Water-Soluble Silicon Quantum Dots with Wavelength-Tunable Photoluminescence

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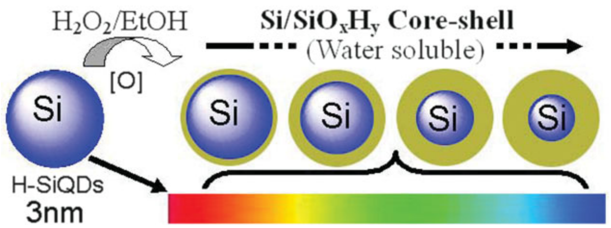
One of the most researched and fastest moving interfaces of nanotechnology is the application of quantum dots (QDs) in biology.[1] The unique advantages of size-tunable fluorescent wavelength by a single wavelength excitation render QDs great application potential in optical encoding detection.[1,2] To date, much emphasis has been placed on using highly fluorescent II-IV QDs (CdSe and CdS, etc) with wavelength-tunable emission as biological chromophores. However, these QDs are highly cytotoxic, and their biological applications are doubtful. Therefore, there the need for a less toxic or nontoxic QD system to replace the Cd-based QDs remains.[1,2]

Silicon is inert, nontoxic, abundant, low-cost, biocompatible, and widely used in microelectronics. Si nanostructures are arguably the most attractive and important material in nanoscience and nanotechnology.[3–6] Quantum-confinement effects can significantly enhance photoluminescence, by increasing radiative recombination via direct band-gap transitions and reducing phonon-assisted indirect band-gap transitions. Such effects become important in Si nanostructures with physical dimensions close to the bulk-Si exciton Bohr radius of about 4 nm.[5a],b Recently, we reported the synthesis of 1–4 nm H-Si QDs (hydrogen-terminated Si QDs) using the polyoxometalate (POM)-assisted electrochemical method.[5a] The wavelength-tunable emission of Si QDs in the visible range suggests that these materials are promising candidates for bioapplications. For such applications, production of Si QDs that can be dispersed in water is the foremost important step.[1,2,7] However, preparation of water-dispersible Si QDs with maintained size-dependent photoluminescence (PL) has been difficult. Recently, surface modification of Si nanocrystals with carboxylic acids or allylamine has yielded aqueous dispersions of these crystals. Nevertheless, the complex strategies, which rely on Si QDs of different diameters as the starting materials, yielded emissions of only single or 2–3 colors, and are thus unsuitable for multiplex imaging.[2,7]

Here, we demonstrate the synthesis of highly monodisperse, water-soluble Si QDs that allow for the fine tuning of emission wavelength. The synthesis was performed with the simple oxidization of ~3 nm H-Si QDs in an ethanol (EtOH)/H_2O_2 solution, in which H-Si QDs are converted to Si/SiO_xH_y core/shell nanostructures with a Si core of different controlled diameters. The resulting nanostructures are water soluble and can emit in seven different colors with fine wavelength increments (see Scheme 1). In addition, the Si QDs exhibit excellent photocatalytic activity, with the blue-emitting dots being the most active ones.

Figure 1a shows the transmission electron microscopy (TEM) image of H-Si QDs of ~3 nm. The fluorescence microscopy image (top inset) shows red color, which is larger in energy than indirect band gap of Si (1.1 eV) due to quantum-confinement effects in Si QDs with sizes smaller than 4 nm. The high-resolution TEM(HRTEM) image of H-Si QDs (bottom inset) reveals a lattice spacing of ~0.32 nm, in good agreement with the ⟨111⟩ spacing of Si crystal. It is well known that H-Si QDs are easily oxidized in water, or even in damp ambient. In the present experiment, H-Si QDs should be gradually oxidized by H_2O_2 and converted into a Si/silica (or Si/SiO_xH_y, in solution) core/shell structure. Since the starting H-Si QDs are only ~3 nm, there would be no significant variation in the size of the products (Si/



Scheme 1. After ~3 nm H-Si QDs are oxidized in EtOH/H_2O_2, and the emission color of the oxidized Si QDs ranges from salmon pink to blue.

