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Environment-dependent photon emission from solid state carbon dots and its mechanism†

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Fluorescent carbon dots (CDs) have received great research interest in recent years, with applications in areas such as bio-imaging and chemical sensing. However, solid state photoluminescence of CDs and its related applications (*e.g.* optoelectronics) is a less explored territory. Here, we have systematically studied the photo emission of CDs in solid state. We found that their blue emission is highly dependent on whether the environment contains polar groups or not. Mechanism studies show that the blue emission of CDs may come from their C=O bonds conjugated with aromatic carbons, and the interaction between polar groups in environment and C=O bonds in CDs is responsible for the environment-dependent photo emission. Our conclusion here should assist the development of CDs' solid state applications.

Introduction

As a novel nanolight, carbon dots (CDs) have attracted increasing interests in recent years.[1] They have sp^2 carbon cores bound with oxygenated functional groups.[2] They are water-soluble and biocompatible, and their raw materials are non-toxic and widely available.[3,4] These features make them potentially an environmentally friendly alternative to quantum dots and phosphor nanocrystals.

It is intriguing that most studies reported so far focus on applications of CDs in aqueous environments, such as bio-imaging and chemical sensing,[5,6] but the development of their solid state applications (*e.g.* optoelectronics) is slow. It has been reported that CDs require either a polymer matrix or surface capping/passivation to be emissive in solid state,[7–11] failing which they would be quenched.[4] A general experiment is to print CDs on cellulose paper to obtain fluorescent words and patterns.[3,4] C. Liu *et al.* invented blue emissive hybrid gel glasses by dispersing carbon dots into silica gel matrix.[7,8] W. Liu *et al.* obtained solid state "fluorescent polymers" from carbon dots copolymerized with several model monomers.[9] Since 2011, two reports have been published on successfully using CDs as the active layer to fabricate light-emitting devices by D. Ma *et al.* and A. L. Rogach *et al.*[10,11] In both of their reports, passivation of CDs with 1-hexadecylamine is required to prepare emissive CDs layer. However, those matrix and surface passivation layer are insulating, thus the obtained CDs-based composite layer is not desirable for optoelectronics. D. Ma *et al.* pointed out that the insulating layer of 1-hexadecylamine on CDs is the reason of limited performance of CDs-based LEDs.[10] However, there are no reports on answering why surface modification is required and no detailed study on photo emission of bare carbon dots in solid state so far. To promote CDs' solid state applications, these questions worth investigating.

In this paper, we systematically studied photoluminescence (PL) of bare CDs in solid state in different environments. We found that CDs prepared by different methods (furnace tube pyrolysis and hydrothermal) exhibited similar behaviour that they are blue emissive in the presence of polar groups (*e.g.* cellulose paper) but are quenched in other cases. Detailed studies on the first kind of CDs show that their PL spectra have two emission peaks p1 and p2. Through steady and transient spectral studies, we found that the bluer and stronger p1 emission is molecular-like and may come from C=O bonds. This idea is further supported by a correlation between quantum yield (QY) of CDs and the amount of C=O bonds conjugated with aromatic carbons that we observed. Based on such photo emission origin, CDs' environment-dependent blue emission is then explained by the interaction between C=O bonds on CDs and polar groups in the environment, according to molecular fluorescence theory.

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Results and discussion

Environment dependent emission of solid state CDs

The furnace tube pyrolysis method to prepare CDs is described in previous reports.[12,13] The transmission electron microscopy (TEM) of the as-prepared sample along with a photograph of the sample dispersed in aqueous solution is presented in Fig. 1a, showing the obtained CDs. The high resolution transmission electron microscopy (HRTEM) of one representative CD presented in Fig. 1b shows that the CDs have crystallized graphite inner cores. The size distribution of CDs in Fig. 1c indicates that most CDs are 1–2 nm in diameter.

