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Solution Synthesis of Germanium Nanocrystals Demonstrating Quantum Confinement

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The solution synthesis of II−VI semiconductor nanocrystals is well established,[1,2] and III−V semiconductors are being heavily investigated.[3−6] The situation is very different with the group IV semiconductors Si and Ge. Since the suggestion by Canham[7] that luminescence in porous Si is caused by quantum confinement, there has been a great deal of interest in both porous Si and Si nanocrystals.[8,9] While there is no general agreement on the mechanism of luminescence in porous Si, consensus is moving toward a quantum confinement (QC) model for Si nanocrystals.[9] Despite the interest, efficient solution synthesis for Si nanocrystals was lacking until recently,[10,11] and surface termination was limited to hydrogen or oxygen.[8,9] Since Ge has semiconducting properties similar to those of Si, Ge nanocrystals are also expected to exhibit quantum confinement. There have been reports of Ge nanocrystals produced by chemical vapor deposition,[12] ion implantation,[13,14] cosputtering with SiO_2 followed by reduction,[15−18] reduction of GeO_2 in zeolite Y,[19] pulsed laser ablation and chemical beam epitaxy,[20] and oxidation followed by reduction of doped aerogels,[21] but much work remains. Similar to silicon, there are few viable solution syntheses for Ge nanocrystals. Previous solution syntheses for Ge nanocrystals required long reaction times at high temperature and pressure[22] or laser annealing,[23] and provided little control over particle size or surface termination.

Herein we report a new synthetic procedure that permits control over both nanocrystal size and surface termination. We also report on the photoluminescence and UV/vis absorption spectra of these particles, which provide strong evidence of quantum confinement. Additionally, the ability to terminate the surfaces of the nanocrystals with lithium alkyls or Grignard reagents is demonstrated.

All manipulations were carried out under dry N_2 or Ar gas, using a glovebox or a Schlenk line. All solvents were dried over Na−K alloy before use. The colloidal solutions of nanocrystals were synthesized as follows: Sodium germanide (NaGe) was prepared according to a literature preparation,[24] and excess Na was removed by vacuum sublimation at 300 °C for 4 h. Purified NaGe (0.105−0.110 g, 1.1 mmol) was added to a silonated 250 mL three-neck round-bottom flask. The flask was silonated by soaking in a solution of 5% $SiCl_3(CH_3)$ (Acros) in toluene (Fisher) for 30 min, rinsed with toluene and methanol, then dried in a 110 °C oven. Approximately 100 mL of freshly distilled, degassed diethylene glycol dimethyl ether (diglyme) or ethylene glycol dimethyl ether (glyme) was added to the NaGe powder. The mixture was heated and allowed to reflux for 12 h, and $GeCl_4$ was added in excess (0.4 mL, 3.4 mmol) to the resulting gray suspension. The reaction mixture was allowed to reflux for 8−120 h. Longer reaction times result in larger nanocrystals. The reaction mixture changed from gray to bright yellow or yellow-brown and became clear over a 3 h interval. The excess $GeCl_4$ was removed by evacuation.

The surface Ge atoms of these nanocrystals are presumably terminated by Ge−Cl bonds. This hypothesis appears valid since since reaction with methyllithium, methylmagnesium bromide, or octylmagnesium chloride produces nanoclusters terminated with methyl or octyl groups. 5.0 mL of methyllithium (1.0 M in Et_2O, Acros), 2.0 mL of methylmagnesium bromide (3.0 M in Et_2O, Aldrich), or 2.5 mL of octylmagnesium chloride (2.0 M in THF, Aldrich) was added, and the mixture stirred overnight at room temperature. A white precipitate formed upon addition of the alkyllithium or

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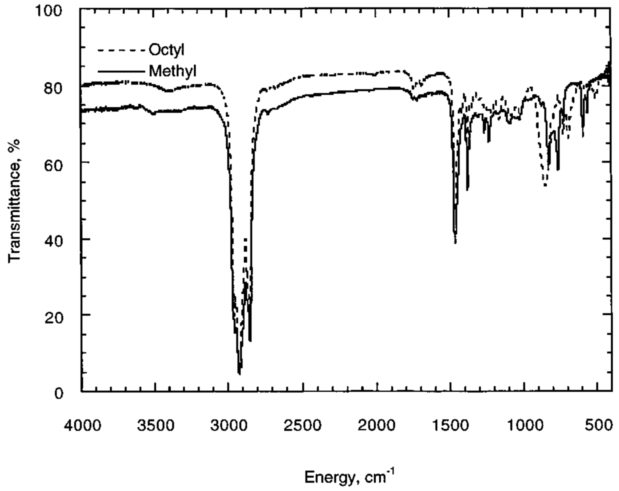

Figure 1. FTIR spectra of methyl- and octyl-terminated Ge nanocrystals.

