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Cite as: AIP Advances **9**, 035135 (2019); <https://doi.org/10.1063/1.5078443>

Submitted: 25 October 2018 . Accepted: 08 March 2019 . Published Online: 18 March 2019

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Submitted: 25 October 2018 • Accepted: 8 March 2019 •

Published Online: 18 March 2019



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ABSTRACT

Luminescent carbon nanodots (CDs) are attracting great interests due to their unique properties in physics and chemistry. In this study we present the experimental evidences of the significant roles of self-absorption and radiative energy transfer in the photoluminescence process of N-doped CDs in water. It is found that the PL spectra, especially the relative intensity between the UV and visible bands, which are the major spectral structures, show a distinctive dependence on the concentrations of CDs, and can be well understood with the well-known Beer-Lambert law. These findings could be very helpful to deepen the existing understanding of the complex luminescence mechanisms of CDs.

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CDs have attracted great attention in fluorescent sensing,¹⁻³ light emitting devices,⁴⁻⁶ nanolasers⁷⁻⁹ and bio-imaging,¹⁰⁻¹² due to their distinctive advantages. All these potential applications rely on the luminescence of CDs,¹³⁻¹⁵ and several models have been proposed to interpret the mechanisms.¹⁶⁻²⁵ In general, these models may be roughly classified into two types: intrinsic edge states and extrinsic impurities.²⁴

Besides high luminescence and multiple colors, some researchers have reported the effect of aggregation-induced emission (AIE).²⁶ Gao *et al.* found that solvents could induce aggregation of CDs and hence enhance emission by reducing the non-radiative pathways.²⁷ Chen *et al.* reported similar AIE effect in graphene quantum dots.²⁸ Zhang *et al.* investigated the roles of photon reabsorption in the red-shifted emission of colloidal CDs.²⁹

However, the luminescence mechanisms, have not yet been fully understood.²⁷⁻³¹ Therefore, it is of great scientific interests to investigate the nature of luminescence and some fundamental photophysical processes in CDs.

In this work, the emissions of N-doped CDs with different concentrations were investigated in detail. It is firmly shown that the self-absorption and resultant radiative energy transfer have significant impacts on the photoluminescence evolution.

A facile method was used to synthesize N-doped CDs.⁹ In brief, urea (6 grams) and citric acid (3 g) were dissolved in water, and then the solution was treated in an 800 W microwave oven for 4 min. The powder of CDs was obtained by centrifugation and evaporation. The N content from urea improved the stability of the CDs in aqueous system. The solution shows

no precipitation after several months' storage under normal conditions.

Transmission electron microscopy (TEM) characterization was performed on a JEOL-2100F transmission electron microscope. UV-visible spectra were acquired on a HALO DB-20S UV-Vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) analyzes were measured on an ESCALAB MK II X-ray photoelectron spectrometer. Fourier-transform infrared spectroscopy (FTIR) spectrum was recorded with a Perkin-Elmer spectrometer. PL measurements were conducted on a home-assembled PL setup consisting of a Spex 750M monochromator and a Hamamatsu R928 photomultiplier detector.³²

As shown in Fig. 1(a), the ethanol solution containing CDs was painted on a glass substrate, which shows strong green luminescence under the excitation of a 405 nm laser diode. However, the luminescence significantly quenched as the ethanol evaporated, as seen in Fig. 1(b). Such concentration quenching (CQ) is common to most aromatic hydrocarbons and their derivatives.³³ Due to its association with the luminophore aggregation, the CQ process has frequently been referred to as aggregation-caused quenching (ACQ).³⁴ For carbon nanodots, due to the aromatic rings of carbon, strong π - π stacking interactions prompts the formation of aggregations when concentration increases. To avoid ACQ, CDs were usually dispersed into various solutions or solid polymer and salt matrix.^{35,36} From the TEM images shown in Fig. 1(c) and (d), the prepared CDs are 2–5 nm in diameter, and have a characteristic interplanar spacing of 0.34 nm which is close to the (002) facet of graphitic carbon.⁹

