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Full-Color Inorganic Carbon Dot Phosphors for White-Light-Emitting Diodes

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Light-emitting carbon dots (CDots) are widely investigated due to their distinct merits. However, it is still a challenge to modulate their bandgap emissions and conquer their aggregation-induced luminescence quenching to achieve full-color highly emissive CDot-based phosphors. Herein, this study proposes an approach toward realization of full-color emissive CDots from two common precursors, citric acid and urea, through employing three different solvents (water, glycerol, and dimethylformamide) and their combinations in a solvothermal synthesis. Employing sodium silicate solution, this study further demonstrates the microwave-assisted method allowing to incorporate CDots into a silica network, which effectively prevents aggregation of CDots and results in strongly luminescent full-color inorganic CDot phosphors with photoluminescence quantum yields of 30–40%. Through deposition of the red- and green-emitting CDot phosphors on blue-emitting InGaN chips, white-light-emitting diodes are fabricated with Commission Internationale de L'Eclairage of (0.34, 0.31) and the color rendering index of 82.4, indicating their promising application for solid-state lighting.

1. Introduction

Carbon dots (CDots) as a novel luminescent material possess a number of distinct merits such as low toxicity, biocompatibility, high photostability, and ease of preparation,[1,2] which render them attractive for applications in bioimaging,[3–5] sensor,[6] photocatalysis,[7] energy storage,[8,9] and optoelectronic devices.[10–12] Luminescence properties of CDots are still under intensive investigations, both to reveal their origin and to optimize them for lighting applications.[13–16] In terms of the emission mechanisms, apart from the recently evolving evidences on the molecular fluorophore formation during the synthesis of CDots and their contribution to the strong emission of the resulting samples in the blue spectral region,[17–19] intrinsic (bandgap related) emission from the CDots core originating from the conjugated sp^2-domains[20,21] is most promising for their development and applications.[22] Theoretical calculations[23] and experimental studies[24] pointed out that the intrinsic emissions of CDots can be tuned by modulating the dimension of conjugated sp^2-domains. However, it is still lack of experimental method to achieve full color emissions through tuning the sizes of sp^2-domains in CDots. Several groups also showed that the emission of CDots can be tuned toward green and red through surface modification.[25,26] Ding et al. prepared a series of CDots with emission tunable from 440 to 625 nm, which has been ascribed to the varying degree of their surface oxidation.[27] Similarly, Bao et al. reported a wet chemical method toward CDots with emission tunable from 430 to 610 nm by surface oxidation.[28] Several other recent studies suggested some strategies to achieve higher photoluminescence quantum yields (PLQYs) in the full-color range by using different precursors.[29] To the best of our knowledge, there is no experimental evidence to achieve full-color emissive CDots in the same precursors and method, which is very important for fundamental understanding and realizing full-color intrinsic emissive CDots.

Apart from their promising biological applications, CDot-based solid state luminescent composites, as emerging environmentally friendly phosphors, have received increasing attentions for carbon-based light emitting diodes (LEDs), and particularly white LEDs (WLEDs).[30,31] However, in realizing efficient CDot-based phosphors, the quenching of emission in the solid state constitutes a severe issue.[32,33] It is important to exploit suitable matrices, surface functionalizing agents and methods to produce well dispersed, environmentally protected,

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strongly emitting CDot-based phosphors. Chen et al. applied polymer coating to prevent the solid state luminescence quenching of CDots.[34] Wang et al. realized solid state blue-emitting composite phosphors (PLQY of 60%) by embedding CDots into a polyhedral oligomeric silsesquioxane matrix.[35] Our group incorporated CDots within starch, barium sulfate ($BaSO_4$), and silica, resulting in CDot-based phosphors with efficient green emission.[36–38] Commercial WLEDs based on blue emitting InGaN chips with YAG:Ce yellow phosphor as color converter[39] usually exhibit color rendering index (CRI) lower than 75. The correct judgment of object color needs the CRI of light source higher than 80. Consequently, high efficient red emitting CDot-based phosphors are strongly desirable. However, most of the reported CDot-based phosphors usually emit in the blue or green spectral ranges.[30,31,36] It is thus still a challenge to prepare full-color, highly emissive CDot-based phosphors, especially the red emissive ones.

In our previous work, we developed blue, green, and orange emissive CDots from two common procures citric acid and urea in different methods (microwave[32] or solvothermal[19,36] methods), which shine a light on revealing the mysterious luminescent mechanism and controlling emissions of CDots. In this work, full-color emissive CDots were prepared from the same precursors citric acid and urea by tuning the solvents in solvothermal conditions. We demonstrate how different solvents—water, glycerol, and dimethylformamide (DMF)—affect the dehydration and carbonization processes occurring during the high-temperature solvothermal reaction, resulting in the different overall sizes of the resulting CDots and thus dimensions of conjugated sp^2-domains, determining their different emission colors. Full-color emissive CDots could thus be synthesized in solvothermal conditions when using mixtures of these three solvents in variable contents. Employing sodium silicate solution, we further demonstrate the microwave assisted method allowing us to functionalize CDots with a silica chains in 2 min time, which effectively prevents aggregation of CDots and results in full-color inorganic CDot phosphors (PLQYs of 30–40% in the solid state). Full-color LEDs were realized using these phosphors. By covering the red and green emitting CDot phosphors on blue emitting InGaN chips, WLEDs were fabricated, based on the pure CDot-based phosphors, with Commission Internationale de L'Eclairage (CIE) of (0.34, 0.31) and the color rendering index of 82.4, which demonstrates strong potential of these materials in solid state lighting.

