

RESEARCH ARTICLE

View Article Online
View Journal | View IssueCite this: *Mater. Chem. Front.*,
2020, 4, 517**Microwave-assisted *in situ* large scale synthesis of a carbon dots@g-C₃N₄ composite phosphor for white light-emitting devices†**Li Meng,^{ab} Elena V. Ushakova,^{id c} Zhengjie Zhou,^{ab} Enshan Liu,^d Di Li,^a Ding Zhou,^a Zhanao Tan,^{id e} Songnan Qu*^{cd} and Andrey L. Rogach^{id cf}Received 25th October 2019,
Accepted 9th December 2019

DOI: 10.1039/c9qm00659a

rsc.li/frontiers-materials

Sustainable, environment-friendly phosphors produced from cheap and readily available precursor materials using green preparation processes are in high demand for lighting applications. Herein, a composite phosphor comprising carbon dots (CDs) and graphitic carbon nitride (g-C₃N₄) is prepared on a large scale from citric acid and urea in water, through a green microwave assisted *in situ* heating method. An optimized CDs@g-C₃N₄ composite with a 1 wt% loading of CDs shows a strong green emission under 410 nm excitation, with a photoluminescence quantum yield of 62% in the solid state. Using this composite as a phosphor in the color conversion layer, a white light emitting diode with a power efficiency of up to 42 lm W⁻¹ is fabricated.

Introduction

Phosphors are highly demanded in the lighting industry, particularly for white light emitting diodes (WLEDs).¹ Currently used commercial phosphors are mostly based on rare-earth materials, which experience issues of severe exploitation and less environmentally friendly refining, and may face a serious shortage in supply.² It is thus of importance to look for alternative sustainable phosphors, which are to be produced using green preparation processes, and from readily available resources.

Carbon dots (CDs) have recently attracted attention in this respect owing to their tunable fluorescence emission, biocompatibility, low toxicity and facile preparation.^{3–13} Increasing efforts have been devoted towards overcoming the luminescence quenching of CDs in the solid state for WLED applications. Wang *et al.* mixed CDs with polystyrene to obtain a CD-based white emissive phosphor with a photoluminescence quantum yield

(PLQY) of 25%, and made a WLED with a power efficiency of 14.8 lm W⁻¹.¹⁴ Wang *et al.* designed a MOF material from CDs and Zr(IV) with white emission at 365 nm excitation with a PLQY of 37%, and fabricated a WLED with a power efficiency of 1.7 lm W⁻¹.¹⁵ Shen *et al.* embedded CDs in trisodium citrate crystals to prepare a green emissive phosphor with a PLQY of 21%, and fabricated a WLED with a power efficiency of 6.9 lm W⁻¹.¹⁶ We combined CDs with starch, polyvinylalcohol, BaSO₄, NaCl, sodium silicate, silica and branched polyethylenimine to prepare phosphors with PLQYs ranging from 26% to 60%,^{17–23} and WLEDs with power efficiencies in the range of 8–28 lm W⁻¹. Even though the PLQYs of CDs in the solid state have been gradually increased, the performances of CD-based WLEDs are still far from practical requirements (60–90 lm W⁻¹) due to their low device power efficiency. Thus, there is still a need to develop new methods towards strongly emissive CD-based phosphors, and to improve the performance of CD-based WLEDs.

Graphitic carbon nitride (g-C₃N₄) is a stable material which has been proved to be an excellent catalyst for photodecomposition of water;^{24,25} it can be easily synthesized from low cost and environment-friendly urea.²⁶ The band gap of bulk g-C₃N₄ is about 2.7 eV, while g-C₃N₄ nanosheets may have wider band gaps, which result in blue emission;²⁷ they can be used as a matrix for preparing luminescent composites. Chen *et al.* reported a phenyl-modified g-C₃N₄-based green emissive phosphor with a PLQY of 38%.²⁸

Herein, we have developed an *in situ* large scale synthetic procedure towards a strongly emissive CDs@g-C₃N₄ composite phosphor with its PLQY reaching 62%, *via* two-step microwave-assisted heating of citric acid and urea precursors. Using this sustainable and low cost synthesized CDs@g-C₃N₄ phosphor,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9qm00659a

WLEDs with power efficiencies up to 42 lm W^{-1} have been realized, which makes an important step towards practical lighting application of CDs.