The XPS analysis was performed to investigate the element composition. As shown in Fig. 2(a) and (b), the C_{1s} spectrum shows five peaks, i.e., 284.5, 285.2, 285.7, 286.7 and 288.7 eV, which represent five main types of carbon bonds: sp^2 , sp^3 , C–N, C–O and C=N/C=O, respectively. The N_{1s} spectrum shows three peaks at 399.8, 400.3 and 401.9 eV which are assigned to the C–N–C, N–(C)₃, and N–H, respectively.^{9,23} Clearly, N atoms were effectively incorporated into CDs. In FTIR spectrum, as shown in Fig. 3(c),

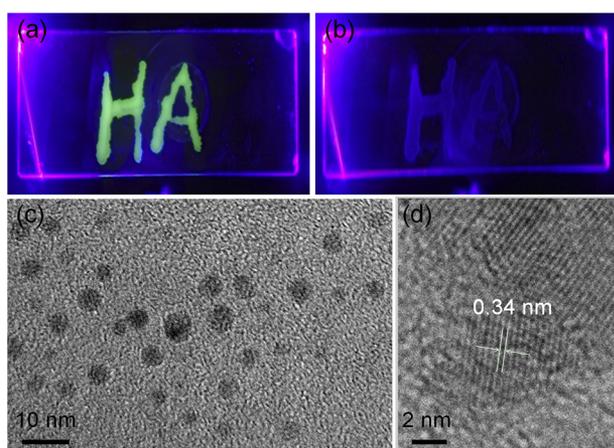


FIG. 1. (a) Digital photos of the CDs ethanol solution freshly painted on a glass substrate, and (b) after the ethanol evaporated under excitation of 405 nm laser; (c) TEM and (d) HRTEM images of the CDs.

the broad absorption bands at 3100–3500 cm^{-1} are assigned to the vibrations of N–H and O–H bonds, while the 1600–1700 cm^{-1} and 1350–1460 cm^{-1} are attributed to $\nu(C=O)$ and $\delta(CH_2)$, respectively.²³ The peak at about 1100 cm^{-1} corresponds to the distinct C–N stretching vibration,^{23,24} giving another spectroscopic evidence of the N incorporation. The UV-Vis absorption spectra of different concentrations were shown in Fig. 2(d). There are three major absorbance bands at 270, 330 and 410 nm respectively, which represent the typical absorptions of aromatic system and extended π - π conjugation in the CDs structure.^{9,10} The normalized spectra show no obvious differences, mean that the absorption bands did not change with concentrations, as shown in the inset of Fig. 2(d).

We employed a Xe lamp (Müller, Germany) + a grating monochromator (Acton SpectraPro 300i) as the excitation source.^{37,38} It can be seen in Fig. 3(a), there are two emission peaks when excited with 325 nm lights. One is centered at 365 nm, the other is about 515 nm. The former can be attributed to the intrinsic states induced by the edge carbons in CDs, while the latter is from nitrogen induced defect states.²⁴ As the excitation wavelength increases, the visible emission becomes dominant. This fact reflects the dominant role of N induced defect states in the absorption and luminescence of visible light. Particularly, when the excitation wavelength was set at 425 nm, the visible emission achieves its maximum intensity due to the almost resonant excitation. For the excitation wavelength longer than 475 nm, the excited visible emission shifts towards the longer wavelength direction and simultaneously the intensity declines rapidly, reflecting the feature of absorption spectrum in the corresponding wavelength range (e.g., Fig. 2(d)).

