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Microscopic Proof of Photoluminescence from Mechanochemically Synthesized 1-Octene-Capped Quantum-Confined Silicon Nanoparticles: Implications for Light-Emission Applications

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ABSTRACT: Silicon nanoparticles (SiNPs) have been explored intensively for their use in applications requiring efficient fluorescence for LEDs, lasers, displays, photovoltaic spectral-shifting filters, and biomedical applications. High radiative rates are essential for such applications, and theoretically these could be achieved via quantum confinement and/or straining. Wet-chemical methods used to synthesize SiNPs are under scrutiny because of reported contamination by fluorescent carbon species. To develop a cleaner method, we utilize a specially designed attritor type high-energy ball-mill and use a high-purity (99.999%) Si microparticle precursor. The mechanochemical process is used under a continuous nitrogen gas atmosphere to avoid oxidation of the particles. We confirm the presence of quantum-confined NPs (<5 nm) using atomic force microscopy (AFM). Microphotoluminescence (PL) spectroscopy coupled to AFM confirms quantum-confined tunable red/near-infrared PL emission in SiNPs capped with an organic ligand (1-octene). Using micro-Raman-PL spectroscopy, we confirm SiNPs as the origin of the emission. These results demonstrate a facile and potentially scalable mechanochemical method of synthesis for contamination-free SiNPs.

1. INTRODUCTION

Silicon is a nontoxic, earth-abundant semiconductor with a bulk indirect band gap of 1.12 eV. It is a suitable material for photovoltaic (PV) applications and currently has the lion’s share in the PV market. Its indirect band gap and low quantum yield, however, make it unsuitable for applications requiring efficient fluorescence, such as LEDs, lasers, displays, photovoltaic spectral-shifting filters, and biomedical applications. High radiative rates are essential for such applications, and theoretically these could be achieved via quantum confinement and/or straining. Wet-chemical methods used to synthesize SiNPs are under scrutiny because of reported contamination by fluorescent carbon species. To develop a cleaner method, we utilize a specially designed attritor type high-energy ball-mill and use a high-purity (99.999%) Si microparticle precursor. The mechanochemical process is used under a continuous nitrogen gas atmosphere to avoid oxidation of the particles. We confirm the presence of quantum-confined NPs (<5 nm) using atomic force microscopy (AFM). Microphotoluminescence (PL) spectroscopy coupled to AFM confirms quantum-confined tunable red/near-infrared PL emission in SiNPs capped with an organic ligand (1-octene). Using micro-Raman-PL spectroscopy, we confirm SiNPs as the origin of the emission. These results demonstrate a facile and potentially scalable mechanochemical method of synthesis for contamination-free SiNPs.

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tunability throughout the entire visible range.\textsuperscript{7,19–22} Such SiNPs are typically synthesized by wet-chemical methods that involve higher temperatures in the presence of carbon sources during the synthesis process that has been recently reported to lead to the cosynthesis of various carbon-related fluorescent material, such as carbon dots,\textsuperscript{23–25} along with the SiNPs in the sample. Recent critical reports have also shown that even without Si precursors, the product still has optical properties similar to those reported for SiNPs,\textsuperscript{26–28} which strengthens the argument of contamination by brightly fluorescent carbon species causing the reported bright PL, instead of silicon.

Thus, several challenges remain: (1) a synthesis method that could produce large quantities of SiNPs without contamination; (2) direct and unambiguous proof of PL emission from SiNPs; and (3) visible-light-tunable PL corroborating the theoretical studies.\textsuperscript{29,30} One way to overcome the issue of carbon contamination and up-scalability is to use a top-down solvent-free approach, starting with pure silicon. Regarding this, in 2007, Heintz et al. first reported the synthesis of luminescent silicon nanoparticles (SiNPs) by high-energy ball-milling.\textsuperscript{31} Millimeter-sized silicon particles were crushed in a mill in the presence of alkennes and alkynes for surface passivation, and blue PL emission was observed. This study shows the potential of mechanochemistry in the synthesis of SiNPs, although the authors observed the debated fast-decaying blue PL and no proof related to carbon contamination of the free SiNPs was provided. Later, Matsumoto et al. observed PL in the blue spectral range from milled SiNPs originating from dimethylanthracene (DMA) impurities in hexane.\textsuperscript{32} In our recent study, we also observed blue PL from high-energy ball-milled SiNPs capped with oxides, likely originating from metallic defects introduced into the SiNPs during the ball-milling from the milling media (balls and vessel).\textsuperscript{33} These experiments highlight the importance of experimental scrutiny to minimize the contamination and assumptions.

