

# Surface passivation dependent photoluminescence from silicon quantum dot phosphors

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We demonstrate wavelength-tunable, air-stable and nontoxic phosphor materials based on silicon quantum dots (SiQDs). The phosphors, which are composed of micrometer-size silicon particles with attached SiQDs, are synthesized by an electrochemical etching method under ambient conditions. The photoluminescence (PL) peak wavelength can be controlled by the SiQD size due to quantum confinement effect, as well as the surface passivation chemistry of SiQDs. The red-emitting phosphors have PL quantum yield equal to 17%. The SiQD-phosphors can be embedded in polymers and efficiently excited by 405 nm light-emitting diodes for potential general lighting applications. © 2012 Optical Society of America

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Semiconductor quantum dots (QDs) with wide-range wavelength tunability, high photoluminescence (PL) quantum yield (PLQY), and narrow emission linewidth have been considered as a potential replacement for rare-earth-element (REE) phosphors used in white light-emitting diodes (LEDs) [1]. Using QDs as phosphors for lighting not only improves the color rendering performance [2,3] but also lessens the demand for REEs and hence the environmental degradation associated with their extraction and refining. However, previous QD-phosphor research was predominately based on II–VI compound semiconductor nanocrystals. Although their exquisite core/shell structures can lead to high PLQY, the heavy-metal toxicity from cadmium ions might limit their potential for wide-spread commercialization.

Previously, we demonstrated air-stable and nontoxic silicon quantum dot phosphors (SiQD-phosphors) with PL wavelengths tunable by a HNO<sub>3</sub>/HF isotropic etching process, which decreases the SiQD sizes. The longer etching time resulted in smaller dot sizes and thus the more PL blueshift due to quantum confinement effect [4]. Here, we demonstrated that in addition to the SiQD sizes, the PL properties (peak wavelength and intensity) are closely dependent on the surface passivation chemistries of SiQDs. Efficient PL with versatile colors can be achieved by effectively controlling these two factors. The red- and yellow-emitting SiQD-phosphors can be efficiently excited by 405 nm InGaN LEDs for potential general lighting applications. The whole synthesis process is performed under ambient conditions, using common chemicals. In contrast, other main strategies for SiQD synthesis, such as solution-based precursor reduction and aerosol decomposition of silane, inevitably require critical conditions, special equipment, or complex reactions [5].

We synthesized the SiQD-phosphors by starting with electrochemical etching on a p-type Si wafer in a mixture of HF and methanol [4,6]. A typical etching condition was at a constant current density of 3.5 mA/cm<sup>2</sup> for 60 min. After the electrochemical etching, we obtained free-standing Si powders, which exhibited weak red-emitting PL from the wafer substrate using a mechanical

pulverization process, and dispersed the Si powders in ethanol. The Si powder suspension was then added with an aqueous mixture of HNO<sub>3</sub> and HF for an isotropic etching reaction. The PL color slowly and continuously shifted from red to yellow as the etching process continued. After the isotropic etching, all the Si powder suspensions were treated with 20% HNO<sub>3</sub> to grow an oxide capping layer (hydroxyl-termination, Si-OH). The silicon oxide shell resulting from the etching process isolated the SiQDs from the PL quenching ethanol [7] and thus increased the PL intensity [4].

For functionalization with alkyl-alkoxysilanes, the luminescent Si powders with hydroxyl-termination were treated with 5 wt. % trimethoxypropylsilane (TMPS) and redispersed in chloroform. For functionalization with amino-alkoxysilanes, the Si powders were treated with 5 wt. % (3-aminopropyl)triethoxysilane (APTES) and redispersed in water. Each surface treatment step was effectively terminated by high-speed centrifugation, decantation of supernatant and redispersion in the desired solvents. A concentration of 1 mg of the SiQD-phosphors in 1 mL of solvent (chloroform or water) was used for all optical characterizations.

The PL and excitation spectra of the SiQD-phosphors with hydroxyl-termination, TMPS-passivation, and APTES-passivation were measured by using a fluorometer (Jobin Yvon Horiba Fluorolog FL-3). All the PL spectra were acquired by using 405 nm excitation. By HNO<sub>3</sub>/HF isotropic etching and subsequent HNO<sub>3</sub> treatment, we first obtained the hydroxyl-terminated SiQD-phosphor suspensions in ethanol with PL peak wavelengths at red (676 nm), orange (630 nm), and yellow (616 nm), as represented by gray dashed curves in Figs. 1(a), 1(c), and 1(d), respectively. Then, half of each hydroxyl-terminated sample was put through functionalization with TMPS, while the other half was treated with APTES. The TMPS-passivated SiQD-phosphor suspensions in chloroform, represented by red, orange, and yellow curves in Figs. 1(a), 1(c), and 1(d), kept almost the same PL peak wavelengths and intensities as the hydroxyl-terminated ones. In contrast, the APTES-passivated SiQD-phosphor suspensions in water, represented by green curves in Figs. 1(a), 1(c), and 1(d),

