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Colloidal Synthesis of Germanium Nanocrystals Using Room-Temperature Benchtop Chemistry

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Nanoparticles of the group IV semiconductors Si and Ge are important materials because of their size-dependent photoluminescence (PL) properties[1] and their potential application in biological imaging,[2] as well as in optical and electronic devices.[3] Ge nanoparticles exhibit quantum confinement effects at larger particle diameters than Si,[4] and there is growing interest in developing synthetic routes to these materials. Many of the strategies for synthesizing Ge nanoparticles involve physical or thin film methods, such as chemical vapor deposition,[5] etching,[6] plasma techniques,[7] and gas-phase pyrolysis.[8] Solution methods have also been used to access Ge nanoparticles, and these are particularly intriguing because of the potential for scalability and facile surface modification. Typical solution routes to Ge nanoparticles include chemical reactions of Ge Zintl salts,[9] thermal decomposition of metal–organic complexes in high-boiling solvents[10] or supercritical CO_2,[11] and chemical reduction of Ge salts using strong reducing agents such as alkali metals,[4,12] *n*-butyllithium,[13] alkali metal naphthalides,[14] and metal hydrides.[15] Here, we report a room-temperature colloidal route to Ge nanoparticles. Using a modified polyol process, Ge nanoparticles stabilized by polyvinylpyrrolidone (PVP) are synthesized by borohydride reduction of $GeCl_4$ in ethylene glycol. This strategy involves simple benchtop chemistry and represents an alternative to the harsh methods and specialized laboratory equipment typically required for synthesizing colloidal Ge nanoparticles.

In a typical synthesis, $GeCl_4$ (267 μL) and PVP (50 mg, MW = 630 000) were dissolved in 10 mL of ethylene glycol. After purging with Ar, 6 mL of a 2 M solution of $NaBH_4$ in triethylene glycol dimethyl ether (triglyme) was added via a two-channel syringe pump at a rate of 1.5 mL/min for the first 2 mL and a rate of 0.15 mL/min for the remaining 4 mL. After 30 min, the precipitate was separated by centrifugation and washed with ethanol to remove undesired reaction byproducts, including organic species. All reactions were carried out in 20 mL sample vials at room temperature on a benchtop under ambient conditions. Ar was continuously bubbled through the samples via a disposable pipet tip attached to a plastic tube connected to an Ar tank. The nanoparticles were dispersible in water, ethanol, and acetonitrile.

Figure 1 shows representative transmission electron microscopy (TEM) images for Ge nanoparticles synthesized as described above. The particles are fairly monodisperse with an average diameter of 5 ± 1 nm, as seen in the large-area and cropped TEM images in Figure 1a,c, respectively, as well as in the size distribution histogram in Figure 1b. Energy-dispersive X-ray spectroscopy (EDS) shows the presence of only Ge, as well as Cu from the TEM grid (Figure 2). The selected area electron diffraction (SAED) pattern in Figure 1 shows rings corresponding to the 111, 220, 311, 331, and 440 planes of diamond-type Ge. A high-resolution TEM image (Figure 1d) indicates that the Ge nanoparticles are highly crystalline, showing lattice fringes that correspond to the 220 plane of Ge (2.0 Å). The powder X-ray diffraction (XRD) pattern for the Ge nanoparticles, shown in

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(1) (a) Wilcoxon, J. P.; Provencio, P. P.; Samara, G. A. *Phys. Rev. B* **2001**, *64*, 035417. (b) Liu, S. M. *J. Nanosci. Nanotechnol.* **2008**, *8*, 1110.

(2) (a) O'Farrell, N.; Houlton, A.; Horrocks, B. R. *Int. J. Nanomedicine* **2006**, *1*, 451. (b) Lambert, T. N.; Andrews, N. L.; Gerung, H.; Boyle, T. J.; Oliver, J. M.; Wilson, B. S.; Han, S. M. *Small* **2007**, *3*, 691.

(3) (a) Bettotti, P.; Cazzanelli, M.; Dal Negro, L.; Danese, B.; Gaburro, Z.; Oton, C. J.; Vijaya Prakash, G.; Pavesi, L. *J. Phys.: Condens. Matter* **2002**, *14*, 8253. (b) She, M.; King, T.-J. *IEEE Trans. Electron Devices* **2003**, *50*, 1934.

(4) Heath, J. R.; Shiang, J. J.; Alivisatos, A. P. *J. Chem. Phys.* **1994**, *101*, 1607.

(5) Dag, O.; Kuperman, A.; Ozin, G. A. *Adv. Mater.* **1994**, *6*, 147.