Grignard reagent. Excess alkyllithium or Grignard reagent was neutralized with deionized water. The reaction was then taken to dryness by gentle heating. The resulting gray powder was sonicated with HPLC grade hexane for approximately 0.5 h, and the mixture was filtered through Whatman #1 filter paper to remove large particles. The solids on the filter paper were identified as NaCl and LiCl by powder X-ray diffraction when RLi was used to terminate the surface. The resulting clear colloid in hexane was washed with deionized water in a separatory funnel to remove any remaining traces of sodium chloride. Hexane can be removed, and the resulting material can be redissolved in a variety of solvents.

High-resolution transmission electron microscopy (HRTEM) analysis of the colloids was performed with a JEOL 200CX TEM at 200 keV. A 5 μL aliquot of the colloid was pipetted onto a lacey carbon substrate on a 300 mesh Cu TEM grid and dried. The colloids produced were diluted with HPLC grade hexane and examined with a HP8452A UV/vis spectrophotometer. A blank of pure HPLC grade hexane was examined before every sample. The fluorescence spectra of these colloids were acquired on a Perkin-Elmer LS50B luminescence spectrophotometer; a slit width of 2.5 nm was used for both the excitation and emission monochromators. The colloids were diluted with HPLC hexane as necessary, and pure solvent was examined with the fluorimeter before acquiring fluorescence spectra. A Mattson Galaxy 3000 FTIR spectrophotometer was used to perform IR spectroscopy on the dried colloids. Each colloid was dried on a CsI plate and then heated at 130 °C for 2 h to remove the solvent; a blank CsI plate was examined before each sample.

The FTIR spectra demonstrate the presence of alkyl groups in the dried colloids. The three peaks at 2955, 2924, and 2853 cm^{-1} (Figure 1) fall where expected for the C−H stretches of methyl and methylene groups. The peaks at 1376 and 1456 cm^{-1} are at the positions expected for the symmetric and asymmetric bends of the methyl group, respectively. The peaks in the fingerprint region show similarity, but not complete agreement with published spectra for Ge tetraalkyls.[25,26]

HRTEM of the samples produced by the above procedures revealed crystalline Ge nanoclusters in all of the samples characterized. In the best samples, the majority of nanoclusters seen in the HRTEM micrographs are between 2 and 5 nm (Figure 2), with an average size of 3.5(1.2) nm. A histogram from several micrographs taken of the same sample shows an approximately log-normal size distribution of nanoparticles. Lattice fringes are clearly visible in the micrographs, indicating that the majority of the small structures seen are crystalline Ge nanoclusters. The lattice fringes imaged in this micrograph show a spacing of 3.27 Å, and the angle between crossed fringes is 70.5°, both consistent with the {111} planes of bulk Ge.[27] Selected area electron diffraction (SAED) patterns obtained in the TEM are consistent with bulk Ge.

