

Research Article

Tuning the Photoluminescence of Graphene Quantum Dots by Fluorination

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Received 18 May 2017; Revised 13 August 2017; Accepted 14 September 2017; Published 7 November 2017

Academic Editor: Liyi Li

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Fluorinated graphene quantum dots (F-GQDs) were prepared by mixing GQDs and XeF_2 in a facile gaseous phase heating method. The F-GQDs with excellent water solubility have a F/C atomic ratio of 84.25% and a diameter of 2–6 nm. The photoluminescence (PL) properties of GQDs and F-GQDs were investigated systematically. The results showed that the PL emission of the F-GQDs exhibited an obvious blue-shift of 90 nm compared to that of the GQDs.

1. Introduction

Graphene quantum dots (GQDs) have been paid attention due to their robust chemical inertness, good biocompatibility, low toxicity, and strong photoluminescence (PL) [1–5]. The modulation of the band gap of GQDs by various means has attracted great interest for potential applications. The band gap properties of GQDs are caused by quantum confinement effects [6–8]. In general, the band gap or the PL emission of GQDs can be modulated by their size and chemical functionalization. Chemical functionalization by doping foreign atoms, such as nitrogen [9], chlorine [10], and sulfur [11], is the main method for tuning the band gap of GQDs. Fluorine has been used to tune the electronic and optical properties of graphene due to its high electronegativity [12–16]. Theoretical calculations also demonstrated that the band gap of graphene can be changed from 0 to 3.13 eV by increasing the fluorination degree, leading to a tunable optical property [17]. However, little work has been made to tune the band gap of GQDs by fluorination [18, 19]. In practice, PL emission of these F-GQDs showed a relatively small shift (usually less than 30 nm) compared to that of the GQDs. Accordingly, it is expected that the PL emission of GQDs can exhibit a large shift by fluorination.

Various methods have been realized in preparation of Fluorinated GQDs (F-GQDs), such as hydrothermal cutting

routes [18] and microwave-assisted technique [19]. Nevertheless, these methods are unsatisfactory due to low yields. Therefore, it is important for both experimental studies and potentially valuable applications to develop a high-yield method for preparation of F-GQDs.

Herein, we synthesize the high-yield F-GQDs by mixing GQDs and XeF_2 through a gaseous phase heating route. The obtained F-GQDs with excellent water solubility have a F/C atomic ratio of 84.25% and diameter of 2–6 nm. The PL properties of the GQDs and F-GQDs were investigated. The PL emission of the F-GQDs exhibited a clear blue-shift of 90 nm compared to that of the GQDs.

2. Methods

GQDs were prepared in large scale through a bottom-up method as reported elsewhere [20]. F-GQDs were synthesized by mixing GQDs and XeF_2 via a gaseous phase heating route. Fluorine atoms of XeF_2 replaced the hydroxyl group on the surface of GQDs during the gaseous phase heating reaction. A mixture of prepared GQDs (50 mg) and XeF_2 (250 mg) was first mixed carefully and transferred to a Teflon-lined stainless autoclave under an Ar atmosphere. The mixture was then heated to 180°C, which was maintained for 12 h. After cooling to room temperature, the obtained F-GQDs were dried at 70°C for 12 h under a vacuum to eliminate excess XeF_2 .

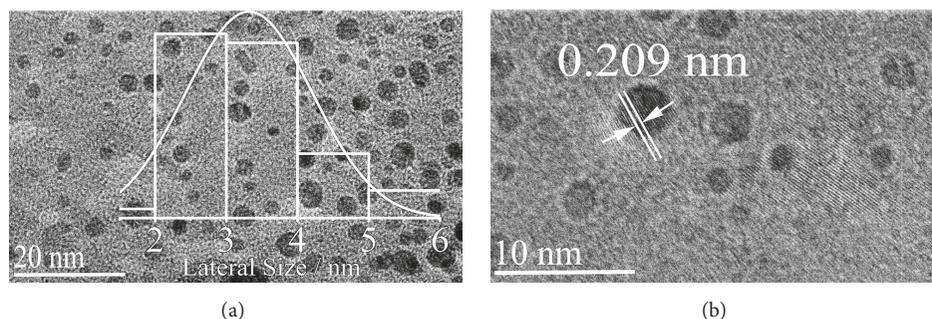


FIGURE 1: (a) TEM image (inset: diameter distribution) of F-GQDs. (b) HRTEM image of F-GQDs.

