

Electrochemical Synthesis of Red Fluorescent Silicon Nanoparticles

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Herein, we report on the preparation of red fluorescent Si nanoparticles stabilized with styrene. Nano-sized Si particles emit fluorescence under UV excitation, which could be used to open up new applications in the fields of optics and semi-conductor research. Unfortunately, conventional methods for the preparation of red fluorescent Si nanoparticles suffer from the lack of a fully-established standard synthesis protocol. A common initial approach during the preparation of semi-conductors is the etching of crystalline Si wafers in a HF/ethanol/H₂O bath, which provides a uniformly-etched surface of nanopores amenable for further nano-sized modifications *via* tuning of various parameters. Subsequent sonication of the etched surface crumbles the pores on the wafer, resulting in the dispersion of particles into the solution. In this study, we use styrene to occupy these platforms to stabilize the surface. We determine that the liberated silicon particles in ethanol solution interact with styrene, resulting in the substitution of Si-H bonds with those of Si-C as determined *via* UV photo-catalysis. The synthesized styrene-coated Si nanoparticles exhibit a stable, bright, red fluorescence under excitation with a 365 nm UV light, and yield approximately 100 mg per wafer with a synthesis time of 2 h. We believe this protocol could be further expanded as a cost-effective and high-throughput standard method in the preparation of red fluorescent Si nanoparticles.

Key Words : Silicon, Nanoparticles, Styrene, Surface functionalization, Fluorescence

Introduction

Fluorescent silicon nanoparticles (Si NPs) have gained a tremendous amount of attention across diverse research fields such as biomedical engineering, photonics, and electronics due to their unique optical properties and small size.¹ With a narrow size range of 1-5 nm, the quantum confinement effect is readily observed since the diameter of the Si NPs is of equal magnitude compared to the wavelength of the electrons. In other words, the band gap of Si NPs becomes size-dependent, resulting in a blue shift in fluorescence as the particles become smaller.²

Silicon is an inexpensive biocompatible material with several promising applications in electronics such as semi-conductors, solar cells, and LEDs. Various methods of preparing Si NPs have been reported: laser pyrolysis,³ thermal decomposition,⁴ chemical synthesis,⁵ electrochemical reduction,⁶ Si wafer etching in hydrofluoric acid,⁷ *etc.* Each protocol has been thoroughly investigated since the 1980's, when L. Canham first reported on the optical properties of nanocrystalline Si particles.⁸ However, a standard protocol for the synthesis of stable and uniformly-sized bright fluorescent Si nanoparticles has not yet been fully established.

Electrochemical Si wafer etching is one of the most desirable and straightforward protocols that originated from an established preparation method for porous silicon.⁹ This method provides a uniformly etched surface of nanopores and upon sonication, results in their disintegration and

dispersion into solution as nanoparticles. The resulting hydrogen-terminated surface of etched Si nanoparticles provides a useful platform for further conjugation of additional chemicals or biomolecules. Furthermore, the narrow size distribution of nanoparticle is desirable in a variety of applications due to the size dependence of the nanoparticle electronic structure. Not surprisingly, various approaches to control the size distribution of Si nanoparticles, such as ultra-centrifugation, dialysis, and size-exclusion chromatography, have been investigated. Unfortunately, a high degree of heterogeneity in particle size and the instability of Si-H due to their constant oxidation has remained a challenge in obtaining stable red fluorescent Si nanoparticles.¹⁰

In this study, we report on a straightforward method in the preparation of large quantities of bright red-fluorescing styrene-stabilized Si nanoparticles by analyzing the transmission electron microscopy (TEM) images and photoluminescence data after passivation of Si NPs, we estimate the average size of nanoparticles directly related to a band gap growth. Importantly, styrene-coating preserves the red fluorescence of Si NPs while ensuring their stability. Specifically, the optical properties were preserved and did not deteriorate for at least 2 months. Furthermore, the resulting Si NPs capped with alkane groups maintain their hydrophobicity and resist continuous oxidation, a highly desirable trait for photovoltaic applications. A relatively homogeneous particle size distribution is obtained after capping with styrene and subsequent filtration through a membrane. The scalable proce-

cedure described herein yields approximately 100 mg per wafer with a synthesis time of 2 hours, and thus has the potential to become a cost-effective and high-throughput standard method in the preparation of red fluorescent Si nanoparticles.

Experimental

Electrochemical Etching of Si Wafer. Silicon wafers (n type, 4 inch, <100> oriented, 0.005 ohm-cm, Arsenic doped) were purchased from iNexus, Inc. (Seongnam, Korea) and all reagents were purchased from Sigma-Aldrich Korea. Si wafers were electrochemically etched in a solution of HF/ethanol/H₂O (3:1:1, volume ratio). Anodic etching of Si wafers was executed in a Teflon-based custom bath that houses a Si wafer in between two other wafers serving as cathodes. The etching solution was added to the bath slowly under a 100 mA constant current, and incubated for approximately 2 hours. The etched wafer was thoroughly washed with deionized water twice and then again with ethanol and dried. Upon UV excitation, etched Si wafers exhibited red fluorescence.

