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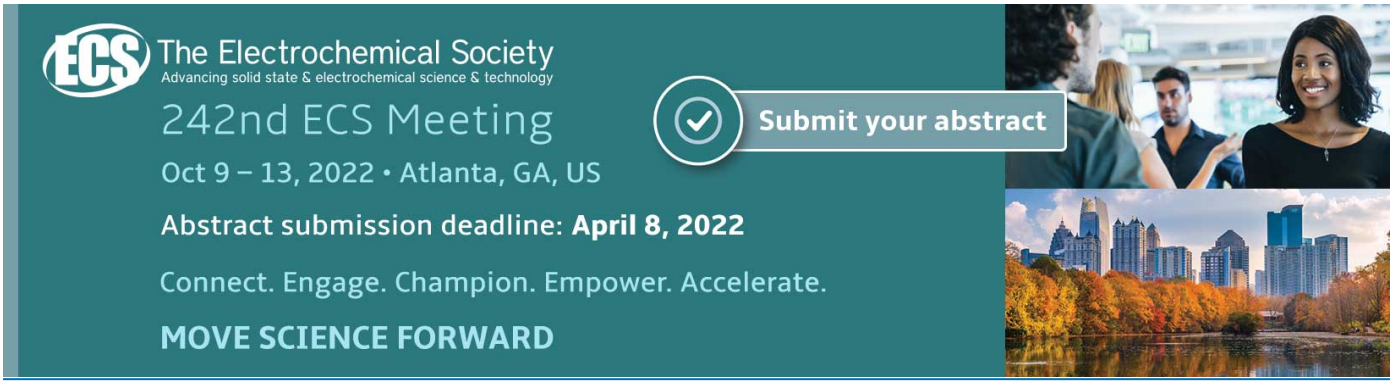

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Superior hydrophobic silica-coated quantum dot for stable optical performance in humid environments

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Abstract

Quantum dot (QD) features many exceptional optical performances but is also vulnerable to moisture which results in structural damage and luminescent decrease. This work provided and fabricated a novel superior hydrophobic methylated core/shell silica-coated QD (MSQ) for high water stability. QD was coated with a silica shell and then surface-methylated by trimethyl silane. Mercaptopropyl trimethoxy silane, tetraethyl orthosilicate, and ethoxy trimethyl silane were utilized as the ligand exchanger, the raw material of silica, and the surface modification, respectively. Characterization results illustrated the core/shell structure of MSQ. In addition, its water contact angle was up to 159.6°. QD-, silica-coated QD(SQ)-, and MSQ-silicone were made and displayed similar absorption, emission, and excitation spectra but different water stabilities. The photoluminescence intensity and photoluminescence quantum yield of MSQ-silicone hardly changed during 15 d of water immersion, in contrast to the dramatical decrease of other two kinds of composite silicone. Specifically, the photoluminescence quantum yield decreases of MSQ-, SQ-, and QD-silicone were 1%, 40%, and 43%, respectively. Therefore, MSQ had a much better water stability. The superior hydrophobic methylated silica-coated QD has a great potential to realize the long-term working stability in a humid environment and the wider application in diverse fields.

Keywords: quantum dots, silicon dioxide, hydrophobicity, stability

(Some figures may appear in colour only in the online journal)

1. Introduction

Colloidal quantum dot (QD), as a class of nanometer-sized semiconductor particles, has gained considerable attention from academia and industry in last decades. The excellent properties of QD, such as size-dependent emission, narrow emission band, high quantum yield, and low production cost, have made it the most promising luminescent material in lighting and display [1–3]. The high quantum yield of QD is guaranteed by the sufficient binding between the organic molecule ligands and the surface atoms of QD. However, the binding between QD and ligands are very vulnerable to moisture, oxygen, chemical, and heat, which lead to the expulsion of ligands and damages of QD [4–6]. Therefore, strategies are badly needed to boost the working stability of QD in harsh conditions.

