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Direct white emissive Cl-doped graphene quantum dots-based flexible film as a single luminophore for remote tunable UV-WLEDs

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ABSTRACT

Herein we first report new chlorine-doped graphene quantum dots (Cl-GQDs) that can be used in solid-state white-light-emitting diodes (WLEDs). The Cl-GQDs with a mean size of 1.53 nm are obtained by one-step hydrothermal method using β -cyclodextrin and hydrochloric acid as the source materials. The PL emission spectra of the Cl-GQDs show an excitation-wavelength-dependent behavior in the range from 300 to 380 nm excitation. Under UV irradiation, the Cl-GQDs can direct emit white light. Given that they are worth using in light-conversion, Cl-GQDs embedded solid composite film (Cl-ESCF), based on

silicon resin as host material, is successfully fabricated by solution-processing approach. The freestanding Cl-ESCF has high transparency and flexibility, excellent photostability and temperature resistance, and retains its optical properties in the solid state. In order to realize its potential, the Cl-ESCF converted remote UV-pumped WLED is demonstrated. The results verify that the Cl-GQDs can be homogeneously dispersed within solid matrix without obvious aggregation so that a uniform and defect-free natural white light can be obtained. In addition, our WLED possesses favorable white-light characters with the CIE of (0.33, 0.34), moderate CCT of 5653 K, and high CRI of 87.6, as well as good color and LED stability. This single-phase rare-earth-free white-luminescent Cl-GQDs may be not only expected to prevent the drawbacks of multicolor phosphors, thereby generating high-quality white emission, but also identified to be a green alternative for conventional emitters.

Keywords: Cl-GQDs, solid luminescent film, GQD WLEDs, flexibility, LED stability

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1. Introduction

White-light-emitting diodes (WLEDs) used in solid-state illumination will gradually displace traditional incandescent and fluorescent bulbs due to their distinct benefits such as compact size, fast response, low power consumption, and long operational life [1–3]. Contemporarily, the mainstream WLEDs couple a blue-LED chip with a yellow phosphor. However, such type of WLEDs has main drawbacks of low color-rendering index (CRI) and blue-light retinal injury due to a strong blue spike of 450–500 nm in the white-light spectrum [4–6]. Ultraviolet (UV)-pumped WLEDs (UV-WLEDs) that use UV-LED chips to excite suitable combinations of phosphors are potential candidates to improve CRI and reduce light toxicity to an eye of the blue-LED chip [7–9]. Nevertheless, it is also noted that a high input current (350–700 mA) leads to a high junction temperature (150–200 °C) of device, which brings about several issues of UV-WLEDs including chromaticity drifts, degradation of luminous efficacy (LE), and final reduction of device stability [10,11].

Advanced remote LED packaging technology, which maintains appreciable distance between UV-chips and converter phosphors [12,13], will overcome these puzzles because it can effectively avoid prolong heating of phosphors, in addition to providing smooth color variation [14,15]. Unfortunately, the need of multicolor rare-earth (RE) phosphors extremely blocks the further development of UV-WLEDs with large emission area [16]. Besides, RE phosphors in general currently show rising prices and a limited supply [17]. Thus, developing a new kind of single RE-free C-based phosphors which absorb only UV light but directly emit white light are intriguingly desirable to replace multicolor RE materials for efficient remote UV-WLEDs.

As a rising star in the fluorescent nanocarbon family, graphene quantum dots (GQDs) have attracted much attention in recent years due to numerous merits such as low toxicity, excellent water dispersibility, superior optical performances (e.g., high photostability and tunable PL), and facile preparation and modification, thus offer a potential alternative to multicolor RE phosphors for remote UV-WLEDs [18–22]. To date, various strategies for the synthesis and doping of the GQDs, however, most of their efforts has focused on the preparation methods and PL characterizations of GQDs in their original aqueous solution, the photo-physical properties of their solid-stated forms are seldom studied and also still not satisfactory largely due to the self-quenching caused by the aggregation of the GQDs [23,24]. This aggregation issue can be avoided by dispersing GQDs in an inert matrix. Meanwhile, the mechanical and chemical stability could be improved [18]. So far, only a few works have been reported on GQDs doped in solid matrices including thermoplastic starch (TPS) [25], poly(methylmethacrylate) (PMMA) [26], and poly(vinylalcohol) (PVA) [27], but they show limited photo- and thermostability improvement upon UV irradiation. Furthermore, white-light emission of the reported results from combination of multiple components causes color variation [18,28]. Hence, it is imperative to exploit single-phase white emissive GQDs for realizing stable and high CRI UV-pumped WLEDs.