Ultrasonic Crumbling of Etched Pores and Passivation of the Surface. The etched Si wafers were sonicated in 100% ethanol for 30 minutes under nitrogen gas purging to remove dissolved oxygen in the solution. After sonication, particles dispersed into solution and exhibited a whitish fluorescence upon UV excitation.

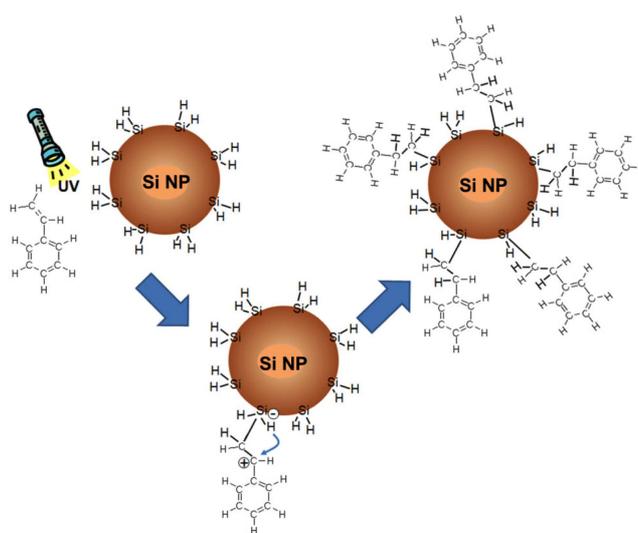
Passivation of the Particles with Styrene. The etched wafers were dispersed in 80 mL of styrene and processed *via* sonication. 20 mL of the resulting solution containing Si NPs was placed into a UV-permeable glass cuvette. The cuvette was then exposed to 365 nm UV for 30 minutes while purging with nitrogen. Due to UV-catalyzed hydrosilylation, the fluorescence of the solution switched to an intense red. Finally, dried particles in the cuvette were re-dispersed in an organic solvent and filtered through Teflon membrane filters to remove inhomogeneous aggregates.

Characterization of Styrene-coated Si NPs. TEM images were acquired using a Cryo Tecnai F20 TEM. A Malvern Zeta-sizer was used to obtain DLS measurements, which portrayed the size distribution profile. The photoluminescence spectra of Si NPs were recorded using a spectrofluorimeter. The absorbance spectra of styrene-coated Si NPs were recorded with an Ocean Optics Chem2000 fiber optic spectrophotometer. FT-IR spectra of Si NPs were recorded using particle samples deposited on Teflon IR cards on a Bruker IFS 66 spectrometer.

Results and Discussion

Scheme 1 depicts a UV-assisted photocatalysis procedure in the passivation of Si NPs with styrene.

Styrene-passivated Si NPs dispersed in toluene exhibit an intense red fluorescence under UV excitation (345 nm) and display maximum emission at 645 nm (Figure 1), representing a blue-shift from the original maximum emission peak at



Scheme 1. UV-assisted hydrosilylation of silicon nanoparticles: Styrene is passivated onto the surface of particles.

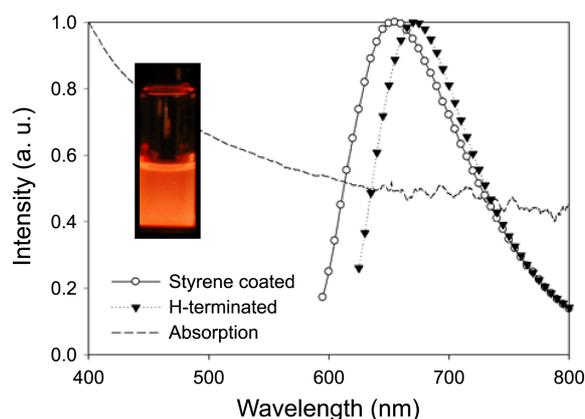


Figure 1. Photoluminescence and absorption spectra of styrene-terminated silicon nanoparticles. Insert represents the red-orange fluorescence of styrene-coated Si nanoparticles upon UV excitation.

approximately 700 nm. This blue shift may be due to partial oxidation of the surface during hydrosilylation, as noted by others.³

TEM images of the styrene-coated particles are acquired on a carbon grid by depositing and evaporating a drop of the particle suspension. We confirm the presence of nanometer-sized crystals (Figure 2, panel A). Furthermore, the particles have an average diameter of 5 ± 0.2 nm, as determined by analyzing 1,000 randomly chosen particles from the TEM images. The deviation (~ 0.2 nm) is similar to a lattice in the crystalline structure of silicon, suggestive of well-defined particles. Due to a lower electron density of carbon chains on the surface of particles, the size analyzed from TEM images corresponds only to the silicon nanoparticles. Finally, we also obtain the particle size distribution *via* dynamic light scattering measurements (Figure 2, panel B).

