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Robust, processable, and bright quantum dot/organosilicate hybrid films with uniform QD distribution based on thiol-containing organosilicate ligandst

Heeje Woo,^a Jaehoon Lim,^a Yeonju Lee,^a Jinwoo Sung,^b Hyunkwon Shin,^b Jin Mok Oh,^b Moongoo Choi,^b Hyunsik Yoon,^c Wan Ki Bae^d and Kookheon Char^{*a}

Robust, processable, and bright quantum dot/organosilicate (QD/OS) hybrid films with uniform QD distribution are successfully demonstrated by grafting thiol-containing polymeric organosilicate (OS) ligands to the surface of QDs. It is found that the surface modified QDs show almost the same optical properties (*i.e.*, in terms of emission PL spectra and quantum yields (QYs)) as those of pristine QDs initially covered with oleic acids. The QD/OS hybrid films based on the surface modified QDs show the uniform distribution of QDs within the films with all the beneficial properties such as high QY, improved environmental resistance against hydrochloric acid, and excellent optical transparency in the visible range. In addition, red, green, blue, and white QD/OS hybrid films with high color purity and a down-conversion film, based on a mixture of red and green QDs, placed on top of a blue LED chip showing white emission were also successfully demonstrated with the QD/OS hybrids. We further demonstrate that cylinder-patterned QD/OS hybrid films are possible simply by applying unconventional imprint lithography. The QD/OS hybrid films with uniform distribution of QDs within the films could thus be applied as practical platforms, which have easy processability, high QY, and environmental stability, for optical devices based on functional nanocrystals.

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Introduction

Colloidal quantum dots (QDs) have received intense attention in recent years as the most practical next generation phosphors for optical and optoelectronic devices due to their excellent optical properties, such as broad absorption, narrow emission spectral bandwidth, emission wavelength tunability ranging from near UV to visible to near-IR, and high photoluminescence quantum yield (PL QY) in the solid state at room temperature.^{1–3} Particularly, in the area of light-emitting devices, many research groups and companies have reported the practical realization of

light-emitting devices utilizing QDs as active materials^{4–7} or down-conversion phosphors.^{8–10}

In order to use QDs for practical applications such as LEDs and photovoltaics,^{11–13} it is necessary to preserve their luminescence efficiency and to extend their lifetime against stringent environmental conditions. For this reason, QDs have often been embedded in matrices such as polymers and epoxy, acrylic, or silicone resins to protect the QDs against the external environment and also, at the same time, effectively improve the processability of QDs.^{14–16} However, the embedding of QDs in unsuitable matrices often causes the opposite effect because QDs are typically immiscible with organic matrices and form massive aggregates due to dissimilar chemical properties between the surfactants covering QDs and matrix materials.

To overcome the problem of the massive aggregation of inorganic nanocrystals, the surface modification of inorganic nanocrystals has been developed based on two different approaches: the simple ligand exchange with oligomeric or polymeric ligands containing functional anchor moieties (such as thiols, amines, carboxylic acids, and phosphine oxides) (the grafting-to approach)^{17,18} and the direct growth of brushes^{19,20} or shells^{21–23} from the surfaces of QDs (the grafting-from approach). Through the surface modification of inorganic nanocrystals such as QDs, surface properties of QDs could be

^aThe National Creative Research Initiative Center for Intelligent Hybrids, The WCU Program of Chemical Convergence for Energy & Environment, School of Chemical & Biological Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea. E-mail: khchar@plaza.snu.ac.kr

^bMaterials and Devices Laboratory, LGE Advanced Research Institute, LG Electronics, 38 Baumoe-ro, Seocho-gu, Seoul 137-724, Korea

^cDepartment of Chemical Engineering, Seoul National University of Science & Technology, Seoul, 139-743, Korea

^dChemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87544, USA

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easily modified such that QDs are well miscible with matrix materials to guarantee the uniform distribution of QDs within matrix materials and additional functionality and processability could also be conferred on the QDs.

In this context, we have already reported that the hybridization of QDs with polymeric ligands based on ligand exchange improved the QD distribution within polymeric matrices.^{24,25} The surfactants covering pristine QDs (*i.e.*, oleic acids) were effectively replaced with conducting polymers containing thiol anchoring blocks and the surface-modified QDs were then incorporated into conducting polymer matrices. As a result, the surface-modified QDs showed the uniform distribution within conducting polymer matrices when compared with pristine QDs, forming massive aggregates within the matrices and the electroluminescence performance of devices based on the QD/conducting polymer hybrids was remarkably improved.

