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COMMUNICATION

One-Pot Synthesis of Functionalized Germanium Nanocrystals from a Single Source Precursor

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One-pot syntheses of surface functionalized germanium nanocrystals (GeNCs) based upon traditional hot injection and microwave-assisted heating of a Ge(II) dihydride single source precursor has been developed. The reported procedures offer *in-situ* hydrogermylation-based covalent attachment of alkene/alkyne derived surface moieties that give access to hydrophobic or hydrophilic GeNCs.

Germanium nanocrystals (GeNCs) are promising materials for optoelectronic applications such as solar cells, flash memory devices, and lithium-ion batteries.^{1,2} In addition, as a result of its large exciton radius (*ca.* 17.7 nm) and possible involvement of quantum confinement in light emission, GeNCs could also display tunable size-dependent photoluminescence (PL) spanning the visible and infrared regions of the electromagnetic spectrum.³⁻⁷ Moreover, GeNCs are biocompatible/non-toxic making them attractive as biological imaging and therapeutic agents.⁸

Recently, Vaughn and Schaak presented a comprehensive review outlining known methods for preparing colloidal GeNCs.⁶ A variety of approaches have been explored including: solution-phase precursor reduction, metathesis of Ge Zintl phases, thermally induced organogermane decomposition, co-reduction of GeI₂ and GeI₄, *etc.*^{1,3,9-23} However precise control of NC dimension and surface chemistry has not yet been achieved. In this regard, methods for preparing well-defined GeNCs are of paramount importance to the future growth of this field.

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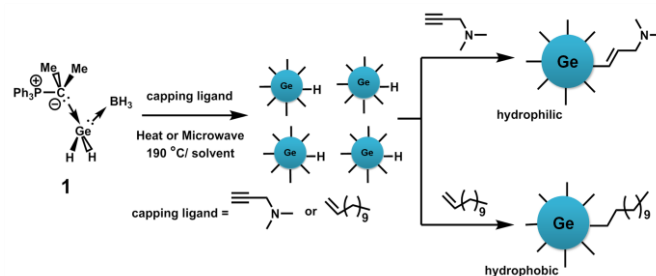
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Group 14 dihydrides (EH₂; E = Si and Ge) have received attention due to their accepted role as key intermediates during the growth of high purity Si and Ge films from SiH₄ and GeH₄.²⁴ Although these species are unstable in the condensed phase at room temperature, the Rivard Group has developed a general donor-acceptor protocol that allows EH₂ units to be handled as isolable complexes.^{25,26} Of particular import here, mild heating of the GeH₂-Wittig adduct Ph₃PCMe₂•GeH₂•BH₃ (**1**) in toluene to *ca.* 100°C yields elemental germanium and soluble byproducts.²⁷ In this communication we describe our successful efforts to harness this decomposition process to access crystalline GeNCs *via* hot injection (HI) and microwave irradiation (MI) induced degradation of **1** (Scheme 1).



Scheme 1 Synthesis and *in-situ* functionalization of hydrophilic and hydrophobic GeNCs upon thermal or microwave irradiation induced decomposition of Ph₃PCMe₂•GeH₂•BH₃ (**1**).

Positing that Ge particle growth could be controlled to enable nanocrystal formation, the requisite germanium (II) dihydride precursor, **1**, was synthesized and subjected to HI or MI protocols at predefined temperatures (*i.e.*, 100, 150, 190, and 250°C; see electronic supplemental information). To realize hydrophobic dodecyl-terminated GeNCs, HI or MI of **1** were performed in a 1:1 (v:v) solution of diphenylether and 1-dodecene. Hydrophilic GeNCs bearing surface bonded

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3-dimethylamino-1-propene moieties (*i.e.*, Me₂N-GeNCs) were generated by subjecting **1** to MI in 3-dimethylamino-1-propyne; this alkyne adopts the dual role of capping ligand and microwave absorber. Unfortunately, the comparatively low boiling point (*i.e.*, 81°C) of this alkyne precluded its application in HI syntheses. Surface functionalized GeNCs were freed from reaction byproducts (*e.g.*, Ph₃P•BH₃) upon sonication in appropriate solvent/antisolvent mixtures followed by centrifugation (see electronic supplemental information).

