Ultra-strong phosphorescence with 48% quantum yield from grinding treated thermal annealed carbon dots and boric acid composite

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Abstract
Metal-free room-temperature phosphorescence (RTP) materials are of great significance for many applications; however, they usually exhibit low efficiency and weak intensity. This article reports a new strategy for the preparation of a high-efficiency and strong RTP materials from crystalline thermal-annealed carbon dots (CDs) and boric acid (BA) composite (g-t-CD@BA) through grinding-induced amorphous to crystallization transition. Amorphous thermal-annealed CDs and BA composite (t-CD@BA) is prepared following a thermal melting and super-cooling route, where the CDs are fully dispersed in molten BA liquid and uniformly frozen in an amorphous thermal annealed BA matrix after super-cooling to room temperature. Upon grinding treatment, the fracture and fragmentation caused by grinding promote the transformation of the high-energy amorphous state to the lower energy crystalline counterparts. As a result, the CDs are uniformly in situ embedded in the BA crystal matrix. This method affords maximum uniform embedding of the CDs in the BA crystals, decreases nonradiative decay, and promotes intersystem crossing by restraining the free vibration of the CDs, thus producing strong RTP materials with the highest reported phosphorescence quantum yield (48%). Remarkably, RTP from g-t-CD@BA powder is strong enough to illuminate items with a delay time exceeding 9 s.

Keywords
boric acid, carbon dots, crystalline state, grinding treatment, room-temperature phosphorescence
1 | INTRODUCTION

Room-temperature phosphorescence (RTP) materials with long emission lifetimes are highly desirable in a wide range of applications, such as anti-fake materials, sensors, and optoelectronic devices.1–4 To date, most efficient RTP materials are limited to metal-doped inorganic complexes and organometallic compounds;5 however, the high cost and cytotoxicity of these materials, owing to the presence of noble metals, limit their practical application. Recently, high-efficiency metal-free organic RTP materials have been realized by several strategies,6–10 including crystal engineering, the heavy atom effect, and host-guest supramolecular systems. Most recently, Huang et al. reported an extra-high phosphorescence quantum yield (PQY, 46.1%) of a supramolecular crystal framework.10 However, organic materials usually display poor photostability and require specific molecular designs to produce the desired photoluminescent properties, while challenges associated with a facile synthetic route remain.

Carbon dots (CDs) are emerging as a new class of phosphorescence nanomaterials,11–17 which have attracted significant attention because of their attractive properties, such as simple synthetic routes, low cost, and high photostability. Recently, a principle on manipulating intersystem crossing (ISC) by incorporating heteroatoms into CDs (e.g., N, P, B, and halogens) was proposed to achieve effective RTP.18–23 Liu et al. obtained N-doped CDs with a PQY of 17.5%,20 while Wang et al. reported B,P-doped CDs that exhibited a high PQY of 23%.20 Additionally, restriction of the CDs, achieved by embedding CDs into solid matrices, have been used extensively to construct effective RTP CD materials.24–32 Liu et al. reported efficient phosphorescence emissive CDs with a PQY of 26.4%, prepared from rice husks through a multiconfinement structure design.27 Notably, although these studies yielded effective RTP CDs, the phosphorescent emission efficiency of the CDs is still low when compared with those reported for organic phosphorescent materials.

Because the rigid crystal matrix can greatly reduce the proportion of nonradiative transitions, the embedding of phosphor into a crystalline material shows great potential in the preparation of high-efficiency RTP materials.13,33–36 Recently, RTP CD@crystal materials were developed by embedding CDs in crystal matrices under hydrothermal or solvothermal conditions.25,37,38 However, CDs are generally prone to disperse in common solvents but tend to agglomerate on or among the crystals, thereby leading to weak intensity due to the low loading capacity in crystals. Moreover, for practical applications, high-performance optoelectronic devices require both a high RTP efficiency and strong RTP output. Thus, exploration of novel fabrication strategies to effectively disperse CDs in crystals to achieve high-efficiency and strong RTP is highly desirable. With these facts in mind, we designed and developed a facile and novel strategy for the preparation of a high-efficiency and strong RTP materials from crystalline thermal-annealed carbon dot (CDs) and boric acid (BA) composite (g-t-CD@BA) through grinding induced amorphous to crystallization transition. The g-t-CD@BA displayed strong phosphorescence with an ultrahigh PQY of 48%, which, to the best of our knowledge, is the highest value reported for RTP CD-based materials to date. Notably, after switching off the 365 nm irradiation, the RTP of the g-t-CD@BA is strong enough to illuminate items with a delay exceeding 9 s and RTP luminance reaches a value of 590 lux at a delay of 1 s.