As stated earlier, we concentrate the present study on the self-absorption of emitted photons and resultant energy transfer within the CDs. We are thus predominately concerned with the PL evolution of the CDs under the excitation of 325 nm UV laser. As shown in Fig. 3(b), much diluted solution sample ($\sim 0.1 \mu g/L$) exhibits luminescence featuring one main peak at 365 nm and a long low energy tail. In contrast, the normal solution sample (e.g., 0.1 mg/L) shows luminescence with two bands. Obviously, the PL spectra of the CDs solution samples show a strong dependence on the concentrations. To elucidate the PL evolution, we did a systematic PL measurements, as shown in Fig. 3(c). In the figure “C” means the ordinary concentration, while “C/2” represents half the ordinary concentration and so on. As can be seen, the relevant intensity between the UV and visible luminescence bands is largely dependent on the concentration of CDs. The relative intensity of the UV band with respect to the visible band increases rapidly as the concentration decreases except the case of much higher concentration (e.g., 2C). Meanwhile, the visible luminescence band shifts substantially towards the higher energy direction. In contrast, the UV band at ~ 365 nm did not exhibit obvious peak shift, but likely broadens at its low energy side, as seen in Fig. 3(d) where all the PL spectra are normalized at the UV peak. For the observed relatively low luminescence intensity of the sample with 2C concentration, it may be interpreted as a result of ACQ effect.^{33,34} For the observed distinct dependence of the relative intensity between the UV and visible bands on the concentration, it may be ascribed to the photon reabsorption and resultant energy transfer.²⁹ In fact, energy transfer mechanisms in liquid and solid systems are an old but still being extensively studied subject due

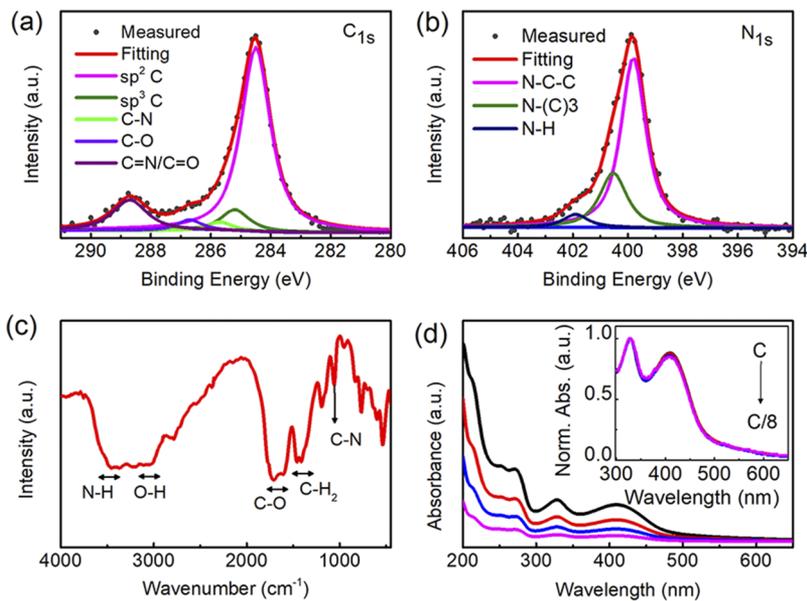


FIG. 2. (a) C1s and (b) N1s XPS spectra of the CDs as prepared; (c) FTIR spectrum of the CDs powder; (d) UV-Vis absorption spectra at different concentrations. Inset: the corresponding normalized UV-Vis absorption spectra.

to their fundamental interest and technological importance.^{39–41} Among them are the Förster-type resonance energy transfer^{39,40} and non-Förster-type energy transfer.^{41,42} When the Förster-type resonance energy transfer is well established as the energy direct transfer from the excited molecules to a surrounding molecule via radiationless processes, the non-Förster-type energy transfer may have a variety of forms. Radiative energy transfer via repeated circles of self-absorption or re-absorption of emitted photons and fluorescence is an important type of non-Förster-type energy transfer mechanism.⁴³ The energy transfer through photon reabsorption is

that the donor emits a photon firstly, and then the photon is reabsorbed by the acceptor. To reflect this difference, we use the concept “radiative energy transfer”. Recently, we have shown that the self-absorption and cascade photon recycling could be significant in ZnO crystal⁴⁴ and GaInP/GaAs solar cells.⁴⁵ As shown below, we argue that the self-absorption and radiative energy transfer play important role in the visible luminescence of N dopant induced defects in the CDs.

