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Synthesis of fluorinated graphene quantum dots by CF_4 plasma

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1. Introduction

Graphene quantum dots (GQDs) are composed of few graphene nanoparticles with a size less than 30 nm. GQDs have attracted research interest due to their unique properties, such as possessing a large surface area, low toxicity and strong and tunable photoluminescence [1]. With these advantageous characteristics, GQDs can be used for bioimaging, biosensing, photovoltaics and optoelectronic devices [1]. Especially, when 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 and possess high potential to use in electrical fields for semiconductor. Various methods to synthesize the F-GQDs are presented including photochemical fluorination, ionic-liquid exfoliation and solvothermal fluorination [2]. However these methods require the complicated synthesis process and use of harmful chemicals. These are cause to increase the impurity of F-GQDs.

Here, we present the simple method to synthesize the F-GQDs by plasma fluorination. 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 [3]. However F-GQDs prepared by plasma fluorination are rarely reported since most of GQDs are produced in solution; RIE process are performed in vacuum state so GQDs in solution can’t be treated with fluorine plasma. In order to treat the GQDs produced by the conventional method with a plasma process, additional process to vaporize the solvent is required.

Besides GQDs in our research can be treated with RIE process because no chemicals and solvent was used during synthesis and formed on substrate by particle type. Our previous research, we reported the direct synthesis of GQDs on silicon carbide (SiC) plate by hydrogen assisted pyrolysis of SiC [4]. GQDs can be etched by fluorine plasma after fabrication without extra process. Therefore, we performed RIE process on GQDs on SiC plate synthesized by our previous study to manufacture F-GQDs. CF_4 gas are treated to source of fluorine plasma. CF_4 gas is used in graphene production through palsma fluorination [3] and this gas is widely used in RIE process to etch the surface of semiconductor. After synthesis, surface morphology and chemical analysis of F-GQDs are conducted. Raman spectra of F-GQDs was measured to determine the graphene quality after plasma fluorination.

2. Methods

2.1 GQDs preparation

GQDs on SiC plate are prepared by hydrogen-assisted pyrolysis of SiC. 4H N-doped SiC plates with cut off-axis angle of 4^{o} relative to the (0001) basal plane was purchased from TankeBlue Co., Ltd. (Beijing, China). SiC plates are cleaned with ultra-sonication process in ethanol and acetone. Washed SiC plates 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℃ 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 CF_4 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 CF_4 gas and produced plasma etched the surface of GQDs on SiC plate from 1min to 10 min to fabricate the F-GQDs. Radio frequency power was kept to 20 W. After RIE process, injection of CF_4 gas was stopped and F-GQDs were put off from the device.

2.3 Characterization of F-GQDs

The surface morphology of F-GQDs was observed using a field-emission scanning electron microscope (FESEM, Hitachi S-4800, Tokyo, Japan). Chemical structure of F-GQDs was characterized by X-ray photoelectron spectroscopy(XPS) using monochromatic

X-ray source (K-alpha, Thermo VG Scientific, MA, USA). Raman spectra of F-GQDs was examined using a Raman spectrophotometer (Horiba, Jobin Yvon, Kyoto, Japan)

Fig. 1. Reactive ion etching device

3. Results and discussion

3.1 Surface morphology of F-GQDs

The morphology of GQDs and F-GQDs etched by fluorine plasma for 1, 5, and 10 min was obtained with FESEM image. Rough surface are observed on SiC plate after pyrolysis of SiC (Fig. 2a) and small GQDs are formed on rough surface (Fig. 3a). When GQDs were etched by fluorine plasma for 1 min, surface became rougher but drastic change of surface was not appeared (Fig. 2b). The morphology of F-GQDs are similar with normal GQDs.

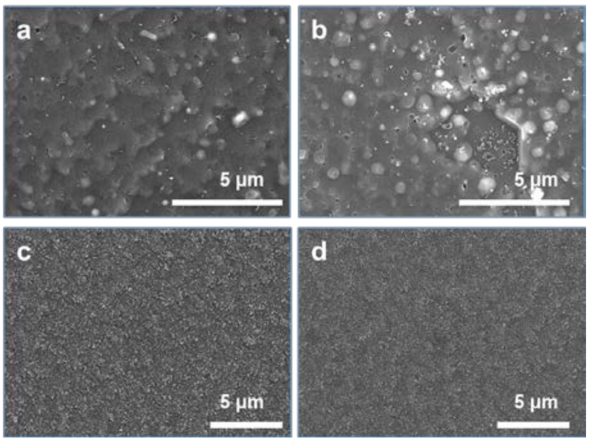

Fig. 2. SEM image of (a) GQDs on SiC and F-GQDs on SiC etched by fluorine plasma for (b)1 min, (c) 5min and (d) 10 min. (Magnification is 10k)

