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Solid-State Fluorescent Carbon Dots with Aggregation-Induced Yellow Emission for White Light-Emitting Diodes with High Luminous Efficiencies

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Supporting Information

ABSTRACT: For practical applications of carbon dots (CDs), a major challenge is to prevent the notorious aggregation-caused quenching (ACQ) effect. Herein, a new type of CDs (CD1) has been developed that can transform from ACQ to an enhancement of fluorescence by aggregation-induced emission (AIE). The blue fluorescence of the CDs is suppressed by ACQ. However, this is accompanied by the phenomenon of AIE at a longer wavelength, resulting in the emergence and gradual enhancement of yellow fluorescence. The obtained CD1 solid powder shows a bright yellow emission with a photoluminescence quantum yield (PLQY) of 65%. The photoluminescence (PL) spectra, absorption spectra, and time-resolved PL decay curves indicate that Förster resonant energy transfer from dispersed CD1 particles to large CD1 agglomerations leads to the enhancement of yellow fluorescence. To exploit its high PLQY and strong AIE, CD1 is applied as a color-converting layer on blue light-emitting diode (LED) chips to fabricate white LEDs (WLEDs). The obtained devices show white light coordinates of



(0.29, 0.38) and (0.32, 0.42), which are close to pure white light (0.33, 0.33), and luminous efficiencies of 97.8 and 93.9 lm·W⁻¹ and show good stability. The low cost, easy fabrication, controllability, and favorable fluorescence properties signify that CD1 of AIE will have superior performance in a variety of applications.

KEYWORDS: carbon dots (CDs), aggregation-caused quenching (ACQ), aggregation-induced emission (AIE), solid-state fluorescence, white light-emitting diodes (WLEDs), luminous efficiency

INTRODUCTION

White light-emitting diodes (WLEDs) have significant application potential in the new generation of lighting and display technologies because of their compact size, fast response, low power consumption, long operational life, and remarkable energy efficiency.¹⁻³ In the design of WLEDs, solid-state phosphors, used as color conversion layers, play a key role in determining the performance parameters, such as luminescent color, Commission Internationale d'Eclairage (CIE) coordinate, color rendering index (CRI), correlated color temperature (CCT), luminous efficiency, and production cost. However, conventional rare-earth-based phosphors are costly and nonrenewable.⁴ Semiconductor quantum dots (QDs) and perovskite QDs are considered to be potential substitutes for rare-earth-based phosphors, but their heavy metal components (such as Cd and Pb) may pose toxicity risks.^{5–7} Consequently, alternative materials that can be easily prepared by green procedures are essential for the development of WLEDs.

Recently, a new branch of carbon-based nanomaterials, namely, carbon dots (CDs), have emerged as promising nanomaterials and aroused great interest in bioimaging, photocatalysis, sensors, lasers, LEDs, and photovoltaic devices because of their excellent luminescence properties, low cost, low toxicity, excellent biocompatibility, and high stability.^{8–15} Recently, numerous reports of CD-based WLEDs have highlighted the potential applications of CDs in this field. Guo synthesized three different types of emissive CDs by controlling the reaction temperature and fabricated 370 nm pumped WLEDs with CIE coordinates of (0.19, 0.28), (0.45, 0.44), and (0.34, 0.37). The photoluminescence quantum yields (PLQYs) of these as-prepared CDs reached up to 47%.¹⁶ Qu reported a warm WLED [CIE coordinate: (0.41, 0.45), CCT: 3708 K] based on starch/CD phosphors, with a PLQY of 23%.¹⁷ Wang prepared red emissive CDs with a PLQY of

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53% and developed an ultraviolet (UV)-pumped CD-based warm WLED with a CRI of 97 by combining the CDs with blue and green emissive CDs.¹⁸ These pieces of information are listed in Table 1 for comparison.

