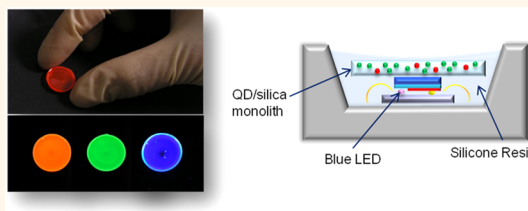


# Highly Luminescent and Photostable Quantum Dot–Silica Monolith and Its Application to Light-Emitting Diodes

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**ABSTRACT** A highly luminescent and photostable quantum dot–silica monolith (QD–SM) substance was prepared by preliminary surface exchange of the QDs and base-catalyzed sol–gel condensation of silica. The SM was heavily doped with 6-mercaptohexanol exchanged QDs up to 12 vol % (26 wt %) without particle aggregation. Propylamine catalyst was important in maintaining the original luminescence of the QDs in the SM during sol–gel condensation. The silica layer was a good barrier against oxygen and moisture, so that the QD–SM maintained its initial luminescence after high-power UV radiation ( $\sim 1$  W) for 200 h and through the 150 °C LED encapsulant curing process. Green and red light-emitting QD–SMs were applied as color-converting layers on blue LEDs, and the external quantum efficiency reached up to 89% for the green QD–SM and 63% for the red one. A white LED made with a mixture of green and red QDs in the SM, in which the color coordinate was adjusted at (0.23, 0.21) in CIE1931 color space for a backlight application, showed an efficacy of 47 lm/W, the highest value yet reported.



**KEYWORDS:** quantum dot · semiconductor nanocrystal · silica monolith · LED

Quantum dots (QDs) are promising light-emitting materials for the next generation of displays because of their high quantum efficiency (QE), good color purity, and tunable emission wavelengths throughout the visible range.<sup>1–9</sup> Various structural types of quantum dots have been produced—core/shell, alloy, gradient alloy—using different elemental compositions to control their optical properties.<sup>1–11</sup> We have previously reported a method for preparing core/multishell QDs having 100% QE and better photostability than simple core/shell structures.<sup>12,13</sup> The resulting color-converting QD–LEDs showed external quantum efficiency (EQE is the number of color-converted photons per the reduced number of photons compared to the originally emitted photons from LED source) of 72% for green QDs and 34% for red QDs; these values are competitive with conventional phosphors for LED applications. In fact, these EQEs can be improved, based on the original QEs of the solutions. It is likely that the luminescence of the original QDs was greatly reduced during the LED packaging process, in which the QDs were mixed with

silicone resin and experienced thermal curing. In general, the ligands on the QD surface can be easily detached, leading to surface defects and particle aggregation. Surface defects could become luminescence quenching traps or starting points for the oxidation of the entire QD structure. Also, the aggregated particles could increase reabsorption and light scattering, reducing the EQEs. To prevent this deterioration in optical properties, QDs can be preliminarily encapsulated in a barrier material.

Several encapsulating methods have been reported for nanoparticles.<sup>14–27</sup> QD–polymer composite with moderate emission efficiency ( $\sim 40\%$ ) was prepared by using poly(ethylmethacrylate) in the presence of trioctylphosphine (TOP).<sup>14</sup> Although TOP enabled retention of the luminescence and better dispersion of QDs, the extra ligands could disturb the polymerization of the acrylate to drop the long-term stability. Silica shell layer also can be grown on the surface of isolated QDs *via* a Stöber process<sup>15,16</sup> in which the silica thickness is finely controlled by the catalyzed hydrolysis and condensation of silane precursors. This method requires initial

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Received for review November 11, 2012 and accepted January 30, 2013.

Published online January 30, 2013  
10.1021/nn3052428

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surface exchange of QDs with a silane coupling agent, and the condensation reaction occurs right above the QD surface. The problem was that the QD/silica prepared *via* the Stöber process suffered from severely reduced photoluminescence (PL).