Results and discussion

CDs were synthesized from citric acid and urea *via* a microwave-assisted heating method, following our previous work.²⁹ Briefly, 6 g urea and 3 g citric acid were dissolved in 30 ml of deionized water, and heated for 3–4 min in a microwave oven to form a dark-brown CD solid, with a chemical yield of approximately 13.0%. This solid could be easily dispersed in water, providing a transparent solution with a yellow color under daylight, which showed green emission under UV light (insets in Fig. S1, ESI[†]). UV-vis absorption and PL spectra (405 nm excitation) of CDs dispersed in water are shown in Fig. S1 (ESI[†]); the PLQY was 15% under 405 nm excitation. $g\text{-C}_3\text{N}_4$ was prepared from urea as follows: 10 g urea was dissolved in 20 ml of deionized water, followed by microwave-assisted heating for 3–4 min.²⁶

To produce composites of CDs with $g\text{-C}_3\text{N}_4$ (denoted CDs@ $g\text{-C}_3\text{N}_4$ hereafter) from citric acid and urea, a two-step microwave-assisted heating method was developed, as illustrated in Fig. 1 and Fig. S2 (ESI[†]). First, appropriate amounts of citric acid (9–216 mg) and urea (18–432 mg) with a weight ratio of 1 : 2 were dissolved in 10 ml of water, followed by the first-step microwave heating for 3–4 min, which resulted in the formation of a non-emissive black powder comprising aggregated CDs. In the next step, 20 ml of 0.5 g ml^{-1} urea aqueous solution was added to dissolve this black powder and to form a transparent yellow solution. This solution was treated with the second-step

microwave heating for 3–4 min, resulting in the formation of a green emissive powder. By controlling the ratio of the initial amount of citric acid and the total amount of urea, CDs@ $g\text{-C}_3\text{N}_4$ composites with 0.5–12 wt% loading amounts of CDs were obtained, with chemical yields of approximately 7.0–7.4%. During the second step of the microwave heating process, the abundant urea forms $g\text{-C}_3\text{N}_4$, whereas CDs become embedded within the $g\text{-C}_3\text{N}_4$ network, which prevents their aggregation-induced luminescence quenching. Such a microwave-assisted method offers combined advantages of a low cost, fast and large-scale production of CD-based phosphors: more than 20 g of CDs@ $g\text{-C}_3\text{N}_4$ composite material can be easily prepared as one batch, as presented in Fig. 2a. Under UV light, this composite exhibits strong green fluorescence, indicating the successful incorporation of CDs within $g\text{-C}_3\text{N}_4$ (Fig. 2b). Fig. 2c shows the fluorescence image of the CDs@ $g\text{-C}_3\text{N}_4$ composite with 1 wt% CD loading concentration. The CDs@ $g\text{-C}_3\text{N}_4$ composite with its particle size distribution ranging from 5 to $40 \mu\text{m}$ exhibits homogeneous intense green emission under blue light, demonstrating the uniform composition of CDs within $g\text{-C}_3\text{N}_4$. As expected, the color of the CDs@ $g\text{-C}_3\text{N}_4$ composite becomes gradually darker upon increasing the CD loading concentration, while the emission was first enhanced and then decreased (Fig. 2d).

