

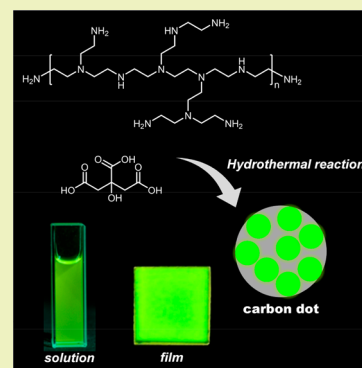
Highly Emissive Carbon Dots in Solid State and Their Applications in Light-Emitting Devices and Visible Light Communication

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S Supporting Information

ABSTRACT: As a new type of luminescent material, carbon dots (CDs) have attracted increased attention for their superior optical properties in recent years. However, CDs generally suffer from aggregation-induced luminescence quenching, which means they are highly emissive in solution or a dispersed state but dramatically quenched in a solid or aggregated state. This problem significantly limits the application of CDs, partially in the solid-state light-emitting devices. In this work, a new kind of solid-state emissive CDs have been synthesized via simple one-step hydrothermal strategy. Under 450 nm excitation, the CDs exhibit bright green luminescence in the solid state, with a quantum yield of 26%. The luminescence lifetime of the CDs is only 4 ns. Employing the CDs as a color converter, white light-emitting diodes were fabricated and a visible light communication system with high performance (modulation bandwidth of 55 MHz, data transmission rate of 181 Mbps) was realized.

KEYWORDS: Carbon dots, Aggregation-induced luminescence quenching, Solid-state luminescence, Light-emitting diodes, Visible light communication



INTRODUCTION

Increasing types of luminescent materials opened up exciting avenues of display and illumination, while luminescent materials made from rare-earth-based materials, quantum dots, and small organic molecules still suffer from problems of limited supply, toxicity, low stability, and high cost.^{1–5} Carbon dots (CDs) are a kind of promising luminescent nanomaterial with the features of tunable color, high-photoluminescence quantum yield (PLQY), good photostability, and excellent biocompatibility.^{6–11} Moreover, CDs can be synthesized from widely available, environment-friendly materials by simple and low-cost methods in comparison with quantum dots and rare-earth-based materials.¹² All these advantages endow CDs distinct benefits for applications in lighting,^{13–15} optoelectronics,^{16–18} sensing,^{19–21} and bioimaging,^{22–26} etc.

In recent years, rapid progress has been made in the optical performance of CDs and their promising applications as color-converting phosphors in white light-emitting diodes (WLEDs) and visible light communication (VLC) have been demonstrated,^{14,27–29} which offer a potential alternative to traditional luminescent materials such as quantum dots and rare-earth-

based materials. However, most of the CDs suffer from aggregation-induced luminescence quenching in the solid state, which is ascribed to excessive resonance energy transfer (RET), interparticle coupled surface states, or direct π – π interactions.^{15,29–32} This drawback prevents all direct applications of CDs in solid-state lighting devices. The usual approach to conquer the self-quenching is generally doping CDs in solid matrices, e.g., polymers, inorganic salts, silica, and layered and mesoporous materials.^{33–39} There are reports that solid-state emissive CDs employing poly(vinyl alcohol) (PVA) as matrix achieved PLQY of 84%, but the loading concentration of CDs is only 0.6 wt %.^{40,41} It is proved that higher loading concentration still leads to a large decrease of PLQY, which is mainly because of local aggregation in the solid state during the preparation process. In addition, these common methods are accompanied by multistep procedures, which are time-consuming and have the issue of instability. Thus, it is urgent to develop self-quenching-resistant CDs to

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Scheme 1. Schematic Illustration of the Preparation of CDs

