Synthesis of Nanometer Size Single Layer Graphene by Moderate Electrochemical Exfoliation

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Electrochemical exfoliation method had been developed for producing nanometer-size single layer graphene. We herein reported a developed method about producing single layer graphene with an average size of about 510 nm² from analysis of scanning tunneling microscopy (STM) measurements. The high resolution STM images also showed clear carbon lattice structure of the produced graphene in an atomic level, indicating that our produced nano meter size graphene is not distorted and oxidized by exfoliation process and preserve pristine graphene lattice structure. Our developed technique provides a preparation of nanometer-size single layer graphene dispersed in a solution.

Key words: Electrochemical exfoliation, Graphene, Scanning Tunneling Microscopy

1. INTRODUCTION

Graphene, a two-dimensional carbon layer with a thickness of a single atom, has been selected as one of the most promising materials in nanotechnology due to its high carrier mobility,[1] flexibility,[2] permeability[3] and electrochemical activity.[4] Possessing such eximious characteristics, graphene has attracted considerable attention for applications such as highly transparent and flexible conductive film, low cost catalyst for oxygen reduction reaction[5] and bio-sensing material. To realize these applications, it is necessary to optimize the structure according to individual needs. For example, in a viewpoint of bio-sensing applications, graphene oxide is one of the suitable forms because of its high water solubility and easy modification of various functional groups. Hence, many researchers have been making great efforts to synthesize graphene oxide.[6] In contrast, high qualitative nanometer size graphene is expected to be appropriate in a viewpoint of catalytic activity for fuel cell because the catalyst need to have high electrical conductivity and high ratio of edge structure which works as active sites. Recently, previous literature has been reported electrochemical exfoliation method of HOPG to obtain high-quality and cost-effective graphene.[7] However, so far as our best knowledge, to synthesize and characterize single layer graphene with nanometer size structure by using electrochemical exfoliation method has not been reported yet. In this study, we ameliorated some electrochemical exfoliation conditions and performed to synthesize nanometer size single layer graphene. By reducing applied potential to the electrode, we could successfully obtain nanometer size graphene with single layer dispersed in solution. Scanning tunneling microscopy (STM) analysis was also carried out, indicating that the produced nano meter size graphene is not distorted and oxidized by exfoliation process and preserve pristine graphene lattice structure.

2. EXPERIMENT

2.1 Synthesis

Fig. 1a is the scheme of the setup of electrochemical exfoliation. Highly oriented pyrolytic graphite (HOPG: 1 cm × 1 cm × 0.3 mm) was employed as carbon source of graphene and anode for electrochemical exfoliation, which is adhered to a tungsten wire by a silver pad (Fig. 1b) and then inserted into the electrolyte. A Pt sheet, acting as cathode, was placed parallel to the HOPG with a distance of 2 cm. The area ratio of two electrodes is approximately 1 : 1. The electrolyte solution was prepared through dropwise added 30% potassium hydroxide water solution into the 0.5 M sulfuric acid water solution, and the pH value of the electrolyte was adjusted to pH = 1.2. The electrochemical exfoliation process was performed by applying such DC bias: +1 V for 10 min and subsequent +4.5 V for 7 min on HOPG electrode. Afterward, the exfoliated graphene pieces in electrolyte solution were

![Fig. 1a: Schematic illustration for electrochemical exfoliation; b: HOPG flake before exfoliation; c: HOPG after exfoliation.](image-url)
filtrated with a 0.2 μm porous filter and washed with milli-Q water. After being dried with nitrogen, they were dispersed in DMF solution by sonication for 20 min to form the suspension. The suspension was centrifugated at 14000 rpm for 30 min to remove the undesired larger size graphite particles, which can then be used for further characterizations and film preparation just by immersing a single crystal Au (111) substrate into such dispersion. All of these procedures were operated at room temperature.

2.2 Characterizations

The STM images were performed in a Veeco Digital Instruments Nanoscope IIIa system at room temperature. Au bead with (111) facet surfaces was prepared by the Clavilier method. Raman spectra measurements were carried out with a Renishaw Raman microscopic system (excitation wavelength is 514 nm and magnification of lens is 50 times). XPS measurements were performed by a JEOL spectrometer with monochromatic Al Ka X-ray radiation (1486.6 eV).

3. RESULTS AND DISCUSSION

The electrochemical exfoliation was carried out in an applied static bias. At first, bias of +1 V for 10 min was applied to HOPG electrode, causing intercalation of anions into inner layers of HOPG. Following that, bias was increased to +4.5 V, and immediately the layers of HOPG expanded due to oxygen evolution. By the bubbles of gas generation, the layers were dissociated into small graphene pieces and dispersed in the solution. Figure 1c shows photograph of HOPG electrode after the exfoliation, and HOPG wholly expanded and crumbled. It was sufficient to obtain plenty of graphene pieces for ~10 min exfoliation. The supernatant solution with light brown color was filtrated and dispersed into DMF solution again, and suspension of exfoliated graphene in DMF solution was centrifuged. According to previous work, the exfoliation was carried out by applying +10 V to the HOPG electrode for 1 min. This condition produces micrometer size and bilayer graphene pieces. Meanwhile, we applied +4.5 V for 7 min, which is milder applied bias and much longer time. It is strongly suggested that our milder exfoliation condition generates small bubbles of oxygen gas compared to previous work and results in gradual dissociation of HOPG into small graphene pieces.