Here, we report the synthesis of very pure 1-octene (alkene)-capped SiNPs by high-energy ball-milling. A custom-built high-energy ball-mill is used in the process to avoid any exposure of oxygen during the process. The insertion of organic ligands was done near the end of the process to avoid the formation of carbon dots during the milling process, which involves high pressures and heat. Tungsten carbide (WC) is used as a milling medium to prevent metallic impurities from inserting into the SiNPs. WC is a harder material than silicon, so the diffusion of WC in silicon is unlikely. We use dry milling to avoid any contamination from the organic solvents. Size-dependent PL is studied using AFM correlated with micro-PL spectroscopy, matching the theory proposed by Wang et al. and Delerue et al.\textsuperscript{29,30} We confirm the origin of the PL to be from 1-octene -capped SiNPs by microscopic Raman-PL correlated spectroscopy. The results of this work offer an unambiguous demonstration of the origin of PL from SiNPs and the potential of mechanochemistry for the synthesis of SiNPs.

2. MATERIALS AND METHODS

Crystalline silicon powder of 20 μm size and 99.999\% purity was purchased from Hongwu International Group Ltd., China. The full process scheme is depicted in Figure 1. We followed the synthesis process as described in our previous reports with a difference in the addition of ligands at the end of the milling process.\textsuperscript{32,33} Silicon powder (1 g) is loaded into a custom-built attritor-type high-energy ball-mill vessel. A WC milling medium is used in the process. The Si powder is ball-milled at 450 rpm at a ball-to-powder weight ratio of 40:1 for 4 h. Milling is performed in steps of 1 h of milling followed by 15 min of cooling, assisted by continuous water circulation around the milling vessel through a jacket to remove excess heat generated during the milling process. Continuous nitrogen gas flow is provided to avoid atmospheric oxygen reacting with the silicon powder during the milling process. After the milling process is finished, a syringe is used to insert 1-octene (ligand) and octane as a solvent through a gas inlet nozzle without opening the milling vessel. The colloidal dispersion of 1-octene-passivated SiNPs in octane is then collected. The SiNP dispersion is centrifuged at 12 000 rpm for 10 min to collect the precipitate. The supernatant is discarded because it contains unreacted ligands and excess solvent. The precipitate is redispersed in octane. For single-nanoparticle PL measurement, we use a Zeiss optical microscope (inverted, 100X, 1.3 NA) to collect the PL from each individual SiNP. The cleaned colloidal dispersion was left to rest overnight to allow the larger particles to sediment at the bottom. The supernatant is collected and then centrifuged again to get the size-separated colloidal dispersion of SiNPs in octane. The collected colloidal dispersion is stored in a glass vial sealed with Teflon tape.

A Bruker Alpha Fourier-transform infrared spectroscopy (FTIR) spectrometer equipped with an attenuated total reflection (ATR) single-reflection crystal (Bruker Optic GmbH, Ettlingen, Germany) was used to record FTIR spectra of unmilled and milled Si powder samples. Dynamic light scattering (DLS) of milled Si samples was measured with a Zetasizer Nano ZS (633 nm, scattering angle 173°, Malvern Instruments, Herrenberg, Germany). For single-nanoparticle PL spectroscopy, SiNPs were dispersed in spectroscopy-grade hexane and drop-cast on a quartz coverslip (SPI supplies 25-mm-diameter coverslips with a thickness of 0.15–0.18 mm) and left to dry in air at room temperature. For the measurement, we use a Zeiss optical microscope (inverted,
Axio Observer 3) coupled to an atomic force microscope (AFM; Nanowizard 3, JPK Instruments). The PL emission is measured using a spectrometer (Princeton Instruments, Acton SP2300) with a charge-coupled detector (CCD; Princeton Instruments, Pylon 400B), coupled to the optical microscope. A diode laser (445 nm, Becker and Hickl GmbH, BDL-445-SMN) is used to excite the samples. The PL from the sample is collected using a 100× objective (Zeiss, Epiplan-Neofluar with NA = 0.75) and is spectrally filtered using a razor-edge 445 nm band-pass filter (Semrock, BLP01−445R-25) to remove the scattered excitation light. Correlated Raman and PL spectroscopy measurements are employed to correlate the particle composition and PL. For this purpose, SiNPs dispersed in octane are drop cast on a sapphire substrate and left to dry in air at room temperature. Measurements are performed on a Witec alpha300R confocal microscope excited by a diode-pumped solid-state 532 nm laser. Alternatively, samples are excited by 455 nm laser light, generated by a NKT Photonics SuperK Extreme white-light supercontinuum laser with a wavelength range of 450−2200 nm, coupled to an NKT Photonics SuperK Select acousto-optical tunable filter for wavelength selection. The excitation light is directed onto the sample via a 100× objective with NA = 0.9 (Zeiss EC Epiplan-Neofluar 100x) which also out-coupled the resultant Raman and PL signals into a spectrograph (Witec UHTS 300 VIS) and detected with a CCD (Ador EMCCD). Raman and PL spectra are measured using 1800 and 150 gr/mm gratings, respectively.