In general, inorganic matrices are known to have distinctive thermal and optical resistances when compared with organic or polymeric counterparts. Thus, we expect that inorganic matrices could be good candidates for QD encapsulants in practical applications such as in optical and optoelectronic devices. Silicone-based resins, for example, have been regarded as promising encapsulants for QDs, replacing conventional epoxy encapsulants with weak environmental stability in optical and optoelectronic devices. Particularly, organosilicates (OS) are well known for their outstanding optical transparency in the visible light range and excellent thermal, chemical, and optical endurance without long-term yellowing problem which occurs with epoxy-based matrices.^{26,27} Furthermore, material properties and functionalities of organosilicate polymers are tunable by controlling the type of precursors and composition ratio, and uniform OS films in large area as well as patterned OS arrays can be readily prepared by simple processes such as spin-casting and unconventional lithography.

Despite the various advantages of organosilicates as matrix materials, QD hybrids based on such organosilicates are quite rare at the moment and no systematic studies on the control of QD morphology within organosilicate matrices have been undertaken.²⁸ In recent studies on QDs for down-conversion phosphor applications, most QDs were just used in the aggregated form, blended or physically mixed with matrix materials such as silicones and organosilicates. And QD morphologies within the matrices in those studies were not clearly defined.

Herein, we propose a simple method to prepare mechanically robust, processable, and bright quantum dot/organosilicate (QD/OS) hybrid films with improved QD distribution within OS matrices using thiol-containing polymeric OS ligands (Fig. 1(a)). The OS ligands used in the present study were easily prepared by the typical sol-gel copolymerization of 3 different OS precursors in the presence of acid catalysts (Fig. 1(b)). The surfaces of QDs, initially covered with oleic acids, were modified with thiol-containing OS ligands by a simple ligand exchange. Since this simple surface modification of QDs neither includes any harmful chemicals causing damage to QDs nor requires any harsh process conditions, the QD/OS hybrid films with the uniform distribution of QDs within the OS matrices were obtained without losing any quantum efficiency and any

emission spectral shift. We also demonstrated that the QD/OS hybrid films are readily processable (with unconventional imprint lithography) and show excellent optical transparency as well as enhanced environmental stability in hydrochloric acid.

Experimental details

Chemicals

Cadmium oxide (CdO, 99.99%), zinc acetate (99.9%, powder), selenium (99.9%, powder), sulfur (99.9%, powder), tri-octylphosphine (TOP, 90%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), and mercaptopropionic acid (MPA, 99.8%), tetraethyl orthosilicate (TEOS, 98%), methyl trimethoxysilane (MTMS, 98%), (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%), trimethyl ethoxysilane (TMES, 98%), hydrochloric acid (aq, 37%), and methylisobutylketone (MIBK, 99%) were used as purchased from Aldrich.

Synthesis of oleic acid coated CdSe@ZnS QDs

The OA-coated red, green, and blue CdSe@ZnS QDs were prepared following the one-pot synthetic method, which has already been reported by our laboratory.^{29–31} The QDs synthesized were purified repeatedly (typically, three times) by precipitation/redispersion methods to remove residual ligands or unreacted precursors. All the QDs were dispersed in toluene (10 mg ml⁻¹) and kept under ambient conditions before use.

Synthesis of (thiol-containing) OS polymeric ligands

The OS polymers employed as the ligands for the surface modification of QDs as well as OS matrices for hybrid film formation were prepared by the sol-gel copolymerization of OS monomers (TEOS, MTMS, and MPTMS) using hydrochloric acid as a catalyst. The hydrochloric acid was completely removed by washing several times with distilled water. For OS ligands, TM37 and TMP371, the feed ratios of TEOS, MTMS, and MPTMS were 3 : 7 : 0 and 3 : 7 : 1 by molar ratio, respectively. The detailed synthetic procedure is described elsewhere.³²

