

Ultraviolet photoluminescence from 6H silicon carbide nanoparticles

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We report stable photoluminescence from 6H silicon carbide nanocrystals dispersed in three different solvents: water, hydrofluoric acid, and toluene. Transmission electron micrograph surveys reveal a size distribution that contains a significant fraction of monocrystal particles with diameters below 3 nm—small enough for quantum confinement to play a role in increasing the effective bandgap energy. The ultraviolet photoluminescence band observed at 3.5 eV in the colloidal solutions is consistent with quantum confinement estimates based on the effective mass model.

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Interest in semiconducting nanocrystals, or quantum dots (QDs), is growing because of their unusual physical properties, reported for particles that are less than few nanometers in diameter.¹ Photoluminescent QDs are increasingly being used as biological tags and are becoming an alternative to traditional organic dye based fluorophores.² Their main advantages over organic fluorophores are superior stability against photobleaching and size-tunable emission wavelength. However, QDs prepared from binary compounds of II-VI or III-V group elements can be toxic and their use in biological assays necessitates encapsulation in a robust inert material shell, which significantly increases the particle diameter and complicates the fabrication process.^{3,4}

Silicon nanoparticles, despite being comprised of an indirect-bandgap material, can exhibit photoluminescence at visible wavelengths, an effect attributed to quantum confinement.⁵ Unlike their direct-bandgap counterparts, silicon nanoparticles are bioinert⁶ but their wider acceptance as alternative fluorophores is presently limited by poor emission stability in aqueous environments.⁷

Silicon carbide (SiC) is a wide bandgap biocompatible⁸ material that was recently shown to exhibit blue/yellow photoluminescence in nanoscale structures.⁹ The three main polytypes of SiC, 3C, 6H, and 4H have bandgap (E_g) values of 2.3, 3.03, and 3.2 eV respectively, and could be expected to emit at wavelengths above their energy gap, when quantum confinement takes place. Indeed, stable emission at 400 nm has been demonstrated from 3C SiC nanoparticles, consistent with the bandgap expansion in nanocrystals that are smaller than the exciton Bohr radius.¹⁰ Increased blue-green photoluminescence from nanoporous 6H SiC was reported by Matsumoto *et al.*,¹¹ but an emission above the energy gap has not been observed, and the below bandgap emission was attributed to surface defects. Clear evidence of quantum confinement in 6H SiC is therefore still lacking.^{12–15}

Porous silicon carbide was fabricated by electrochemical etching of a monocrystal 6H SiC wafer [*n*-type 10^{19} cm⁻³, Cree Inc., Durham, NC (Ref. 16)]. Galvanostatic etching with current density of 6 mA/cm² was carried out in the

dark using a polytetrafluoroethylene electrochemical cell, containing a 3:1 volume mixture of 48% HF and ethanol. Following 10 min of etching, the wafer was thoroughly rinsed with de-ionized water, ethanol, and then dried in a stream of N₂. The porous silicon carbide films were then immersed in three different solvents (water, toluene and hydrofluoric acid) and sonicated for 10 min each to form the nanoparticle suspensions.

Figure 1 shows transmission electron microscope (TEM) images of the representative silicon carbide nanoparticles, with diameters ranging from 1 to 8 nm. The clear visible fringes in the TEM image [Fig. 1(b)] and the far-field electron diffraction pattern [Fig. 1(c)] suggest that the 6H crystalline structure is retained during the process of nanoparticle production. There was no evidence of the amorphous phase as all of the nanoparticles that were randomly analyzed in the TEM image area displayed clear diffraction patterns.

Figure 2 is a photograph showing visible photoluminescence of three colloidal suspensions of SiC nanoparticles in water, toluene, and the HF-based electrolyte, when illuminated by a common UV lamp.