2. Results and Discussion

2.1. Preparations and Optical Properties of CDots

The CDots were prepared according to our previous works. In detail, citric acid (1 g) and urea (2 g) were reacted at 160 °C for 4 h under solvothermal condition in 10 mL water, glycerol, and DMF, respectively, and then cooled to room temperature. The resulting solvent was further mixed with 20 mL ethanol and then centrifuged at 8000 r min^{-1} for 10 min. The precipitate was collected, dispersed in ethanol, and centrifuged (8000 r min^{-1}, 10 min) twice to wash off residual solvents and small organic molecules, and then freeze-dried to give the dark products of CDot-water, CDot-glycerol, and CDot-DMF. **Figure 1**d shows absorption and PL spectra of CDot-water, CDot-glycerol, and CDot-DMF in dilute aqueous solutions, which gradually shift toward longer wavelengths. Considering that the absorption bands of CDots are related to the sizes of conjugated sp^2-domains,[23] this provides us a hint that the sizes of sp^2-conjugated extensions in CDots can be tuned by varying solvents in solvothermal synthesis.

2.2. Morphologies and Structures of CDots

To understanding the origin of the tunable optical properties, morphological and structural analyses of CDot-water, CDot-glycerol, and CDot-DMF were carried out. The morphologies of the three CDots were characterized using transmission electron microscopy (TEM). As shown in Figure 1, CDot-water, CDot-glycerol, and CDot-DMF samples are demonstrating well separated nanoparticles with a rather broad size distribution (shown on the corresponding size histograms in Figure 1a–c) with average diameters of 1.7, 2.8, and 4.5 nm. High-resolution TEM (HRTEM) images show that CDot-water, CDot-glycerol, and CDot-DMF exhibit similar well-resolved lattice fringes with a spacing of 0.21 nm, which fits with the (100) crystallographic facet of graphitic carbon,[40] indicating their similar core structures.

The chemical composition of CDot-water, CDot-glycerol, and CDot-DMF has been studied by X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS). XPS spectra of CDot-water, CDot-glycerol, and CDot-DMF (Figure 1e) show three peaks at 284.0, 400.0, and 531.5 eV, which are attributed to C_{1s}, N_{1s}, and O_{1s}, respectively.[41] Relative atomic ratios of oxygen-to-carbon (O/C) estimated by EDS gradually decrease in CDot-water (77%), CDot-glycerol (59%), and CDot-DMF (29%) samples, and all these numbers are significantly lower than the O/C atomic ratio in the precursor molecules citric acid (92%) and urea (93%). The decreasing oxygen content can be seen as a measure of the increasing degree of the dehydration and carbonization of the precursors in a solvothermal synthesis, which is apparently different for the CDots samples synthesized in water, glycerol, and DMF. The EDS data agree with the following XPS data analysis. The XPS O_{1s} spectra of the three samples can be deconvoluted into two peaks at 530.9 and 532.4 eV (Figure 1f), which are attributed to C=O and C—OH/C—O—C groups, respectively.[42] From Figure 1f we can see that the ratios of C—OH/C—O—C and C=O related peaks gradually decrease for CDot-water, CDot-glycerol, and CDot-DMF samples, which provides further evidence on the gradually increasing dehydration and carbonization degree for the CDots samples synthesized in water, glycerol, and DMF under solvothermal conditions, when sp^3-hybridized carbon in the precursors partially transforms into sp^2-hybridized domains in CDots. In previous report, increased surface oxidation degree could red-shift the PL emissions of CDots.[27] It should be noted that the calculated relative atomic ratios of $O_{(C=O)}/C$ from XPS results also gradually decreased from for CDot-water, CDot-glycerol, and CDot-DMF samples, indicating that the red-shifted absorption and emission bands are not related to the surface oxidation degree. The anticipated increase of the size