In this research, we derive Cl-GQDs for the first time by one-pot hydrothermal route using β -cyclodextrin as carbon source and hydrochloric acid as Cl source. The Cl-GQDs have excellent water solubility, excitation-dependent PL and directly white-light emission. To overcome self-quenching of Cl-GQDs in solid state, we prepare Cl-GQDs embedded solid composite film (Cl-ESCF) by a simple solution-processing method based on silicon

resin as matrix. No additional additives or encapsulants are needed for the film formation. The Cl-ESCF owns flexibility in shape, high photo- and thermostability, and retains its optical property in solid state. To realize its potential, remote WLED has been fabricated by integrating Cl-ESCF with UV-LED chips. Our results demonstrate that Cl-GQDs are homogeneously dispersed in solid matrix without obvious aggregation so that a uniform and defect-free white-light with Commission Internationale de L'Eclairage (CIE) of (0.33, 0.34), moderate CCT of 5653 K, and high CRI of 87.6 is achieved. This WLED also has good color and device stability. To our knowledge, luminescent film containing Cl-GQDs has not reported before, and such white emissive GQD-based solid film under single UV excitation could be used in pliable high ending lighting.

2. Experimental

2.1. Chemicals

β -cyclodextrin and hydrochloric acid (HCl, 32% *wt.*) were purchased from Aladdin. Silicon resin (SR) was acquired from Sigma-Aldrich. All chemicals are used as received. Deionized (DI) water (resistivity 18.2 M Ω cm at 25 °C) obtained through a Milli-Q (MQ) water system was used in all experiments. Dialysis bags (Membrane Filtration Products, Inc. Product number 1-0150-45) were used to purify the GQDs.

2.2. Synthesis of Cl-GQDs

The Cl-GQDs were synthesized *via* a facile hydrothermal technique. In detail, 1 g of β -cyclodextrin and 1.5 mL of HCl were dissolved in 25 mL of DI water under continuous ultrasonic at room temperature (RT). Then the mixture was sealed into a 50 mL autoclave with a Teflon inner vessel and placed in an oven at 160 °C over 2 h. After cooling to RT

naturally, the products were filtered through a 0.22 μm microporous membrane to remove large aggregates. The filtrate was further dialyzed in a dialysis bag (1000 Da, molecular weight cut-off) against fresh DI water every 24 h for 6 days. The resulting solution was lyophilized to obtain Cl-GQD powders.

2.3. Preparation of solid luminescent film

To fabricate the composite film, various amounts of the as-purified Cl-GQDs (0, 0.5, 1.0, 1.5, and 2.0 mL) and 11 g of SR (10 g silicone-A & 1 g silicone-B) were dissolved in 20 mL of DI water using magnetic stirring at RT to fully dissolve the polymer solution. Additional bath sonication for 20 min was used to ensure a good dispersion of Cl-GQDs. Then we drop cast ~5 mL of each polymer/Cl-GQDs solution on a cleaned Teflon mould. The mould was put in an oven at 50 °C for 24 h to evaporate the solvent. Finally, a series of 3 mm solid films were **peeled** off from the mould and stored in a desiccator for use.

2.4. Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a FEI Tecnai-G2-F20 TEM at 200 kV. Atomic force microscopic (AFM) image was taken with SPM-3100 (VEECO). X-ray diffraction (XRD) pattern was obtained on Rigaku D/max-2500 using Cu $K\alpha$ radiation. Raman spectrum was measured on a Renishaw InVia microscope with a 532 nm laser. Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet 6700 spectrograph in the form of KBr pellets. X-ray photoelectron spectroscopy (XPS) spectra were done on an ESCALAB 250 spectrometer with a monochromatic Al $K\alpha$ as exciting source. Ultraviolet–visible (UV–Vis) absorption spectrum was recorded on a Shimadzu UV-3600 spectrophotometer. Photoluminescence

(PL) and the time-resolved PL decay spectra were measured with an Edinburgh FLS980 spectrophotometer. Stability test of product was determined *via* contrast the PL intensity upon different conservative times at RT. The pH value was adjusted by HCl and NaOH solution using Mettler-Toledo FE-28 pH meter. Absolute PL quantum yield (PLQY) was obtained in a calibrated integrating sphere in FLS980 spectrometer. Thermal gravimetric (TG)-differential scanning calorimetry (DSC) was conducted on a NETZSCH STA 449C analyzer in N₂ atmosphere with the flow rate of 100 mL/min. Electroluminescence (EL) properties and the values of the correlated color temperature (CCT), CIE, CRI, and LE of remote WLEDs were assessed by a LABSPHERE light measurement system with a fiber optic spectrometer and an integrating sphere under different drive currents.

