Brightly photoluminescent phosphor materials based on silicon quantum dots with oxide shell passivation

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Abstract: We demonstrate silicon-based phosphor materials which exhibit bright photoluminescence from near-infra-red to green. The colloidal composites which are composed of silicon quantum dots (SiQDs) attached on micro-size silicon particles are synthesized by electrochemical etching of silicon wafers and then dispersed in ethanol. Subsequently, isotropic etching by HF/HNO_3 mixture controls the size so as the emission wavelength of SiQDs, and forms an oxide passivating shell. The phosphors can further react with alkoxysilanes to form a stable suspension in non-polar solvents for solution-processing. The resulting red-light-emitting SiQD-based phosphors in chloroform exhibit photoluminescence external quantum efficiency of 15.9%. Their thin films can be efficiently excited by InGaN light-emitting diodes and are stable in room condition.

OCIS codes: (160.2540) Fluorescent and luminescent materials; (160.4236) Nanomaterials; (250.5230) Photoluminescence.

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#156055 - $15.00 USD Received 6 Oct 2011; revised 16 Nov 2011; accepted 18 Nov 2011; published 8 Dec 2011

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1. Introduction

Semiconductor quantum dots (QDs) with size-tunable band gaps, high photoluminescence (PL) quantum efficiency (QE), and high color purity have shown a great potential for next-generation lighting and displays [1]. Light-emitting devices embodied by QDs have two general forms: First, hybrid QD-organic light-emitting diodes (LEDs), which utilize QDs as the electroluminescent layer while the organic semiconductor layers are responsible for electron-hole injection [2–4]. Second, light-converting LEDs, in which QDs are excited by wide band gap LEDs and emit the desired PL in longer wavelengths [5–7]. Recently, using a state-of-the-art white QD-LED backlight system composed of InGaN blue LEDs and multiply passivated green- and red-light-emitting QDs as light converters, a high performance LCD panel was successfully demonstrated for the first time [8]. However, it is worthy of notice that previous QD-light-emitting research was predominantly based on group II-VI semiconductor QDs, such as CdSe, CdZnSe or CdZnS cores with single or multiple shells. Although such complex and exquisite hetero-structures often lead to outstanding specifications, for instance almost 100% PL QE [8], however, the high synthesis cost and the toxicity from their heavy-metal ingredients might shadow their potential for large-scale production and wide-spread commercialization.

Group IV silicon QDs (SiQDs), on the other hand, have gradually received more attention, owing to their heavy-metal-free composition, chemical stability [9] and abundant starting materials. Recently, hybrid SiQD-organic LEDs have demonstrated electroluminescence from infra-red (IR) to visible wavelengths [10–12]. Extensive works have been contributed to the synthesis of SiQDs. To date, main strategies include solution-based precursor reduction [13], heat-, laser- or plasma-induced aerosol decomposition of SiH_4 [14, 15], thermal processing of sol-gel polymers derived from $HSiCl_3$ [16] and harvesting from nano-porous silicon [17]. Except the last one, all the other methods inevitably require critical conditions, special equipment or complex chemical reactions, all of which make them hard to achieve cost-down and scale-up. In contrast, the porous silicon can be easily prepared by electrochemical etching in a mixture of common chemicals under ambient condition. The subsequent physical harvesting can effectively separate the SiQDs from the silicon substrate. Noticeably these highly luminescent powders mostly comprise micro-size silicon pieces with PL-emitting nanocrystal SiQDs trapped on their surfaces, rather than free-standing SiQDs.

Here we demonstrate low-cost, heavy-metal-free, air-stable and wavelength-tunable SiQD-based phosphor materials which are synthesized by the electrochemical etching method. Although containing micro-size particles, the colloidal red-light-emitting phosphors in chloroform exhibit PL external QE (EQE) of 15.9%. Furthermore, their thin films can be efficiently excited by InGaN LEDs and are stable in room condition owing to an oxide passivating shell. All these properties enable the SiQD-based phosphor materials a good candidate as light converters for lighting and displays applications.