Table 1. PLQYs, ACQ or AIE Properties of CDs, CIE Coordinates, and Luminous Efficiencies of CD-Based WLEDs of Several Representative Literature Studies

			CDs based WLEDs		
references	solution	solid	AIE	CIE	luminous efficiency
16	47%	N/A	no	(0.34, 0.37)	N/A
17	46%	23% for CD/starch phosphors @ 1.41 wt %	no	(0.41, 0.45)	N/A
18	53%	50% for CD/PMMA film @ 6.83 wt %	no	(0.39, 0.39)	31.3
our work	84% for blue dispersed emission	65% @ pure CD powder with yellow AIE	yes	(0.29, 0.38)	97.8

However, the luminous efficiencies of these obtained WLEDs were either not mentioned or less than 50 $\text{lm}\cdot\text{W}^{-1}$. The PLOYs of the above CDs were based on solution luminescence. This is because CDs in the solid state suffer from the aggregation-caused quenching (ACQ) effect, that is, the emission is weakened in comparison to that in solutions because of aggregation.^{19,20} This would undoubtedly have reduced the luminous efficiency of the above-described WLEDs. The ACQ problem must be effectively solved because most luminophores are used in the solid state for practical applications, such as opto-electronic devices, lasers, and fluorescent diagnostic kits. A common method to resist ACQ is the dispersion of CDs into solid matrices such as a transparent polymer,²¹⁻²⁴ starch,²⁵ or silica xerogel.^{26,27} However, under these conditions, high PLQYs can usually only be realized at rather low concentrations. For instance, CD@poly(vinyl alcohol) (PVA) composites possess high PLQYs (up to 84%) with a CD concentration of 0.6 wt %, whereas their PLQYs decline to 16% when increasing the CD concentration to 7.4 wt %.28 In practice, these methods, though commonly used, do not actually eliminate the inherent ACQ characteristics of CDs. A more effective strategy would be to fabricate CDs as solid powders with emissive properties determined not by ACQ but by the reverse phenomenon, aggregation-induced emission (AIE), leading to high PLQYs.

We here developed a simple strategy to synthesize yellow emissive CDs with AIE by a one-pot microwave heating method. The CDs transformed from aggregation-quenched blue fluorescence to an AIE-induced enhancement of yellow fluorescence with the increase of CD concentration. The CD powder reached a PLQY of 65% in the range of 500–620 nm, and WLEDs with high luminous efficiencies (>90 lm·W⁻¹) were realized using the CDs (Table 1).

MATERIALS AND METHODS

Materials. Citric acid (CA, 99.5%), L-cysteine (CYS, 99%), and KCl (99.5%) were purchased from Aladdin. All of the chemicals used were commercially available and of analysis-grade purity without further purification. The ultrapure water used in all of the experiments was from a Millipore system.

Synthesis of CD1 Powder. CA (3 g), 2 g of CYS, and 1 g of KCl were dissolved in 10 mL of ultrapure water, and the solution was heated in a microwave oven. Regular intervals are needed every 20 s to avoid bumping, and stirring was necessary during these intervals to ensure a homogeneous reaction. By keeping at medium heating for 5 min, CD1-containing powder was obtained. Then the powder was dissolved in a dilute hydrochloric acid solution (pH = 1), which was dialyzed against ultrapure water using a membrane (molecular weight cutoff = 1 kD) for 1 week. The purified aqueous solution of CD1 was condensed by vacuum-rotary evaporation, and then it was freeze-dried to powder and collected.

Synthesis of CD2 Powder. CA (3 g) and 2 g of CYS were dissolved in 10 mL of ultrapure water following the procedure for the synthesis of CD1 powder.

Preparation of WLEDs. To fabricate WLEDs, polydimethylsiloxane (PDMS) and CD1 powder were mixed with a certain mass ratio to form a uniform gel, which was then directly coated onto a commercially available 460 nm GaN LED, followed by curing at 60 °C for 30 min without need of any other matrices. Different emissive WLEDs were obtained using different concentrations of CD1 in CD1/PDMS color conversion layers.

Stability Measurement. To test the stability of the WLED device, the emission spectrum of the WLED was measured against working time at an operating current of 20 mA, and the electroluminescence (EL) intensity and luminous efficiency were also measured when enhancing the drive current from 20 to 90 mA. To test the thermal stability of CD1, the photoluminescence (PL) intensity of CD1 and CD1/PDMS was measured against temperature (from 25 to about 100 $^{\circ}$ C).

