

Long lifetime pure organic phosphorescence based on water soluble carbon dots†

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Carbon dots show potential in lighting and displays. However, only their fluorescence has been observed so far. Here we report the observation of phosphorescence from carbon dots in a polyvinyl alcohol matrix. The phosphorescence is attributed to C=O bonds on the surface of carbon dots and has a very long lifetime (~380 ms).

Room temperature phosphorescent (RTP) materials have shown tremendous applications in sensing, bio-imaging and light-emitting, but so far they have been generally inorganics or metal complexes¹ which usually contain heavy metals that are toxic, expensive and unstable. Thus efficient pure organic RTP materials are highly desired. But they are still very rare, partially because the spin-orbit coupling of electrons in pure organic compounds is so weak that it could not assist efficient intersystem crossing. Fortunately, some pure organic RTP materials have been successively realized in recent years.² But most of them have lifetimes in the millisecond order. Therefore, obtaining pure organic RTP materials with longer emission lifetimes is still a challenge.

In this communication, a pure organic RTP material was obtained based on water soluble carbon dots and its phosphorescent lifetime was enhanced to the sub-second order. As newly discovered bio-compatible, water soluble and stable fluorescent nanomaterials,³ carbon dots have attracted increasing attention for their potential applications in imaging, sensing or photocatalysis.⁴ Although fluorescence from carbon dots has been well documented and studied, phosphorescence has not been reported before. Interestingly, we have found that by dispersing carbon dots into a polyvinyl alcohol (PVA) matrix, obvious phosphorescence could be observed at room temperature when excited by ultraviolet (UV) light.

The phosphorescence was centered at ~500 nm with a long lifetime (~380 ms). Primary investigations suggested that the phosphorescence originated from triplet excited states of aromatic carbonyls on the surface of carbon dots and the PVA molecules effectively protected their energy from rotational or vibrational loss by rigidifying these groups with hydrogen bonds.

The carbon dots were prepared by pyrolysis of ethylenediamine-tetraacetic acid disodium salt (EDTA-2Na) at 400 °C under a N₂ atmosphere, modified from a previous report.^{3d} Most of them are smaller than 5 nm, as shown in the transmission electronic microscopy (TEM) image in Fig. 1a. The high resolution TEM (HRTEM) images reveal their lattice fringes to be 0.337 nm, 0.214 nm and 0.199 nm, which are in agreement with lattice spacings of the (002), (100) and (101) planes of graphite (PDF 12-0212).⁵ This result indicates that carbon dots have a

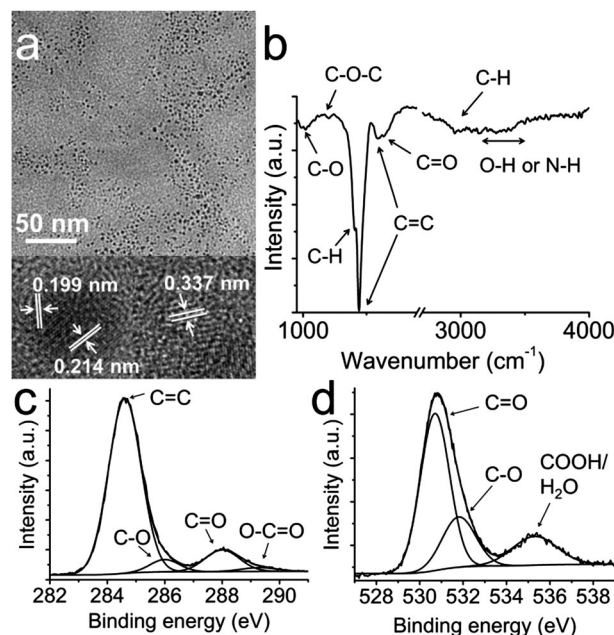


Fig. 1 (a) TEM and HRTEM images of the as prepared carbon dots. (b) The ATR-FTIR spectrum of carbon dots. (c) The XPS spectrum of C 1s. (d) The XPS spectrum of O 1s.