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DOI: 10.1002/adma.200801642

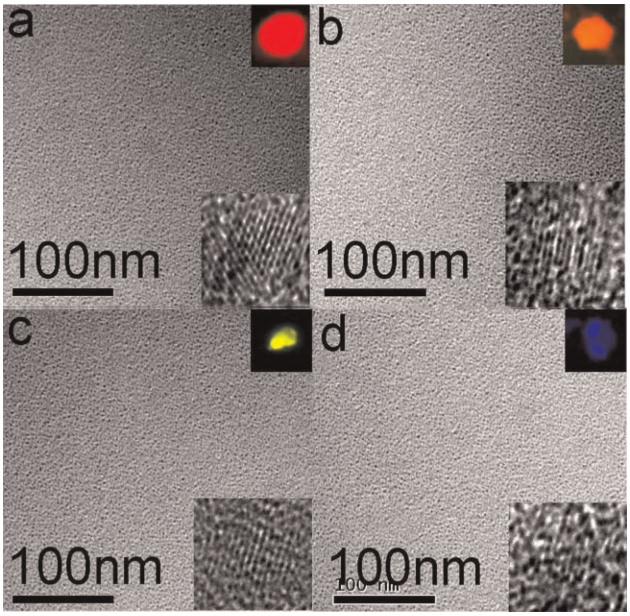

Figure 1. TEM images of a) ~3 nm H-Si QDs and b–d) Si QDs after 0.5, 3.5, and 24 h oxidation, respectively. Insets are the corresponding fluorescence microscopy (top) and HRTEM (bottom) images.

SiO_xH_y QDs) after oxidation. Figure 1b–d are TEM images of Si QDs after 0.5, 3.5, and 24 h oxidation, respectively, showing that Si QDs remain well dispersed and highly uniform in size after oxidation. The inset HRTEM images (Fig. 1b–d) reveal that the core size of the Si/SiO_xH_y QDs decreases with increasing oxidation time, with the Si core size reduced to 2.8, 2.1, and 1.2 nm after 0.5, 3.5, and 24 h oxidation, respectively. The lattice fringe spacing of 0.32 nm (in all insets) agrees well with the $\langle 111 \rangle$ spacing of Si crystal. The corresponding fluorescence microscopy images show that the water-soluble Si/SiO_xH_y QDs emit salmon pink, yellow, and blue light, for Si QDs of core sizes 2.8, 2.1, and 1.2 nm, respectively.

