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Towards efficient solid-state photoluminescence based on carbon-nanodots and starch composites†

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A new type of environmentally friendly phosphor based on carbon nanodots (CDs) has been developed through the dispersion of CDs by integrating the CDs with starch particles. The starch particles contain large numbers of hydroxyl groups around the surfaces, which can effectively absorb the CDs, whose surfaces are functionalized by lots of carboxyl and amide groups, through hydrogen bonding. Effective dispersion of CDs on the surfaces of starch particles can suppress the non-radiative decay processes and photoluminescence (PL) quenching induced by aggregation of CDs. The starch matrix neither competes for absorbing excitation light nor absorbs the emissions of CDs, which leads to efficient PL emitting. As a result, the starch/CD phosphors with a quantum yield of ~50% were obtained. The starch/CD phosphors show great potential in phosphor-based light emitting diodes, temperature sensors, and patterning.

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Introduction

Luminescent carbon nanodots (CDs) have been regarded as viable alternatives to organic dyes and heavy-metal-based (Cd, Pb, *etc.*) semiconductor quantum dots (QDs) (CdSe, PbS, *etc.*) in many fields such as bioimaging and biosensing,^{1–8} patterning,^{9,10} coding,¹¹ and optoelectronic devices,^{12–16} due to their water solubility, good stability, low toxicity, superior resistance to photobleaching, and excellent biocompatibility.^{17–19} Until now, a great number of synthetic methods toward CDs are available, such as laser ablation, electrochemical oxidation, hydrothermal synthesis, and microwave synthesis route, *etc.*^{17–19} High photoluminescence (PL) quantum yield (QY) is primary to optimize the performances and expand the application fields of CDs. The PL QY higher than 60% was achieved in several CDs in their aqueous solutions, which is comparable to the commercial CdSe/ZnS QDs.^{5,10,17–21} Such excellent lumi-

nescence properties greatly promote CDs in biological applications and other scientific fields.

Recently, great interest has been focused on using CDs as an photoactive material in lighting and display applications.^{9,12–14,22–24} The performances of CD-based solid-state luminescent devices are still not satisfactory, due to strong luminescence quenching in the solid aggregate state.^{11,22,24} Only a few cases for CD-based solid-state materials with high luminescence have been reported.^{9,10,22–28} In these systems, to prevent solid-state luminescence quenching, the CDs are generally dispersed in a polymer matrix to achieve luminescent films or gel glasses. To the best of our knowledge, there is no report on the effect of the dispersion matrix on the PL QY of CDs. Furthermore, these reported CD-based polymer materials generally have a fixed shape, which are inconvenient to use compared with phosphors in some applications. Thus, there is a strong need to understand the effect of the dispersion matrix on the PL QY of CDs and develop environmentally friendly CD-based phosphors with high PL QY.

Starch is environmentally friendly, low-cost, and rich on earth, which can be regenerated by the process of plant photosynthesis. The starch particles contain large number of hydroxyl groups functionalized around the surfaces.²⁹ It is well known that the CDs are biocompatible. So it is promising to integrate CDs with starch particles through chemical adsorption to produce environmentally friendly CD-based phosphors. In this work, we provided a universal technique for preparing efficient CD-based phosphors through effective dispersion of CDs by integrating the CDs with starch particles. Effective dis-

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phosphors on the surfaces of starch particles can suppress the non-radiative decay processes and PL quenching induced by aggregation of CDs. The starch matrix neither competes for absorbing excitation light nor absorbs the emissions of CDs, which leads to efficient PL emitting. As a result, the starch/CD phosphors with QY of ~50% were obtained. The starch/CD phosphors show great potential in phosphor-based light emitting diodes (LEDs), temperature sensors, and patterning.

