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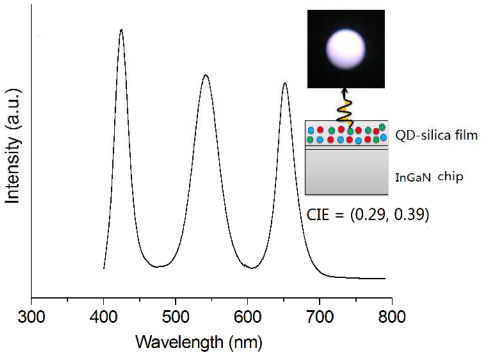

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ARTICLE

Magic sol-gel silica films encapsulating hydrophobic and hydrophilic quantum dots for white-light-emission

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A sol-gel SiO_2 film prepared from 3-aminopropyltrimethoxysilane (APS) has been developed as an excellent medium to encapsulate both hydrophobic and hydrophilic quantum dots (QDs). The film was fabricated by spin and dipping coating on flat substrates as well as by a spraying approach on various substrates with 3-dimensional (3D) surface. Pre-heat-treatment of the substrate plays an important role for creating homogeneous films on a 3D surface. In the case of aqueous CdTe and $ZnSe_{0.9}Te_{0.1}$ QDs, APS did not decrease photoluminescence (PL) efficiency of the QDs. For hydrophobic QDs, a phase transfer from oil to water phase was first performed through the ligand exchange process between APS and the capping agent. By mixing QDs with different emitting colors, silica gel with white-light emission was obtained. Based on hydrophobic and hydrophilic QDs, the white-light-emitting diodes with adjustable chromaticity coordinates were fabricated using a UV-emitting InGaN chip as excitation source. Because of facile preparation procedure, high stability, and high PL efficiency, the magic film shows great potential for use in white-lighting-emission applications.

Introduction

In recent year, increasingly serious energy crisis have drawn much attention, which triggered tremendous interest to develop various materials for illuminance and luminescence devices. Thin films have numerous electrical, optical, and wear-resistant applications. Especially, functional thin films can be tailored for various applications in energy conversion processes (solar cell coatings), window coatings, or greenhouses for heat and sunlight control. Because of the interesting properties of quantum dots (QDs) including the tunability of the energy of the electronic levels, control over the photoluminescence (PL) color and yield, carrier multiplication, and chemical flexibility,[1, 2] Thin films with QDs are attractive and have been studied during the last decade because of their potential applications in many areas of technological importance, such as photonic crystals, light-emitting devices, and biological labels.[3, 4] Colloidal QD solutions are stabilized due to a layer of ligands on the surface. The ligands passivate the surface dangling bonds, which can act as traps for electrons and holes. High fluorescence quantum yields can be achieved by modifying the surface of the QDs in solutions. However, the ligands may be removed during the preparation of thin films, in which the fluorescence quantum yields of the QDs in the films decreased. Therefore, it is urged to develop a thin film for incorporating QDs that can keep their high fluorescence efficiency.

Various techniques are applied to prepare films with QDs, including layer by layer assembly, physical vapour deposition, chemical vapour deposition, covalent attachment of polymers, and sol-gel processes etc.[5] Thin films created via the immobilization of organic polymers on substrates have widespread applications in areas including biosensing assemblies, biomedical devices, and light-emitting diodes.[6] Organic polymers are chemically compatible with the organics-capped QDs, but suffer from UV sensitivity and limited thermal range.[7] The poor thermal conductivity of such organic films limits their applications. Therefore, matrices incorporated QDs provide platforms with high optical quality and improved thermal resilience that can be integrated into optical devices. Sol-gel derived metal oxide films have been exploited as optical gain media, exhibiting tunable amplified spontaneous emission. Because of ideal mechanical properties and chemical and thermal stability, sol-gel silica films are great interest for optical applications.[8]