2 | RESULTS AND DISCUSSION

The CDs were synthesized by one-pot hydrothermal treatment of lycorine hydrochloride at 200°C for 2 h, and then composited with BA through thermal melting followed by super-cooling treatment to prepare amorphous CDs and BA composite (t-CD@BA). (Figure 1, detail in the Supporting Information Material). During this process, molten BA acts as a medium to allow the CDs to fully disperse into the matrix and is then uniformly frozen in the amorphous thermal annealed BA matrix after super-cooling to room temperature. Upon mechanical grinding, a sharply increased surface energy of the ground fine fragments drives the rearrangement of the contained disordered BA molecules to an ordered structure, resulting in BA crystallization. Notably, in this process, the CDs are in situ and homogeneously embedded in the crystalline BA matrix. This method affords maximum uniformly embedded CDs in the BA crystals. It also decreases nonradiative transition and increases ISC in the CDs by restraining the vibrational freedom of the CDs as a result of the rigid BA crystal matrix.

In the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (Figure 2A), the CDs show an average diameter of 5 ± 1.2 nm and a well-resolved lattice spacing of 0.21 nm, corresponding to the (100) facet of graphite carbon.14 The chemical structure and photophysical properties of the CDs and t-CD@BA were investigated. The Fourier transform infrared (FTIR) spectra (Figure 2B) reveal that the CDs exhibit characteristic absorption peaks at 3400, 1631, and 1617 cm−1, assigned to the O–H, C=O, and C=C stretching vibrations, respectively.27 After incorporating the CDs into the thermal annealed BA matrix, new absorption peaks can
be observed at 941 cm$^{-1}$, corresponding to the C$\equiv$B stretching vibration$^{18,21,22}$ indicating BA molecules functionalized on the CDs after thermal treatment. In the XPS results, the high-resolution B 1s spectrum of t-CD@BA (Figure 2C) displays three bands centered at 194.6, 193.6, and 192.7 eV, assigned to B$\equiv$O, B$_2$O$_3$, and BCO$_2$, respectively,$^{18}$ implying dehydration process occurs among CDs and BA molecules. These results indicate that the CDs were chemically bonded in the BA matrix.

In the photoluminescence (PL) spectra (Figure 3A), the CD aqueous solution comprises a main emission peak at 430 nm, while the t-CD@BA displays two significant emission peaks approximately at 430 and 530 nm, respectively. Moreover, the emission peak at 530 nm in the PL spectrum of t-CD@BA almost coincides with its peak in the RTP spectrum. When t-CD@BA is fully dissolved in water, the peak at 530 nm nearly disappears in FL spectrum and no phosphorescent emission is observed (Figure S1). It is well known that
phosphorescence quenching usually occurs in the presence of water owing to the presence of dissolved oxygen as well as the occurrence of solvent-assisted relaxation. These results indicate that the peak at 530 nm in the form is mainly derived from phosphorescence. Thermal annealed BA sample exhibited negligible fluorescence and phosphorescence compared with that of t-CD@BA at room temperature (Figure S2), indicating the RTP mainly comes from the chemically embedded CDs.