Our initial attempts to prepare hydrophobic GeNCs at 100 and 150°C *via* HI or MI thermolysis of **1** in 1-dodecene/diphenyl ether yielded only trace product. Bright field transmission electron microscopy (TEM) images of the NCs synthesized *via* MI of **1** at 150°C showed sparse polydisperse particles of ca. 3-5 nm dimensions (ESI, Fig S1); HRTEM highlights their crystallinity, however limited yield prevented further characterization.

GeNC size and yield increased with HI and MI reaction temperature. TEM images (Fig. 1a) of dodecyl-GeNCs synthesized by HI at 190°C show pseudospherical particles with average diameters (d_{avg}) of 10.1 ± 1.65 nm. Dodecyl- and Me₂N-terminated GeNCs (Figs. 1b,c) synthesized *via* MI at 190°C are smaller (*i.e.*, $d_{\text{avg}} = 5.35 \pm 0.96$ nm, dodecyl-GeNCs; $d_{\text{avg}} = 5.41 \pm 0.85$ nm, Me₂N-GeNCs). In all cases HRTEM images show d-spacings of 0.33 nm that is readily attributed to the Ge(111) plane of diamond-structured Ge.¹⁹ To evaluate the role of precursor concentration on NC size we performed MI induced decomposition of **1** at concentrations of 10 and 20 mg/5 mL in 1:1 (v:v) 1-dodecene/diphenylether. A clear trend emerges that sees smaller particles produced with decreased precursor concentration (see ESI Figs. S2–S4).

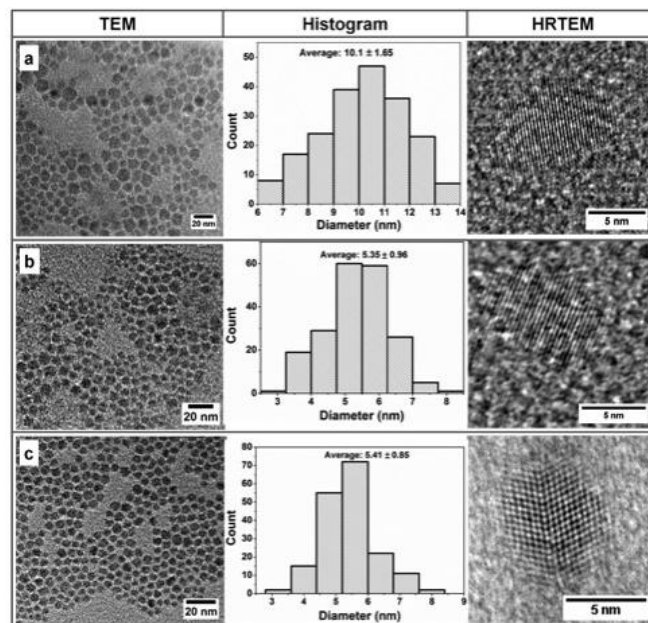


Fig. 1 Representative TEM evaluation of GeNCs obtained from decomposition of **1** at 30 mg/mL at 190°C. (a) Dodecyl-GeNCs obtained from HI. (b) Dodecyl-GeNCs and (c) Me₂N-GeNCs synthesized by MI.

The FTIR spectra (Figs. 2a, b) of dodecyl-terminated GeNCs synthesized by HI and MI methods show absorptions attributable to NC surface coverage by alkyl functionalities. Specifically, absorptions present at 2800-3000 cm⁻¹ are readily attributed to C-H stretching within a saturated hydrocarbon residue, while accompanying C-H bending appears at 1475 and 1365 cm⁻¹. The FTIR spectrum of the Me₂N-GeNCs (Fig. 2c) shows features consistent with surface-bonded 3-dimethylamino-1-propene moieties. The identity of the surface species on Me₂N-GeNCs was further confirmed by direct comparison of the IR spectra obtained for Me₂N-GeNCs and neat 3-dimethylamino-1-propene (ESI, Fig. S5). These IR data are consistent the HI and MI induced decomposition of **1** yielding hydride-terminated GeNCs that are subsequently functionalized *via* hydrogermylation of 1-dodecene (dodecyl-GeNCs) or 3-dimethylamino-1-propyne (Me₂N-GeNCs). The hydrogermylation reaction yields substitutionally inert Ge-C bonds on the NC surface while the terminal alkyl chains and dimethylamino groups impart hydrophobicity or hydrophilicity, respectively.