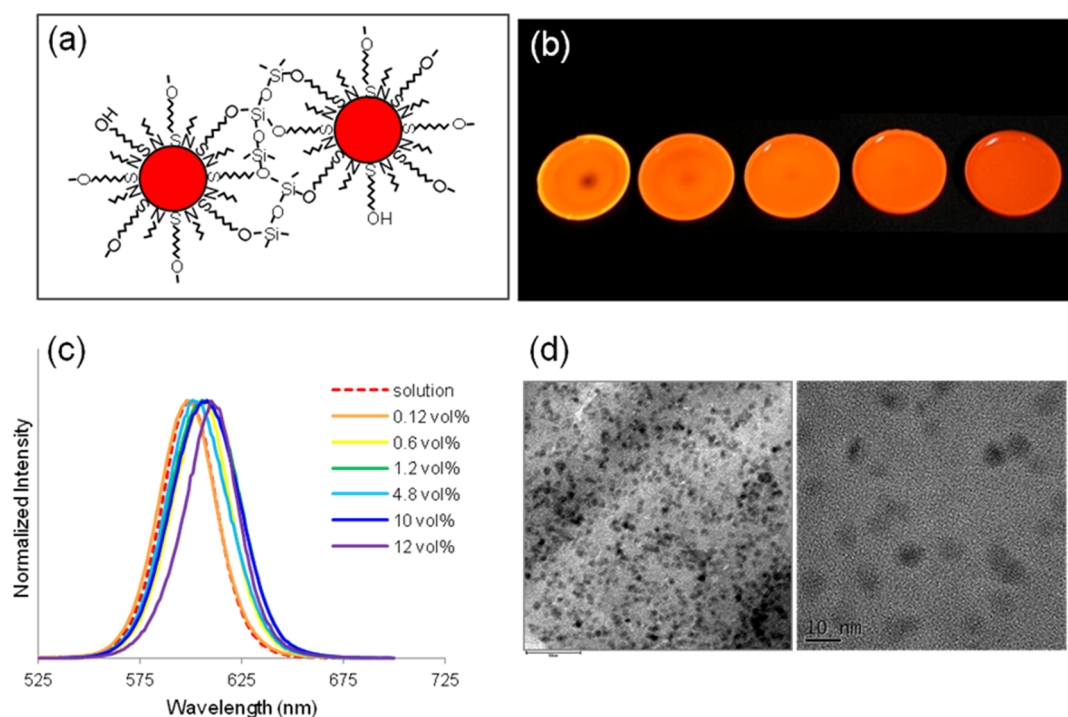
A reverse microemulsion method, taking place between water and oil phases, has been applied to prepare silica-coated QDs.<sup>17–19</sup> The QD/silica prepared by the microemulsion method showed relatively improved QE by 20–30% compared to the QD/silica prepared by Stöber process, but the thick silica layer (silica particle diameter >20 nm) had critical limitation of the QD concentration in the composite.<sup>19</sup> QDs have also been incorporated in the silica matrix as a film or a monolithic item.<sup>20,21,24–27</sup> The QD–silica composite was prepared by surface exchange with 3-mercaptopropyltrimethoxysilane followed by the silica sol–gel reaction, and it retained stable optical properties under ambient conditions for many months.<sup>19</sup> Various surface exchanging ligands, such as 11-mercatoundecanoic acid, 3-aminopropyltriethoxysilane (APS), and 5-aminopentanol, have been used.<sup>25–27</sup> QD–silica composites prepared with water-soluble QDs with APS precursor showed 20–40% PL efficiency that was maintained at the level of the original solution.<sup>20,21</sup> However, the QD–silica composites prepared with QDs, which were originally synthesized with hydrophobic ligands and solvent and experienced a surface exchange step, did not present quoted luminescence efficiency.<sup>25–27</sup> Below, we present detail methods for preparing homogeneously doped QD–silica monolith (SM) while retaining the original PL efficiency and set out their applications to LEDs. 6-Mercaptohexanol (6-MHOH) was used to exchange initial surfactants on the multishell passivated QDs, and propylamine was used as a catalyst for the silica sol–gel condensation. Both reagents proved important for the homogeneous dispersion and the PL efficiency, such that the resulting LED involving the QD–SM had high EQE of up to 89% on the LED.