2. Experiment

We electrochemically etched p-type boron-doped Si wafers with (100) orientation and 5 – 20 ohm-cm resistivity in a mixture of HF and methanol [17, 18]. A typical etching condition was at a constant current density of 3.5 mA/cm^2 for about an hour under stirring. After rinsing with isopropanol and drying in air, the wafer surface exhibited bright orangish/reddish PL and became highly hydrophobic as a result of complete hydride termination (Si-H). By simply adjusting the electrolyte ratios, etching current density and etching time, the PL peak wavelength can vary from 710 nm to 650 nm after the electrochemical etching. The luminescent powders harvested from the wafer surface were then dispersed in ethanol uniformly with the help from ultra-sonication. For the synthesis of near-IR- to red-light-emitting phosphors, HNO_3 was slowly added to the Si powder suspension under stirring, resulting in a final concentration of 20%. For the synthesis of orange-, yellow- and green-light-emitting phosphors, both HNO_3 and diluted HF were added to yield a final concentration of 20% for HNO_3 and 0.5-1% for HF. During the isotropic etching, the PL intensity gradually increased and the PL color continuously blue-shifted from red to orange, yellow and green in the case of HNO_3/HF etching. Once the desired PL wavelength was reached, the reaction was effectively stopped by taking the suspension to centrifugation (4000 rpm for 20 minutes), decanting the supernatant and re-dispersing the precipitate in ethanol. The process can be repeated several times to remove residual HNO_3 and HF.

For further functionalization with alkoxysilanes, the luminescent silicon powders, treated as described above to obtain hydroxyl termination (Si-OH), were dispersed in ~5 wt % trimethoxypropylsilane (TMPS) in ethanol, and then refluxed with stirring for about 12 hours. Subsequently, the suspension was taken to centrifugation (4000 rpm for 20 minutes) and the precipitate can form a stable suspension in non-polar solvents, such chloroform and hexanes. A typical concentration of 1 mg / ml was used for optical characterizations and 10 mg / ml for thin film fabrication. The PL and excitation spectra of all liquid samples were measured by using a fluorometer (Jobin Yvon Horiba Fluorolog FL-3) with xenon short arc lamp as light source. The PL EQE of all liquid and solid-state thin film samples were measured by using an integrating sphere system (Hamamatsu Absolute PL Quantum Yield Measurement System).

3. Results and discussion

The normalized PL and excitation spectra of colloidal SiQD-based phosphors in ethanol are shown in Fig. 1(a) and (b), respectively. The PL of near-IR- (708 nm), red- (674 nm), orange- (624 nm), yellow- (610 nm) light-emitting samples were measured with 405 nm excitation, while the PL of yellow-green- (585 nm) and green- (549 nm) light-emitting samples were measured with 365 nm excitation. Specifically, the red-light-emitting phosphors which were treated by HNO_3 have a broadband excitation spectrum, maintaining 70% of excitation efficiency from 345 nm to 475 nm (the red-line in Fig. 1(b)). Similar results were also observed for the near-IR-light-emitting phosphors. However, with HNO_3/HF etching, the orange-, yellow-, yellow-green-, and green-light-emitting phosphors can only be efficiently excited by a narrow band of ultra-violet (UV) light and the excitation spectra slightly blueshift for the longer HNO_3/HF etching time. Note that several energy lines around 475 nm in the excitation spectra likely originate from the xenon lamp.