Ultraviolet photoelectron spectroscopy (UPS) measurement: UPS was performed with an $h\nu = 21.22$ eV, He I source (AXIS ULTRA DLD, Kratos). The analysis room vacuum was 2.0×10^{-8} Torr, and the bias voltage for test was -5 V. The Cl-GQDs thin film was prepared from spin-coating on ITO substrate for UPS measurement.

Ultrafast transient absorption (TA) setup: The TA setup consisted of pump pulses doubled from laser pulses (~ 100 fs pulse width, 250 Hz repetition rate) generated from a mode-locked Titanium:Sapphire laser/amplifier system (Solstice, Spectra-Physics) and broadband white-light probe pulses generated from 2-mm-thick water. The TA data were collected by a fiber optic spectrometer connected to a computer. The relative polarization of the pump and probe beams was set to the magic angle. The group velocity dispersion of the transient spectra was compensated by a chirp program. All the measurements were performed at RT.

3. Results and discussion

3.1. *Structural and composition characterizations of Cl-GQDs*

Typical plane-view TEM image (Fig. 1a) reveals that Cl-GQDs are nearly spherical and well dispersed without apparent aggregation. HRTEM image in Fig. 1b suggests the high crystallinity of Cl-GQDs, they have a significant standard sixfold symmetry in real and reciprocal spaces (Fig. 1b and inset, respectively), and the interlayer spacing of ~0.21 nm corresponds to the (100) lattice planes of the graphite [29]. The diameter of Cl-GQDs (Fig. 1c) is mainly distributed in the range of 1–2 nm (1.53 nm average size). The AFM topography (Fig. 1d) reveals that the Cl-GQDs thickness is 1–3 nm, namely, between one and three layers of graphene sheets [30]. The XRD pattern (Fig. S1) of Cl-GQDs shows one prominent peak around $2\theta = 27.18^\circ$ which corresponds to the value of the basal plane distance [31]. Raman spectrum of Cl-GQDs (Fig. S2), which provides information on the defect density, is characterized by D and G bands at 1339 and 1586 cm^{-1} , corresponding to the vibrations of C atoms with dangling bonds of the disordered sp^3 C structure and sp^2 bonded C atoms in a 2D hexagonal lattice of a graphite cluster, respectively. The D-to-G intensity ratio is about 0.88, indicating that sp^2 carbons are mainly present, with some sp^3 hybrid carbons in Cl-GQDs.

In order to determine the chemical compositions and surface states of the Cl-GQDs, FTIR and XPS measurements were undertaken. Fig. 2a exhibits the FTIR spectrum of Cl-GQDs, the broad absorption bands at 3200–3600 cm^{-1} are assigned to the stretching vibrations of O–H. This indicates that there are a large number of hydroxyl groups on the surface of Cl-GQDs, which results in the Cl-GQDs having good hydrophilic properties.

The bands at 2926 and 1397 cm^{-1} are attributed to the stretching vibration and bending vibration of C–H, respectively. The peak at 1719 cm^{-1} is corresponded to C=O stretching. The bands at 601 and 1024 cm^{-1} are from the stretching vibration of C–Cl [29,32–34].