## RESULTS AND DISCUSSION

QDs were synthesized according to the previous method by using CdO, Zn(OAc)<sub>2</sub>, oleic acid, Se/TOP, S/TOP, and tri-*n*-octylamine.<sup>7,12,13</sup> CdSe/CdS/ZnS QDs showed first absorption maximum peak at 580 nm and band edge emission peak at 597 nm with high quantum efficiency (QE) of 95%. The particle size of the QDs was  $7.5 \pm 0.44$  nm and showed fine crystalline structure (Figure S1, Supporting Information). The initial surfactants of the QDs after the synthesis were too oily to be compatible with reagents for the silica sol–gel reaction, so 6-MHOH was chosen as a ligand to alter the surface of the QDs to be more hydrophilic. To fully replace initial surfactants such as oleic acid and triocetylphosphine, the QDs were first dispersed in pyridine solvent. Pyridine was effective in removing excess

ligands and ripping the bound ligands off from the QD surface mildly. After the first pyridine solution containing initial ligands and solvent was removed after centrifuge, QDs were dispersed in pyridine solvent and 6-MHOH was added to the QD and pyridine solution. Then, hexane was added to separate hydrophilic, 6-MHOH coordinated QDs from the pyridine solution. 6-MHOH coordinated surface was confirmed with IR patterns showing characteristic vibration at  $1048\text{ cm}^{-1}$  (Figure S2, Supporting Information). The QDs with hydroxyl terminal functional groups became miscible with the silica precursor, tetraethylorthosilicate (TEOS), and the base catalyst, propylamine, when the mixture ratio was adjusted appropriately. Full details of the method for preparing the QD–SM are set out in the Experimental Section. A previous study found that octylamine performed the roles of both a ligand on the QD surface, so as to preserve the original optical properties, and a catalyst for the sol–gel condensation.<sup>28</sup> The absorption and PL emission spectra were measured at each step: initial preparation, 6-MHOH surface exchange, mixing with silica sol reagents, and after 24 h condensation (Figure S3, Supporting Information). The QE was slightly reduced after 6-MHOH surface exchange step and recovered during the silica sol mixing and initial condensation. Primary alkylamine also makes less hydrophilic QDs more compatible with TEOS, by controlling the solution polarity. Alkylamines with low boiling point, such as propylamine, are easy to remove and assist in forming more condensed silica framework. The elemental analysis for nitrogen in the QD–SM with 1.2 vol % QD showed that about 91% of the propylamine used was removed after drying for 3 days, and more than 94% was removed after the thermal treatment at 100 °C (Table S1, Supporting Information). About 5% of the propylamine remained after the thermal treatment to passivate the QD surface; the QD–SM did not exhibit browning or cracks even under the high UV radiation dose.

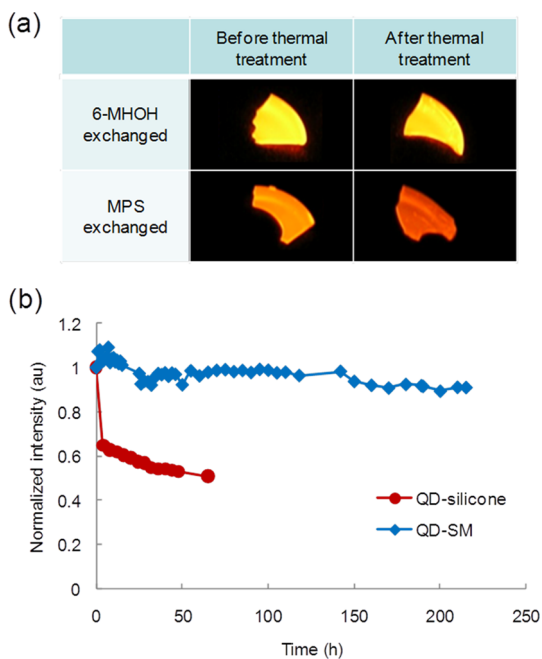
Figure 1a shows a schematic diagram of the QD–SM, in which the initial ligands were replaced by 6-MHOH and propylamine. The terminal OH functional group of 6-MHOH reacts with TEOS precursors and gives rise to a more condensed silica framework. The QD concentration increased from 0.12 to 12 vol % in the SM, maintaining a homogeneous dispersion by using more propylamine relative to the QD concentration. The 12 vol % of QD in the silica matrix is quite a high volume fraction compared to the former highest value of 12 vol % CdSe QD in silica film.<sup>26</sup> QD–SMs with 0.12, 0.2, 0.6, 1.2, 4.8, and 12 vol % QD concentration were prepared and viewed under 365 nm UV light (Figure 1b). Figure 1c shows PL spectra of the QD–SM with different QD concentrations after the thermal treatment. The PL peak wavelength of the QD–SM red-shifted as the QD concentration increased because of the reabsorption. Both PL peaks of the QD–SMs and