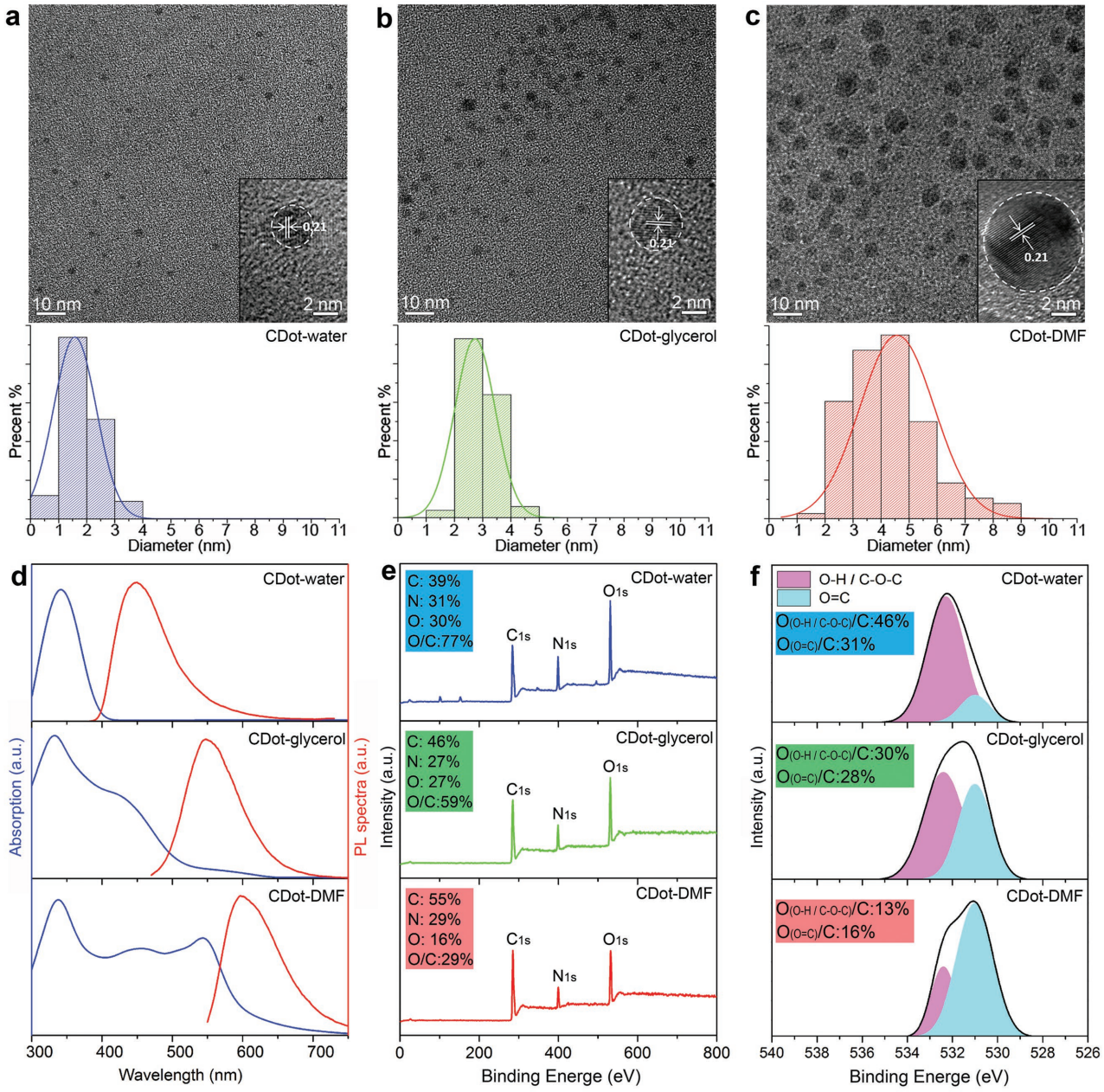
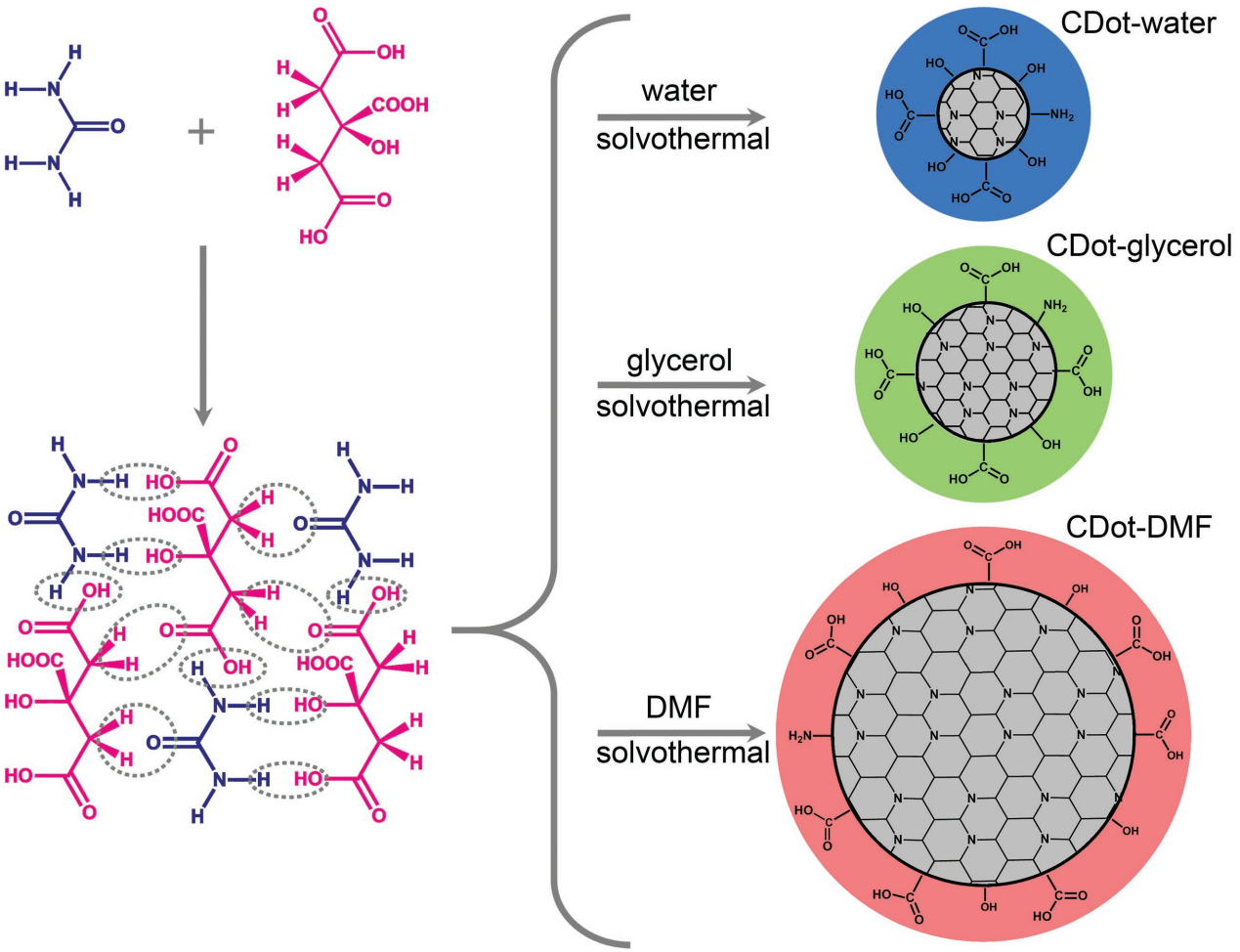