However, when etching time increased to 5 min, surface morphology of GQDs on SiC are significantly changed (Fig. 2c). Sharp and bumpy structure are observed in SEM image when compared with GQDs on SiC. This surface was induced by fluorine plasma which etched the surface. Morphology of GQDs are also altered by etching time. A lot of F-GQDs have rough surface are observed (Fig. 3c). Surface morphology of F-GQDs on SiC etched for 10 min also showed the sharp bumpy structure (Fig. 2d). Especially, a lot of F-GQDs particles were observed in SEM image (Fig. 3d). These size are less than those of F-GQDs etched for 5 min. Thus, it is indicated that Etching time affect the surface morphology of GQDs on SiC.

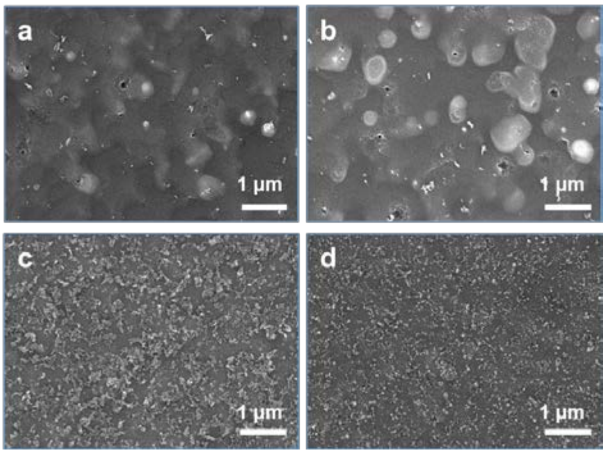

Fig. 3. SEM image of (a) GQDs on SiC and F-GQDs on SiC etched by fluorine plasma for (b) 1 min, (c) 5min and (d) 10 min at higher magnification. (Magnification is 20k)

3.2 Chemical analysis of F-GQDs

Chemical structure of F-GQDs were measured by XPS spectra. Drastic change of atomic ratio of F-GQDs are observed by etching time (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 5 and 10 min, F atomic ratio significantly increased to 26.90 % and 34.78%, respectively. It means that F radicals in plasma are absorbed to surface of GQDs. Especially, atomic ratio of carbon was reduced while that of silicon increased, because plasma removed the C atoms on surface of SiC plate with GQDs during etching process.

Table I: Atomic ratio of GQDs and F-GQDs by etching time

(at.%)	0 min	5 min	10 min
F	0	26.90	34.78
C	76.25	44.18	39.19
O	14.06	6.97	13.47
Si	9.69	21.95	12.56

Reduction of graphene thickness in F-GQDs due to etching process was proven by Raman spectra of F-GQDs (Fig. 4a). Raman intensity of each F-GQDs are normalized. In the Raman spectra of GQDs on SiC, sharp and clear D, G and 2D bands were observed. However, all of F-GQDs showed low and broad 2D band and peaks attributed by SiC plate. It is induced that graphene layer and aromatic C=C bonds in GQDs are destroyed by etching process of plasma. Nevertheless, the D to G peak ratio (I_D/ I_G) of the F-GQDs are comparably high (Fig. 4b) and it indicated that F-GQDs maintain high crystallinity.

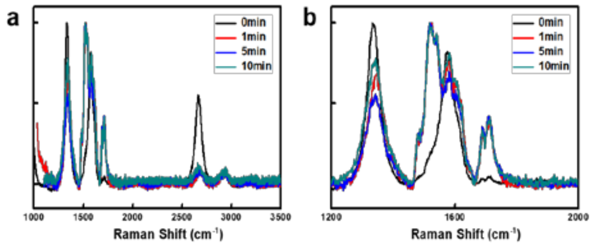

Fig. 4. Raman spectra of GQDs and F-GQDs etched by fluorine plasma for 1 min, 5min and 10 min. (a) Range from 1000-3500 cm^{-1} and (b) 1200-2000 cm^{-1}

4. Conclusions

We have presented a facile route to F-GQDs by plasma fluorination. CF4 plasma changed to fluorine plasma contains F radicals by RF powe. Fluorine plasma etched the surface of GQDs on SiC and F radicals are absorbed to surface of GQDs. FESEM images showed the bumpy structure and F-GQDs with rough surface after RIE process. Absorption of F atoms and removal of C atoms are proved by XPS spectra. Although plasma etched and destroyed the graphene in GQDs, F-GQDs still showed the high crystallinity in Raman spectra.

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