To date, different methods have been reported to alleviate the vulnerability of QD, such as surface ligand modification, encapsulating in particle, coating of shell, binding with matrix, and packaging engineering. Some researchers found more stable and proper ligands for QD [7–9], such as moisture-tolerant molecules. Others encapsulated QD in silicon dioxide (SiO_2) particles [10–12], waterproof aerogels [13], mesoporous particles [14, 15], and so on. This encapsulation was often accompanied by different degrees of aggregation of QD inside the particles [16]. Others endowed

QD with siloxane ligands to react with the siloxane matrix for long-term stability and homogeneous dispersion [17–19]. Others coated the surface of QD-added silicone film with hydrophobic particles to isolate moisture [20]. And others coated the single QD with a shell of SiO_2 or epoxy resin to protect QD from oxidation and aggregation [21–24]. Although the ring-open polycondensation of epoxy resin shell of QD happens in the waterless condition, epoxy resin has an aging problem under UV light [25]. Therefore, the epoxy resin shell need proper light stabilizers or stable groups to deactivate the free radicals. As a result, the preparation of epoxy resin-coated QD is more complex, expensive, and time-consuming than that of the SiO_2 shell-coated [26, 27]. The SiO_2 shell is usually generated by the hydrolytic polycondensation at ambient temperature, which is simple and economic. The SiO_2 shell is hydrophilia due to the hydroxy on its surface, and its permeability is much bigger than that of SiO_2 glass produced at high temperature [22]. So, the hydrophilia and permeability of the SiO_2 shell still threaten the long-term water stability of SiO_2-coated QD.

In this work, we provide and fabricate the superior hydrophobic core/shell SiO_2-coated QD for a highly water stability. Physicochemical characteristic, optical performance, and water stability of the hydrophobic SiO_2-coated QD are investigated.

2. Experiments

2.1. Materials

Chemical reagents including tetraethyl orthosilicate (TEOS), mercaptopropyl trimethoxy silane (MTS), ethoxy trimethyl silane (ETS), ethyl alcohol, ammonium hydroxide, deionized water, and n-hexane were purchased from Aladdin and used without purification. Red-light-emissive CdSe/ZnS QD with oleic acid ligands and a peak wavelength of 633 nm, named QD-OA, was provided by Poly Opto Electronics Ltd Dow corning 184 was used to make the mixed silicone slices added by QD or modified QD.

2.2. Fabrication of methylated silica coated QD (MSQ)

Figure 1 shows the fabrication process of MSQ, including three steps-ligand changing, SiO_2 coating, and surface methylation. After the ligand changing, MTS substitutes the original OA ligands on the surface of QD. The thiol end of MTS is coupled to the surface of QD. The other three methoxy ends of MTS are reactive to TEOS. The SiO_2 shell-coated QD (SQ) is generated by the hydrolytic condensation of TEOS. Finally, the SQ is surface methylated by ETS, namely MSQ. In MSQ, the methyl ends of ETS turn the hydrophilic surface of SQ to hydrophobic.

There are the details in the fabrication process. In the first step, MTS was used to exchange the initial OA ligands and played a role as the bridge connecting QD and the SiO_2 coating layer. 0.5 ml of MTS was ionized with 0.1 g of sodium hydroxide. 20 ml of ethyl alcohol, 0.5 ml of QD-OA chloroform solution (10 mg ml^{-1}), and 0.5 ml of sodium

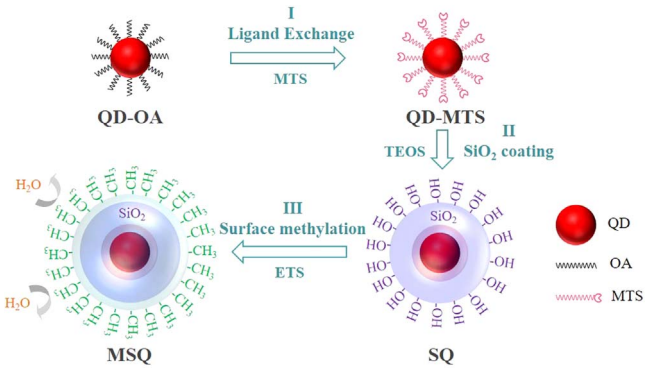

Figure 1. Schematic of the preparation process of MSQ.