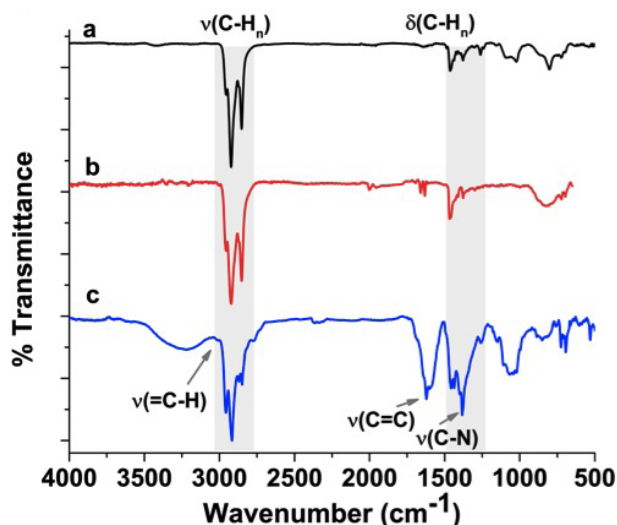


Fig. 2 FTIR spectra of GeNCs obtained from decomposition of **1** at 30 mg/mL at 190°C. (a) Dodecyl-GeNCs synthesized by HI. (b) Dodecyl-GeNCs and (c) Me₂N-GeNCs synthesized by MI.

To gain insight into the elemental composition and speciation of the GeNCs obtained from the solution-phase decomposition of **1**, X-ray photoelectron spectroscopy (XPS) was performed.²⁸ Survey spectra of all dodecyl-GeNCs confirm only Ge, C, and O are present at the sensitivity of the XPS technique. The relative atomic compositions are Ge (19.6%), C (62.7%), O (17.7%) and Ge (21.3%), C (61.5%), O (17.2%) for NCs prepared using HI and MI, respectively. Similarly, survey spectra indicate the relative atomic composition of NMe₂-GeNCs is N (5.2%), Ge (12.5%), C (63.6%) and O (18.7%) (ESI, **Fig. S6**). The carbon content detected in the present samples arises from surface bonded moieties on the NCs, omnipresent adventitious carbon, and potential impurities. It is non-trivial to account for the contributions of these carbon components, however a survey spectrum of commercial Ge powder (not shown) provides a baseline estimate of ca. 37% adventitious carbon content. Based upon this value, the N:C ratio found for Me₂N-GeNCs is ca. 0.2 and is in excellent agreement with the composition of the expected 3-dimethylamino-1-propene surface termination; from this we conclude the present NCs contain negligible C contamination. Similar compositional analyses for dodecyl-GeNCs are not possible because of the lack of a heteroatom (*i.e.*, N), however it is reasonable the contribution from C impurities is negligible. The oxygen content in the presented NCs is consistent with the complexities of Ge surface chemistry. It can be reasonably attributed to the hydrolysis and oxidation of residual Ge-H surface functionalities during work up and/or high temperature reaction with the diphenyl ether solvent.^{5,14,29} The origin of these oxygen-based species is the subject of ongoing investigation.

The Ge 3d region of the high resolution XP spectra (**Fig. 3** and ESI **Fig S7**) show a broad emission centred at ca. 30.5 eV that is confidently fit to components at 29.0, 29.8, 30.8, 31.6, and 32.4 eV. The emission at 29.0 eV is characteristic of core

Ge atoms; surface atoms bonded to alkyl and alkenyl groups, as well as surface suboxides account for higher oxidation state components.

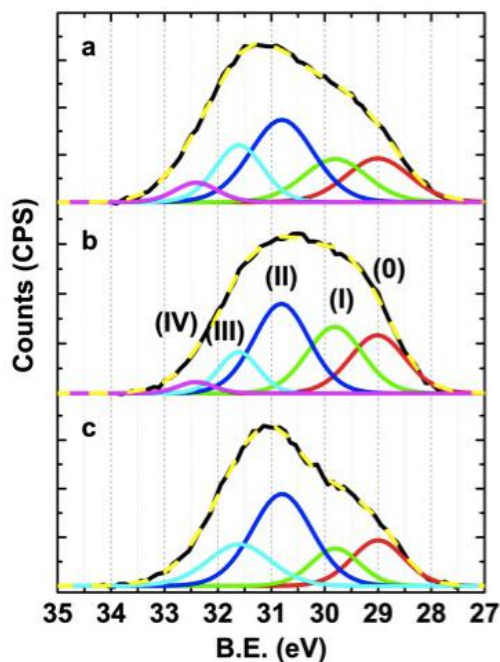


Fig. 3 High-resolution XP spectra of the Ge 3d region for GeNCs obtained from decomposition of **1** at 30 mg/ml at 190°C. (a) Dodecyl-GeNCs synthesized by HI. (b) Dodecyl-GeNCs and (c) Me₂N-GeNCs synthesized by MI. Ge 3d_{3/2} fitting components have been omitted for clarity.

