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ARTICLE TYPE

Carbon dot-doped sodium borosilicate gel glasses with emission tunability and their application in white light emitting diodes†

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Carbon dot (CD)-doped sodium borosilicate gel (CD-NBS gel) glasses were successfully prepared by incorporating the CDs into sodium borosilicate networks. The structural and luminescent properties of highly flexible CD-NBS gel glasses with 5% wt.% to 70 wt.% CDs were studied. Images of the CD-NBS gel glasses captured through a transmission electron microscope demonstrated the uniformity and good dispersibility of the glasses. Red-shifted emission and enhanced quantum efficiency were observed when the doping concentration of CD in the NBS gel glasses increased. The enhanced fluorescent properties of the CD-NBS gel glasses were considered to originate from the surface modification of CDs with high dopant concentration in the gel glasses. CD-based white light-emitting diodes (W-LEDs) were developed by combining the yellow-emitting CD-NBS gel glasses with blue GaN-based LED chips. The as-fabricated W-LEDs exhibited the optimised colour coordinate of (0.32, 0.33), the colour rendering index up to 78.9, and the maximum luminous efficacy exceeding 58.1 lm/W by the use of the CD-NBS gel glasses with different concentrations of CDs. These results indicate that the new kind of CD-NBS gel glasses would be a promising candidate for W-LEDs.

Introduction

Photoluminescent carbon dots (CDs) have received considerable attention as potential replacements for the currently used toxic metal-based semiconductor quantum dots (QDs) because of their unique properties such as high photo stability, low environmental toxicity and excellent biocompatibility.¹⁻⁴ Since their serendipitous discovery in 2004,⁵ CDs have been produced from all sorts of carbon precursors and have been used in a wide range of technologies. Moreover, the surface of CDs can easily be functionalised, thus making them useful components for various luminescent hybrids.⁶⁻⁸ Although extensive work has been conducted on their synthesis and characterisation, the doping of CDs in solid matrices is still at the early stages of development.

In applying the low-toxicity, eco-friendly CDs in real device applications, CDs should be embedded in an appropriate solid matrix or be prepared in solid-state architectures.⁷ In addition, in spite of the many efforts to tune the size and shape of CDs, preventing luminescence quenching with aggregation and controlling the uniformity as well as the emission properties of CDs remain as difficult tasks. A significant number of methods optimised for the synthesis of CDs use laser-activated ablation of grapheme sheets,⁸ plant-based materials⁹⁻¹³ and electrochemical synthesis.¹⁴ Obviously, gel glasses that can enhance the uniform size distribution of QDs are often considered good matrices for loading different nanocrystals. To date, only a few studies have reported on CDs embedded in gel glasses such as silica gel glass,⁷ silica aerogel¹⁵ and CDs fluid doped silica gel glass¹⁶. However, to the best of my knowledge, the use of sodium borosilicate (NBS)

gel glasses as embedded matrices of the CDs has not been reported. The sodium borosilicate matrix is a good host material because of the advantages of good transparency, facile preparation and designable microstructures. The research on NBS

glass as a representative low-melting glass would offer a strong potential way to achieve highly luminescent CD doped glass. Therefore, a significant amount of work is still highly needed in this area, including using stable transparency and flexible materials and finding effective strategy in practical solid state lighting.

The use of white-light-emitting diodes (W-LEDs) has been considered a promising energy-saving technique for sustainable development because of their long working lifetime, low power consumption and fast response times.¹⁷ At present, the most popular W-LEDs are based on a blue GaN chip with YAG: Ce yellow phosphor as colour converter.^{18,19} However, these W-LEDs often involve costly raw materials and high reaction temperature (> 1000 °C). Another newly developed strategy is the use of semiconductor QD-based W-LEDs with high colour rendering index (CRI). Nevertheless, the fabrication and isolation process of the QDs often involve the intrinsic toxicity and potential environmental hazards, greatly limiting their practical applications.²⁰⁻²⁴ Recently, some studies have reported on the potential application of CDs in W-LEDs²⁵⁻²⁹ because of their unique properties of being low-cost and environment-friendly. Liu et al. first fabricated electroluminescent W-LEDs by using

