

NEWS & VIEWS

Open Access

An innovative way to modulate the photoluminescence of carbonized polymer dots

Pengfei Li¹ and Zaicheng Sun¹✉

Abstract

Cross-linking enhances the photoluminescence quantum yield of carbonized polymer dots, in which confined-domain promotes the energy level overlap, redshifts emission wavelength, and facilitates phosphorescence generation.

Carbon dots (CDs) were first observed during the preparation of single-walled carbon nanotubes in 2004. And then in 2007, CDs were defined in detail as zero-dimension carbon nanomaterials with diameters of 2–10 nm. It possesses wide and fantastic potential applications in optoelectronic devices, biomedicine, photocatalysis, etc. as the excellent optical properties, good biocompatibility, simple preparation. Thus, it also becomes hot material in a lot of fields. Depending on the composition and structure of the CDs, they can be divided into graphene quantum dots (GQD), graphitic carbon nitride quantum dots (CNQD), carbon quantum dots (CQDs), carbon nanodots (CNDs), and carbonized polymer dots (CPDs).

CDs have been rapidly developed and made great achievements in the last decade, various researchers put enormous enthusiasm and energy to regulate their optical properties. Up till the present, CDs can achieve full spectral emission and the maximum emission wavelength can reach far IR. However, it is still far from practical application. The major cause is the controversial photoluminescence (PL) mechanism. As is well known “properties depend on the structure”, without doubt, the optical properties of CDs also depend on the structure. Therefore, the intricate and ambiguous structures naturally become the greatest hindrances in the process of researching the CDs PL mechanism.

Of course, the PL mechanism has been studied since CDs were discovered, the carbon core state, surface state, and molecule state as the mainstream views are widely recognized by researchers^{1,2}. The core state fluorescence caused by $\pi-\pi^*$ electron transitions, the size of isolated sp^2 subdomain determines PL property^{3,4}. This PL mechanism is extensively applicable for CDs that possess large pure sp^2 carbon crystalline structure sizes. The surface state is considered that surface functional groups regulate the electronic structures and energy levels of CDs to control the bandgap of CDs, to lead the PL^{5,6}. This type of CDs usually has the conjugated carbon backbone and the surface contains abundant functional groups. The molecule state refers to molecular fluorophores carried by CDs dominating the PL property, it is often formed in the early stage of the synthesis process by bottom-up routes. Moreover, the type of CDs through the preparation method are CQDs, CNDs, and CPDs^{2,7}. However, the aforesaid cannot explain the unconventional PL behaviors exhibited by the sub-luminophores in non-conjugated polymer dots, the unconventional PL behaviors always present to CQDs. Therewith Yang et al. proposed the pioneering concept of cross-link-enhanced emission effect (CEE) to reveal the PL behaviors, which has been widely applied and exploited⁸.

Generally, some electron-rich heteroatom functions groups (such as C=O, C=N, N=O, and N–O) transition back to ground states from the excited states through the non-radiative pathways without luminescence. In the CEE PL mechanism (Fig. 1), these electron-rich heteroatom functions groups defined as sub-luminophore, it is