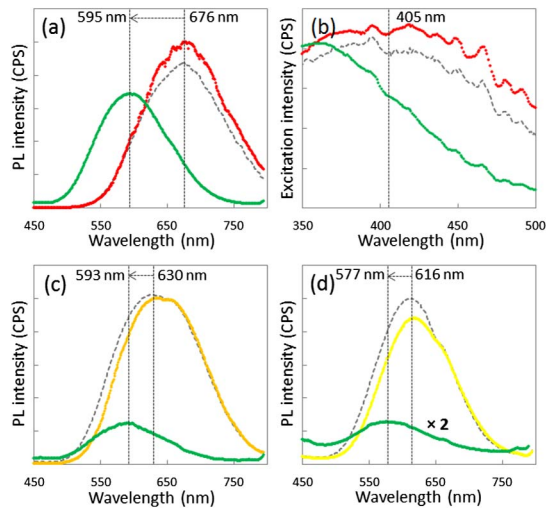


Fig. 1. (Color online) (a), (c), and (d) PL spectra of the SiQD-phosphors with hydroxyl-termination (grey dotted curves), TMPS-passivation (red, orange, and yellow curves), and APTES-passivation (green curves). (b) Excitation spectra of the SiQD-phosphors in (a). CPS, counts per second.

showed significant PL blueshift in different amounts: from 676 to 595 nm, 630 to 593 nm, and 616 to 577 nm for the red, orange, and yellow samples, respectively. At the same time, the PL intensity became lower than the hydroxyl-terminated ones, and more intensity decrease was observed for samples with shorter starting wavelengths. The decrease of PL intensity is likely due to the strong polarity nature of the passivating ligands (APTES) and the solvent environment (water). The dipoles attract either electrons or holes to surface trap states and therefore reduce the PL intensity [7].

As shown in Fig. 1(b), the TMPS-passivated (red curve) and the hydroxyl-terminated (grey dashed curve) SiQD-phosphors showed broadband excitation spectra, maintaining excitation efficiency of more than 70% from 350 to 473 nm. In comparison, the APTES-passivated SiQD-phosphors (green curve) showed a narrower excitation bandwidth, however still maintaining about 70% of excitation efficiency at 405 nm. This property ensures the red- (red curve) and the yellow-emitting (green curve) phosphors in Fig. 1(a) can be excited efficiently by conventional 405 nm InGaN LEDs.

From the scanning electron microscope images [4], the phosphors are composed of micrometer-size Si particles (diameters ranging from around 1 to 5  $\mu\text{m}$ ) with nanoporous surfaces. The visible photoluminescent SiQDs (diameter less than around 3.5 nm) are embedded in the porous Si layer as nanosize columnar structures [8]. The surface chemistries of TMPS- and APTES-passivated SiQD-phosphors are shown in Fig. 2(a). Both TMPS and APTES have three carbons in the hydrocarbon chains, while APTES is terminated with an additional amino group at the end, which gives APTES a much higher polarity than TMPS. We used Fourier transform infrared spectroscopy in attenuated total reflectance mode to determine the surface compositions of the SiQD-phosphors in dry powder forms. Both TMPS- and APTES-passivated samples showed similar spectra. The most prominent peak was at 1050 to 1100  $\text{cm}^{-1}$ , which can be a joint

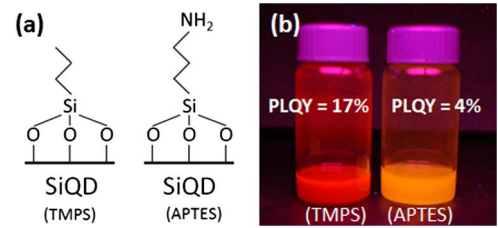


Fig. 2. (Color online) (a) Surface chemistries of TMPS- and APTES-passivation. (b) Photograph of the SiQD-phosphors with TMPS- and APTES-passivation, under 365 nm UV excitation.

contribution from Si-O-Si and Si-C bonds of the attached TMPS or APTES ligands [9]. A smaller peak was observed at 2350  $\text{cm}^{-1}$ , which is likely attributed to either O-Si-H or Si-H bonds [9]. Although the Si surface had been treated with 20%  $\text{HNO}_3$ , some hydride groups were still not oxidized to hydroxyl groups.

The red-emitting TMPS-passivated SiQD-phosphors in chloroform and the yellow-emitting APTES-passivated SiQD-phosphors in water are shown in Fig. 2(b), under 365 nm ultraviolet (UV) excitation. Their corresponding PL spectra can be found in Fig. 1(a). Note that the phosphors under 365 nm excitation exhibit almost the same PL spectra as under 405 nm excitation. The absolute PLQY of both liquid samples were measured by using an integrating sphere system (Hamamatsu Absolute PL Quantum Yield Measurement System). The PLQY = 17% and 4% for the TMPS- and APTES-passivated samples, respectively. The red-emitting phosphors have shown PLQY close to previously reported SiQDs with visible PLQY = 20% to 30% and synthesized by more complex methods [10,11]. It is worth noticing that during the PLQY measurements, a significant portion of the PL photons emitted by the SiQDs were reabsorbed by the micrometer-size Si particles in the integrating sphere and hence were not collected by the spectrometer, and cannot contribute to the PLQY tally. Therefore, to improve PLQY, we will need to increase the production yield of free-standing SiQDs and decrease the amount of micrometer structures in the phosphors.

