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White light-emitting diodes using thermally and photochemically stable fluorescent silica nanoparticles as color-converters†

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Trialkoxysilyl terminal groups were directly introduced into fluorescent organic dye molecules by consecutive allylation and hydrosilation reactions; the derivatized dye molecules were then successfully embedded into silica nanoparticles by the Stöber method. Those fluorescent silica nanoparticles (FSNPs) had emission colors corresponding to each fluorescent organic dye used (yellowish-green and red) and showed excellent thermal and photochemical stabilities. A white light-emitting diode (WLED) was fabricated by combining the FSNP/silicone encapsulant composite incorporated with FSNPs having yellowish-green and red emission with a blue InGaN LED (BLED). The resulting three-color RGB FSNP-LED exhibited a good color rendering index (CRI), Ra 86.7, at the correlated color temperature of 5452.6 K and CIE coordinates of (0.3334, 0.3360), indicating that the combination of highly fluorescent silica nanoparticles with LEDs can offer a promising solution for white light sources with high color rendering properties.

Introduction

Approximately 20% of global energy consumption is used for the production of light.[1] Increasing energy demands along with mounting concerns of global warming and climate change have placed an enormous emphasis on the exploration of high-efficiency light sources to reduce energy consumption.[2–4] Solid-state lighting devices such as light-emitting diodes (LEDs) are the most promising alternative, because they provide high luminescence efficiencies, quick response times, long lifetimes and high mechanical stabilities.[5,6] Currently, white LEDs (WLEDs) have attracted a great deal of attention as their commercialization continues to expand to high-volume applications, including general lighting and liquid crystal displays (LCDs) of digital cameras, cellular phones, and monitors of notebook computers.[7,8]

Although red, green, and blue emissions are commonly mixed together to generate white light, this can also be achieved by simply adding blue to yellow light. In recent years, the most popular commercial WLEDs are based on a blue InGaN LED chip with a yellow-emitting phosphor of cerium-doped yttrium aluminum garnet (YAG:Ce^{3+}). The ubiquity of YAG:Ce^{3+} phosphors in commercial devices is attributed to their simpler and more cost-effective fabrication as well as their long term stability, which is attributed to the high melting point, high hardness, and stable thermal and chemical properties.[9,10] However, YAG:Ce-based WLEDs have a low color rendering index (CRI) because of their lack of color in the red region. In an attempt to improve color rendering properties, green-emitting $SrGa_2S_4:Eu^{2+}$ or green-emitting α-sialon:Yb^{2+} phosphors have been mixed with red-emitting $Ca_{1-x}Sr_xS:Eu^{2+}$ or red-emitting $Sr_2Si_5N_8:Eu^{2+}$ phosphors respectively.[11,12] Unfortunately, sulfide phosphors are thermally and chemically unstable and tend to reach luminescence saturation with increasing applied current when incorporated into WLEDs.[11,13] With respect to nitride phosphors, extreme preparation conditions, including high temperature and high nitrogen pressures, are required.[12,14,15] Moreover, the phosphors commonly exhibit fluorescence reabsorption and non-uniformity of luminescent properties, resulting in the loss of luminous efficiency and time-dependent shift of color point.[16]

With this background in mind, organic luminescence converters are attractive alternatives because of their broad absorption and emission, moderate price, and ease of fabrication. There have been attempts to use organic luminescence converters for LED applications,[17–19] but there are concerns over their stability.[20] In order to create more robust emitters, researchers have developed hybrid organic/inorganic nanoparticles from organic dye molecules and amorphous silica. As a matrix material, silica provides chemical and mechanical stability, which can protect the encapsulated dye molecules from external perturbations, while exposing a hydrophilic and easily functionalized surface to the environment, in some cases enhancing the photophysical properties of the encapsulated dyes.[21–23]

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† Electronic supplementary information (ESI) available: Reaction conditions for size-controlled FSNPs, photographs of various mixed conditions of FSNPs with silicone polymer in acetone solvent, and SEM images of the cross-sectioned area of the FSNP/silicone polymer composite. See DOI: 10.1039/c3tc30967c