Preparation of QD/OS hybrid films

Pristine QDs in toluene were first precipitated by centrifugation and redispersed in OS solutions (OS polymers dissolved in MIBK, 100 mg ml⁻¹) for the QD surface modification. The QD solutions in MIBK were sonicated until they became clear. The surface-modified QD solutions were washed with *n*-hexane and redispersed in MIBK. Additional OS solutions were added to adjust the QD loading amount in OS polymer matrices. The QD loading content was varied from 0.5 to 10 wt% of total OS polymers. To prepare free-standing QD/OS thin films to study the QD morphology, the QD/OS mixture solutions with 10 wt% of OS concentration dissolved in MIBK were spun-cast on PAH (poly(allylamine hydrochloride))-coated Si wafers. The QD/OS hybrid films were further annealed at 70 °C for 1 h. After thermal annealing, free standing QD/OS hybrid films were obtained by the removal of the sacrificial PAH layer in distilled water (film thickness: ~150 nm). To characterize the PL QY, environmental stability, and transmittance, the QD/OS hybrid

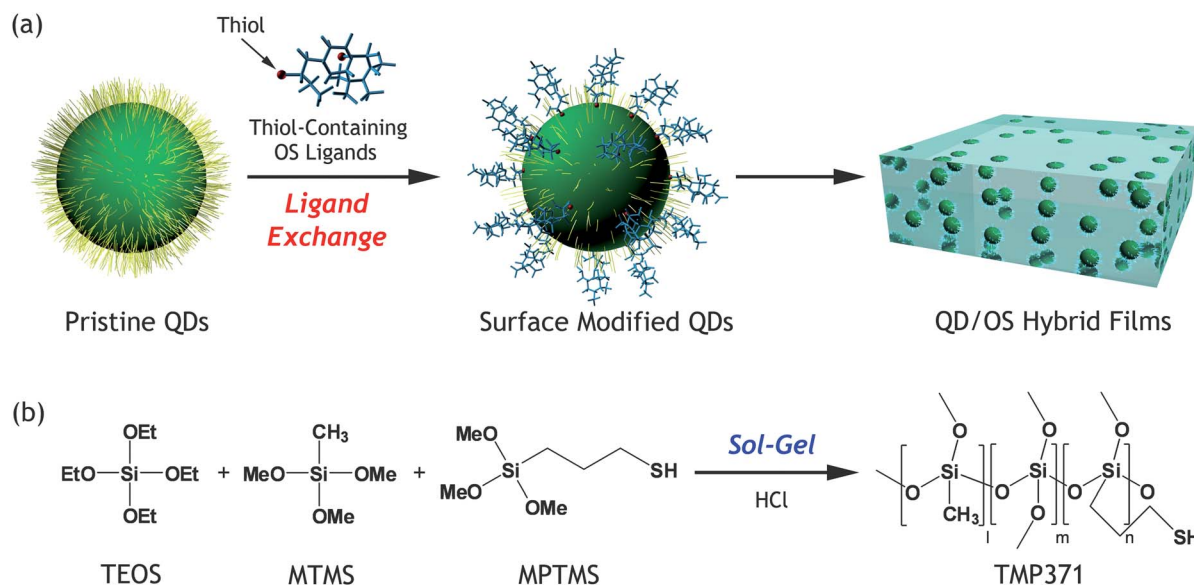


Fig. 1 (a) A schematic of the preparation of QD/OS hybrid films and (b) a schematic illustration for the synthesis of thiol-containing polymeric OS ligands (TMP371).

films with 5 wt% of QDs were prepared by drop-casting (film thickness: $\sim 6 \mu\text{m}$). The QD/OS hybrid films prepared were then subject to further curing at 70°C for 1 h.

Characterization of QD/OS hybrid films

The molecular structure and composition of OS polymeric ligands prepared in the present study were characterized by FT-IR (FT-IR200, JASCO), NMR (500 MHz, Avance500, Bruker), solid-state NMR (500 MHz, Avance II, Bruker), and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass spectroscopy (Voyager-DETM STR Biospectrometry Workstation, Applied Biosystems Inc.). The QD morphologies within OS matrices were obtained by using an energy-filtered transmission electron microscope (EF-TEM; LIBRA 120, Carl Zeiss) and the cross-sectional TEM samples were obtained with an ultra microtome (AT/ULTRACUT R, LEICA Microsystems). The PL spectra and quantum yields of QD solutions as well as QD/OS films were obtained with an absolute photoluminescence (PL) quantum yield measurement system combined with an integrating sphere detector (C9920-02, Hamamatsu). The transmittance of QD/OS films was measured with a UV-Vis spectrometer (Lambda 35 UV/VIS Spectrometer, PERKIN ELMER Instruments). The patterned QD/OS films were characterized by using a Field-Emission Scanning Electron Microscope (FE-SEM; JSM 6071F, JEOL) and an Image Restoration Microscope (Delta Vision RT, Applied Precision).

