

Graphene Nanoplatelets via Exfoliation of Platelet Carbon Nanofibers and Its Electric Double Layer Capacitance

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Graphite oxide nanoplatelets with thickness of approximately 1 nm were synthesized via exfoliation of platelet carbon nanofibers with average diameter of 150 nm. The lateral size of the graphite oxide nanoplatelets was in accord with the diameter of the parent platelet carbon nanofibers. Subsequent chemical reduction of the graphite oxide nanoplatelets resulted in graphene nanoplatelet aggregates. Specific capacitance of 132 F g^{-1} in sulfuric acid electrolyte was obtained for the graphene nanoplatelet electrodes, which is about 1.6 times higher than graphene nanosheet aggregates obtained from natural graphite. The capacitive properties are discussed based on the size of the graphene nanoplatelets.

Graphene, a single layer of graphite, is a nanoscopic two-dimensional crystallite with an ultimate thickness of one carbon atom. It has attracted great interest from many researchers in recent years as a new nanocarbon.^{1,2} Graphene has been used as an integral part of 3D structures, normally grown epitaxially on the top of single crystals³ or mechanically cleaved from graphite.⁴ These methods yield small quantities of so-called “multilayered graphene” useful for fundamental studies. Agglomerates of single-layered graphene with a restacked structure, often simply called graphene for simplicity, can be obtained in large quantities via exfoliation of graphite oxide and subsequent reduction.^{5,6} Due to its good electronic conductivity and theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, graphene may be a candidate for electrode material for electric double layer capacitors.⁷⁻¹⁰ Reported capacitance values for graphene electrodes range from 100 to 200 F g^{-1} . This rather wide range of capacitance may be due in part to the difference in the synthetic procedure as well as the starting material.^{7,8} Such difference may affect the electrochemically active surface area, ionic accessibility into inner pores of graphene aggregates, and electric conductivity.

Studies relating to graphene have so far been limited to natural or synthetic graphite with particle size in the micro- to submicrometer regime. As the ionic accessibility should be limited to the lateral size of the aggregated individual graphene crystals, it can be anticipated that easier access into the inner pores of the graphene aggregate might be achieved by downsizing the lateral size of graphene. A recent study has highlighted this effect by mechanical downsizing the lateral size of graphene, resulting in easier access of electrolyte to graphene aggregate.¹¹

In this work, in an attempt to obtain nanoscale graphene, we focused on platelet carbon nanofibers (PCNFs) as a starting material. Here, we describe the preparation and electric double layer capacitance of graphene nanoplatelets obtained through exfoliation of oxidized PCNFs and subsequent reduction. As far as we are aware of, this is the first example of the synthesis of

graphene nanoplatelets with lateral dimension in the nanometer scale through oxidation–exfoliation–reduction of PCNFs.

Graphite oxide (GO) was prepared following the Hummers method¹² using PCNFs (150 nm average diameter) as a starting material. GO (100 mg) was dispersed in 100 mL of ultrapure water ($> 18 \text{ M}\Omega \text{ cm}$) and subjected to ultrasonication for 10 min in order to obtain a colloid containing exfoliated GO nanoplatelets. Non-exfoliated impurity was removed by centrifugation at 8000 rpm for 30 min. 20 mol L^{-1} hydrazine monohydrate (500 μL) was then added and allowed to react for 24 h at 60°C to reduce GO nanoplatelets into graphene nanoplatelets. The solid product was filtered, washed with ultrapure water, and dried under vacuum overnight. A similar procedure was adopted to prepare GO nanosheets and graphene nanosheets from natural graphite (3 μm average particle size). In this paper, the exfoliated substance derived from PCNFs and natural graphite will be termed nanoplatelet and nanosheet, respectively.

Powder XRD patterns of GO obtained from PCNFs and natural graphite both exhibited an increase in basal spacing from 0.34 nm to approximately 0.8 nm, and no graphite residue is evident (Figure S1¹⁴). Figure 1 shows typical AFM images of exfoliated GO nanoplatelets and nanosheets deposited on a Si substrate. Height profile analysis shows that the individual exfoliated GO nanoplatelets and nanosheets both have thickness of ca. 1.1 nm, indicating exfoliation of graphite oxide into single layers. The lateral size of GO nanosheets was in the order of a few micrometers, while the GO nanoplatelets had a substantially smaller lateral size ranging from 60 to 400 nm (average 170 nm of 150 specimens, see Figure S2¹⁴ for histogram). The lateral

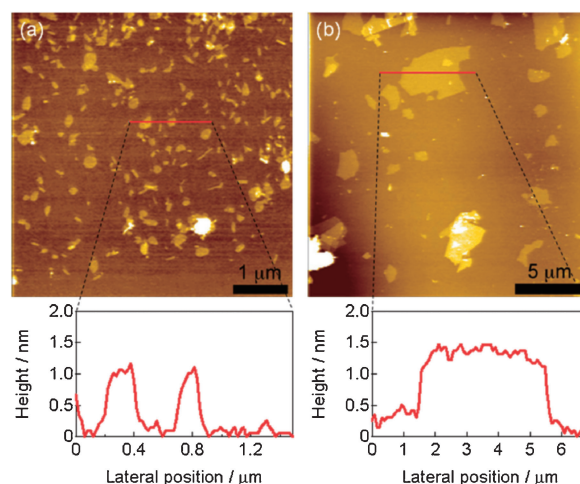


Figure 1. Typical AFM images and height profiles of exfoliated graphite oxide nanoplatelets derived from (a) PCNF and (b) natural graphite.

