Activating Room Temperature Long Afterglow of Carbon Dots via Covalent Fixation

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Supporting Information

ABSTRACT: The achievement of long afterglow in aqueous solution and as well as with small effects of dissolved oxygen is critical for its applications, but this is still a highly difficult and challenging task. Herein, a novel strategy for covalently fixing carbon dots (CDs) onto colloidal nanosilica (nSiO₂). The as-obtained materials (named m-CDs@nSiO₂) show not only an unexpected long afterglow emission in water dispersion (lifetime as high as 0.703 s) but also with small effects of the dissolved oxygen. Further studies revealed that the observed long afterglow of m-CDs@nSiO₂ possesses a predominant delayed fluorescence nature and mixed with a portion of phosphorescence. Some key knowledge that can be concluded from this study are (i) covalent interaction could be employed as an option to fix and rigidify triplet emission species; (ii) covalent bonds fixation strategy could behave as a better alternative than that of the frequently used hydrogen/halogen bonds for stabilizing triplets, because this benefits in extending the occurrence of long afterglow from only solid to solution/dispersion forms; and (iii) the containing unsaturated bonds (e.g., C≡C) on the surface of CDs make them to be self-protection agents against the effects of dissolved oxygen. These CDs are not only showing long afterglow emission in water dispersion and oxygen insensitivity, but also a moisture-related strategy for high-level information protection is proposed and demonstrated.

INTRODUCTION

Afterglow materials, including phosphorescence, persistent luminescence, and delayed fluorescence (DF) materials, continuously stimulate the extensive interests due to their widespread applications in light-emitting devices, sensing, biomedicine, and security systems.1–10 To date, the afterglow materials are still mainly limited to rare earth (RE)-containing inorganic materials,4,13,14 noble metal (NM)-containing complexes,7,15 and pure organic compounds.7,8,15–19 All of these materials, however, suffered from high cost, cytotoxicity, complicated preparation process, sensitivity to oxygen, and/or observable only at low temperature or in the solid/crystalline forms.1–19 In addition, most of the reported afterglow materials present relatively short emission lifetimes (i.e., several microseconds to a few milliseconds), and such short decay times do not meet the applications of persistent luminescence, because tens of milliseconds is generally required for the common human to recognize the afterglow emission.20 Therefore, it is still highly desirable to develop new types of long afterglow materials that are inexpensive, facile preparation, low cytotoxicity, and RE-/NM-free. More specifically, to apply the afterglow materials in certain high-tech fields (e.g., time-resolved sensing and imaging), they are expected to be dissolvable/dispersible in water and observable in the presence of atmospheric oxygen at room temperature. This is actually a more challenging task due to the intrinsic limitations for producing efficient afterglow emission. For instance, fixation and rigidification of chromophores via crystallization or embedding in a solid matrix with the assistance of hydrogen bonding are generally needed to prevent nonradiative decay of the excited triplet state and inhibit quenching from atmospheric oxygen.18–22