From the absorption spectra in Fig. 2(d), we know that the absorption of incident 325 nm UV light predominately occurs at

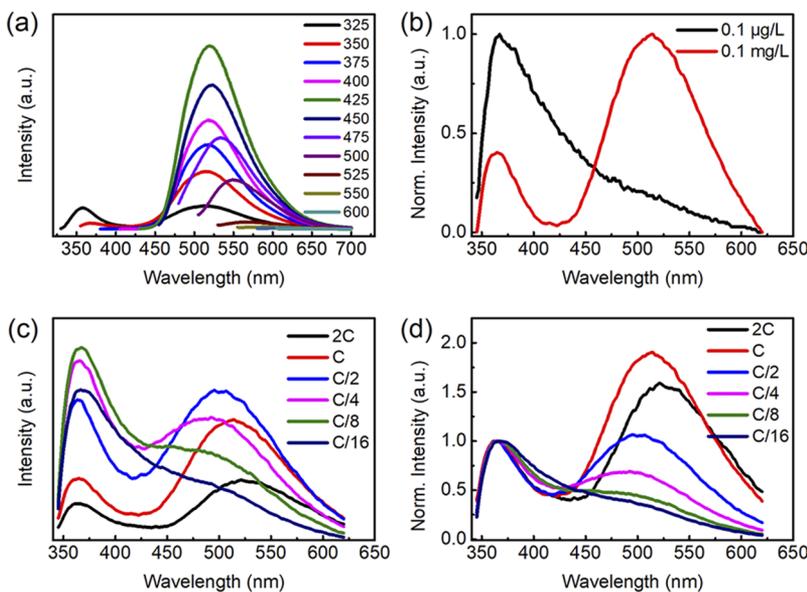


FIG. 3. (a) Excitation-wavelength dependent PL spectra of CDs in water at room temperature; (b) PL spectra of the CDs solutions at concentrations of ~ 0.1 mg/L and ~ 0.1 μ g/L; (c) PL spectra and (d) normalized PL spectra of the CDs aqueous solutions at different concentrations under the excitation of 325 nm laser.

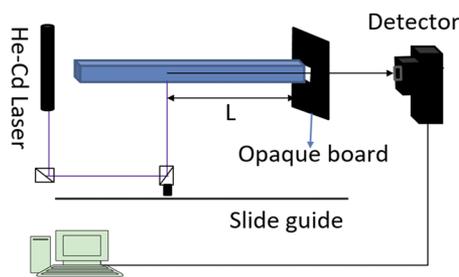


FIG. 4. Schematic of side-detection PL arrangement for the traversing-distance-dependent PL spectral measurement.

the intrinsic electron states of hexagonally bonded carbons in the CDs.⁹ Then efficient luminescent transitions take place between the electronic levels of edge-carbons to give the UV emission peaking at ~ 365 nm.²⁴ The partial emitted UV photons will be immediately absorbed by the electronic states of extended π - π conjugation bonds and even directly by the defect states induced by N dopants in the CDs themselves and neighboring CDs. Such radiative energy transfer will result in the excitation and visible luminescence of N defect states in the CDs. Moreover, such self-absorption and luminescence may continuously repeat during the propagation of emitted photons with higher energy until partial photons successfully escape from the luminescent sample.⁴⁵ According to this picture, the visible luminescence of N dopants induced defect states is mainly due to the self-absorption of the emitted UV photons and the radiative energy transfer. Therefore, the self-absorption shall be essential for the luminescence. Consequently, measured luminescence spectrum shall be strongly dependent on both concentration and absorption coefficient of emitters. As observed in Fig. 3(b) and (d), the PL spectra, especially the relative intensity between the UV and visible luminescence bands, show a distinctive

dependence on the concentration of CDs. For instance, the intensity of the visible band relative to the UV band remarkably increases with increasing the concentration of N-doped CDs. PL spectral shape change can be ascribed to the dependence of absorption coefficient on wavelength, as seen in the absorption spectra in Fig. 2(d).

It is well known that optical absorption induced light intensity variation can be interpreted by the Beer-Lambert law. We have also proven that the self-absorption within luminescent body strictly obeys the law too.⁴⁴ Following the previous experimental arrangement such as the geometric configuration of front excitation and side detection,⁴⁴ we did a testing experiment on a quartz tube containing the CDs-water solution, as illustrated in Fig. 4. Only those photons escaped from the side end of quartz tube can be collected and detected. Moreover, traversing distance of emitted photons inside the tube can be tuned by moving the focusing spot of the excitation laser along the quartz cell.