The scanning electron microscopy (SEM) image of $g\text{-C}_3\text{N}_4$ provided in Fig. 3a shows that it exhibits a layered morphology. The transmission electron microscopy (TEM) image further reveals that it consists of multiple nanosheets, with a lattice spacing of 0.32 nm as identified by a high resolution TEM (HRTEM) shown in the inset of Fig. 3b, corresponding to the (002) plane of graphitic carbon nitride.³⁰ A TEM image of the CDs@ $g\text{-C}_3\text{N}_4$ composite is shown in Fig. 3c. The layered structure

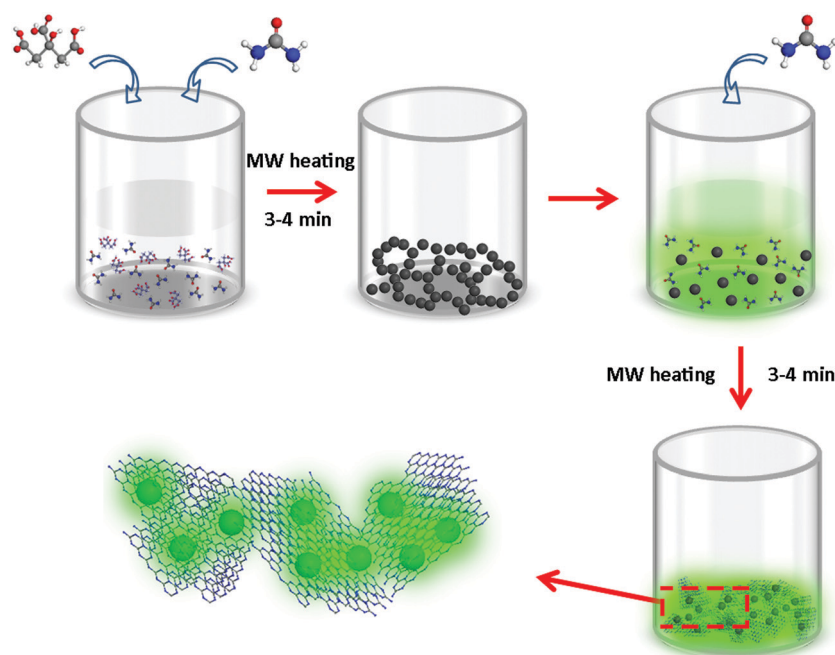


Fig. 1 Schematic representation of the synthesis of CDs@ $g\text{-C}_3\text{N}_4$ composites *via* a two-step microwave-assisted *in situ* heating method using citric acid and urea as precursors in water (MW: microwave).

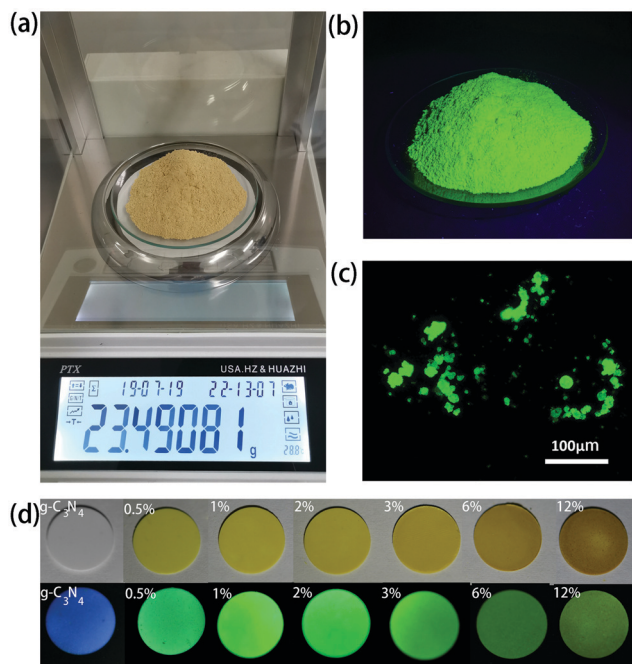


Fig. 2 Photographs of a CDs@g-C₃N₄ composite (approximately 23.5 g) with 1 wt% CDs taken under daylight (a) and under UV light (b). (c) Fluorescence image of the CDs@g-C₃N₄ composite with 1 wt% CD loading concentration taken under a fluorescence microscope with blue excitation. (d) Photographs of the pressed tablets of bare g-C₃N₄ (far left) and a number of CDs@g-C₃N₄ composites with different weight loadings of CDs, taken under daylight (top row) and UV light (bottom row).