XPS full survey (Fig. 2b) demonstrates that besides carbon (C, 285 eV) and oxygen (O, 532 eV), distinct chlorine (Cl, 197 eV) signal is also observed near the surface of the Cl-GQDs, suggesting the effectiveness of the Cl-doping in the GQDs. The corresponding doping concentration is about 2.8 at. %. To be specific, deconvolutions are performed on all high-resolution XPS spectra. As illustrated in Fig. 2c, four characteristic curves are seen in the XPS spectrum of C 1s, that is, C–C/C=C peak at 284.6 eV, C–OH/C–O–C peak at 285.9 eV, C=O peak at 287.5 eV, and COOH peak at 289.1 eV [35]. The O 1s spectrum (Fig. 2d) is deconvoluted into two main peaks, centered at 532.2 eV (C=O) and 533.4 eV (C–OH/C–O–C), respectively [36]. As shown in Fig. 2e, substitutional dopants in GQD skeletons are verified by peak of Cl 2p, which displays three peaks, located at 199.3 eV ($-\text{OC}_6\text{Cl}_4\text{O}$), 200.4 eV ($-\text{C}_6\text{H}_4\text{Cl}$), and 201.6 eV ($-\text{CH}_2\text{Cl}$), respectively [34,37]. On the basis of the FTIR and XPS findings, we can conclude that the obtained Cl-GQDs are doped with Cl in both site surface and lattice substitutional manners, with diverse oxygen-containing functional groups, including carbonyl, carboxyl, epoxy, and hydroxyl groups at the edges and/or onto the basal plane, as schematically displayed in Fig. 2f. The presence of these groups endows Cl-GQDs soluble in water and various organic solvents (such as Ethanol, DMF, and THF).

3.2. Optical behaviors and PL mechanism of Cl-GQDs

To study the optical properties of Cl-GQDs, the UV–Vis and PL spectra of Cl-GQDs

solution were measured (Fig. 3a). For UV–Vis spectrum, except three predominant bands at 202, 272, and 353 nm were observed, a lower-energy absorption exists. For PL spectra, two dominant peaks at 448 and 587 nm can be observed when the specimen was excited by different excitation wavelengths (λ_{Ex}). Although the PL intensities of the two peaks are dependent on λ_{Ex} , the positions of them do not change significantly. One of the important purposes of doping C-based material is to regulate its properties. Fig. S3 manifests the PL spectra of Cl-GQDs with various dopant concentrations. It is seen that the PL intensity of Cl-GQDs remarkably increases and reaches a maximum when the HCl content is 1.5 mL, followed by a decline with the further increased doping content because of the decreased disorder-induced defect states between gap of π and π^* [35,38]. Thus, the Cl atom doping in the GQDs plays vital roles in tuning the PL properties of Cl-GQDs. The corresponding CIE values of Cl-GQDs excited using different λ_{Ex} are depicted in inset of Fig. S4. As the λ_{Ex} increases from 300 to 380 nm, the coordinates of the samples are varied from (0.2816, 0.3035) to (0.3658, 0.3672), and their hues can be tuned from the border of bluish white to yellowish white. In particular, when the $\lambda_{\text{Ex}} = 360$ nm (d point in Fig. S4), the CIE is realized at (0.3289, 0.3348), which is quite close to the pure white light (0.33, 0.33).

Bandgap energy of Cl-GQDs (3.17 eV) was calculated using the equation $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{edge}}$, where λ_{edge} is the onset value of the first excitonic absorption band in the direction of longer wavelength [39]. The highest occupied molecular orbital (HOMO) level (5.98 eV) is determined by means of the UPS (Fig. 3b) and the lowest unoccupied molecular orbital (LUMO) level (2.81 eV) is deduced from energy gap and HOMO level. The PLQY of the as-prepared Cl-GQDs at 360 nm excitation was determined to be 6.2%,

which is comparable to the yields of other methods derived GQDs [32,40–42]. The effect of solvent's environment on the PL responses were investigated after dispersing 50 μ L of Cl-GQDs in 10 mL different solvents. Intriguingly, the Cl-GQDs have solvent-dependent PL properties. As illustrated in Fig. S5a, the highest solubility in THF, partially induces the π conjugated system throughout the molecule (i.e., sp^3 gets partially converted to sp^2) thereby raising the PL intensity compared with other solvents (THF > DMF > Ethanol > Water) [43], and the emission under UV illumination can be adjusted by controlling the solvent class (Fig. S5b), which offers new advantage for Cl-GQDs meeting requirements. Furthermore, Cl-GQDs are highly stable, even after being kept for 8 months in air at RT, they still exhibit homogeneous phase without any clear sediment and strong PL emission, facilitating their storage and application.