The sol-gel method is an emerging route with high promise for very homogeneous films at molecular scale and control of chemical purity, which can form at relatively low temperatures.[9-12] Silica films have advantage in various applications because of the stability. Mulvaney's group prepared luminescent silica gel using hydrolysis-condensation reaction of silicon alkoxide ($Si(OR)_4$) in alcoholic solutions.[13] The sol-gel process makes functional QDs homogeneous dispersion in the films. In addition, the composition of sol-gel matrices can be adjusted at a molecular level. Murase's group introduced Zr into the glass network of silica to derived $Si_{1-x}Zr_xO_2$ glass with high PL efficiency.[14] Rare research focused on hydrophobic QDs embedded in sol-gel matrices. Sol-gel silica gel is normally obtained using hydrolysis-condensation reaction of silicon alkoxide ($Si(OR)_4$) in alcoholic solutions. The hydrolysis and condensation of silane agents are complex and difficult to control. Traditional sol-gel matrix can be fabricated using tetraethyl orthosilicate (TEOS). The hydrolysis of TEOS occurs in an acid (e.g., HCl as a catalyst) or alkaline (e.g., ammonia as a catalyst). These catalysts result in the decrease of PL efficiency or PL quenching of the QDs. Namely, it is difficult to prepare large crack-free film for traditional sol-gel materials because of a condensation process with large shrinkage. To extend the application of QDs in thin film devices, it is important to develop novel strategies for films with QDs. 3-aminopropyltrimethoxysilane (APS) has relatively slow hydrolysis and gentle condensation due to its aminopropyl group in the silica network and thus results in a smaller shrinkage.

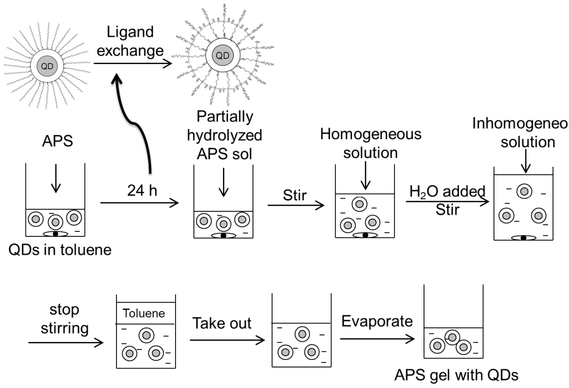
Significant progress has been reported in fabricating silica films with hydrophilic CdTe QDs using APS in our previous research.[5] Because of the properties of silica sol created using APS, the sol is ideal for preparing thin films on flat substrates by the simple coating methods such as dipping, spinning, or spraying. However, no literature reported on such film encapsulating hydrophobic QDs. Compared with hydrophilic QDs such as CdTe QDs, hydrophobic QDs, especially CdSe-based QDs, revealed high stability and great PL properties.[15] However, organic QDs prepared at high-temperature are not compatible to directly encapsulate sol-gel films due to their hydrophobic properties. So ligand exchange is often required for the introduction of surface functionality to the QDs, in which the PL properties were deteriorated during incorporation. It is still desirable to create highly luminescent sol-gel films with various QDs to study their properties for applications.

In this article, we described a novel method for preparing optically transparent, crack-free and luminescent sol-gel silica films using a silane coupling agent (APS) as a precursor. Hydrophilic and hydrophobic QDs embedded in the sol-gel film preserved high PL efficiencies. In particular, a direct ligand exchange by APS molecules was used for the incorporation of hydrophobic QDs. The substrates with various morphologies such as bulb, bottle, and ball were coated with these films by spinning, dipping, and spraying coating. The white-light-emitting diodes were fabricated using a UV InGaN chip (a PL peak of less than 400 nm) as the excitation source. The Commission Internationale de L'Eclairage chromaticity (CIE) coordinates are easily adjusted through changing the amount of QDs with different emitting color. Because the film revealed high PL efficiency, it is utilizable in white-light-emitting. This film also can be used for encapsulating other functional nanoparticles such as magnetic and noble metal for various applications due to facile preparation procedure and high stability.