Characterization. High-resolution transmission electron microscopy (HRTEM) images were taken with a FEI-Tecnai G2 transmission electron microscope operating at 200 kV. The TEM sample was prepared by depositing CD dilute solution on a carboncoated copper grid. X-ray photoelectron spectroscopy (XPS) was determined by using a Thermo Scientific ESCALAB 250 for multitechnique surface analysis. A Bio-Rad Excalibur FTS 3000 spectrometer with KBr tablets was used to measure Fourier transform infrared (FTIR) spectra of CDs. A F-7000 Hitachi fluorescence spectrometer was used to detect PL emission spectra. Fluorescence lifetimes and absolute PLQY were determined by using an Edinburgh FLS920 fluorescence spectrometer (Figures S1-S4). UV/visible absorption spectra were measured by a Shimadzu UV-3101 spectrophotometer. The photoelectric properties of the WLEDs were measured using a HAAS 2000 photoelectric measuring system (350-1100 nm, EVERFINE, China). The forward bias current for WLEDs was 20 mA.

RESULTS AND DISCUSSION

The one-pot microwave heating synthesis was performed as follows (Scheme 1). CA (3 g), CYS (2 g), and KCl (1 g) were dissolved in ultrapure water (10 mL) (the left side of Scheme 1). The solution was heated under microwave radiation, during which the precursor materials swelled into porous foam (the foamy object in a beaker) as the water evaporated and the byproduct gas was released (the middle part bubbles in the

Scheme 1. Schematic of Growth Mechanism of CD1 Synthesized by the One-Step Microwave Heating Method





Figure 1. (a) Excitation–emission matrix of the 0.2 mg mL⁻¹ CD1 solution; (b) top: fluorescent photographs of CD1 solutions at concentrations of 0.2, 20, 50, 100, 250, 500, and 1000 mg mL⁻¹, bottom: the corresponding normalized PL spectra; (c) excitation–emission matrix of solid CD1 powder (the inset is the corresponding fluorescent photograph). (d) Excitation–emission matrix of the 0.2 mg mL⁻¹ CD2 solution; (e) top: fluorescent photographs of CD2 solutions at concentrations of 0.2, 10, 20, 50, 100, 250, and 500 mg mL⁻¹, bottom: the corresponding normalized PL spectra; (f) excitation–emission matrix of solid CD2 powder (the inset is the corresponding fluorescent photograph). The color bar in Figure 1 is the normalized intensity of luminescence, the reddest part of the top color bar means the maximum value of 1, the bluest color at the bottom represents the minimum value of 0, and the middle colors are distributed from the reddest to bluest color in a linear equidistant manner.



Figure 2. TEM images of (a) CD1 and (b) CD2 (top inset is the size distribution histogram, bottom inset is the HRTEM image); (c) FTIR spectra of CD1 and CD2; XPS spectra of (d) full scan, (e) C 1s, (f) N 1s, (g) O 1s, and (h) S 2p of CD1 and CD2.

right-side figure). KCl acted as a temperature-conducting medium, so that the precursor materials could be uniformly heated to form CDs. Moreover, KCl also isolated these nascent CDs to prevent them from interfering with each other in the process of growth. This formation of CDs within the confined spaces of the foam walls (the rightmost graphic) effectively prevented the excessive growth of CDs, endowing them with uniform particle sizes. Highly luminescent CD-containing foams with yellow emission were obtained after 5 min. Subsequent purification was performed to remove metal ions, residual salts, and unreacted small molecules to ensure highpurity CDs (CD1). To confirm the necessity of KCl, a control experiment was carried out without KCl but otherwise using the same microwave heating method. The product was denoted CD2.

Table 2. Relative Contents of Various Chemical Bonds in CD1 and CD2 As Determined by XPS

		N 1s		O 1s		S 2p		
sample	C 1s	pyrrolic-N	graphitic-N	C=0	С-ОН/С-О-С	S-C	S-H	S-S
CD1	1	0.07	1.5×10^{-2}	0.55	0.06	3.2×10^{-2}	1.2×10^{-2}	1.6×10^{-2}
CD2	1	0.12	0.5×10^{-2}	0.37	0.13	3.1×10^{-2}	2.1×10^{-2}	4.8×10^{-2}