In this study, we report the synthesis of yellowish-green and red emitting fluorescent organic dye molecules, by facile derivatization of pigment red 254 and rhodamine B with trimethoxysilane through a consecutive allylation and hydrosilation reaction sequence. These derivatized fluorescent dye molecules were successfully incorporated into silica nanoparticles through the Stöber method, with the resultant fluorescent silica nanoparticles (FSNPs) denoted as SiO_2(PR254H) and SiO_2(RhBH), respectively. The two different types of FSNPs showed the similar optical properties of parent dye molecules. We also fabricated homogeneous FSNP/silicone polymer composites by dispersing the FSNPs into an acetone solvent and mixing in silicone polymer as the encapsulating material, followed by solvent removal under vacuum. Moreover, a white light emitting FSNP-based LED was fabricated by combining FSNP/silicone polymer composites, incorporated with yellowish-green and red emitting FSNPs, with a blue InGaN LED. The resulting three-band RGB FSNP-based WLEDs showed good performances, suggesting that the combination of highly fluorescent FSNPs with LEDs can offer a promising solution for the manufacturing of white light sources with high color rendering properties.

Experimental

Materials

Rhodamine B, allyl iodide, allyl bromide, cesium carbonate (Cs_2CO_3), potassium carbonate (K_2CO_3), chloroform, trimethoxysilane ($HSi(OMe)_3$), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt(dvs)), and *N*,*N*-dimethylformamide (DMF) were purchased from Aldrich. Pigment red 254 and TEOS (tetraethyl orthosilicate) were purchased from TCI. Ethanol (EtOH) was purchased from J. T. Baker. $CDCl_3$ was purchased from Cambridge Isotope Laboratories for use as an NMR solvent. Dichloromethane (CH_2Cl_2), magnesium sulfate ($MgSO_4$), methanol and ammonium hydroxide solution (NH_4OH) were purchased from Samchun Chemical Co. All organic solvents were used without any further purification. SMD 5050 blue LED chip was purchased from ENTEC L&E Ltd. OE-6560 A/B kit (optical encapsulant) was purchased from Dow Corning Korea Ltd.

Synthesis of 2,5-diallyl-3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (PR254A)

PR254A was prepared following a procedure similar to that previously reported.[24] Pigment red 254 (86 mg, 0.24 mmol) and K_2CO_3 (350 mg, 2.5 mmol) were added to DMF (8 mL). After heating to 130 °C under N_2 atmosphere, a solution of allyl bromide (0.23 mL, 2.8 mmol) in DMF (2 mL) was added dropwise and stirred for 5 h at 130 °C. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 and water. The mixture was extracted with CH_2Cl_2 and washed sequentially with brine (2×) and water. The organic layer was dried over $MgSO_4$, filtered, and solvent was removed *in vacuo*. The residue was purified by column chromatography (SiO_2, eluent: CH_2Cl_2) to afford 58 mg of orange powder in 56% yield. ^1H NMR (500 MHz, $CDCl_3$): δ ppm 4.29 (m, 4H), 5.14 (d, 2H), 5.20 (d, 2H), 5.88 (m, 2H), 7.41 (d, 4H), 7.80 (d, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ ppm 162.2, 147.7, 137.7, 133.2, 130.3, 129.3, 126.1, 117.0, 109.6, 44.4. Anal. found: C, 66.02; H, 4.88; N, 5.95%. Calcd for $C_{24}H_{18}Cl_2N_2O_2$: C, 65.91; H, 4.15; N, 6.41%.

Synthesis of 3,6-bis(4-chlorophenyl)-2,5-bis(3-(trimethoxysilyl)-propyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (PR254H)

PR254A (35 mg, 0.08 mmol) was dissolved in anhydrous $CHCl_3$ (5 mL), followed by the addition of $HSi(OMe)_3$ (0.04 mL, 0.32 mmol) and a catalytic amount of Pt(dvs). The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the mixture was immediately filtered through a Celite pad. Solvent and excess $HSi(OMe)_3$ were removed *in vacuo*. PR254H was obtained as orange sticky oil (46 mg, 85%). This compound was used for the next reaction immediately after the confirmation of the disappearance of the allyl moiety in PR254A by NMR.