Experimental

The pure water obtained from a Milli-Q synthesis system (ρ ~ 18 MΩ·cm^{-1}) was used for all experiments. The chemicals were of analytical grade and used directly without any further purification unless otherwise stated. Methods of preparations of hydrophobic CdSe/$Cd_{0.5}Zn_{0.5}S$ and hydrophilic CdTe, QDs were reported in our previous papers.[15-18] Aqueous $ZnSe_{0.9}Te_{0.1}$ QDs were fabricated using thioglycolic acid (TGA) as a capping agent. Typically, Zn precursor solutions with a PH of 6.3 were prepared by mixing $Zn(ClO_4)_2$.$6H_2O$ and TGA. After the solution was degased in N_2 for 30 min, a mixed gas of H_2Se and H_2Te was passed through it. The H_2Se and H_2Te were fabricated by reacting Al_2Se_3/Al_2Te_3 with H_2SO_4. Finally, a light irradiation was used to increase the PL efficiency of the prepared samples.

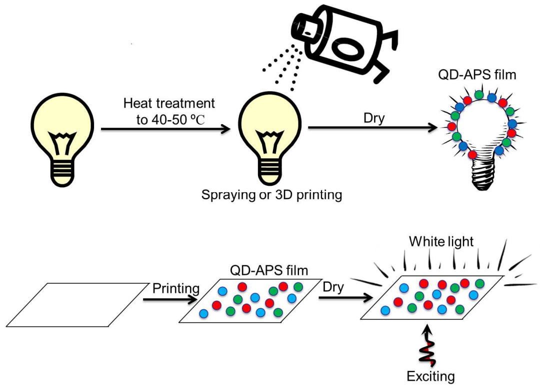
For sol-gel films encapsulating hydrophilic QDs, a precursor gel was prepared through the hydrolysis and condensation of APS. Briefly, the precursor sol of APS was obtained in a beaker with a cover by mixing APS and ethanol (molar ratio- 1:20), followed by adding 2 mL of water and stirring for 24 h at room temperature. Then, the sol was kept for 10-20 h in the atmosphere until its viscosity reached 1000-1500 mPa • s. About 1-2 mL of CdTe or $ZnSe_{0.9}Te_{0.1}$ colloidal solution was added into the above APS gel. The mixture was stirred and kept in a clean room for the evaporation of water that increased the viscosity.



Scheme 1. Preparation procedure of QD-silica gel.

For hydrophobic CdSe/$Cd_{0.5}Zn_{0.5}S$ QDs, a ligand exchange process was first performed. Scheme 1 illustrates the preparation procedures of ligand exchange of hydrophobic QDs and QD-silica gel. Typically, 2 μL of APS was added in the QD solution with stirring for 24 h to produce APS-capped QDs. The pre-hydrolyzed APS sol was prepared by mixing APS and water with a molar ratio of 1 : 2 in ethanol with stirring for 24 h. the sol was kept in clean room for evaporating ethanol. Note that ethanol must be removed in order to retain a high PL efficiency of QDs. The pre-hydrolyzed APS sol was added into the APS-coated QD toluene solution with stirring for 10 h to obtain a clear solution. Water was then added in the solution with vigorous stirring for 20 h. Being stopped stirring, the solution was into two layers (toluene and aqueous solution). All QDs and APS sol was transferred into the water phase, which was then taken and kept in the clean room for the removal of solvents to obtain QD-silica gel.

Acetone, ethanol, and de-ionized water were used to clean substrates. The dried substrates were coated with QD-silica films. The flat substrates were coated by dipping and spin coating. The substrates with special morphologies (e.g., bulb, ball, and bottle) were coated by a spraying route through a pre-heat-treatment of the substrates. The preparation of white-light-emitting diodes was carried out by coating a QD-silica film on an InGaN light-emitting diode (LED) chip. Scheme 2 illustrates the preparation process.