The photoluminescence spectra for all three colloidal solutions were collected using a spectrofluorimeter (SLM 8000) with optical photoexcitation at either 300 nm (4.13 eV) or 450 nm (2.75 eV). It is notable that PL emission was significantly less intense when a below-bulk bandgap excitation (2.75 eV) was used (dashed traces in Fig. 3).

Figure 3(a) plots the measured photoluminescence spectra for nanoparticles dispersed in water, showing a broad-band centered at 2.78 eV when excited at 4.13 eV. While the majority of the photoluminescence occurs at energies below the 6H SiC bandgap ($E_g = 3.03$ eV), we observed an emission tail that extends well above the bulk bandgap, in agreement with earlier reports.¹⁷ The photoluminescence band below the energy gap was extensively studied by several authors and was attributed to radiative recombination by surface states or radiative recombination processes involving a nitrogen donor center.^{18,19} In our observations the strength of the photoluminescence band centered at 2.78 eV depends strongly on the solvent in which the nanoparticles are dispersed.

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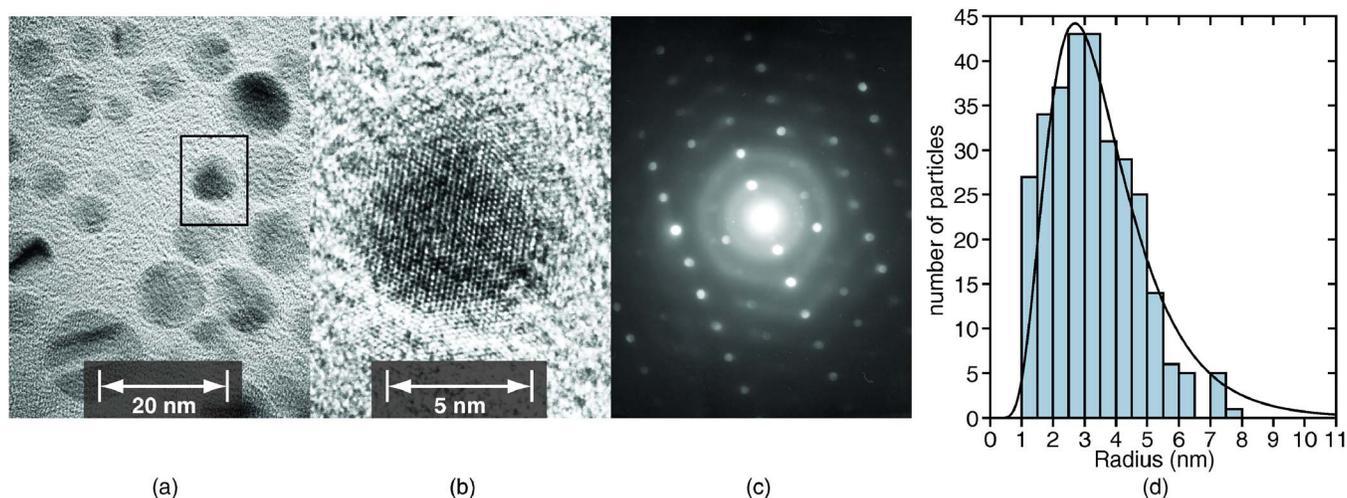


FIG. 1. (Color online) (a) TEM image of 6H SiC nanoparticles. (b) Enlarged image of isolated silicon carbide nanoparticle showing visible lattice fringes from a single SiC nanoparticle. (c) Measured electron diffraction from representative nanoparticle. (d) Particle size distribution obtained from TEM image analysis.