Results and discussion

Two different types of OS ligands, TM37 and TMP371, were prepared for the surface modification of CdSe@ZnS QDs covered with oleic acids (pristine QDs). To prepare the OS ligands for the QD surface modification, TEOS and MTMS were used as main silicate precursors and a small amount of MPTMS

was employed as a precursor containing thiol groups, which we believe have energetically favorable interactions with the QD surfaces. TEOS (tetravalent precursor) should make up the network-type OS polymers with relevant molecular weights and MTMS (trivalent precursor) should enable stress relaxation and uniform film formation without forming cracks of TEOS-based OS films.²⁶ The MPTMS precursors containing propyl thiol end groups should yield OS ligands for effective QD surface modification. The molecular structure and composition of the two different OS ligands prepared in this study were analyzed by FT-IR, $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, and MALDI-TOF (see ESI[†]). The TM37 OS ligands which were prepared with TEOS and MTMS precursors are the network-type organosilicate polymers containing a residual amount of silanol end groups while the TMP371 OS ligands, prepared with TEOS, MTMS, and a small amount of MPTMS, showed almost the same molecular structure and composition as those of the TM37 except a small amount of additional propyl thiol end groups. To prepare QD/OS hybrid nanoparticles, the OA surfactants covering the pristine QDs were replaced with the OS ligands based on the simple ligand exchange. The QDs, surface modified with either TM37 or TMP371, were denoted as QD-TM and QD-TMP, respectively.

The surface modification of QDs with OS ligands could be easily monitored with the solubility change of QDs during the surface modification procedure.²⁴ While pristine QDs stabilized with oleic acids are dispersed in non-polar solvents (*e.g.*, hexane, cyclohexane, toluene), QDs modified with OS ligands are only dispersed in polar organic solvents, such as acetone, ethanol, DMF, and MIBK (Fig. 2(a)). During the surface modification, QDs maintain their optical properties (*e.g.*, peak PL emission wavelength (λ_{peak}) and full-width at half maximum (FWHM)) (Fig. 2(b)), indicating that the OS ligands replace oleic acids by adsorbing on the surfaces of QDs without causing severe damage on QD emission itself. Interestingly, QD-TMP

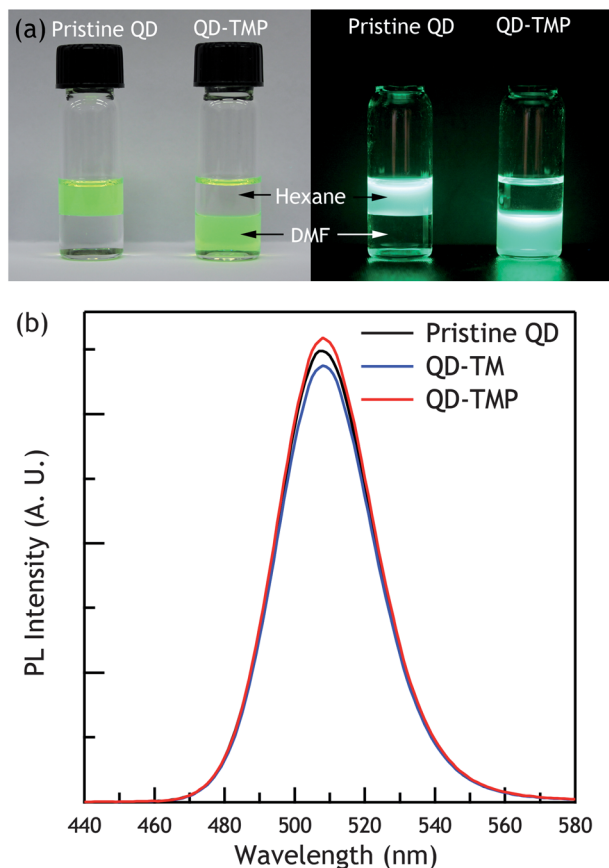


Fig. 2 (a) Photographs illustrating the solubility change of QDs by the hybridization with OS ligands (TMP371) under room light (left) and UV exposure (right, $\lambda_{\text{ex}} = 365$ nm). Left vial: pristine QDs dispersed in hexane. Right vial: QDs surface modified with thiol-containing OS ligands dispersed in DMF. (b) PL spectra of pristine QD, QD-TM, and QD-TMP solutions in THF. The excitation wavelength for the PL measurement was fixed at 440 nm.

solution samples show the slight enhancement in PL QY whereas QD-TM solution samples display the slight decrease in PL QY. We attribute these different trends in the PL QY during the ligand exchange to the improved surface passivation with longer TMP ligands, which, in turn, suppress the exciton loss through the energy transfer process or the re-absorption/re-emission process in contact with polar solvent.