3. Characterization

The morphologies of the F-GQDs were characterized by transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB using an Al K α radiation. Ultraviolet-visible spectroscopy was characterized with an UV/VIS/NIR spectrometer. The PL spectra and fluorescence emission spectra were recorded using a fluorescence spectrophotometer. All measurements were performed at room temperature.

4. Results and Discussion

Figure 1(a) shows the TEM images of the synthesized F-GQDs. The F-GQDs clearly exhibit a distribution of 2–6 nm (inset of Figure 1(a)) and are obviously smaller than GQDs prepared with a distribution of 2–10 nm (Figure S1, in Supplementary Material, available online at <https://doi.org/10.1155/2017/9682846>), similar to a previous report [17]. This may result from further decomposition during the gaseous phase heating treatment. The high-resolution TEM (HRTEM) images (Figures 1(b) and S2) indicate the high crystallinity of both GQDs and F-GQDs with a lattice of 0.209 nm, which is consistent with the (102) diffraction plane of sp² graphitic carbon [21, 22].

The XPS measurements affirm the composition of GQDs and F-GQDs. As shown in Figure 2(a), there are peaks at 284 eV (C 1s), 400 eV (N 1s), and 533 eV (O 1s), which are present in both GQDs and F-GQDs, as well as a weak signal from Na impurity. Notably, a peak at 686 eV (F 1s) can only be observed in the XPS spectra of F-GQDs. It is obvious that the F atom from XeF₂ has been doped into the GQDs. The atomic analyses resulting from XPS measurements are exhibited in Table S1. The unavoidable emergence of O and N in GQDs comes from the nitration process of pyrene. The C, F, and O contents of F-GQDs are 41.26%, 34.76%, and 20.82%, respectively. The F/C atomic ratio was calculated to be 84.25%. To get information on the incorporation of C, N, and F, fine-scanned XPS spectra were performed. The C 1s spectra of GQDs and F-GQDs (Figures 2(b) and 2(c)) were fine-scanned into several components.

The intense peaks at 284.6 eV, 285.6 eV, 286.2 eV, and 288.1 eV, which are due to the graphitic C=C, C–N bonding, C–O bonding, and C=O bonding, respectively, can be

observed in the C 1s spectrum of both GQDs and F-GQDs. By contrast, some new peaks appear in the C 1s XPS spectra of F-GQDs. This analysis also demonstrates the presence of oxygen-rich functional groups that provide F-GQDs with excellent water solubility for practical applications. Combined with the clear fluorine peak at 686 eV, the intense peak at 287.1 eV confirms the existence of C–F covalent bonding in F-GQDs [23]. Figure 2(d) reveals two kinds of bonding in the F 1s spectra, 685.9 eV owing to the semi-ionic C–F bonding and 688.6 eV is due to a covalent C–F bonding pattern [24]. Obviously, F is in the form of functional groups within the F-GQDs, not in the form of elemental crystal physically adsorbed or wrapped within them.

The UV-vis absorption spectra of the GQDs and F-GQDs can be seen in Figure 3(a). Aqueous solutions of GQDs and F-GQDs reveal black and achromatic colors, respectively, under sunlight [25]; Figure 3(a) (inset) shows that GQDs and F-GQDs emit bright yellow and green photoluminescence under irradiation by a 365 nm UV lamp, respectively. The GQDs have a weak absorption at 342 nm, which is close to previous reports [26], and a strong broad absorption at 480 nm, which is in the visible light range. F-GQDs have a typical absorption peak at 337 nm corresponding to the $n \rightarrow \pi^*$ transition of the C=O bond. The excitation wavelength dependence of the emission wavelength and intensity is normal in carbon-based fluorescent materials. This behavior is caused by the distribution of particles of different emissive sites on each nanoparticle.