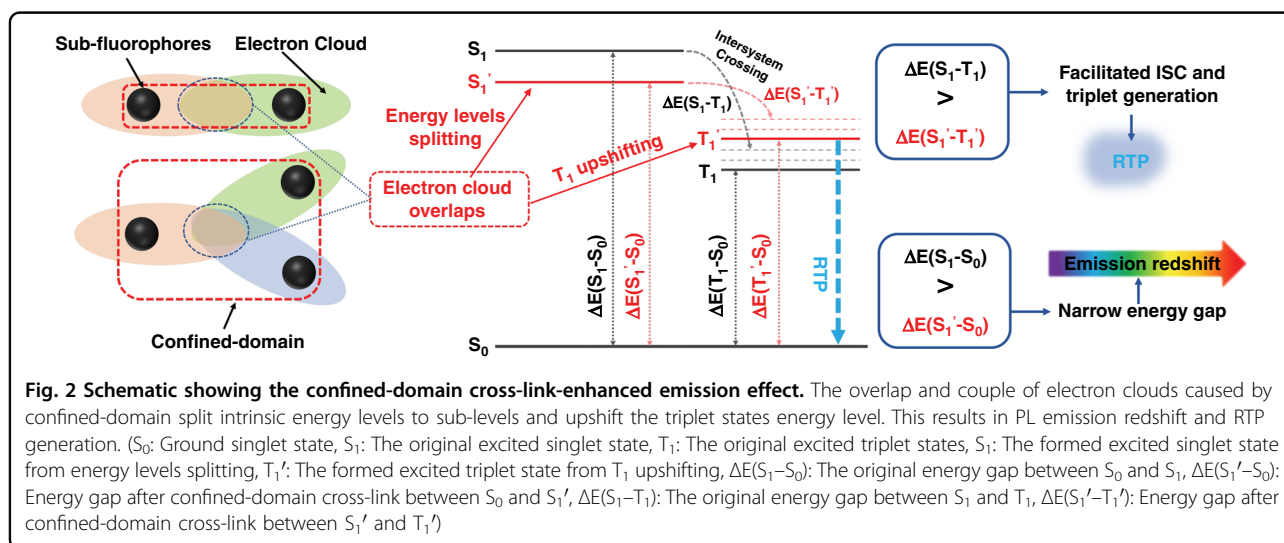
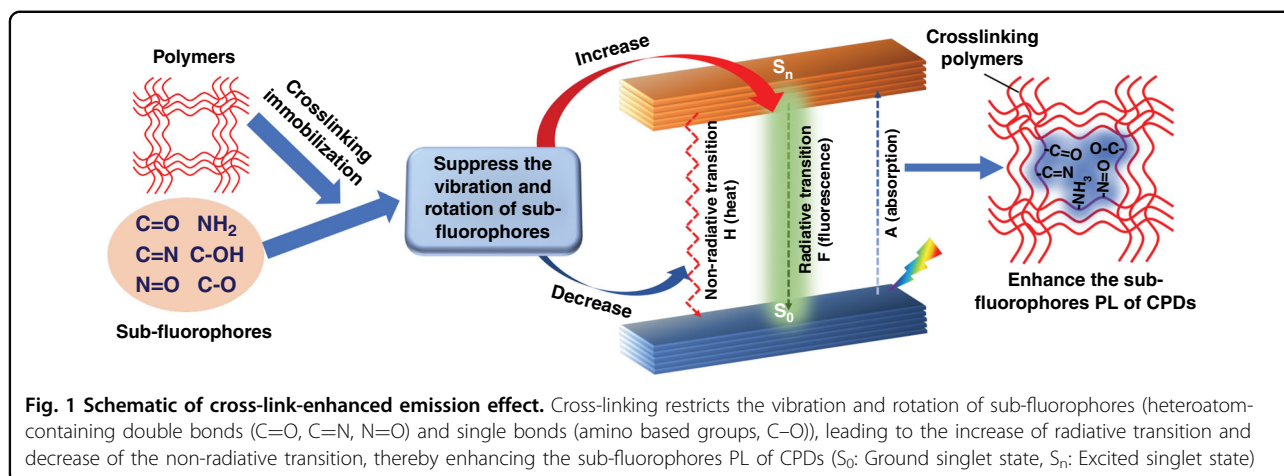
Correspondence: Zaicheng Sun (sunzc@bjut.edu.cn)

¹Center of Excellence for Environmental Safety and Biological Effects, Beijing Key Laboratory for Green Catalysis and Separation, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, P. R. China

© The Author(s) 2022



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.



immobilized by cross-linking polymers to restrict the vibration and rotation of sub-fluorophores, leading to the increase of radiative transition and decrease of the non-radiative transition, thereby enhancing the sub-fluorophores PL of CPDs^{9,10}. Nevertheless, this only improves the quantum yield (QY) of CPDs but does not explain the change of the energy level and the conversion of the radiative process from fluorescence to phosphorescence. In a recent publication by Tao et al.¹¹, the confined-domain CEE effect on luminescence properties of CPDs was investigated deeper perspective by combining characterizations and theoretical calculations, revealing the photophysical process.