Fig. 3 (a) SEM image of g-C₃N₄. (b) TEM image of g-C₃N₄, with a HRTEM image shown in the inset. (c) TEM image of a CDs@g-C₃N₄ composite with 1 wt% CDs, with a HRTEM image in the inset. (d) XRD patterns of bare g-C₃N₄ (red line) and the CDs@g-C₃N₄ composite with 1 wt% CDs (blue line).

related to g-C₃N₄ can be clearly seen alongside with dispersed dark dots with sizes of 2–8 nm. The HRTEM image shown in the inset of Fig. 3c shows that dots have a lattice spacing of 0.21 nm, corresponding to the (100) crystallographic facet of graphite-like carbon cores,³¹ which can be attributed to the CDs. XRD patterns of g-C₃N₄ and CDs@g-C₃N₄ are very similar (Fig. 3d),

both exhibiting a dominating major peak at 27.8 degrees, which can be attributed to the (002) reflection of the graphite phase of g-C₃N₄.³² The g-C₃N₄ prepared by microwave heating is similar to that prepared from urea in a tube furnace (Fig. S3, ESI[†]).

g-C₃N₄ synthesized *via* microwave heating is slightly water soluble. The excitation–emission maps of g-C₃N₄ in aqueous solution and of the g-C₃N₄ powder are shown in Fig. 4a and Fig. S4 (ESI[†]), respectively. Both samples show a single emission band at around 400 nm. From the excitation–emission map of a dilute ethanol solution of the CDs (Fig. 4b), it can be seen that CDs exhibit excitation-dependent PL with two bands at 390 nm and 520 nm, as reported in our previous work.³³ The strongest emission is observed at around 520 nm under 410 nm excitation. Fig. 4c shows that CDs@g-C₃N₄ composites mostly inherit the luminescence from the CDs, namely two bands at 390 nm and 510 nm, while the PL band from g-C₃N₄ at 400 nm cannot be observed. The effective excitation spectral region for the green emission band of the CDs@g-C₃N₄ composite is broader than that of the ethanol solution of CDs (Fig. 4d). Considering that the emission of g-C₃N₄ well overlaps with the PLE spectrum of CDs (Fig. 4d) and the emission band of g-C₃N₄ is observed in the PLE spectrum of CDs@g-C₃N₄ (Fig. 4d), it can be inferred that in the CDs@g-C₃N₄ composite an efficient resonant energy transfer occurs from g-C₃N₄ to the embedded CDs, and contributes to the enhancement of the green emission of the latter.

Fig. 4e shows PL spectra of CDs@g-C₃N₄ composites with different loadings of CDs, all collected under 360 nm excitation. For the loading amounts of CDs lower than 1 wt%, both bands at 390 and 520 nm are present in the PL spectra. The strongest emission was observed for the CDs@g-C₃N₄ composite with 1 wt% of CDs. Upon further increase of the CD loading, the band at 390 nm vanished, while the band at 520 nm slightly red-shifted and gradually decreased in intensity. Both processes can be ascribed to the increasing re-absorption of the emitted light at higher loading amounts of CDs, while the decreased intensity of the green emission is probably related to the aggregation-induced luminescence quenching of CDs. A clear blue emission from the back of the pressed tablets of bare g-C₃N₄ can be seen when excited with UV light that passed through the tablets of bare g-C₃N₄ (Fig. S5, ESI[†]). Fig. 4f shows PL decay curves of CDs@g-C₃N₄ composites with different loading amounts of CDs, recorded under 375 nm excitation. At lower CD amounts (up to 1 wt%), the average PL lifetime derived from these curves is 11.6 ns. Upon increasing the CD loading the PL lifetime gradually decreased, which further confirms the assumption that the aggregation-induced luminescence quenching of CDs occurs in the composites. The highest PLQY of the CDs@g-C₃N₄ composite was measured to be 62% for 1 wt% CD loading (Fig. S6, ESI[†]).