hydroxide ionized MTS were mixed and stirred for 10 min at 25 °C and 600 RPM. The mixture was centrifuged and the collected QD-MTS sediment was washed twice with ethyl alcohol. In the second step, the QD-MTS sediment and 0.1 ml of TEOS were added to 100 ml of ethyl alcohol, followed by the dropwise addition of 4 ml of ammonium hydroxide solution with a concentration of 28%. After 60 min of hydrolytic condensation of TEOS at 40 °C and 800 RPM, the mixture was centrifuged and the collected SQ sediment was washed twice with ethyl alcohol. The low concentrations of QD-MTS and TEOS avoid the agglomeration of SiO_2 and make sure the SiO_2 shell-coated QD. Meanwhile, the adjusted pH value of 8 and the reaction temperature of 40 °C can result in a high coating speed which prevented QD from severe water erosion. In the third step, the SQ sediment, 5 ml of ETS, a single-alkoxy alkyl silane, and 4 ml of ammonium hydroxide were added to 100 ml of ethyl alcohol and stirred for 12 h at 25 °C and 800 RPM. It's noted that multi-alkoxy alkyl silane is able to polymerize, which will lead to the aggregation of MSQ. The mixture was centrifuged and the MSQ sediment was washed and dispersed in ethyl alcohol. As shown in figure 2(a), QD (QD-OA), SQ, and MSQ are uniformly dispersed in ethyl alcohol solution, respectively.

2.3. Packaging of MSQ in silicone

For the water stability test, QD, SQ, and MSQ were uniformly mixed with the Dow Corning 184 silicone, respectively. Then, the mixture was air-removed by vacuuming and then poured into a metal mold for thermal curing at 85 °C for 20 min. The shaped QD-, SQ- and MSQ-silicone slices had a diameter of 12 mm and a height of 1 mm, as shown in figure 2(b).

2.4. Measurements

The water contact angle of MSQ particles was tested by a KRÜSS Drop Shape Analyzer and the Laplace-Young Fitting method. Transmission electron microscopy (TEM) images and energy disperse spectroscopy (EDS) were measured by Talos F200X. Fourier transform infrared spectroscopy (FTIR) images were tested by NICOLET 5700. The absorption spectra were tested by Solid Spec 3700 UV–visible Near Infrared Spectrophotometer. The photoluminescence emission and excitation spectra were tested by FP6500 Fluorescence Spectrophotometer.

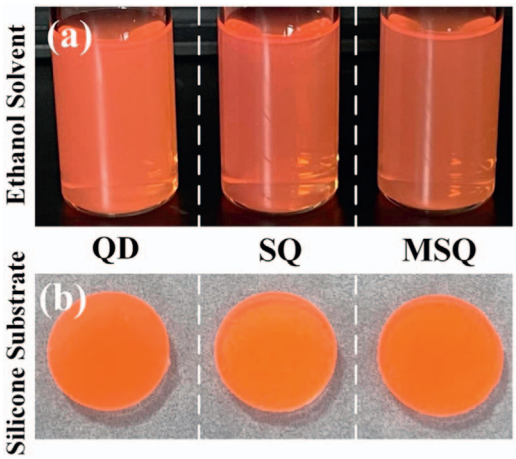

Figure 2. (a) QD, SQ, and MSQ in ethanol solutions. (b) QD-, SQ-, and MSQ-silicone.

The excitation wavelength of the emission spectra was 450 nm. The absolute photoluminescence quantum yields (PLQY) were measured by the FLS980 Series of Fluorescence Spectrometers at an excitation wavelength of 450 nm. The spectra of the QD-, SQ-, and MSQ-silicone excited by a LED light source were tested by an Everfine ATA-1000 Integrating Sphere.

3. Results and discussions

3.1. Characteristic of MSQ

The water contact angle of MSQ was measured. MSQ particles were spread on a glass dish for test. Then a water droplet was dripped on the surface of the dry MSQ, as shown in figure 3(a). The average water contact angle of MSQ in figure 3(b) was up to 159.6°, signifying the superior hydrophobicity (contact angle larger than 150°) of MSQ.

For the morphology investigation, the TEM images, figures 4(a) and (b), show the core/shell structures of SQ and MSQ, respectively. The average diameters of SQ and MSQ were 24.5 and 27.7 nm in turn. This small diameter difference was attributed to the ETS molecule layer on the surface of MSQ. Besides, the cubic nanocrystal structure of QD in figure 4(c) is clearly observed in the core of MSQ in figure 4(d), illustrating the core of MSQ was QD.

EDS result in figure 5(a) provides the element comparison of QD and MSQ. It is noted that the high contents of Cu and C are attributed to carbon film-coated copper grid used as the supporter in the test.The component elements in QD, Cd, Se, Zn, and S were detected in both QD and MSQ. Besides, there was a peak of element O coming from the surface ligands of QD. By contrast, MSQ displaied an additional peak of element Si and stronger peak of O reusulting from the SiO_2 coating. Figure 5(b) is the dark-field TEM image of MSQ. The element distributions of Cd, Si, Se, and O in MSQ are shown in figures 5(c), 4(d), (f), and (g), respectively. Combined with the cenrtral overlaping of Cd and Si in figure 5(e), it is evident that QD only existed in the core of MSQ. Furthermore, the full overlaping of Si and O in figure 5(h) was credited to the silica shell.