The emission behaviors of CD1 and CD2 were explored first. A dilute (0.2 mg mL^{-1}) CD1 solution showed an emission peak at 435 nm, which was independent of the excitation wavelength (the strong blue fluorescence can be seen in the inset photo of Figure 1a), with a PLQY of 84%. The top part of Figure 1b shows fluorescent photographs of CD1 solutions at different concentrations, and the bottom part shows the corresponding normalized PL spectra. As can be seen, CD1 exhibited concentration-dependent luminescence: as the concentration of CD1 increased, new emission peaks appeared at longer wavelengths and were red-shifted to 550 nm while becoming gradually more intense (Figure S5). The CD1 powder showed excellent hydrophilicity: 1 g of CD1 powder could be dissolved in 1 mL of water instantly without heating or ultrasound treatment. The peak at 550 nm became the dominant emission, while the blue emission became almost invisible compared with the yellow one (Figure S5f). The bright yellow fluorescence of the CD1 powder, corresponding to the emission peak at 550 nm, is shown in the inset of Figure 1c. Importantly, the PLOY of the powder was measured to be 65% in the range of 500-620 nm. The above finding, that as the CD1 concentration increased the blue emission around 450 nm gradually weakened, is attributed to ACQ, as in conventional CDs.^{19,20} Meanwhile, the gradual strengthening of the yellow emission around 550 nm after its initial appearance is attributed to AIE. These observations indicate that CD1 can transform from ACQ to AIE and possesses tunable PL. To the best of our knowledge, this is the first report of CDs with both ACQ and AIE. Compared with the liquid samples, a new emission center appeared in the powder sample under the excitation range of 300-420 nm, which were caused by the different measurement approach used for solids (Figure S6). As can be seen, transmissive measurement is used to record the spectra of solutions, which causes strong absorption at short wavelengths, whereas the reflective measurement approach is suitable for solid samples, which does not affect the short wavelengths. The two emission centers in Figure 1c match with the main emission peaks of dilute and concentrated solutions in Figure 1b, but the maximum intensity of blue emission (around 450 nm) is about a quarter of that of the yellow ones (around 550 nm).

In the case of CD2, the 0.2 mg mL⁻¹ solution possessed the most intense emission peak at 440 nm and showed excitationdependent emission (see the inset photo of blue fluorescence in Figure 1d), with a PLQY of 54%. As the concentration increased, the emission wavelength was red-shifted, while the fluorescence intensity decreased rapidly (Figures 1e and S7). The fluorescence of CD2 solutions with concentrations of 250 and 500 mg mL⁻¹ was hardly observable by the naked eye. Meanwhile, no PL peaks could be detected in the visible light region for the solid powder (Figure 1f), indicating that its fluorescence was completely quenched in the solid state. This behavior indicates the phenomenon of ACQ, which is very common for conventional CDs. In our experiments, the fluorescence usually decayed too fast at higher concentration to develop tunable PL for practical applications.

The morphologies and chemical compositions of CD1 and CD2 were characterized to probe the origin of their luminescence properties, respectively. Figure 2a shows the TEM image of the CD1 sample prepared from the dilute solution, which demonstrates that the CD1 particles are torispherical. The top inset picture of Figure 2a shows that the size distribution is consistent with a Gaussian function, with an average diameter of 2.1 nm and a full width at half-maximum of 0.7 nm, indicating that the particle sizes are relatively uniform. HRTEM (bottom inset of Figure 2a) reveals a lattice spacing of 2.1 Å, which corresponds to the in-plane lattice spacing of graphite (100 facet). Larger CDs are observed in the CD2 TEM image (Figure 2b), where the average size is 5.2 nm and its Gaussian distribution ranges from 2 to 8 nm. Considering the different spectral properties of CD1 and CD2, it is reasonable to suppose that the homogeneous structure of CD1 would lead to uniform energy levels, which would help to avoid nonradiative energy transfer among CDs in aggregates and thus to prevent ACQ.