Notably, the difference of UV-vis spectra between GQDs and F-GQDs confirms that fluorination causes an obvious absorption shift toward short wavelengths. To explore the optical properties of the F-GQDs, a detailed PL study was carried out by using different excitation wavelengths. As shown in Figure 3(b), it is found that (i) the PL peak shifts to longer wavelength as the excitation wavelength is increased from 310 to 390 nm and (ii) on excitation at 324 nm, the maximum PL intensity of F-GQDs appears at 450 nm with a Stokes shift of 126 nm (1.07 eV). Interestingly, one can find that, compared to GQDs, the maximum PL peak of the F-GQDs shows a blue-shift of 90 nm in the PL emission spectrum (Figure 3(c)). This indicates that the PL blue-shift may result from the relatively strong electron affinity of F atoms in the F-GQDs. Furthermore, the PL excitation (PLE)

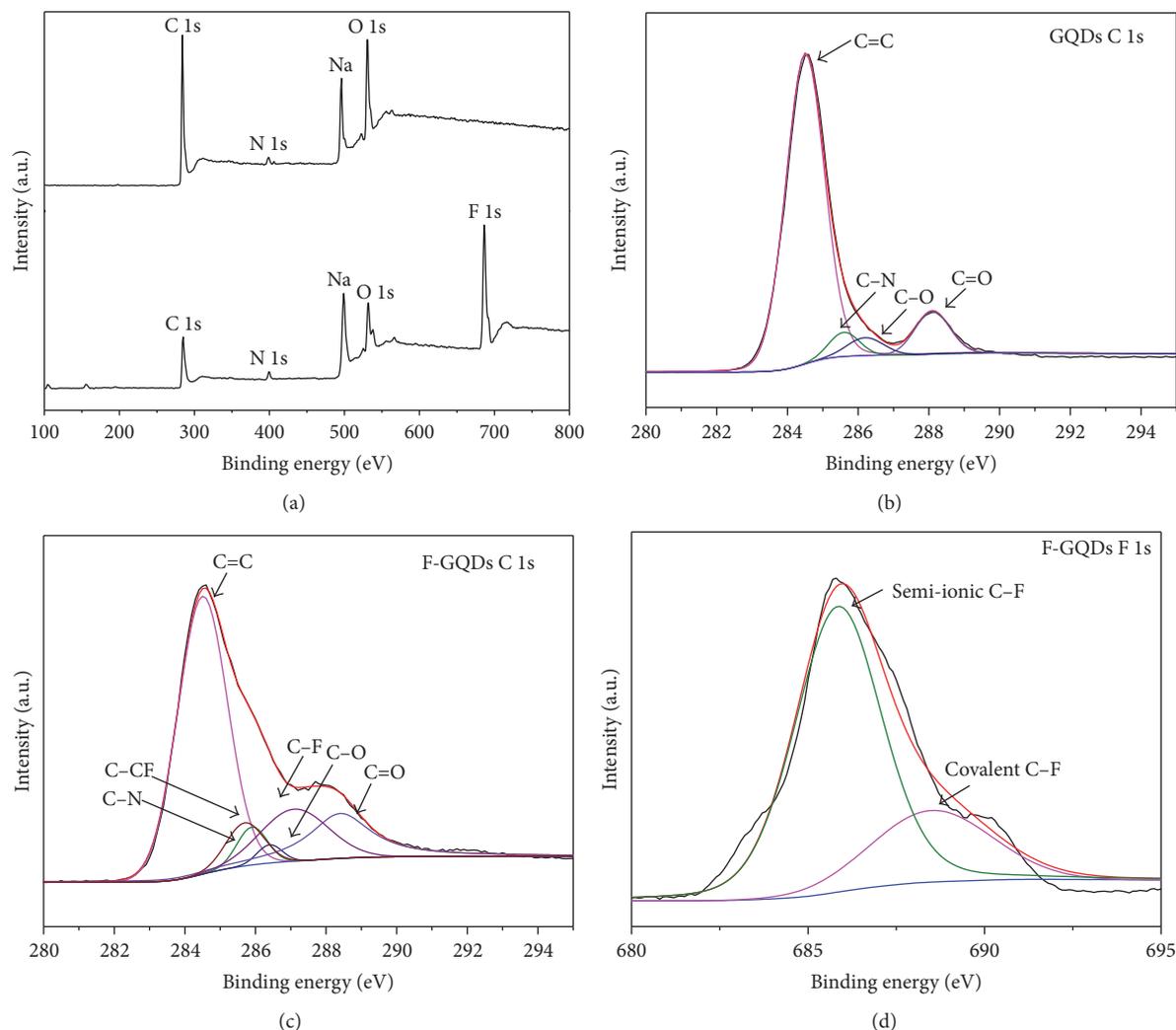


FIGURE 2: (a) XPS full spectra of GQDs and F-GQDs. High-resolution C 1s spectra of (b) GQDs and (c) F-GQDs. (d) High-resolution F 1s XPS spectrum of F-GQDs.

spectrum recorded with the strongest luminescence shows two sharp peaks at 247 nm and 324 nm (Figure 3(d)). It indicates that the luminescence of the F-GQDs is correlated with the two transitions of 247 nm (5.03 eV) and 324 nm (3.83 eV), which can be regarded as transitions from the σ and π orbitals of sp^2 triple carbenes (HOMO) to LUMO (Figure 3(e)). In addition, the quantum yield of F-GQDs is 5.2%, using quinine sulfate as a reference (shown in Table S2).