In order to exclude possible emission from the Si oxide surface states,²⁰ we also measured the photoluminescence of SiC nanoparticles suspended in a mixture of hydrofluoric acid and ethanol. This solvent is the same as the electrolyte originally used to etch the porous silicon carbide wafers and ensures that the particle surface is oxide-free. The photoluminescence spectrum for the nanoparticles suspended in HF/ethanol [Fig. 3(b)] exhibits a prominent above-bandgap UV emission band with maximum intensity around 3.5 eV, when excited at 4.13 eV. The sub-band-gap emission is suppressed relative to that of the nanoparticles in aqueous suspension. These results are in general agreement with a recent *ab initio* study that predicts that the silicon carbide bandgap is sensitive to the particle environment and suggests that silicon carbide nanoparticles with hydrogen termination are likely emitters in the UV.^{21,22} In particles smaller than 3 nm, the surface termination is thought to affect the bandgap both by modifying the electronic structure of the nanoparticle and by inducing a physical expansion of the lattice.²²

The photoluminescence spectrum of 6H SiC nanoparticles dispersed in toluene [Fig. 3(c)] shows a broadband emission from 4 to 2.2 eV, even though at lower intensity

compared to the water or HF/ethanol suspensions. It is notable that the PL emission spectrum of the SiC nanoparticles is strongly influenced by the surrounding media, a result, which differs from earlier reported observations of 3C SiC nanoparticles,²³ where the PL spectra were similar in ethanol, water, and toluene solutions. Apparently, emission above the bandgap in 6H crystallites is produced when both conditions regarding crystallite dimensions and surface termination are met.

Several theoretical models have been proposed to evaluate the band gap widening in nanocrystals due to quantum confinement. The effective mass model predicts that the energy gap ΔE between valence and conduction bands will grow with the decreasing crystal size according to^{24,25}

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 1.786 \frac{e^2}{\epsilon R} - 0.248 R_{\infty} hc, \quad (1)$$

where R is the particle radius, m_e^* and m_h^* are the electron and hole effective masses, respectively, ϵ is the dielectric constant, and R_{∞} is the Rydberg constant. Using published effective masses of SiC (Refs. 26 and 27) ($m_e^* = 1.1m_0$ and $m_h^* = 0.71m_0$), Eq. (1) predicts that the bandgap of 6H SiC will increase to 3.5 eV in particles with radius of 1.35 nm. The measured nanoparticle size distribution presented in Fig. 1(d) confirms that there is a significant population of nanoparticles with diameters below 2.7 nm that could contribute to the observed above-bandgap UV emission (Fig. 3).

The nature of the previous above-bandgap PL emissions in nanoporous 6H SiC has been disputed^{12-14,17,28} in part because the reported crystallites sizes were outside the quantum confinement range.^{11,14} Also, as was recently demonstrated, the bandgap in SiC nanocrystals is highly sensitive to surface termination with the largest values (above 3 eV) expected for carbon terminated and hydrogen rich crystallites of about 2.5 nm in diameter.²² Our measurements in water, HF/ethanol, and toluene confirm that both visible and UV photoluminescence emission bands are susceptible to the particle environment in the 6H polytype.

We have observed an ultraviolet emission band from the 6H SiC nanoparticles dispersed in three different solvents. Although the emission spectrum depends on the surrounding particle environment and surface termination, in all cases we

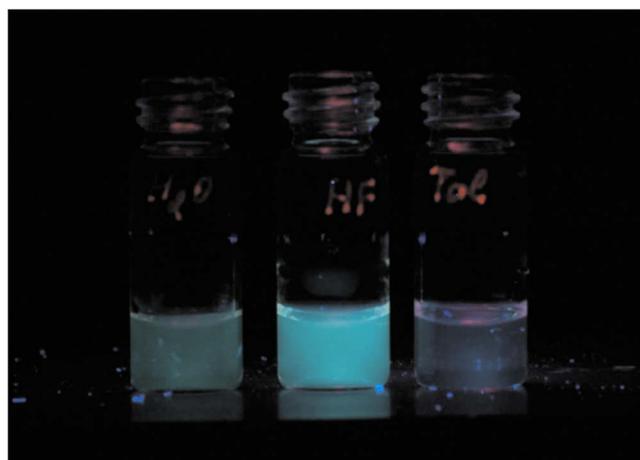


FIG. 2. (Color online) The visible photoluminescence of SiC nanoparticle colloidal solutions in water, toluene, and in a mixture of hydrofluoric acid and ethanol (electrochemical etching bath) under UV illumination (365 nm, $h\nu = 3.40$ eV).

