using Na/K[7] to simultaneously reduce $GeCl_4$ and $RR'MX_2$ (M = Si or Ge), the reaction of Zintl salts (*e.g.*, Mg_2Ge) with GeX_4,[7b–e] and the metal hydride reduction of micelle solutions containing GeX_4.[6] Many of these methods have disadvantages arising from the extreme reactivity of the reagents (*i.e.*, Na/K), poorly defined surface chemistry,[6,7a] the need to prepare precursors (*e.g.*, Mg_2Ge) at high temperatures (*i.e.*, 650 °C),[7b–e] or the requirement to purify samples by physical methods (*i.e.*, size exclusion chromatography).[6] Although attempts to tailor Ge quantum dot surface chemistry have been somewhat limited, Kauzalarich *et al*. successfully attached a variety of organic functionalities to the surface of Ge quantum dots *via* the Zintl salt reduction procedure noted above.[7b–d] This irreversible attachment was achieved by the reaction of Grignard or organolithium reagents with a crude reaction mixture believed to contain chloride terminated Ge quantum dots, although this intermediate was never isolated.

Here, we report an alternative method for the synthesis of surface functionalized Ge quantum dots that exploits a hydrogermylation reaction (Scheme 1(A)) known to alkylate the surfaces of porous germanium.[8] Our solution-based approach offers a convenient method for tailoring Ge quantum dot surface chemistry, while also providing a reactivity-based, low-temperature method for the preparation and purification of alkyl surface functionalized Ge quantum dots.

Wilcoxon *et al*. claim hydride-terminated Ge quantum dots can be prepared *via* metal hydride reduction of GeX_4 (X = Cl, Br, I) and purified by high-pressure size exclusion chromatography. These authors did not characterize the Ge quantum dot surface chemistry and the mechanism of size control in their procedure remains poorly understood.[9] Here we use lithium aluminium hydride to reduce GeI_4 (Scheme 1(B)(i)).‡ Unlike $GeCl_4$ which is a highly volitile liquid, GeI_4 is a convenient, easy to handle, solid source of Ge whose colour allows for qualitative monitoring of reaction progress.

Following the reduction process, a sample of the resulting mixture was analyzed by FT-IR spectroscopy (Fig. S1B, ESI†), confirming surface termination by Ge–H (ν Ge–H_x = 2067 cm^{-1}).[10] The same analysis of the reaction mixture obtained from $LiAlD_4$ reduction shows no absorption in the Ge–H region of the spectrum and a shoulder at 1455 cm^{-1} suggesting the presence of a Ge–D surface. Refluxing with excess *n*-alkene causes the surface of hydride-terminated quantum dots to undergo hydrogermylation (Scheme 1) to yield *n*-alkyl surface termination. ^1H NMR spectra of *n*-undecyl terminated quantum dots showed broad, structureless aliphatic CH signals indicative of multiple, surface bound environments. There is no evidence of any alkene protons or Ge–H. FT-IR spectra of all *n*-alkylated fquantum dots (Fig. S2, ESI†) show characteristic aliphatic ν C–H = 2922 and 2850 cm^{-1}, $\delta_{as}CH_2$ 1460 cm^{-1}, and ν Ge–C = 850 cm^{-1}. There is no evidence of Ge–



Scheme 1 (A) The hydrogermylation surface reaction of terminal *n*-alkenes with hydride terminated Ge. (B) The general reaction scheme for the synthesis and surface derivatization of Ge quantum dots.

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† Electronic supplementary information (ESI) available: FT-IR spectra of the hydride terminated reaction intermediate and *n*-undecyl surface Ge nanoclusters. See http://www.rsc.org/suppdata/cc/b3/b314887d/

DOI: 10.1039/b314887d

O (ν Ge–O 870–910 cm^{-1}) or remaining Ge–H. While the lack of Ge–O absorption does not rule out trace oxide on the surface of our nanoparticles it is unlikely that significant quantities are present since FT-IR is known to be more sensitive to Ge–O than Ge–C stretches.[7b]

TEM specimens were prepared by drying sample solutions on ultra-thin homemade carbon support films. The selected area electron diffraction pattern (Fig. 1 inset) is consistent with crystalline Ge. The size distribution of the particles was determined from TEM analysis of 400 particles from different regions of the grid (Fig. 1). The average particle size was determined to be 5 nm with 88% of the particles being within the range of 2–7 nm. We also noted some large agglomerations of particles (up to 18 nm) randomly distributed over the grid.