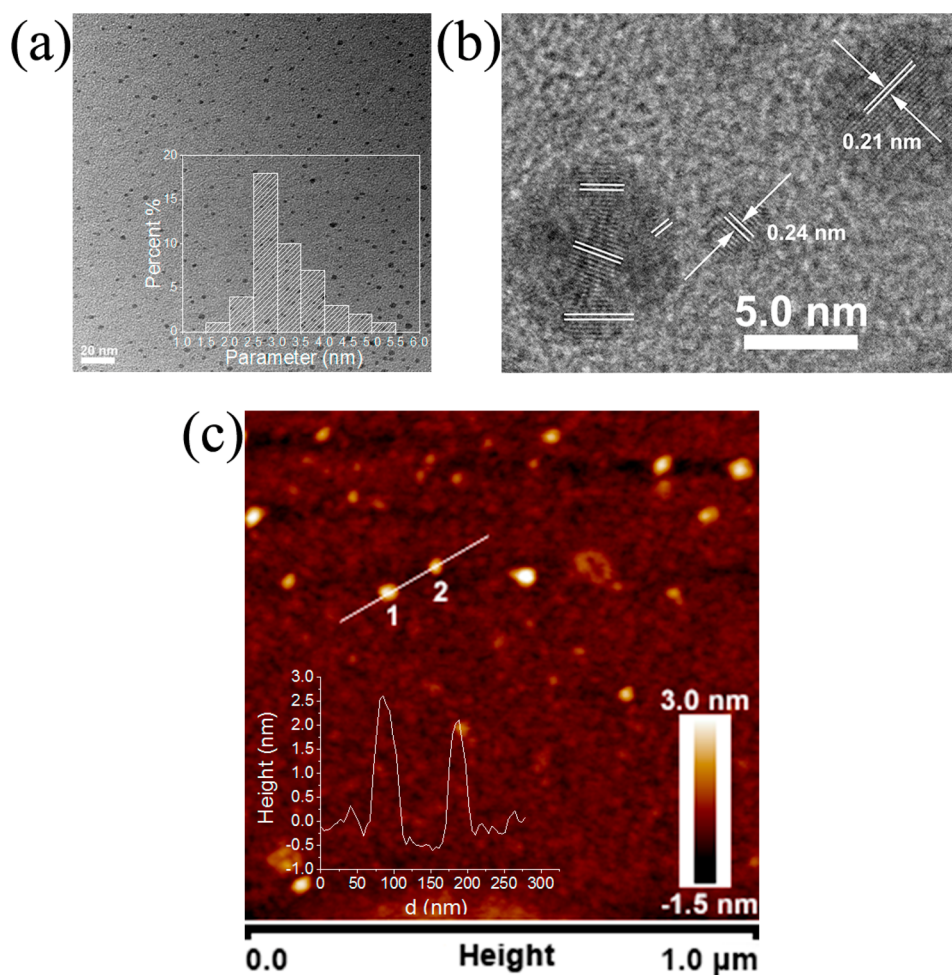
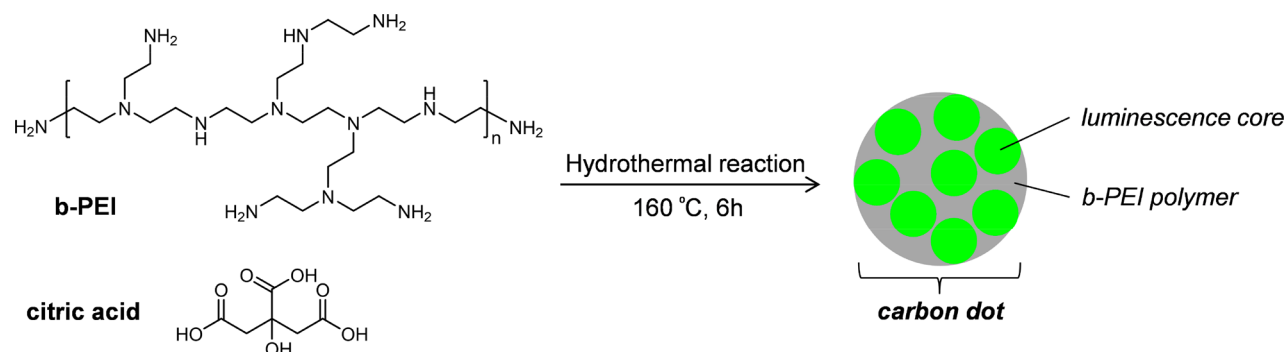


Figure 1. (a) TEM images of CDs (inset, size distribution histograms of CDs); (b) HRTEM image of the particles; (c) AFM image (inset, height profile along the line in the AFM image).