**Figure 1.** (a) Schematic diagram of the QD–SM. (b) Photographs of red light-emitting QD–SM with various concentrations of QDs in the silica matrix (from left: 0.12, 0.6, 1.2, 4.8, and 12 vol %) under UV light. (c) PL spectra of QD–SMs with different QD concentrations after 100 °C thermal treatment and the QD–toluene solution (0.12 vol %). (d) TEM images of sliced QD–SM with 12 vol % QD.

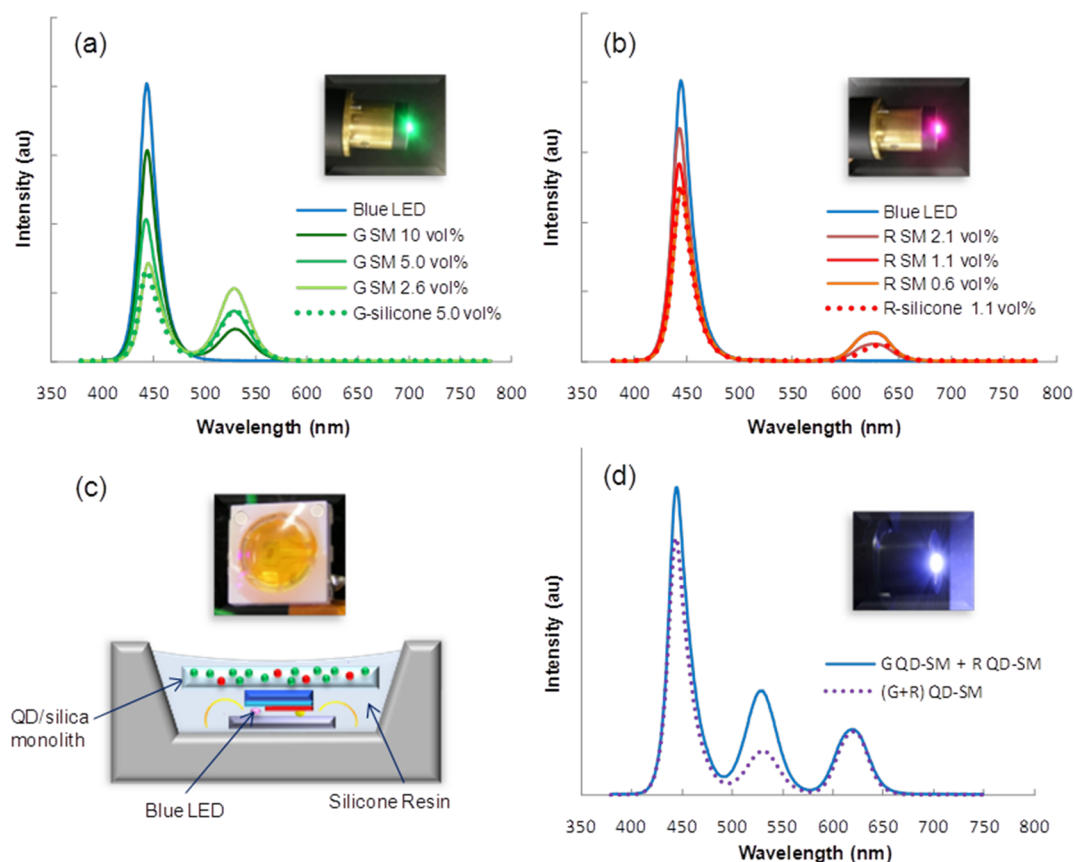
the QD–toluene solutions with same QD concentrations showed similar red-shift level. Therefore, it was expected that the dispersion of the QDs in SM was similar to the QDs in toluene solvent (Figure S4, Supporting Information). The 12 vol % QD–SM was cryogenically sliced and analyzed by TEM (Figure 1d), STEM, and SEM (Figure S5, Supporting Information). It was found that QDs exist as isolated nanoparticles in the silica matrix, indicating that the PL peak wavelength was not affected by the aggregation of QDs. The QD concentration in the SM is  $1.6 \times 10^{-3}$  mol/L for 12 vol % QD–SM. In this case, the mutual average distance should be about 10 nm, similar to the value shown in the Figure 1d. Since the 12 vol % QD–SM is estimated to have enough space between the surfaces of the QDs ( $\sim 7.5$  nm) for homogeneous dispersion of QD spheres, the shift in the PL peak could be caused by reabsorption rather than by the Förster resonant energy transfer (FRET) mechanism, which is known to occur from smaller to larger QDs in the ensemble for a densely packed QD monolayer.<sup>29</sup> The previous paper, in which the concentration of QDs were more than  $1 \times 10^{-5}$  mol/L in glass composite showed red shift due to the reabsorption.<sup>20</sup> Also, the QD–polymer composite with  $1 \times 10^{-3}$  mol/L also showed a red shift due to the reabsorption.<sup>14</sup>