Many Ge nanoparticles synthesized *via* solution-phase routes show photoluminescence (PL) in the visible spectral region with blue-light emission often being reported.^{10,30,31} The appearance of blue emission is not readily explained in the context of quantum confinement; in fact, the effective-mass approximation predicts GeNCs of this dimension should emit in the near-IR or IR regions.^{32,33} **Figs. 4a** and **4b** show the PL excitation and PL spectra of Me₂N-GeNCs. Upon excitation at 365 nm blue luminescence is observed. Similar to other reports of blue/green-emitting GeNCs,^{10,30,31} we note the PL maximum shifts with excitation wavelength (**Fig. 4b**). The PL quantum yield was determined (ESI, **Fig. S8**) to be ca. 1.8% for Me₂N-GeNCs. PL lifetimes of the Me₂N-GeNCs (**Fig. 4c**) at predefined emission wavelengths were obtained using time-correlated single photon counting methods. The short-lived lifetime components (*i.e.*, 0.42 ns and 3.31 ns) at λ_{em.} = 510 nm are consistent with previous reports of GeNCs with faster recombination decay.^{31,34} The origin of excitation wavelength dependent PL is currently unclear and may result from preferential excitation of NCs of specific sizes, or surface state emission.³⁵ This, and direct measurement of the band gap of individual NCs are the subject of ongoing investigations in our laboratory.³⁶

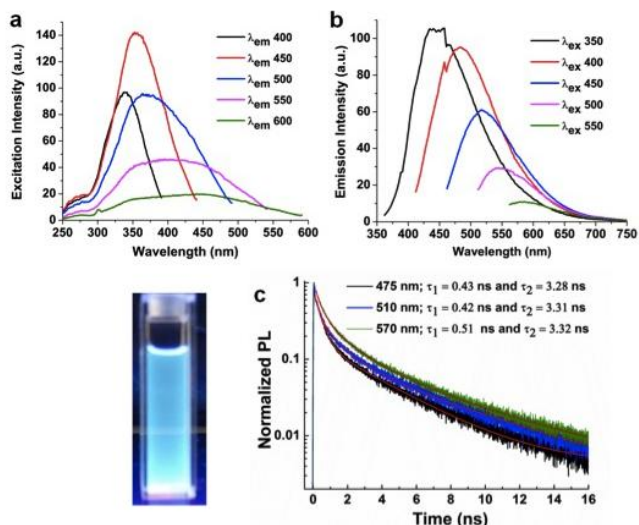


Fig. 4 Photoluminescent properties of $\text{Me}_2\text{N-GeNCs}$ obtained from MI induced decomposition of **1** at 30 mg/ml at 190°C . (a) Excitation spectra obtained while monitoring emission at the indicated wavelengths. (b) Emission spectra obtained upon excitation at the indicated wavelengths. (c) PL decay at indicated emission wavelengths for $\text{Me}_2\text{N-GeNCs}$. (Solid red lines show the two component fits of the exponential decays).

Conclusion

In conclusion, we have developed a facile method that provides surface functionalized GeNCs *via* one-pot hot injection or microwave-irradiation induced decomposition of a “bottleable” GeH_2 -based precursor. While hot injection and microwave irradiation provide GeNCs, the microwave-initiated method is particularly advantageous as it provides access to GeNCs of different sizes through variation of precursor concentration as well as surface modification using volatile capping ligands. Adding to the appeal of the presented approach surface Ge-H residues afford sites for incorporating hydrophobic or hydrophilic groups on the periphery of the nanoparticle *via* hydrogermylation. Furthermore, we have prepared GeNCs of near identical dimension that differ only in surface functionality, yet they exhibit very different optical properties. These observations may arise from surface doping and could open the door to future tailoring of electronic and optical response and are the subject of ongoing investigations.

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Notes and references

† Electronic Supplementary Information (ESI) available. Experimental details, FTIR, TEM images and XPS of thermally functionalized GeNCs. See DOI: 10.1039/b000000x/

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