To reveal the advantages of the microwave-assisted *in situ* synthesized CDs@g-C₃N₄ composite, composites of g-C₃N₄ and CDs were also prepared *via* physical mixing processing. g-C₃N₄ and CDs were separately synthesized *via* the above-mentioned microwave-assisted method, mixed in 30 ml of deionized water followed by stirring for 5 h, and freeze-dried to form composites (denoted CDs/g-C₃N₄) with CD loading amounts in the range of

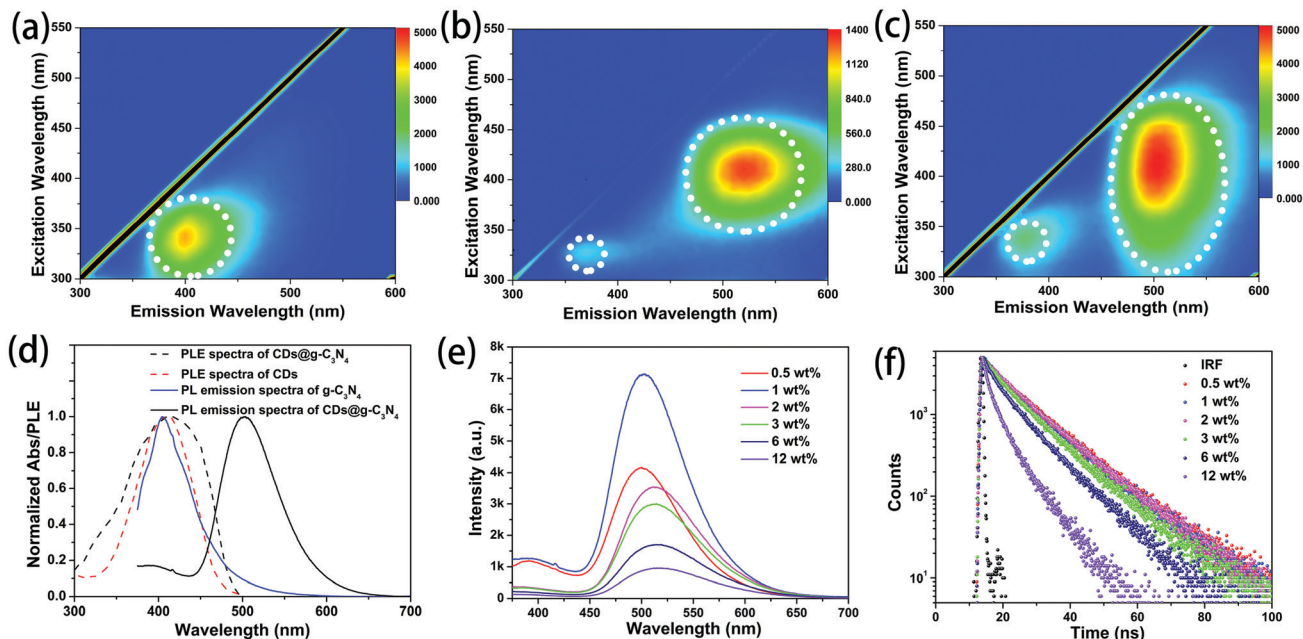


Fig. 4 Excitation–emission maps of (a) g-C₃N₄ solid powder, (b) an ethanolic solution of CDs and (c) a solid powder of a CDs@g-C₃N₄ composite with 1 wt% CDs. (d) PLE spectra (monitored at 510 nm) of CDs (red dotted curve) and CDs@g-C₃N₄ (black dotted curve), and PL emission spectra (excited at 360 nm) of g-C₃N₄ (blue curve) and CDs@g-C₃N₄ (black curve). (e) PL spectra of CDs@g-C₃N₄ composites with different loadings of CDs, all excited at 360 nm. (f) PL decay curves of g-C₃N₄ and CDs@g-C₃N₄ powders with different loadings of CDs, monitored at 510 nm under 375 nm excitation.