Scheme 2. Preparation procedure of sol-gel films with emitting QDs (upper part, substrate with a 3D surface. Lower part, flat substrate)

Optical absorption and PL spectra of samples were recorded using conventional spectrometers, Hitachi U-4100 and F-4600, respectively. The PL efficiency was estimated by comparing samples with Rhodamine 6G in ethanol (PL efficiency ~ 95%) at room temperature.[16, 17] Transmission electron microscope (TEM, JEM-100CX) was used to observe the size and morphology of the samples.

Result and Discussion

Figure 1 shows the PL spectra of green- and red-emitting CdTe QDs prepared using TGA as a capping agent. The PL peak wavelength of green- and red-emitting CdTe QDs are 541 and 650 nm, respectively. The PL properties of the QDs are summarized in Table 1. The red QDs revealed a high PL efficiency (65%) while that of green ones is 24%. This is ascribed to the CdS-like layer formed on the surface because of a long reflux time (more than 2 days). The CdS-like layer formed by Cd^{2+} and S^{2-} ions generated by the decomposition of TGA. Figure 2b shows a PL spectrum of aqueous $ZnSe_{0.9}Te_{0.1}$ QDs using TGA as capping agent. The PL peak wavelength and full width at half maximum (FWHM) of the QDs is 425 and 23 nm, respectively. The PL efficiency of the QDs after irradiation is 21% as shown in Table 1.

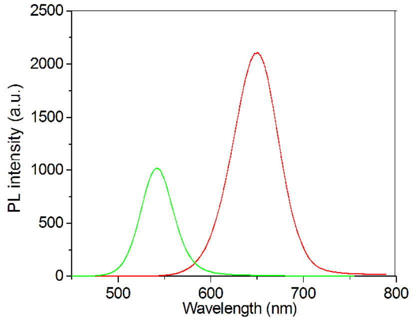


Figure 1. PL spectra of hydrophilic green- and red-emitting CdTe QDs.

Table 1 PL properties of hydrophilic and hydrophobic QDs*

Sample	QDs	PL peak wavelength (nm)	Average diameter (nm)	FWHM (nm)	PL efficiency (%)
1	CdTe	541	2.8	41	24
2	CdTe	650	3.9	58	65
3	$CdSe/Cd_{0.5}Zn_{0.5}S$	589	6.8	26	80
4	$CdSe/Cd_{0.5}Zn_{0.5}S$	652	10.2	28	75
5	$ZnSe_{0.9}Te_{0.1}$	425	4.0	23	21

*CdTe and $ZnSe_{0.9}Te_{0.1}$ QDs are hydrophilic. $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs is hydrophobic.

Hydrophilic $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs with two different sizes were fabricated through adjusting preparation conditions using an organic synthesis at a high temperature (e.g., 300 ºC). Figure 2a shows absorption and PL spectra of hydrophilic $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs. The PL peak wavelengths of QD 3 and QD 4 are 589 and 652 nm, respectively. The QDs revealed narrow PL spectra (FWHM ~ 26 and 28 nm) and high PL efficiencies (~ 80% and 75 %) as shown in Table 1. This is ascribed to the $Cd_{0.5}Zn_{0.5}S$ alloy shell. Because CdSe/CdS QDs have less lattice mismatch (~3.9%) than that of CdSe/ZnS QDs (~12%),[15] the alloy shell can improve the QD stability due to smaller lattice mismatch between CdS and ZnS, though it may also cause some leakage of charge carriers.