meet the practical demand. For instance, by hydrothermal treatment of PVA and ethylenediamine, Chen and co-workers synthesized solid-state fluorescent CDs with strong yellow-green fluorescence in the aggregation state and a PLQY of 35%.¹⁵ Recently, our group has developed several approaches to construct CDs with efficient emissions in the solid states. We successfully prepared uniform-sized CDs in a foam structure. The homogeneous structure of CDs results in a uniform energy band gap, which significantly suppresses the energy transfer among CDs in aggregates and thus overcomes the aggregation-caused quenching.⁴² In another way, treating blue-emissive CDs with aqueous hydrogen peroxide (H_2O_2)

provides green-emissive CDs with PLQY up to 25% in the solid state.²⁹ However, the reported self-quenching-resistant CD powders are still scarce and require a relatively rigid process or post-treatment. It is very necessary to develop new approaches to construct solid-state luminescent CDs for WLEDs and VLC applications.

To solve the aforementioned problem, herein, we developed a new type of self-quenching-resistant CDs via a one-step hydrothermal strategy, using citric acid as the carbon source and branched poly(ethylenimine) (b-PEI; molecular weight, 2000) as the nitrogen source and surface passivation agents (Scheme 1). Under 450 nm excitation, the CDs in solid state

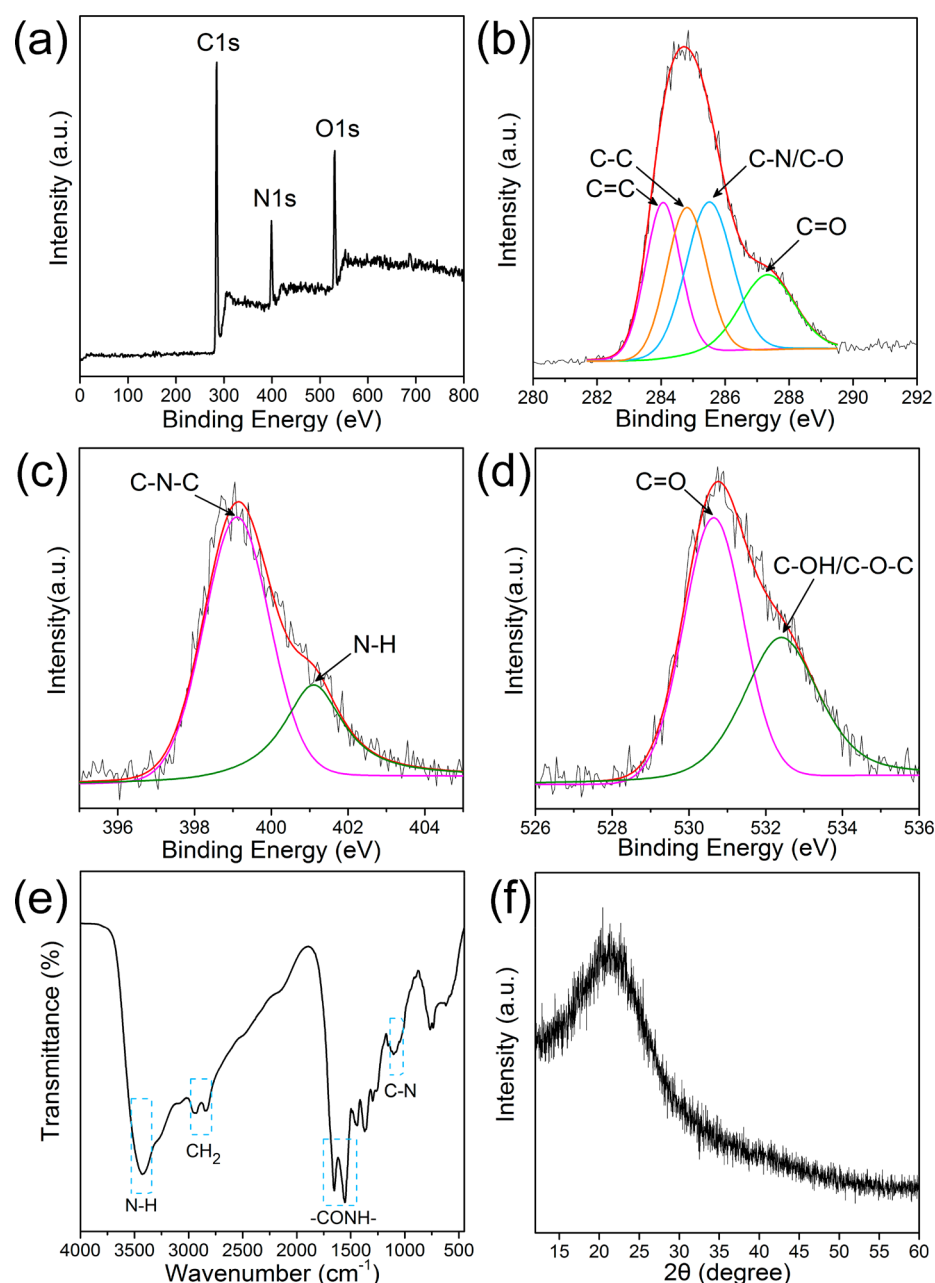


Figure 2. (a) Full survey XPS spectra; (b) C 1s, (c) N 1s, and (d) O 1s XPS spectra of CDs; (e) FT-IR spectrum of the CDs; (f) XRD pattern of the CDs.

exhibit bright green luminescence without any dispersed matrices and feature a PLQY of 26% and short luminescence lifetime of 4 ns. By combining the CD phosphors with an InGaN blue chip (450 nm), WLEDs were successfully constructed. Taking advantage of the short luminescence lifetime of CDs (4 ns), a VLC system was also constructed. The modulation bandwidth of the system is 55 MHz, and the data transmission rate is 181 Mbps. Compared with our recently reported strategy to achieve self-quenching-resistant CD phosphor by H_2O_2 treating,²⁹ this method is versatile and simple without post-treatment. This study not only provided a new method for preparing self-quenching-resistant solid-state luminescent CDs but also demonstrated promising utilizations of CDs for lighting and VLC.