Experimental section

Chemicals and materials

Citric acid (99.5%) and urea (99%) were purchased from Beijing Chemical Works. The potato starch and commercial fluorescent dye ink were directly purchased from the supermarket. The epoxy silicone resin A and B components were purchased from Ausbond (China) Co., Limited. All chemicals were used without further purification. The GaN LEDs (peak wavelength: 450 nm) were purchased from Changzhi High-Tech Arima Optoelectronics Co., Limited. The water used in all experiments was purified with a Millipore system.

Synthesis of green luminescent CDs (g-CDs)

The g-CDs were prepared according to our previous work.²¹ 1 g of citric acid and 2 g of urea were added to 20 ml of deionized water to form a transparent solution. Then the mixed solution was heated in a domestic 750 W microwave oven for about 5 minutes, during which the solution changed from a colorless liquid to a light brown and finally dark brown clustered solid, indicating the formation of CDs. The solid was then dissolved in water and centrifuged to remove agglomerated particles at a speed of 8000 rpm for 20 min three times.

Synthesis of blue luminescent CDs (b-CDs)

The b-CDs were prepared according to previous work.³⁰ 1 g of citric acid and 2 g of urea were added to 20 ml of deionized water to form a transparent solution. The mixed solution was transferred into a 50 ml Teflon-lined stainless-steel autoclave. Then the sealed autoclave was heated to 160 °C and kept for about 4 h.

Preparation of starch/CD phosphors

The starch/g-CD phosphors (mass ratio: 20 : 1–450 : 1) were prepared by simply mixing the g-CDs and starch in water under constant stirring for 24 h. The reaction mixtures were filtered to remove the unadsorbed g-CDs, and the remaining solid blocks on filter paper were freeze-dried in a vacuum freeze dryer. The starch/g-CD phosphors were then obtained by grinding the dried blocks in agate mortar and screening by mesh sieve. The coverage degree of g-CDs on starch particles was controlled by regulating the mass ratio of starch powder and g-CDs from 20 : 1 to 45 : 1, 70 : 1, 200 : 1, and 450 : 1. The blue luminescent starch/b-CD phosphors were prepared in the same route as green luminescent starch/g-CD phosphors. The

phosphors were then kept in a vacuum oven for further experiments and measurements.

Fabrication of phosphor-based LEDs

The starch/g-CD phosphors (mass ratio: 45 : 1 and 70 : 1) were dispersed in toluene and then dropped on commercial GaN LEDs (peak wavelength: 450 nm). The starch/g-CD phosphors covered GaN LEDs were then dried in air naturally and encapsulated with transparent epoxy silicone resin.

Fabrication of phosphor-based luminescent blocks and various patterns

The epoxy silicone resin A and B components (volume ratio: 1 : 1) were mixed with chloroform. The starch/CD phosphors were then added to the epoxy silicone resin mixtures under mechanical stirring for 20 min. The mixtures were poured into specific moulds and dried naturally. Then starch/CD phosphor-based luminescent blocks were obtained after removing from the moulds. Various patterns were fabricated by adhering different luminescent starch/CD phosphors on transparent tapes in specific shapes.

Results and discussion

The green luminescent CDs (g-CDs) were synthesized according to our previous work with the starting materials of 1 g citric acid and 2 g urea.²¹ The obtained solid g-CDs were dissolved in water and centrifuged to remove agglomerated particles at a speed of 8000 rpm for 20 min three times. The g-CDs have the strongest PL emission band with excitation at 420 nm and a PL QY of 18% in water as in our previous work.²¹ The PL was significantly quenched when the g-CDs were deposited on glass, metal, or plastic substrates due to the formation of aggregates.¹¹ The g-CDs contain a lot of carboxyl and amide groups on the surfaces as demonstrated in our previous work,^{11,21} which can be effectively adsorbed on starch particles through hydrogen bonding. The formation mechanism of the starch/g-CD phosphors is schematically illustrated in Fig. 1. The g-CDs and starch were simply mixed in water under constant stirring for 24 h. The reaction mixtures were filtered to remove unadsorbed CDs, and the remaining solid blocks on filter paper were freeze-dried in a vacuum freeze-