Figure 1. a–c) TEM images (top) of CDot-water, CDot-glycerol, CDot-DMF and their corresponding size histograms (bottom). Insets show HRTEM images of the corresponding CDots. d) Absorption and PL spectra of CDot-water, CDot-glycerol, CDot-DMF at 360, 420, 540 nm excitations, respectively. e) Full survey XPS spectra of CDot-water, CDot-glycerol, and CDot-DMF. The insets show their elemental atomic contents estimated from EDS, together with the relative atomic ratios of oxygen to carbon (O/C). f) XPS O_{1s} spectra of CDot-water, CDot-glycerol, and CDot-DMF, deconvoluted by two peaks. The insets show atomic ratios of $oxygen_{(C-OH/C-O-C)}$ and $oxygen_{(C=O)}$ to carbon from XPS results.

of sp^2-domains in CDot-water, CDot-glycerol, and CDot-DMF samples could agree with their gradually increasing overall particle sizes and red-shifted absorption and emission bands.

2.3. Full-Color Emissive CDots

In previous reports, two approaches were developed to tune the emissions of CDots, which are sizes separation[27] and surface chemical modifications.[28] However, size-dependant wide-range emissions of CDots were only observed in a few cases, while the emission tunable ranges of CDots through surface chemical modifications are limited.[43] Both of these two methods cannot give a clear picture on full-color range controlling of CDots. Based on the results above, a possible growth mechanism for CDot-water, CDot-glycerol, and CDot-DMF is proposed in **Scheme 1**. Citric acid and urea first assemble into a nanoplate structure through the intermolecular H-bonding.



Scheme 1. Schematic of a possible growth mechanism for CDot-water, CDot-glycerol, and CDot-DMF.

Under solvothermal conditions, dehydration process happened between citric acid and urea to form nitrogen-rich CDots with abundant carboxyl, hydroxyl, and amide groups on the surface. In the solvothermal processes, solvents can affect the extents of dehydration and carbonization processes between citric acid and urea. It can be inferred that the degrees of dehydration and

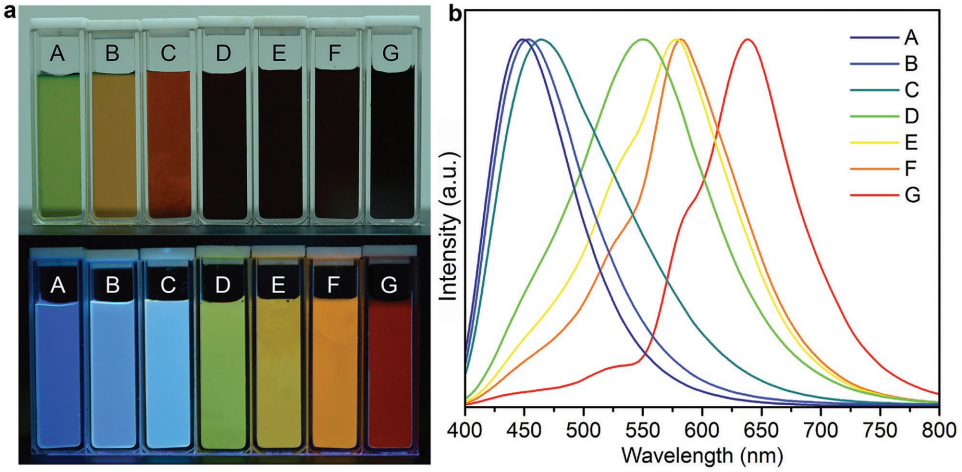
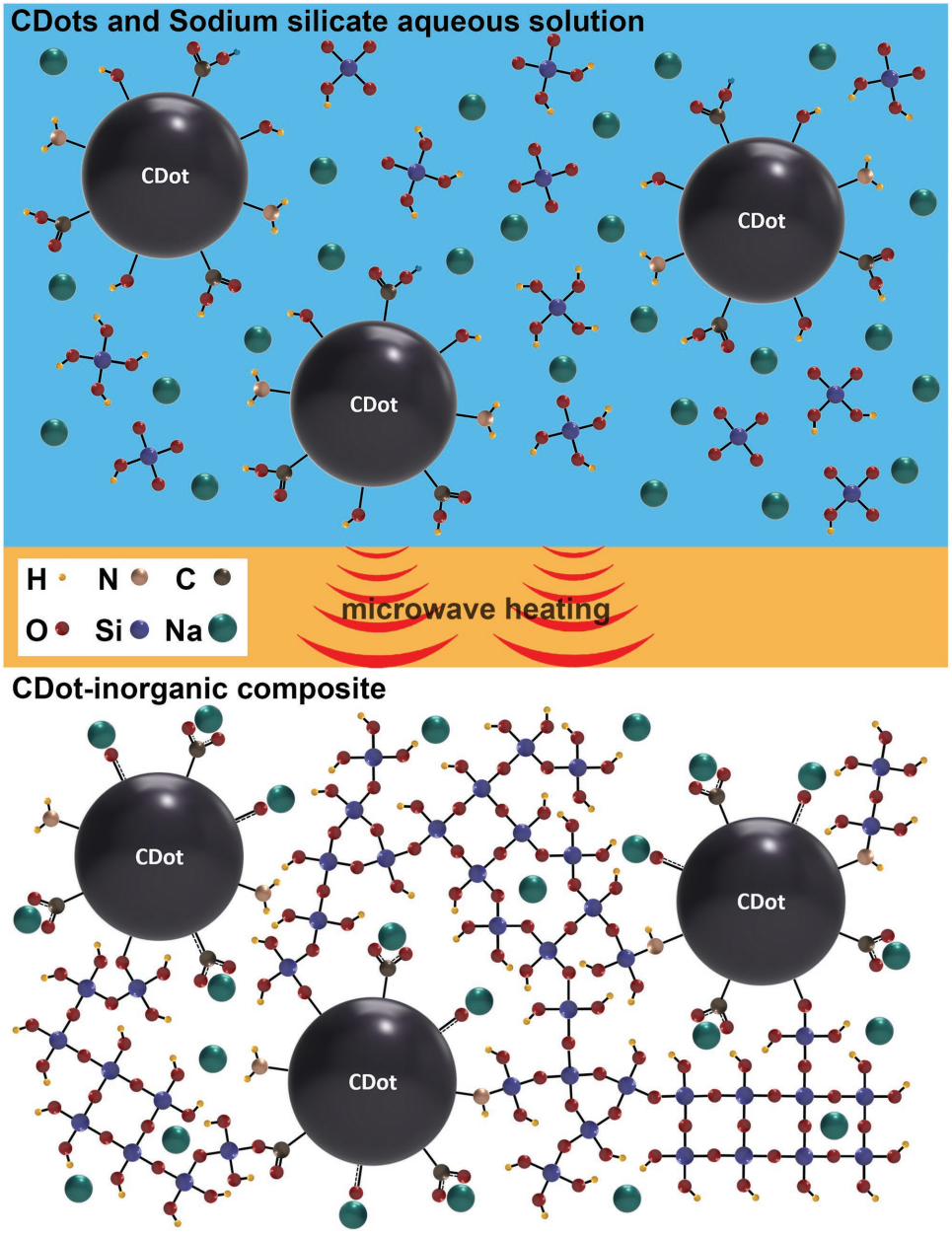