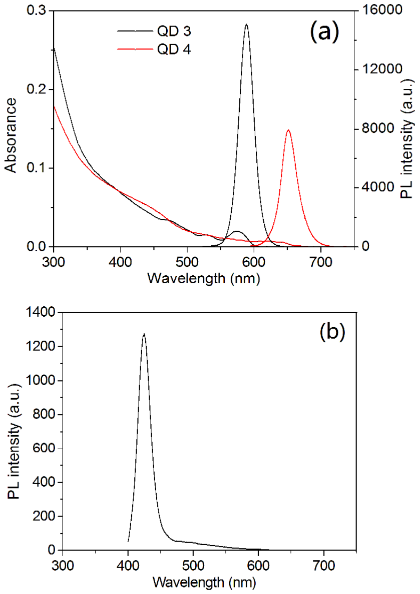


Figure 2. (a) Absorption and PL spectra of hydrophilic $CdSe/Cd_{0.5}ZnS$ QDs (QD 3 and QD 4). (b) PL spectrum of QD 5.

Figure 3 shows the transmission electron microscopy (TEM) images of QD 1 and QD 4, (a) QD 1 (green-emitting aqueous CdTe QDs) and (b) QD 4 (red-emitting hydrophobic $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs). Well-defined lattice fringes were observed in the images. The average diameters of QD 1 and QD 4 are 2.8 and 10.2 nm, respectively. Compared with green-emitting CdTe QDs (QD 1), red-emitting $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs (QD 4) have a narrower size distribution and higher crystallinity, which is ascribed to their high synthetic temperature.

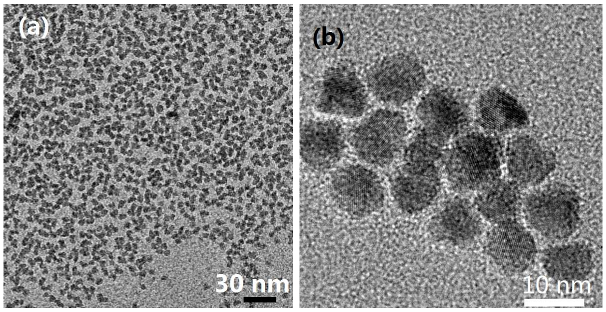


Figure 3. TEM images of QD 1 and QD 4. (a), QD 1 (green-emitting aqueous CdTe QDs). (b), QD 4 (red-emitting hydrophobic $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs).

A multiple step sol-gel process was developed to encapsulate QDs in silica sol. Because the hydrolysis time of APS in ethanol was long, the silica sol needed to be prepared in advanced to avoid the surface deterioration of the QDs in the process. Such deterioration can decrease the PL efficiency of the QDs. For aqueous QDs, the colloidal solution of the QDs was first precipitated for the removal of the ligand in solution. The precipitated QD solution was added into the silica sol. In this case, the QDs were well dispersed in the silica molecular network and the aggregation of the QDs could be prevented. For hydrophobic $CdSe/Cd_{0.5}Zn_{0.5}S$ QDs, the ligand exchange process is shown in Scheme 1. When APS was added in the QDs toluene solution, the amino group of APS can attach to the surface of the QDs to replace the initial ligand. After that, the partially hydrolyzed APS sol was added. Because of the hydrolysis and condensation of APS molecules, the hydrophobic QDs were transferred into the water phase. The viscosity of the APS sol was adjusted for the preparation of films.

Table 2. PL properties of sol-gel films with QDs

Sample	QDs used	PL peak wavelength (nm)	FWHM (nm)	PL efficiency (%)
1	CdTe	539	40	20
2	CdTe	650	58	65
3	CdSe/$Cd_{0.5}Zn_{0.5}S$	589	26	40
4	CdSe/$Cd_{0.5}Zn_{0.5}S$	652	28	55
5	$ZnSe_{0.9}Te_{0.1}$	428	25	18