In recent years, luminescent carbon dots (CDs) have attracted tremendous attention thanks to their numerous merits (e.g., superior optical and chemical properties, facile preparation and modification, and excellent biocompatibility), consequently demonstrating many potential applications including sensing, theranostics, bioimaging, optoelectronic devices, and so on.23–25 More interestingly, the room temperature phosphorescence (RTP) and DF phenomena of CDs have also been reported recently, but only observable through fixing in certain matrices (e.g., poly(vinyl alcohol)
nSiO2 (i.e., m-CDs@nSiO2) could be obtained facilely via a hydrothermal treatment of m-CDs and nSiO2. Further studies were carried out to investigate the morphology of the as-prepared m-CDs@nSiO2. Interestingly, the high resolution TEM (HR-TEM) observation of the nSiO2, but with slight aggregation (Figure 2b). Upon the excitation of 365 nm, which is similar as that of the free m-CDs in water (i.e., 23.0%). This result indicates that nearly no emission property of m-CDs changes after connecting to nSiO2. Subsequently, transmission electron microscopy (TEM) was performed to investigate the morphology of the as-prepared m-CDs@nSiO2. As shown in Figure 2a and Figure S2 (SI), the m-CDs and nSiO2 display well-dispersed nanoparticles with average diameters of about 3.5 nm (size distribution 2−5 nm) and 25 nm, respectively. After the hydrothermal treatment, the m-CDs@nSiO2 was found to be similar in diameter as that of the nSiO2 but with slight aggregation (Figure 2b). Interestingly, the high resolution TEM (HR-TEM) observation reveals that the m-CDs evidently covered on the surface of nSiO2 (Figure 2c). To further determine how m-CDs cover on nSiO2 (e.g., physical adsorption or chemical bonding), the Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) characterizations of m-CDs@nSiO2 were carried out. As shown in Figure 3a (red line), the emergence of absorption peaks at ca. 2848 and 2920 cm−1 (the aliphatic C−H stretching vibrations of m-CDs) indicates successfully combining m-CDs and nSiO2. Importantly, two new characteristic peaks at about 1460 and 871 cm−1 are also observed from the FT-IR spectrum of m-CDs@nSiO2, which can be attributed to the C−Si and N−Si stretching vibrations, respectively. These findings imply that covalent coupling reactions should have occurred during the hydrothermal treatment process of the m-CDs and nSiO2. To further confirm this deduction, the XPS surveys of m-CDs@nSiO2 are also performed and compared with the free m-CDs (Figure S3, SI). Figure 3b demonstrates that this composite mainly includes C, N, O, and Si.
Si elements, supporting the successfully combining m-CDs and nSiO2. The deconvoluted C 1s, N 1s, and Si 2p XPS spectra confirm the formation of C−Si and N−Si bonds (Figure 3c−e). For instance, the C 1s XPS can be fitted with four binding energies at 283.9, 284.6, 285.4, and 286.6 eV, attributed to the C−Si, C−C/C≡C, C−N/C=N, and C−O bonds, respectively (Figure 3c);35,39 the N 1s XPS spectrum contains four components that can be assigned to N−Si (397.5 eV), pyridinic-like N (398.4 eV), amino N (399.1 eV), and pyrrolic-like N (400.0 eV) (Figure 3d);35,40 and the Si 2p XPS spectrum can be deconvoluted into three binding energies at 102.5, 103.2, and 104.0 eV, resulting from C−Si/N−Si, SiO2, and SiO2 (gel), respectively (Figure 3e).39,41 These characterizations and analysis clearly evidence that the m-CDs are immobilized on the surface of nSiO2 through covalent bonds.

Afterglow Emission Properties and Mechanism of m-CDs@nSiO2. Since the composite of m-CDs@nSiO2 has shown an unprecedented long afterglow in air-saturated aqueous dispersion at ambient condition (Figure 1), their afterglow emission properties and what underlies for producing such an interesting phenomenon are thoroughly investigated and discussed. Note that, as we described before, no afterglow emission can be observed from the free m-CDs both in solid and in dispersion forms.31 First of all, we attempted to determine the afterglow nature of m-CDs@nSiO2. As shown in Figure 4a, the similarities between steady-state PL and afterglow emission spectra of m-CDs@nSiO2 imply their nature of delayed fluorescence (DF). Generally, DF can be divided into three types: E-type DF (emission arising from the lowest singlet excited state (S1) that populated by a reverse intersystem crossing (RISC) from the lowest triplet excited state (T1));15,44,45 P-type DF (triplet−triplet annihilation);46 and recombination fluorescence (recombination of radical ions or opposite charges).47 Among them, the E-type DF or called thermal active delayed fluorescence (TADF) is the most cases of reported and has attracted much attention in recently years due to its high significance in fabricating a new generation of optoelectronic devices.1,2,48,49 To make further clarifications, relevance of this afterglow with the triplet excited states is investigated. Since oxygen is a well-known quencher to the excited triplet state (T1),15,44,45 P-type DF (triplet−triplet annihilation);46 and recombination fluorescence (recombination of radical ions or opposite charges).47 Among them, the E-type DF or called thermal active delayed fluorescence (TADF) is the most cases of reported and has attracted much attention in recently years due to its high significance in fabricating a new generation of optoelectronic devices.1,2,48,49 To make further clarifications, relevance of this afterglow with the triplet excited states is investigated.

Figure 2. TEM images of m-CDs (a) and m-CDs@nSiO2 (b), and HR-TEM image of m-CDs@nSiO2 (c). Insets of (a) and (b) display the size distributions of m-CDs and m-CDs@nSiO2, respectively.

Figure 3. FT-IR and XPS characterization. (a) FT-IR spectra of m-CDs, nSiO2, and m-CDs@nSiO2. (b) XPS survey spectrum of m-CDs@nSiO2. (c−e) High resolution XPS spectra and fitting results of C 1s (c), N 1s (d), and Si 2p (e) of m-CDs@nSiO2, respectively.
afterglow of m-CDs@nSiO2, temperature-dependent afterglow emission spectra were also measured. As shown in Figure 4c, the afterglow intensities are observed to increase gradually with the temperature from 298.15 to 423.15 K, confirming the existence of a thermally assisted process. Consequently, it could be tentatively ascribed the observed afterglow emission of m-CDs@nSiO2 to be TADF.