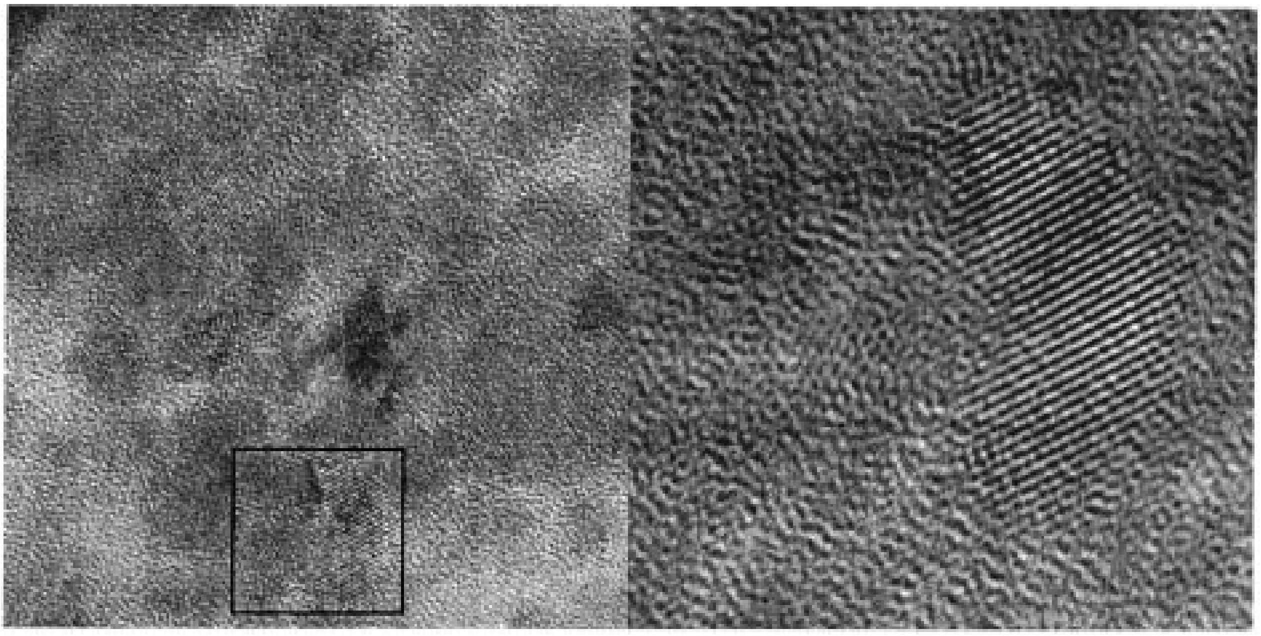

Figure 2. High-resolution TEM micrograph of GE nanocrystals. The inset area has been rotationally filtered to reduce background from amorphous carbon substrate. The lattice fringes seen correspond to the {111} planes of Ge.

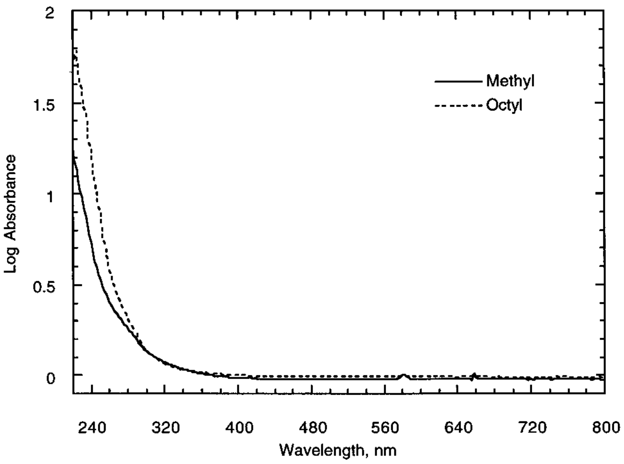

Figure 3. Absorption spectra of methyl- and octyl-terminated Ge nanocrystals. Spectra are normalized to correct for difference in concentration. Note onset of absorption from 300 to 400 nm.

While bulk Ge absorbs weakly in the infrared, nanocrystals produced by this method absorb strongly in the ultraviolet (Figure 3). The spectrum of methyl-terminated nanocrystals is slightly blue-shifted, suggesting that the nanocrystals in that sample are slightly smaller than the octyl-terminated nanocrystals. This behavior is consistent with quantum confinement models.[28−31] In addition, both methyl- and octyl-terminated Ge nanocrystals have similar absorption spectra for the same size nanocrystals. This strongly argues against surface effects as being responsible for these results.

Size-selective photoluminescence (PL) spectroscopy was also performed on the colloids of Ge nanocrystals produced by this method. According to quantum confinement models, the optical properties of quantum-confined nanocrystals are highly size dependent.[28−31] Nanocrystals of a specific size absorb and emit light at a specific wavelength. Since the present synthesis produces a continuous size distribution of nanocrystals, the overall PL spectrum is inhomogeneously broadened. One manifestation of quantum confinement in such a sample is a monotonic shift of emission wavelength as the excitation wavelength is changed. The Ge nanocrystals produced by this method show such a continuous shift in emission wavelength with excitation wavelength (Figure 4). This provides further support for quantum confinement in these Ge nanocrystals.

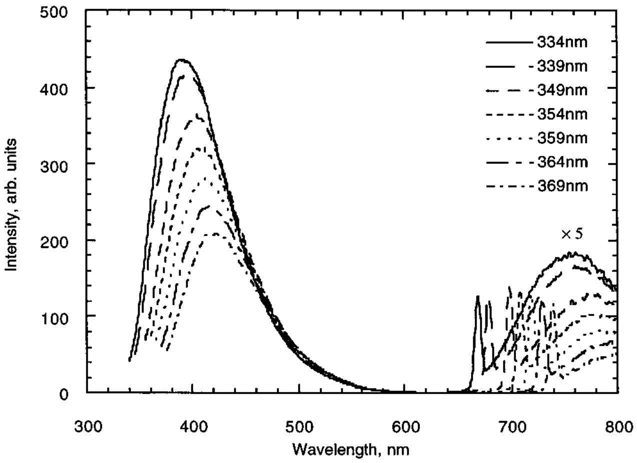

Figure 4. Size-selective photoluminescence spectra of Ge nanocrystals. A smooth shift of the emission wavelength with excitation wavelength is a necessary though not sufficient condition for quantum confinement.

In summary, reaction between the Zintl salt NaGe and $GeCl_4$ provides a novel synthetic route to Ge nanocrystals. The synthesis of the methyl-terminated nanocrystals resulted in an average particle size of 3.5(1.2) nm, by HRTEM. FTIR spectroscopy is consistent with alkyls attached to the Ge nanoparticles. The size dependence of the intense absorption, the blue shift of the absorption to the ultraviolet, and the monotonic shift of the emission wavelength with excitation wavelength all provide strong evidence for quantum confinement in these Ge nanocrystals.

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