Figure 2. a) Photographs of the CDots solutions synthesized a three-solvent mixture (samples A, B, C, D, E, F, G) under daylight (top) and UV light (bottom), and b) their corresponding PL spectra at 375 nm excitation.

carbonization are gradually increased in water, glycerol, and DMF, resulting in the gradually increased sp^2-domains and red-shifted absorption and emission bands, which agree well with their increased particle sizes. Thus, it can be concluded that the emissions of the prepared CDots are related to the particle sizes, which can be tuned by solvents in solvothermal conditions.

Aprotic solvent such as DMF appears to provide higher degree of dehydration and carbonization of CDots precursors than the protic one such as water. Based on this observation, we were able to synthesize full-color emissive CDots simply by tuning the volume ratios of water, glycerol, and DMF employed as solvents in a reaction mixture, using selected volume ratios of water, glycerol, and DMF as 1:0:0, 1:1:0, 1:3:0, 0:1:0, 0:4:1, 0:3:1, 0:0:1 (samples A, B, C, D, E, F, G, respectively) and performing solvothermal treatment for 4 h as described above. Under UV light, the respective solutions exhibit bright luminescence covering the whole blue to red spectral range (**Figure 2**a) with the emission peaks gradually shifting from 448 nm to 453 nm, 465 nm, 550 nm, 578 nm, 583 nm, and finally 638 nm for samples A to G, respectively (Figure 2b). Figure S1 (Supporting Information) shows absorption spectra of samples A–G in dilute aqueous solutions, which are gradually broadened and red-shifted.



Scheme 2. A possible formation mechanism of inorganic functional CDot-based phosphors from the CDot-sodium silicate solution under microwave assisted treatment.

2.4. Full-Color Emissive Inorganic CDot Phosphors

Sodium silicate is a widely used material with low toxicity and low cost, which is readily available as a colorless aqueous solution, often called liquid glass[44] because it is able to dehydrate and solidify at elevated temperatures forming 3D glassy-like structures. We chose aqueous solution of sodium silicate (Na_2SiO_3•$9H_2O$ aqueous solution with molar ratio of 3.3 and Baume degrees of 40) as a transparent matrix and surface functionalizing agent for fabrication of inorganic CDot phosphors. Because of good water solubility, the prepared CDots could well disperse in sodium silicate aqueous solution. Dehydration process in sodium silicate at temperature lower than 60 °C is very slow. Obvious microphase separation between CDots and sodium silicate occurred during drying of the mixed solutions, which leads to luminescence quenching due to induced aggregation of CDots. As shown in Figure S2 (Supporting Information), after drying at 60 °C, CDots tend to cluster obviously.

Microwave assisted synthesis is a powerful technique to rapidly increase the reacting temperature and accelerate dehydration process and chemical reactions. We used microwave assisted heating to accelerate dehydration processes in sodium silicate, where adjacent silanol groups (Si—OH) form Si—O—Si bonds and further develop silica network structure,[45] which could be supported by EDS and thermogravimetric analysis (TGA) data (Figure S3, Supporting Information). **Scheme 2** shows a possible formation mechanism of inorganic CDot phosphors. As demonstrated above by XPS, there are plenty of hydroxyl and carboxyl groups on the surface of CDots (Figure 1e,f), so that dehydration processes happen not only between sodium silicate entities but also involve CDots thus preventing their phase separation and aggregation. Bearing this in mind, the following fabrication procedure for inorganic CDot phosphors has been adopted. 0.1 mL of CDots solutions A–G, 2 mL aqueous solution of sodium silicate (Baume degree is 40), and 1 mL of deionized water were mixed under stirring to form homogeneous solution. The mixture was treated under 500 W microwave irradiation for 2 min to form swelled solid foams (Figure S2, Supporting Information), which were subsequently ground into powders, thoroughly washed with ethanol, and dried at 60 °C to provide powdered CDot phosphors (samples denoted as P-A, P-B, P-C, P-D, P-E, P-F, P-G).