Under the frontal illumination of 325 nm laser, PL spectra obtained at six different traversing distances (e.g. $L = 0.5, 0.8, 1.0, 1.5, 2.0, 2.5$ and 3.0 cm, respectively) are depicted in Fig. 5(a). As can be seen, both UV and visible bands weakened with L increased, and the UV band attenuated much faster than the visible one. At the same time, some red shift of the visible band occurred, as clearly seen in Fig. 5(b), where the PL spectra in Fig. 5(a) were renormalized at the visible band and replotted. This may be because self-absorption, energy transfer and reabsorption occurred concurrently, the longer the photons traveled in solution, the stronger reabsorption occurred, as a result, the total PL attenuated and shifted to long wavelength direction.

According to the Beer-Lambert law, $I(L) = I_0 \exp[-\alpha(\lambda)L]$, where $\alpha(\lambda)$ is absorption coefficient which is sensitive to wavelength, and L is travelling distance of photons in medium, the intensity of UV band shall follow the tendency predicted by the Beer-Lambert law. As expected, the peak intensity evolution of UV band with the traversing distance conforms to the law very well, which can

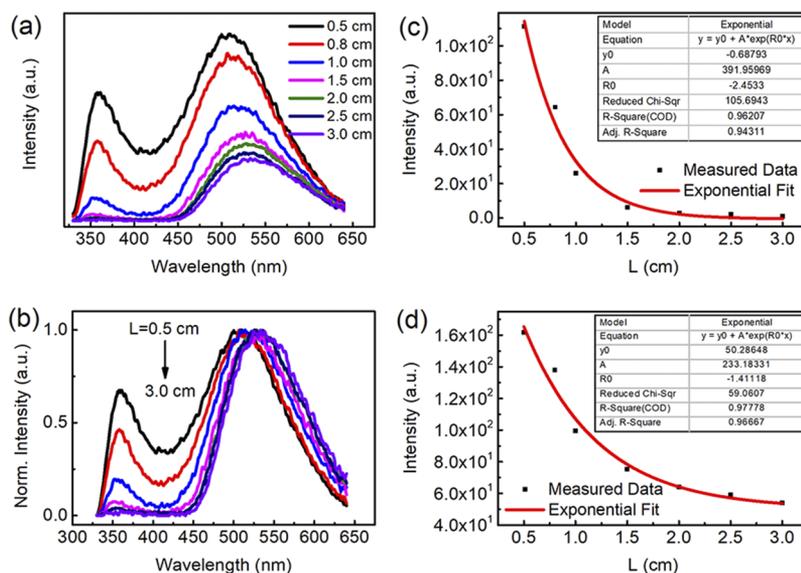


FIG. 5. (a) PL and (b) Normalized PL spectra measured with the side-detection mode at different travelling distances; (c) Exponential fit of the UV luminescence and (d) the visible luminescence intensities at different travelling distances.

be seen in Fig. 5(c). Since the visible luminescence is mainly caused by self-absorption and resultant energy transfer, its intensity shall follow the UV band. It is thus well described by the Beer law too, as shown in Fig. 5(d). The absorption coefficients of UV and visible emissions are different, which may be due to the different varieties of the energy level distributions of intrinsic and defect states of N-CDs.

In summary, the PL spectra of the aqueous N-doped CDs are studied at different concentrations. Two main luminescence bands, namely UV band and visible band, are observed for the solution sample with ordinary CDs concentration. But, the PL spectra, especially the relative intensity between the two bands, show a distinctive dependence on the CDs concentration. By taking the experimental arrangement of front-excitation and side-detection, we show that the luminescence intensities of both bands obey the Beer-Lambert law. These data and phenomena indicate that the self-absorption and the radiative energy transfer deeply influence the PL spectra of CDs in solution.

The study was financially supported by the National Natural Science Foundation of China (Grant No. 11374247), Shenzhen Municipal Science and Technology Innovation Council (Grant No. JCYJ20170818141709893), and Natural Science Research Projects in Jiangsu Higher Education Institutions (Grant No. 16KJB430004).

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