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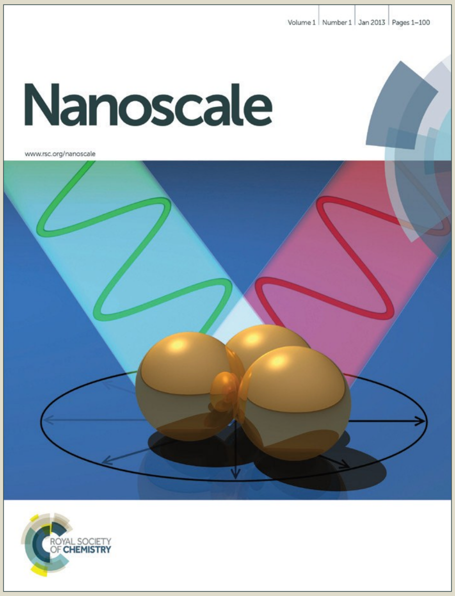

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One-pot and ultrafast synthesis of nitrogen and phosphorus co-doped carbon dots possessing bright dual wavelength fluorescence emission

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Very brief microwave heating of aniline, ethylene diamine, and phosphoric acid in water at ambient pressure generated nitrogen and phosphorus co-doped carbon dots (N,P-CDs) that exhibit bright dual blue (centred at 450 nm; 51% quantum yield) and green (centred at 510 nm, 38% quantum yield) fluorescence emission bands. The N,P-CDs were characterized using TEM, XRD, XPS, IR, UV-vis, and fluorescence spectroscopy, demonstrating their partially crystalline carbon, partially amorphous structures, and the incorporation of O, N, and P into the carbogenic scaffold. The N,P-CDs demonstrated excitation-dependent and nearly pH-independent emission properties. The unique dual emission properties lay the foundation for the use of N,P-CDs in ratiometric sensing applications.

Fluorescent carbon dots (CDs) and carbon nanoparticles have attracted much attention in chemical and biological sensing and bioimaging applications because of their excellent optical properties, biocompatibility, photo-stability, and ease of synthesis.[1-4] Carbon dots can be prepared by a number of methods but that all generally fall into two broad categories: top-down and bottom-up approaches.[5, 6] In top-down methods, the nanoparticles are formed by breaking down larger pieces of material into the desired nanostructures through arc discharge, laser ablation, chemical, or electrochemical oxidation. In bottom-up approaches, the CDs are obtained from assembling molecular precursors under a range of different reaction conditions, including solvo-thermal, and microwave-assisted conditions. Particularly the latter approach has become popular due to its simplicity, low-costs, and the ability to generate a variety of CDs in a single step.[7]

Most CDs emit in the blue range under ultraviolet excitation. Many efforts are underway to develop synthetic methods for CDs with emission in the green, yellow, or red. However, many syntheses reported are complex, involve toxic components, or the resulting CDs suffer from low emission quantum yields.[5, 7-11] The ability to freely tune the fluorescence emission of CDs has been considered as a key requirement for the broad application of CDs, but this tunability was achieved only rarely.[9] The emission of CDs could be adjusted by controlling the condensation reaction that generated the CDs, chemical manipulations, or most commonly by doping in of other elements.[6, 9, 12] Nitrogen (N) is by far the most prominent doping candidate but boron (B), and sulfur (S) and phosphorus (P) were also used in combination with nitrogen.[12-17] Excitation-dependent fluorescence emissions of single CD preparations were reported, but generally there is a significant decrease in the fluorescence intensity upon modulation of the excitation wavelength.[1, 2, 18] Thus, it is still difficult to synthesize bright CDs with different fluorescence emission wavelengths using a simple strategy.

We report here on a rapid and simple microwave-assisted method for the synthesis of N- and P-co-doped CDs (N,P-CDs). The N,P-CDs exhibit very bright dual (blue – 51% quantum yield/green – 38% quantum yield) emissions. We are not aware of a prior report using N and P as co-dopants for the synthesis of colour-tuned CDs or the description of bright dual fluorescence emissions in CDs. The dual emission properties lay the foundation for the use of N,P-CDs in ratiometric sensing or other applications that can take advantage of a material with dual wavelengths emission properties.

Thus, a homogenous aqueous solution of *m*-phenylenediamine (mPDA), *ortho*-phosphoric acid and ethylenediamine (EDA) in the stoichiometric ratio 1:3.2:1.6 was heated in a domestic 800 W microwave for 40 s. Upon cooling, mixture had solidified into a dark brown gel that could be dissolved/suspended by the addition of water. The supernatant following centrifugation contained the N,P-CDs. The homogeneous solution was stable at room temperature for months.