To investigate the PL properties of QDs in films, sol-gel silica films were prepared by spin coating (3000 rpm) with APS gel containing CdTe, $ZnSe_{0.9}Te_{0.1}$, or CdSe/$Cd_{0.5}Zn_{0.5}S$ on a glass substrate. Table 2 shows the PL data of the films. These samples retained their initial PL properties for half year in air. The PL peak wavelength of green-emitting CdTe (QD 1) exhibited a small blue shift (~ 2 nm) in the film. This is ascribed to a partial removal of the ligand (TGA) on the QDs during the preparation. In contrast, red-emitting CdTe QDs retain their PL properties including PL peak wavelength, PL efficiency, and FWHM in the film, which is ascribed to the CdSe-like layer on the QDs due to a long reflux time in the synthesis (2 days). The CdS layer was formed by Cd^{2+} and S^{2-} ions generated from the decomposition of TGA during reflux. On the other hand, $ZnSe_{0.9}Te_{0.1}$ QDs in the film exhibited red-shifted PL peak wavelength (~ 3 nm), decreased PL efficiency (~ 18%), and broad FWHM (25 nm). As for hydrophobic CdSe/$Cd_{0.5}Zn_{0.5}S$ QDs, The PL peak wavelength and FWHM remained unchanged. However, their PL efficiencies decreased (40, and 50 % for QD 3 and QD 4, respectively). This is due to the phase transfer process from oil phase to water one. Although the PL efficiency of the QDs in films decreased, the PL efficiencies reported here are still high compared with those reported in literature.[19]

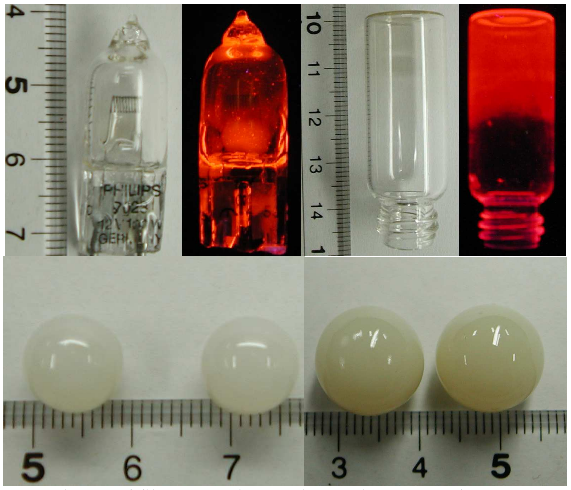


Figure 4. Photos of films coated on various substrates under 365 nm UV light (red-emitting) and room light.

A novel method has been developed to prepare silica film on 3-dementional surface such as bottle, bulb, and ball. Scheme 2 shows the preparation procedure. Pre-heat-treatment of the substrates plays an important role to obtain homogeneous films. The substrates were pre-heated to 40-50 ºC, followed by coating APS-QDs gel on them, where the solvent was slowly evaporated to form a film on the substrate surface. Such low temperature did not affect the PL efficiency of the QDs during the coating process. Figure 4 shows photos of samples under UV light and room light. The bulb, bottle, as well as nylon and polystyrene beads were coated with silica film incorporating CdTe QDs. Homogeneous film was coated on the matrix. The bright PL was observed. As a result, the film can be applied to encapsulate other functional micro- and nano-particles. Fig. 5 shows the TEM image of sol-gel film with CdTe QDs (sample 2). The QDs were uniformly dispersed in the film without aggregation. Other samples have a similar situation to sample 2.

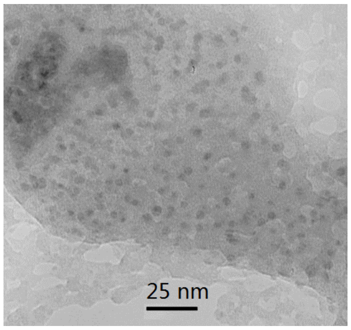


Figure 5. TEM image of sol-gel film incorporating CdTe QDs (sample 2).