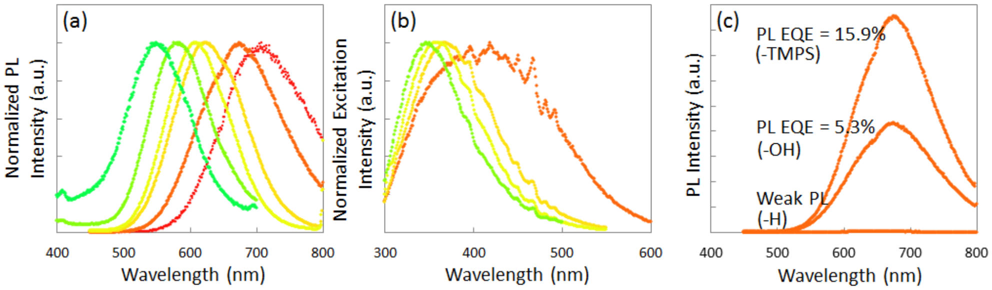

Fig. 1. (a) The normalized PL spectra of near-IR-, red-, orange-, yellow-, yellow-green- and green-light-emitting colloidal SiQD-based phosphor materials in ethanol. (b) The normalized excitation spectra of the red-, orange-, yellow- and yellow-green-light-emitting phosphors measured in (a). (c) The PL spectra and EQEs of the red-light-emitting phosphors passivated with hydrides, hydroxyl groups and TMPS.

The PL spectra and EQEs of the colloidal red-light-emitting phosphor suspension with different kinds of surface passivation are shown in Fig. 1(c). The electrochemical etching resulted in bright orangish/reddish PL on the wafer surface. However, after the fluorescent powders were suspended in ethanol, the PL intensity became significantly quenched. The PL quenching due to ethanol has also been observed in hydrogen-terminated porous silicon [19]. The following HNO_3 treatment essentially grew a high-quality oxide capping which isolates the PL-emitting SiQDs from the environment [20]. Experimentally, the enhancement of PL intensity in ethanol was clearly observed for samples treated by either HNO_3 only or HNO_3/HF mixture. The PL EQE of red-, orange-, yellow-, and yellow-green-light-emitting phosphors in ethanol were measured to be 5.3%, 6.3%, 3.6% and 1.4%, respectively. (All samples were excited by 405 nm, except the yellow-green sample which was excited by 365nm.) To improve solubility in non-polar solvents, the phosphor materials with hydroxyl termination reacted with alkoxysilanes (here we used TMPS) through the silanization reaction. In Fig. 1(c), the TMPS-treated red-light-emitting phosphors in chloroform showed a much improved PL EQE of 15.9% (with 405 nm excitation). The improvement possibly arises from the higher degree of oxide capping as a result of reflux and the solvent environment changed from polar to non-polar systems. The PL peak wavelength slightly red-shifted (from 656 nm to 674 nm) from hydride to hydroxyl termination both in ethanol, while there was almost no change of PL peak position from hydroxyl termination in ethanol to alkyl termination in chloroform, as shown in Fig. 1(c). Although containing a certain amount of micro-size silicon particles, the PL EQE (15.9%) achieved here is comparable to a recent result in literature (SiQD-ensemble PL QE of 20% [21],). However, their synthesis required multiple sedimentation processes and the capping structures involved complex organic residues. To further improve the PL EQE, an efficient separation technique to harvest SiQDs from the wafer with high production yield has been investigated. After extended ultra-sonication and centrifugation, we obtained a clear red-light-emitting suspension containing only nano-size particles in ethanol, and the PL EQE of that sample was measured to be 9.4%, compared to 5.3% with both nano- and micro-size particles in ethanol.

The red-light-emitting phosphors in non-polar solvents can be processed into thin films by drop-casting or spin-coating. Figure 2(a) and (b) show the scanning electron microscope (SEM) images of the thin film in low and high magnification, respectively. For the micro-size silicon particles, they are mostly of sizes ranging from 1 to 5 µm. Some submicron-size clusters can also be found among the gaps between particles. In high magnification, nano-porous surfaces which are mostly composed of PL-emitting SiQDs can be found on top of each micro-size silicon particle. Figure 2(c) shows “UW” painted a glass slide by using the red-light-emitting phosphors suspending in hexanes/octanes. The photograph was taken under illumination from a 365 nm UV lamp.

