

Electrochemically Generated Highly Fluorescent Boron-Doped Graphene Quantum Dots for Fluorescent Crystal, Sensors and Bioimaging

Louzhen Fan*, Zetan Fan

Department of Chemistry, Beijing Normal University,
Beijing, 100875, China
E-mail: lzf@bnu.edu.cn

Graphene is a zero-bandgap semiconductor, no optical luminescence is observed in pristine graphene. A bandgap, however, can be engineered into graphene quantum dots (GQDs) due to quantum confinement and edge effects. As a result, luminescent GQDs have attracted great attention as one of highly promising nanomaterials due to their exceptional advantages of low cytotoxicity, excellent solubility, stable photoluminescence (PL), fine biocompatibility as well as low-cost.^[1] Above these fascinating merits in GQDs distinguish themselves from traditional fluorescent materials, making them perfect alternatives for numerous exciting applications: bioimaging,^[2] fluorescence sensors,^[3] fuel cells,^[4] photovoltaic devices.^[5]

Doping carbon materials with heteroatoms can effectively tune their intrinsic properties, thus producing new phenomena and unexpected characteristics. Although various heteroatom-doped carbon materials have been reported, doped GQDs have been much less studied. Herein, we report a facile one-pot electrochemical approach for the synthesis of boron(B) doped GQDs (B-GQDs) with B content of 5.24 at %, in which only borax was used as the electrolyte without any other chemical additives. The as obtained water-soluble B-GQDs feature intriguing tunable fluorescence, act as a Al^{3+} fluorescent sensor, cellular imaging and electrocatalysts for the oxygen reduction reaction. With the existence of borax, they show strong green luminescence with a quantum yield as high as 13%. Significantly, green fluorescent crystals were obtained from evaporating the aqueous solution in the presence of borax at room temperature.

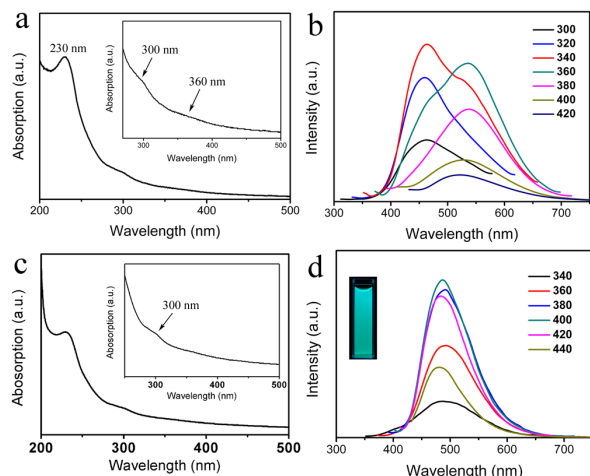


Figure 1. UV-vis absorption spectra of the B-GQDs aqueous solution (a) in the absence of borax and (c) in the presence of borax. PL spectra of the B-GQDs aqueous solution (b) in the absence of borax and (d) in the presence of borax at different excitation wavelengths. The inset in (d) is a photograph of the solution under 365 nm UV irradiation.

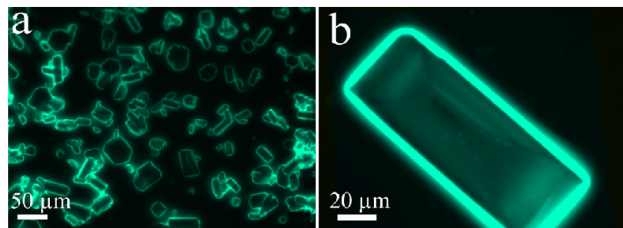


Figure 2. (a, b) Fluorescence microscopy images of crystals at the excitation wavelength of 405 nm.

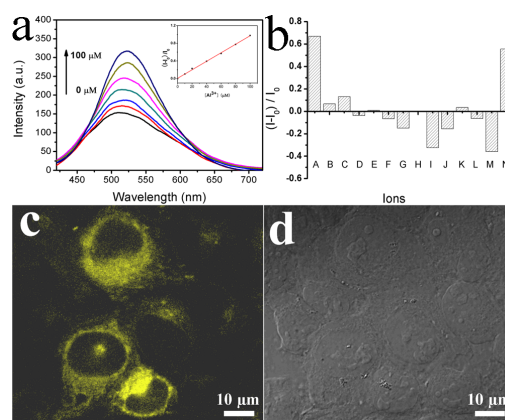


Figure 3. (a) PL emission spectra of B-GQDs aqueous solution upon addition of Al^{3+} at 405 nm excitation. The Al^{3+} concentrations are 0, 10, 20, 40, 60, 80, 100 μM , from bottom to top. (b) Maximum fluorescent response of B-GQDs upon addition of different metal ions (100 μM) listed from left to right: (A) Al^{3+} , (B) Ag^+ , (C) Na^+ , (D) K^+ , (E) Mg^{2+} , (F) Ca^{2+} , (G) Ba^{2+} , (H) Cd^{2+} , (I) Pb^{2+} , (J) Fe^{2+} , (K) Zn^{2+} , (L) Fe^{3+} , (M) Cr^{3+} , (N) $\text{Al}^{3+} + \text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{Ba}^{2+} + \text{Fe}^{3+}$. The relationship between $(I-I_0)/I_0$ and Al^{3+} from 0 to 100 μM . I and I_0 are the PL intensities of B-GQDs at 400 nm excitation in the presence and absence of Al^{3+} , respectively. (c) Confocal fluorescence microscopy images of A549 with the fluorescent B-GQDs incorporated at the excitation wavelength of 405 nm and corresponding image under bright field (d).

Acknowledgements

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