Interestingly, the t-CD@BA sample after grinding (g-t-CD@BA) displayed an unprecedented RTP enhancement phenomenon (~3.2-fold increase) (Figure 3B). In phosphorescence decay curves (Figure 3C and Table S1), enhanced average lifetime and strength of RTP were detected from g-t-CD@BA compared with that of t-CD@BA. The total QY and PQY of t-CD@BA were measured to be 19% and 15%, respectively. In contrast, the total QY and PQY of g-t-CD@BA significantly increased to 64% and 48%, respectively. The g-t-CD@BA not only exhibits a high RTP efficiency but also an extraordinarily strong RTP intensity. Remarkably, after switching off the 365 nm irradiation source (5 W), the intense green RTP from a plate (5 × 5 cm) filled with g-t-CD@BA can illuminate items for more than 9 s (Figure 3D and Movie S1). The RTP luminance value of g-t-CD@BA can reach 590 lux at a delay of 1 s, which is exceedingly higher than the brightness (97 lux) of commercial mobile phone screens (Figure 3E and Movie S2). For comparison, some typical luminance
values in real environments are sunrise/sunset on a clear day (400 lux), office lighting (320–500 lux), and typical TV studio lighting (1000 lux). Interestingly, even after being excited by sunlight on a dark or cloudy day, the g-t-CD@BA still exhibited a bright green RTP, visible to the unaided eye, with a delay of 9 s (Figure 3F and Movie S3), which, to the best of our knowledge, has never been reported. Phosphorescence excitation (PLE) spectra of the g-t-CD@BA indicate ultraviolet light in sunlight plays a major contribution to phosphorescence emission (Figure S3). In addition, the phosphorescence of the g-t-CD@BA can last for about 13 s, visible to the unaided eye, after being excited by 365 nm light (Figure S4).

To reveal the grinding-induced RTP enhancement phenomenon, we next investigated the changes between the structures of t-CD@BA and g-t-CD@BA. Under mechanical grinding, large lumps (>1 × 1 mm) of t-CD@BA are ground into g-t-CD@BA in fine particles in the size of 40–60 μm, as shown in Figure S5. The X-ray diffraction (XRD) spectrum (Figure 4A) for the t-CD@BA presented broadened and weak peaks, indicative of an amorphous phase.39–41 Following grinding, the spectrum of the g-t-CD@BA presented several sharp diffraction peaks which is similar to crystalline BA powder (Figure S6), indicating a grinding induced structural transition from an amorphous to a crystal phase. In the differential scanning calorimetry (DSC) curves on heating above melting point (Figure 4B), the t-CD@BA exhibited two weak endothermic peaks at 110°C and 152°C with total enthalpy of 333 J/g. On the other hand, for the g-t-CD@BA, the endothermic peaks became much stronger with total enthalpy of 1080 J/g, indicating that g-t-CD@BA possesses much lower energy than t-CD@BA.40 This further confirms the grinding induced transition from the high-energy amorphous phase to a low-energy crystal phase. The formation of the amorphous t-CD@BA mainly occurs because the molten BA molecules are unable to rearrange into a crystalline lattice and are therefore “frozen” into a more disordered state during the rapid cooling process. Compared with the amorphous environment, a more rigid crystalline environment can effectively restrict the freedom of the embedded CDs by restraining the vibrations of their surface groups to reduce nonradiative relaxation and enhance the ISC process, leading to greatly enhanced RTP.

Based on the results above, it can be inferred the rapid change of the specific surface area of t-CD@BA from large lumps to fine particles, results in a sharply increased surface energy, which is not stable in room temperature.41,42 Thus, a more stable crystal phase with lower energy is formed from amorphous phase of the thermal annealed BA matrix, resulting in the formation of crystalline g-t-CD@BA.