RESULTS AND DISCUSSION

Citric acid was used as the carbon source, and b-PEI (molecular weight, 2000) was used as the nitrogen source and surface passivation agents. Under hydrothermal condition, these two components mixed in H_2O were heated at 160 °C for 6 h. Products of hydrothermal reaction were further purified by dialyzing against H_2O for 1 week (refer to [Experimental Section](#)), and finally solid-state luminescent CDs were obtained. We also tested *N,N*-dimethylformamide (DMF) as the solvent instead of H_2O for preparing the carbon dots. Under the same reaction condition, the carbon dots prepared from DMF display the same emission property as those prepared from H_2O . However, the reaction using DMF as solvent would produce some cross-linked byproducts

of carbon dots which were insoluble in common solvents, e.g., DMF, DMSO, and H₂O.

We employed transmission electron microscopy (TEM) and atomic force microscopy (AFM) to characterize the morphologies and structures of the CDs. As shown in Figure 1a, TEM analysis revealed that the sizes of CDs distributed in the range of 2–6 nm (Figure 1a). High-resolution transmission electron microscopy (HRTEM, Figure 1b) image disclosed the crystalline nature of CDs with lattice fringes of 0.21 and 0.24 nm, corresponding to the [110] plane of graphene and (1120) lattice fringes of graphite, respectively.⁴³ Thus, the CDs have a graphite structure. The HRTEM image of “aggregated” CDs provides the size distribution of about 2–6 nm (Supporting Information Figure S1). In the AFM image (Figure 1c), the heights of the CDs were distributed in the range of 2–6 nm. The results of AFM and TEM indicated that the CDs were quasi-spherical and the mean particle size was 3 nm. The CDs purified via dialysis have a broad size distribution, and we suppose that homogeneous CDs with narrow size distribution may be obtained via size-exclusion chromatography, which has been recently employed to separate crude CDs on the basis of their sizes.⁴⁴