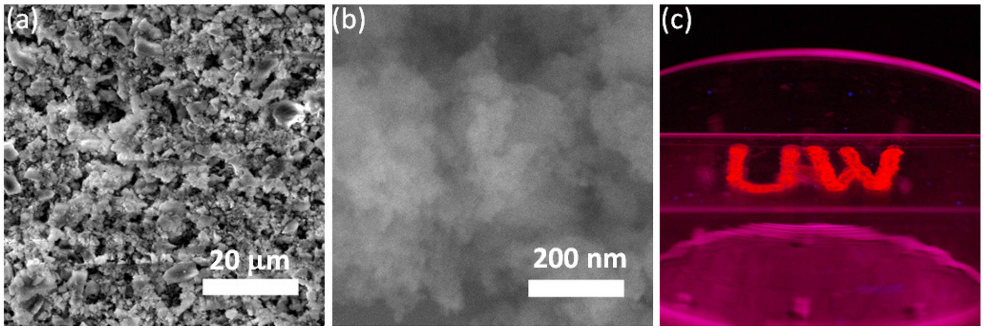

Fig. 2. (a) and (b) The SEM images of a drop-casted phosphor thin film by low (10^3 ×) and high (10^5 ×) magnification, respectively. (c) “UW” painted with the red-light-emitting phosphors on a glass slide.

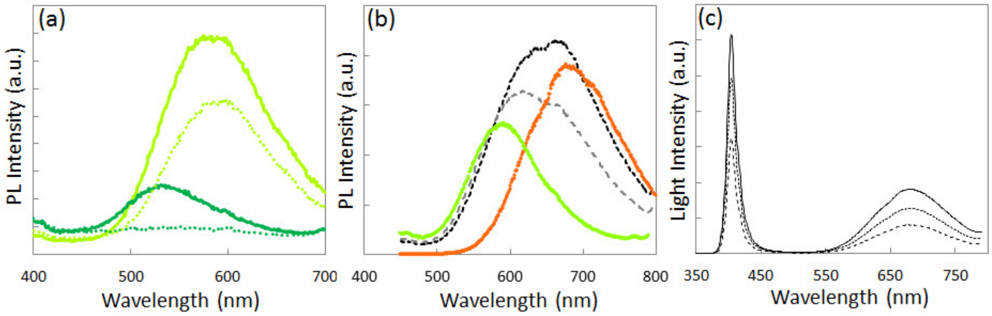

Fig. 3. (a) The PL spectra of colloidal green-light-emitting phosphors before (solid lines) and after oxidation (dot lines). (b) The PL spectra of a mixture of colloidal red- and yellow-green-light-emitting phosphors, where the black- and grey-dot lines represent different mixing ratios. (c) The light spectra from a 405 nm InGaN LED with the red-light-emitting phosphor thin film as light converters, as a function of increasing LED intensity (from the bottom-dash line to the top-solid line).

For applications in lighting and displays, the air-stability of all phosphor materials has been an important requirement. To verify such quality, the PL EQE of the red-light-emitting phosphor thin film, such as the one in Fig. 2(c), was initially measured to be 13.2% (with 405 nm excitation), and it maintained more than 10% for the following two weeks when the thin film was stored in room condition. Meanwhile, the PL peak position also remained unchanged. This high stability likely arising from the oxide passivation was also found in near-IR-, orange- and yellow-light-emitting samples. For yellow-green- and green-light-emitting phosphors whose PL peak at <590 nm, although capped with an oxide passivating shell, their PL peak wavelengths still slowly red-shifted toward yellow as exposed in air. This phenomenon is likely attributed to the electron- and hole-trap-states resulting from Si═O bonds which form localized energy levels in the bandgap of SiQDs and therefore red-shift the PL peak to around 590 nm [22]. For example, in Fig. 3(a), the PL peak of a colloidal phosphor suspension in ethanol (yellow-green-solid line) red-shifted from its original 583 nm to 590 nm upon oxidation by mixing with H_2O_2 (yellow-green-dot line). Noticeably, the PL peak intensity dropped about 30% at the same time. For comparison, the same colloidal phosphor suspension was first treated with diluted HF to remove the surface oxide passivation, then re-dispersed in ethanol (green-solid line), and mixed with H_2O_2 at the end (green-dot line). Upon HF treatment, the PL peak wavelength blue-shifted from its original