CDs as the emission layer and reported the CRI of 82.²⁵ Chen's and Rhee's groups demonstrated colour-conversion W-LEDs by combining LED chips with CDs phosphors and a CDs-PMMA film.²⁶⁻²⁸ More recently, Zeng et al. reported an ion-free inter-crossed carbon nanoring (IC-CNRS)-based W-LEDs with the colour coordinate at (0.28, 0.27).²⁹ Although the CD-based W-LEDs have been attempted by many groups, the use of CD solid monolithic gel directly in W-LEDs has not been reported yet. Without doubt, the best way to report their use is to achieve high quality luminescence in the solid state for fluorescent CDs and then to directly use them in W-LEDs. Therefore, developing solid monolithic materials of CD-based W-LEDs to achieve highly efficient luminescence and high stability is necessary.

In this study, CD-doped sodium borosilicate gel (CD-NBS gel) glasses were successfully prepared by incorporating the yellow CD into sodium borosilicate networks. The structural and luminescent properties of the CD-NBS gel glasses with doping concentration of 5% wt.% to 70 wt.% CD were studied using transmission electron microscope (TEM), X-ray diffraction (XRD) and steady-state and time-resolved PL spectroscopy. The CD-NBS gel glasses exhibited the highest PL quantum yield (QY) up to 78%, and the red-shifted emission increased when the doping concentration of CDs in the gel glasses. Significantly, the PL properties of the CD-NBS gel glasses with varying dopant concentrations of CD were mainly influenced by surface modification. Finally, CD-based W-LEDs were developed by combining the yellow-emitting CD-NBS gel glasses with blue GaN-based LED chips. The as-fabricated W-LEDs with the colour coordinate of (0.32, 0.33), the CRI of 78.9, and the maximum luminous efficacy exceeding 58.1lm/W were obtained by the use of the CD-NBS gel glasses with different concentrations of CDs.

Experimental Method

Materials

Anhydrous citric acid, N-(β -aminoethyl)- γ -aminopropyl methyldimethoxy silane (AEAPMS), tetraethyl orthosilicate (TEOS), boracic acid (H_3BO_3), metallic sodium (Na), 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) and all other chemicals were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). All the chemicals were of analytical grade and were used as received without any further purification.

Preparation of luminescent CDs

The CDs were synthesised according to a previous report.⁶ Briefly, 20 mL AEAPMS were placed into a three-necked flask and were degassed with nitrogen for 10 min. When the temperature reached 220 °C, 1.0 g citric acid dissolved uniformly with 4 mL ethanol was quickly injected into the solution with vigorous stirring. The mixture was kept at the temperature for 2 min, during which the solution changed from a colourless liquid to yellow and then finally dark brown clustered solid, indicating the formation of CDs.

Preparation of the CD-NBS gel glasses

The NBS glass containing CDs was prepared by the sol-gel

method. The synthetic process of stiff gel was similar to our previous work.³⁰ All the composition of the gel matrix was 5.74Na₂O-21.38B₂O₃-72.88SiO₂ (in wt.%). Sodium borosilicate system gels containing CDs were prepared using TEOS, H₃BO₃, and Na as precursors, 2-methoxyethanol and ethanol as precursor solvents, and hydrochloric acid as catalyst. Afterward, the CD ethanol solution was added to the sol. The schematic synthesis for the construction of the CD-NBS gel glasses is shown in Fig. 1. After the resultant gel glasses aged at 100 °C for 2–3 weeks, the resulting indehiscent, bright and transparent stiff gel glasses were obtained.

Preparation of W-LEDs

For the fabrication of W-LED, the blue GaN-based LED chips with the peak wavelength centred at 460 nm were used and attached to the bottom of the LED base. The two leads of the LEDs were prepared to be connected to the power supply. Afterward, epoxy resin B was mixed with the CD-NBS gel glasses dispensed on the blue GaN-based LED chip and thermally cured at 100 °C for 1 h. All the optical performances were measured using a ZWL-600 instrument with an integral sphere.