The chemical constitution and structure of CDs were characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). The XPS spectra revealed the existence of C_{1s}, N_{1s}, and O_{1s} which located at 284, 400, and 531 eV, respectively (Figure 2a). In the high-resolution spectra of C_{1s} (Figure 2b), peaks at 284.1, 284.8, 285.5, and 287.3 eV were attributed to C=C, C–C/adventitious carbon, C–N/C–O, and C=O groups.^{45–48} The high-resolution N_{1s} XPS spectra have two peaks located at 399.1 and 401.1 eV (Figure 2c), which correspond to pyridinic N (C–N–C) and amino N (N–H), respectively.⁴⁹ In the O_{1s} spectra (Figure 2d), two peaks located at 530.6 and 532.4 eV were assigned to C=O and C–OH/C–O–C groups.⁵⁰ The FT-IR spectrum (Figure 2e) of CDs exhibited characteristic absorption bands of N–H at 3440 cm^{−1}, CH₂ at 2950 and 2840 cm^{−1}, and C–N at 1122 cm^{−1}, which indicated the existence of the b-PEI fragment in CDs.⁵¹ In addition, sharp peaks associated with amide linkage (–CONH–) at 1650 and 1556 cm^{−1} (corresponding to amide I and II bands),⁴² proved the dehydration condensation of citric acid and b-PEI during the formation of CDs. The XRD pattern of the CDs showed a broad diffraction peak at 2 θ = 21° (Figure 2f), suggesting the formation of amorphous carbon in CDs.^{2,52} The broadened peak and large layer spacing (0.41 nm) compared with those in reported CDs (2 θ = 27°, *d* = 0.32 nm) were probably because polymer chains on the surface and edges of CDs partially broadened and disordered the close-packed structure of graphite-like cores in CDs.⁵³

The CDs could disperse in water easily, and the color of the solution is light yellow. After drip coating, a smooth CD film can be easily obtained on the quartz substrate (Figure S2). The absorption spectrum of CD aqueous solution (Figure S3a) exhibits a major absorption band that peaked at 360 nm with an absorption tail extended to the visible region. The absorption peak at 360 nm is attributed to the n– π^* transition of C=O.^{54,55} In the excitation–emission map of CD dilute aqueous solution (Figure S3b), the luminescence occurs in the blue to green region, with the main emission band around 440–480 nm under the excitation of 395–415 nm. The PLQY of CD solution is 6% under 450 nm excitation. In the solid state, CDs exhibited identical absorption spectra (Figure 3a)

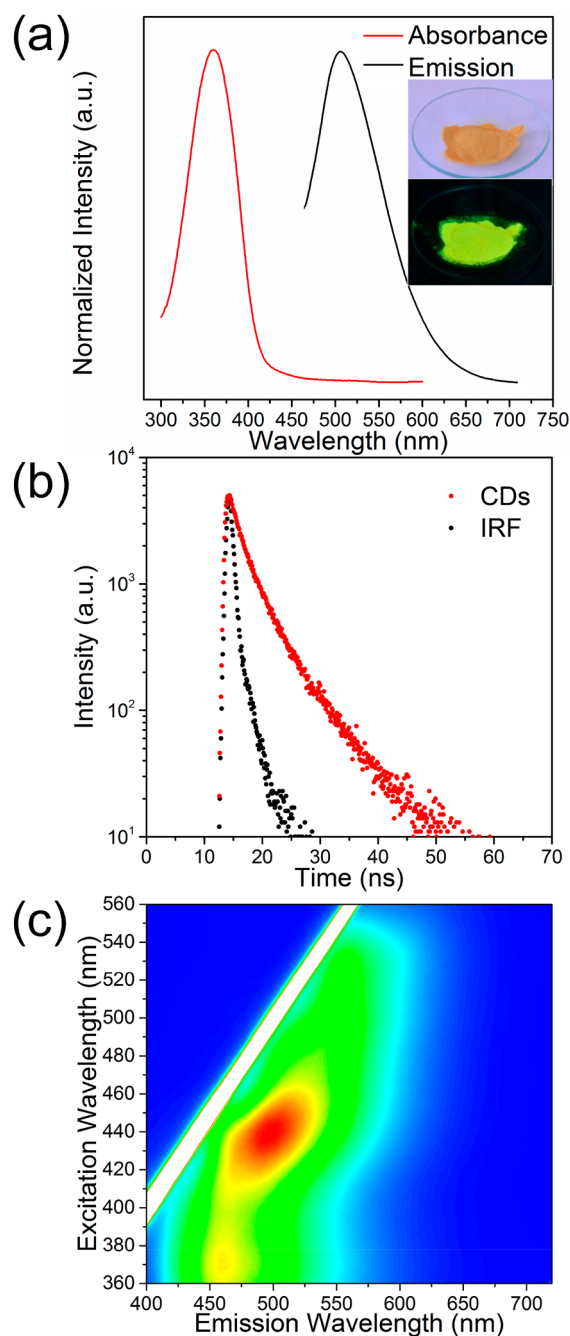


Figure 3. a) UV–vis absorption spectrum and emission spectrum of CD film (excited by 450 nm; inset, photographs of the CD powders under daylight and blue light); (b) PL decay curve of the CD film excited at 405 nm and collected fluorescence intensity at 510 nm (IRF, for instrumental response function); (c) excitation–emission map of CD film.