0.5–6 wt%. From the TEM image of CDs/g-C₃N₄ (Fig. S7, ESI[†]), we can recognize that the CDs tend to form clusters at the edges of g-C₃N₄. It can be seen from Fig. 5a and Fig. S8, S9 (ESI[†]) that under UV light excitation the green emission from the CDs@g-C₃N₄ is much stronger than that of the CDs/g-C₃N₄ at the same CD loading. The values of the PLQYs and PL intensities of

both CDs@g-C₃N₄ and CDs/g-C₃N₄ under 410 nm excitation are summarized in Fig. 5b. It can be seen that both the PLQY and PL intensity of CDs@g-C₃N₄ with 1 wt% CD loading concentration are the highest compared to CDs/g-C₃N₄, and the PLQY of CDs/g-C₃N₄ gradually decreases upon increasing the CD loading concentration. Thus, it can be inferred that the microwave-assisted *in situ* synthesis promotes the successful inclusion of CDs within the g-C₃N₄ network without evident agglomeration, while the synthesis of composites *via* physical mixing is not able to provide a homogeneous CD distribution upon increasing the CD loading concentration, which in turn results in CD aggregation-induced luminescence quenching.

Previous reports pointed out the fact that CDs exhibit much better photostability than fluorescent organic dyes.^{18,34,35} We conducted a study of the photo- and thermal stability of the CDs@g-C₃N₄ composite, in terms of preserving its emission intensity. As shown in Fig. 5c and d, the PL intensity of the reference organic dye (fluorescein sodium) decreased to less than 70% and 50% of their initial PL intensity after continuous UV irradiation (1.6 W cm⁻¹) for one hour and heating up to 160 °C, respectively, while the PL intensity of the CDs/g-C₃N₄ composite retained 85% and 65% of their initial PL intensity values. In contrast, the CDs@g-C₃N₄ composite maintained its emission stability, retaining 92% and 80% of the initial PL intensity after the same treatment, due to the beneficial protection of the homogeneously embedded CDs in the g-C₃N₄ matrix formed in the second-step of the microwave heating.

A CDs@g-C₃N₄ composite with 1 wt% CDs, as the one with the most favorable light-emitting characteristics, was selected for WLED fabrication. InGaN LED chips (1 W) were covered

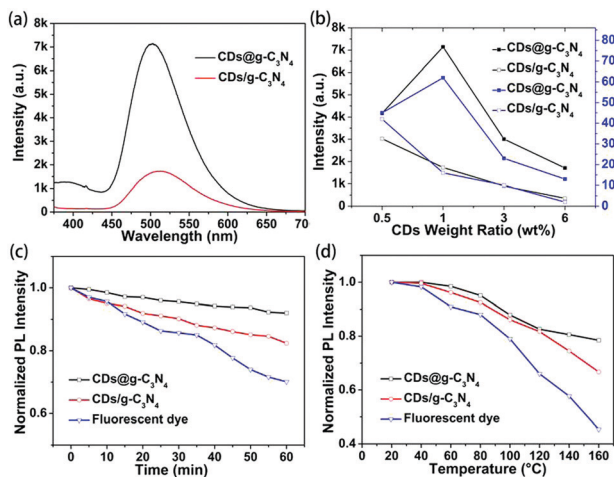


Fig. 5 (a) PL spectra of CDs@g-C₃N₄ and CDs/g-C₃N₄ composites with 1 wt% CD loading concentration under 360 nm excitation. (b) Peak PL intensities under 360 nm excitation of CDs@g-C₃N₄ and CDs/g-C₃N₄ with different CD loading concentrations (black curves) and PLQYs of CDs@g-C₃N₄ and CDs/g-C₃N₄ composites with different CD loading concentrations under 410 nm excitation (blue curves). Evolution of the PL intensities of CDs@g-C₃N₄, CDs/g-C₃N₄ and organic dye (fluorescein sodium): (c) under UV light exposure (1.6 W cm⁻¹) and (d) upon heating to 160 °C.