In order to obtain better insights into the afterglow characteristics of m-CDs@nSiO2, their steady-state PL and afterglow lifetimes were also measured. As expected, the m-CDs@nSiO2 aqueous dispersion shows nanoseconds level PL lifetime (7.56 ns, Figure S5, SI). However, a long afterglow lifetime of the m-CDs@nSiO2 is confirmed by their decay spectrum (Figure 4d), which can be fitted by a triexponential function with three components of lifetime to be 7.65 ms (1.13%), 182.12 ms (10.09%), and 717.68 ms (88.78%), respectively. This result implies that there are two decay channels to be mainly responsible for the observed afterglow emission (the component of 1.13% (7.65 ms) could be ignored). According to the following equation (1),

$$\tau_{av} = \sum \alpha \tau_i / \sum \alpha \tau_i$$

an average lifetime was thus calculated to be 0.703 s (under 365 nm excitation).

Boltzmann statistics indicate that a smaller energy gap between the lowest $T_1$ and the lowest $S_1$ ($\Delta E_{ST}$) benefits faster RISC, and thus a small $\Delta E_{ST}$ is generally required for producing an efficient TADF. Since the RISC determines the lifetime of DF, so its decay rate constant ($k_{RISC}$) can be used to estimate $\Delta E_{ST}$. According to the literatures, the energy gap $\Delta E_{ST}$ can be calculated by the following equation (2),

$$k_{RISC} = A \exp(-\Delta E_{ST}/k_B T)$$

where $A$ is a constant, $k_B$ is the Boltzmann’s constant, and $T$ is the absolute temperature. Consequently, the temperature-dependent afterglow lifetime measurements for m-CDs@nSiO2 from 298.15 to 473.15 K were carried out (Figure S6 and Table S1 in the SI). Then, these decay rates were plotted as a function of temperature and fitted based on eq 2 (Figure 4e), from which, the energy gap $\Delta E_{ST}$ could thus be determined to be 0.298 eV. Since TADF would be eliminated at low temperature, so the $\Delta E_{ST}$ of m-CDs@nSiO2 could also be estimated through its low temperature fluorescence and phosphorescence spectra. As shown in Figure S7 (SI), the low temperature (77 K) afterglow spectrum of m-CDs@nSiO2 only displays phosphorescence emission at $\lambda_{max} = 508$ nm (no TADF). From these low temperature fluorescence and phosphorescence spectra, the $\Delta E_{ST}$ is calculated to be 0.290 eV. Moreover, the afterglow emission spectra at different temperatures were analyzed by fitting with Gaussian functions. As shown in Figure S8 (SI), all these spectra could be fitted with two simple Gaussian peaks locating at ca.
461 and 518 nm, corresponding to an energy gap of 0.296 eV. The high consistency of this value with that obtained by fitting eq 2 and low temperature fluorescence and phosphorescence spectra indicates that the two fitting peaks in Figure S8 (SI) could be attributed to the emission of excited S1 and T1 states, respectively, i.e., DF and phosphorescence (Figure 4f). This conclusion is also supported by different afterglow lifetimes at 461 and 518 nm, i.e., 0.69 and 0.73 s, respectively (Figure S9 and Table S3, SI). Therefore, we can conclude that the observed afterglow of m-CDs@nSiO2 is actually a mixture of TADF and RTP, but the former represents a major contribution based on the relative integrated emission intensity of the two fitting peaks (Figure S8 and Table S2, SI). Note that the higher percentages of TADF emission were also found with increasing temperatures (Table S2, SI), and this is in good accordance with the facts that the molecular vibrations, k_RISC, and nonradiative loss would greatly increase under higher temperatures.20,49

The reasons why the m-CDs@nSiO2 composite attracted so much of our attention are the observations of two unique afterglow properties: (i) being able to disperse in water and showing strong and long lifetime emission at room temperature, and (ii) small quenching effects from dissolved oxygen (i.e., only ca. 20% differences between argon and air-saturated conditions). In fact, these features are unusual in comparison with the traditional TADF and RTP materials, which are usually only observable in the forms of crystallization (or embedded in a solid matrix), with strict deoxygenation, and/or at low temperature.5,16,18,19,22 Consequently, the origins of such unique afterglow features of m-CDs@nSiO2 are explored. On the basis of the TEM results and properties of nSiO2, it is easier to understand the dispersibility of m-CDs@nSiO2 in water. However, it is really astonishing to us to directly observe a long afterglow emission from m-CDs@nSiO2 aqueous dispersion at room temperature, even at air-saturated condition.

