Construction of Carbon Dots with Wavelength-tunable Electrochemiluminescence and Enhanced Efficiency

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Abstract: Tuning electrochemiluminescence (ECL) wavelength of carbon dots (CDs) with enhanced efficiency is essential for multiplexed biosensing, bioimaging, and energy applications but remains challenging. Herein, we reported a facile route to finely modulate the ECL wavelength of CDs from 425 to 645 nm, the widest range ever reported, along with a more than 5-fold enhancement of ECL efficiency via phosphorous (P) incorporation. The molecular mechanism was explored experimentally and theoretically, which revealed the unusual dual roles of P dopants in the form of P-C and P-O bonding, i.e., importing shallow trapping states and promoting an effective intra-molecular charge transfer. This work would allow unlocking the key factors of ECL kinetics for heteroatom doped-CDs appearing out of reach, and open a new avenue for the rational design of nanocarbon for desirable applications.

Keywords: carbon dots, electrochemiluminescence, phosphorus doping, wavelength-tunable, mechanism
Introduction

Electrochemiluminescence (ECL) is a light-emitting process excited through electrochemical reactions, showing remarkable merits of high sensitivity, low background, quick response, ease of operation, and low cost of equipment.\textsuperscript{1-7} Recently, multicolor ECL has attracted considerable attention for ECL-based biomedical applications ranging from multiplex bioassay to bioimaging, raising an increasing demand for exploiting luminophores with tunable emission wavelength.\textsuperscript{8-14} Along this line, several pioneer works have been reported that multicolor ECL could be realized by combining or modifying ruthenium (II) and iridium (III) complexes.\textsuperscript{15-17} Although organic molecules hold great potential for multicolor ECL due to their structural versatility and ease of modulating the electronic and optical properties, most of these studies have been performed in organic media. Inorganic nanocrystals have also been employed for this purpose, mainly using Pb and Cd-based quantum dots (QDs).\textsuperscript{18-22} Nonetheless, the organic media and biocompatibility concerns hamper their future bio-/environmentally friendly applications.

Carbon dots (CDs) have been emerged as potential emitting materials for ECL due to their merits of ease of surface functionalization, high water dispersibility, favorable biocompatibility, and excellent environmental friendliness.\textsuperscript{23-30} It has been generally believed that the ECL emission of CDs is mainly dominated by surface energy levels and surface chemistry, while photoluminescence (PL) is primarily produced from the core.\textsuperscript{31} In this context, numerous efforts have been devoted to the ECL enhancement of CDs by heteroatom doping,\textsuperscript{32-34} hybridization with dye\textsuperscript{25} or graphene\textsuperscript{35}, and the oxidation of CDs surface.\textsuperscript{36-37} However, despite these great successes in ECL of CDs, the fine tuning the ECL wavelength in a wide range, along with an understanding of the mechanism in the molecular level, has been rarely reported.
Herein, we report a facile way to modulate the ECL wavelength of CDs in an aqueous solution by phosphorus (P) doping (Figure 1). Thanks to the high electron-donating property of the P dopants, the surface state, band gap, and electrochemical activity of CDs were significantly altered. As a result, the ECL wavelength was finely tuned from 425 to 645 nm solely by adjusting the concentration of P dopants; meanwhile, the ECL efficiency of CDs was boosted more than 5 folds maximumly. The mechanism for this unusual regulation of the ECL wavelength with enhanced efficiency was further explored by experimental and theoretical investigations. It was disclosed that P dopants in the form of P-C and P-O groups not only imported shallow trapping states but also promoted intramolecular charge transfer (ICT) in ECL. This work would provide new insight into the ECL mechanism of the heteroatom-doped CDs, and open a new avenue for the rational design of nanocarbon towards desirable applications.

**Experimental Section**

**Reagents and Materials.** 2-aminoterephthalic acid (ATA), and bis[tetrakis(hydroxymethyl)phosphonium] sulfate solution (THPS, 75%) were purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Potassium persulfate (K$_2$S$_2$O$_8$) and Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru(bpy)$_3$Cl$_2$·6H$_2$O) were purchased from Sigma-Aldrich Chemical Co. (USA). Ultrapure water was obtained from a Millipore water
purification system (18.2 MΩ·cm).