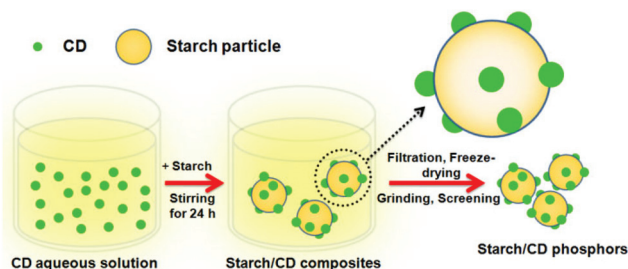


Fig. 1 Schematic illustration of the formation mechanism of starch/CD phosphors.

drying machine. The starch/g-CD phosphors were then obtained by grinding dried blocks in agate mortar and screening out by mesh sieve. The coverage degree of g-CDs on starch particles was controlled by regulating the mass ratio of starch powder and g-CDs from 20:1 to 45:1, 70:1, 200:1, and 450:1. Optical images of the starch/g-CD phosphors with different g-CD contents are shown in Fig. S1 in ESI.† The color of the starch/g-CD phosphors gradually changes from white to yellow-green with the g-CD content increasing (Fig. S1†), demonstrating the integrating of g-CDs with starch particles. Fig. 2 shows the fluorescence images of the starch/g-CD phosphors (mass ratio: 70:1). The starch/g-CD phosphors with particle size distribution ranging from 20 to 40 μm exhibit intense light emitting under photoexcitation as seen from Fig. 2. A visualized excitation-wavelength-dependent emission is observed from the fluorescence images (Fig. 2a–c), which is considered to be a peculiar property of CDs.¹ The homogeneous blue-green, yellow-green, and red light emitting are detected from the whole surfaces of starch particles under UV, blue, and green light excitation (Fig. 2d–f), demonstrating the uniform adsorption of g-CDs on the surfaces of starch particles. It can be concluded that the chemical adsorption of g-CDs on the surfaces of starch particles can result in effective dispersion of CDs and prevent solid-state PL quenching.

The UV-Vis absorption spectra (converted from diffuse reflection spectra) of pure starch, g-CDs in water, and starch/g-CD phosphors (mass ratio: 70:1) were recorded as shown in Fig. 3a. Pure starch powder has almost no absorption above 400 nm, while the starch/g-CD phosphors have continuous broad absorption in the visible region ranging from 400 to 600 nm, similar to the absorption spectrum of CDs in water, demonstrating the adsorption of CDs on the starch particles. It can be seen that the starch powder has almost no absorption between 400 and 600 nm (main absorption and emission band of CDs), which means that the starch matrix neither competes for absorbing excitation light nor absorbs the emissions of g-CDs, leading to efficient PL emitting from g-CDs. Fig. 3b shows the excitation-wavelength-dependent PL spectra of the starch/g-CD phosphors with the strongest emission peak of 515 nm under excitation at 420 nm. The excitation spectrum

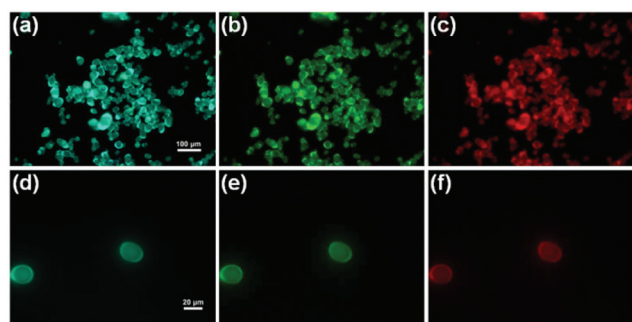


Fig. 2 Fluorescence images of the starch/g-CD phosphors (mass ratio: 70:1) under UV (a and d), blue (b and e), and green (c and f) light excitation. The exposure time is 100, 150, and 6000 ms for (a and d), (b and e), and (c and f), respectively.