The PL of CDs in water excited by a 325 nm He–Cd laser through a confocal microscope is presented in Fig. 2a. The spectrum can be fitted by two peaks: p1 is at ~395 nm with full width at half maximum (FWHM) of ~40 nm and p2 is at ~440 nm with FWHM of ~120 nm. The higher and narrower p1 contributes to the overall blue emission (insert in Fig. 2a), which is common in CDs[1,2] and fluorescent graphene oxide (GO).[14–16]

However, when CDs are deposited on a Teflon substrate and dried, the blue emission is quenched (Fig. 2b). They tend to aggregate into a "ring" pattern because Teflon is hydrophobic. From the spectrum we can see that the relative intensity of p1 decreases from 43% to 4% by area. The second peak p2 becomes dominant and shifts to a longer wavelength (515 nm). A third peak p3 appears at even longer wavelength (~630 nm) with the FWHM of ~80 nm. It should be noted that the emission of CDs on Teflon substrate is so weak that to collect sufficient signal the slit width of spectrometer needs to be increased.

Next we devised a way to transfer CDs from the Teflon substrate onto a polyethylene glycol (PEG) 20000 substrate. We poured melted PEG 20000 (at 90 °C) onto the CDs-coated Teflon and then peeled it off along with CDs after cooling. The "ring" pattern of CDs originally on Teflon is intact on PEG 20000 (Fig. 2d), indicating that the CDs are in the same aggregated state. However, on PEG 20000, the blue emission is recovered (Fig. 2c) under UV light. The relative intensity of p1 increases back to 33%. Since the only difference is substrate, thus the blue emission might be environment-dependent and the quenching of CDs on Teflon should not be concentration quenching. It should be noted that PEG 20000 itself is non-emissive, as is shown in Fig. S1 of ESI.†

We found that not only PEG, but also polyvinyl alcohol (PVA), cellulose paper, cotton and polyacrylamide (PAM) support the blue emission (ESI, Fig. S2†), while substrates such as Teflon, indium tin oxide (ITO), silicon and SiO_2 do not. The common feature of the first group of materials is they all have abundant polar groups. We have conducted the same experiment with CDs prepared by hydrothermal method reported elsewhere[3] and have observed the same phenomenon (ESI, Fig. S3 and S4†). Thus it is a general property of CDs.

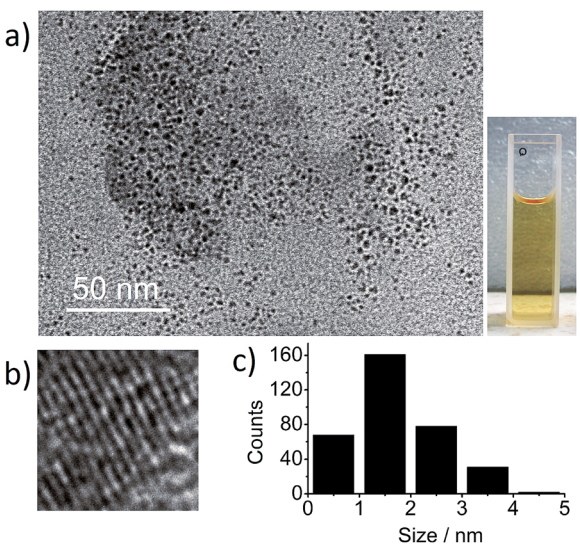


Fig. 1 (a) Transmission electron microscopy (TEM) of as-prepared CDs. The digital image of aqueous solution of CDs is placed alongside. (b) High resolution transmission electron microscopy (HRTEM) of one representative CD, showing its crystallized graphite inner core. (c) Diagram of size distribution of CDs.