Characterisation techniques

Fluorescence spectra and PL QYs were recorded with a Horiba Jobin Yvon Fluoromax-4P spectrophotometer equipped with absolute QY measurement apparatus. For the UV/vis absorption, the UV-2450 spectrometer was used at room temperature. Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) lifetime spectroscopy system with a picosecond-pulsed diode laser (EPL-400 nm) as the single wavelength excitation light source. The TEM and high-resolution TEM (HRTEM) measurements were carried out with a FEI Tecnai F20 performing with an acceleration voltage of 200 kV. In obtaining the Fourier transform infrared (FTIR) spectra, the sample was grounded with KBr power and was measured using Bruke Equinox 55 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out using an Axi Ultra DLD spectrometer with monochrome Al K α as the excitation source. The XRD patterns were obtained using an X-ray diffract meter (Bruker D8 Advance) in the 2 θ range of 10–80° using Cu K α radiation with wavelength λ of 1.5406 Å. Nitrogen desorption isotherms and BJH pore size distribution were recorded using an ASAP 2020 specific surface area and porosity analyser. Optical properties such as CRI, chromaticity coordinates (CIE), correlated colour temperature (CCT) and luminous efficacy (LE) were evaluated using an integrating sphere (PMS-50, Everfine, China) under a forward current of 20 mA. All the measurements were carried out at room temperature.

Results and discussion

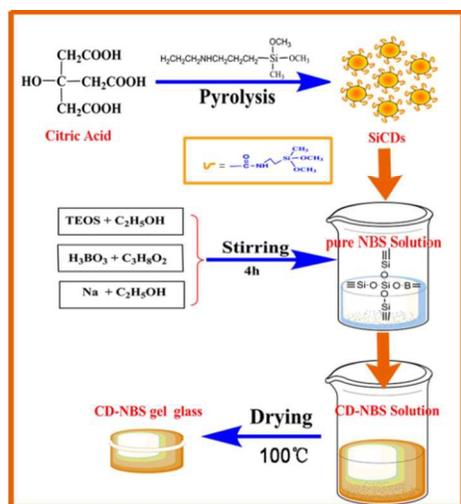


Fig. 1 Schematic of synthesis for the construction of the CD-NBS gel glasses.

The methodology for the formation of the CD-NBS gel glasses is illustrated in Fig. 1. The hydrolysis and condensation reactions of the AEAPMS capping of the CDs in ethanol leads to formation of an inorganic NBS framework with the amino groups of AEAPMS acting as basic catalysts for the sol-gel process.³¹ The doping concentration of CD in the NBS gel matrix can be easily controlled from 5% wt.% to 70 wt.% by changing the weight ratio of the CD to the NBS gel, which is several orders of magnitude larger than conventional QD composites. The colour of the CD-NBS gel glasses gradually changes from yellow to reddish brown with increasing CD content. These CD-NBS gel glasses are both highly flexible and transparent (Fig. S1†), demonstrating the successful integration of CDs into NBS gel glasses.

Characterization and optical properties of the CDs

The size and morphology of the obtained CDs under optimal synthesis conditions were characterised by TEM and HRTEM. The TEM (Fig. 2a) and HRTEM images (Fig. 2c) clearly confirm that as-prepared CDs exhibit a relatively uniform and well-dispersed spherical shape with lattice spacing of about 0.32 nm corresponding to the 002 facet of graphite. Fig. 2b shows that the aqueous dispersion of CDs, having a narrow size distribution with an average diameter of 3.15 nm (50 random nanoparticles were analysed), is consistent with that estimated from the HRTEM image. Fig. S2† shows the XRD patterns of the CDs. One broad peak is observed around $2\theta = 20^\circ$, indicating the amorphous phase of CDs as reported in the literature.^{6,32,33} The FTIR spectrum is used to identify the surface functionalisation of CDs and the structure of final CD-NBS gel glasses as shown in Fig.

S3†. Typical signals for $-\text{NH}_2$ groups at $3,450\text{ cm}^{-1}$ and the $\text{C}=\text{O}$ vibration at $1,654\text{ cm}^{-1}$ are observed in the CDs and the CD-NBS gel glasses. For the FTIR spectra of the CD-NBS gel glasses and the pure NBS gel glasses, Si-O-Si stretching ($1070\text{--}1098\text{ cm}^{-1}$), Si-CH₂ stretching (790 cm^{-1}) and Si-O-B swing symmetrically (695 cm^{-1}) bands appear in all spectra. In addition, the Si-CH₂ stretching peaks become prominent with the increasing doping concentration of CD in the NBS gel network, which implies that the number of silyl groups increased because the doping concentration of CD increased. This variation of the Si-CH₂ stretching peaks of the CD-NBS gel glasses mainly resulted from the correlation between the CDs and the NBS gel network.