X-ray diffraction (XRD) studies are performed using a Rigaku Miniflex II Desktop X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) measurements are performed using a Verios 460 STEM. An energy-dispersive spectroscopy (EDX) Oxford Xmax 80 mm² silicon drift detector is attached to a STEM setup to study elemental composition. Transmission electron microscopy (TEM) is performed using the Technai G2 20 X-Twin equipped with a field emission gun (FEG) as the electron source. X-ray photoelectron spectroscopy (XPS) is performed in an ultrahigh vacuum setup (base pressure better than 1.0 × 10⁻⁹ mbar) equipped with a Scienta Omicron R4000 HiPP-3 hemispherical analyzer (swift acceleration mode, 1 mm slit entrance) and a monochromated Al Kα X-ray source (1486.6 eV). The samples are mounted on standard Omicron flagpoles with double-sided Cu tape. The spectra are acquired at 100 eV of pass energy (PE) and calibrated to the peak position of O 1s in SiO₂ (532.9 eV binding energy).

3. RESULTS AND DISCUSSION

We start our analysis by characterizing the particle size of the silicon powder before and after the milling process using SEM, where images of unmilled particles indicate the presence of micrometer-sized particles, (Figure 2a) which are downsized to SiNPs by the high-energy ball-milling process (Figure 2b). The SEM images clearly show the presence of nanosized Si particles in the milled Si sample. The presence of SiNPs with sizes below 20 nm is further confirmed by TEM measurements (Figure 2c). Next, we assess the capping and surface termination by FTIR (Figure 2d), which show evidence of organically capped Si particles in the milled Si sample. The presence of SiNPs with sizes below 20 nm is further confirmed by TEM measurements (Figure 2c). Next, we assess the capping and surface termination by FTIR (Figure 2d), which show evidence of organically capped Si particles in the milled sample, noted by the presence of peaks at 1257 and 806 cm⁻¹ corresponding to Si−C and Si−Si bonds, suggesting the formation of organic bonds on the surface of the SiNPs. However, the sample also reveals Si−O bonds, suggesting that the sample is not completely capped with 1-octene and may have a mixture of 1-octene and oxygen-capped SiNPs. This has also been reported in similar synthesis methods. It could be caused by the fact that the starting Si microparticles are oxide-capped, which might also persist in the final product. The presence of oxygen in the silicon particles before and after milling is confirmed by the XPS measurements (Figure S1).

In addition to SEM, TEM, and FTIR analysis, we employ a series of additional characterization methods to analyze the sample. XRD demonstrates that the milling process does not change the phase of the particles (Figure S2). DLS is used to characterize the particle size distribution, indicating a

Figure 2. (a) SEM image of the micrometer-sized silicon particles before milling. (b) SEM image of size-separated SiNPs after milling. (c) TEM image of size-separated SiNPs. (d) FTIR spectrum of milled SiNPs.
reduction of particle sizes from ~20 to 0.1–1 μm after milling (Figure S3).

EDX analysis (Figure S4) shows the presence of silicon, carbon, and oxygen in the sample, which is expected, considering the composition of the starting material (pure silicon) and the use of carbon ligands. Oxygen was present in trace amounts in the starting material. The absence of other elements suggests negligible contamination in the milled samples.

