Synthesis of Fluorescent Fluorinated Graphene Quantum Dots by Plasma Treatment

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1. Introduction

Graphene quantum dots (GQDs), which are nanosized graphene particle with size less than 30 nm, have attracted to researchers due to their unique properties, such as high dispersibility in water, low toxicity and tunable photoluminescence (PL) [1]. Thus, GQDs have high potential applications in bioimaging, biosensing, drugy delivery and photocatalysis [1]. Especially, when specific elements are doped on GQDs, it can adjust the electrical and chemical properties of GQDs and allows to various application, thus a variety of synthesis of N- and F-doped GQDs were presented. Fluorinated GQDs (F-GQDs) have a wide energy gap strong PL. Therefore, F-GQDs possess high potential to use in electrical fields for semiconductor and bioimaging fields. Various methods to synthesize the F-GQDs are developed including ionic-liquid exfoliation, solvothermal fluorination and photochemical fluorination [2]. However, these conventional methods require the complicated synthesis process and use of harmful chemicals; these can increase the impurity of F-GQDs.

Here, we presented a simple method to fabricate the fluorescent F-GQDs dispersed in water by plasma fluorination of GQDs on silicon carbide (SiC) and sonication process. In our previous study, we synthesized the F-GQDs on SiC plate by employing hydrogen-assisted pyrolysis of SiC followed by plasma fluorination of GQDs [3]. Surface fluorination attaches the functional groups including F and O atoms on the surface of GQDs and these functional groups improve the dispersibility of GQDs in water. Therefore, in this research, we detached the F-GQDs from SiC plate by sonication process to disperse the F-GQDs in water.

Plasma fluorination use a reactive ion etching (RIE)process. During plasma fluorination, fluorine plasma are generated and reactive F radicals are absorbed onto target materials while etching the surface of materials. This process doesn’t required the harmful chemicals and complicated process. Surface structure of target materials are altered by the experimental condition such as RF power and etching time. Following these advantages, several researches to fabricate the fluorinated graphene by plasma fluorination are reported [4].

CF₄ gas are treated to source of fluorine plasma. CF₄ gas is used in graphene production through palasma fluorination [4] and this gas is widely used in RIE process to etch the surface of semiconductor. After synthesis and plasma treatment, F-GQDs show the blue light emission under UV lights. Chemical properties of F-GQDs were analyzed by X-ray photoelectron spectroscopy (XPS).

2. Methods

2.1 High-quality GQDs preparation

GQDs on SiC plate are fabricated by hydrogen-assisted pyrolysis of SiC. 4H N-doped SiC plates with cut off-axis angle of 4° relative to the (0001) basal plane was purchased from TankeBlue Co., Ltd. (Beijing, China). Washed SiC plates with ethanol and acetone were placed in center of alumina furnace and internal pressure of furnace was kept to 80 mTorr by mixed gas comprising argon (96 at.%) and hydrogen (4 at.%). SiC plates were annealed to 1500°C that was maintained for 30 min.

2.2 Plasma fluorination on GQDs

Plasma fluorination on GQDs were performed by RIE process. GQDs were placed in PE-RIE system (AllForSystem, Korea), (Fig.1) and internal pressure was kept to vacuum by rotary pump subsequently CF₄ gas was injected to the device with flow rate of 10 sccm and pressure was maintained to 150 mTorr. Then, radio frequency was operated to generate a fluorine plasma from CF₄ gas and produced plasma etched the surface of GQDs on SiC plate for 10 min to fabricate the F-GQDs. Radio frequency power was kept to 20 W. After RIE process, injection of CF₄ gas was stopped and F-GQDs were put off from the device. F-GQDs formed on the SiC plates were detached from the SiC surface through sonication at 80 kHz in 3 mL of ethanol for 3 min. The separated F-GQDs were centrifuged with 10,000 MWCO micro-filters to remove large graphene particles. Ethanol in F-GQDs ethanol dispersion was vaporized. Then dried F-GQDs were dispersed in deionized water by sonication for 2 min.