Synthesis of (9-(2-((allyloxy)carbonyl)phenyl)-6-(diethylamino)-3-xanthenylidene)diethylammonium chloride (RhBA)

RhBA was prepared according to a previous report.[23] Rhodamine B (0.5 g, 1.04 mmol), allyl iodide (0.54 g, 3.12 mmol), and Cs_2CO_3 (1.02 g, 3.12 mmol) were added in 30 mL of DMF, and the mixture was stirred at 60 °C for 1 day. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 and washed with water (3×). The CH_2Cl_2 layer was collected and concentrated *in vacuo*, followed by further drying under vacuum. A dark reddish powder (0.481 g, 88.8%) was isolated by column chromatography (SiO_2, eluent: CH_2Cl_2/MeOH = 10/1). ^1H NMR (500 MHz, $CDCl_3$): δ ppm 8.31 (d, 1H), 7.82 (tt, 2H), 7.34 (d, 1H), 7.10 (d, 2H), 6.93 (dd, 2H), 6.80 (d, 2H), 5.70 (m, 1H), 5.20 (dd, 2H), 4.53 (d, 2H), 3.68 (q, 8H), 1.34 (t, 12H). ^{13}C NMR (500 MHz, $CDCl_3$): δ ppm 164.61, 158.62, 157.65, 155.45, 133.48, 133.20, 131.28, 131.19, 131.04, 130.41, 130.18, 129.81, 119.04, 114.30, 113.43, 96.21, 66.02, 46.23, 12.70. HR-MS(FAB+) Calcd for 483.2642 *m*/*z*, Obsd for 483.2640 *m*/*z*.

Synthesis of (6-(diethylamino)-9-(2-((3-(trimethoxysilyl)-propoxy)carbonyl)phenyl)-3-xanthenylidene)diethylammonium chloride (RhBH)

RhBA (35 mg, 0.07 mmol) was dissolved in anhydrous $CHCl_3$ (5 mL), followed by the addition of $HSi(OMe)_3$ (0.04 mL, 0.28 mmol) and a catalytic amount of Pt(dvs). The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the mixture was immediately filtered through a Celite pad. Solvent and excess $HSi(OMe)_3$ were removed *in vacuo*. RhBH was obtained as orange sticky oil (33 mg, 81%). This compound was used for the next reaction immediately after the confirmation of the disappearance of the allyl moiety in RhBA by NMR.

General method for synthesizing fluorescent silica nanoparticles

The modified fluorescent dye molecules were dissolved in EtOH and H_2O, followed by the sequential addition of NH_4OH and TEOS (solution compositions are found in Table S1†). The mixture was stirred at 400 rpm for 12 h at room temperature. The mixture was centrifuged and the precipitate was redispersed in EtOH, followed by centrifugation. This reprecipitation–redispersion procedure was repeated three more times. The sizes of fluorescent silica nanoparticles were controlled by varying the amounts of TEOS, H_2O, and NH_4OH.

Fabrication of FSNP-assisted phosphor-converted WLEDs

WLEDs were fabricated by combining InGaN based blue LEDs with as-synthesized FSNPs and OE-6560 resin. The FSNPs were dispersed in acetone to avoid aggregation after mixing with OE-6560B resin. The mixture solution was blended by vortex mixing for 15 min until the mixture became transparent. Next, the acetone was removed *in vacuo*. The mixture of FSNPs and OE-6560B resin was further mixed with the OE-6560A resin at a weight ratio of 1 : 3 (OE-6560A:OE-6560B). The mixture was well-stirred until it became homogeneous. The mixture was dropped on a BLED and heated in a vacuum oven at 80 °C for 30 min and finally at 170 °C for 90 min.