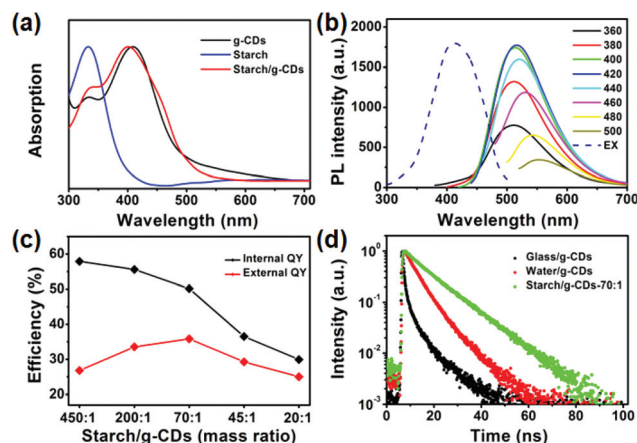


Fig. 3 (a) UV-Vis absorption spectra of pure starch, g-CDs in water, and starch/g-CD phosphors (mass ratio: 70:1). (b) Excitation-wavelength-dependent PL spectra (solid lines) and excitation spectrum (dashed line) (emission wavelength: 515 nm) of the starch/g-CD phosphors (mass ratio: 70:1). (c) PL QYs of starch/g-CD phosphors with different g-CD coverage degrees (excitation at 420 nm). (d) PL dynamics of g-CDs in water, g-CDs on the glass substrate, and starch/g-CD phosphors (mass ratio: 70:1).

also indicates the most effective excitation at ~ 420 nm (Fig. 3b). The PL spectra (excitation at 420 nm) of the starch/g-CD phosphors with different g-CD contents exhibit a red shift upon increasing the g-CD coverage as shown in Fig. S2,† which might be due to self-absorption of g-CDs in high contents. The PL QYs of starch/g-CD phosphors with different g-CD coverage degrees were measured as shown in Fig. 3c (excitation at 420 nm). The internal QYs gradually decrease from 58% to 30% with the g-CD content increasing, which might be due to increasing self-absorption of g-CDs in high contents. The external QYs show an optimized value of 36% for starch/g-CD phosphors (mass ratio: 70:1, internal QY: 50%). It can be concluded that the adsorption of g-CDs on starch particles can effectively avoid PL quenching of g-CDs in the solid state. Thus, a new environmentally friendly phosphor was obtained based on g-CDs and starch composites. To acquire a deeper understanding of the mechanisms of solid-state PL quenching of g-CDs, the PL dynamics of g-CDs in water, g-CDs on the glass substrate, and starch/g-CD phosphors (mass ratio: 70:1) were collected as shown in Fig. 3d. The PL decay curves were fitted with bi- or tri-exponential decay kinetics and the calculated average lifetimes are summarized in Table 1. Then, we estimated the radiative and non-radiative decay rates of g-CDs in water, g-CDs on the glass substrate, and the starch/g-CD phosphors as listed in Table 1 from eqn (1) and (2):

$$\text{QY} = \frac{k_r}{k_r + k_{nr}} \quad (1)$$

$$\frac{1}{\tau} = k_r + k_{nr} \quad (2)$$

where k_r and k_{nr} are the radiative and non-radiative decay rates, τ is the average lifetime. As seen from Table 1, the k_{nr} of

Table 1 Fit parameters of the PL decay curves of g-CDs deposited on the glass, dispersed in water, and adsorbed on starch particles (mass ratio: 70 : 1)^a

Samples	τ_1 (ns)	a_1 (%)	τ_2 (ns)	a_2 (%)	τ_3 (ns)	a_3 (%)	χ^2	τ_{ave} (ns)	k_r (10^7 s^{-1})	k_{nr} (10^8 s^{-1})
Glass/g-CDs	0.23	53.10	2.57	26.62	9.33	20.28	1.23	2.70	~0	3.70
Water/g-CDs	4.47	64.51	9.24	35.49			1.13	6.16	2.92	1.33
Starch/g-CDs	4.39	9.36	12.53	90.64			1.18	11.77	4.25	0.43