The compositions of the two types of CDs were determined by FTIR spectroscopy and XPS. In Figure 2c, for both materials, the broad absorption band at 2575 cm^{-1} is assigned to the stretching vibrations of $-SH_{2}^{29,30}$ and the strong peak at 1717 cm⁻¹ is attributed to the vibrational absorption band of C=O in carboxyl groups. Meanwhile, the peaks at 1638 and 1395 cm⁻¹ are characteristic of the two stretching vibrations of C=O in carboxylate.^{18,31,32} The peaks at 1220 and 1019 cm⁻¹ correspond to the two stretching vibrations of C-O-C.³³ The peak at 1520 cm⁻¹ is the in-plane bending vibration of N-H and that at 1075 cm⁻¹ is the stretching vibration of C-N.³⁴ CD2 shows weaker absorption bands of C=O in carboxyl groups and stronger peaks of asymmetric stretching (ν_{as}) of COO⁻, which implies the transformation from carboxyl groups to carboxylates. The enhanced peaks of $\delta(N-H)$ and $\nu(C-N)$ denote more nitrogen doping in CD2. Additionally, CD2 presents an obviously reinforced peak of symmetric stretching $(\nu_{\rm S})$ of C–O–C, implying more abundant C–O–C groups in CD2 than in CD1.

These compositions were further confirmed by the XPS results (Figure 2d-h). The full survey scans indicate that both CDs are mainly composed of carbon, nitrogen, sulfur, and oxygen (Figure 2d). The high-resolution C 1s spectra show the existence of graphene-like sp² C in C=C groups at 284.6 eV, sp³ C in C-N/C-O/C-S groups at 286.2 eV, and sp³ C in C=O groups around 288.2 eV (Figure 2e).^{35,36} The high-resolution N 1s scans (Figure 2f) illustrate two different types of nitrogen doping: pyrrolic-N around 399.8 eV and graphitic-N around 401.3 eV.³⁷ The O 1s spectra (Figure 2g) exhibit peaks at 531.8 and 533 eV, corresponding to C=O and C-OH/C-O-C groups, respectively.^{35,36} The high-resolution spectra of S 2p reveal the presence of S-C, S-H, and S-S units (Figure 2h).³⁸⁻⁴⁰

The relative contents of different chemical bonds are presented in Table 2 for detailed comparisons between CD1 and CD2. The differences in composition between the two materials are consistent with the FTIR analysis. Comparing the



Figure 3. Absorption spectra of (a) CD1 and (d) CD2 in solution with different concentrations; time-resolved spectroscopy curves of (b) CD1 and (e) CD2 solution with different concentrations monitored at 450 nm under excitation at 365 nm; time-resolved spectroscopy curves of (c) CD1 and (f) CD2 solution with different concentrations monitored at 550 nm under excitation at 460 nm.

N 1s results, CD2 has a higher level of N-doping, which is mainly pyrrolic-N, so that the peak of δ (N–H) is stronger than that of CD1. In addition, the large gap in graphitic-N contents between the two types of CDs may be responsible for the clear difference between their PLQYs.^{34,41,42} On the other hand, the doping of sulfur introduced thiol groups, which is also an electron-donating group similar to the hydroxyl group, so that the synergy of graphitic-N and thiol groups leads to high PLQY to CD1.³⁴ More importantly, CD2 contains more than twice the contents of C–OH/C–O–C as those of CD1, which may be related to their different spectral characteristics.

To clarify the mechanisms behind the AIE and ACQ of the two types of CDs, absorption spectroscopy and time-resolved spectroscopy were performed. Figure 3a shows the absorption spectra of CD1 solutions with different concentrations. As shown, the dilute CD solution (0.2 mg mL⁻¹) possesses a strong peak at 350 nm arising from the $n-\pi^*$ transitions, which presumably predominates because of the existence of C=O bonds.⁴³ A new absorption peak appears at 470 nm as the concentration increases. In Figure S8, the PL peak at 550 nm overlaps with the band at 470 nm, implying that the yellow light emission originates from the transition of the absorption band at 470 nm rather than the band at 350 nm.⁴⁴ In short, the blue emission at 450 nm is contributed by the monodisperse CDs, whereas the yellow emission at 550 nm is attributed to the aggregated CDs. Remarkably, there is a large overlap between the new absorption peak (470 nm) and the PL peak (450 nm) of the dilute CD1 solution (0.2 mg mL⁻¹) (Figure S8), which indicates effective Förster resonant energy transfer (FRET) from dispersed CD1 particles to agglomerated ones.⁴⁵⁻⁴⁸ A series of time-resolved spectra of CD1 were measured to verify this hypothesis, as illustrated in Figure 3b. The excited-state lifetime of CD1 monitored at 450 nm gradually decreased as the concentration increased (Table S1), indicating the formation of alternative recombination channels in the aggregated state.⁴⁹ However, no obvious changes as a function of concentration were observed in the decay curves monitored at 550 nm (Figure 3c). These results reveal the gradually reduced lifetime of blue emission centers with the increase of concentration and confirm the FRET from dispersed CDs to agglomerated ones.