The QD–SM prepared with 6-MHOH coordinated QDs showed higher luminescence efficiency and thermal stability than the QD–SM prepared with 3-mercaptopropyltrimethoxysilane (3-MPS) coordinated QDs. The QD–SMs were prepared with both ligands according to



**Figure 2.** (a) Photos taken under a 365 nm UV lamp of QD–SM prepared with 6-MHOH and 3-MPS before and after the thermal treatment. (b) Changes in the emission intensities of the QD–SM prepared with 6-MHOH and the bare QD–silicone composite during the operation with a high-power UV LED (peak at 400 nm,  $\sim 1$  W, driving current at 350 mA).

the same protocol, and the QD concentrations were controlled identically at 3.6 vol %. Each monolith was dried at room temperature for 3 days and was then divided into two pieces. One of the pieces was treated at



**Figure 3.** (a) Spectra of blue LED, green QD–SM LEDs containing various QD concentrations and bare QD–silicone LED. Inset shows a green QD–LED operating at 60 mA. (b) Same as (a) except for using red QDs. (c) Schematic diagram of the LED using QD–SM as a color-converting layer. Photo shows the real device with the mixed green and red QD–SM. (d) Spectra of white LEDs made with separately prepared green QD–SM and red QD–SM and mixed green and red QD–SM. Inset shows white LEDs with separately prepared green QD–SM and red QD–SM.

100 °C in air for 1 h, and the brightness of each QD–SM piece was compared before and after thermal treatment under a UV lamp of wavelength 365 nm (Figure 2a). The QD–SM prepared with 6-MHOH was much brighter than the QD–SM prepared with 3-MPS, even before the thermal treatment. After the 100 °C thermal treatment, the brightness of the QD–SMs prepared with 6-MHOH made almost no difference, but the brightness of the QD–SM prepared with 3-MPS was severely impaired. This can be explained by oxidative damage to the ZnS shell caused by hydroxide ions that formed during the base-catalyzed sol–gel reaction.<sup>25</sup> 6-MHOH, with a small OH headgroup and a long alkyl chain, has an advantage in the dense packing on the QD surface over 3-MPS, with its bulky Si(OMe)<sub>3</sub> headgroup and short alkyl chain. As a result, densely coordinated 6-MHOH protects the QD surface more effectively against hydroxide ion attack during the sol–gel reaction, preventing generation of surface defects and maintaining the original PL. For the QD–SM prepared with 3-MPS, the hydroxide ions ravaged the QD surfaces during the sol–gel reaction and further heat treatment, even in the presence of propylamine, which could also bind to the surface dangling bonds, resulting in severe PL quenching. To apply QDs in practical devices, such as LEDs, it is

necessary to have high photostability for the high-energy excitation source. The stability of the QD–SM was tested in a UV LED (peak at 400 nm) with 155W/cm<sup>2</sup> light intensity operating at 350 mA and 3.2 V and was compared with the bare QD–silicone composite. Emission from the QD–SM was maintained about 90% of the initial intensity without any change of the PL wavelength for more than 200 h of operation, whereas the emission from the bare QD–silicone composite fell to about 65% of the initial intensity after 4 h of operation because of the heat and photon energy produced by the high-power LED (Figure 2b). The improved stability of the QD–SM compared to the bare QD–silicone composite was due to a more condensed silica framework that worked as a barrier preventing oxygen and moisture from reaching the QDs. It was confirmed that QD–SM displayed no porosity in the N<sub>2</sub> adsorption/desorption isotherm (Figure S6, Supporting Information). Drying the sol–gel mixture of QD–SM at room temperature for 72 h by controlling vapor pressure would be important to prepare a highly cross-linked QD–SM showing no porosity and a crack-free, smooth surface without particulates, as shown in SEM images (Figure S5, Supporting Information), while the porosity was generated by fast sol–gel condensation at higher