To explain the above phenomena, an energy level structure model was established to study the PL properties of the F-GQDs. A schematic illustration of the typical electronic transition processes of F-GQDs is shown in Figure 3(f). The PL spectrum can be regarded as a transition from LUMO to HOMO. That is, when the electrons of the σ orbital are excited, the σ electrons transition to the LUMO, and then the electrons go back to a low-energy state [27]. As is known, this is caused by the carbene ground-state multiplicity to

the energy levels of σ and π orbitals, which is related to the energy difference (δE) between the σ and π orbitals [28]. The δE should be below 1.5 eV, as proposed by Hoffmann [29]. Notably, the δE in the PL process of F-GQDs is 1.2 eV. Theoretical calculations indicate that the band gap widens with increasing F coverage, which is due to interaction of the p orbitals of F with the π orbitals of C producing sp^3 bonds that modify the charge densities. As a consequence, the F-GQDs show a blue-shift in the position of the PL peak with respect to that of GQDs.

In summary, we synthesized high-yield F-GQDs by mixing GQDs and XeF_2 through a facile gaseous phase heating approach. The F-GQDs have a F/C atomic ratio of 84.25% and a diameter of 2–6 nm. The PL emission of the F-GQDs exhibits an obvious blue-shift of 90 nm compared to that of the GQDs. This suggests that the adsorption of fluorine on the GQDs is a promising approach to modify the properties