The absorption and time-resolved spectra of CD2 were also measured for comparison. Unlike CD1, the significant enhancement in the absorption spectra of CD2 occurred in the broad range of 400–650 nm rather than for a specific peak, as the concentration increased (Figure 3d). As shown in Figure 3e,f and Table S2, the monitored lifetimes all decreased as the concentration increased, meaning that the energy in monodisperse CD2 was transferred to aggregated CD2 and then mostly dissipated by nonradiative transitions.

The absorption spectra were converted to Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ to estimate the optical band gaps (E_g) of these CDs, in which α , h, and ν are the absorption coefficient, Planck constant, and light frequency, respectively.^{15,50} As shown in Figure 4a, the E_g values of CD1 at different concentrations were thus determined to be 3.25, 3.08, 3.05, 3.01, 2.98, 2.94, 2.91, and 2.83 eV, respectively (Table S3). The E_g values of CD2 are also given in Figure 4b and Table S3, and these decrease rapidly with increasing concentration.

According to first-principles calculations by Yan et al., the C-O-C and C-O-H groups of sp²-hybridized carbon can induce hydroxy- (or epoxide)-related electronic states within the $n-\pi^*$ gap and create excited energy levels.^{51,52} This phenomenon depends on the contents of C-O-H/C-O-C groups (Table 2), which explains why the excited energy levels are relatively concentrated in CD1 but more widely separated in CD2.⁵³ By carefully inspecting and analyzing the emission spectra of the CDs, for example, Figure S7b, we divide the spectra into three parts: the front peak, main peak, and rear peak. The main peak is the strongest peak in the fluorescence spectra, the front peak refers to the weakest emission peak that can be detected before the main peak, and the rear peak is the weakest emission peak that can be detected after the main peak. The blue, green, and red lines connect the energy levels of the front, main, and rear peaks at different concentrations, respectively, showing the trends in the energy levels after the concentration changes. The gap between the front and rear peaks denotes the width of the excited energy band (the distance between two dashed lines in Figure 4c,d), while the position of the main peak represents the Fermi level (green line, the core level of the excited energy band), which determines the PL behavior. The emission band gaps



Figure 4. (a) $(\alpha h\nu)^2$ vs $h\nu$ curve of CD1 solutions with different concentrations. The black lines are the tangents of the curves. The intersection value on the *X*-axis is the band gap. (b) $(\alpha h\nu)^2$ vs $h\nu$ curve of CD2 solutions with different concentrations. (c) Energy-band level alignments of CD1, the solid arrow refers to the reduction of the band gap as the concentration increases and the distances between two dashed lines are excited energy levels within the $n-\pi^*$ gap; (d) energy-band level alignments of CD2. Schematic of energy transfer that occurs in the aggregation process of (e) CD1 and (f) CD2.

calculated on this basis are given in Table S3, Figure 4c,d. For CD1, regardless of the concentration, the front peak is located around 450 nm (2.76 eV) and represents the excited level of the monodisperse CD1. The position of the rear peak is determined by the concentration and represents the excited level of the aggregated CD1. The main emission peak gradually approaches the rear peak in this excited state energy band as the concentration increases, and the emission peak reaches 550 nm at the concentration of 1 g mL^{-1} . According to the quantum confinement effect, energy level splitting and broadening occur in CDs' aggregation process as the concentration increases and leads to a reduction in the band gap.^{54,55} Therefore, as the concentration of CD2 increases, first, the E_{σ} values decrease rapidly, and furthermore, the wide range of excited-state energy levels in the band gap also splits and broadens, and the separated excited energy levels within the $n-\pi^*$ gap can easily enter into the broadening lowest