The photoluminescence spectrum (Fig. 2) of the *n*-undecyl functionalized Ge quantum dots shows a broad, well-defined peak centered at 390 nm. The emission extends throughout the visible spectrum and tails off into the red. This is consistent with other reports of Ge particles of similar size and distribution.[7f] We are currently investigating the influence of surface chemistry on photoluminescence and developing surface reactivity-based methods for narrowing particle size distribution – both are important considerations if optoelectronic applications of these quantum dots are to be realized.

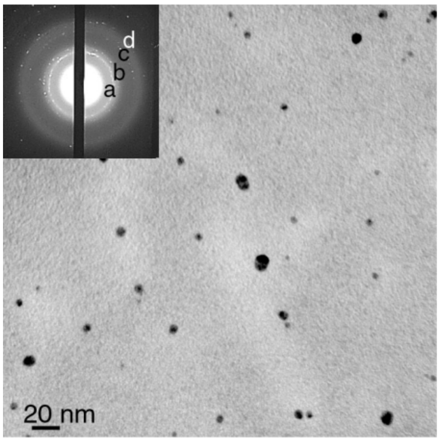

Fig. 1 Bright-field image of *n*-undecyl surface functionalized Ge quantum dots. An electron-diffraction pattern is shown in the inset. The four bright lines labeled a, b, c and d correspond to the 220, 311, 331 and 440 lattice spacings of Ge, respectively.

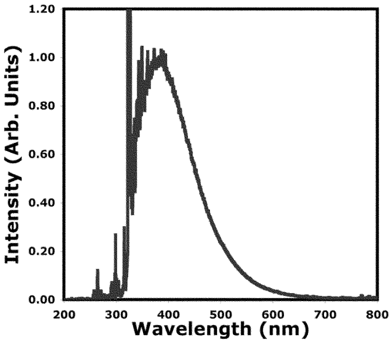

Fig. 2 Photoluminescence (PL) spectrum of *n*-undecyl surface functionalized Ge quantum dots in THF. The intense line at 325 nm is due to the pump laser. No luminescence was observed from a pure THF reference solution. Sharp peaks below ~400 nm can arise from the procedure used to correct for the response curve of the CCD spectrometer (the intensity of the black-body radiator used for this purpose becomes quite low below 400 nm, resulting in a "noisier" corrected spectrum).

The above results demonstrate that hydride terminated Ge quantum dots can be prepared *via* metal hydride reduction of nonpolar solutions of surfactant and GeI_4 at room temperature. Subsequent thermally initiated reaction of these quantum dots with terminal *n*-alkenes results in the particle surface with *n*-alkyl chains. Our procedure renders Ge quantum dots air- and water-stable, as well as solution processable.

C. Blois and A. Hryciw assisted with the TEM and PL. Thanks are given to the NSERC URSA program for a summer research fellowship to M. S. and University of Alberta for funding. M. Miskolzie and D. Formanski are thanked for assistance with NMR and FT-IR spectroscopy.

Notes and references

‡ *Experimental*: All reactions were performed using standard Schlenk-line techniques. All spectroscopic samples were prepared in a nitrogen filled glovebox (< 0.1 ppm O_2, < 0.1 ppm H_2O). Over a period of 5 min a solution of $LiAlH_4$ (0.98 ml, 0.1M in THF, 0.98 mmol) was added to a rapidly stirring toluene solution of GeI_4 (0.50 g, 0.86 mmol) containing cetyltrimethylammonium bromide (0.024 g, 0.065 mmol, Aldrich). The reaction progress was monitored qualitatively by observing a series of distinct colour changes (orange → yellow → faint yellow) and the precipitation of a light yellow solid. An excess of n-alkene was added and the mixture was refluxed for 2 hours. The supernatant containing nanoparticles, excess alkene and solvent was removed and evaporated to dryness to give an oily yellow–orange residue. Upon trituration with diethyl ether a waxy yellow solid was obtained (0.050 g). This solid was freed from organic and salt impurities upon repeated sonication/centrifugation cycles in pentane (3×), absolute ethanol (3×), and water (3×). Samples were dried *in vaccuo* (10 mTorr, 110 °C) and under subdued light for 2 h over NaOH desicant.

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