Figure 3 shows the FTIR spectra of Si NPs recorded after the styrene conjugation procedure. The spectrum recorded following the UV-assisted hydrosilylation contains features

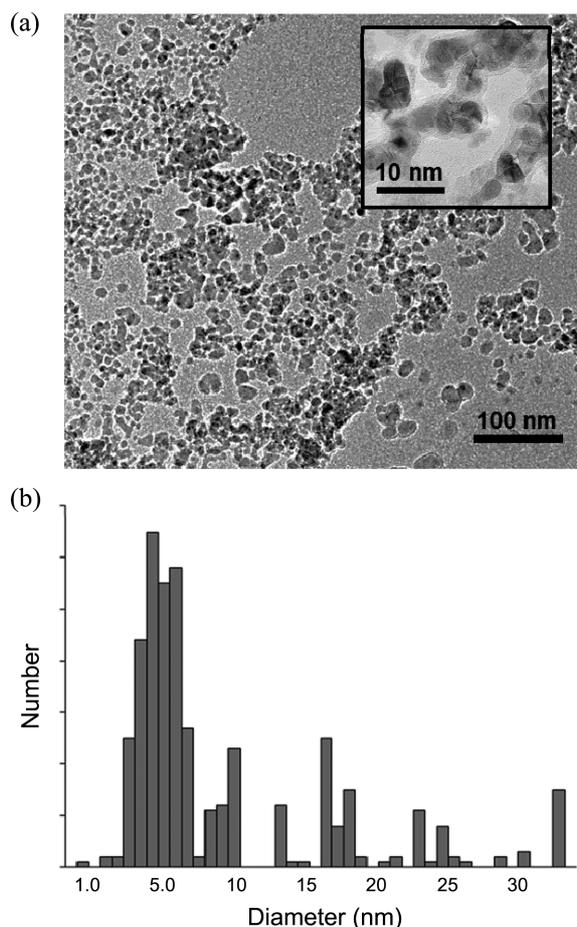


Figure 2. Transmission electron microscope image of styrene-coated silicon nanoparticles (a). Inset is a high resolution TEM image of the particles, describing lattice structures of the silicon nanocrystals. Nanoparticle size distribution as determined *via* dynamic light scattering (b).

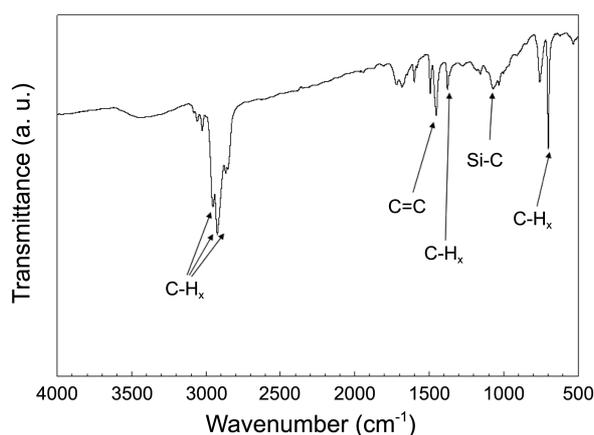


Figure 3. Fourier transform infra-red spectra of styrene-coated silicon nanoparticles. Characteristic IR peaks of Si-C surface bondings and C-H from styrene validate surface hydrosilylation.

assigned to Si-C stretch (1274 cm^{-1}), C-H stretch (2965 , 2928 , 2964 cm^{-1}), and methylene bending (1463 cm^{-1}) modes, and is consistent with the presence of alkane groups on the surface of silicon nanoparticles. C-H peaks correspond to

symmetric C-H₂, antisymmetric C-H₂, and asymmetric C-H₃ stretching vibrations. The observed vibrational bands of Si-C bonds display a covalent conjugation between Si-H and alkyl groups. The weak peaks of Si-O correspond to a small number of Si-O bonds present on the Si nanoparticle, indicating a relatively thorough substitution of Si-O with Si-C. Furthermore, there are no bands observed for Si-H at 2100 cm^{-1} . The small peaks observed at approximately 3000 cm^{-1} may be from unreacted CH-CH₂ bonds. Alkyl linkages to Si NPs provide improved stability and serve as potential intermediates for further nanoparticle conjugation. Finally, we envision that the total mass recovered (approximately 100 mg per Si wafer with a synthesis time of 1 h) is scalable for further application beyond the bench-top.

In view of a relatively straightforward reaction setup, etching with ultrasonic activation may open new avenues for large-scale production of alkyl-terminated silicon nanoparticles.

Conclusion

In summary, red fluorescent Si NPs are synthesized using a photocatalyzed hydrosilylation reaction of H-terminated Si nanoparticles, which are obtained *via* electrochemical etching of Si wafers. By measuring both the absorbance and the photoluminescence of styrene-coated Si NPs, we confirm that the particle band gap is related to its size. Particles with a considerably narrow particle size distribution and of excellent stability are observed. The absorbance, fluorescence, TEM, and DLS results suggest a median particle diameter of approximately 5-6 nm. Further studies would be focused on the precise tuning of the particle size and surface functionalization to optimize the production of monodisperse, stable, bright Si NPs. The simple and scalable synthesis method reported herein may become a standard protocol in the preparation of stable Si NPs for various applications.

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