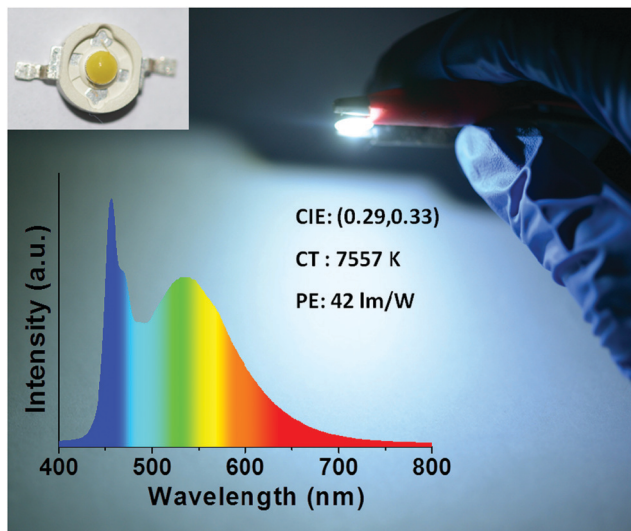


Fig. 6 Photograph of a CD-based working LED prototype utilizing a $\text{CDs@g-C}_3\text{N}_4$ composite with 1 wt% CDs as a phosphor, and its emission spectra with the related characteristics. CIE: CIE color coordinates, CT: color temperature, PE: power efficiency.

with this phosphor dispersed in epoxy silicone resin (mass ratio 1 : 2), followed by heating in an oven at 80 °C for 1 h. A device which emitted cold white light with CIE color coordinates of (0.29, 0.33) and a color temperature of 7557 K was realized (Fig. 6), with a power efficiency of 42 lm W^{-1} , which favorably compares with the performance of other CD-based down-conversion WLEDs reported in the literature (Table S1, ESI[†]).

Conclusions

$\text{CDs@g-C}_3\text{N}_4$ composite phosphors were conveniently fabricated on a large scale using a two-step microwave-assisted heating method from the cheap and environmentally friendly precursors citric acid and urea. CDs were *in situ* homogeneously embedded and bonded within the $\text{g-C}_3\text{N}_4$ network to prevent CD aggregation-induced luminescence quenching. Compared to a physical mixture of CDs and $\text{g-C}_3\text{N}_4$, composite $\text{CDs@g-C}_3\text{N}_4$ phosphors exhibited higher PLQYs with better photo- and thermal stability. The $\text{CDs@g-C}_3\text{N}_4$ composite with an optimal loading amount of CDs (1 wt%) emitted bright green light with a PLQY of 62% under 410 nm excitation, and retained 92% and 80% of its initial PL intensity after continuous UV irradiation (1.6 W cm^{-2}) for one hour and heating up to 160 °C, respectively. Using this $\text{CDs@g-C}_3\text{N}_4$ composite as the color conversion layer, a WLED emitting cold white light with CIE color coordinates of (0.29, 0.33) and a color temperature of 7557 K was fabricated, with a high power efficiency of 42 lm W^{-1} . The results of this work will further promote the development of environment-friendly CD-based phosphors for lighting applications.

Materials and methods

Citric acid (99.5%) was purchased from Aladdin. Urea (99%) was purchased from Macklin. All chemicals were used as

received without further purification. The deionized water used in all the experiments was purified using a Millipore system.