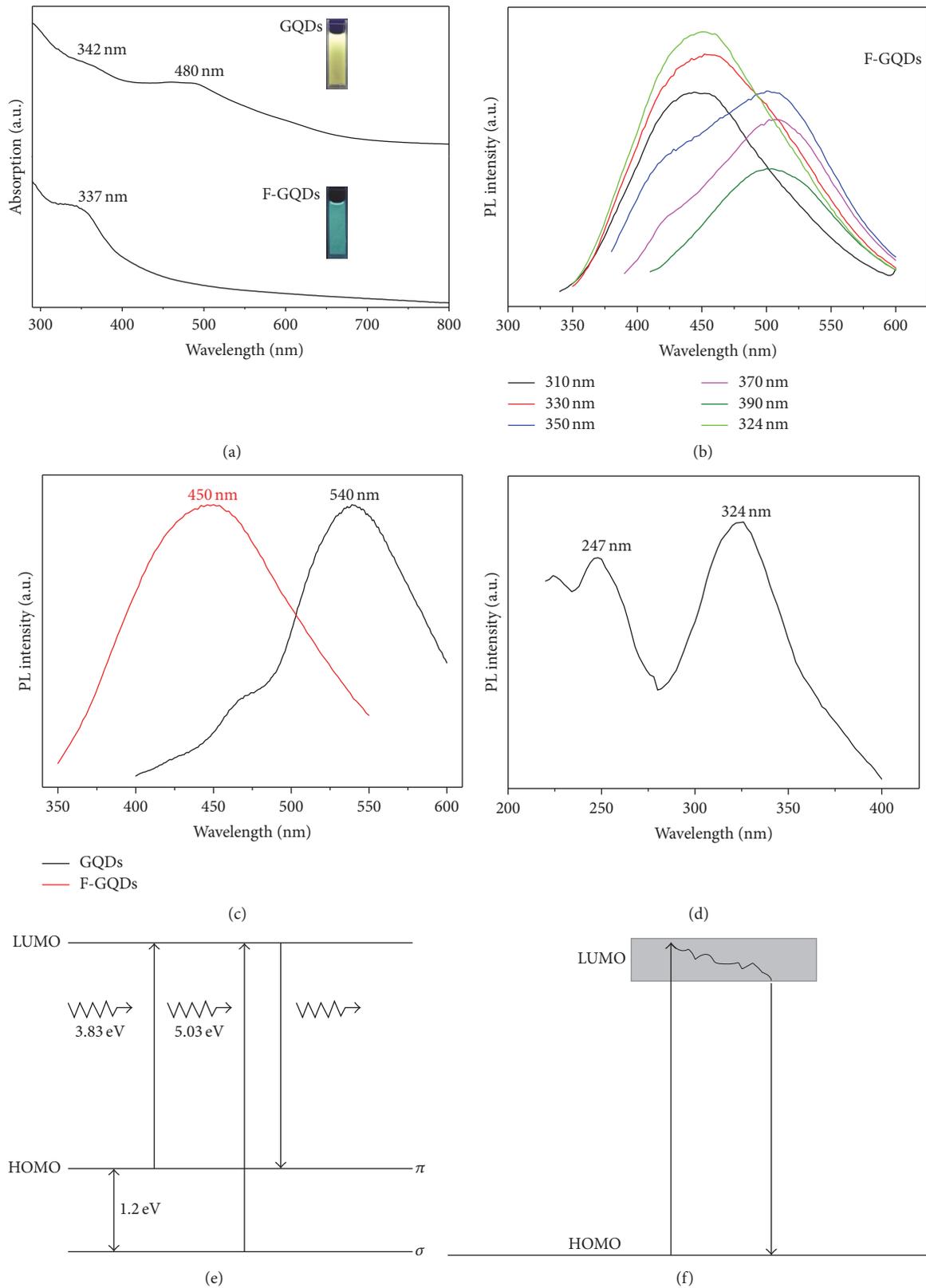


FIGURE 3: (a) The UV-vis absorption spectra of the GQDs and F-GQDs dispersed in water, and the insets are the optical photographs of the corresponding samples under the excitation with the wavelength of 360 nm. (b) The PL spectra of F-GQDs under excitation with different wavelengths. (c) The comparison of PL spectra of GQDs with F-GQDs under the irradiation with the wavelength of 324 nm. (d) The PLE spectrum of F-GQDs when fixing the emission wavelength at 450 nm. (e) The typical electronic transitions of triple carbene in the optical spectrum of the F-GQDs. (f) The schematic illustration of the typical electronic transitions processes of F-GQDs.

of GQDs, which would lead to more flexible electrooptical applications of graphene-based materials in the future.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Yi Luo and Yongjie Xu contributed equally to this work.

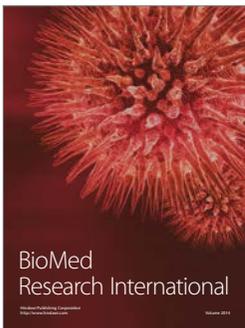
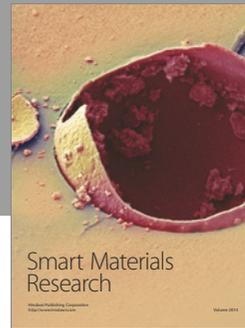
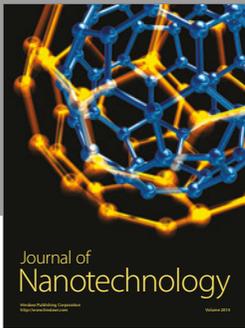
Acknowledgments

This work was financially supported by NSFC (nos. 11364010, 11764011, and 51662004) and Natural Science Foundation of Guangxi Province, China (nos. 2016 GXNSFAA380008 and 2015GXNSFBA139002).

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