Figure 3a shows fluorescence images of these CDot phosphors under UV light, whose emissions are red-shifted from blue to red for the samples P-A to P-G. No absorption or PL was observed in the visible spectral range for the silica sample without addition of CDots. Figure 3b shows that the diffuse reflectance absorption and emission spectra of the CDot phosphors are similar to their loading CDots, indicating that inorganic silica has been deposited on CDots without changing their optical properties. Remarkably, PLQYs of the powdered CDot phosphors are in the range of 30–40%, which is even higher than that of the respective CDots in aqueous solutions (**Table 1**). The reason for the improved PLQYs of CDots in the composites can be related to the existence of Na^+ ions present in the silica network structure, which, as previously reported,[36] can be attached at the surface of the embedded CDots to form metal-cation-functionalized CDots with an increased PLQYs.

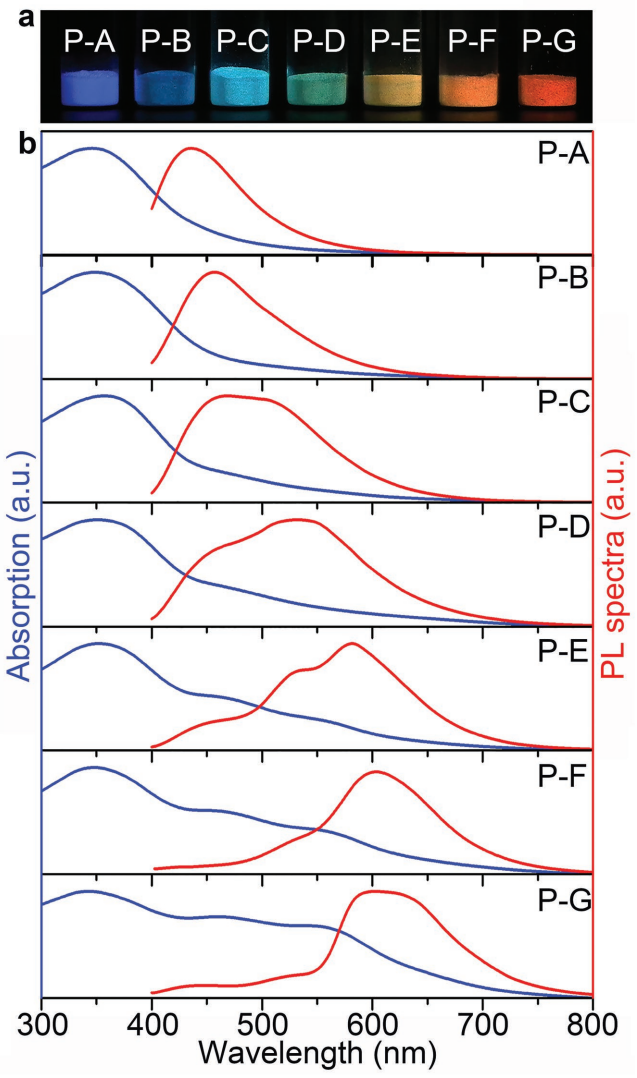


Figure 3. a) Fluorescence images of CDot phosphors P-A, P-B, P-C, P-D, P-E, P-F, P-G under 365 nm UV light, and b) their corresponding diffuse reflectance absorption spectra (in blue) and PL spectra (in red) under 375 nm excitation.

Table 1. PLQYs of the CDots in aqueous solutions (samples A to G) and the CDot phosphors (samples P-A to P-G) at the optimal wavelength excitations.

	PLQY[a)]/λ_{ex} [nm]		PLQY[b)]/λ_{ex} [nm]
A	0.32/360	P-A	0.40/360
B	0.22/390	P-B	0.35/390
C	0.16/410	P-C	0.37/410
D	0.13/470	P-D	0.34/470
E	0.11/520	P-E	0.32/520
F	0.09/530	P-F	0.30/530
G	0.08/540	P-G	0.30/540

[a)]Measured in dilute aqueous solutions; [b)]Measured in solid state.