Synthesis of CDs

Green-emissive CDs were synthesized using a microwave-assisted method, from citric acid as the carbon source and urea as the nitrogen source according to our previous work.³² 6 g urea, 3 g citric acid and 20 ml of deionized water were mixed in a 100 ml beaker to form a colorless transparent solution. The beaker was transferred to a domestic 750 W microwave oven, and heated for 3–4 min. Upon heating, the water began to boil and gradually evaporated, resulting in the formation of a brownish solid.

Preparation of $\text{g-C}_3\text{N}_4$

10 g urea was dissolved in 20 ml of deionized water, followed by heating in a 750 W microwave oven for 3–4 min. Upon heating, the water gradually evaporated, resulting in the formation of a $\text{g-C}_3\text{N}_4$ powder, which was ground and used for further measurements.

Preparation of $\text{CDs@g-C}_3\text{N}_4$ composites

To prepare composite materials with different loading amounts of CDs, citric acid (9 mg, 18 mg, 36 mg, 54 mg, 108 mg, 216 mg) and urea (18 mg, 36 mg, 72 mg, 108 mg, 216 mg, 432 mg) were added into 20 ml of deionized water, and the mixtures were stirred for a period of time until both precursors were completely dissolved. Each solution was transferred to a 750 W microwave oven and heated for 3–4 min. Upon heating, the water began to boil and gradually evaporated, resulting in the formation of a brownish solid. Subsequently, addition of 20 ml of 0.5 g ml^{-1} urea to the solid made CDs fully soluble. This solution was placed into a 750 W microwave oven again and heated for 3–4 min until the water completely evaporated, which resulted in the formation of a $\text{CDs@g-C}_3\text{N}_4$ composite solid. The solid was ground and used for further measurements.

Preparation of $\text{CDs/g-C}_3\text{N}_4$ composites by means of physical mixing

Separately synthesized CDs (5 mg, 10 mg, 30 mg, 60 mg) were mixed with $\text{g-C}_3\text{N}_4$ (1 g) under continuous stirring in deionized water for 2 h, and then placed into a lyophilizer for vacuum freezing. The resulting powders were ground and used for further measurements.

Fabrication of WLEDs based on $\text{CDs@g-C}_3\text{N}_4$ phosphors

InGaN LED chips (emission peak at 450 nm, operating under a voltage of 3.0 V) were purchased from Shenzhen Xinhongxian Optoelectronics Technology Co., Ltd. For the preparation of the color conversion layer, the $\text{CDs@g-C}_3\text{N}_4$ composites were mixed with the epoxy silicone resin precursors with a mass ratio of 1 : 2. The mixtures were deposited on the LED chip followed by heating at 80 °C for 1 h.

Characterization

UV-visible absorption spectra were measured on a Shimadzu UV-3101PC spectrophotometer. PL and PL excitation spectra were measured on a Hitachi F-7000 spectrophotometer. Absolute PLQYs

were measured in a calibrated integrating sphere using an FLS920 spectrofluorimeter (Edinburgh Instruments Ltd). PL lifetimes were measured *via* time-correlated single-photon counting using an FLS920 spectrometer under 405 nm excitation. Fluorescence microscopy images were obtained on a C2+ confocal microscope system (Nikon confocal instruments). X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer. Transmission electron microscopy (TEM) was performed on an FEI Tecnai-G2-F20 microscope at 200 kV. Scanning electron microscopy (SEM) was performed on a JEOL FESEM 6700F microscope with a primary electron energy of 3 kV. The emission spectra of WLEDs were measured on a Fu Xiang NOVA-EX fiber optic spectrometer.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was funded by the Science and Technology Development Fund, Macau SAR (0040/2019/A1), the National Natural Science Foundation of China (No. 61975200), the Youth Innovation Promotion Association of CAS (2018252), Jilin Province Science and Technology Research Projects (No. 20170101191JC, 20180101190JC and 20170101042JC), and the Ministry of Science and Higher Education of the Russian Federation (Grant No. 14. Y26.31.0028).

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