Photostability test

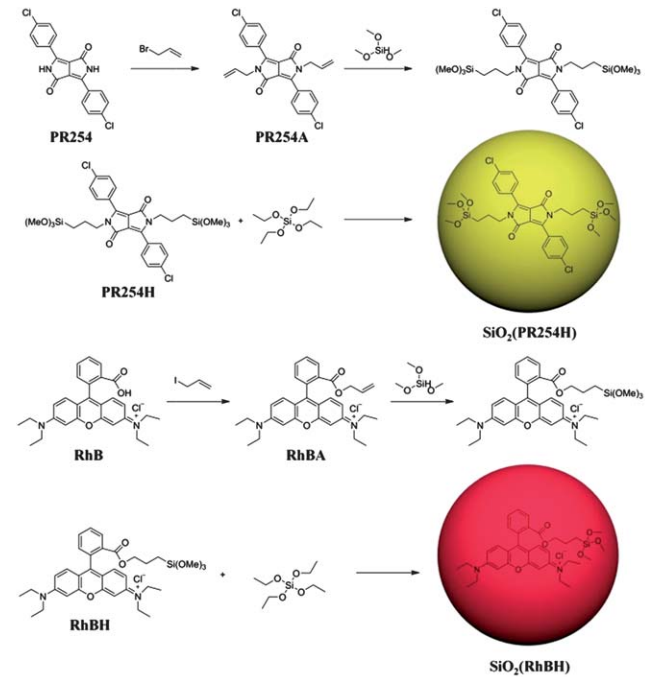
PR254A, RhBA, SiO_2(PR254H), and SiO_2(RhBH) were dissolved in various amounts of EtOH such that all solutions possessed the same UV absorbance. Samples were exposed to UV light under a Tungsten-Halogen lamp (200 W, PHILIPS) with a light intensity of 757 mW cm^{-2}. Emission spectra for all samples were taken after appropriate illumination times.

Characterizations

The absorption and emission of fluorescent organic dye molecules and FSNPs were measured by UV-Vis spectrometry (Sinco, S-3100) and fluorophotometry (JASCO, FP-6500), respectively, at room temperature. The synthetic dye was characterized by ^{1}H- and ^{13}C-NMR (Varian NMR System 500 MHz), mass spectrometry (JEOL, JMS-AX505WA), and elemental analysis (CE Instrument, Flash2000). The size and shape of silica nanoparticles were characterized by transmission electron microscopy (TEM) (Hitachi, H-7600). The EL spectra, the CIE chromaticity coordinates, and the CRI values of the as-fabricated FSNP-LED were collected by a quantum efficiency measurement system (QE-2000, Photal OTSUKA ELECTRONICS) at room temperature.

Results and discussions

The overall scheme for the synthesis of FSNPs is described in Scheme 1. Trialkoxysilyl terminal groups could be directly introduced into the fluorescent dye molecules by the sequential allylation and hydrosilation reactions. These allyl terminal groups in the derivative dye molecules could then be quantitatively converted into trialkoxysilyl groups by hydrosilation in the presence of catalytic Pt(dvs). Two types of modified fluorescent dye molecules were successfully incorporated into silica nanoparticles by co-condensation with TEOS in basic ethanol solution with NH_4OH (Fig. 1). The size of the FSNPs could be controlled in the range from 20 to 130 nm by varying the concentration of TEOS, water and ammonia in ethanol solution (Table S1†). The amount of incorporated RhBH and PR254H relative to TEOS in generated FSNPs could be estimated to be about 0.75 and 0.29 mol%, respectively, based on ^{29}Si-NMR and thermogravimetric analysis (TGA) data (Fig. S1 and S2 and Table S2†), which were relevant to the mixing percentage of dyes to TEOS in Table S1† (0.73 and 0.27 for RhBH and PR254H, respectively).



Scheme 1 Schematic illustration of the synthesis of FSNPs.

The photographs of modified fluorescent dye molecules (PR254A and RhBA), SiO_2(PR254H) and SiO_2(RhBH), respectively, can be clearly observed through the entire dispersion, suggesting that FSNPs can be well-dispersed in EtOH (Fig. 2a and b). The UV-vis absorption and photoluminescence spectra of the fluorescent dye molecules and FSNPs are shown in Fig. 2c and d. SiO_2(PR254H) and SiO_2(RhBH) exhibited main absorption bands at 468 nm and 561 nm, respectively. SiO_2(PR254H) had a suitable absorption range from the near-UV to the visible

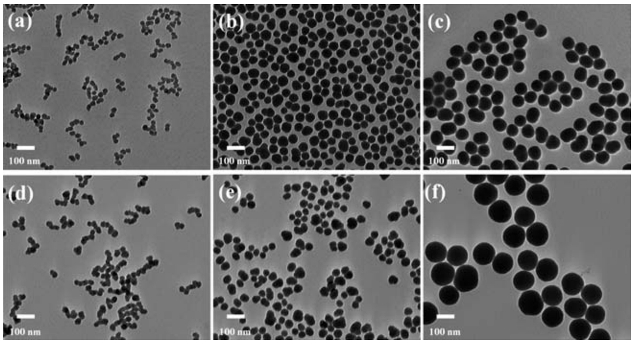


Fig. 1 TEM images of FSNPs: (a) 20 nm; (b) 50 nm; (c) 80 nm of SiO_2(PR254H); and (d) 30 nm; (e) 50 nm; (f) 130 nm of SiO_2(RhBH).