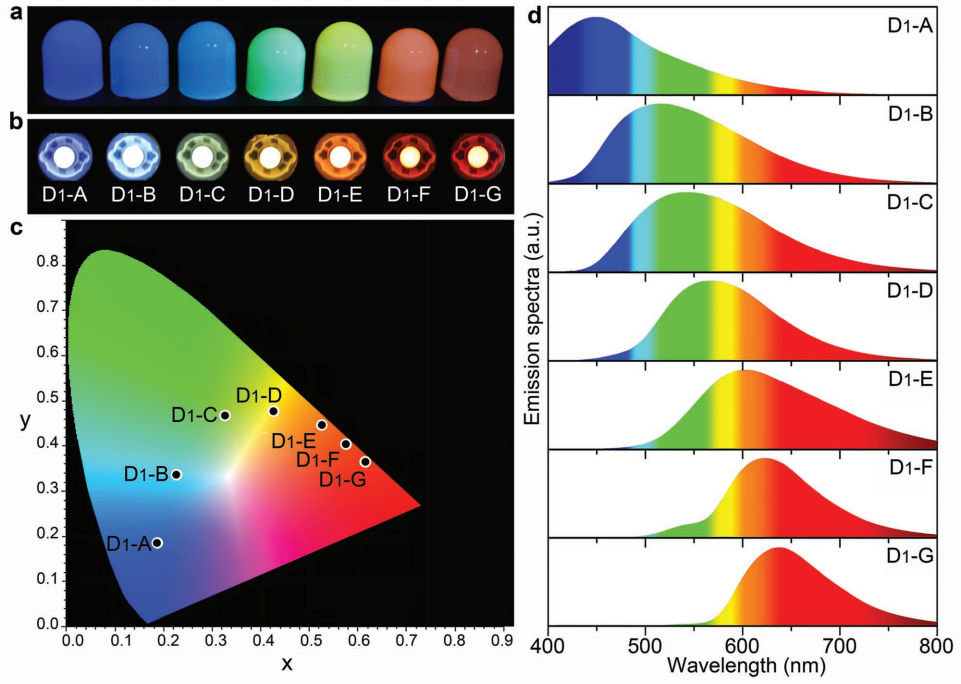


Figure 4. a) Fluorescence images of the CDot phosphors/PDMS composites under 365 nm UV light. b) Photographs and c) CIE coordinates of the single color CDot-based LEDs operating under the voltage of 3.0 V. d) Their corresponding emission spectra. Devices D_1-A, D_1-B, D_1-C, D_1-D, D_1-E, D_1-F, D_1-G were fabricated by covering inorganic functional CDot phosphors/PDMS composites as color conversion layer on 395 nm emissive InGaN chips. The inorganic functional CDot phosphors used for D_1-A, D_1-B, D_1-C, D_1-D, D_1-E, D_1-F, D_1-G are P-A, P-B, P-C, P-D, P-E, P-F, P-G, respectively.

Thus, sodium silicate can not only be used as an inert matrix but also as the surface functionalizing agent to improve the emission of CDots in the solid state.

2.5. CDot-Based LEDs

Mixing the inorganic CDot phosphors with polydimethylsiloxane (PDMS) and solidifying the mixtures at 80 °C for 1 h allows us to obtain strongly luminescent solid-state materials easy to cast into different shapes (**Figure 4**a), which can be employed as color convertors in down-conversion LEDs. Thus, full-color LEDs were fabricated by using 395 nm emissive InGaN chips as excitation sources. Figure 4b shows the photographs of operating monochrome CDot-based LEDs (devices D_1-A, D_1-B, D_1-C, D_1-D, D_1-E, D_1-F, D_1-G). The maximum emission peaks of single color CDot-based LEDs were 448, 515, 540, 570, 603, 622, 638 nm, respectively (Figure 4d). We mention that on the 440 nm emissive InGaN chips, the maximum emission peaks of the green and red emissive inorganic functional CDot phosphors (P-C, P-G) were 540 and 640 nm, respectively (**Figure 5**a), which pave the way to fabricate WLEDs with high CRI. The WLEDs were fabricated by successively covering red and green light inorganic functional CDot phosphors (samples P-G and P-C) on the 440 nm emissive InGaN chips. Figure 5b shows the emission spectra of CDot-based WLEDs (device D_2-C) operating under the voltage of 3.0 V. Devices comprised the green conversion layer deposited on top of the red conversion layer, which helped to avoid the absorption of green light by the red phosphors and improve the luminous efficiency of the LEDs. Figure 5c–e shows photographs of fruits and pen caps with different colors under CDot-based WLEDs array and under daylight. Figure S4 (Supporting Information) shows CDot-based WLEDs are performed well for the 14 kings of standard colors of CIE. With the CRI of 82.4, luminous efficiency of 8.34 lm W^{-1}, color temperature (CT) of 5048 K, and CIE coordinates of (0.34,0.31), the CDot-based WLEDs show great prospect in high CRI lighting field.

3. Conclusions

In summary, we proposed an approach toward controlling the bandgap emissions of CDots to realize full-color emissive CDots from citric acid and urea, employing three different solvents (water, glycerol, and DMF) and their combinations in a solvothermal synthesis. The solvents govern the degree of dehydration and carbonization processes of precursors, which results in formation of differently sized sp^2-conjugated domains within the prepared CDots, leading to different colors of their emission ranging from blue to the red. To prevent aggregation induced luminescent quenching of CDots, we employed a microwave assisted treatment of CDots dispersed in aqueous solutions of sodium silicate, which immobilize well-dispersed CDots in the silica network, effectively preventing aggregation of CDots and producing strongly luminescent inorganic CDot phosphors with PLQYs in the range of 30–40% in the solid state. By covering the red and green CDot phosphors on blue emitting InGaN chips, WLEDs were fabricated, solely based on CDot phosphors, with CIE of (0.34, 0.31) and the