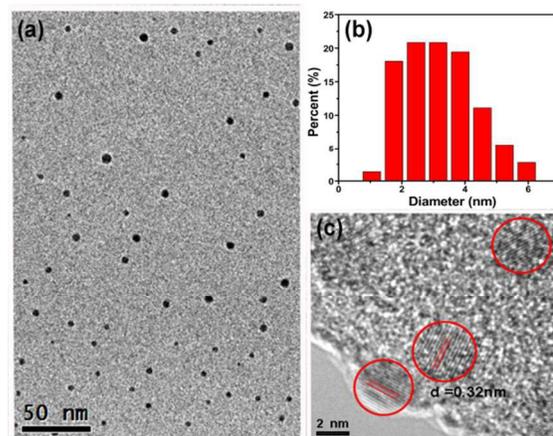


Fig. 2 The TEM image (a), diameter distribution (b) for over 50 particles, and HRTEM image (c) of prepared CDs.

Fig. 3 shows characteristic absorption peaks of as-prepared CDs centred at $\sim 260\text{ nm}$ and $\sim 360\text{ nm}$ in the UV-vis absorption spectrum, which can be assigned to the $\pi\text{-}\pi^*$ transition of the $\text{C}=\text{C}$ bonds and the $n\text{-}\pi^*$ transition of the $\text{C}=\text{O}$ bonds, respectively. The absorption spectrum is similar to that of the CDs reported previously in the literature.³²⁻³⁴ The emission peak shifting with the changing excitation wavelength (shifting fluorescence) is a common phenomenon observed in CDs.^{32,34,35} In our work, the non-shifting orange fluorescence emission peak of the CDs at $\sim 610\text{ nm}$ with increasing excitation wavelength is observed as shown in Fig. 3, whereas the PL intensity is significantly enhanced and accompanied by the remarkable narrowing of its full width at the half maximum (FWHM) from 121 nm to 105 nm. The fluorescent QY of the CDs is 43%. The surface status of CDs significantly affects the PL properties. In addition, the similar excitation wavelength-independent emissions were observed in CDs in other reports.³⁶⁻⁴⁰

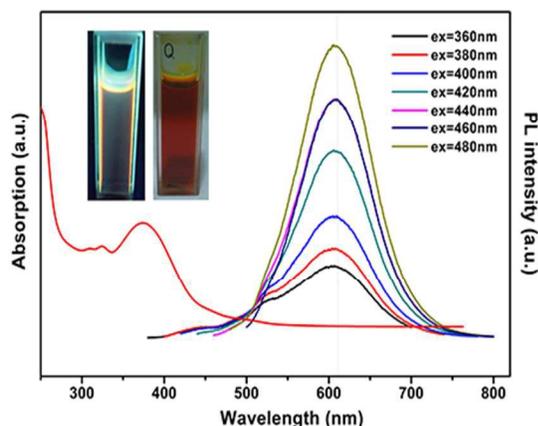


Fig. 3 UV-vis absorption and PL emission spectra of the CDs at different excitation wavelengths (recorded from 360 nm to 480 nm in 20 nm increments). The inset shows photographs of CDs taken under UV (365 nm) irradiation and sunlight, respectively.

Photoluminescent properties of the CD-NBS gel glasses

The CD-NBS gel glasses with 5% wt.% to 70 wt.% CDs were prepared successfully. The TEM images of the CD-NBS gel glasses are shown in Fig. 4, illustrating their uniformity and good dispersion, which exhibit similar statistical diameters of 2.9 ± 0.7 nm. In addition, the HRTEM image of the CD-NBS gel glasses indicates that the lattice spacing is about 3.18 \AA , corresponding to the 002 facet of graphite. In addition, the pore size distribution of the CD-NBS gel glasses is characterised by Brunauer-Emmett-Teller (BET) measurement and N_2 adsorption-desorption measurement. The characteristic hysteresis loop of the type-IV isotherm is indicative of a mesoporous structure (Fig. S4†). The result reveals that the pore size distribution of the CD-NBS gel glasses is centred at 2.47 nm (Fig. S4†), and their specific surface area is about $275.57 \text{ m}^2 \text{ g}^{-1}$. Furthermore, the narrow pore size distribution confirms the highly ordered uniform pore structure.