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graphitic structure. The attenuated total reflection Fourier transformed infrared (ATR-FTIR) spectrum of carbon dots is shown in Fig. 1b. The two peaks at 1021 cm^{-1} and 1200 cm^{-1} are assigned to $\nu(\text{C-O})$ and $\nu(\text{C-O-C})$; the peak at 1635 cm^{-1} could be attributed to $\nu(\text{C=O})$ of aromatic carbonyl; the two peaks at 1441 cm^{-1} and 1590 cm^{-1} originate from $\nu(\text{aromatic C=C})$; the peak at 1408 cm^{-1} and the band at $\sim 2950\text{ cm}^{-1}$ represent $\delta(\text{C-H})$ and $\nu(\text{C-H})$, respectively; the band at $3000\text{--}3400\text{ cm}^{-1}$ is indicative of $\nu(\text{O-H})$ and $\nu(\text{N-H})$.^{3c,4c,6} The presence of C-O and C=O bonds could be further confirmed using X-ray photoelectron spectroscopy (XPS) of C 1s and O 1s (Fig. 1c and d). For C 1s, the curve is fitted into four peaks, which are attributed to graphitic C=C bonds (284.6 eV), C-O bonds (285.4 eV), C=O bonds (288 eV) and O-C=O bonds (289.3 eV).⁷ And the O 1s spectrum could be deconvoluted into three peaks of C=O (530.7 eV), C-O (531.8 eV) and chemisorbed oxygen (COOH) and/or bound water (535.3 eV).⁸ Therefore, the carbon dots are graphite nanoparticles with a highly oxidized surface.

The carbon dots dispersed in water emit blue light under 365 nm UV light illumination (Fig. 2a, upper left). While the carbon dots dispersed in a PVA matrix emit cool white light under the same UV light excitation (lower left). Interestingly, we have also observed an afterglow of the film when we turned off the UV light (lower right), which is observable for seconds by the naked eye (a corresponding video is provided in the ESI†). Fig. 2b shows the corresponding steady state photoluminescence (PL) spectra of carbon dots dispersed in water (blue line) and in the PVA film (cyan line) by 325 nm excitation. Though both of their peaks center at $\sim 400\text{ nm}$, the film shows an enhancement in the longer wavelength region (400–600 nm). This enhancement correlates with the film's afterglow spectrum (olive line) centered at 500 nm. So the steady state PL spectrum of the film is actually a mixture of fluorescence and phosphorescence of carbon dots. The Stokes shift between

fluorescence and phosphorescence is 100 nm with an energy gap of 0.62 eV.

In order to explore the origin of phosphorescence, we compared the phosphorescence excitation spectrum of the carbon dot-PVA composite film and the absorption spectrum of carbon dots diluted in water (Fig. 2c). In the absorption spectrum, there is a peak at 220 nm and a broad band centered at 300 nm, which could be attributed to $\pi\text{--}\pi^*$ transition of C=C bonds and $n\text{--}\pi^*$ transition of C=O bonds, respectively.^{2a,9} In the phosphorescence excitation spectrum with emission at 500 nm, only a broad band at 260–340 nm appears and overlaps the absorption band of C=O bonds, suggesting that the phosphorescence may come from the C=O bonds on carbon dots. In addition, it should be noted that the aromatic carbonyl group has been generally considered an origin of RTP. This is because its singlet and triplet states are close in energy, the spin-orbit coupling is efficient, and then the intersystem crossing is efficient as well.^{2,10} Therefore, it is reasonable to suppose that the RTP observed here comes from aromatic carbonyls on carbon dots.

The phosphorescence decay spectrum is shown in Fig. 2d. The curve can be fitted into a multiexponential function with four lifetimes of 6 ms (51.0%), 40 ms (26.7%), 186 ms (16.9%) and 677 ms (5.4%). The average lifetime calculated using eqn (1)

$$\langle \tau \rangle = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i \quad (1)$$

is 380 ms. The multiple lifetimes of the phosphorescence imply various emission species, which may be a wide range of chemical environments on the surface of carbon dots for aromatic carbonyls.

Although the triplet state of aromatic carbonyls is where the phosphorescence originates, similar RTP cannot be observed from carbon dots dispersed in water, cellulose paper or PEG 20 000. They are strongly fluorescent. Indeed, the triplet state with a long lifetime would be effectively quenched by nonradiative processes, so the PVA matrix must play a key role in protecting them. Hydrogen bonding is usually important for RTP because they could effectively lock the emissive species and inhibit their intramolecular motions, the nonradiative relaxation channel.^{2b} There is a large amount of hydroxyl groups on PVA molecules,^{2d} so we suggest that these groups could effectively form hydrogen bonds to rigidify C=O bonds on carbon dots, limiting the intramolecular motions and preventing the nonradiative relaxation (Scheme 1). Besides, oxygen is a strong quencher of the triplet state^{10a} while PVA has a good oxygen barrier performance,¹¹ therefore another possible role of PVA would be effectively hindering the direct collisions between aromatic carbonyls and oxygen molecules, thus promoting the phosphorescence.