with that in solution and bright luminescence in the blue to yellow spectral region, with a major emission band centered at around 488–535 nm under the excitation of 420–460 nm (Figure 3c). The emission spectra of CDs display a certain dependence on the excitation wavelengths. This may be due to the emissions originating from the conjugated π -domains as well as the surface defects.⁵⁶ Under 450 nm excitation, the CD film shows bright green luminescence (λ_{em} = 510 nm) with a PLQY up to 26% (Figures 3a and S2). The photoluminescence

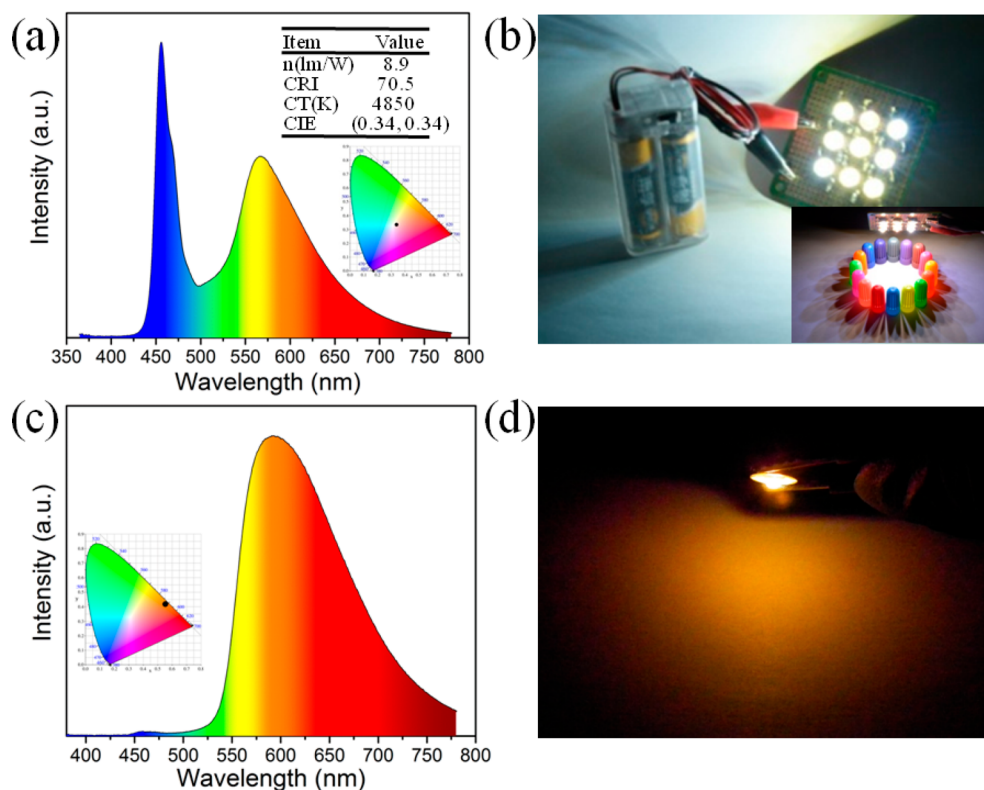


Figure 4. (a) Emission spectrum of working WLED and its performance parameters; (b) photograph of the battery-powered WLEDs array (operating on 3.0 V; inset, image of pen caps under the working WLEDs array); (c) emission spectrum of CDs-based LEDs with yellow light; (d) photograph of the working yellow LED.