**Synthesis of PNCDs and NCDs.** PNCDs-m-n were synthesized from THPS and ATA with different molar ratios (m : n = 1:2 to 1:1, 2:1, 3:1, 4:1, and 5:1) as shown in Table S1. Specifically, for the synthesis of PNCDs-5-1, 0.073 g (0.4 mmol) of ATA was dissolved in 20 mL of ultrapure water, and 0.78 mL THPS (2.0 mmol) was added, then the mixture was sonicated for 30 min. After that, the mixture was transferred into the Teflon-lined autoclave chamber and reacted at 180 °C for 8 h. After natural cooling to ambient temperature, the mixture was centrifuged at 5000 rpm for 5 min, and then filtered with 0.22 μm cellulose filter paper to remove large precipitates to obtain PNCDs-5-1 crude product. The pH of the crude product was mediated to around 7.0 by the addition of NaOH solution (2 M). After that, the crude product was firstly dialyzed in a dialysis bag with a cut-off molecular weight of 500-1000 Da for 24 h. Then, the solution inside the dialysis bag was further dialyzed in a dialysis bag with a cut-off molecular weight of 3500 Da for 72 h. The final solution outside the dialysis bag was collected and concentrated by rotary evaporation. The solid powder of PNCDs-5-1 was finally obtained via vacuum freeze-drying for 12 h. This powder was dispersed in ultrapure water or PBS and stored at 4 °C for further use. The synthesis and purification processes of NCDs and other PNCDs-m-n are similar to that of PNCDs-5-1.

**ECL Measurements and Efficiency Calculation.** Firstly, the GCE was polished with 0.3 μm alumina slurry and then ultrasonically cleaned in ethanol and ultrapure water. Then, ECL measurements were performed with an MPI-E ECL analyzer system (Xi’an Remex Analysis Instruments Co., Ltd., Xi’an, China) in a three-electrode cell in the potential range from −0.2 to −1.8 V at a 650 V photomultiplier tube (PMT). A coupled fluorescence spectrometer (Fluoromax-4, Horiba, Japan)-potentiostat (CHI660E, CHI, China) system was employed for the acquisition of ECL spectra. The supporting electrolyte was 0.1 M PBS (pH=7.5) with 0.1 M K₂S₂O₈. According to the previously reported work, the ECL efficiency (Φₑₑₑ, %) of PNCDs-m-n (or NCDs)/K₂S₂O₈ was determined by the ratio of the generated photon number per consumed electron relative to the Ru(bpy)₃²⁺/K₂S₂O₈ standard using equation 1. The aqueous electrolytes for the Φₑₑₑ measurements were 0.1 M K₂S₂O₈ in 0.1 M PBS (pH=7.5)
containing 0.5 mg/mL PNCDs-m-n or NCDs and 0.5 mg/mL Ru(bpy)$_3^{2+}$, respectively. The bias potential during the ECL measurement is $-1.8$ V, and the scan rate is 0.1 V/s.

$$\Phi_{ECL} = \left( \frac{\int ECL \, dt}{\int \text{Current} \, dt} \right)^X \times 100\% \quad (1)$$

**Theoretical Calculations.** Density functional theory (DFT) calculations were carried out to investigate the energy band structures of the PNCDs-0, PNCDs-I, and PNCDs-II. The DFT and linear-response time-dependent DFT (TDDFT) calculations were performed with the Gaussian16 (revision A03)$^{40}$ using the hybrid B3LYP functional and the 6-31G(d,p) basis set. Grimme's D3BJ dispersion correction was used to improve calculation accuracy. The hole-electron analysis was performed with the Multiwfn 3.8(dev) code.$^{41}$ The total DOS was obtained from Multiwfn (revision 3.8) by Hirshfeld method with the full width at half maximum of 0.3 eV.$^{41}$ The graphs were rendered by Visual Molecular Dynamics (VMD).