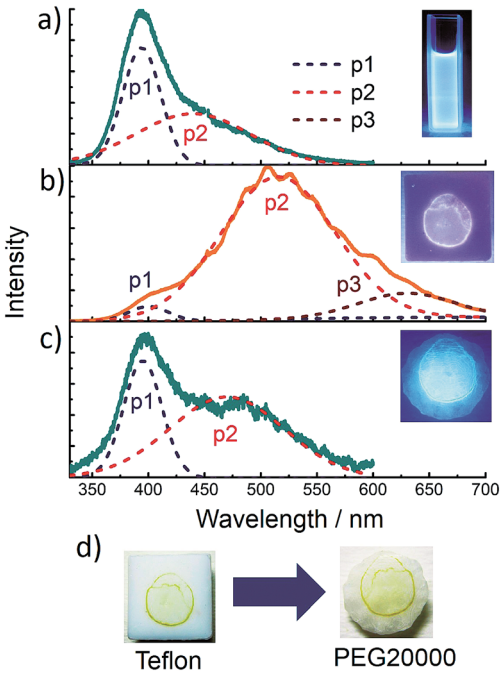


Fig. 2 PL of CDs excited by a 325 nm He–Cd laser in (a) water, (b) in solid state on a Teflon substrate and (c) on PEG 20000. Insets are corresponding images illuminated by a 365 nm UV lamp. (d) The "ring" pattern of CDs is transferred from Teflon substrate (left) to PEG 20000 (right).

Blue emission origin of CDs

To understand the environment-dependent blue emission of CDs, we investigated the origin of blue emission. When varying excitation from 300 nm to 380 nm using a Hitachi F4500 fluorescence spectrometer, two peaks fixed at 395–398 nm and 414–417 nm respectively are identified (Fig. 3a). They correspond to p1 emission. The excitation-independent emission is the

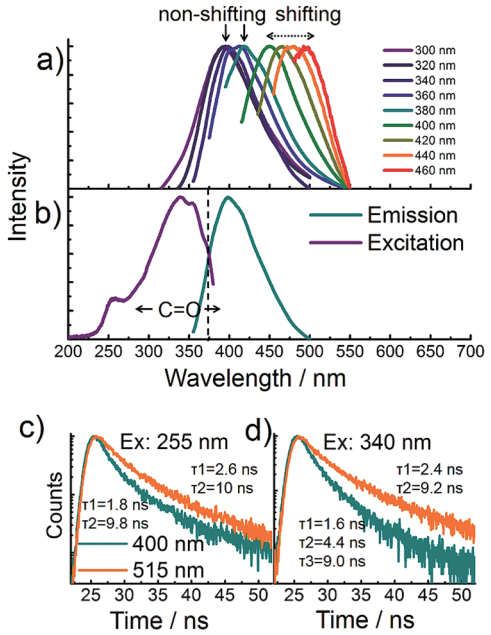


Fig. 3 (a) PL of CDs in water excited by 300–460 nm with a Hitachi F4500. (b) PLE and PL spectra of CDs in water with emission at 395 nm and excitation at 340 nm, respectively. (c) TRPL spectra of CDs on PEG 20000 with excitation at 255 nm and 340 nm and emission at 400 nm and 515 nm.

feature of molecular fluorescence.[17,18] Their small energy gap (~0.17 eV) suggests that they come from the same fluorophore but different vibrational levels. Similar immoveable emissions can be observed in CDs and GO in other reports.[18–20]

Note that there are excitation-dependent emissions from 450 nm to 500 nm, corresponding to the broad p2 emission. Such a moveable emission was observed in previous reports of carbon dots; however, the specific emission origin is unknown so far. Generally, such emission is attributed to "defect states" with a broad energy distribution on either graphitized core of carbon dots[18] or oxygenated groups.[21] Such broad energy distribution results in the broad emission peak (FWHM = 120 nm) and moveable emission wavelength by different excitation wavelengths. Because the p2 emission is not the focus of this paper, we did not study its emission origin further.

The PL excitation (PLE) spectroscopy of p1 detected at 395 nm is presented in Fig. 3b. A major peak at 340 nm is near mirror-symmetric to the p1 emission excited by 340 nm. This is another feature of molecular fluorescence.[17,18] The PLE peak at 340 nm is in the range of electronic transition on C=O bonds,[22,23] thus p1 emission may specifically come from C=O bonds.

Furthermore, from the time-resolved PL (TRPL) spectra, we can see that the emission at 400 nm excited by 340 nm (p1 emission) has lifetimes of 1.6 ns, 4.4 ns and 9.0 ns (Fig. 3d). The lifetime of 4.4 ns has been suggested to come from oxidized state or molecular-like state.[24,25] The other two life-times (1.6–2.6 ns and 9.0–10 ns) at both 400 nm and 515 nm excited by either 255 nm or 340 nm (Fig. 3c and d) should represent p2 emission, which expands across a wide range of wavelength of excitation and emission.