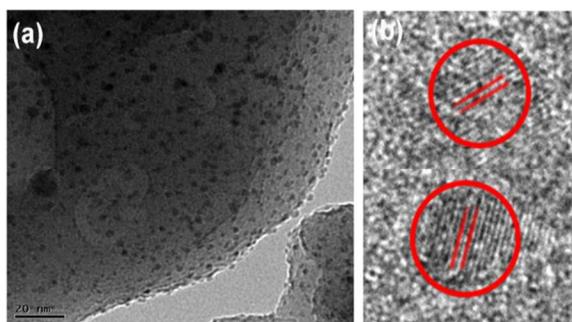


Fig. 4 TEM (a) and HRTEM images (b) of the obtained CD-NBS gel glasses.

Fig. 5 show the emission spectra of the CD-NBS gel glasses under several excitation wavelengths from 360–480 nm.

Fluorescence wavelengths for all types of CD-NBS gel glasses are independent of the excitation wavelength, whereas the PL intensity remarkably increase, which is similar to that observed in typical CDs. Moreover, the fluorescence emission peak clearly red-shifts to 560 nm, 575 nm and 600 nm for 20 wt.%, 50 wt.% and 70 wt.% CD-NBS gel glasses, respectively, from 550 nm for 5 wt.% CD-NBS gel glasses when the doping concentration of CDs increases (Fig. S5†). What are responsible for the emission red shift? Surface states influenced by surface modification can serve as capturing centres of excitations, thereby giving rise to the surface-state-related fluorescence.^{41,42} The silane-pre-functionalised CDs contain many alkyloxysilyl groups, similar to the silane coupling agent. After hydrolysis, many organic compounds will form silano groups⁷ which are highly reactive intermediates in bonding and the self- or hybrid- condensation with the NBS gel structure.

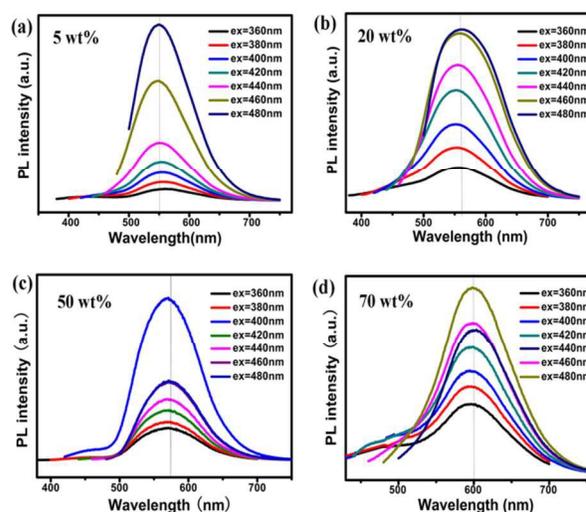


Fig. 5 PL emission spectra of the CD-NBS gel glasses with various CD loading fractions of (a) 5 wt.%, (b) 20 wt.%, (c) 50 wt.% and (d) 70 wt.% under different excitation wavelengths recorded from 360 nm to 480 nm in 20 nm increments.

To verify the involved mechanism, the surface chemical composition characteristics of CDs and CD-NBS gel glasses were investigated by XPS spectra. Fig. S6† shows the C1s XPS spectra indicating that the following contribution can be assigned: C=C (284.3 eV), C-O (285.7 eV) and Si-CH₂ (282 eV). As the doping concentration of CD increases from 5 wt.% to 70 wt.%, the relative peak intensity of the C1s XPS increases in the range of 280–283 eV, and the C-O peak gradually shifts towards the low binding-energy side (Si-CH₂), implying that the interaction becomes obvious between the reactive intermediates on the surface of the CDs and the NBS network as the doping concentration of CDs in the CD-NBS gel increases, which is consistent with the FTIR results. The highly reactive intermediates on the surface of the CDs are responsible for the bonding or hybrid condensation with the NBS gel network and affect the surface states influenced by the surface modification of

the CDs in the CD-NBS gel glasses. As the doping concentration of CDs increases, the interactions such as bonding or hybrid condensation between the varieties of reactive intermediates on the surface of the CDs and NBS network become obvious. The higher degree interaction between the varieties of reactive intermediates on the surface of the CDs and the NBS network also modified effective CD surface, more surface defects are present on the CDs.^{7,43,44} Such a change consequently narrows the energy levels and causes the red-shift fluorescence emission of the CDs.⁴⁵ Therefore, the PL peaks of the resulting CDs move to longer wavelengths as the interaction between reactive groups and the NBS gel network increases. This behaviour is consistent with previous studies,^{9,46} suggesting surface-state-related fluorescence from CDs. Additionally, the increase in the doping concentration of CDs will result in a decrease in the degree of carbon crystallisation, changing the nature of surface-state emission.⁴⁷