**Results and Discussion**

**Synthesis and Characterization of PNCDs and NCDs.** Since surface functional groups play a critical role in ECL generation, ATA was selected as a precursor for synthesizing CDs with ECL properties due to its amine and carboxyl groups (the as-obtained CDs were denoted as NCDs).$^{39,42}$ Given the sizeable atomic radius and high electron-donating ability of P, THPS was chosen as an additional precursor for P source to produce P-doped CDs (PNCDs). By adjusting the molar ratio of THPS (m) and ATA (n), different PNCDs-m-n were obtained (Table S1). The transmission electron microscopy (TEM) images of PNCDs and NCDs revealed homogeneous and monodispersed nanoparticles with an average size of 3-8 nm (Figure 2 and Figure S1). The high-resolution TEM (HRTEM) images and corresponding fast Fourier transform (FFT) patterns of PNCDs and NCDs (Figure 2 and Figure S1) demonstrated a structure with three main types of lattice fringe distance of 0.21 nm, 0.28 nm, and 0.32 nm, corresponding to the (100), (020) and (002) planes of graphitic carbon, respectively.$^{43-46}$ Interestingly, compared to the NCDs, the X-ray diffraction (XRD) patterns of PNCDs showed an obviously broadened peak (Figure S2), attributing to the defects in the crystal structure, which was also revealed by the increased ratio of the disordered D band and crystalline G band.
(D/G) in the Raman spectra (Figure S3).

Figure 2. TEM images of PNCDs-5-1 (a0) and NCDs (b0) with the size distribution in the inset, HRTEM images of PNCDs-5-1 (a1 and a2) and NCDs (b1 and b2) with insets of zoomed-in images showing crystalline lattice fringes, and FFT patterns of PNCDs-5-1 (a3 and a4) and NCDs (b3 and b4).

The Fourier transform infrared (FTIR) spectra of both PNCDs and NCDs manifested the presence of C=\(\text{C}\), C=O, C=\(\text{N}\), C=\(\text{H}\), O=\(\text{H}\), and N=\(\text{H}\) bonds (Figure 3a).\(^{43,47-51}\) Noteworthily, the distinct peaks at 1138 cm\(^{-1}\), 928 cm\(^{-1}\), and 618 cm\(^{-1}\) from the FTIR spectrum of PNCDs, attributing to the P=O\(^-\)-C, P=O, and P=\(\text{C}\) bonds, respectively,\(^{52-55}\) demonstrated the successful doping of P into the PNCDs, which was also verified by the X-ray photoelectron spectroscopy (XPS) results (Figure S4). The slightly increased intensity of the stretching vibration of \(\text{\(\sim\)}\text{CH}_2\text{-OH}\) (1043 cm\(^{-1}\)) and \text{COOH} (1740 cm\(^{-1}\)) in PNCDs implied that the P doping gave rise to the surface defects,\(^{56-58}\) consistent with the XRD and Raman results. The C1s bands (C=O/C=\(\text{P}\) at 285.6 eV) and P2p bands (P-C at 131.7 eV and P-O at 132.5 eV) of PNCDs were detected, suggesting the formation of C=O\(^-\)-P and C=\(\text{P}\) (Figure 3b, 3c, 3e, and Figure S5, S6), indicative of the covalent binding of P with the framework of PNCDs.\(^{47,59-61}\) It should be noted that the N1s band of PNCDs and NCDs displayed similar peaks (Figure S7), indicating that the binding information of N was not affected by P doping. As summarized in Figure 3f and Figure 3g, PNCDs displayed a higher ratio of O/C and P/C, higher relative content of C=O\(^-\)-\(\text{P}\) and C=\(\text{P}\),
and lower aromatic C than those in NCDs (Figure 3d, S4, S5 and Table S2).

**Figure 3.** (a) FTIR spectra of NCDs and PNCDs-m-n. The C1s XPS spectra of PNCDs-5-1 (b), PNCDs-1-1 (c), and NCDs (d). (e) The P2p XPS spectrum of PNCDs-5-1. (f) The molar ratio of O/C (black) and P/C (red) in NCDs and PNCDs-m-n summarized from XPS results. (g) The percentage of C from C-O-P/C-OH groups (blue) and aromatic ring (pink) in total carbon for NCDs and PNCDs-m-n summarized from XPS results.

Hence, the above results validated the successful synthesis of PNCDs with the formation of more surface functional groups and effective doping in the graphitic carbon framework, which
altered the optical properties of the PNCDs with respect to that of NCDs (see UV-vis and PL spectra in Figure S8-S10 and more discussion in Supporting Information). It should be noted that different from NCDs, the PNCDs displayed prominent excitation-dependent properties in the whole wavelength range, which could be ascribed to different surface states introduced by P doping.

