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Femtosecond Ligand/Core Dynamics of Microwave Assisted Synthesized Silicon Quantum Dots in Aqueous Solution

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Abstract

A microwave-assisted reaction has been developed to produce hydrogen-terminated silicon (Si) quantum dots (QDs). The Si QDs were passivated for water solubility via two different methods: hydrosilylation produced 3-aminopropenyl-terminated and a modified Stöber process produced silica-encapsulated Si QDs. Each method produces water soluble QDs with maximum emission at 414 nm and after purification exhibit intrinsic fluorescence quantum yield efficiencies of 15 % and 23 %, respectively. Even though the QDs have different surfaces, they exhibit near identical absorption and fluorescent spectra. Femtosecond transient absorption spectroscopy was used to temporally resolve the photoexcited carrier dynamics between the QDs and ligand. The transient dynamics of the 3-aminopropenyl-terminated Si QDs is interpreted as a formation and decay of an excited-state charge transfer (CT) state between the delocalized π electrons of the carbon linker with the Si core excitons. This CT state is stable for ~4 ns before reverting back to a more stable long-living species. The silica-encapsulated Si QDs show a simpler spectrum without CT dynamics.

Keywords

Silicon nanoparticles; Si QDs; transient absorption spectroscopy; microwave synthesis

Silicon (Si) quantum dots (QDs) are of great interest for applications in biomedicine, electronics, optoelectronics, nonlinear optics, and solar energy.^{1,2} As seen from the variety of possible uses, silicon QDs have significant potential, but solution or colloidal synthetic methods remain underdeveloped. Although a variety of high temperature methods exist to prepare Si QDs, such as laser pyrolysis, plasma decomposition, and heat treatment under reducing atmospheres, colloidal chemistry approaches provide the unique opportunity to control the size and surface of the QDs simultaneously.^{1,3–7} While there has been promising progress on preparing Si QDs in solution, the application of microwave-assisted solution synthesis has not yet been demonstrated. The synthetic method presented herein provides an efficient synthesis of hydrogen-terminated Si QDs without the use of HF. Transient absorption spectroscopy provided insight to the nature of the photocarriers indicating that with appropriate ligand conjugation, complex photodynamics exist between the ligand environment and the Si QD core suggesting an energy or electron transfer process can be

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Supporting Information Available: Detailed synthesis protocols, experimental methods and additional transient data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

tuned to optimize the photophysical processes for a variety of applications (e.g., increased fluorescence quantum yield).

During the past two decades microwave chemistry has been growing as a successful means of controlled synthesis in organic chemistry. While there have been reports of successful microwave assisted synthesis of II-IV semiconductor QDs,^{8–10} microwave assisted synthesis has not been demonstrated for Si QDs. Microwave-assisted synthesis has advantages such as uniform heating of solvents and localized heating of reactants. Microwave dielectric heating can also accelerate reactions a thousand-fold depending on the solvent.¹¹ Moreover, doped Si has been shown to efficiently absorb microwaves and microwave irradiation has been demonstrated as an efficient method to passivate porous silicon surfaces with 1-alkenes.^{12,13} A simple, rapid, and efficient synthetic route to water soluble Si QDs would be advantageous to further develop their use in fields such as molecular biology and biomedical engineering where use of air-sensitive reactive precursors may be a significant barrier.

Solution phase chemistry, either of metal silicides with silicon halides and ammonium halides or via oxidation or reduction routes, has introduced many new pathways to generate organically capped and stable Si nanoparticles.^{14–19} One successful example is the reaction of sodium silicide, Na_4Si_4 , with ammonium bromide, NH_4Br , performed through standard Schlenk techniques to produce hydrogen terminated Si nanoparticles.²⁰ These Si QDs can be produced in a three day period by refluxing the starting reagents followed by isolation and purification. Alkylamine- and acid-terminated silicon nanoparticles have also been demonstrated and shown to be water stable for biological imaging applications.^{18,21} Use of metal silicides as reactive precursors exhibit additional versatility in generating water soluble magnetic resonance/optical multimodal probes.^{22,23}