^a The average lifetimes were calculated using the equation $\tau_{\text{ave}} = \sum_{i=1}^n a_i \tau_i$.^{31,32}

the g-CDs dispersed in water is $1.33 \times 10^8 \text{ s}^{-1}$. When the g-CDs were deposited on the glass substrate, almost no PL emission was detected using a spectrophotometer, indicating an extremely low PL QY, which may be close to zero. The serious aggregation of g-CDs on the glass substrate enhances the interaction between g-CDs, resulting in the k_{nr} to as quick as $3.70 \times 10^8 \text{ s}^{-1}$, which leads to inferior PL properties of pure g-CD solid-state films. By adsorbing the g-CDs on starch particles, the k_{nr} greatly decreases to $0.43 \times 10^8 \text{ s}^{-1}$, meaning that the surfaces of starch particles can effectively disperse g-CDs, which suppresses non-radiative decay processes and avoids PL quenching induced by the aggregation of g-CDs. It is also worth noting that the k_{nr} of the g-CDs adsorbed on starch particles is even slower than that of the CDs in water, indicating that the water is not an ideal matrix for g-CDs with high PL QY compared with starch. So the QY of starch/g-CD phosphors can reach ~50%, while it is only 18% for g-CDs dispersed in water. In addition, the k_r is $4.25 \times 10^7 \text{ s}^{-1}$ for g-CDs dispersed on starch particles, which decreases to $2.92 \times 10^7 \text{ s}^{-1}$ and $\sim 0 \times 10^7 \text{ s}^{-1}$ for g-CDs dispersed in water and deposited on the glass, respectively, indicating that a non-ideal matrix and ineffective dispersion can all interfere with the radiative decay processes and weaken the PL of g-CDs.

The temperature-dependent PL for traditional QDs has been extensively investigated, while a little research has been done for CDs. The temperature-dependent PL not only provides unique insight into the understanding of the PL mechanisms of QDs,³³ but also offers the potential for the application in temperature sensors.³⁴ The temperature-dependent PL spectra of the starch/g-CD phosphors (mass ratio: 70 : 1) from 90 to 370 K were recorded as shown in Fig. 4a. The PL intensity exhibits an obvious decrease as the temperature increases. The enhanced non-radiative recombination is possibly the main factor for the PL thermal quenching due to the activation of non-radiative recombination centers with temperature increasing.^{33–36} The PL peak of starch/g-CD phosphors shows a red shift of ~100 eV from 90 to 370 K, which is generally attributed to stronger electron–phonon interaction as the temperature increases (Fig. 4b).^{33,35,36} The full width at the half-maximum (FWHM) of the starch/g-CD phosphors were also investigated (Fig. 4c). A small change for the FWHM is observed with the temperature increasing, due to dominant temperature-independent electron–electron interaction compared with the temperature-dependent electron–phonon interaction.³³ The PL thermal stability performances of the starch/g-CD phosphors were also measured at the temperature of

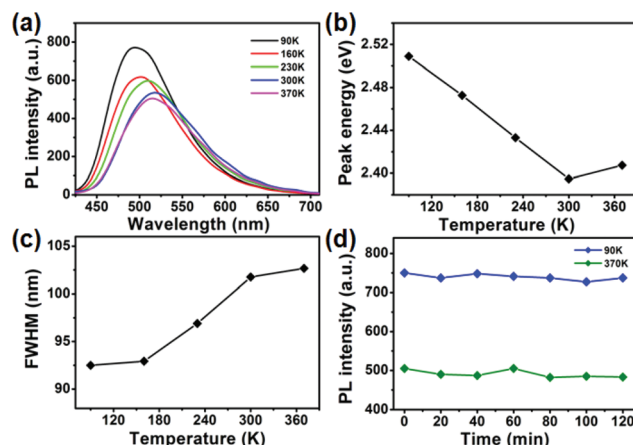


Fig. 4 Temperature-dependent PL spectra (a), PL peak (b), and FWHM (c) of the starch/g-CD phosphors (mass ratio: 70 : 1) at the temperature ranging from 90 to 370 K (excitation at 405 nm). (d) Thermal stability performances of the starch/g-CD phosphors (mass ratio: 70 : 1) during holding at the temperature of 90 and 370 K for 2 h in air.