To characterize the QD morphology within OS matrices, QD/OS films with two different types of OS polymers were prepared. In contrast to the similar change in colloidal solubility with both types of OS ligands, a huge difference in their morphology in the films has been observed: QDs are homogeneously dispersed within the TMP371 matrices, as confirmed by plan- and cross-sectional TEM images regardless of the variation in QD contents, while QDs are likely to aggregate within the TM37 matrices (Fig. 3). This clear difference in their final morphology suggests that the silanol anchor groups of TM37 do not readily bind to the QD surface to uniformly disperse QDs within the OS matrices, while thiol anchor groups in TMP OS ligands provide the enthalpic attractions between QDs and OS ligands so that QDs are uniformly dispersed within the OS matrices.²⁴ Consequently, QDs surface-modified with TM37

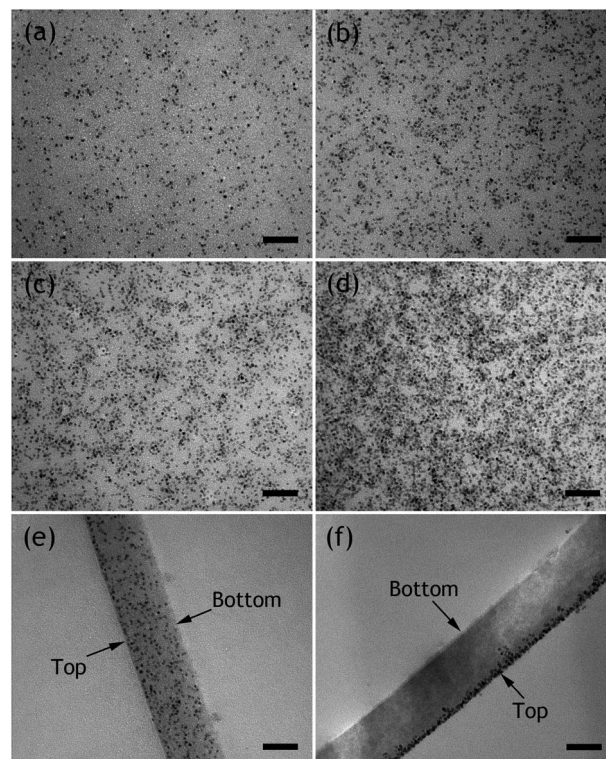


Fig. 3 The plan-view TEM images of QD/TMP hybrid films containing different amounts of QDs within the films ((a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 10 wt% of QDs). The cross-sectional views of (e) a QD/TMP hybrid film and (f) a QD/TM blend film containing 5 wt% of QDs. All the films were prepared by spin-casting QD/OS solutions with 10 wt% of OS concentration in MIBK (scale bars: 100 nm).

(QD-TM) were partially miscible with the TM37 matrices and the phase separation between QDs and OS matrices occurred during the film formation. Since TMP371 surface modifiers with strong binding thiol anchors could effectively replace the OA surfactants covering pristine QDs, thus improving the miscibility with TMP371 matrices, the QDs surface-modified with TMP371 (QD-TMP) were uniformly distributed within the entire matrices of TMP371 films.

The morphological difference in the QD/OS hybrid films significantly influences their optical properties and chemical stability. For the comparative study on the influence of QD morphology within OS matrices on the ensemble PL QY of QD/OS films, the PL QY of QDs within two different types of OS matrices was characterized as a function of QD content (Fig. 4(a)). It is well known that the ensemble PL QY of fluorophores decreases at higher concentration (*i.e.*, concentration quenching) due to an unexpected energy transfer process or re-absorption/re-emission process among closely located fluorophores. As the QD content is increased, the PL QY of QD/TM blend films gradually decreases from 60% to 55% due to the concentration quenching, while QD/TMP hybrid films based on TMP371 matrices maintain almost constant PL QY around 65–68% in the range of QD content chosen in the present study, which, in turn, indicates that QDs are uniformly distributed in the QD/TMP hybrid films whereas QDs are significantly aggregated in the case of the QD/TM blend films.