Fig. 2: Representative Raman spectrum of the exfoliated graphene pieces on Au (111) surface.

We analyzed the exfoliated graphene pieces by Raman spectra measurement. Fig. 2 shows representative Raman spectrum for the exfoliated graphene pieces deposited on Au (111) surface. These three intense peaks are clearly appeared at 1350 cm⁻¹, 1580 cm⁻¹ and 2700 cm⁻¹, which correspond to defect structures (D-band), in-plane vibration of sp² carbon atoms (G-band) and the stacking orders (2D-band). Observation of sharp G-band and 2D-band means that the exfoliation process provides graphene pieces, and little decomposed carbon such as amorphous like carbon generates. However, we always observed strong D-band peaks arising from defect structure, suggesting two possible reasons. One is that the exfoliated graphene contains a large amount of defect structure by the exfoliation process. The other reason is that nanometer size graphene pieces are produced because smaller graphene has a lot of edge structures, resulting in the enhancement of the intensity of D-band.

To confirm the origin of intense D-band, STM measurement was carried out. Fig. 3a shows STM image of deposited exfoliated graphene on Au (111) surface, and individual nanometer size graphene could be clearly observed. We also performed analysis of size distribution, which is statistically derived from the STM image in Fig. 3a, and resultant size histogram shows in Fig. 3b. Observed size distribution follows the Gaussian distribution, and the average size of the produced
graphene is about 510 nm$^2$ with standard deviation of 197 nm$^2$. Fig. 3c is the height analysis of the selected position lined out in Fig. 3a. The height of the first step is 0.15 nm and is similar to a diameter of carbon atom (0.14 nm). The height of the second step is approximately 0.30 nm, which is near the theoretical value of layer distance of graphite (0.33 nm). This profile analysis means that the exfoliated graphene is monolayer piece with partial bilayer fragment on it. The monolayer pieces which possess the height of 0.15 nm are in majority as shown Fig. 3a. According to previous works,[7] AFM measurement showed that exfoliated graphene sheets had a lateral size in a range from 1 µm to 40 µm with a thickness in a range from 1 to 3 nm. In comparison with their results, our milder electrochemical exfoliation condition produces nanometer size graphene with almost single layer.

Further STM analysis was performed to confirm the crystal structure of the exfoliated graphene. Fig. 4 showed the magnified STM images of graphene on Au (111) at the atomic level. STM images of graphene revealed atomic distinct graphene lattice structure and periodicity, and the distance between carbon atoms was approximately 0.3 nm, which is almost good accordance with the distance of graphite lattice. Previous STM observations of graphene oxide were already reported that graphite lattice is hardly observed because of presence of oxygen-containing groups and disorder structure induced by oxidation. Our STM results proved that the exfoliated graphene is non-distorted single nano sheet and preserves pristine graphene lattice structure. In addition, we also conclude that observed intense D-band peak of Raman spectrum as shown Fig. 2 is not origin from a large amount of defects structure but a lot of edges of nanometer size single graphene. It is noteworthy that produced nanometer size mono graphene with high quality is significant benefit for future application such as conductive transparent films and catalyst for fuel cell.

To confirm chemical conditions for the exfoliated graphene, XPS measurements were recorded. Fig. 5 shows the XPS of O1s and C1s regions of the exfoliated graphene is shown in Fig. 4: atomically resolved STM images of the exfoliated graphene, showing the graphene lattice. $V_{bias} = +20$ mV; $I = 0.1$ nA.

**Fig. 4:** atomically resolved STM images of the exfoliated graphene, showing the graphene lattice.

**Fig. 5:** XPS of a: graphene C1s; b: graphene O1s; c: HOPG C1s; d: HOPG O1s.

**Fig. 5:** XPS of a: graphene C1s; b: graphene O1s; c: HOPG C1s; d: HOPG O1s.
graphene and HOPG, respectively. In case of the exfoliated graphene, both C1s and O1s spectra showed broad shoulder at higher energy region, expecting to consists of several components (Fig. 5a and 5b). Peak-fitting analysis indicates that the most intense peak (C-C: 284.3 eV) represents the sp² graphitic carbon, and the broad and weak shoulder peak consists of sp³ carbon structure (C-C*: 285.1 eV), carbon-oxygen bond (C-O: 286 eV) and carbonyl group (C=O: 287.2 eV) structures. The small peak which can be assigned to sp³ carbon structures may arise from contamination in the atmosphere or defect in sample because the same weak peak is always observed at the same region with the C1s peak of HOPG (Fig. 5c). No observation of O1s peak of HOPG also indicates that O1s peak of the exfoliated graphene originates from the electrochemical exfoliation. In the consideration of STM results, observed intense peaks of oxygen-containing groups such as C-O and C=O groups are expected to mainly originate from oxygenated carbon species at edge of nano meter size graphene due to oxidization during exfoliation or exposure to air. Compared with the XPS spectra in previous works, our graphene has relatively much smaller intensity of peaks of O-containing groups, which is the specific evidence that we obtained high purity nano meter size single layer graphene successfully.

4. CONCLUSION
We have succeeded in the synthesis and characterizations of nanometer size and high quality single layer graphene by improving electrochemical exfoliating method. STM analysis revealed that the size of graphene pieces possess nanometer size at an average about 510 nm² and preserve pristine graphene lattice structure. We believe that our developed technique for preparation of nanometer size single graphene is important for realization of conductive film and catalytic material for fuel cell and will open future applications using graphene.

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5. REFERENCES

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