90 and 370 K holding for 2 h in air. No obvious changes in the PL spectra were found in the measured period (Fig. 4d). It is noted that the variation in the PL intensity and peak position are found to be obvious in a low temperature range (90–300 K), as seen from Fig. 4a and b. These results mean that the starch/g-CD phosphors can be potential material for temperature sensors, especially low-temperature sensors.

The photostability of the starch/g-CD phosphors was tested as shown in Fig. 5a and b. The starch/g-CD phosphors (mass ratio: 45 : 1) and the commercial fluorescent dye ink were deposited on glass and exposed under a 500 W xenon–mercury lamp under the same conditions (Fig. 5a). The green fluorescence emission of the fluorescent dye is mostly unobserved after 4 hour irradiation, due to serious photobleaching (Fig. 5b), while the starch/g-CD phosphors show good resistance to photobleaching under strong UV light as seen in Fig. 5a and b. The good optical properties indicate that the starch/g-CD phosphors have a great potential to fabricate phosphor-based LEDs.³⁷ The starch/g-CD phosphors (mass ratio: 45 : 1) were dispersed in toluene and then dropped on commercial GaN LEDs (peak wavelength: 450 nm). The starch/g-CD phosphor covered GaN LEDs were then dried in air naturally and encapsulated with transparent epoxy silicone resin. The PL QYs of starch/g-CD phosphors with excitation at 450 nm were measured as shown in Fig. S3 in ESI.† Fig. 5c

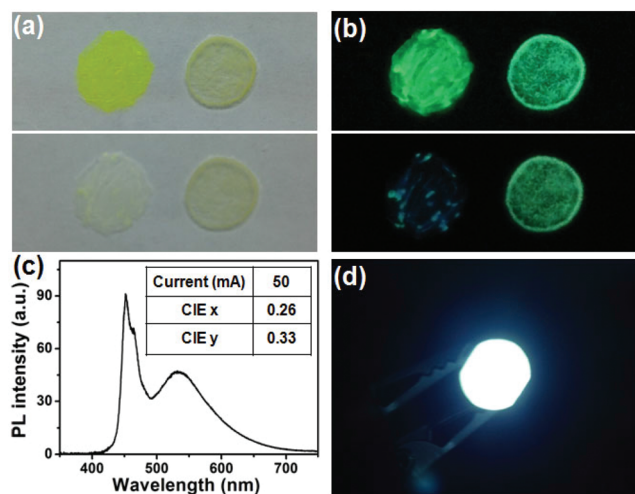


Fig. 5 Optical images under room (a) and UV (b) light of the commercial fluorescent dye ink (left column) and starch/g-CD phosphors (mass ratio: 45 : 1) (right column) deposited on glass substrates exposed under a 500 W xenon–mercury lamp for 0 (above) and 4 h (below). (c) Emission spectrum of the starch/g-CD (mass ratio: 45 : 1) phosphor-based LEDs. (d) Optical image of the corresponding LEDs at the current of 50 mA.

shows the emission spectra of starch/g-CD phosphor-based LEDs at an optimized current of 50 mA (~ 2.8 V), and a cool white light with CIE coordinates of (0.26, 0.33) was obtained (Fig. 5d). Starch/g-CD phosphor-based LEDs with lower g-CD content (mass ratio: 70 : 1) were also fabricated, which emitted a bluish white light with CIE of (0.23, 0.27) (Fig. S4 in ESI†) due to weaker absorption of blue excitation light. So the color composition can be regulated by changing the g-CD contents in starch/g-CD phosphors to meet special needs. It is concluded that the starch/g-CD phosphors are promising candidates for practical lighting applications.