For clarifying the responsible PL mechanisms of the white emissive Cl-GQDs, TA measurements were performed at 360 nm excitation. From Fig. 3c, one can observe that it gives the small negative signals at around 380 nm, which are in accordance with the energy band structure in the steady-state absorption spectrum at similar wavelength. Thus, we assign this state to the ground-state bleaching (GSB) signal. In the wavelength range of 400 to 600 nm corresponding to PL, the pronounced positive signals can be attributed to excited-state absorption (ESA). In the red side of ESA, there is another subtle negative signal, which can be assigned to the stimulated emission (SE). These transient behaviors reflect that the components of ESA and SE signals could be responsible for the white PL. More interestingly, we further find that the intensities of white-light emission decrease in the solution of high or low pH value but almost remain constant in a solution of pH 4–10

(Fig. S6). Such pH-sensitive feature is attributed to changes in the surface charge induced by protonation-deprotonation [44], which may affect the PL center. Based on the above results, we propose that the synergistic effect of the C core and surface states contributes to the white fluorescence [45,46]. The physicochemical analysis from the FTIR and XPS has proved the presence of O- and Cl-containing functional groups on the GQDs surface. These chemical species hybridize with the conjugated C sp^2 skeleton of the carbogenic core play the role of white-light emission.

In order to further explore the recombination dynamics of the Cl-GQDs, we perform time-resolved PL (TRPL) experiments by changing the λ_{Ex} . All the PL decay curves show a double-exponential function with a fast decay component plus a slow decay component (Fig. 3d), which correspond to recombination from the intrinsic states and defect states, respectively [47–49]. In a general way, the PL that from defect states exhibits a longer recombination decay lifetime than that from intrinsic states [50]. As the λ_{Ex} varies from 300 to 380 nm, the PL decays of Cl-GQDs are found to remarkably depend on the λ_{Ex} . Here we assume that the fluorescent lifetime of Cl-GQDs can be divided by the weight coefficient of the fast and slow decay components. By fixing the fast ($\tau_1 = 1.18$ ns) and slow ($\tau_2 = 4.87$ ns) decay times, we compute the relative weight coefficients of Cl-GQDs (inset of Fig. 3d). The fast decay component is dominant when the Cl-GQDs are excited by 300 nm, while the slow decay component governs the PL emission as the λ_{Ex} increases up to 380 nm. The observed increase of the effective PL decay with longer λ_{Ex} strongly indicates that the change of predominant excited state in the Cl-GQDs depends on the excitation-energy. We therefore conclude that most PL originates from the intrinsic states

upon $\lambda_{\text{Ex}} = 300$ nm, whereas, vacancy or interstitial atoms involved in defect states can be efficiently excited by λ_{Ex} beyond 380 nm. The excitation-energy-dependent PL and TRPL results tie in well with the corresponding intrinsic and defect-related absorption states of Cl-GQDs as seen in the UV-absorption spectrum (Fig. 3a).

With the help of the above studies, the growth process and energy-level structure of Cl-GQDs can be understood as below. (1) Under hydrothermal treatments, β -cyclodextrin molecules dehydrate intra- and inter-molecularly, forming a honeycomb carbon skeleton. The presence of HCl catalyzes the dehydration polymerization between β -cyclodextrin and the aqueous solution, the crystal nucleus of Cl-GQDs is then formed. Afterwards, the growth of Cl-GQDs occurs at the surface as active functional groups are present (Fig. 3e). The catalytic effect of HCl is crucial for the formation of Cl-GQDs at ambient condition. HCl also acts as a reactant and provides chlorine as dopant. Cl is incorporated into the C matrix in different configurations. (2) Modulation of the optical properties by effectively Cl-doping has been demonstrated in this work, which brings unique energy-level into the electronic structure. The presence of Cl gives rise to additional energy levels between C π and C π^* , leading to new UV absorbance at 272 and 353 nm. When Cl-GQDs are excited by a certain energy light, the absorbed photons may cause electron transitions of 6.1 eV (202 nm, $\pi \rightarrow \pi^*$ of C=C), 4.6 eV (272 nm, $\pi \rightarrow \pi^*$ of C-Cl) and 3.6 eV (353 nm, $\pi \rightarrow \pi^*$ of C=O), creating three absorption bands in the UV spectrum. The excited electrons can be deactivated by two paths. One is through direct recombination after vibration relaxation, generating photoluminescence. Another is undergoing intersystem crossing, followed by vibration relaxation, and finally radiative recombination occurs. These two ways result in

excitation-dependent PL [51–53]. Obviously, the ‘bridge-effect’ of Cl is beneficial to the intersystem crossing ($C \pi^* \rightarrow Cl \pi^*$ and $Cl \pi^* \rightarrow O \pi^*$) among the Cl-GQDs. Role of the Cl doping in white emission can be further evidenced by the UV–Vis and PL spectra of the undoped GQDs. No characteristic peaks can be observed in the UV absorbance (Fig. S7), and the undoped GQDs can not direct emit white light at single UV excitation (Fig. S8). These results forcefully confirm that Cl-induced energy level plays a vital role in altering the band gap and conduction type, endowing Cl-GQDs a promising fluorescent material.