A microwave-assisted reaction has been developed to produce hydrogen-terminated Si QDs that are further reacted via hydrosilylation²⁴ or via a modified Stöber process²⁵ to form photoluminescent QDs (Scheme 1). The 3-aminopropenyl-terminated Si QDs were produced by a simple microwave assisted reaction as a one pot, two step reaction as illustrated in Scheme 1A. Scheme 1B shows the reaction scheme used to produce the silica-encapsulated Si QDs. The optimal reaction parameters are indicated in Scheme 1. In a typical reaction Na_4Si_4 and NH_4Br were loaded into a microwave reaction vessel and dimethylformamide (DMF) was added under an inert atmosphere before the reaction vessel was sealed and placed into the microwave reactor. After heat treatment, the reaction vessel was allowed to cool and propargylamine was added under inert atmospheric conditions. The reaction vessel was sealed and placed into the microwave reactor for a second short heating step. The final product was purified via dialysis or chromatography. The silica-encapsulated Si QDs produced by Scheme 1B were separated from the salt by-product via dialysis and transferred to ethanol. The silica shell was formed by the base catalyzed reaction of tetraethoxysilane. The silica-encapsulated Si QDs consisted of both multiple Si QDs encased in silica and individual Si QDs with a silica coating as shown in Scheme 1B. A thermal reaction under similar conditions in a pressure vessel resulted in negligible yields suggesting that the microwave absorption of the rapidly formed Si QDs is important.

A typical Transmission Electron Microscopy (TEM) image of 3-aminopropenyl-terminated Si QDs produced in the microwave, along with a High Resolution Scanning Transmission Electron Microscopy (HRSTEM) image are shown in Figure 1. The average particle diameter of 3.4 ± 0.7 nm was obtained, as indicated in the inset histogram. The STEM Bright Field image of the 3-aminopropenyl-terminated Si QDs resolved the lattice fringes consistent with the (111), 0.313 nm, and (220) spacing, 0.192 nm, of diamond structured silicon, upper left and lower right circle, respectively. Silica encapsulated Si QDs were synthesized via Scheme 1B by a modified Stöber method. The TEM image indicates that Si

QDs are completely encapsulated in silica (Figure 2), which imparts water solubility without introducing additional organic moieties.

The absorption and photoluminescence emission spectra of the 3-aminopropenyl-terminated and the silica-encapsulated Si QDs, are strikingly similar and the strongest emission is in the blue (Figure 3). The excitation and emission spectra are similar to those alkyl- and alkylamine-terminated Si QDs reported in the literature which are all prepared by solution colloidal routes.^{7,17,18,20,23,26} Moreover, the maximum wavelengths for all samples produced under the reaction parameters investigated were nearly identical, suggesting that this method generates Si QDs with similar size populations. TEM characterization is consistent with this hypothesis. Longer reaction times at a given temperature did not drive Ostwald ripening to produce larger Si QDs emitting at longer wavelengths. However, it appears at least for the 20 min. reaction time that a slight increase in the number of smaller sized QDs is observed. The general lack of Si QD growth with increasing time was confirmed from the TEM characterization that consistently showed small diameter QDs (3–4 nm). This suggests that unlike reduction routes where size is correlated to the ratio of precursor to reducing agent, the particle size for this reaction may be limited by the solubility of Na_4Si_4 and/or the concentration of precursors in solution.¹⁴

The 3-aminopropenyl-terminated Si QDs exhibit an average fluorescence quantum yield (QY) of ~15% (average for 3 different samples) in water after purification, similar to that reported for 3-aminopropyl-terminated Si QDs obtained by thermal methods.^{7,27} Typical QYs for silicon QDs capped with alkylamine in water have been reported to be $13.2 \pm 0.6\%$.⁷ Nanocrystalline silicon light emission has been attributed to both quantum confinement effects and reduction in the rate of nonradiative combinations.^{28,29} Prior to purification, the particles' QY was significantly higher (~26%) in water. Evidence for the presence of polymer in the unpurified product and the removal of the polymer via dialysis was apparent from both the changes in QY as well as in TEM when the as-prepared product was compared to the purified product (Supporting Information).