**P doping Triggers Efficiency- and Wavelength-Tunable ECL.** The unique solubility and photophysical properties make NCDs and PNCDs very promising as ECL luminophores in an aqueous solution. As annihilation-type ECL was not observed, the coreactant-type ECL was comprehensively exploited and optimized using K$_2$S$_2$O$_8$ as the coreactant (Figure S11). As shown in Figure 4a and Figure 4b, the ECL of NCDs and PNCDs onsets at about $-1.2$ V during the negative scan from $-0.2$ V to $-1.8$ V, following a traditional “reduction-oxidation” mechanism (Equations S1-S5). The ECL was stable and repeatable under consecutive cyclic potential scans (Figure S12), and after storage in 0.1 M PBS (pH=7.5) at 4 °C under darkness for 30 days (Figure S13). Moreover, with the increase of P dopants, both the ECL intensity (Figure 4a, 4b, and Figure S14) and efficiency (Figure S15) increased gradually, implying the critical role of P dopants in ECL.

For more details about the ECL emission of PNCDs, the ECL spectra at different potentials were collected. The maximum ECL emission wavelength almost kept constant when the potential varied from $-1.2$ V to $-2.0$ V (Figure S16), manifesting that there was only one single excited state corresponding to the ECL emission.$^{38, 62}$ Notably, an evident P-relevant redshift of ECL emission was observed. As shown in Figure 4c and Figure S17, the ECL spectrum of NCDs displayed a maximum emission at about 425 nm, while the PNCDs-1-2 with a small number of P dopants showed a maximum emission at 535 nm. Further increasing the P dopants resulted in a longer ECL emission wavelength at 645 nm was observed for PNCDs-5-1. It is worth noting that the facile and controllable regulation of ECL wavelength from 425 nm to 645nm only via a single element doping was rare (Table 1). Moreover, a dual ECL emission at 425 nm and 645 nm was observed from the mixture of NCDs and PNCDs-5-1 at the same concentration (Figure S18), ascribed to the emission of NCDs and PNCDs-5-1, respectively, displaying a tremendous potential scheme for the wavelength-resolved ECL in the application
of multiplexed analysis. In contrast, a maximum redshift of about only 85 nm for the PL emission was observed when varying the amount of P dopants (Figure 4c and Figure S9). The comparison of ECL and PL in the dependence of wavelength change on the P dopants demonstrated that ECL was more sensitive to the P doping. Strikingly, the ECL emission of PNCDs-m-n with the same surface properties displayed distinct redshift up to 155 nm relative to their corresponding PL emission (Figure 4c and Figure S19, S20). The apparent difference between the ECL and PL emission highlighted the different emitting states of ECL and PL for PNCDs.

**Figure 4.** (a) CV (blue line) and ECL-potential (red line) curves of the PNCDs-5-1/K₂S₂O₈ system. (b) ECL-potential curves of NCDs and PNCDs-m-n. (c) PL emission spectra (dash line) and ECL emission spectra (solid line) of NCDs and PNCDs-m-n. λₒ for the PL spectra of NCDs and PNCDs-m-n are 305 nm and 365 nm, respectively. All ECL experiments were performed in 0.1 M PBS (pH=7.5) containing 0.1 M K₂S₂O₈ and 0.5 mg/mL NCDs or PNCDs-m-n at a scan rate of 0.1 V/s. The bias potential for (c) is −1.8 V.
Table 1. Comparison of different emitters with tunable ECL emission.

<table>
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<tr>
<th>Emitter Type</th>
<th>PL Emission Wavelength (nm)</th>
<th>ECL Wavelength (nm)</th>
<th>Maximum ECL Shift (nm)</th>
<th>Ref.</th>
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<tr>
<td>Cd-based QDs [a]</td>
<td>549 ~ 643</td>
<td>549 ~ 643</td>
<td>94</td>
<td>18</td>
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<tr>
<td>Ru/Ir complexes [b]</td>
<td>476 ~ 610</td>
<td>491 ~ 636</td>
<td>145</td>
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<td>Organic dyes [c]</td>
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<td>450 ~ 517</td>
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<tr>
<td>CN-NVs [d]</td>
<td>446 ~ 468</td>
<td>450 ~ 516</td>
<td>66</td>
<td>9</td>
</tr>
<tr>
<td>PNCDs</td>
<td>405 ~ 490</td>
<td>425 ~ 645</td>
<td>220</td>
<td>This work</td>
</tr>
</tbody>
</table>

[a] CdSe/CdS/ZnS core/shell/shell QDs; [b] ruthenium (II) and iridium (III) complexes; [c] bifunctional organic dyes; [d] graphitic carbon nitride modified with nitrogen vacancy.