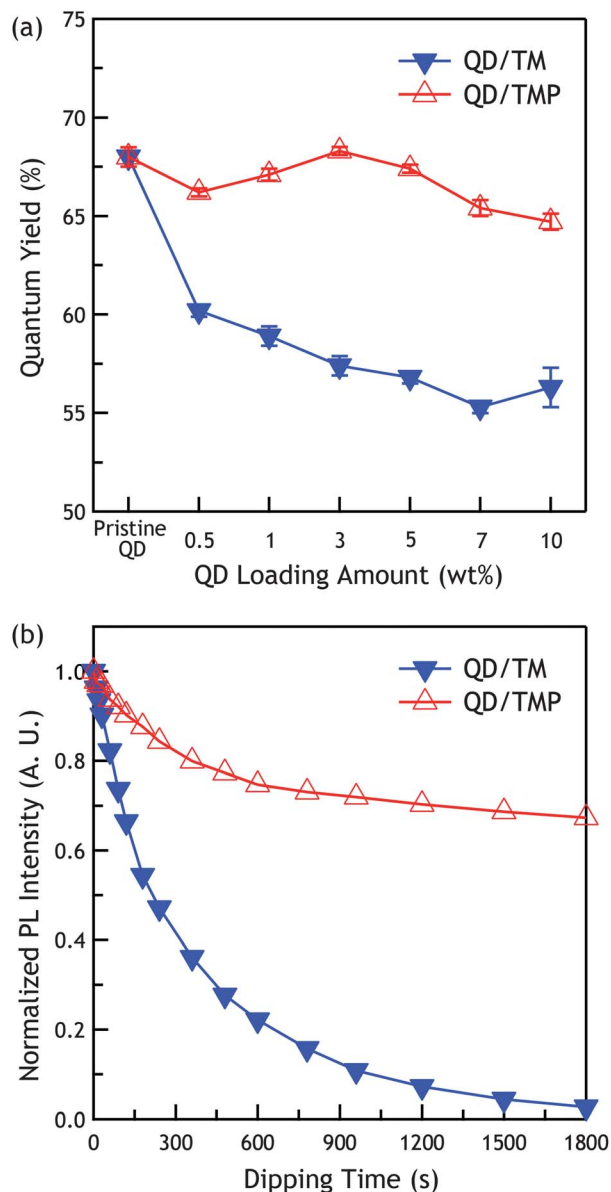


Fig. 4 (a) PL quantum yield (QY) of pristine QD solution in THF and QD/OS films (QD/TM and QD/TMP) with different QD loading amounts. (b) The change in PL intensity of QD/TM blends and QD/TMP hybrid films exposed to hydrochloric acid solution (aq., 18.5%) as a function of dipping time. The excitation wavelength for both characterizations was fixed at 440 nm.

To investigate the influence of QD morphology on the environmental stability of QD/OS films, the QD/OS films containing 5 wt% of QDs were exposed to acidic atmosphere. The QD/OS films were placed in hydrochloric acid solution (aq., 18.5%) and the emission PL intensity of the QD/OS films was monitored as a function of dipping time (Fig. 4(b)). The emission PL intensity of the QD/TM blend films rapidly decreases and all the QDs were almost completely quenched within 30 min of dipping in hydrochloric acid solution while the emission PL intensity of the QD/TMP hybrid films is maintained at 68% of the initial PL intensity up to 30 min of dipping. The reason for the improved stability in hydrochloric acid of the QD/TMP hybrid films is again due to the uniform QD morphology within the TMP OS

matrices. In the case of the QD/TM blend films, all the QDs are located at the top surface of the OS thin films and QDs at the top of the surface are quickly quenched upon exposure to hydrochloric acid. On the other hand, QDs in the QD/TMP hybrid films are slowly quenched upon exposure to hydrochloric acid since the QDs within the TMP matrices are uniformly distributed within the matrix and the penetration of hydrochloric acid within the TMP matrix is purely diffusional. As a result, QDs in the QD/TMP hybrid films are environmentally much more stable, which is directly related to the degree of QD distribution within OS matrices.²³

To determine the effect of QD morphology on the transparency of QD/OS films, the transmittance of OS matrices and QD/OS films was measured with a UV-Vis spectrometer (Fig. 5(a)). Both OS films, TM37 and TMP371, show extremely high transmittance of more than 99% in the visible wavelength range. The QD/TMP hybrid films also show high transparency similar to the pure OS films due to the uniform QD distribution except for a short wavelength range (<500 nm) due to the absorption by QDs. In the case of the QD/TM blend films, the films appear to be a little bit opaque (Fig. 5(b)) and the transmittance measured is also lower than the transmittance of the QD/TMP hybrid films in the whole visible range. Because all the QDs were located at the top surface of the QD/TM blend films, forming an aggregate layer of bigger size, the incident visible light is scattered off the film surface by the QD aggregate layer at the surface, ultimately lowering the transmittance.