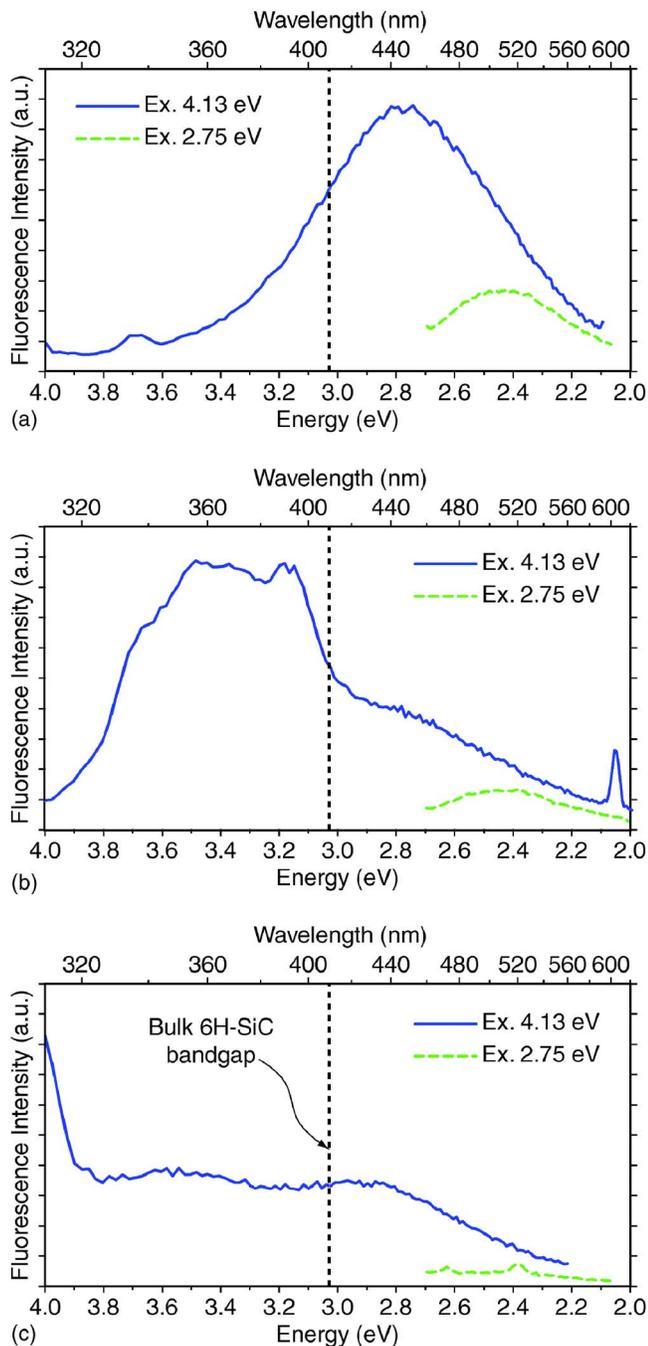


FIG. 3. (Color online) PL emission spectra of 6H SiC nanocrystals dispersed in (a) water, (b) HF/Ethanol, and (c) toluene. The labels indicate exciting photon energies.

see clear evidence of the above-bandgap photoluminescence, even with particles in a hydrofluoric acid solution that precludes surface oxidation. The unambiguous above-bandgap photoluminescence, together with the observed size distribution, strongly supports the theory that quantum confinement plays a role in determining the photoluminescence spectrum

for 6H SiC nanoparticles. The above three colloidal solutions have been stored for up to four months and did not display any appreciable photoluminescence spectral shifts or intensity loss. Given their high stability, small size, and material biocompatibility,²⁹ 6H SiC nanoparticles could be a viable fluorophore for biological labeling.

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