Received 6 Oct 2011; revised 16 Nov 2011; accepted 18 Nov 2011; published 8 Dec 2011

583 nm to 533 nm as a result of decreased QD size by HF etching, while the PL peak intensity also dropped about 70% likely due to ethanol quenching on the hydride-terminated surface [19]. After adding H_2O_2, the PL dramatically disappeared due to the formation of efficient non-radiative channels. Similar results have been found in the previous study of porous silicon that poorly oxidized surface leads to catastrophic loss of PL, while high-quality oxide passivation formed chemically or thermally can enhance PL efficiency [23].

White light generation has drawn much attention owing to the expanding market of general lighting and backlight for liquid-crystal displays (LCDs). Mixing the light from a blue InGaN LED and that of yellow phosphors (cerium-doped yttrium aluminum garnet (YAG)) has been the most efficient and cost-effective way for obtaining a white LED. However, the resulting pale white light cannot display color faithfully due to a relatively small color gamut. As shown in Fig. 3(b), here we demonstrate mixing colloidal yellow-green- (585 nm) and red- (677 nm) light-emitting SiQD-based phosphors to yield a yellow-to-orange broadband emission (full-width-at-half-maximum (FWHM) = 181 nm). By mixing with more colors especially in the blue to green wavelengths, the phosphor materials can potentially generate continuous emission covering the whole visible spectrum for the general lighting application [24]. Furthermore, to demonstrate the integration with conventional LEDs, Fig. 3(c) shows the light spectra from a 405 nm InGaN LED (purchased from Thorlabs, Inc.) with the red-light-emitting phosphor thin film as light converters, as a function of increasing LED intensity. Similar demonstration of using CdSe/ZnSe QDs as light converters in comparison with conventional YAG phosphors was found in literature [5]. To achieve a white LED consisting of a blue LED with red and green SiQD-based phosphors as three primary colors, the low excitation efficiency of green phosphors in blue wavelengths is now the main obstacle, as shown in Fig. 1(b). The studies of green phosphors of higher blue excitation efficiency and better passivation to prevent PL red-shifting due to Si═O trap-states [22] are currently in progress.

4. Conclusion

In summary, we have demonstrated colloidal SiQD-based phosphor materials which emitted bright PL from near-IR to green. The phosphors were first synthesized by the electrochemical etching method. The subsequent HNO_3 or HNO_3/HF isotropic etching not only controlled the QD size so as the PL emission due to quantum confinement effect, but also capped the material surface with a high-quality oxide passivating shell. The red-light-emitting phosphors with HNO_3 treatment can be efficiently excited by blue light, while the other phosphors with HNO_3/HF treatment can be excited by a relatively narrow band in UV. The phosphor materials with hydroxyl termination can further react with alkoxysilanes to become stable suspensions in non-polar solvents. The TMPS-modified red-light-emitting phosphors in chloroform showed PL EQE of 15.9%, and their thin films are stable in room condition (PL EQE equal to 13.2% initially and kept more than 10% for two weeks). The SiQD-based phosphor materials presented here have shown a great potential as low-cost, heave-metal-free, air-stable, and wavelength-tunable light-converters for applications in general lighting and display backlight systems.

Acknowledgments

This paper is based on work supported by the National Science Foundation (DMR 1035196) and the Royalty Research Fund of the University of Washington.