Red, green, blue, and white QD/TMP hybrid films were prepared with three different QDs (with red, green, and blue emissions) and TMP371 matrices (Fig. 5(c)). The QD/TMP hybrid film with white emission was prepared by mixing red, green, and blue QDs in 1 : 4.5 : 2.2 of weight ratio.³³ All the QD/TMP hybrid films showed high transparency under room light and emitted vivid light under UV exposure ($\lambda = 365$ nm), exciting QDs. The QD/TMP hybrid films with red, green, and blue emissions showed high color purity and their chromaticity coordinates reside outside the current National Television System Committee (NTSC) standard color triangle in the Commission Internationale de l'Eclairage (CIE) chromaticity diagram. The white QD/TMP hybrid film also retains the reasonable chromaticity coordinate located within the white light region of the CIE chromaticity diagram (see ESI†).

A white-emitting LED for back-light unit of liquid crystal displays also has been demonstrated using a commercial blue InGaN LED chip ($\lambda_{\text{peak}} = 447$ nm, Haewon Semiconductor, Korea) and a red/green mixed QD/TMP hybrid film as a down-conversion phosphor. The QD/TMP hybrid film with 5 wt% QDs was deposited on the blue LED chip surface by drop casting and then cured at 70 °C for 1 h. The white LED shows trigonal white emission from the blue LED chip and the color-converted green and red emissions from QDs (Fig. 5(d)) with a chromaticity coordinate of (0.34, 0.35) within the CIE chromaticity diagram and a color temperature of 5300 K.

Patterned QD/TMP hybrid films could also be prepared using PDMS stamps by an unconventional imprint lithographic method (Fig. 5(e)).^{34,35} A PDMS stamp with inverted cylindrical patterns was prepared with a Si master template, which was