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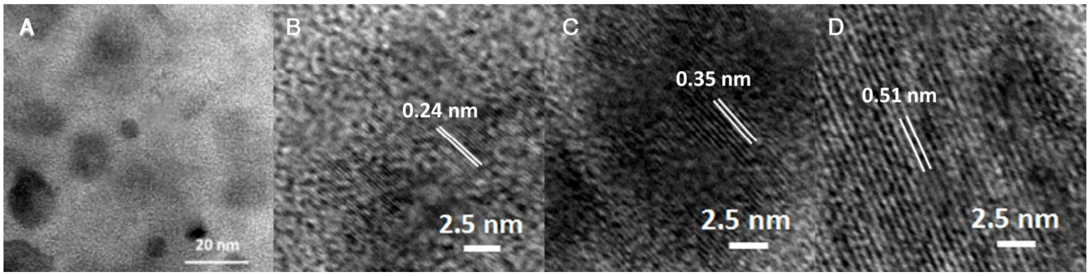

Fig. 1 (A) TEM graph of the N,P-CDs prepared; (B-D) HRTEM images and lattice structures of different N,P-CDs.

The transmission electron microscopy (TEM) image (Fig. 1A) shows the size and morphology of the as-prepared N,P-CDs. Due to the presence of carbon in the TEM grid, the particles have very low contrast, especially for completely amorphous CDs. Nonetheless, the diameters of the N,P-CDs could be determined to average 8.1±2.7 nm, with some particles larger than 15 nm. High-resolution TEM (HRTEM) images (Fig. 1B-D) suggest that multiple types of particles are present and that single N,P-CDs may also possess domains of different structures. Some nanoparticles are amorphous while some show crystallinity, with lattice spacings of 0.24 nm, 0.35 nm, and 0.51 nm, corresponding well to the spacing of the planes of carbon materials, respectively. Powder XRD spectra of the N,P-CDs confirmed the d-spacing obtained by HRTEM (see Fig. S1 in ESI).

Elemental composition and speciation within the N,P-CDs were determined by XPS. The XPS survey spectrum (Fig. 2A) indicates that the N,P-CDs are composed of carbon (66.6%), oxygen (27.8%), nitrogen (3.3%) and phosphorus (2.3%), i.e. suggestive of the incorporation of all reagents into the particles. The O1*s* XPS spectrum (Fig. 2B) could be de-convoluted into four peaks, at 529.9 eV (C=O), 531.2 eV and 532.4 eV (P=O or N,N-P=O), and 533.8 eV (H_2O).[19, 20] The N1s spectrum (Fig. 2C) reveals the presence of tertiary amines of the type X_3-N (403.3 eV, X = C, N, or P), X_2-N (pyridinic- and pyrrolic N, 400.7 eV, X=C, N or P) and N-H (398.5 eV) groups, respectively.[20]

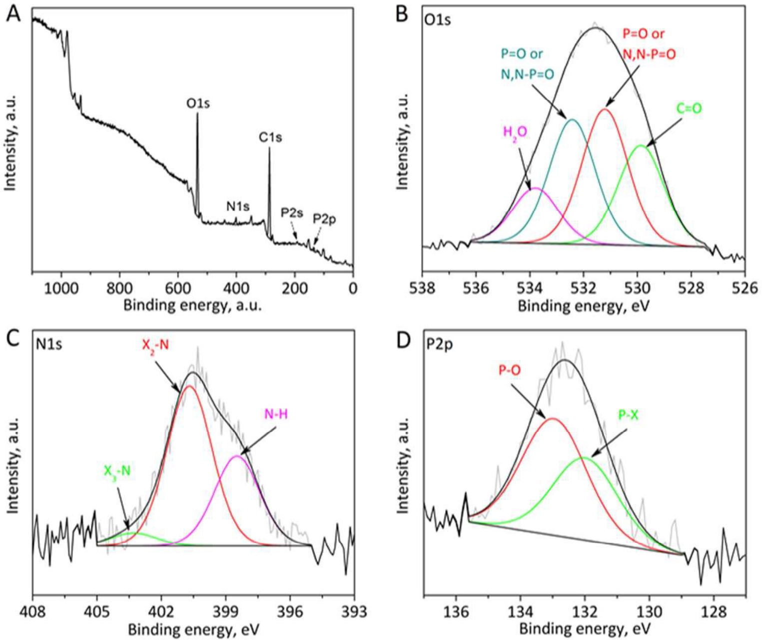

Fig. 2 XPS spectra of N,P-CDs. (A) XPS survey spectrum. High resolution XPS spectra of the O1*s* (B) N1*s* (C), and P2p (D) lines, in grey, including their fitted peaks.