Figure 2 shows the scheme of confined-domain CEE effect on energy level and electron transition, stable and compact environment of CPDs can greatly promote the electron-cloud overlaps and couple, split intrinsic energy levels, generates sub-levels, resulting in emission wavelength shift. In addition, The coupled units also possible

to narrow the energy gap between the excited singlet state and triplet excitons state (ΔE_{S-T}), which change the pathway of radiative transitions, facilitated intersystem crossing (ISC) and triplet generation. Herein, the CPDs system model with different strengths of confined-domain CEE was constructed by modulating the content of methyl groups in copolymers. Increasing methyl groups content weakened the cross-linking degree and strength of confined-domain CEE, but they process the same PL centers (bear amide or imide groups). From the above of femtosecond transient absorption (TA) spectroscopy, the great degree cross-linking CPDs appeared more energy-level structures at excited state, indicating that confined-domain CEE stimulates the production of abundant sub-levels, increase the number of transition channels through space interaction, which is a benefit to PL. The theoretical calculations studied the spin-orbit coupling (SOC) coefficients which can quantitatively estimate the probability of ISC and triplet emission. The results suggested that the

generation ability of the triplet excitons and the extent of phosphorescence emission gradually decreased with the strength weakened of confined-domain CEE, weakened room-temperature phosphorescence (RTP) performance of CPDs. This is possible because the confined-domain CEE upshifts the triplet state's energy level, narrowing the ΔE_{S-T} , and making the ISC easier. Furthermore, this also can extend the phosphorescence lifetime¹².

The confined-domain CEE involved multiple photo-physical processes. Based on the concept of confined-domain CEE, the CPDs emission of both fluorescence and phosphorescence can be modulated and targeted synthesis. More and more diverse features and extensive functions can be developed, for example, tuning the RTP lifetimes of CPDs by confined-domain CEE can develop the potentially smart materials apply to multi-level anti-counterfeiting technology^{13,14}. However, Variability in the properties of CPDs arising from methyl groups is relatively limited as methyl group is simple in structure. A variety of other substituents, such as aromatic rings and halogens, can be introduced into the structures of precursors for developing novel CPDs¹⁵.

Published online: 30 March 2022

References

1. Zhu, P. P. et al. Origins of efficient multiemission luminescence in carbon dots. *Chem. Mater.* **31**, 4732–4742 (2019).
2. Zhi, B. et al. Multicolor polymeric carbon dots: synthesis, separation and polyamide-supported molecular fluorescence. *Chem. Sci.* **12**, 2441–2455 (2021).
3. Wang, Z. F. et al. 53% Efficient red emissive carbon quantum dots for high color rendering and stable warm white-light-emitting diodes. *Adv. Mater.* **29**, 1702910 (2017).
4. Tepliakov, N. V. et al. sp^2 - sp^3 -hybridized atomic domains determine optical features of carbon dots. *ACS Nano* **13**, 10737–10744 (2019).
5. Jing, P. T. et al. Surface related intrinsic luminescence from carbon nanodots: solvent dependent piezochromism. *Nanoscale Horiz.* **4**, 175–181 (2019).
6. Nguyen, H. A. et al. Unraveling the fluorescence mechanism of carbon dots with *sub*-single-particle resolution. *ACS Nano* **14**, 6127–6137 (2020).
7. Schneider, J. et al. Molecular fluorescence in citric acid-based carbon dots. *J. Phys. Chem. C* **121**, 2014–2022 (2017).
8. Zhu, S. J. et al. The crosslink enhanced emission (CEE) in non-conjugated polymer dots: from the photoluminescence mechanism to the cellular uptake mechanism and internalization. *Chem. Commun.* **50**, 13845–13848 (2014).
9. Zhu, S. J. et al. Non-conjugated polymer dots with crosslink-enhanced emission in the absence of fluorophore units. *Angew. Chem. Int. Ed.* **54**, 14626–14637 (2015).
10. Tao, S. Y. et al. Crosslink-enhanced emission effect on luminescence in polymers: advances and perspectives. *Angew. Chem. Int. Ed.* **59**, 9826–9840 (2020).
11. Tao, S. Y. et al. Confined-domain crosslink-enhanced emission effect in carbonized polymer dots. *Light: Sci. Appl.* **11**, 56 (2022).
12. He, Z. K. et al. White light emission from a single organic molecule with dual phosphorescence at room temperature. *Nat. Commun.* **8**, 416 (2017).
13. Yu, X. W. et al. Lifetime-engineered phosphorescent carbon dots-in-zeolite composites for naked-eye visible multiplexing. *CCS Chem.* **3**, 252–264 (2021).
14. Liang, Y. C. et al. Lifetime-engineered carbon nanodots for time division duplexing. *Adv. Sci.* **8**, 2003433 (2021).
15. Yang, H. Y. et al. Hydrophobic carbon dots with blue dispersed emission and red aggregation-induced emission. *Nat. Commun.* **10**, 1789 (2019).