(6) (a) Kamins, T. I.; Ohlberg, D. A. A.; Williams, R. S.; Zhang, W.; Chou, S. Y. *Appl. Phys. Lett.* **1999**, *74*, 1773. (b) Kartopu, G.; Sapelkin, A. V.; Karavanskii, V. A.; Serincan, U.; Turan, R. *J. Appl. Phys.* **2008**, *103*, 113518.

(7) Gresback, R.; Holman, Z.; Kortshagen, U. *Appl. Phys. Lett.* **2007**, *91*, 093119.

(8) Stoldt, C. R.; Haag, M. A.; Larsen, B. A. *Appl. Phys. Lett.* **2008**, *93*, 043125.

(9) (a) Taylor, B. R.; Kauzlarich, S. M.; Delgado, G. R.; Lee, H. W. H. *Chem. Mater.* **1999**, *11*, 2493. (b) Ma, X.; Wu, F.; Kauzlarich, S. M. *J. Solid State Chem.* **2008**, *181*, 1628.

(10) (a) Gerion, D.; Zaitseva, N.; Saw, C.; Casula, M. F.; Fakra, S.; Buuren, T. V.; Galli, G. *Nano Lett.* **2004**, *4*, 597. (b) Gerung, H.; Bunge, S. D.; Boyle, T. J.; Brinker, C. J.; Han, S. M. *Chem. Commun.* **2005**, 1914. (c) Zaitseva, N.; Dai, Z. R.; Grant, C. D.; Harper, J.; Saw, C. *Chem. Mater.* **2007**, *19*, 5174. (d) Wu, H. P.; Ge, M. Y.; Yao, C. W.; Wang, Y. W.; Zeng, Y. W.; Wang, L. N.; Zhang, G. Q.; Jiang, J. Z. *Nanotechnology* **2006**, *17*, 5339.

(11) (a) Lu, X.; Ziegler, K. J.; Ghezelbash, A.; Johnston, K. P.; Korgel, B. A. *Nano Lett.* **2004**, *4*, 969. (b) Lu, X.; Korgel, B. A.; Johnston, K. P. *Nanotechnology* **2005**, *16*, S389.

(12) Wang, W.; Huang, J.; Ren, Z. *Langmuir* **2005**, *21*, 751.

(13) Lee, D. C.; Pietryga, J. M.; Robel, I.; Werder, D. J.; Schaller, R. D.; Klimov, V. I. *J. Am. Chem. Soc.* **2009**, *131*, 3436.

(14) (a) Kornowski, A.; Giersig, M.; Vogel, R.; Chemseddine, A.; Weller, H. *Adv. Mater.* **1993**, *5*, 634. (b) Chiu, H. W.; Chervin, C. N.; Kauzlarich, S. M. *Chem. Mater.* **2005**, *17*, 4858. (c) Hope-Weeks, L. J. *Chem. Lett.* **2005**, *34*, 1526. (d) Chiu, H. W.; Kauzlarich, S. M. *Chem. Mater.* **2006**, *18*, 1023.

(15) (a) Fok, E.; Shih, M.; Meldrum, A.; Veinot, J. G. C. *Chem. Commun.* **2004**, 386. (b) Lu, X.; Korgel, B. A.; Johnston, K. P. *Chem. Mater.* **2005**, *17*, 6479. (c) Wu, H. P.; Liu, J. F.; Wang, Y. W.; Zeng, Y. W.; Jiang, J. Z. *Mater. Lett.* **2006**, *60*, 986. (d) Warner, J. H.; Tilley, R. D. *Nanotechnology* **2006**, *17*, 3745.

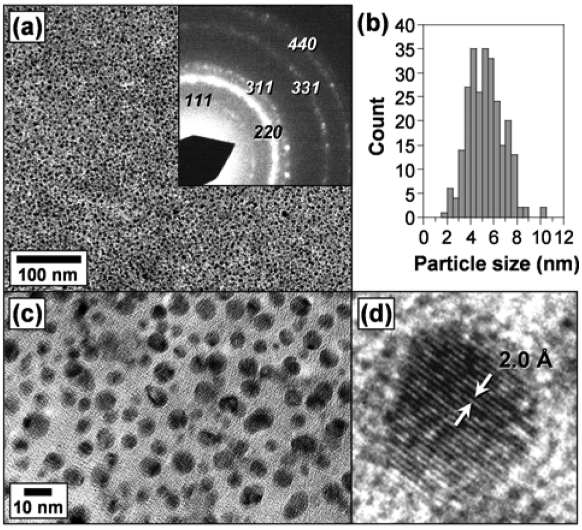

Figure 1. TEM images of Ge nanoparticles (different magnifications) synthesized by reducing $GeCl_4$ in ethylene glycol with $NaBH_4$ in triglyme as described in the text. The inset in (a) shows the SAED pattern for the Ge nanoparticles and the HRTEM image in (d) shows lattice planes corresponding to the 200 plane of diamond-type Ge. A size distribution histogram for the sample in (a) is shown in (b).