unoccupied molecular orbital levels (Figure 4d), which further promotes the red shift of the PL spectra of CD2. According to our calculations, this red shift of PL moves out of the visible range when the concentration of CD2 exceeds 500 mg mL⁻¹ (>1.52 eV, Table S3), and no visible fluorescence can be detected. On the other hand, the self-absorption is greatly enhanced when increasing the concentration (Figure 3d), causing a decrease in PL intensity. In addition, the uneven size distribution of CD2 leads to diversification of the energy levels, increasing the concentration strengthens nonradiative energy transitions among different-sized CD2 and aggregated CD2, resulting in a rapid decrease in PL intensity, so that a rapid red shift and decrease of the PL happen as the concentration increases, which is the ACQ phenomenon of the conventional CDs. As for CD1, the band gap reduction did not overlap with the excited energy levels within the $n-\pi^*$ gap when increasing the concentration (Figure 4c). The size distribution of CD1 is quite uniform, so the energy levels of CD1 are relatively close, so that even after increasing the concentration, the band gap of CD1 undergoes little change. Hence, the excited-state energy levels in the band gap are relatively concentrated, so the CDs exhibit a transformation from ACQ to AIE.

On the basis of the above results, a possible mechanism for ACQ and AIE phenomena of the CDs is given in Figure 4e,f. As the concentration increases, monodispersed CDs gather into aggregates. The residual dispersed CD1, whose own emissive wavelength is blue (left side of Figure 4e), can transmit their energy to the large aggregates of CD1, which have yellow emission (right side of Figure 4e). Meanwhile, the blue light emitted by the dispersed CD1 will be reabsorbed by the agglomerated CD1, resulting in the enhancement of yellow emission with increasing concentration (Figure 4e). These effects finally lead to a bright yellow fluorescence of CD1 powder with a PLQY of 65%. For CD2, no fluorescence of the aggregates can be detected (right side of Figure 4f). Instead, because the absorption band of the aggregates is both broad and strong, the energy of the residual dispersed CDs will be dissipated through the nonradiative transition of aggregates (Figure 4f). Therefore, increasing concentration ultimately leads to the quenching of fluorescence.

WLEDs have diverse applications, including lighting and display, benefiting from their low power consumption, long lifetime, fast response, and compact size.^{1–3} CD1 can be used to prepare WLEDs in combination with blue GaN LED chips, with the benefits of simple, low-cost preparation and easily realized solid-state yellow emission with high PLQY. To fabricate WLEDs, PDMS and CD1 powder were mixed to form a uniform gel, which was then directly coated onto a 460 nm GaN LED, followed by curing at 60 °C for 30 min without



Figure 5. (a) EL spectra of WLEDs with different concentrations of CD1 in CD1/PDMS color conversion layers and (b) their corresponding photographs and color coordinates of these devices under working conditions.

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need of any other matrices to obtain the WLED (the schematic diagram is shown in the inset of Figure 5a). Different colorconverting layers, generated from different mass ratios of CD1 to CD1/PDMS, led to differently illuminated WLEDs. Figure 5a shows the emission spectra of the WLEDs under working conditions, wherein two discrete emission peaks located at 460 and 550 nm can be clearly observed, which are attributed to the blue chip and solid-state CD1, respectively. Figure 5b shows photographs of the working devices with their corresponding CIE coordinates. When the concentration of CD1 reaches 63.6 and 70 wt %, the color coordinates of the obtained WLEDs are (0.29, 0.38) and (0.32, 0.42), respectively, close to pure white light (0.33, 0.33), and their corresponding luminous efficiencies reach 97.8 and 93.9 lm- W^{-1} , respectively (Figure S9), which are much higher than the WLEDs based on conventional CDs, semiconductor QDs, and perovskite QDs.^{17,18,56,57} As shown in Figure 5a, as the concentration of CD1 in the CD1/PDMS complex increases from 50.0 to 87.5 wt %, the PL peak of CD1 gradually shifts from 542 to 558 nm. This red shift of PL wavelength is caused by the increased aggregation of CD1. Most CDs are hydrophilic, whereas PDMS is hydrophobic, and then the CD/PDMS complex formed in a physically mixed manner exacerbates the aggregation of the CDs (Figure S10); this phenomenon undoubtedly hinders the use of traditional CDs with ACQ to prepare WLEDs. However, CD1 possesses AIEinduced enhancement of yellow fluorescence, and because of the hydrophobicity of PDMS, the degree of CD1 aggregation is further increased, and its PL wavelength is 8 nm larger than that of pure CD1 powder when CD1 concentration is 87.5 wt %. Therefore, in the CD1/PDMS complex, CD1 is allowed to exist in a large concentration, which increases the effective light absorption of the blue light emitted by the LED GaN chip without increasing the thickness of the color-converting layer. Increasing the thickness always enhances the blue light scattering and the optical loss. On the one hand, a large concentration of CD1 leads to AIE-induced yellow light enhanced emission, and its 65% PLQY of pure solid powder and the measured external PLQY of 60% of the WLED color conversion layer (CD1: 63.6 wt %, measurement shown in Figure S11) ensure its high light conversion efficiency in WLED.