temperature to activate the catalytic reaction. Also, the condensed QD–SM was protected from the acidic platinum catalyst or hydrosilane, which chemically damaged the QD surface and caused PL quenching during silicone curing for LED encapsulation. It is therefore expected that the QD–SM would have higher EQE and photostability as color-converting structures for LEDs than bare QD–silicone composites.

Green and red light-emitting QD–SMs containing differing QD concentrations were prepared and applied to blue LEDs.<sup>12,13</sup> The QD–SM was molded as a disk with a diameter of 3 mm and placed on the LED chip, followed by silicone encapsulation, as shown in Figure 3c. The EQEs of the green QD–SM in LEDs were 68, 71, and 89% for QD concentrations of 10, 5, and 2.6 vol %, respectively. The EQEs of red ones were 48, 62, and 60% for QD concentrations of 2.1, 1.1, and 0.6 vol %, respectively (Figure S7, Supporting Information). These EQE values are much higher than the previous highest EQEs of color-converting QD–LEDs;<sup>12</sup> for red QDs, with thinner passivating shell than green QDs, the EQEs of the QD–SM were improved by 3-fold over bare QD–silicone composite. However, the EQE of the QD–SM still showed slightly reduced efficiency compared to the photoluminescence efficiency after the sol–gel condensation. It was expected that this was due to the thermal quenching and back scattering in the LED packages. The heavily doped green QD–SM with 10 vol % QD had peak emission at 530 nm (fwhm = 37 nm), a value which is red-shifted from the original solution peak emission at 523 nm (fwhm = 39 nm), as in the heavily doped red QD–SM. We also prepared two different types of white LEDs. One is made with separately prepared green and red QD–SMs on a blue LED; the other is made with a mixture QD–SM containing

green and red QDs together in the same silica matrix. The concentrations of the green QD–SM and red QD–SM were, respectively, 2.6 and 1.1 vol % QD; the same concentrations of green and red QDs were used for the QD–SM mixture. The white LED with separately prepared green and red QD–SMs gave 47 lm/W, a figure which is 10% higher than the previous best efficacy of 41 lm/W (Figure 3d).<sup>12</sup> The white LED with the green and red mixture QD–SM gave only 33 lm/W due to reabsorption between the densely located green and red QDs in the limited silica network. To obtain efficient QD–LEDs, it is therefore important to prepare high-quality QDs with high QE, to protect the QD surfaces from chemical damage caused by the fabrication process and to control the QD concentration in limited spaces so as to prevent reabsorption.

## CONCLUSION

In summary, we prepared a highly luminescent and photostable QD–SM that was homogeneously doped with up to 12 vol % QD, using 6-MHOH for the QD surface exchange and propylamine as a catalyst for the silica sol–gel condensation. The QD–SM maintained the initial PL after thermal curing at 100 °C and exhibited strong photostability against high-power UV radiation for at least 200 h. For the green and red QD–SM embedded in the blue LED, the EQE was 89 and 63%, respectively; the EQE values decreased as the QD concentration increased because of reabsorption between the QDs. The white LED suitable for display backlight, made with separately prepared green QD–SM and red QD–SM, had the highest efficacy yet reported (47 lm/W). The QD–SM structure has great potential in color-converting materials in the next generation of LEDs.