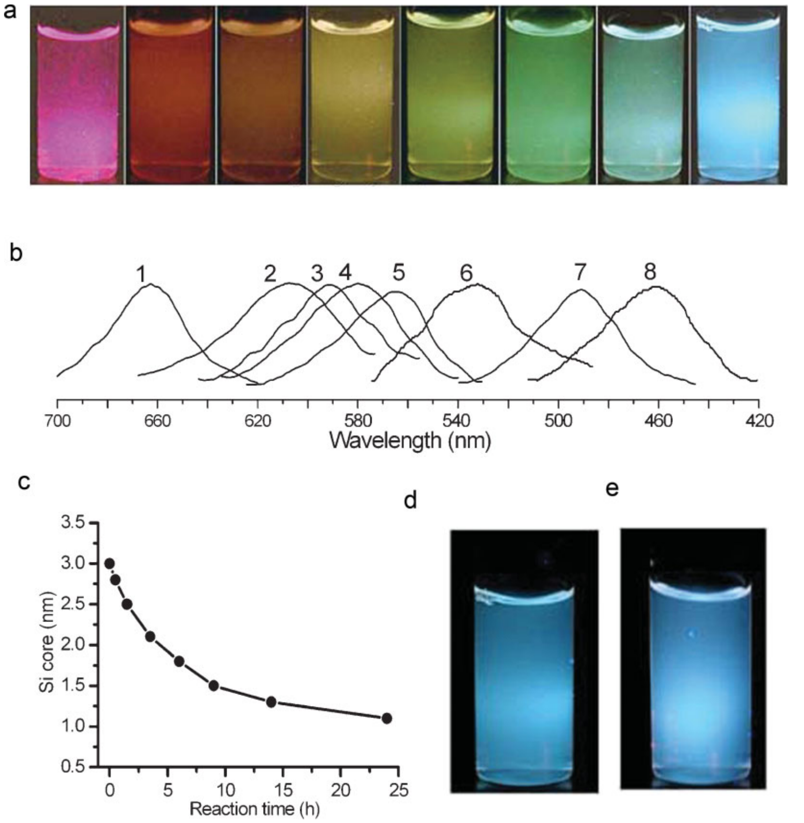

Figure 2. a) Photograph (under UV light) of H-Si QDs (left, red emission) and seven water-soluble Si QDs (yielding seven distinct emission colors). b) PL spectra of H-Si QDs (curve 1) and Si QDs after 0.5, 1.5, 3.5, 6, 9, 14, and 24 h oxidization (curves 2 to 8), respectively (excitation wavelength: 360 nm). c) Plot of the oxidation time versus Si core size. d,e) Photographs of the blue-emitting Si QDs (under UV light) before and after HF treatment, showing the same color.

Upon controlled oxidation, Si QDs can be tuned to emit light of seven different colors: salmon pink, orange, yellow, kelly green, green, cyan, and blue. Figure 2a shows a photograph (under UV light) of the red-emitting H-Si QDs (left) and the seven water-soluble oxidized Si QDs yielding seven distinct emission colors. Figure 2b shows the corresponding PL spectra (excitation light is 360 nm) of H-Si QDs (curve 1) and the seven Si QDs oxidized for different times: curves 2–8 correspond to 0.5, 1.5, 3.5, 6, 9, 14, and 24 h oxidization, respectively. Figure 2c shows the decrease in Si core size with increasing oxidation time. In the quantum-confinement region, for sizes smaller than 4 nm (for Si), the PL properties (e.g., wavelength) of H-Si QDs are very sensitively dependent on dot size, and the emission color changes substantially even with a 0.1 nm change in size. Unfortunately, fine size control in H-Si QDs is very difficult to obtain. The full-width at half-maximum (FWHM) of the luminescence peak of previously reported Si QDs was usually about 100 nm.[5a] In contrast, the FWHM of the luminescence peak of the present Si/SiO_xH_y core/shell QDs is only ~60 nm (Fig. 2b), which is significantly narrower. Notably, the present Si/SiO_xH_y core/shell QDs from controlled oxidation can be freely dispersed in water, with transparent appearance and without the need for further ultrasonic dispersion; so they are called "water-soluble Si QDs". From the above results, we conclude that the fine tuning in emission color can be attributed to the finely-tuned core size of Si QDs due to controlled oxidation in $EtOH/H_2O_2$ solution. To confirm that the emission of SiQDs comes from the Si core, we performed the following control experiment. After HF (5–10%) treatment was applied to remove the oxide shell, the blue-emitting Si QDs still showed bright blue-light emission with little change (PL spectra shown in Supporting Information Fig. S1 and S2), as evidenced by comparing the photographs (under UV light) shown in Figure 2d (before HF treatment) and 2e (after HF treatment). Thus, by controlling the oxidation time of ~3 nm H-Si QDs, we can tune the Si core size so that the resulting Si QDs can yield photoluminescence with finely tuned wavelengths.[4,5] The intense, wavelength-tunable visible emission of the water-soluble

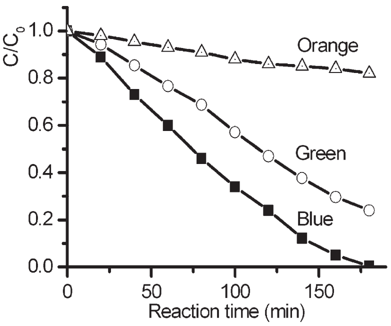

Figure 3. Photocatalytic activity of Si QDs with different emitting colors.

monodisperse Si QDs suggests these are promising candidates for biomarker applications. We point out that controlled oxidation of ~4 nm H-Si QDs can also produce similar Si/SiO_xH_y core/shell nanostructures; these, however, cannot produce blue emission, even after a long oxidation time of 48 h. On the other hand, the oxidation reaction of <3 nm H-Si QDs was too fast to control, and is impractical.