Taking advantages of the phosphorescence observable by the naked eye which can last for seconds, the carbon dot-PVA composite film could be used as a security feature. Phosphorescence has rarely been employed as an anti-counterfeiting method before,¹² but it should have several advantages over its traditional fluorescent counterparts: firstly, pure organic RTP materials are much less available, making them more inconvenient to be duplicated; secondly, the phosphorescence has a typical duration of time that is less likely to be reproduced than just the color emitted. Besides, due to the easy attachment

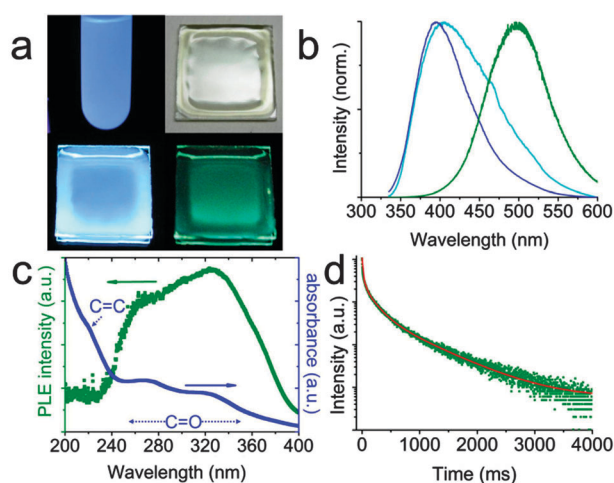
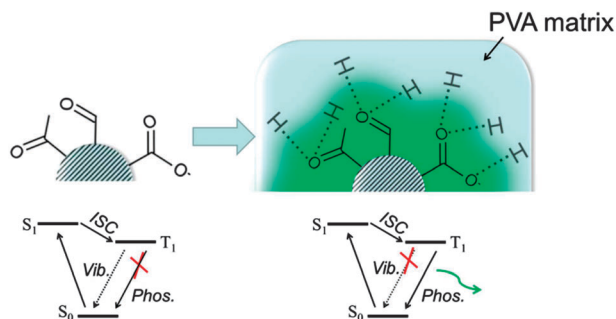


Fig. 2 (a and b) Digital photographs and the corresponding spectra of carbon dots: dispersed in water under UV light (a: upper left; b: blue line); dispersed in the PVA matrix under daylight (upper right), UV light (a: lower left; b: cyan line) and right after UV light has been turned off (a: lower right; b: olive line). The UV excitation for the photographs is 365 nm while for the spectra it is 325 nm. (c) Phosphorescence excitation spectrum (olive dots) and absorption spectrum of carbon dots dispersed in water (blue dots). (d) Time-resolved phosphorescence spectrum.



Scheme 1 Proposed phosphorescence mechanism of carbon dots dispersed in the PVA matrix.

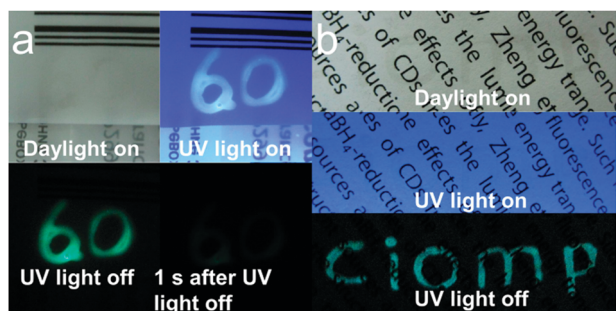


Fig. 3 (a) Fig. "60" written using the carbon dot-PVA composite film on a plastic package. The typical duration of afterglow is ~ 1 s, which could be employed for time-resolved anti-counterfeiting. (b) Letters "ciomp" written on a common printing paper are invisible under daylight and even UV light, but appear when the UV light has just been turned off in a darkroom.

of PVA to glass, plastic or paper, and the biocompatibility of both PVA and carbon dots, the security features can be printed on various packages of merchandise, especially food and drugs, for authentication. A concept of time-resolved phosphorescence anti-counterfeiting is shown in Fig. 3a.

The composite film could also be used as a secret information carrier on paper documents, as shown in Fig. 3b. Letters have been written on a common printing paper using carbon dot-PVA mixed solution as the ink. After drying, the letters are hardly observable under a daylight lamp. They are even invisible under UV light, because of the strong fluorescence background of the common printing paper. However, right after the UV light has been turned off, the strong fluorescence background vanishes and the letters "ciomp" emitting phosphorescence can be clearly observed. This method could be employed for advanced authentication or hiding important information from unanticipated people.

In conclusion, we have obtained pure organic RTP based on a carbon dot-PVA composite film. The phosphorescent emission peak was located at 500 nm with an average lifetime of 380 ms under the 325 nm excitation. The phosphorescence was suggested to originate from the aromatic carbonyls of carbon dots, and the PVA matrix effectively protects their triplet states from being quenched by intramolecular motions and oxygen. The pure organic, water-soluble and biocompatible RTP material can be readily used in novel anti-counterfeiting, especially for food and drugs. Its potential applications include chemical and

biological sensing and time-resolved imaging. The long lifetime of the triplet state in carbon dots is worth further study, because it means slow carrier recombination, which is especially beneficial for carrier collection in photovoltaic devices.

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