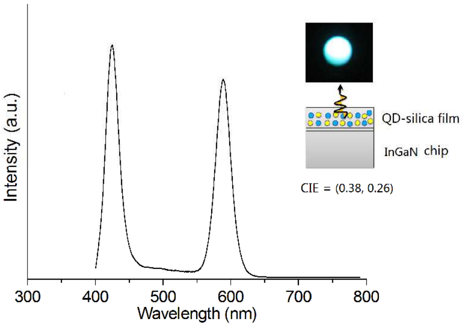


Figure 6. Emission spectrum of two-band white LED device consisted of an InGaN chip and CdTe–$ZnSe_{0.9}Te_{0.1}$ QDs. The inset image shows a photo (top) of the LED driven at 3.0 V/20 mA and the structure of the device (bottom). The measurement was performed using a filter of 390 nm.

To investigate application of highly luminescent QD-silica films, QD-silica gel was coated onto an InGaN chip to fabricate a QD-phosphor-converted white LED. In order to obtain white light, QDs with two (blue- and yellow-emitting) or three (blue-, green-, and red-emitting) colors or size distributions were mixed for creating white light. We can simply mix aqueous multiple color QDs such as CdTe and ZnSeTe to obtain thin film with high quality. Moreover, hydrophobic QDs can also be mixed with aqueous QDs after ligand exchange. For example, figure 5 shows an emission spectrum of a two-band white LED using dual-emitting QDs. The CIE-1931 chromaticity coordinates are estimated to be (0.38, 0.26), however, the colour-rendering-index (CRI) is low (< 10) because of lacking green emission (~ 500 nm). Fig. 6 shows a spectrum a three-band blue-green-red white LED device using triple-emitting QDs as phosphors. The CIE coordinates and CRI values are (0.29, 0.39) and 45, respectively. As a result, it is possible to use the mixture of blue-, green-, and red-emitting QDs as phosphors in white LEDs.

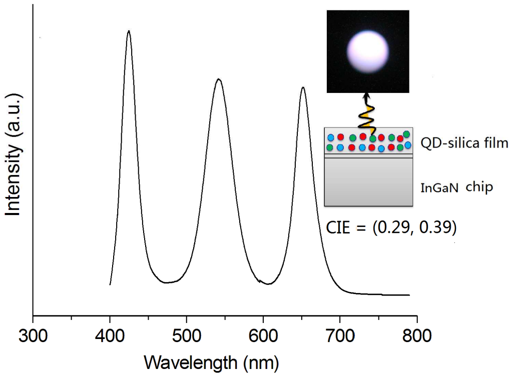


Figure 7. Emission spectrum of three-band white LED device consisted of InGaN chip, CdTe, CdSeCd$_{0.5}$Zn$_{0.5}$S, and ZnSe$_{0.9}$Te$_{0.1}$ QDs. The top part in the inset image shows a photo of the LED driven at 3.0 V/20 mA and the bottom part shows the structure of the device. The measurement was performed using a filter of 390 nm.

Conclusions

We have developed luminescent QD-silica films and approach to coating films on 3-demensional substrates including bulb, bottle, and balls. The silica matrix was prepared from the hydrolysis of APS. The film revealed high stability against harmful environment. A multiple step sol-gel process was developed to encapsulate various QDs including aqueous CdTe and ZnSeTe QDs as well as hydrophobic CdSe/Cd$_{0.5}$Zn$_{0.5}$S QDs in a sol-gel silica matrix. The red-emitting CdTe QDs retained their initial PL efficiency because of the amino group in APS can attach with carboxyl group on the QDs, in which surface ligands on the QDs were retained in the film. As for hydrophobic QDs, a phase transfer of the QDs firstly occurred through the ligand exchange between APS and capping agent of the QDs. By mixing QDs with different emitting colors, white-light emitted APS gel was obtained. Based on hydrophobic and hydrophilic QDs, the white-light-emitting diodes were fabricated using a UV emitting InGaN chip as the excitation source. Three-band red–green–blue WLED with CIE-1931 coordinates (0.29, 0.39) was successfully assembled by using a UV InGaN chip, blue-, green-, and red-emitting QDs-silica phosphors. Because of facile preparation procedure, high stability, and high PL efficiency, these magic silica films show a great potential for use in white lighting applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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