After being embedded in a polymer matrix, such as polydimethylsiloxane (PDMS) used in this work, the SiQD-phosphors showed consistent PL colors as they have in solution or powder forms. The inset of Fig. 3 shows the PDMS thin films embedded with the red-emitting TMPS-passivated and the yellow-emitting APTES-passivated SiQD-phosphors, under 365 nm UV excitation. We placed the film in front of 405 nm InGaN LEDs and characterized the spectra of light passing through the film, as shown in Fig. 3. With only the red-emitting PDMS film (solid curve), the spectrum was composed of one blue (405 nm) and one red (674 nm) peak, resulting in a purple color. With the red-emitting PDMS film stacking on top of the yellow-emitting one (dotted curve), the peak was shifted to yellow (608 nm) and was broadened, i.e., FWHM increasing from 142 to 153 nm, and the integrated PL intensity became almost half. To cover the whole visible spectrum, we are currently developing green-emitting SiQD-phosphors with PL peak wavelengths at around 500 nm. However, blue- or green-emitting SiQDs with enlarged bandgap, due to quantum confinement effect, suffer from

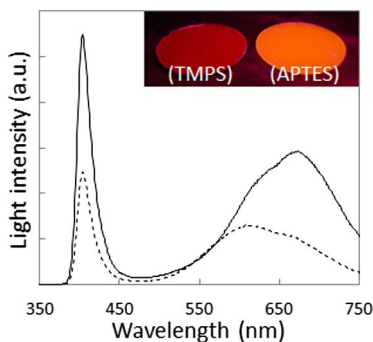


Fig. 3. (Color online) Lighting spectra of 405 nm InGaN LEDs covered with only the red-emitting PDMS film (solid curve), and with the red- and the yellow-emitting PDMS films (dotted curve). Inset: a photograph of the PDMS films, under 365 nm UV excitation.

surface trapping states associated with Si=O bonds, which limit the radiative recombination energy to around 590 nm [12]. Therefore, rather than oxide capping, an oxygen-free surface passivation method, such as hydrosilylation with alkenes or alkynes, will be preferred for blue- or green-emitting SiQDs.

APTES is only different from TMPS by having an additional  $\text{-NH}_2$  termination at one end, as shown in Fig. 2(a). However, while almost no change of PL peak wavelength with TMPS-passivation, the APTES-passivated SiQD-phosphors showed significant PL blueshift compared to the hydroxyl-terminated ones. It is likely that the much stronger polarity of APTES changes the charge distribution within the SiQDs and thus affects their PL spectra. Similarly, computational studies have shown that covering SiQDs with alkyl-groups (Si-C) resulted in minimal changes in PL spectra. In contrast, SiQDs with  $\text{-HN}_2$ ,  $\text{-SH}$ , and  $\text{-OH}$  terminations exhibited obvious PL changes compared to hydride-capped SiQDs [13]. Experimentally, 1 to 2 nm SiQDs capped with either allylamine ( $\text{CH}_2 = \text{CH-CH}_2\text{-HN}_2$ ) or 1-heptene ( $\text{CH}_2 = \text{CH-(CH}_2)_4\text{-CH}_3$ ) have also shown remarkably different PL properties. Similar to our case, both ligands have short alkyl-chains, but allylamine has an  $\text{-HN}_2$  termination at one end [14].

By using time-correlated single photon counting technique with 375 nm laser pulses repeated in more than 1  $\mu\text{s}$ , we found that both TMPS- and APTES-passivated SiQD-phosphors have PL decay in the microseconds range. Such slow PL, compared to fast PL in nanoseconds range of direct bandgap CdSe QDs, is likely due to ultra-fast trapping into, and then slow decay from, the oxide surface states that form within the bandgap during

oxidation [15]. In our SiQD-phosphors, the silicon oxide capping layer resulting from the  $\text{HNO}_3$  treatment should be responsible for the air-stable and long-lifetime PL.

In conclusion, the SiQD-phosphors with hydroxyl-termination were synthesized by electrochemical etching, followed by  $\text{HNO}_3/\text{HF}$  isotropic etching for controlling the PL peak wavelength and  $\text{HNO}_3$  treatment for capping with an oxide shell. Subsequent functionalization with APTES induced significant PL blueshift. In contrast, functionalization with TMPS resulted in almost no change of PL peak wavelength. All the SiQD-phosphors have shown air-stable and consistent PL in solution or powdered forms, or after being embedded in a polymer matrix. The red-emitting TMPS-passivated phosphors (PLQY = 17%) and the yellow-emitting APTES-passivated phosphors (PLQY = 4%) can be efficiently excited by 405 nm InGaN LEDs for potential applications in general lighting.

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