In addition to the above evidences that the blue emission is molecular-like and probably comes from C=O bonds, we observed a correlation between the amount of C=O bonds and QY of CDs. We found that acetone precipitates CDs from their aqueous solution, and the addition of more acetone leads to more precipitation. We labelled CDs that precipitate first as S1, those that precipitate later as S2, and the remaining CDs as S3. The images of S1 and S2 precipitation are shown in Fig. S5, ESI.† The images of S1–S3 re-dispersed in water under day-light and UV light are shown in Fig. 4a and b, respectively. Their PL spectra are presented in Fig. 4c. All of them are blue emissive with a major peak located at ~400 nm. Further studies on their emission and excitation spectra show that their spectra shape are nearly the same (ESI, Fig. S6†), thus they should share the same photoluminescence origin. However, their QY are different (Fig. 4b). The absolute QY measurement indicates that their QY increases from 0.7% for S1 to 9.8% for S2 and then to 17.1% for S3.

On the other hand, there is a surface chemical composition transition from S1 to S3 as well. In their UV-vis spectra (Fig. 5a), there are three absorption peaks corresponding to C=C bonds (217 nm), aromatic rings (265 nm), and C=O bonds (320 nm).[26–28] The absorption of C=O bonds increases from S1 to S3 (indicated by the green dashed line), indicating a growing amount of C=O bonds. X-ray photoelectron spectroscopy (XPS) of C1s signal of.S1–S3 is presented in Fig. 5b. The peaks at 284.6 eV, 285.8 eV, 287.9 eV and 289.2 eV are attributed to C=C, C–O, C=O, and C(O)OH species, respectively.[24,29] Peak fitting indicates that the percentage of C=O bonds increases appreciably from S1 (4.74%) to S2 (9.09%) and then to S3 (12.53%).

Functional groups on CDs directly link to the inner core composed of sp^2 aromatic carbon.[2] Therefore, most C=O groups observed here should conjugate with aromatic carbon, forming aromatic carbonyl structures. This is confirmed by Fourier transformed infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy (ESI, Fig. S7†). Fig. 5c shows FTIR spectra of S1–S3. The peak at 1656 cm^{-1} is from

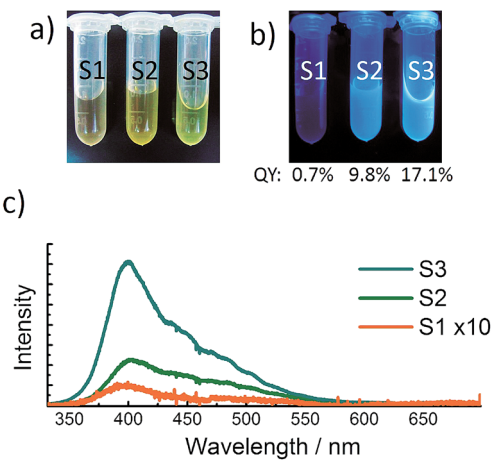


Fig. 4 Images of S1–S3 under (a) daylight and (b) UV light along with their PL QY data. (c) Corresponding PL spectra of S1–S3 under 325 nm He–Cd laser excitation. The intensity of S1 emission is magnified by 10 times to make a clearer comparison.