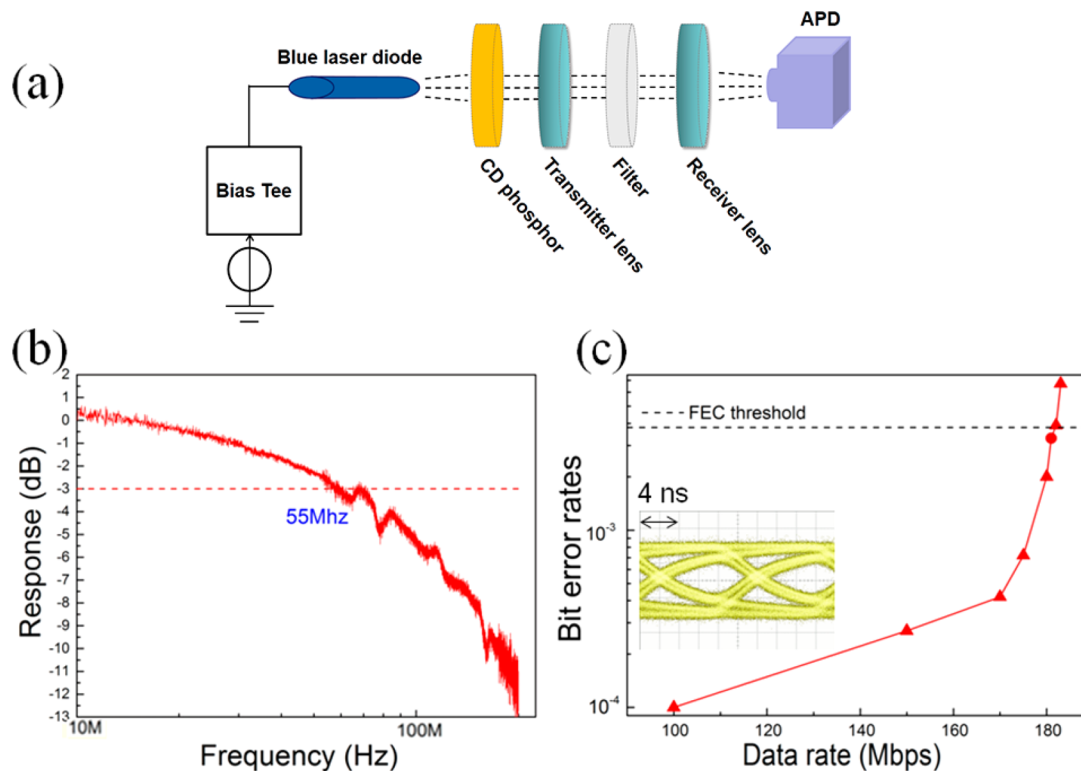


Figure 5. (a) Schematic illustration of the measurement of VLC system; (b) frequency response of the VLC system (dotted line, bandwidth of -3 dB); (c) dependence of the bit error rate (BER) on the data transmission rate (dashed line, threshold of forward error correction (3.8×10^{-3}); inset, eye diagram at the transmission rate of 100 Mbps).

(PL) decay curve of the CD film is shown in Figure 3b. The lifetime monitored at 510 nm is only 4 ns.

On basis of the structure and photophysical characterizations of CDs, b-PEI is speculated to play a key role in the luminescence behavior of CDs. On one hand, the amino-enriched branched chains of b-PEI provide abundant reactive sites for dehydration and N doping to support the formation of emissive carbon cores. On the other hand, the polymer backbones and branched chains can homogeneously disperse and restrain the adjacent luminescence centers in the aggregate state and thus prevent interparticle surface electron transitions as well as π - π interactions of graphitizing cores. As a result, CDs can maintain efficient luminescence in the aggregate state with no need of additional dispersion matrix. Moreover, from the absorption spectrum of the CD film, it is evident that the absorption band is narrow and the overlap between absorption spectrum and the PL spectrum is small. The weak self-absorption property also contributes to the efficient solid-state luminescence of CDs.

The branched polymer b-PEI serves as not only the nitrogen source of CDs but also the surface passivation agent to avoid the aggregation-induced luminescence quenching. The reaction between b-PEI and other carbon sources, instead of citric acid, may provide new solid-emissive CDs with various emission colors. Moreover, this result will inspire employment of other branched polymers to prepare solid-emissive CDs.