The average lifetime of CDs and CD-NBS gel glasses were determined using the TRPL technique. The TRPL spectra of the CDs and the CD-NBS gel glasses with different doping concentrations of CDs are shown in Fig. 6 under the excitation of 400 nm. The PL decay curves are fitted by a double exponential function: $Y(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2)$ (1) where α_1 and α_2 are the fractional contributions of decay lifetimes τ_1 and τ_2 . The average lifetime can be calculated by a relation: $\tau_{av} = (\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2) / (\alpha_1 \tau_1 + \alpha_2 \tau_2)$ (2). The emission decays of all the CD-NBS gel glasses are composed of two processes: a short-lived component τ_1 (1~4 ns) and a long-lived component τ_2 (7~10 ns), which are related to the electronic transitions in the CDs, indicating the strong coupling between the core and surface states similar to the luminescent Si nanoparticles.^{37,48} The fitting parameters are summarised in Table 1, the average lifetimes of CD-NBS gel glasses are clearly dependent of the doping concentrations of CDs which are evidently increased when the doping concentration of CDs increased. In addition, the enhancement of the fluorescent QYs to 45%, 64% and 78% for 20 wt.%, 50 wt.% and 70 wt.% CD-NBS gel glasses, respectively, from 25% for 5 wt.% CD-NBS gel glasses were observed under excitation at 460 nm as shown in Table 1. Compared with the average lifetime and QYs of CDs, that of CD-NBS gel glasses with high dopant concentration of CDs is longer, so it can prevent solid-state luminescence quenching at some level.

Table 1 Biexponential fit values and QYs of CDs and CD-NBS gel glasses with different fraction of CDs

Sample	λ_{ex} [nm]	α_1 [%]	τ_1 [ns]	α_2 [%]	τ_2 [ns]	τ_{av} [ns]	QY
CDs		20.6	2.27	79.4	8.73	8.32	43%
5%	400	20.9	1.84	79.1	6.95	6.62	25%
20%		17.8	2.01	82.2	9.27	8.94	45%

50%	23.7	3.17	76.3	10.18	9.56	64%
70%	27.1	4.04	72.9	10.85	10.02	78%

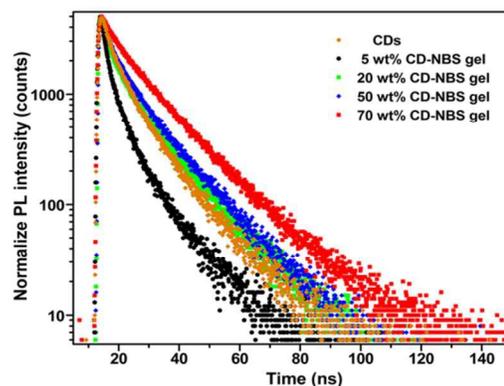


Fig. 6 Fluorescence decay curves for CDs and CD-NBS gel glasses with different fraction of CDs

Application

The as-prepared CD-NBS gel glasses show superior properties, such as excellent fluorescence, easy access, low cost and low toxicity. Perhaps more importantly, by virtue of the white-emitting ability of CD-NBS gel glasses, they show enormous practical applications in the lighting and display fields. Therefore, we directly employed CD-NBS gel glasses in solid-state lighting applications in the form of W-LEDs. Fig. 7a shows the fabrication strategy of W-LEDs based on CD-NBS gel glasses with blue-GaN LED chip and the photograph of the device.