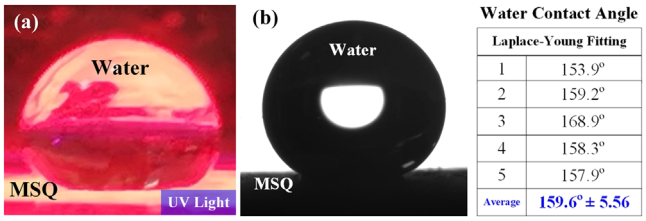

Figure 3. (a) A droplet on MSQ particles at ultraviolet (UV) light. (b) The test scene of water contact angle.

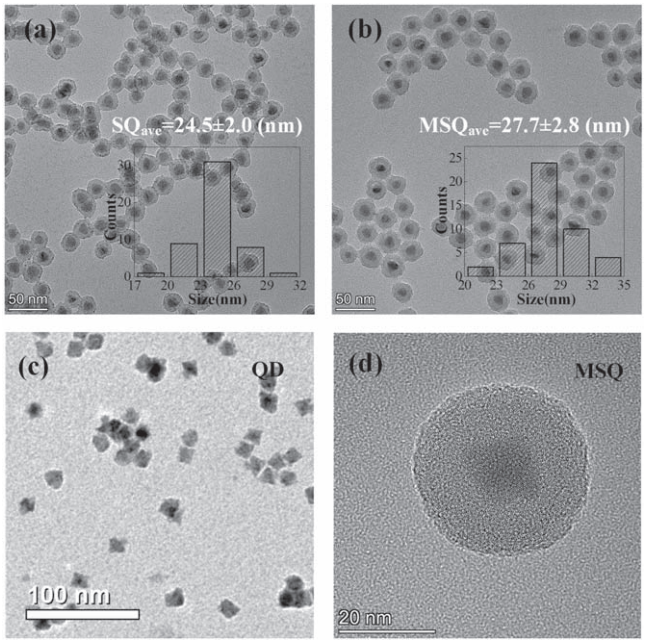

Figure 4. TEM images of (a) SQ, (b) MSQ, (c) QD, and (d) one MSQ.

As further proof for the MSQ preparation process, the FTIR spectra of QD-OA, QD-MTS, SQ, and MSQ are shown in figure 6. There were a few similar characteristic peaks in QD-OA and QD-MTS. But the absorption peak of the S–H bond at 2552 cm^{-1} only existed in QD-MTS, indicating the ligand exchange by MTS which contains the sulfydryl (-SH) group. There was a wide and strong Si–O peaks from 980 cm^{-1} to 1300 cm^{-1} in both SQ and MSQ, illustrating to the coating of SiO_2 shell. Besides, MSQ exhibited a obvious peak at 1403 cm^{-1} which was ascribed to the stretching vibration of C–H in methyl (-CH_3) and proved the surfacial methylation by ETS. It is noted that C–H (CH_3) also appeared in both QD-OA and QD-MTS because OA and MTS have methyl groups. Whereas the SiO_2 coating made the C–H (CH_3) peak almost vanish in SQ. Due to the methylation, the C–H (CH_3) peak became prominent again in MSQ. In short, the difference in absorption peaks demonstrated the successful reactions of ligand exchange, SiO_2 coating, and surfacial methylation.

3.2. Optical parameter of MSQ

The normalized absorption spectra and photoluminescent emission spectra of QD-OA, QD-MTS, SQ, and MSQ added