Mechanism Study. To gain more insight into the P-relevant ECL intensity and wavelength of PNCDs, the photoelectrochemistry was firstly explored by measuring the open circuit potential (OCP) and Mott-Schottky (M-S) plots. The generation of a large OCP upon irradiation is usually considered to be a symbol of high excited electron storage ability. As shown in Figure 5a, with higher P concentration, the OCP curve of PNCDs under irradiation showed a more increased ΔV₁. With the light off, the OCP of all PNCDs dropped gradually (ΔV₂). The ratio of ΔV₂/ΔV₁ for PNCDs was closer to 1 with higher P dopants, demonstrating less surface deep electron-trapping state. As revealed by the M-S plots (Figure 5b), PNCDs with higher P dopants had higher charge carrier density, suggesting higher electron-hole separation and electron conductivity. Thereby, both the OCP and M-S results illustrated that P doping in PNCDs could reduce the surface deep electron-trapping state, promote the electron-hole separation, and enhance the electron conductivity, all of which boosted the ECL performance of PNCDs.
Figure 5. (a) OCP and (b) M-S plots of NCDs and PNCDs-m-n in 0.1 M KCl aqueous solution. (c) Onset reduction potentials of NCDs and PNCDs-m-n obtained from CV curves measured in the degassed PBS (0.1 M, pH = 7.5) in Figure S21. (d) PL lifetimes of NCDs and PNCDs-m-n. (e) Plots of $(\alpha h \nu)^2$ vs. photon energy and (f) energy band information of NCDs and PNCDs-m-n.

The electrochemical reduction behavior of NCDs and PNCDs was further investigated in 0.1 M degassed PBS (pH=7.5) by cyclic voltammetry (CV) (Figure S21). As summarized in Figure 5c, upon increasing P dopants, the onset reduction potential gradually shifted positively from −0.48 V (for NCDs) to −0.37 V (for PNCDs-5-1), suggesting that PNCDs were more easily to
be reduced than NCDs, which was one of the most critical factors for promoting ECL reactions. The facile electrochemical reduction of PNCDs could be explained by the high electron-donating property, and large atom radius of the doped P atom.\textsuperscript{64-65} For additional insight into the influence of P doping on the transition processes of PNCDs, the fluorescence decay spectra of NCDs and PNCDs were measured (Figure S22). Notably, the lifetimes gradually decreased from 7.11 ns (for NCDs) to 5.67 ns (for PNCDs-5-1) with the increased P dopants (Figure 5d), reminiscent of an enhancement of radiative rate induced by the P doping,\textsuperscript{66} which matched well with the OCP and M-S results. Hence, introducing P dopants in PNCDs not only facilitated the electrochemical reduction but also promoted the photoelectrochemical processes of PNCDs, which explained well that the PNCDs with higher P dopants displayed higher ECL efficiency.

To reveal the energy band structures of PNCDs and NCDs, the UV-vis diffuse reflectance spectra (UV-vis DRS) and ultraviolet photoelectron spectroscopy (UPS) were measured. As shown in Figure 5e and Figure 5f, the band gap was achieved from the plots of $(\alpha h\nu)^2$ vs. photon energy (h\nu) via the transformed Kubelka–Munk function based on the UV-vis DRS analysis (Figure S23). The conduction band (CB) level of PNCDs and NCDs was further acquired based on corresponding band gap values and valence band (VB) levels from the UPS analysis (Figure S24). It was observed that the band gap became narrower gradually, and the CB level descended progressively with the increased P dopants (Figure 5f), demonstrating that the P doping narrowed the energy band gap, which was consistent with the red-shifted PL emission of PNCDs-m-n with higher P dopants.
Figure 6. (a) The simplified structural units of PNCDs-0, PNCDs-I, and PNCDs-II. (b) Hole-electron analysis and hole-electron composition fragment heat map of S1 state. Green regions denote the electron distribution and blue regions denote the hole distribution. (c) The calculated molecular orbitals and density of states of the PNCDs-0, PNCDs-I, and PNCDs-II. 1, 2, 3, 4, and 5 in (b) and (c) represent the corresponding molecular fragment marked in (a). (d) Proposed mechanism for the wavelength-tunable ECL and enhanced efficiency of carbon dots by P-doping.
To get more insight into the ECL mechanism of PNCDs and the effect of P-doping in molecular level, computational simulations were further undertaken. Three simplified structural units, a dimer of ATA for NCDs (denoted as PNCDs-0), and that of ATA with one P-containing group (designated as PNCDs-I) or two P-containing groups (defined as PNCDs-II), were proposed for NCDs and PNCDs-m-n according to above structural characterization results (Figure 6a and Figure S25). Density functional theory (DFT) calculations were carried out to assess the energy levels of the ground and excited states of these simplified structural units (Figure S26). A hole-electron composition fragments heat map was obtained from the hole-electron analysis in intrafragments (Figure 6b and Tables S3, S4). Compared with PNCDs-0, the PNCDs-I in the relaxed \( S_1 \) state displayed higher hole density in the P-containing groups and higher electron density in the aromatic rings. With increasing the number of P-containing groups (for PNCDs-II), such electron and hole density change became more evident, suggesting that the electron can flow from the P-containing groups to the aromatic ring due to the significant electron-donating effect of the P dopants. Consequently, the incorporation of P dopants led to ICT in the excited state, resulting in substantial spatial separation of electron and hole distribution, which promoted the ECL process.