region. Generally, UV (360–410 nm) or blue light (420–480 nm) LEDs are used as light sources for WLEDs; therefore, broad absorption is an advantage of the organic dye-encapsulated silica nanoparticles. The photoluminescence maximum was red-shifted from 532 nm for PR254A to 547 nm for the SiO_2(PR254H) nanoparticle when excited at 450 nm. In the case of the SiO_2(RhBH), the maximum photoluminescence wavelength also red-shifted from 588 nm for RhBA to 601 nm for the SiO_2(RhBH) nanoparticle. The red-shift of the emission band to longer wavelengths as well as bandwidth change in PL spectra was very likely due to the difference in environmental properties such as hydrogen bonding and polarity between the solvent and silica matrix as reported in the literature.[25–28] This red emission helps wide expression and would lead to a high CRI of white emission. With excitation at 450 nm, SiO_2(PR254H) had a photo-luminescence maximum at 547 nm, which overlaps with the absorption of SiO_2(RhBH). It is expected that some of the emission energy of SiO_2(PR254H) would transfer to SiO_2(RhBH) if they are both incorporated into a system.

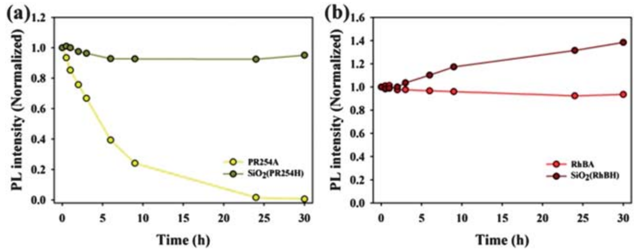


Fig. 3 (a) Photostability of fluorescent dye molecules and FSNPs as a function of light exposure time.

Fig. 3a and b show the maximum photoluminescence intensity as a function of light exposure time for photostability verification. Modified fluorescent dye molecules were subject to photobleaching in the EtOH solution by a tungsten halogen lamp excitation. The photoluminescence intensity of the PR254A decreased to approximately 50% from the initial intensity after 5 h of exposure time, indicating that the dye is discolored because of photodegradation. However, RhBA retained its photoluminescence of approximately 90% after 30 h. It is worthy to note that, owing to their excellent photostability and photophysical properties, rhodamine dyes are widely used as laser dyes, fluorescence standards (for quantum yield and polarization), pigments, and fluorescent probes.[29] In the case of the FSNPs, the photoluminescence intensity is maintained or slightly increased at the initial state. Because these dye molecules are chemically bound to the silica matrix, they cannot be easily removed by extracting with a large amount of solvent or applying sonication; furthermore they are not easily photo-bleached as reported in the literature because of the restricted movement of dye molecules after being embedded in the silica matrix.[22,23,30] These properties make fluorescent silica nanoparticles very useful for WLED applications.

To adopt FSNPs as light conversion materials in LEDs, it is necessary to homogeneously disperse FSNPs into a polymer matrix for the fabrication of FSNP/silicone polymer composites.[31] Matrix dispersion may influence the uniformity of light that is emitted from an LED device, depending on the viewing angle.[7] Therefore, the FSNPs were dispersed in acetone solvent