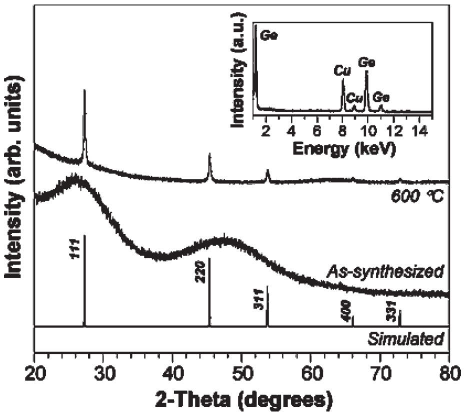

Figure 2. Powder XRD data for Ge nanoparticles as-synthesized (room temperature) and after heating to 600 °C. The simulated XRD pattern for diamond-type Ge is shown for comparison. Inset: EDS data for Ge nanoparticles (Cu comes from the TEM grid).

Figure 2, indicates that they are amorphous as synthesized at room temperature. Crystallization and concomitant particle growth occur after heating to 600 °C under Ar. This is consistent with previous reports.[9,14] Comparing the TEM and XRD data, we speculate that the Ge nanoparticles are amorphous as-made but crystallize in the TEM beam.

By changing the reaction conditions, other particle sizes, size distributions, and shapes are also accessible. At higher concentrations of $GeCl_4$ (300 μL using otherwise identical conditions), a bimodal distribution of 8 ± 2 nm and 2.2 ± 0.7 nm particles is observed (Figure 3a). This is consistent with previous reports indicating that higher concentrations of Ge salts can lead to larger particle sizes.[14c,15b] However, using ethanol as a solvent instead of ethylene glycol led to more uniform larger particles. Figure 3b shows a TEM image of larger Ge nanoparticles with an average diameter of 50 ± 18 nm. While significantly larger, these particles are more polydisperse and coalesced than those synthesized in ethylene glycol.

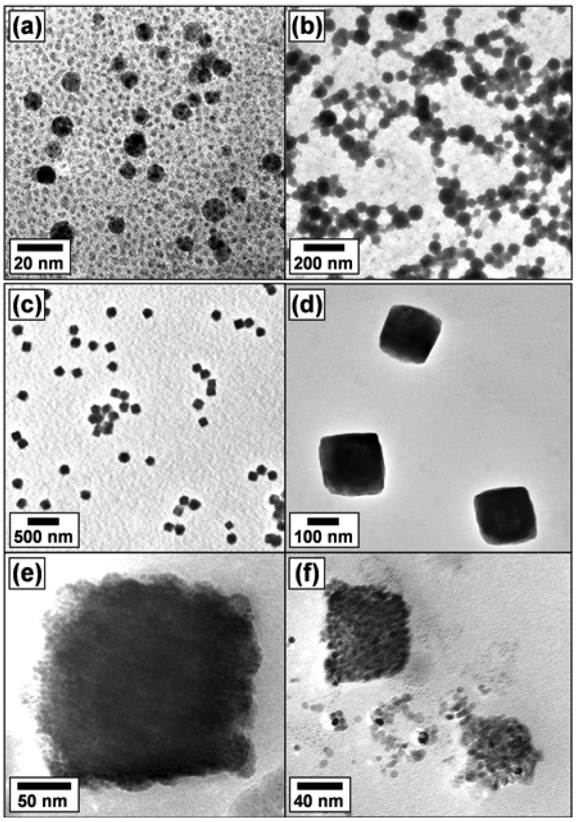

Figure 3. TEM images of (a) Ge nanoparticles with a bimodal size distribution synthesized using a higher concentration of $GeCl_4$, (b) larger Ge nanoparticles synthesized in ethanol, and (c−f) large Ge nanocubes synthesized using a faster reduction rate (see text for details). The TEM images in (e) and (f) were taken at intermediate stages of the reaction and show that the nanocubes form from aggregates of smaller nanoparticles.