Porous Si and Si nanoparticles are known to be good photosensitizers and powerful singlet-oxygen generators in solution.[6] Similarly, the size-controlled Si QDs with tunable band-gap emissions from near-infrared to blue are promising candidates for applications in photoreduction, dye photodegradation, and photocatalyzed selective oxidation.[5b] Thus, we performed degradation of methyl red to evaluate the photocatalytic activity of the Si QDs. A mixture of 10 mL Si-QDs colloidal solution and 40 mL methyl red solution (methyl red/DI water, about 2.5×10^{-4} M) was illuminated by a 150 W halogen lamp (visible light, the spectrum is shown in Fig. S3 of the Supporting Information). Samples were collected every 20 minutes from the system. Methyl red was spectrophotometrically determined at $\lambda_{\max} = 490$ nm. The UV-vis absorption spectrum of the methyl red solution is shown in Figure S4 of the Supporting Information. After the solution containing the blue-emitting Si QDs and methyl red was irradiated by visible light for 3 h, reduction of methyl red was almost complete, or 100%. However, under the same conditions, reduction of methyl red was only 70%, 10%, and 0%, respectively, when green-emitting, orange-emitting, and salmon-pink-emitting Si QDs were used as catalysts (see Fig. 3). This distinctly different photocatalytic activity can be attributed to blue- and green-emitting Si QDs having a larger electron/hole pair energy than orange- and salmon-pink-emitting Si QDs; therefore, only the former two Si QDs have sufficient energy to induce photodegradation of methyl red.[4,5]

In summary, we have demonstrated the controlled conversion of ~3 nm H-Si QDs to water-soluble, uniform-sized Si QDs (or Si/SiO_xH_y core/shell nanostructures in solution) of different core sizes, via controlled oxidation in $EtOH/H_2O_2$ solution. The uniform-sized Si QDs of different sizes can be finely tuned to emit light of seven different colors, due to emission from the quantum-sized Si cores. The Si QDs, especially the blue-light-emitting ones, exhibit excellent photocatalytic activity in the visible range. The active surface of silica,[8] together with the proper surface functionality and tunable band gap, will enable SiQDs or Si/SiO_xH_y core/shell nanostructures in solution to have widespread applications in the biological field and in photocatalysis.

Experimental

All chemicals were purchased from Sigma–Aldrich. In a typical experiment, ~3 nm H-Si QDs were synthesized by the POM-assisted electrochemical method (current density: 4–10 mA cm^{-2}, about 75% of the as-produced dots have the size (3 ± 0.2) nm), and then dispersed in absolute ethanol. 3–8 mL 30% H_2O_2 and 100 mL colloidal solution of H-Si QDs in ethanol were mixed and then refluxed for 24 h. Samples were collected after 0.5, 1.5, 3.5, 6, 9, 14, and 24 h. After oxidation under reflux, the samples were passed through a 0.45 μm filter, and clear solutions were collected. The estimated yield of the blue-light-emitting product was ~75%, while that of other light-emitting products was ~85%. The products (Si/SiO_xH_y core/shell QDs) obtained by controlled oxidation can be freely dispersed in water, with transparent appearance (without further ultrasonic dispersion) and good photostability (luminescence properties and appearance remain unchanged after over 20 days in air at room temperature). The quantum yield of the yellow-emitting product was estimated to be 8–10% using Rhodamine B in ethanol as reference, whose quantum yield is regarded as 97%. TEM images of Si QDs were obtained using a FEI/Philips Techal 12 BioTWIN TEM, while high-resolution TEM (HRTEM) images were captured using a CM200 FEG TEM. PL studies were carried out using a PERKIN ELMER Luminescence Spectrometer LS50B (excitation light: 360 nm), while UV-vis spectra were obtained using an Aglient 8453 UV-Vis Diode Array Spectrophotometer.

Acknowledgements

This work is supported by the Research Grants Council of the Hong Kong (CityU 102206), the CityU Strategic Research Grants (7002275), a 973 Program (2006CB933000, 2007C B936000), National High-tech R&D Program of China (2006AA03Z302), and Natural Science Foundation of China (NSFC) (No. 20801010 and 20803008). Supporting Information is available online from Wiley InterScience or from the authors.

Received: June 17, 2008
Revised: August 25, 2008
Published online:

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