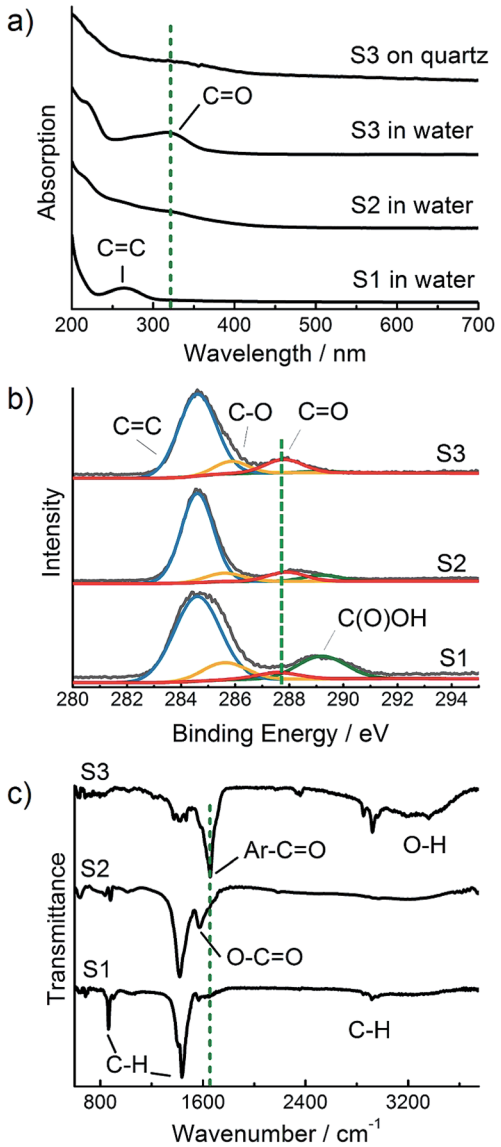


Fig. 5 (a) UV-vis absorption spectra of S1–S3 in water and S3 dried on quartz. (b) XPS spectra of C1s of S1–S3. (c) FTIR spectra of S1–S3. The increment of C=O bonds from S1–S3 is guided by the green dashed line in each graph.

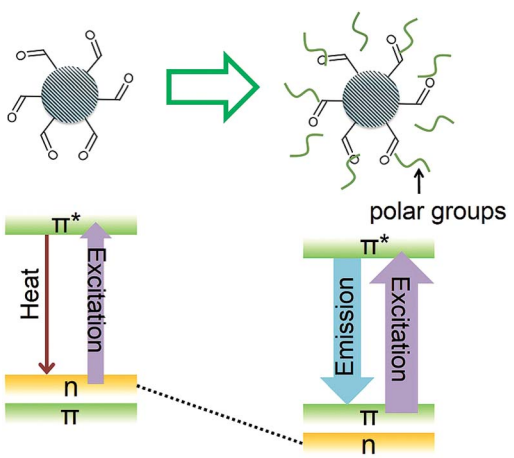
ν(C=O) of Ar-C=O (C=O bonds conjugated with aromatic carbons); the peak at 864 cm^{-1} and the band at 1374–1469 cm^{-1} originate from δ(C–H); the band at 2850–2960 cm^{-1} represents ν(C–H); the band at 3000–3400 cm^{-1} represents ν(O–H).[30] We can see that there is an obvious increment of Ar-C=O signal from S1 to S3.

In fact, the increase in C=O bonds is easy to understand. Acetone has C=O bonds; therefore, CDs with more C=O bonds are less likely to precipitate, according to "like dissolves like" rule.[31] What is noticeable is that the consistency between the amount of C=O bonds and QY of S1–S3 should support the idea that the blue emission is from C=O bonds (conjugated with aromatic carbons).

The blue emission mechanism of CDs and GO is a hot topic and several theories have been proposed, such as surface oxidized state,[24] sp^2 nano-domains embedded in carbon–oxygen sp^3 boundary,[14,29] and molecular-like fluorophore.[18,25] More recent studies, however, integrate these theories and suggest that the emission is from the interaction between sp^2 nano-domains and functional groups on the boundary.[32–34] D. Kozawa *et al.* suggested that the UV-blue emission of graphene oxide is from sp^2 fragments consisting of small number of aromatic rings with oxygenated functional groups.[34] P. Johari *et al.* specifically pointed out the key role of C=O bonds conjugated with GO plane in fluorescence through theoretical studies.[35] Besides, according to molecular fluorescence theory, C=O bonds conjugated with aromatic carbons are potentially phosphorescent.[17] We have indeed observed phosphorescence from PVA-protected CDs,[12] which lends further support to our viewpoint here.