3.3. Properties of freestanding luminescent film

The unique direct white emission and excellent stability of Cl-GQDs, coupled with their low-cost and eco-friendly are compelling for application in high-performance LEDs. However, the luminescence of GQDs is highly quenched in the solid aggregate states. In our previous work, we reported a universal technique for making efficient GQD-based color conversion through effective dispersion of GQDs by incorporating GQDs and RE phosphors with PVA [13]. Follow this line, solid luminescent films, based on SR as the supporting material and freshly Cl-GQDs, were made by solution-processing approach. Here, SR was selected as base material due to its superb heat resistance, stable electrical specification, and good water tolerance. A schematic presentation of preparing Cl-ESCF is exhibited in Fig. 4a. The as-fabricated Cl-ESCFs are of uniform thickness and show high optical quality under daylight, and single emit white light under UV light excitation (Fig. S9). Moreover, the Cl-ESCF is flexible and can be bent and fully restored freely. As we know, flexible device like organic LED (OLED) looking ductile, thinner, and durable have demonstrated innovative display technology [54]. Thereby, the fluorescent Cl-ESCF

has a bright future in collapsible lighting apparatus. Besides, the prepared Cl-ESCF also has physical advantages such as harmlessness, mechanical strength, and air stability.

A typical TEM image of Cl-GQDs distribution in Cl-ESCF (Fig. S10) shows almost no aggregation, indicating the achievement of uniform Cl-GQDs dispersion in the matrix. Transmission spectra (Fig. 4b) reveal that the Cl-ESCFs have high optical transparency (OT) at 500–900 nm. The corresponding dependence of film's OT on the Cl-GQDs dose (Fig. S11) testifies that when the Cl-GQDs are increased up to 1.0 mL, the Cl-ESCFs still maintain high OT (85.6%) that is comparable with the baseline (85.8%). Further increase in Cl-GQDs dose leads to particle agglomeration, near their volumetric saturation, which is strongly evidenced by a drop in OT. This allows the prediction that the Cl-ESCF would pursue excellent optical performances when Cl-GQDs dosage not exceeding 1.0 mL.

To investigate the luminescence properties of the composite film, PL measurements in the solid state were done (Fig. S12). It can be found that the PL intensity of the films is concentration-dependent and shows a tendency of gradual increase till peaking at 1.0 mL of Cl-GQDs, followed by a decline as the increasing Cl-GQDs. To obtain the maximum output efficiency of composites in terms of their luminescence level, the recommended loading of GQDs is 1.0 mL. In consequence, we choose the Cl-ESCF containing 1.0 mL Cl-GQDs for following related investigations. Fig. S13 describes the PL spectrum ($\lambda_{\text{Ex}} = 360$ nm) of the solid Cl-ESCF, no obvious change in emission wavelength was detected compared to the liquid Cl-GQDs, which implies that no PL self-quenching interaction is occurred after the formation of the SR/GQD composites [24]. What's more, the formation of GQDs-doped cross-linked network results in a solid film which inhibits the PL shifts

and suppresses the intermolecular vibration and non-radiative transition, in contrast to the systems requiring additives.