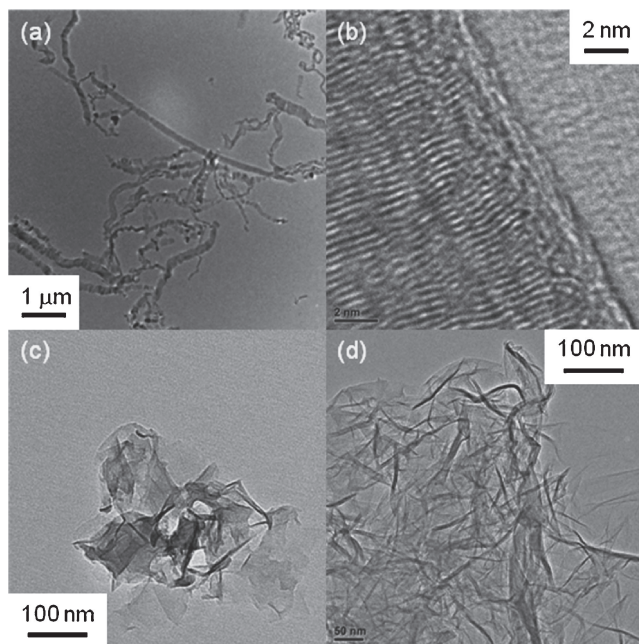


Figure 2. Typical TEM images of (a, b) PCNF, (c) graphene nanoplatelets derived from PCNF, and (d) graphene nanosheets derived from natural graphite.

size of GO nanoplatelets is governed by the diameter of PCNFs, which ranges from 40 to 550 nm (average 150 nm).

Reduction of GO nanoplatelets by adding hydrazine into the GO nanoplatelet colloid resulted in a blackish sedimentation. The change in color from the brownish GO nanoplatelet to black accompanied by a decrease in basal spacing from 0.8 to 0.39 nm are strong evidence of successful reduction of GO nanoplatelets to graphene nanoplatelets. Figure 2 shows typical TEM images of graphene nanoplatelet aggregates. The aggregates are composed of nanometer-sized graphene. Individual graphene nanoplatelets could not be observed by TEM, as graphene nanoplatelets have a strong tendency to restack due to π - π interactions once GO nanoplatelets are reduced to graphene nanoplatelets, similar to carbon nanotube bundles. The dimension of the loosely stacked graphene nanoplatelets matches that obtained for GO nanoplatelets by AFM (Figure 1a).

Figure 3 compares cyclic voltammograms of as-received PCNFs and graphene nanoplatelet aggregates. A clear increase in electric double layer capacitance was achieved compared to the pristine parent graphitic material; graphene nanoplatelets afforded 132 F g^{-1} at 2 mV s^{-1} , while the specific capacitance of PCNFs was only 7 F g^{-1} . On the other hand, aggregates of graphene nanosheets having larger lateral sizes exhibited 82 F g^{-1} at 2 mV s^{-1} . A plausible explanation for the higher specific capacitance of graphene nanoplatelets may be the smaller lateral size. The edge of graphite is generally accepted to have larger capacitance than the basal plane.¹³ The capacitance retention at high rate (95 F g^{-1} at 500 mV s^{-1} , 72% compared to the value at 2 mV s^{-1}) is slightly superior for graphene nanoplatelets compared to graphene nanosheets (52 F g^{-1} at 500 mV s^{-1} , 63% compared to the value at 2 mV s^{-1}) (Figure S6¹⁴). As the individual nanoplatelets are smaller in lateral size compared to the nanosheets, the diffusion length through the slit

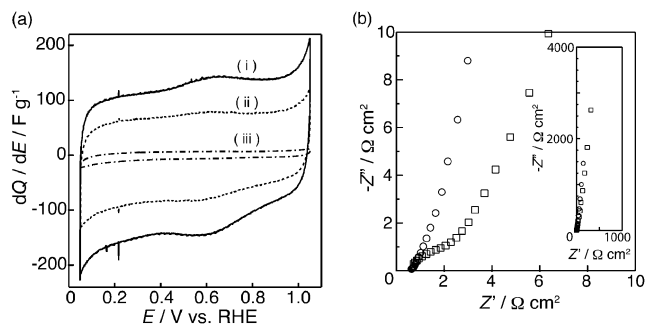


Figure 3. (a) Cyclic voltammograms of (i) graphene nanoplatelets derived from PCNF, (ii) graphene nanosheets derived from natural graphite, and (iii) as-received PCNF. (b) Nyquist plots of graphene nanoplatelets derived from PCNF (circles) and graphene nanosheets derived from natural graphite (squares).

pores should be shorter, which may explain the enhanced rate performance of graphene nanoplatelets. Electrochemical impedance spectroscopy supports this possibility, showing a resistive arc at high to medium frequency in the case of graphene nanosheets (Figure 3b).

In conclusion, graphene nanoplatelets with lateral size of ca. 170 nm and thickness of ca. 1 nm have been synthesized from platelet carbon nanofibers. Graphene nanoplatelets exhibited higher capacitance and rate performance than micrometer-size graphene nanosheets obtained from graphite powder, which is tentatively attributed to the higher utilization of graphene edges and shorter ion diffusion length in slit pores.

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