To clarify the effect of P doping on the redshift of ECL emission, the total density of states (DOS) was also fitted by molecular orbitals, which revealed the contribution from different fragments (Figure 6c). The solid black line represents total DOS, the color lines correspond to the contribution from different fragments to DOS, and the black dash lines represent the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). In the undoped PNCDs-0 (without P doping), HOMO and LUMO are mainly composed of fragments 3 and 1, as indicated in Figure 6a. Compared with PNCDs-0, the energy level of LUMO in PNCDs-I decreased slightly, which may be caused by the increase of electron cloud density of the conjugated system ascribed to the P doping as discussed in the hole-electron analysis. It is worth noting that HOMO in PNCDs-I is mainly composed of the P-containing group (fragment 4). In contrast, fragment 1, which dominates HOMO in PNCDs-0, contributes mainly to HOMO-1 in PNCDs-I, and the energy level of HOMO-1 does not change significantly with respect to that of HOMO in PNCDs-0. Notably, the HOMO in PNCDs-I, i.e., the new orbital
introduced by fragment 4 can be regarded as a new energy level generated between HOMO and LUMO of undoped PNCDs-0, which reduced the HOMO-LUMO gap from 3.40 eV to 2.28 eV (Figure S26), and further reduced the transition energy and increased the emission wavelength of ECL. In PNCDs-II, the composition of HOMO and LUMO is similar to that of PNCDs-I, except that more P dopants further narrowed the HOMO-LUMO gap to 1.92 eV and increased the emission wavelength of ECL. Thus, the incorporation of P dopants with high electron-donating ability in PNCDs not only resulted in the significant ICT effect but also led to the formation of a new energy level, narrowing the HOMO-LUMO gap, which jointly boosted the ECL performance of PNCDs (Figure 6d). The newly generated orbital was ascribed to the surface functional groups introduced by P doping, which endowed the redshift of the ECL emission.

Conclusions

In summary, we reported the design and facile synthesis of CDs with multiwavelength ECL and enhanced efficiency through a facile P-doping route by taking advantage of the electron-donating properties of P dopants. Varying the concentration of P dopants would lead to changes in surface functional groups and surface states, allowing fine-tuning of the ECL wavelength from 425 nm to 645 nm, the widest range ever reported, along with a more than 5-fold enhancement of ECL efficiency. The kinetics studies illustrated that the enhanced ECL performance was ascribed to the P doping-induced decrease of surface deep electron-trapping state, which promoted the electron-hole separation, and enhanced the electron conductivity. Moreover, P doping regulated the energy band structures of PNCDs, e.g., the band gap was shrinking, and CB levels were progressively descended with the increased P dopants. The theoretical calculations based on a simple molecular model supported our results, which showed that the incorporation of P dopants with high electron-donating ability in CDs not only resulted in the formation of a new energy level, but also led to a significant ICT effect, which jointly boosted the ECL performance and induced the redshift of ECL emission of PNCDs. This work would provide a general and facile way to design highly efficient ECL systems with modulable emission wavelengths for various applications.
Supporting Information

Apparatus, ECL mechanism of PNCDs, TEM, XRD, Raman, XPS, UV-vis, PL, ECL, CV, UV-vis DRS, UPS characterizations of PNCDs-m-n, reaction conditions for the synthesis of PNCDs-m-n, theoretical calculation results.

Notes

The authors declare no conflict of interest.

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