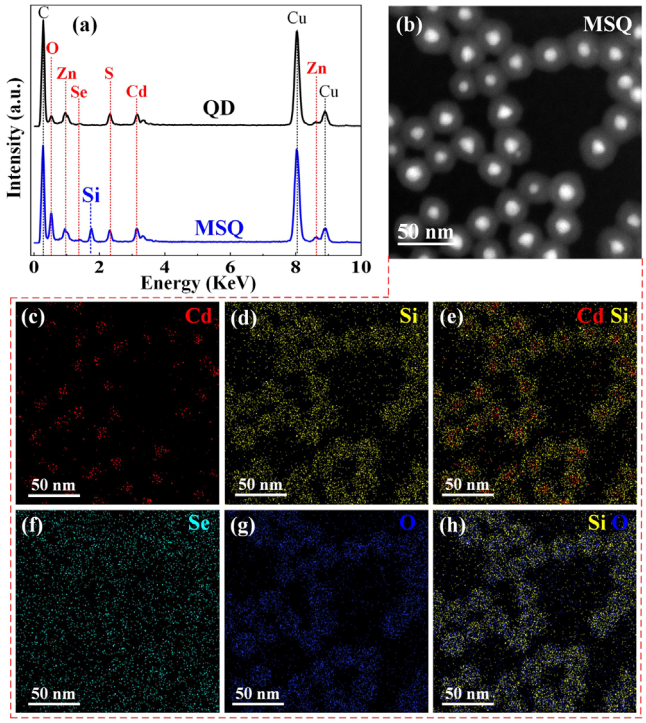

Figure 5. (a)EDS spectra of QD and MSQ. (b) Dark-filed TEM of MSQ and the element distribution of (c) Cd, (d) Si, (e) Cd overlaping Si, (f) Se, (g) O, and (h) Si overlaping O.

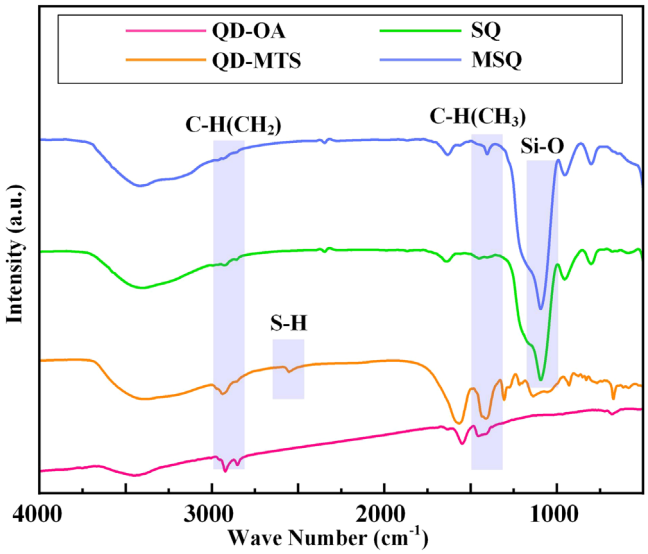

Figure 6. FTIR absorption spectra of QD-OA, QD-MTS, SQ, and MSQ.

silicone are shown in figure 7(a), as well as their excitation spectra in figure 7(b). There was a decrease of absorption of QD-MTS, SQ, and MSQ compared to that of QD-OA, especially at long wavelengths larger than 420 nm. In addition, the emission peak wavelength of QD-OA was 633 nm, but those of QD-MTS, SQ, and MSQ were 629 nm. It was speculated that the 4 nm blue shift was attributed to the better compatibility of QD-MTS in silicone than that of QD-OA because of the shorter chain of MTS [28]. On the other hand,

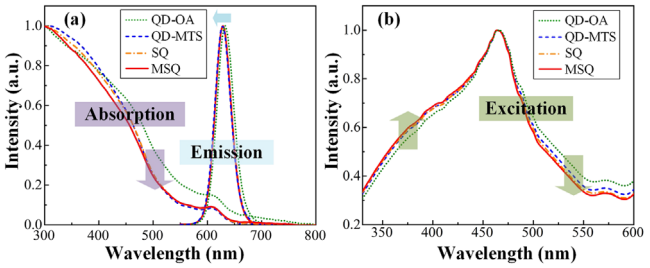

Figure 7. Photoluminescent (a) emission spectra, (b) excitation spectra.

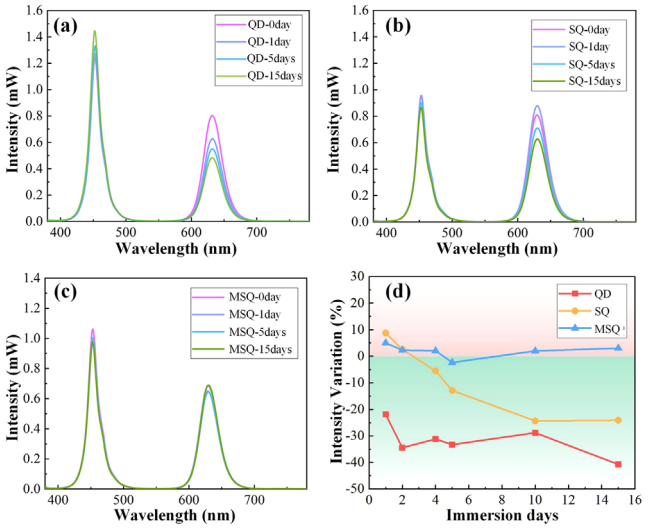

Figure 8. Photoluminescent spectra of (a) QD-silicone, (b) SQ-silicone, and (c) MSQ-silicone during the 15 d water immersion, and (d) the responding intensity variations of emitting light.