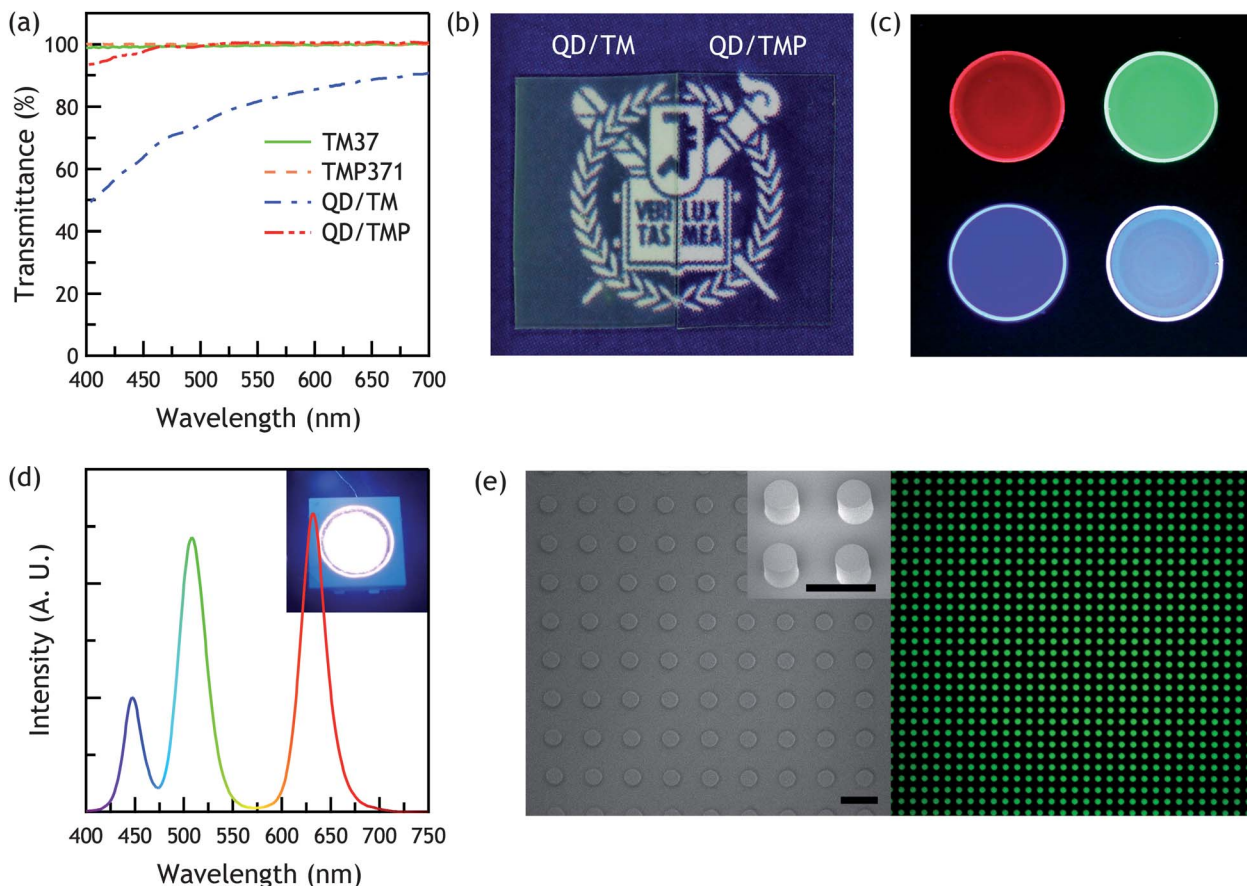


Fig. 5 (a) Transmittance of OS (TM37 and TMP371) and QD/OS (QD/TM and QD/TMP) films in the visible range and (b) photograph showing the QD/TM blend film (left) and the QD/TMP hybrid film (right) under room light (QD content: 5 wt%, film thickness: 6 μm). (c) Red, green, blue, and white QD/TMP hybrid films under UV exposure ($\lambda = 365$ nm). The white QD/TMP hybrid films were prepared using a mixture of red, green, and blue QDs (total QD content: 5 wt%). (d) The spectrum of a white LED prepared with a red/green mixed QD/TMP film placed on top of a blue LED chip. The inset photograph showing the white LED. (e) FE-SEM (left) and fluorescence microscopy (right) images of cylinder-patterned QD/TMP hybrid films. The inset picture shows the tilted FE-SEM image (scale bars: 20 μm). The excitation wavelength for fluorescence microscopy was fixed at 490 nm.

originally fabricated by the conventional lithographic process. The diameter, center-to-center distance, and depth of the inverted cylindrical patterns in a PDMS stamp are 9, 21, and 10 μm , respectively. The 20 wt% QD/TMP solution containing 5 wt% of QDs in MIBK was first deposited on a PET substrate by drop casting and remained for 20 min to evaporate the solvent. A PDMS stamp was then placed on top of the semi-dried QD/TMP solution and mildly pressed to transfer the cylinder patterns to the QD/TMP hybrid films. After thermal treatment at 70 $^{\circ}\text{C}$ for 1 h, the PDMS stamp was removed, leaving behind the solidified QD/TMP patterns. The pattern size and shape of the QD/TMP replicas were exactly copied from the original PDMS stamp and the cylinder height is about 7 μm . From the fluorescence measurement, the cylinder patterns with green emissions from the QDs embedded within TMP matrices are clearly evident.

Conclusions

QD/OS hybrid nanoparticles were first prepared by the surface modification of QDs using thiol-containing OS ligands through the ligand exchange. The QD/OSs obtained from such

surface modification showed the solubility change from nonpolar solvents to polar solvents maintaining excellent optical properties (such as peak emission PL wavelength (λ_{peak}), FWHM, and quantum yield). The QD/OS hybrid thin films based on thiol-containing OS ligands (QD/TMP) showed the uniform QD distribution across the entire OS films due to the improved miscibility between QDs and OS matrices employed. The QD/OS hybrid films also showed the enhanced quantum yield and resistance against hydrochloric acid with excellent optical transparency due to the uniform QD distribution within the TMP OS matrices. Using red, green, blue QDs, and their mixture, the QD/OS hybrid films with red, green, blue, and white emissions were obtained and a white LED was fabricated using a blue LED chip as a light source and a red/green mixed QD/OS hybrid film employed as down-conversion phosphors. In addition, a cylinder-patterned QD/OS hybrid film was demonstrated using the unconventional imprint lithographic method. Based on the several advantages deriving from the hybrid films with uniform QD distribution within OS matrices, we expect that the QD/OS hybrid films would be good candidate materials for optical device applications.

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