This type of CD-based phosphors can also be prepared from other CDs. The synthesis method of the blue luminescent CDs (b-CDs) was reported in recent work.³⁰ The blue luminescent starch/b-CD phosphors were prepared in the same route as green luminescent starch/g-CD phosphors, indicating that our method is a universal technique for preparing CD-based phosphors. We then examined the versatile patterning abilities of the starch/CD phosphors as shown in Fig. 6. Fig. 6a shows the optical images of the blue and green luminescent starch/CD phosphors under room light and a UV lamp. Strong emissions are observed when the phosphors are excited by UV light. To reveal the versatile processing of the starch/CD phosphors, the starch/CD phosphors were dispersed in a transparent epoxy silicone resin matrix. The luminescent blocks with specific shape can be easily composed by mixing starch/CD phosphors in epoxy silicone resin, as shown in Fig. 6b. The starch/CD phosphors can be easily adhered on transparent tape in specific shapes (Fig. 6c). The rhombus is composed of starch/b-CD phosphors, and the arrow is composed of starch/g-CD phosphors. The patterns show strong blue and green luminescence under UV light excitation as seen from Fig. 6c. It

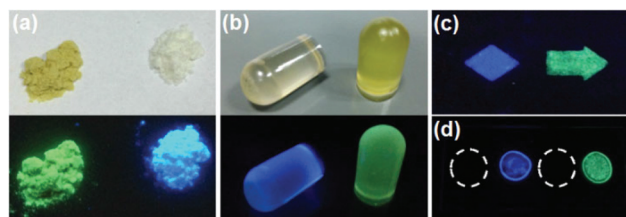


Fig. 6 (a) Optical (top) and luminescence images (down) of starch/g-CD (left) and starch/b-CD (right) phosphors. (b) Luminescent blocks prepared from starch/b-CD (left) and starch/g-CD (right) phosphors in epoxy silicone resin under room light (above) and UV lamp (below). (c) The patterns composed by starch/b-CD (left) and starch/g-CD (right) phosphors in specific shapes on transparent tape under UV light excitation. (d) Luminescence images of starch/b-CD and starch/g-CD phosphor coatings from their chloroform suspensions on glass substrates under UV light excitation. The dashed circle areas are b-CD and g-CD coatings from their aqueous solutions.

should be mentioned that neither g-CDs nor b-CDs can be dissolved in apolar organic solvents and the PL can be strongly quenched when the CDs are deposited on glass substrates due to aggregation (Fig. 6d). It is interesting to find that the starch/CD phosphors can suspend well in chloroform with strong luminescence and the strong emission can also be observed when the starch/CD phosphor chloroform suspensions are deposited on glass substrates (Fig. 6d), indicating that the starch/CD phosphors can be used as good luminescence coatings. These results demonstrate that the starch/CD phosphors have versatile abilities in patterning applications.

Conclusions

In conclusion, we have provided a universal technique for preparing efficient CD-based phosphors through effective dispersion of CDs by integrating the CDs with starch particles. The starch particles contain a large number of hydroxyl groups on the surfaces, which can effectively absorb the CDs, whose surfaces are functionalized by lots of carboxyl and amide groups, through hydrogen bonding. The PL dynamic results indicate that effective dispersion of the CDs on the surfaces of starch particles can suppress the non-radiative decay processes and PL quenching induced by aggregation of CDs. Moreover, the starch matrix neither competes for absorbing excitation light nor absorbs the emissions of CDs, which leads to efficient PL emitting. As a result, the starch/CD phosphors with QY of $\sim 50\%$ were obtained. The starch/CD phosphors show great potential in phosphor-based LEDs, temperature sensors, and patterning. We propose that this research could promote the practical application of the CDs in solid-state luminescence related fields.

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