In addition to concentration and solvent, reduction rate can be used to influence morphology, as previously reported for indium nanoparticles made using similar chemistry.[16] For example, cube-shaped Ge particles are accessible using a faster reduction rate under otherwise identical conditions: 2.5 mL/min for the first 2 mL of the $NaBH_4$/triglyme solution and 0.15 mL/min for the remaining 4 mL. The TEM images in Figure 3c,d show large 160 ± 30 nm cubes. However, higher-resolution images acquired at intermediate stages of the reaction (Figure 3e, f) show evidence that the cube-shaped particles consist of aggregates of smaller 5−8 nm particles. While the exact formation mechanism is unknown, we speculate that the cube-shaped particles form via a polymer-mediated assembly process. (High-resolution TEM images show that the constituent particles are randomly oriented, and control experiments with molecular stabilizers do not result in the formation of cube-shaped aggregates.) Similar cube-shaped Ge nanoparticles formed by the aggregation of smaller particles have been previously reported via reduction of $GeCl_4$ with Na metal in a pressurized

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(16) Chou, N. H.; Ke, X.; Schiffer, P.; Schaak, R. E. *J. Am. Chem. Soc.* **2008**, *130*, 8140.

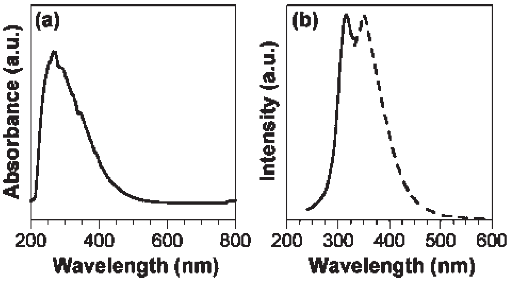

Figure 4. Optical data for 5 nm Ge particles in acetonitrile: (a) UV−visible absorption spectrum and (b) photoluminescence spectra (solid line, excitation spectrum detected at 352 nm; dashed line, emission spectrum at an excitation wavelength of 310 nm).

reactor.[12] Taken together, our data provide evidence that this simple room-temperature benchtop method for synthesizing Ge nanoparticles can be used to generate particles with a range of morphological features that are typically also observed using more harsh chemical methods.

Ge nanoparticles are known to be highly photoluminescent, with intense absorption and emission at ultraviolet and visible wavelengths. The UV−visible absorption spectrum for the as-synthesized amorphous 5 nm Ge particles in acetonitrile (Figure 4a), after washing with ethanol to remove as much of the organic byproducts as possible, shows intense absorption in the ultraviolet region near 275 nm. Bulk Ge absorbs near this wavelength as well, but so do very small Ge nanoparticles.[4,11] The PL excitation and emission spectra for the as-synthesized amorphous 5 nm Ge particles in acetonitrile, washed as described above, are shown in Figure 4b. Excitation at 310 nm produces primarily UV emission with a maximum at 352 nm, although weak luminescence trailing into the visible region is also observed. The corresponding excitation spectrum is shown as well, with λ_{max} = 314 nm (detected at λ = 352 nm). Most colloidal Ge nanoparticles have optimal excitation and emission at longer wavelengths, which suggests that our sample contains very small Ge particles based on the documented trends in PL wavelengths as a function of particle size.[9,11,17] Since our Ge nanoparticles are only weakly passivated with PVP, they are not stable for long periods of time and begin to degrade quickly (within 30−60 min under ambient conditions), as evidenced by a disappearance of the light orange/yellow color that is characteristic of the as-synthesized nanoparticles. It is likely that the effective particle size in solution, an environment that facilitates sample degradation, is smaller than the 5 nm observed for dried nanoparticle samples (which are stable for longer periods of time) because of surface oxidation and subsequent particle etching. It is also known that the PL data for Ge nanoparticles can be extremely sensitive to surface chemistry,[18] and the presence of the PVP polymer and possibly amorphous oxides could also affect the optical properties. Regardless, the data confirm that luminescent Ge nanoparticles have indeed been produced by this simple benchtop chemistry method and provide motivation for studying and modifying the surface chemistry and improving the stability of the nanoparticles.

In conclusion, relatively uniform photoluminescent Ge nanocrystals have been synthesized using a simple and mild room-temperature benchtop chemistry method, and the morphology and size can be modified by changing the reaction conditions. While colloidal stability is an issue that can be addressed with further investigation into surface chemistry and modification, the successful synthesis of Ge nanocrystals using such a mild chemical method is an interesting result that we anticipate will lead to other novel Ge nanostructures.

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Supporting Information Available: Characterization details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Henderson, E. J.; Hessel, C. M.; Veinot, J. G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3624.

(18) (a) Okamoto, S.; Kanemitsu, Y. *Phys. Rev. B* **1996**, *54*, 16421. (b) Reboredo, F. A.; Zunger, A. *Phys. Rev. B* **2001**, *63*, 235314.