In our previous study, we had found a long lifetime RTP emission from the composite film of m-CDs-PVA,31 but no RTP can be detected when this film is wetted. This can be explained by the disruption of hydrogen bonds between m-CDs and PVA and consequent loss of rigidity of the emissive species. In addition, based on the consistencies between the UV–vis absorption of m-CDs and afterglow excitation spectra of m-CDs@nSiO2 (Figure S10, SI), we can deduce that the C–N/C=N bonds containing moieties on m-CDs should also be responsible for the observed afterglow emission, and this is the same origins as that of the RTP from m-CDs-PVA film.31 In the above FT-IR and XPS measurements and analysis, it has been confirmed that the m-CDs are immobilized on the surface of nSiO2 through the formation of C–Si and N–Si bonds. These covalent bonds are believed to be able to lock the emission species (i.e., C–N/C=N containing moieties) on the m-CDs, thus promoting their triplet relevant emissions. Therefore, we tentatively ascribe the observed long afterglow of m-CDs@nSiO2, which decreases the ΔE_ST from ~0.5 eV for m-CDs-PVA film.
(ref 31) to ~0.3 eV for m-CDs@nSiO2. Moreover, although this smaller $\Delta E_T$ facilitates the process of TADF for m-CDs@nSiO2, it is still larger than the ideal value (<0.1 eV) for efficient TADF, and this also explained why their afterglow is a mixture of TADF and RTP.

The other very unique afterglow feature of the m-CDs@nSiO2 aqueous dispersion is the small quenching effects from the dissolved oxygen. This observation is unusual, but highly significant, in extending their ranges of application. It is known that an energy transfer from the triplet excited state of a chromophore to oxygen (forming $1O_2$) is responsible for its strong quenching to triplet relevant emissions. In addition, the m-CDs had shown covering abundant unsaturated bonds on their surface (e.g., C=C bonds). Thus, the observed small quenching effects of dissolved oxygen to the afterglow emission of m-CDs@nSiO2 aqueous dispersion is considered to be due to the unsaturated bonds on the surface of m-CDs consumed dissolved oxygen during the irradiation process. To confirm this assumption, the FT-IR measurement of m-CDs after a treatment with light irradiation (365 nm) during air bubbling was performed. As shown in Figure S11 (SI), new FT-IR peaks emerged at about 3420, 1730, and 1100 cm$^{-1}$ (<20%), but the m-CDs-PVA still show very good reversibility with drying and wetting treatments, and the afterglow emission intensity from m-CDs@nSiO2-PVA film only change slightly (~20%), but the m-CDs-PVA film exhibit ca. 80% alterations (Figure S12).

On the basis of the unique afterglow features of the m-CDs@nSiO2-PVA and m-CDs-PVA films under dry and wet conditions, a novel moisture-related information protection strategy is proposed in this study. First, the nearly colorless m-CDs@nSiO2-PVA (DF ink), m-CDs-PVA (RTP ink), and m-CDs-PEG (FL ink) aqueous dispersions were prepared and loaded in the gel pen’s refills, which can be handwritten on a filter paper. As shown in Figure 5c, all the writings are invisible under daylight after thoroughly drying at ambient condition. In the information encryption process, the intended protection data or information (e.g., 315201, the zip code of our institute) was handwritten using DF ink (i.e., m-CDs@nSiO2-PVA), then the RTP and PL inks (i.e., m-CDs-PVA and m-CDs-PEG) were used to provide interferences with long lifetime RTP and short lifetime PL. Therefore, the wrong information of “896883” and “946807” was observed either at PL or at RTP modes, indicating that the original data or information can be concealed very well. For decryption, the filter paper is first wetted thoroughly, and then obtains the right information (i.e., “315201”) by observing the afterglow emission. These results demonstrate that the m-CDs@nSiO2 composite could be potentially applied in certain high-level counterfeiting and information protection systems like classified documents and banknotes, thanks to their very rare long afterglow features.

### CONCLUSIONS

In summary, we herein for the first time reported CDs-based long afterglow materials (i.e., m-CDs@nSiO2) that are applicable at room temperature and even observable directly in air-saturated aqueous media. Further studies revealed that the afterglow from m-CDs@nSiO2 has a major TADF nature and mixed with a portion of RTP. In addition, the new knowledge that can be obtained from this study are (i) covalent bond interaction could be considered as an option to fix triplet excited states, which would help to extend production of an efficient triplet relevant emission even in solution/dispersion forms, and (ii) CDs could behave as self-protection agents from oxygen quenching triplets, resulting in an oxygen insensitive afterglow system. Finally, by combining water and oxygen insensitive afterglow of m-CDs@nSiO2 and water sensitive RTP of m-CDs-PVA, a moisture-related data and information protection strategy with PL and RTP as interferences is proposed and demonstrated. Other potential applications of m-CDs@nSiO2, such as in time-resolved sensing and bioimaging, are still undergoing in our lab.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00831.

Experimental section and additional supporting figures and tables (PDF)

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**Notes**

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