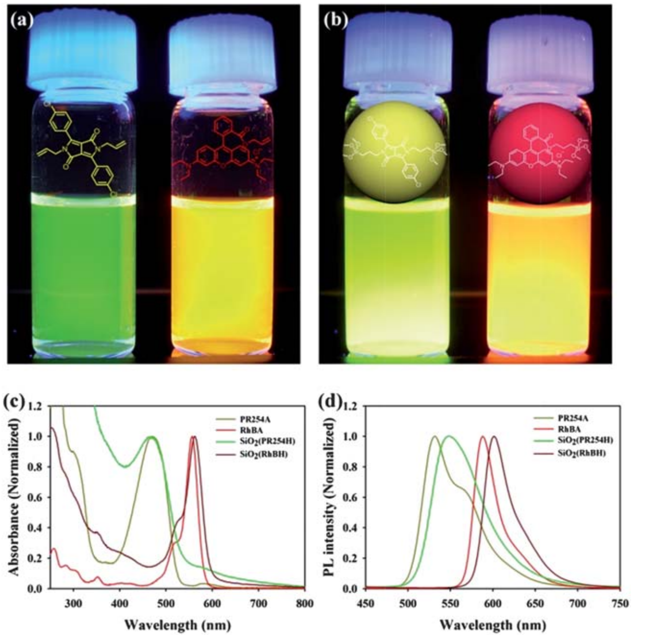


Fig. 2 (a) Photographs of red and yellowish-green fluorescent organic dye molecules and (b) FSNPs under UV excitation at 365 nm; (c) normalized UV-vis absorption; and (d) photoluminescence spectra of PR254A, RhBA, SiO_2(PR254H) and SiO_2(RhBH) in EtOH.

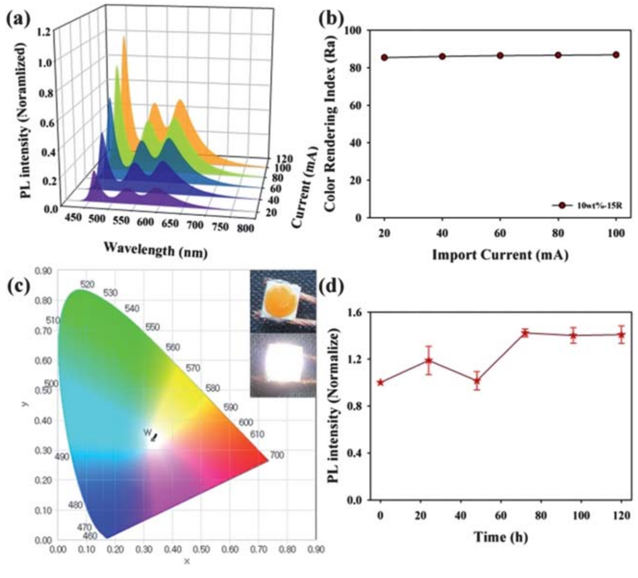


Fig. 4 (a) EL spectra and (b) CRI of the as-prepared FSNP-based WLEDs under different forward bias currents; (c) CRI of the as-prepared FSNP-based WLEDs. Insets show photographs of the as-prepared FSNP-based WLED (460 nm InGaN blue LED chip encapsulated with FSNPs (547 nm and 601 nm)/silicone polymer composite) and the FSNP-based WLED operated at 80 mA; (d) thermal stability of the FSNP/silicone polymer composite film by monitoring the photoluminescence intensity as a function of heating time at 120 °C.

and mixed with a silicone polymer instead of a dry FSNP powder to prevent aggregation of nanoparticles (Fig. S3 and S4†). These composites were applied as light conversion materials onto a blue InGaN LED. Fig. 4c inset shows photographs of the as-prepared and white light emitting FSNP-based WLEDs operated at a current of 80 mA to obtain a clear emission image of the fabricated FSNP-based WLED. Bright white light was emitted from the as-prepared FSNP-based WLED with a CRI (Ra) of 86.7 under a forward bias current of 80 mA, which is much higher than that of the YAG:Ce-based commercial WLEDs (Ra ~ 70). It also showed the Commission Internationale de l'Eclairage (CIE) color coordinates of (0.33, 0.33) and a color temperature (T_c) of 5452.6 K, corresponding to warm white light. As shown in Fig. 4b and c, the CIE coordinates and CRI of the FSNP-based WLED under different currents changed only slightly, which indicates a good PL stability of the FSNP-based WLEDs. The long-term thermal stability of the FSNP/silicone polymer composite was also investigated (Fig. 4d). It was observed that the original photoluminescence of the FSNP/silicone polymer composite was maintained and even slightly increased at 120 °C, supporting the effectiveness of FSNPs for LED application along with photochemical stability as shown in Fig. 3. The electroluminescence (EL) spectra of the as-fabricated FSNP-based WLED under different forward bias currents are shown in Fig. 4a, in which the emission peaks of the blue LED chip, the yellowish-green and red light-emitting FSNPs were located at 460 nm, 533 nm, and 594 nm, respectively. Accordingly, the RGB emission band intensities of the underlying blue LED chip can be tuned by varying the amount of FSNPs incorporated in the silicone polymer.