The P2p XPS spectrum (Fig. 2D) shows two peaks at 132.1 eV and 133.2 eV, which can be assigned to P-$X_{aromatic}$ (X=C or N) and P-O groups.[21] Furthermore, FTIR was used to characterize the carbon dots (see Fig. S2 in ESI), further corroborating the functional group identifications by XPS. The XPS and IR spectra suggest the successful incorporation of nitrogen and phosphorus into the carbon material with diagnostic signals present to identify some of the functional groups present. Thus, we hypothesize that mPDA, EDA, and H_3PO_4 condensed and partially carbonized under the strongly acidic, likely dehydrating, and oxidizing conditions (oxygen was not excluded during the synthesis), likely forming multiple chromophore types. The optical spectra of the N,P-CDs do not suggest the presence of polyaniline-like structures, though the presence of phenyl-NR-phenyl building blocks cannot be excluded.[22] The fluorescence properties of a number of aryl-substituted phosphazenes of different ring sizes were reported (for the optical properties of the N,P-CDs, see also below).[23, 24] Thus, the presence of phosphazene-like structures is not unlikely. Additionally, ammonium phosphate functionalities could provide the excellent water-solubility of the N,P-CDs.[25]

The UV-vis absorption spectrum of a diluted sample of N,P-CDs in water (Fig. 3) exhibits an intense absorption band centred at 288 nm, attributed to π-π* transitions of C=C, C=N, or N=P groups. Although at much lower intensities, two more bands centred at 355 and 444 nm are also observed (inset of Fig. 3), indicative of extended conjugation (aromatic) structures.[26, 27]

The excitation spectra of the N,P-CDs are shown in Fig. 4, clearly demonstrating the presence of a minor and (at least) two major chromophores, with emission maxima at 340, 450 and 510 nm, respectively. The excitation wavelength-dependent emission spectra of the N,P-CDs at the excitation wavelengths from 290 to 500 nm are shown in Fig. 5A. At excitation wavelengths of under 300 nm, all three types of chromophores get excited. With an increase of the excitation wavelengths (to 320-370 nm), only one blue emission peak (centred at ~450 nm) is observed. Further increasing the excitation wavelengths (380, 390 nm) excites both a blue and green emission; while at even higher excitation wavelengths (400-470 nm), only the green emission peak (centred at about 510 nm) is observed. Above 480 nm, no fluorescence emission is recorded.

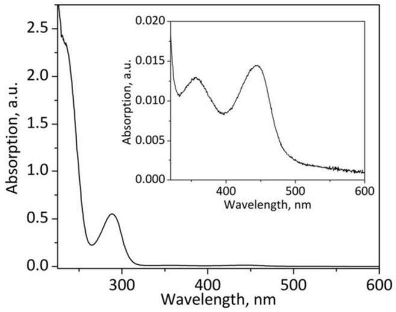

Fig. 3 UV-vis absorption of a dilute sample of N,P-CDs in water; subset shows the UV-vis absorption spectrum in the range of 320-600 nm.

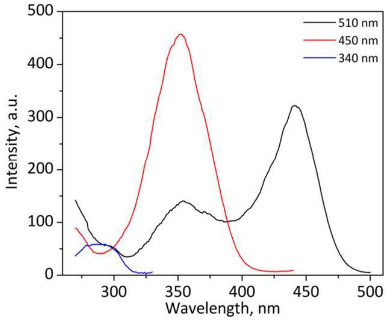

Fig. 4 Excitation spectra of N,P-CDs using the emission wavelengths indicated.

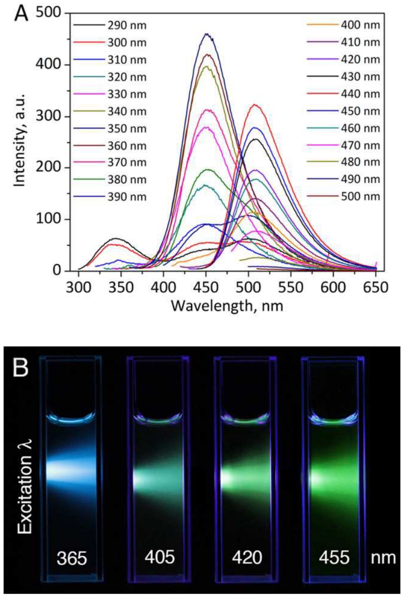

Fig. 5 (A) Emission spectra (in water) of N,P-CDs at the various excitation wavelengths indicated. (B) Photographs of diluted N,P-CDs solutions (in water; quartz cuvettes) excited with fibre-optics-coupled LEDs of the wavelengths indicated, showing their excitation dependent emission properties.

The dual fluorescence emission of the N,P-CDs in the visible region of the spectrum is also clearly visible to the naked eye (Fig. 5B). Fibre-optics-coupled LEDs of the wavelengths indicated elicited differently coloured emissions (blue, cyan, muted green, and grass-green).