the excitation peak wavelengths of the four kinds of QD were the same. Interestingly, the excitation intensities of QD-MTS, SQ, and MSQ at the wavelength smaller than peak wavelength slightly increase compared to that of QD-OA. But it is on the contrary for that at the wavelength larger than the peak wavelength. In short, the ligand exchange by MTS had a few effects on the absorption, emission and excitation spectra of QD.

3.3. Water-resistant stability of MSQ in silicone

The QD-, SQ-, and MSQ-silicone were immersed in water for a water stability test for 15 d. Their photoluminescent spectra during the water immersion are shown in figures 8(a)–(c), respectively. Besides, figure 8(d) provides the corresponding variation percentage curves of photoluminescence intensity. Figure 8(a) shows that the intensity of the red-emitting light from QD-silicone sharply reduces with the increasing immersion time in water. Specifically, the photoluminescence intensity of QD-silicone decreased by 22% after 1 d of water immersion and 41% after 15 d, respectively. As for SQ-silicone, its photoluminescence intensity increased by 9% after 1 d of water immersion due to the initial oxidation passivation of the surface of QD, however decreased after longer

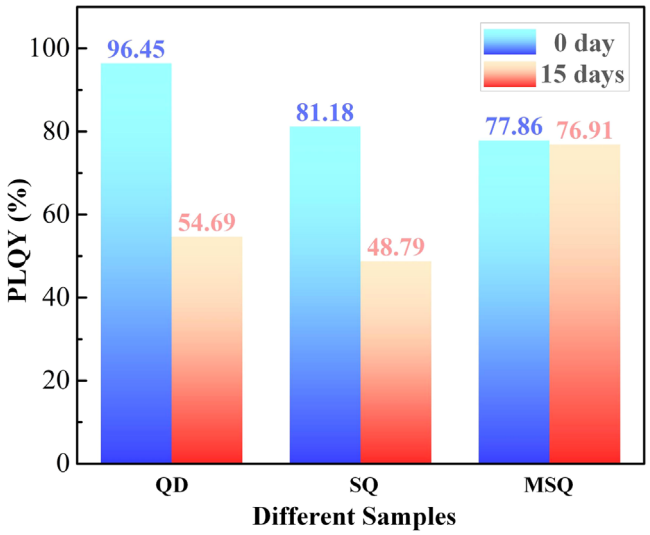

Figure 9. PLQY of QD-, SQ-, and MSQ-silicone before and after the 15 d water immersion.

immersing time along with further oxidation erosion and eventually decreased by 24% after 15 d of water immersion. The above results indicated that both QD- and SQ-silicone had the poor water-resistant ability. It's noted that the photoluminescence intensity variation percentage of the SQ-silicone after 9 d water immersion was comparable to that of the QD-silicone after 1 d water immersion. It proved that the moisture permeability velocity into SQ was decreased by the SiO_2 shell. The thicker SiO_2 shell could result in a smaller moisture permeability velocity into SQ, but it could also cause a worse irreparable light refraction loss [29]. As for MSQ, there is a group of stable photoluminescent spectra of MSQ-silicone in figure 8(c). Particularly, the photoluminescence intensity of MSQ-silicone just rose by 3% after whole water immersion test.

The PLQY of QD-, SQ-, and MSQ-silicone before and after 15 d water immersion are shown in figure 9. QD- and SQ-silicone suffered huge decreases in PLQY after water immersion. By contrast, MSQ-silicone maintained its PLQY well. Specifically, the PLQY of QD-, SQ-, and MSQ-silicone reduced by 43%, 40%, and 1%, respectively, after water immersion. Although MSQ-silicone had a good water stability, its initial PLQY was 0.769 less than that of QD-silicone as 0.964 and that of SQ-silicone as 0.812. The inevitable water erosion during the hydrolytic condensation of TEOS was mostly responsible for the initial PLQY decrease of SQ-silicone compared to that of QD-silicone [21.] In addition, the further decrease of initial PLQY of MSQ was probably because the moisture still permeated through the SiO_2 shell during the early methylation procedure.