2.3 Characterization of F-GQDs

Chemical structure of F-GQDs was characterized by XPS using monochromatic X-ray source (K-alpha, Thermo VG Scientific, MA, USA). The UV-vis absorption spectra of F-GQDs were analyzed with a UV-Vis spectrophotometer (Lambda 1050, Perkin
Elmer, USA) at room temperature. PL spectra of F-GQDs were obtained using a fluorimeter (QM-400, HORIBA, Japan) equipped with a xenon lamp.

Fig. 1. Reactive ion etching device

3. Results and discussion

3.1 Chemical analysis of F-GQDs

Chemical structure of F-GQDs detached from SiC plate was measured by XPS spectra. Drastic change of atomic ratio of F-GQDs are shown in Table 1. In the XPS spectra of GQDs on SiC after annealing process, C, O and Si atoms are appeared and F atoms are not detected. However, when GQDs were etched by fluorine plasma for 10 min, F atomic ratio significantly increased to 34.78%, respectively. It means that F radicals in plasma are absorbed to surface of GQDs.

Table I: Atomic ratio of GQDs and F-GQDs on SiC and F-GQDs after sonication process.

<table>
<thead>
<tr>
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<th>0 min (on SiC)</th>
<th>10 min</th>
<th>After detachment</th>
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<tr>
<td>F</td>
<td>0</td>
<td>34.78</td>
<td>3.5</td>
</tr>
<tr>
<td>C</td>
<td>76.25</td>
<td>39.19</td>
<td>76.54</td>
</tr>
<tr>
<td>O</td>
<td>14.06</td>
<td>13.47</td>
<td>19.96</td>
</tr>
<tr>
<td>Si</td>
<td>9.69</td>
<td>12.56</td>
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After sonication process, the atomic ratio of dried F-GQDs were changed; F atomic ratio was decreased to 3.5%. Furthermore, atomic ratio of oxygen and carbon increased and Si was not observed. Binding energy of C-F bonds are not strong, thus this bond was destroyed during sonication process. This result means that F-GQDs without Si atoms are separated from SiC plate.

3.2 Optical properties of F-GQDs

Optical properties of F-GQDs were obtained by UV absorption spectrum and PL emission spectra. UV absorption spectrum of F-GQDs (Fig. 2) exhibits high absorbance of UV to 300 nm, resulting from $\pi-\pi^*$ transition of aromatic C = C bonds. Moreover, F-GQDs show an absorption band at 325 nm, which can be attributed to $\pi-\pi^*$ transition, indicating that functional groups including O and F atoms are passivated on the surfaces of F-GQDs.

Fig. 2. UV-vis absorption spectrum of F-GQDs

PL emission spectra of F-GQDs excited at various wavelengths from 250 nm to 375 nm is shown in Fig. 3. The F-GQDs dispersed in water show the strong UV/blue light emission and excitation wavelength-independent PL behavior; the positions of the PL peaks are not altered by excitation wavelength. The PL emission peaks were observed at 333, 348, 358, 382 and 402 nm. The PL emission of F-GQDs are attributed by intrinsic emission. Intrinsic emission of F-GQDs are induced by sp$^2$ carbon domains produced by surface functional groups. Collectively, Fluorescent F-GQDs which have high dispersibility in water are synthesized by Plasma fluorination and sonication process.

Fig. 3. PL emission spectra of F-GQDs from 250 nm to 375 nm

4. Conclusions

In summary, we have presented a facile route to fluorescent F-GQDs by plasma fluorination and sonication process. CF$_4$ plasma changed to fluorine plasma contains F radicals and it etched the surface of
GQDs and functional groups are attached to the surface of F-GQDs. F-GQDs are separated from the SiC plates by sonication process and F-GQDs are well dispersed in water. XPS and UV absorption spectra show that functional groups are attached to the surface of the F-GQDs. PL emission spectra of F-GQDs exhibit the strong blue emission.

REFERENCES