Thermal stability of Cl-ESCF is studied using TG and DSC. As exhibited in Fig. 4c, the incorporation of Cl-GQDs in the SR influences the TG behaviors of the polymer. The maximum weight loss temperature decreases from 510 °C for SR to 430 °C for Cl-ESCFs, which are in complete agreement with the DSC results (Fig. S14). This is an indication of the change in the polymer degradation mechanisms, probably induced by Cl-GQDs, that needs further study since it remains unclear. The amount of the residue formed in the process of SR decomposition increases with the addition of the Cl-GQDs. Below 700 °C, the SR decomposes 26% residues, while the Cl-ESCFs decompose 37% residues, that is, considerable amounts of carbonized residues (at least ~11%) remain after the composite's burnout [27]. Also, it is noted that the weight of diverse films (0.5–1.5 mL Cl-GQDs dose) can be maintained above 90% even the temperature achieves 350 °C (Fig. 4c), thus this material for normal working temperature (< 50 °C) of remote WLED is very hopeful. The weight loss of the Cl-ESCF between 300 and 400 °C is primarily caused by the breakage of the partial Si–O–Si group and decomposition of the residual carboxyl group. When the temperature is higher than 400 °C, the mass loss would mainly come from Si–O–Si group, bringing in small and ring molecules [17]. We further heat the Cl-ESCF from RT to 80 °C and finally to 120 °C and find its PL intensity decreases gradually, however, a complete recovery to its original intensity can be obtained after cooling to RT (Fig. 4d), indicating that the Cl-ESCF has outstanding heat resistance. In comparison to Cl-GQDs, Cl-ESCF has a SR matrix as a buffer, which can absorb damages from thermal shock and thereby

contributes to its superior thermal stability.

In addition to high thermal stability, the fluorescence stability of the Cl-ESCF is also crucial criteria in practical applications. Although with many active groups, the Cl-ESCF shows prominent stability after continuous excitation under visible light for 48 days (blue curve in Fig. 4e) or UV irradiation (150 W xenon lamp with center wavelength at 360 nm, 50 h, red curve in Fig. 4e) at RT, which is very positive to promote its actual UV-pumped WLEDs. All the results are testament to the fact that the Cl-ESCF has astonishing photo- and thermostability, which is ascribed to an ordered and fine distribution of the Cl-GQDs within SR matrix with the absence of chromophore migration upon external stimulation.

3.4. Potential of remote tunable UV-pumped WLEDs

High spectral purity and broad PL emission covering most of the visible range make Cl-ESCF suitable replacement of RE phosphors in remote WLEDs. The configuration of remote WLEDs consists of four parts: (1) a power supply is used as LED driver; (2) an aluminum heat sink is used to dissipate device heat; (3) an array of custom-made 360 nm UV-LED (EPISTAR LED chip) is used to excite the Cl-ESCF; (4) a light concentrator is placed between the UV-LED array and Cl-ESCF to concentrate light onto the Cl-ESCF. Fig. 5a compares the distribution of light intensity from the surface of the Cl-ESCF. The variation of intensity was examined along two orthogonal directions of the Cl-ESCF. It is seen that the intensity distribution from both directions is identical and the corresponding radiation profile is mainly related to the LED array and light concentrator. This indicates that homogeneous light emission from the surface of the Cl-ESCF is obtained, which can be owed to the confined 2D microenvironment offered by SR in which a homodisperse of

Cl-GQDs without apparent agglomeration is achieved. As exhibited in the inset of Fig. 5a, a uniform and defect-free natural white-light emission with the CIE of (0.3254, 0.3445), CCT of 5653 K, and luminous efficacy of 5.1 lm/W is obtained. In addition, our WLED has a high CRI of 87.6, which is even comparable to some state-of-the-art WLEDs based on carbon QDs [9], semiconductor QDs [55], and RE phosphors [56].

Color deviation of a WLED operated under different bias currents is usually used to evaluate the LED stability for high-quality lighting. We therefore measure the EL spectra of the Cl-ESCF based WLEDs at various bias currents (20–500 mA) (Fig. 5b). Spectral details and EL data are shown in Fig. 5c and listed in Table 1. The CIE coordinates of the WLEDs at different currents are marked in CIE-1931 color space and the color points are laid on the black body Planckian locus (Fig. 5c), suggesting that the WLEDs produce a gratifying illumination. Also, the adjustable luminescent color evolves from cool-white to warm-white presented in Fig. 5c implies the feasibility of a fine LED control for ensuring good white-light character. The lower luminous efficacy but much higher drive current is attributed to the increasing PN junction temperature caused by excessive heat dissipation. Besides, the relatively small LE values (5.1–8.6 lm/W) highly depend on the type of LED chips, and we expect that further optimization of the chip efficiency will lead to a greatly improved LED performance. The inset of Fig. 5c plots the variation of CIE worked under various currents. With increasing the current from 20 to 500 mA, the CIE are found to be blue-shifted from (0.3716, 0.4117) to (0.3254, 0.3445), which agree with the CCT results. The change of CRI (82.2–87.6) is also negligible (Table 1). These findings indicate that Cl-ESCF has superb color stability, promising for the use in high-power WLEDs. Fig. 5d

shows the EL intensity of Cl-ESCF based WLED against time. Generally, as the working time increases, the thermal stress arises and reduces the luminescence. However, usage of our WLEDs is stable and invariant, still maintaining 94% of the initial emission intensity over 180 min of operation, demonstrating good LED stability. We highlight that the GQD WLEDs have a great prospect in stable and high CRI lighting.