In neutral pH water, the amine group on the 3-aminopropenyl-terminated Si QDs are protonated. The FTIR (Supporting Information) indicates that while the microwave assisted hydrosilylation on the Si QD is successful, the surface of the Si QD shows oxidation, similar to what is observed for porous Si.¹² The FTIR spectra (Fig. SI2) for the silica-encapsulated Si QDs exhibit both O-H and Si-O-Si stretches along with at least one resonance that might be attributed to the C=O stretch of DMF suggesting that the surface capping is more complex. The femtosecond transient absorption signals (vide infra) suggest a photoinduced distonic (charge transfer, CT) population exists to give rise to the enhanced QY (26%) of the polymer and Si QD mixture. The polymer is removed via dialysis or chromatography. This results in a QY of 12–15% for the purified 3-aminopropenyl-terminated Si QDs. In the case of a reaction without propargylamine, that is for the silica-encapsulated QDs, a QY of $23.3\% \pm 0.3$ was obtained (Scheme 1B). The higher QY in the silica encapsulated sample may result from temperature localized heating of the sample via microwave absorption along with more efficient passivation of the surface with an inorganic silica shell.

The near identical absorption and emission spectra of the 3-aminopropenyl-terminated Si QDs, and silica-encapsulated Si QDs (Figure 3) hinders characterization and differentiation of the influence of the surface passivating 3-aminopropenyl ligand and silica environments on the electronic structure and photo dynamics including the fluorescence QYs of the Si QD cores. To unravel this, 400-nm initiated dispersed ultrafast transient absorption signals were measured and compared. The silica-encapsulated Si QDs signals (Figure 4A) exhibit little resolvable spectral evolution of a broad positive induced absorption. Significantly richer dynamics is observed in the 3-aminopropenyl-terminated Si QDs sample (Figure 4B) with a

structure induced absorption that evolved into a negative signal from 500 to 600 ns within 100 ps. (this better seen in the kinetic traces in Figure SI6).

These data were modeled using global analysis to estimate Evolutionary Associated Difference Spectra (EADS) with associated concentration profiles of the underlying dynamic populations (Figure 5).³⁰

$$\frac{dn_i}{dt} = A_i I(t) + \sum_j K_{ij} n_j \quad (1)$$

where n_i represents the population of interest, $A_i I(t)$ is a correlation of the 125-fs pump pulse duration with the initial distribution of excitation used to describe the rise, and K_{ij} is the rate constant describing the flow of population from one compartment into another. Only three compartments were required to fully describe the silica-encapsulated Si QDs data (3.7 ps, 72 ps, and ~12 ns) (Figures 5A, B) with the induced absorption ascribed to trapped charges based on the observed relaxation time constants.^{31,32} Similar kinetics and spectra were observed in octyne-capped Si QD dynamics, demonstrating that the SiO₂ passivates surface traps of the Si QD equally well as long-chained alkanes.³¹ The faster decay kinetics (72 ps) observed on the blue edge vs. the red edge (12 ns) is a signature of excited-state inhomogeneity and is similar to the photoluminescence signals resolved in alkane-terminated Si QDs by Klimov et al. that were ascribed to core and surface trapped excitations, respectively.³³

Five characteristic populations (200 fs, 2.4 ps, 32 ps, 3.7 ns, and 3) were required to describe the 3-aminopropenyl-terminated Si QDs data with EADS that extend across the entire spectral and temporal windows. The initial spectrum is largely positive (red curves, Figure 5C, D) that decays on a 2.4 ps to 32 ps timescale into populations with a clear stimulated emission (SE) contribution peaking at 535 nm and overlapping a broad positive induced absorption signal. This population persists for ~4 ns before reverting to a stable long-living species (magenta curves, Figure 5C, D) that qualitatively resembles the final spectrum in the SiO₂ encapsulated Si QD signals (green curve, Figure 5A). The populations responsible for the SE closely resemble the spectra for transient emissive populations in organic molecules, suggesting that the 3-aminopropenyl ligand is excited in the sample.