To clarify the superiority of our method, we next performed control experiments to compare as-prepared samples with those attained by traditional crystallization process. Thus, CDs and BA composites through evaporative crystallization (e-CD@BA) with different CDs loadings were prepared by low-temperature evaporation of mixture solutions of CDs and BA molecules, where CDs and BA were in the same proportions as in the t-CD@BA samples. The results clearly revealed that all the t-CD@BA samples were transparent without any apparent aggregation and delamination under daylight (Figures 5A and S7). The PL and RTP images (Figure 5A) reveal uniform luminescence for t-CD@BA and g-t-CD@BA, implying the homogeneous dispensation of the CDs into the thermal annealed BA matrices. In contrast, the CDs were severely agglomerated among the BA

![Figure 4](image-url) **Figure 4** XRD and DSC characterization of the CD@BA composites. (A) XRD spectra, (B) DSC curves of t-CD@BA and g-t-CD@BA on the heating run. BA, boric acid; CD, carbon dot; DSC, differential scanning calorimetry; XRD, X-ray diffraction
crystals, even under low-loading conditions. Nonuniform PL and RTP from e-CD@BA and ground e-CD@BA (g-e-CD@BA) were observed at different CD concentrations (Figures 5B and S8).

In the phosphorescence spectra (Figures 5C and S9a), the phosphorescence emission intensity of g-t-CD@BA gradually increases with increasing CDs loading fraction, reaching the maximum value at a concentration of 4.5 mg/g. However, for g-e-CD@BA, the strongest phosphorescent emission was only obtained at a lower concentration of 0.3 mg/g, which is much lower than that for g-t-CD@BA, implying a low loading capacity of the CDs in evaporative crystallized BA matrix (Figures 5C and S9B). The absorbance spectrum of g-e-CD@BA at a concentration of 1.5 mg/g exhibits enhanced tails at the longer wavelength region compared with that of the g-t-CD@BA (Figure 5D), indicating CDs aggregation among the evaporating formed BA crystals. During evaporative crystallization, the CDs are more prone to aggregate on or among the BA crystals, resulting in a weak
intensity due to the low loading capacity in the crystals. On the other hand, for the g-t-CD@BA, maximum uniform embedding of the CDs in the BA samples is observed. Thus, g-t-CD@BA can still hold high optical quality, even under high-loading conditions.

Based on the above results, we propose a grinding-induced crystallization strategy for the preparation of high-efficiency and strong RTP from CDs and BA composite according to the schematic illustration presented in Figure 6. First, amorphous t-CD@BA facilitates uniform embedding of the CDs into the thermal annealed BA matrix, which effectively avoids agglomeration of CDs. The higher energy amorphous t-CD@BA is not stable, which tends to transform to lower energy crystalline state upon external mechanical stimulus. After grinding, the sharply increased surface energy of the ground fine fragments drives the rearrangement of the contained disordered BA molecules to an ordered structure, thus leading to instant transition from amorphous to crystal phase, as demonstrated by XRD results. Thus, the CDs are in situ and homogeneously embedded in the crystalline BA matrix. Compared with the amorphous environment, a more rigid crystalline environment can effectively reduce nonradiative transitions and enhance the ISC process by restraining the vibrations of CDs, thus leading to greatly enhanced RTP. For the evaporative crystallization method, the CDs are generally more prone to aggregate on or among the developed BA crystals, thus leading to low RTP efficiency and weak emission.

3 | CONCLUSION

In summary, we have successfully exploited a new grinding-induced amorphous-to-crystalline transition method for the preparation of high-efficiency RTP materials. The as-prepared g-t-CD@BA exhibits both a high RTP efficiency (PQY of 48%) and strong RTP emission. Remarkable, RTP from g-t-CD@BA is strong enough to illuminate items with a visible time exceeding 9 s to the unaided eye, and RTP luminance value of 590 lux at a delay of 1 s. The excellent RTP properties were mainly attributed to the proposed newly fashioned grinding-induced phase transformation method. In this method, thermal annealed amorphous BA facilitates maximum uniformly embedding of the CDs into the matrix. Moreover, the grinding-induced instant crystallization allows the CDs to be in situ and homogeneously embedded into the crystal BA matrix, greatly surpassing the nonradiative transition and promoting the ISC of CDs. This study provides a practical synthetic strategy for the large-scale preparation of high-efficiency RTP materials for various applications.
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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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