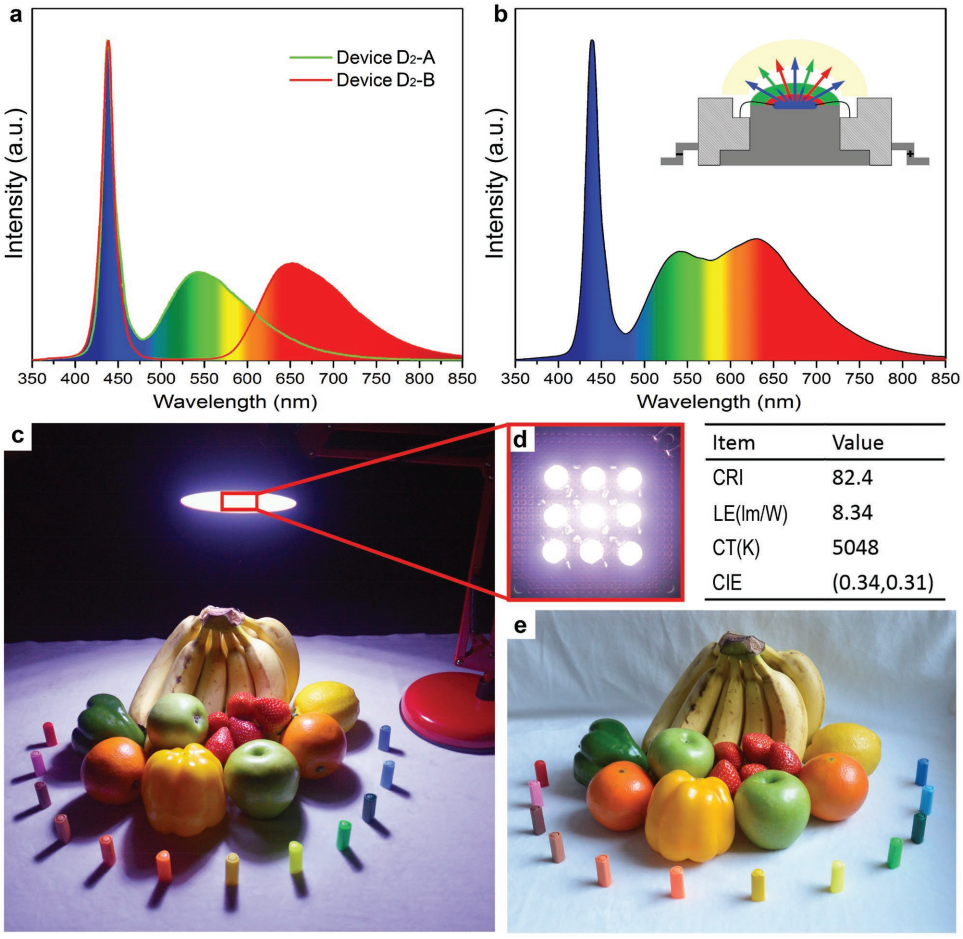


Figure 5. a) Emission spectra of operating devices D_2-A and D_2-B, which were fabricated by covering P-C/PDMS and P-G/PDMS composites on 440 nm emissive InGaN chips, respectively. b) Emission spectra of operating CDot-based WLEDs (device D_2-C), which were fabricated by successively covering P-G/PDMS and P-C/PDMS composites on 440 nm emissive InGaN chips (inset shows its structural representation). c) Photograph of fruits and pen caps with different colors under CDot-based WLEDs array and e) photograph of the same fruits and pen caps under sunlight. d) Photograph of the operating CDot-based WLEDs array and its performance parameters. These devices were operated under voltage of 3.0 V.

color rendering index of 82.4. We anticipate that the full-color emissive CDots and their inorganic phosphors are beneficial for applications in solid state lighting.

4. Experimental Section

Materials: Citric acid (99.5%) and urea (99%) were purchased from Aladdin. Sodium silicate (Na_2SiO_3•$9H_2O$, Baume degree is 40) were purchased from Usolf. PDMS elastomer kits (Sylgard 184) were purchased from Dow Corning (Midland, MI, USA). 395 nm emissive InGaN chips (emission peak at 395 nm, operating under voltage of 3.0 V) and 440 nm emissive InGaN chips (emission peak at 440 nm, operating under voltage of 3.0 V) were both purchased from Greatshine Semiconductor Technology Company Limited. All chemicals were used without further purification.

Preparation of Inorganic CDot Phosphors: 0.1 mL of CDots solutions A-G, 2 mL sodium silicate (Baume degree is 40), and 1 mL of deionized water were mixed under stirring to form homogeneous solution. The mixture was treated under 500 W microwave irradiation for 2 min to form swelled solid foams, and subsequently ground into powders. The as-prepared inorganic functional CDot phosphors were washed by ethanol through centrifugation at 2000 r min^{-1} for 5 min three times.

Fabrication of LEDs from CDot Phosphors: Commercially available 395 nm emissive InGaN chips were used at the bottom of the LED base. For the preparation of the color conversion layer, the CDot phosphors were foremost mixed with PDMS with mass ratios of 1:1. The mixtures were covered on InGaN chips and after curing at 80 °C for 1 h, the LEDs CDot phosphors were obtained. In addition, CDot-based WLEDs (device D_2-C) were fabricated from 440 nm emissive InGaN chips covered with red emitting phosphors CDots (sample P-G mixed with PDMS under mass ratio of 1:1), cured at 80 °C for 1 h, and followed by the deposition of the green emitting phosphors mixtures (sample P-C mixed with PDMS under mass ratio of 1:1) and curing at 80 °C for 1 h. The mass ratio of red to green CDots in the resulting devices was 1:3. CDot-based WLED array was fabricated by parallel connection of 9 CDot-based WLEDs with the same performance parameters.

Characterization: UV–visible absorption spectra were obtained on a Shimadzu UV-3101PC spectrophotometer. PL spectra were collected on a Hitachi F-7000 spectrophotometer. The PLQYs of CDots aqueous solutions and inorganic functional CDot phosphors were measured in a calibrated integrating sphere in FLS920 spectrometer. TEM was performed on a FEI Tecnai-G2-F20 TEM at 200 kV. Fourier transform infrared spectroscopy spectra were recorded using the KBr pellet method (Jasco FT/IR-4100 type-A spectrometer). Scanning electron microscopy was done on a JEOL FESEM 6700F electron microscope

with primary electron energy of 3 kV. EDS and elemental mapping were conducted on an Inca X-Max instrument (Oxford Instruments). TGA was done on an American TA Q500 analyzer under N_2 atmosphere with the flow rate of 100 mL min^{-1}. XPS analyzes were measured on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source. The fluorescence microscopy images were obtained on a C2+ confocal microscope system (Nikon confocal instruments).The emission spectra were obtained using an Ocean Optics Maya 2000 Pro Fiber Optic Spectrometer and Fu Xiang NOVA-EX Fiber Optic Spectrometer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon dots, full-color emission, phosphors, sodium silicate, white-light-emitting devices

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