However, since the energy of the HOMO-LUMO gap for isolated 3-aminopropenyl ligands is ~330 nm (based on the UV-vis spectrum; Fig. SI4), direct excitation of the ligand with the ultra-fast 400-nm pulses is negligible. Consequently, excitation of 3-aminopropenyl ligand (via the observed SE signals) primarily results from the interactions (e.g., charge or energy transport) with photoexcited Si excitons. We suggest a charge (electron or hole) transfer reaction possible involving the lone-pair on the amine N that is facilitated by conjugation from the Si QD through the C=C double bond (Scheme 1A). Vertical excitation of the Si QD core with 400-nm light induces a rapid charge transfer (likely between the lone pair electrons of the -NH₂ or -NH₃⁺ groups on the 3-aminopropenyl ligand and the Si core) to generate a metastable CT state. This state persists for 3.7 ns before a back transfer occurs to form a stabilized localized excited state (Fig. 5, magenta curves). It is unclear if the CT state is formed from electron transfer from the core to the ligand or from the ligand to the core, although the latter is more likely given the high reduction potential of NH₂.

This mechanism is different from that observed by Krysch et al., who recently proposed a photo-initiated charge- or electron-transfer mechanism from direct photoexcitation of the 3-vinylthiophene ligands that capped Si QD's via high energy two-photon excitation.³² The signals presented above are one-photon initiated with a linear dependence on excitation power.

The microwave-assisted synthesis of Si QDs has been demonstrated to be easily performed, efficient and reproducible. Highly photoluminescent Si QDs can be obtained as little as 12 minutes compared to several days in typical thermal reactions. In this study, hydrosilylation and a modified Stöber method have been investigated and this microwave-assisted synthesis can be further expanded to other ligands and capping agents. Microwave-assisted heating produced Si QDs with QYs as high as 23% in water. Femtosecond transient absorption spectroscopy could temporally resolve the photoexcited carrier dynamics between the QDs and ligand. The transient dynamics of the 3-aminopropenyl-terminated Si QDs is interpreted as an admixture of the silica-encapsulated Si QDs dynamics with an excited-state charge transfer (CT) process between the delocalized π electrons of the carbon linker with the Si core excitons. The silica-encapsulated Si QD show a simpler spectrum without charge-transfer dynamics. These results suggest that the charge transfer process may be tuned to optimize the photodynamic processes. The ability to electronically couple nanomaterials has potential applications for designing new multi-component systems with desired charge transfer properties and opens up new opportunities in opto-electronic applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. (A) TEM image and histogram (inset) of 3-aminopropenyl-terminated Si QDs, and (B) STEM Bright Field image of Si QDs showing lattice fringes consistent with the (111) and (220) spacing of diamond structured silicon.

Figure 2. (A) TEM image of silica-encapsulated Si QDs and (B) higher magnification image showing that the silica nanoparticles contain small silicon nanoparticles.

Figure 3. Normalized static emission (solid curves) and absorption spectra (dashed curves) of 3-aminopropenyl-terminated Si QDs (red curves) and silica-encapsulated Si QDs (blue curves) in water. The absorption spectra were normalized at 310 nm.

Figure 4. Transient absorption contour plots depicting the spectral evolution of (A) Si-SiO₂ and (B) Si-C₃H₄NH₂ suspended in H₂O. Data were collected at a flux of 26.5 $\mu\text{J}/\text{Pulse} \cdot \text{mm}^2$.

Figure 5.

Global Analysis (A – C) EADS extracted from a five compartment sequential Global Analysis fitting scheme associated with Si-C₃H₄NH₂ (A,B) and a three compartment scheme associated with Si-SiO₂ (C,D). Concentration profiles of each population. The fast 220-fs EADS in panels A and C are not shown to aid in interpretation, but displayed in Figure S14.

Scheme 1.

(A) Microwave-assisted synthesis of 3-aminopropenyl-terminated Si QDs. (B) Microwave-assisted synthesis of silica-encapsulated Si QDs.