To our delight, the emitters are very bright, and the quantum yield of the two main emission bands is very high. The strongest green fluorescence emission centred at 510 nm ($\lambda_{excitation}$ = 440 nm) possesses a high quantum yield of 0.38, while the strongest blue fluorescence emission band at 450 nm ($\lambda_{excitation}$ = 350 nm) has a quantum yield of 0.51. Thus, the quantum yields of the N,P-CDs are higher than those of most previously reported CDs, and the highest for green CD emitters.[5, 8-11, 26, 28, 29]

The N,P-CDs possess robust emissions that are only modulated to a minor degree (by about 30% at the extremes) by very high or low pH values. The halochromic responses of the emissions of the N,P-CDs at two wavelength in the range between pH 2 and 12 are shown in Fig. 6. The absence of a very strong halochromic response is surprising in light of the fact that most previously reported CDs exhibit pH-dependent emission properties.[1, 2] In case of the N,P-CDs it may indicate the absence of (many) amine-type nitrogens. On the other hand, the phosphoramide-type nitrogens proposed to be present in the N,P-CDs are expected to be much less pH-sensitive, thus the pH-insensitivity provides another evidence for the presence of this functionality.

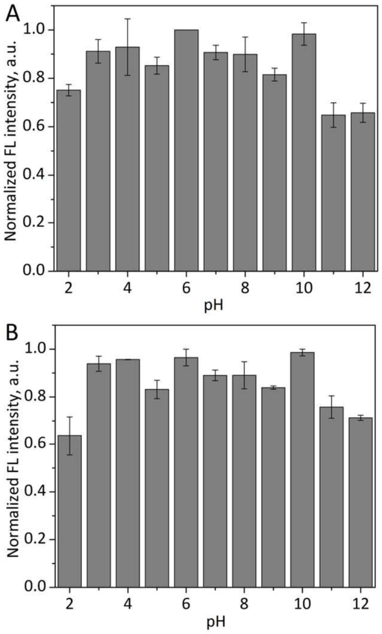

Fig. 6 Normalized fluorescent intensity of the N,P-CDs in the pH range indicated (in buffers of the pH values indicated). (A) Fluorescent intensities at 450 nm ($\lambda_{excitation}$ = 350 nm) and (B) at 510 nm ($\lambda_{excitation}$ = 440 nm).

Nitrogen is the most common dopant for fluorescent CDs.[3, 6] Co-doping a second heteratom into N-doped carbon nanomaterials can modulate the electronic properties, tune the carbonaceous structure, polarizability, and affect the catalytic activity.[25, 30, 31] Phosphorus-doping was introduced for the synthesis of almost all previously reported green fluorescent CDs.[8-11, 26, 28] Theoretical studies have predicted that defects induced by P doping or P,N co-doping can lead to the presence of a highly localized state close to the Fermi level.[30, 32] Possibly co-doping of nitrogen and phosphorus affects the degree of polymerization and graphitization. A higher graphitization degree induces a red-shift of fluorescence, resulting from the enhanced degree of π-conjugation and the decreased band gaps.[8, 33] Other researchers proposed that formation of p-n type photochemical diodes through nitrogen and phosphorus co-doping into carbon dots increased quantum yield greatly.[34] We also believe that the co-doping of nitrogen and phosphorus into the N,P-CDs gives rise to their bright dual emission, but the exact structures and emission mechanisms of the N,P-CDs remain elusive. We are currently studying the molecular origin of the emission and the possible interplay between the carbogenic core and the surface/molecule states.[29]

In conclusion, we synthesized nitrogen and phosphorus co-doped CDs. A facile, one-pot and very rapid microwave-assisted process was used to condense mPDA, phosphoric acid, and EDA in aqueous solution. The N,P-CDs found in the preparation show dual (blue and green) fluorescence emission under different excitation wavelengths, with very high quantum yields, that are relatively insensitive to changing pH values. Their ease of synthesis using inexpensive materials lends itself to scale-up. The unique emission properties are attributed to the synergistic effect of co-doping of nitrogen and phosphorus into the carbogenic material.

The work presented provides basic insights into the development of bright fluorescent carbon dots with varying emission wavelength. In addition, the N,P-CDs prepared could be utilized in a broad range of illumination, sensing and imaging applications, as well as energy storage applications[35]. Particularly their dual wavelength emission could find use in the ratiometric or multiplexed chemosensing applications, such as selective detection and differentiation of nitro-explosives (TNT and picric acid) and the corresponding results and discussion have been presented in Supplementary Materials (Fig. S3). More other applications are also currently under pursuing in our group.

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