To test the stability of the WLED (CD1: 63.6 wt %) device, the emission spectrum of the WLED was measured against working time at an operating current of 20 mA. As shown in Figure S12, after the WLED worked 10 h, there was no obvious change in its EL spectrum, demonstrating a reasonable stability. The EL intensity of the WLED (CD1: 63.6 wt %) lamp increased when enhancing the drive current from 20 to 90 mA (Figure S13). The luminous efficiency of the WLED lamp slightly dropped from 97.8 to 91.4 lm W⁻¹ when the drive current increased from 20 to 90 mA (Figure S14). The good stability of the device is due to the tolerance of CD1 to device heating. To test the thermal stability of CD1, the PL intensity of CD1 and CD1/PDMS (CD1: 63.6 wt %) was measured against temperature (from 25 to 150 °C). As shown in Figure S15, the PL intensities only have 21.5 and 13.8% decay of CD1 and CD1/PDMS at 150 °C, respectively, indicating that CD1 shows high thermal stability. The luminous efficiencies could be further improved by optimizing the structure. In view of these impressive performances and the advantages of simple synthetic method, low cost, stability, and

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controllable fabrication, CD1 has potential applications in solid-state lighting and display.

CONCLUSIONS

In summary, we have synthesized CDs (CD1) with concentration-dependent fluorescence, which transform from ACQ to AIE, by one-pot microwave heating of CA, CYS, and KCl. With increasing solution concentration, the blue fluorescence of CD1 is suppressed by ACQ, which is accompanied by the AIE-promoted emergence and gradual enhancement of yellow fluorescence. During the synthesis, KCl performs two roles: conducting heat evenly to the precursors and isolating these nascent CDs to prepare uniformly sized CD1 particles. Another material, CD2, was also prepared using the same synthesis method but without KCl. The occurrence of only conventional ACQ in CD2 confirmed the necessity of KCl in preparation of CD1 and provided a universal route for synthesizing CDs that exhibit AIE. The obtained CD1 solid powder showed a bright yellow emission with a PLQY of 65%, but no fluorescence was detected in the CD2 solid powder. The PL and absorption spectra and time-resolved PL decay curves indicated the existence of FRET from residual dispersed CD1 to large agglomerations, while the light emitted by dispersed CD1 was reabsorbed by agglomerated CD1, which led to the enhancement of yellow fluorescence of the CD1 solid powder. In contrast, in CD2, the phenomenon of ACQ was further strengthened by the nonuniformity of the particle size and the higher contents of C-O-C and C-O-H groups containing sp²-hybridized carbon. In view of the high PLQY and intense AIE, CD1 was applied as a color-converting layer on blue LED chips to fabricate WLEDs. The obtained devices showed white light coordinates of (0.29, 0.38) and (0.32, 0.42)and high luminous efficiencies of 97.8 and 93.9 $\text{lm}\cdot\text{W}^{-1}$, respectively. We believe that CD1 of AIE property could have superior performance in the fields of lighting and displays, biology, EL, and photovoltaic devices.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b04600.

PLQY measurements; PL spectra; scheme of PL measurement; normalized absorption and PL spectrum; calculated lifetimes; band gap values; luminous efficiencies; CD1/PDMS structure; external PLQY measurement; and stability of CD1 and WLED (PDF)

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Notes

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