Through the water immersion test, MSQ-silicone displayed a much higher photoluminescence stability than QD- and SQ-silicone. The photoluminescence intensity of QD-silicone reduced more rapidly than that of SQ-silicone. Therefore, the SiO_2 shell only slowed down the moisture permeability velocity, rather than isolated moisture and avoided moisture erosion. Only by coating the surface of SQ with hydrophobic alkyl groups, can the moisture be prevented into MSQ.

4. Conclusion

Although QD has many exceptional optical performances, it also suffers from moisture erosion which causes luminescent decrease of QD. This work fabricated the superior hydrophobic SiO_2-coated QD for high water stability. The comprehensive analysis of TEM, EDS, and FTIR results illustrated the monodispersed core/shell structure of SQ and MSQ. QD, SQ, and MSQ displayed similar absorption, emission, and excitation performances, but MSQ had a much better water stability than QD and SQ. The photoluminescence intensity of QD- and SQ-silicone were dramatically reduced after 15 d of water immersion comparing to that of MSQ-silicone. Meanwhile, the PLQY of QD- and SQ-silicone were respectively reduced by 43% and 40%, however that of MSQ-silicone only 1%. We also found out that MSQ was superior hydrophobic with a water contact angle up to 159.6°. In short, the superior hydrophobic MSQ has the potential to greatly enhance the long-term working stability of QD in a humid environment, which is beneficial to the further popularization and wide application of QD.

Acknowledgments

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Kim J Y, Voznyy O, Zhitomirsky D and Sargent E H 2013 25th anniversary article: colloidal quantum dot materials and devices: a quarter-century of advances *Adv. Mater.* **25** 4986–5010

[2] Kagan C R, Lifshitz E, Sargent E H and Talapin D V 2016 Building devices from colloidal quantum dots *Science* **353** aac5523

[3] Xie B, Hu R and Luo X 2016 Quantum dots-converted light-emitting diodes packaging for lighting and display: status and perspectives *J. Electron. Packag.* **138** 020803

[4] Kim H Y, Yoon D E, Jang J, Choi G M, Lee D C and Bae B S 2016 Quantum dot/siloxane composite film exceptionally stable against heat and moisture *J. Am. Chem. Soc.* **138** 16478–85

[5] Huang B, Yang H, Zhang L, Yuan Y, Cui Y and Zhang J 2018 Effect of surface/interfacial defects on photo-stability of thick-shell CdZnSeS/ZnS quantum dots *Nanoscale* **10** 18331–40

[6] Orfield N J, Majumder S, Hu Z, Koh F Y C, Htoon H and Hollingsworth J A 2020 Kinetics and thermodynamics of killing a quantum dot *ACS Appl. Mater. Interfaces* **12** 30695–701

[7] Lesyuk R, Cai B, Reuter U, Gaponik N, Popovych D and Lesnyak V 2017 Quantum-dot-in-polymer composites via advanced surface engineering *Small Methods* **1** 1700189

[8] Xie Y, Geng C, Liu X, Xu S, Xing W, Zhang X, Zhang Z H, Zhang Y and Bi W 2017 Synthesis of highly stable quantum-dot silicone nanocomposites via *in situ* zinc-terminated polysiloxane passivation *Nanoscale* **9** 16836–42

[9] Ozerova V V *et al* 2021 Spectacular enhancement of the thermal and photochemical stability of $MAPbI_3$ perovskite films using functionalized tetraazaadamantane as a molecular modifier *Energies* **14** 669

[10] Jang E P, Jo J H, Lim S W, Lim H B, Kim H J, Han C Y and Yang H 2018 Unconventional formation of dual-colored InP quantum dot-embedded silica composites for an operation-stable white light-emitting diode *J. Mater. Chem.* C **6** 11749–56

[11] Kim Y H, Lee H, Kang S M and Bae B S 2019 Two-step-enhanced stability of quantum dots via silica and siloxane encapsulation for the long-term operation of light-emitting diodes *ACS Appl. Mater. Interfaces* **11** 22801–8

[12] Lai C F, Zhong C Z, Tong H C and Lee Y C 2020 High luminous efficacy and enhanced stability of QDs via a network silica and methylphenyl silicone hybrid for the long-term operation of on-chip white light-emitting diodes with a wide color gamut *Appl. Mater. Today* **20** 100739