The main challenge lies in the unambiguous identification of the PL emission source. In particular, the PL emission originates from the SiNPs and not some carbon-related fluorescent material and is proof of its tunability by the nanoparticle’s size rather than being impurity-related. We solve these challenges using two correlated measurements: (1) microscopic PL spectroscopy correlated with size measured by coupled AFM and (2) microscopic Raman spectroscopy correlated with PL measurements.

After the size-separation process described in the Materials and Methods section, we could identify a fraction of nanosized (<10 nm) particles in the sample (Figure 2b). A diluted dispersion of SiNPs is then drop cast on a transparent quartz substrate (~150 μm thickness). We perform AFM to measure particle sizes in the size-separated milled sample (Figure S5). A histogram obtained from AFM is shown in the inset of Figure S5, suggesting particle sizes ranging from 2 to 6 nm with an approximated average size of ~4.2 nm, well within the onset of the regime of quantum confinement in silicon. The SiNPs show size-dependent PL emission, an expected result from quantum confinement. We measure PL from single SiNPs using our optical microspectroscopy setup, and the size of the emitting particles is directly measured using a coupled AFM. First, we record a PL image in wide-field imaging mode (Figure 3a) with an acquisition time of 10 s to avoid photobleaching of the SiNPs. The PL image shows PL emission ranging from 550 to 700 nm.

Figure 3. (a) 2D PL micrograph of emitting SiNPs. The red square indicates the region corresponding to the AFM scan in the figure below. (b) Corresponding AFM scan of a similar area showing agglomerated SiNPs. Black and white arrows are used to show the single nanoparticles and clusters of particles, respectively. (c) Gaussian peak fitting of the measured PL spectrum shows PL emission ranging from 550 to 700 nm.

The recorded spectrum lies in the range of the single-particle spectra peaking between 1.8 and 2.5 eV and is close to the measured ensemble spectrum (Figure 3c).

A correlated measurement of an SiNP-like PL spectrum (Figure 4d) (that closely resembles the ensemble PL spectrum) from the same particle that exhibits a Raman spectrum expected for 1-octene-capped SiNPs (Figure 4b) confirms that the PL does indeed originate from 1-octene-capped SiNPs. It also shows the important role and potential of the correlative micro-Raman-PL spectroscopy technique in the
development and analysis of novel nanomaterials with a complex PL origin, such as SiNPs. The results also suggest that the solvent-free high-energy mechanochemistry is successful in producing visibly emitting SiNPs without the carbon-related nanomaterial fluorescent contaminants.

4. CONCLUSIONS

By combining various microscopic techniques, we show evidence of PL from quantum-confined SiNPs emitting in the visible spectral range. Size-tunable PL emission spectra are observed by AFM-correlated micro-PL spectroscopy. To exclude the role of carbon-related byproducts in the observed PL, we further employ correlative micro-Raman-PL spectroscopy which verifies the PL origin to be from organically capped SiNPs. In this way, we demonstrate a reliable top-down, solvent-free synthesis method with the potential for scale-up for SiNPs with PL in the visible spectral range, which is free of the lately debated fluorescent carbon contaminants. Also, we demonstrate the acute need for correlative microscopy methods in the analysis of the origin of emission from complex nanosized systems. Silicon nanoparticles could be a nontoxic, earth-abundant alternative for light emission applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03396.

XPS measurements of the silicon particles, XRD patterns of the unmilled and milled Si particles, DLS results of milled Si nanocrystals, EDX spectrum of the milled Si nanocrystals, and AFM image of 1-octene-capped SiNCs (PDF).

Figure 4. Micro-Raman-correlated PL spectroscopy of the 1-octene-capped SiNPs. (a) Dark-field optical image of the SiNPs drop cast on a sapphire substrate. (b) Micro-Raman spectrum of the SiNPs (in red), showing the presence of vibrations related to the nanocrystalline silicon and organic ligands. The bulk Si Raman spectrum is shown (in blue) for reference. (c) Comparison of the Raman spectrum of the bulk and the ball-milled SiNPs at a ~500 cm⁻¹ shift showing a clear shift in the spectrum. (d) Micro-PL spectrum of SiNPs upon excitation with 455 and 532 nm wavelength lasers. PL emission of sapphire substrate was measured and subtracted from the signal of the SiNPs to obtain the presented graphs. Laser artifacts are present in the data marked with blue arrows. Dotted lines represent spectral filters used to cut off excitation laser light.

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