It should be noted that if the blue emission indeed comes from C=O bonds on CDs, its environment-dependency can be conveniently explained, as is shown in Scheme 1. According to molecular fluorescence theory, the fluorescence of molecules containing C=O bonds is polarity dependent.[17,36] Because of the nonbonding electron pairs on oxygen atom of C=O bonds, such molecules often have low-lying and closely spaced n and π orbitals on their HOMO level. The quantum yield of n–π^* transition is much lower than that of π–π^* transition, because n–π^* transition is symmetry-forbidden while π–π^* transition is symmetry-allowed.[17] When the polarity of the environment increases, n electrons with higher polarity are more stabilized than π electrons through dipole–dipole interaction or hydrogen bonding with polar groups in the environment, thus n orbital shifts to lower level and leaves more π orbital component on the HOMO level, promoting π–π^* transition.[17,36] As a result, C=O bonds become more efficient in both absorbing and emitting photons.

To support this mechanism, we compared the absorption of highly diluted CDs (10 $\mu g\ ml^{-1}$) with and without polar groups in the environment (Fig. 5a). We can see that the absorption of S3 at 320 nm (C=O bonds) is more pronounced when S3 is in



Scheme 1 Proposed mechanism of environment-dependent blue emission of CDs.

water than when S3 is dried on quartz. This result should confirm the interaction between C=O bonds and polar groups.

Experimental

Furnace tube pyrolysis method to prepare carbon dots (CDs)

1.6 g EDTA-2Na placed in a quartz boat was heated in a furnace tube under N_2 atmosphere at a rate of 10 °C min^{-1} to 400 °C. After being annealed for 4 h at 400 °C and then cooled to room temperature, the black product was collected and dispersed in deionized water (80 ml) under ultrasonication for 30 min. Then the solution was centrifuged at 9500 rpm for 16 min to remove larger and insoluble particles. The supernatant was collected, which contains fluorescent CDs.

To further collect S1–S3, the supernatant was heated at 80 °C till ~60 ml of water had evaporated. Then 60 ml acetone was introduced into the solution, which became turbid. After ultrasonication, the solution was centrifuged at 9500 rpm for 16 min. The precipitate is S1. The supernatant was collected and further evaporated to 5 ml at 80 °C. Then 75 ml acetone was introduced into the solution, which became turbid again. After ultrasonication, the solution was centrifuged at 9500 rpm for 16 min. The precipitate is S2. The supernatant is S3. All samples were dried and re-dispersed in water for further characterizations.

Hydrothermal method to prepare carbon dots (CDs)

1.05 g citric acid and 335 μl ethylenediamine were dissolved in 10 ml deionized water. Then the solution was transferred to a Teflon-lined autoclave (30 ml) and heated in an oven at 150 °C (ref. 21) for 5 h. After that, the brown-black product was collected and subjected to dialysis to obtain the CDs.

Characterizations

The photoluminescence was performed with a Hitachi F4500 fluorescence spectrophotometer and a confocal Raman microscope with a 325 nm He–Cd laser. The absolute quantum yield is collected with a Hamamatsu Quantaurus-QY C11327-11 instrument. The absorbance spectra were collected by a Shimadzu UV-3101PC spectrometer. The X-ray photoelectron spectra (XPS) were collected with a Thermo ESCALAB 250 photoelectron spectrometer. The attenuated total reflection Fourier transformed infrared (ATR-FTIR) spectra was recorded with a Bruker ALPHA spectrometer. The nuclear magnetic resonance (NMR) spectra were collected with a Bruker Avance500 spectrometer using D_2O as the solvent. The time-resolved photoluminescence spectra were recorded using a FLS920 time-corrected single photon counting system. All of the digital pictures were captured by a Canon digital IXUS 9515 camera.

Conclusions

In summary, we revealed a phenomenon that the blue emission of solid state CDs is highly dependent on polar groups in the environment and explained it by the interaction between C=O bonds on CDs and polar groups in the environment. The dipole–dipole interaction or hydrogen bonding between C=O bonds and polar groups modifies the electronic structure of C=O bonds and enhances their absorption and emission efficiency. This mechanism explains why matrix or surface modification is always required to make CDs emissive in solid state and should promote CDs' solid state applications. Our discussions also have general significance in understanding the mechanism of fluorescent carbon-based materials, since the properties of CDs studied here are shared by CDs and GO, as reported in other studies.

Acknowledgements

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