4. Conclusions

In summary, the application of using novel Cl-GQDs in solid-state WLEDs has been reported for the first time. The Cl-GQDs are prepared *via* one-pot hydrothermal strategy using β -cyclodextrin as C source and HCl as Cl source, respectively. The Cl-GQDs have superior water dispersibility, excitation-dependent PL characteristic and direct white-light emission using single UV excitation. Then we make Cl-GQDs embedded solid composite film (Cl-ESCF) by a simple solution casting based on a silicon resin matrix. The polymer matrix can not only provide mechanical support but also disperse the Cl-GQDs to prevent luminescence quenching. The Cl-ESCF is eco-friendly, easily scalable, fully flexible, and highly photo- and thermostable so that it can play a key role in using solid-state lighting. In this regard, the Cl-ESCF based remote UV-WLED device is demonstrated. The results prove that the Cl-GQDs can be well dispersed in matrix without migration/aggregation in order that high-quality white emission with CIE coordinates of (0.33, 0.34) and high CRI of 87.6 can be achieved. Also, this WLED possesses gratifying color and device stability. We anticipate that further improving the QY of the white emissive Cl-GQDs and better controlling device fabrication will make leaps and bounds in GQD-based LEDs. Detailed follow-up work is underway in our laboratory and will be reported in due course.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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Figure Captions

Fig. 1. (a) TEM, (b) HRTEM, and FFT images (inset) of Cl-GQDs. The dashed circles in panel (b) indicate lattice imaging. (c) Size distribution of Cl-GQDs, based on over 300 HRTEM-imaged particles. (d) AFM topography image and analysis (inset) of Cl-GQDs.

Fig. 2. (a) FTIR spectrum of Cl-GQDs. (b) XPS full scan, high-resolution XPS (c) C 1s spectrum, (d) O 1s spectrum, and (e) Cl 2p spectrum of Cl-GQDs. (f) Schematic diagram showing the structure of Cl-GQDs.

Fig. 3. (a) UV–Vis absorption and PL spectra and (b) UPS data of Cl-GQDs. (c) Ultrafast TA spectra of Cl-GQDs expressed in ΔOD (the change of the absorption intensity of the specimen after excitation) as a function of probe wavelength. (d) PL decay of Cl-GQDs excited at different wavelengths. Inset shows the relative weight coefficients determined using a double-exponential function by fixing the fast and slow decay components upon different λ_{Ex} . (e) The growth process of the Cl-GQDs.

Fig. 4. (a) Schematic illustration of preparing solid luminescent film. (b) Transmittance and (c) TG data of blank silicon resin and composite films with various Cl-GQDs doses. (d) Reversible PL response of the solid composite film in a heating–cooling cycle. (e) Photostability of composite film under visible light (blue curve) and under UV light (red curve). F_0 and F are PL intensities at the outset and specified times, respectively.

Fig. 5. (a) Light intensity distribution of two orthogonal directions from the surface of composite film. Inset shows a photograph of the operating remote WLED device at 500 mA. (b) EL spectra of the WLED at the current regulation (20–500 mA). Inset shows the schematic presentation of remote UV-pumped WLED. (c) The corresponding CIE-1931

color space diagram. Inset plots the variation of the chromaticity coordinates at different bias currents. (d) EL intensity of the composite film against time (at 500 mA).

Tables

Table 1. EL properties of the Cl-ESCF based WLEDs at applied drive currents.

Drive current (mA)	CIE coordinates (x , y)	CCT (K)	CRI	Luminous efficacy (lm/W)
20	(0.3716, 0.4117)	4029	82.2	8.6
120	(0.3567, 0.3937)	4604	83.8	7.4
240	(0.3438, 0.3739)	5047	84.9	6.1
350	(0.3315, 0.3588)	5341	86.1	5.6
500	(0.3254, 0.3445)	5653	87.6	5.1

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5