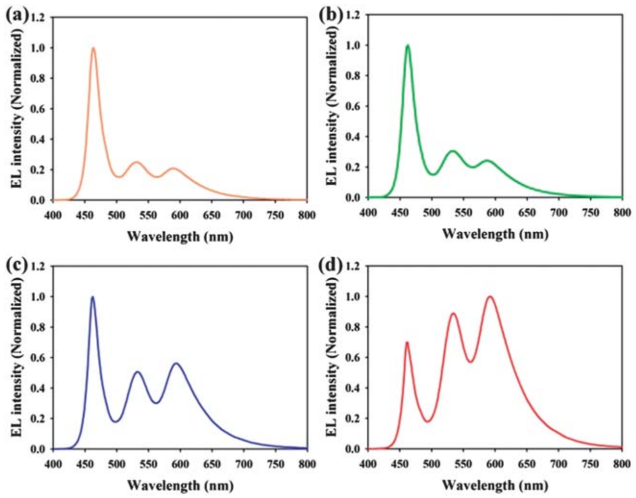


Fig. 5 EL spectra of various FSNP-based LEDs with various compositions of wt% and R/G ratios: (a) 5 wt%, R : G = 1 : 15; (b) 5 wt%, R : G = 1 : 20; (c) 10 wt%, R : G = 1 : 15, and; (d) 10 wt%, R : G = 1 : 20.

Table 1 The CIE color coordinates, color rendering index (Ra), and color temperature (T_c) of various FSNP-based WLEDs

	Weight%	R to G ratio	CIE (x, y)	Ra	T_c (K)
A	5	1 : 15	(0.2565, 0.2667)	76.5	17 042.2
B		1 : 20	(0.2658, 0.2825)	80	12 421.6
C	10	1 : 15	(0.3434, 0.3499)	85.4	5060.8
D		1 : 20	(0.4067, 0.4342)	75.5	3783.1

By controlling the concentration and the SiO_2(PR254H)/SiO_2(RhBH) ratio, various LEDs were fabricated with a CRI ranging from 75 to 85 (Fig. 5 and Table 1). In addition, the color temperature was easily tuned from 3783.1 K to 17 042.2 K and the CIE color coordinates of various FSNP-based LEDs could be easily controlled as shown in Fig. 5 and Table 1. The FSNP-based WLED was found to have a higher CRI compared to the YAG-based WLED, as the combination of SiO_2(PR254H) and SiO_2(RhBH) compensates for the poor emission of the YAG phosphor in the red and green regions. An explanation for why a large amount of SiO_2(PR254H) is required compared to SiO_2(RhBH) for white emission follows: because of the overlap of the emission band of SiO_2(PR254H) and the absorption band of SiO_2(RhBH), the green emission from SiO_2(PR254H) is reabsorbed by SiO_2(RhBH) (Fig. 2c and d, and 4a). When green and red dyes are in close enough proximity, energy transfer occurs from green to red and photoluminescence overlaps. The remaining green dyes, which are not involved in energy transfer, emit a green emission around 532 nm.

Conclusions

FSNPs, in which two types of dyes are covalently incorporated into silica nanoparticles, have been successfully synthesized using the Stöber method. The obtained nanoparticles have a broad absorption in the near-UV to blue region and a broad emission, thereby achieving wide color expression. The modified fluorescent dye molecules that are covalently attached to silica nanoparticles have better photostability and less photo-dependent photoluminescence. The FSNP/silicone polymer composite also shows excellent long term thermal stability at 120 °C. By controlling the portions of red and green species, the FSNPs exhibit broad color tunability and a high CRI for white emission from a blue LED. These results demonstrate that the fluorescent dye molecules with an appropriate structure could replace phosphors for LED applications. The described photostable FSNPs potentially allow for new WLED designs, in place of inorganic phosphor-based LEDs, for direct and simple fabrication of lighting devices with superior performance.

Acknowledgements

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