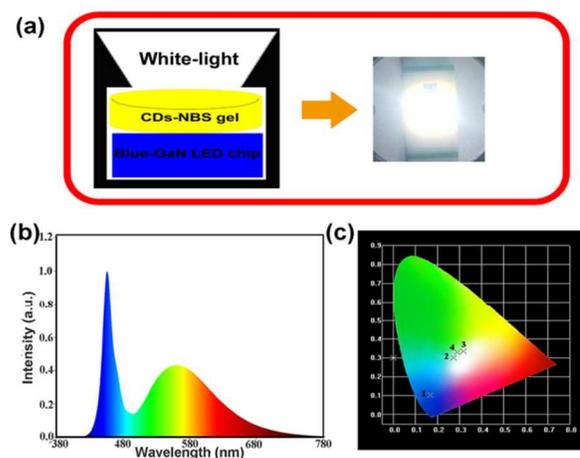


Fig. 7 (a) Fabrication strategy of W-LEDs based on CD-NBS gels with blue GaN LED chip and the photograph of a device. (b) Emission spectrum of the white LED lamp (Color figure online) 50 wt% CD-NBS gels and (c) The CIE of CD-NBS gel glasses with different loading fraction of CDs on the CIE chromaticity chart: 1) 5%. 2) 20%. 3) 50%. 4) 70 wt%, respectively.

The light-emission property of the prototype W-LED was investigated. The emission spectrum of the white LED consists of two emission bands: a blue emission centred at 460 nm from the blue GaN-based chip and a broad yellow emission from 50% CD-NBS gel glasses (Fig. 7b). These two emission bands are combined to produce warm white light. The as-prepared W-LED displays the CIE of the CD-NBS gel glasses with different concentrations of CDs for the 50 wt.% and 70 wt.% CD-NBS gel glasses (Fig. 7c), as their CIE are (0.32, 0.33) and (0.29, 0.33), respectively, which are close to that of balanced white-light emission (0.33, 0.33). In addition, the measured optical parameters of the CD-NBS gel glasses with various concentrations are shown in Table 2. The LE of CD-NBS gel glasses increased with increasing the doping concentrations of CDs, consistent with the PL QY measurements. The optimum CRI is 78.9, which is comparable to commercial W-LEDs. These results demonstrate that W-LEDs are successfully fabricated based on the yellow emission of CD-NBS gel glasses. Although a few LED applications have been demonstrated recently, most of them employed CD hybrid powder and films. This study is the first report to demonstrate the direct application of CD-NBS gel glasses for W-LEDs. The CD-NBS gel glasses as a solid matrix have many advantages such as improved fluorescent QYs and average lifetime, which can prevent solid-state luminescence quenching, provide flexibility and enhance physical stability. Thus, such solid gel may have several advantages over a solid array of CDs or its powdered form. Therefore, the solid-state CD-NBS gel glasses monolith could have wide applications in the next generation of LEDs.

Table 2. Measured optical parameters of CD-NBS gel glasses with various concentrations

Sample	drying temperature	CIE	LE (lm/w)	CRI	CCT(K)
5 wt%	100°C	(0.17,0.10)	10.38	13.5	--
20 wt%	100°C	(0.27,0.30)	28.23	78.9	~10000
50 wt%	100°C	(0.32,0.33)	48.59	74.8	6192
70 wt%	100°C	(0.29,0.33)	58.14	71.7	7818

Conclusions

In conclusion, a controllable sol-gel method for synthesising excitation wavelength-independent monolithic CD-NBS gel glasses with high QYs has been developed. In particular, the red-shift of emission peaks clearly depend on the dopant concentration of CDs in the CD-NBS gel glasses (from 5 wt.% to 70 wt.%). Significantly, using surface analytical techniques such as TRPL spectroscopy, we have revealed that the PL properties of CD-NBS gel glasses are mainly influenced by the surface functional groups: surface modification can result in a red shift of

CD emission in CD-NBS gel glasses. More importantly, to use CD-NBS gel glasses with strong PL emission and high QY, we have developed CD-based W-LEDs by combining the yellow-emitting CD-NBS gel glasses with blue GaN-based LED chips. For their practical application, the resulting W-LEDs exhibited the CIE of (0.32, 0.33), which were close to that of balanced white-light emission (0.33, 0.33), with maximum LE exceeding 58.1 lmW⁻¹ at the CCT of ~6190 K and with the CRI up to 78.9. These results would offer a new kind of CD-NBS gel glass that could become an alternative material for LEDs compared to the most commonly reported CD hybrid powder and films.

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Notes and References

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