## EXPERIMENTAL SECTION

**Synthesis of QDs.** CdSe core QDs were synthesized by injecting 0.2 mL of 2 M Se (Alfa, 200 mesh, 99.99%)/trioctylphosphine (TOP, Aldrich, 90%) into the hot solution mixture of 2.4 mmol of cadmium oxide (Aldrich, 99.99+%), 9.6 mmol of oleic acid (Aldrich, 90%), and 60 mL of trioctylamine (Aldrich, 95%) at 300 °C and reacting for 2 min. The CdSe QDs were separated by centrifugal step, and the precipitates were dispersed in toluene. The optical density of the 100 times diluted CdSe core solution was adjusted as 0.1 at first absorption maximum (560 nm), and 0.05 mmol of cadmium acetate (Sigma-Aldrich, 97%), 0.4 mmol of zinc acetate (Aldrich, 99.99%), and 1.5 mmol of oleic acid were mixed in 20 mL of trioctylamine. The mixture was degassed and heated to 120 °C, and then the temperature was further increased to 320 °C under N<sub>2</sub> flow. Then, 0.6 mL of the CdSe solution was injected into the Cd and Zn containing solution. Right after the core injection, 2 mL of 0.4 M S (Sigma-Aldrich, 99.98%)/TOP was added to the reaction mixture at the rate of 1 mL/min, and the mixture was rapidly stirred for 30 min at the reaction temperature. After synthesis, the CdSe/CdS/ZnS QDs were separated by the addition of ethanol and centrifuge. The UV, PL spectra, and TEM images of the QDs are shown in Figure S1. For the green light-emitting QDs, CdSe/ZnS core QDs (first absorption maximum at 463 nm) were used instead of the

CdSe core. The detailed preparation method was introduced in ref 13.

**Preparation of QD–SMs.** The QDs were precipitated and dissolved in pyridine solution to remove initial surfactant on the QD surface. After the QD and pyridine solution was stirred for 2 h, the QDs were precipitated by adding hexane and then dissolved in pyridine solution with 6-MHOH. For the comparison, we prepared QDs coordinated with 3-MPS through the same surface exchange procedure except using 3-MPS instead of 6-MHOH. The QDs coordinated with 6-MHOH were precipitated again by adding hexane and then dissolved in a mixture of 200  $\mu$ L of TEOS, 50  $\mu$ L of 3-MPS, 100  $\mu$ L of ethanol, propylamine, and 50  $\mu$ L of water. The amount of propylamine was controlled from 50  $\mu$ L (<2 vol %) to 200  $\mu$ L (>10 vol %) according to the QD concentration to increase the compatibility. The resulting solution was transferred to a mold, and gelation took place within a few minutes. The gel was dried in a solvent-saturated environment at room temperature for 72 h and was further cured at 100 °C for 1 h for complete hydrolysis and drying. The volume concentration of the QDs in the silica monolith was obtained based on the ICP-AES analysis. For example, ICP-AES analysis showed that the 10 vol % QD–SM contained 0.105 mmol of Cd, 0.0028 mmol of Se, and 0.031 mmol of Zn per 100 g of QD–SM, and the volume of each CdSe, CdS, and ZnS could be obtained

as 0.092, 3.07, and 0.75 mL, respectively (CdSe 0.0028 mol from Se, CdS 0.102 mol from remained Cd, ZnS 0.031 mol from Zn) based on each molar mass and bulk density. Silica volume (35.7 mL) could be obtained by subtracting total weight of QD (16.8 g/100 g QD–SM) from the QD–SM and dividing by silica density (2.33 g/mL for amorphous silica).

**Preparation of LEDs with QD–SMs.** Blue InGaN LEDs with peak emission at 445 nm (Seoul Semiconductor Inc.) were used. The LED package consisted of a 300  $\mu\text{m}$   $\times$  300  $\mu\text{m}$  chip, and the average efficacy of the blue LED was 8 lm/W when it was operated with 60 mA at 3.3 V. The QD–SM piece, which was molded as a disk with 3 mm diameter, was placed on the top of the LED chip, and the empty space in the package was encapsulated with silicone (Dow Corning, EG6301) at 150 °C for 2 h under air. A calibrated spectrophotometer with an integrating sphere (CAS 140CT compact array spectrometer, Instrument Systems) was used to measure the spectrum. The EQEs of the QD–SM were calculated as the ratio of the emission of the QDs to the blue light reduction.

**Conflict of Interest:** The authors declare no competing financial interest.

**Supporting Information Available:** Absorption, PL emission spectra, and TEM image of CdSe/CdS/ZnS QDs, IR spectra of QDs after surface exchange, absorption and PL emission spectra after surface treatment and sol–gel condensation, absorption and PL emission of QD solution with different concentration, STEM and SEM images of QD–SM,  $\text{N}_2$  isotherm of QD–SM, and EQEs of green QD–SM and red QD–SM on blue LEDs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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