To verify the potential application of the CDs as solid-state luminescence materials in lighting, WLEDs were fabricated using the CDs as an emitting layer. By depositing the CDs on the surface of blue-emissive LED chips and adjusting the concentration, CIE coordinates and the color temperature (CT) of LEDs can be controlled. As shown in Figure 4a, the CDs-based WLED with CIE coordinates of (0.34, 0.34), CT of 4850 K, and CRI of 70.5 has been fabricated. By improving the concentration of CD powders, yellow LEDs with CIE coordinates of (0.56, 0.43), CT of 1849 K, dominant wavelength of 588.4 nm, and color purity of 97.9% have also been realized (Figure 4c,d). In comparison to the CDs in the film with the emission maximum of 510 nm, the emissions of CD phosphors in WLED (maximum of 565 nm) and yellow LED (maximum of 590 nm) are gradually red-shifted, which is ascribed to self-absorption effects of CD phosphors. As shown in Figure 4b, connecting multiple WLEDs in parallel, an area light was fabricated. Powered by two batteries (total voltage, 3 V), the area light can work well.

Besides illumination, VLC based on WLEDs has attracted increasing interest in recent years.⁵⁷ In comparison with traditional radio frequency (RF) communication (e.g., Wireless-Fidelity (Wi-Fi) and Bluetooth), VLC has a lot of superiority, such as unregulated communication spectrum, no RF interference, higher security, and environmental friendliness.⁵⁸ Rare-earth luminescent materials have been successfully applied in VLC. However, these materials have the serious drawbacks of not only limited reserves but also long luminescence lifetimes. The long lifetimes directly limited the intrinsic system bandwidth of VLC, because this value is inversely proportional to the luminescence lifetime.⁵⁹ Taking advantage of the efficient luminescence and short luminescent lifetime (4 ns) in solid state, the CDs were explored as a color converter for VLC applications. The experimental method (Figure 5a) is similar to our previous report.²⁹ A blue laser diode (450 nm) powered by a bias-tee was used to excite the CDs. The generated emission successively passed through the

transmitter lens, 495 nm long-pass filter, and the receiver lens. Finally, the emission was transformed into the electrical signal by the photoelectric converter (APD). As shown in Figure 5b, the CD phosphor-based VLC system exhibited a bandwidth of up to 55 MHz (current, 60 mA), which is significantly larger than the representative rare-earth-based phosphor (3–12 MHz). Figure 5c displays the dependence of the bit error rate (BER) on the data transmission rate of the CD phosphor-based VLC system. On the premise of error-free operation (BER of 3.3×10^{-3}), the maximum data transmission rate is 181 Mbps. The eye diagram for the CD phosphor-converted light at 100 Mbps is shown as the inset of Figure 5c. The open eyes indicate that high and low electrical levels can be well distinguished at a high transmission rate of 100 Mbps. The outstanding performance highlights the potential utility of CDs in VLC.

CONCLUSIONS

In conclusion, a new kind of self-quenching-resistant CDs were synthesized by a facile one-step approach with efficient luminescence (PLQY = 26%), and short PL lifetime (4 ns). Making use of CDs as color converter, WLEDs and a VLC system have been realized. The VLC system displayed a high performance with modulation bandwidth of 55 MHz and data transmission rate of 181 Mbps, much higher than that of rare-earth phosphors. Therefore, the CD phosphor represents a new generation material for high-performance solid-state illumination and VLC.

EXPERIMENTAL SECTION

Citric acid (3 g) and branched PEI (molecular weight, 2000; 6 mL) were dissolved in deionized water (20 mL). Then, the mixture was placed in a Teflon-lined stainless steel autoclave and reacted at 160 °C for 6 h. After cooling to room temperature, a light yellow solution was obtained. The light yellow solution was filtrated to remove the large precipitate and agglomerated particles. Further, using a dialysis bag (molecular weight cutoff, 3500), the CDs were dialyzed against distilled water for a week to remove low molecular weight impurities. At last, the purified products (inner of the dialysis bags) were lyophilized and collected for further use. Other experimental details including chemicals and materials, fabrication of CDs-based WLEDs, characterization experiment, and VLC experiment are exhibited in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b00325.

Experimental section about chemicals and materials, construction of CDs-based WLEDs, VLC and characterization; photographs of CD solution and film and of different colored pen caps taken under sunlight; absorption spectrum of CD aqueous solution; excitation–emission spectrum of CD aqueous solution (PDF)

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Notes

The authors declare no competing financial interest.

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