[13] Hsieh Y T, Lin Y F and Liu W R 2020 Enhancing the water resistance and stability of $CsPbBr_3$ perovskite quantum dots for light-emitting-diode applications through encapsulation in waterproof polymethylsilsesquioxane aerogels *ACS Appl. Mater. Interfaces* **12** 58049–59

[14] Li J, Tang Y, Li Z, Ding X, Yu B and Lin L 2019 Largely enhancing luminous efficacy, color-conversion efficiency, and stability for quantum-dot white LEDs using the two-dimensional hexagonal pore structure of SBA-15 mesoporous particles *ACS Appl. Mater. Interfaces* **11** 18808–16

[15] Jo J H, Heo H S and Lee K 2020 Assessing stability of nanocomposites containing quantum dot/silica hybrid particles with different morphologies at high temperature and humidity *Chem. Mater.* **32** 10538–44

[16] Li Z T, Li J X, Deng Z H, Liang J Y and Li J S 2021 Unraveling the origin of low optical efficiency for quantum dot white light-emitting diodes from the perspective of aggregation-induced scattering effect *IEEE Trans. Electron Devices* **68** 1738–45

[17] Jang J, Yoon D E, Kang S M, Kim Y H, Lee I, Lee H, Kim Y H, Lee D C and Bae B S 2019 Exceptionally stable quantum dot/siloxane hybrid encapsulation material for white light-emitting diodes with a wide color gamut *Nanoscale* **11** 14887–95

[18] Kim Y H, Koh S, Lee H, Kang S M, Lee D C and Bae B S 2020 Photo-patternable quantum dots/siloxane composite with long-term stability for quantum dot color filters *ACS Appl. Mater. Interfaces* **12** 3961–8

[19] Zhang S, Li C, Wang Q, Zhou L, Saeed M H, Wang X, Zhang L, Yang Z and Yang H 2020 Fluorescence enhancement and encapsulation of quantum dots via a novel crosslinked vinyl-ether liquid crystals/polymer composite *Film Polym.* **207** 122834

[20] Yu X, Pei N, Zhou S, Zhang X and Luo X 2019 Enhancing light efficiency and moisture stability of the quantum dots-light-emitting diodes by coating superhydrophobic nanosilica particles *IEEE Trans. Electron Devices* **66** 5196–201

[21] Wang N *et al* 2017 Highly luminescent silica-coated CdS/CdSe/CdS nanoparticles with strong chemical robustness and excellent thermal stability *Nanotechnology* **28** 185603

[22] Murase N, Li C and Gunshi T 2020 Improved photostability of silica bead impregnated with cdse-based quantum dots prepared through proper surface silanization *Colloids Surf.* A **600** 124811

[23] Li M, Zhang X and Yang P 2021 Controlling the growth of a SiO_2 coating on hydrophobic $CsPbBr_3$ nanocrystals towards aqueous transfer and high luminescence *Nanoscale* **13** 3860–7

[24] Wei H, Ying Z, Yu Y and Yuan Y 2007 Studies on UV-stable silicone–epoxy resins *J. Appl. Polym. Sci.* **104** 3954–9

[25] Ai J, Cheng W, Wang P, Qian W and Chen Q 2021 Silica solid particles toughening, strengthening and anti-aging on epoxy resin *J. Appl. Polym. Sci.* **138** e50331

[26] Lin C H, Whang W T, Chen C H, Huang S C and Chen K C 2020 Novel siloxane-modified epoxy resins as promising encapsulant for LEDs *Polymers* **12** 21

[27] Kim Y H, Lee I, Lee H, Kang S M, Lee Y, Kim S and Bae B-S 2021 Sol–gel synthesized siloxane hybrid materials for display and optoelectronic applications *J. Sol-Gel Sci. Technol.* (https://doi.org/10.1007/s10971-021-05491-4)

[28] Kim Y K, Choi K C, Ahn S H and Cho Y S 2012 A Facile synthesis of SiO_2-based nanocomposites containing multiple quantum dots at high concentration for LED applications *RSC Adv.* **2** 6411–3

[29] Li Z, Li J, Li J, Deng Z, Deng Y and Tang Y 2020 Scattering effect on optical performance of quantum dot white light-emitting diodes incorporating SiO_2 nanoparticles *IEEE J. Quantum Electron.* **56** 3600109