

# TRANVESERAL CUTTING OF PLATELET CARBON NANOFIBERS TO ISOLATE GRAPHENE DISCS

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## Introduction

Graphene, a single layer of carbon atoms arranged in a 2D hexagonal lattice, is a basic building block for graphitic materials of all other dimensionalities<sup>[1,2]</sup>. It can be wrapped up into 0D fullerene, rolled into 1D nanotube or stacked into 3D graphite. Only recently this atomically thin 2D material became experimentally accessible though isolation from its bulk structure, which spawned intensive research into its physical, chemical, and mechanical properties, and aimed for a wide-ranging and diversified technological application. The common source of graphene is high-quality graphite crystals. However, their irregular geomorphology makes it very difficult to produce graphene sheets with defined shape.

In this work, we employ a new starting material, platelet carbon nanofiber (PCNF), to isolate the graphene layers with defined disc shapes. Unlike the multi-walled carbon nanotubes composed of the concentric curved graphene sheets, the platelet carbon nanofibers were formed by the perpendicular stacking of graphene sheets, giving a large amount of free edges on the external surface and easy access to interlay spaces<sup>[3,]</sup>. Through the simple chemical oxidation and exfoliation, the disc-type graphene layers were isolated. That is, to the best of my knowledge, the first report that using platelet carbon nanofibers to produce defined disc-shape graphene sheets.

## Experimental

PCNFs were prepared by the decomposition of carbon monoxide over iron metal particles operated at 600 oC. The as-prepared samples were treated in 10 wt. % HCl until the metal content was less than 0.2 wt. %. The purified CNTs were further heat-treated at 2800 oC for 10 min to obtain graphitized PCNFs (GPCNF).

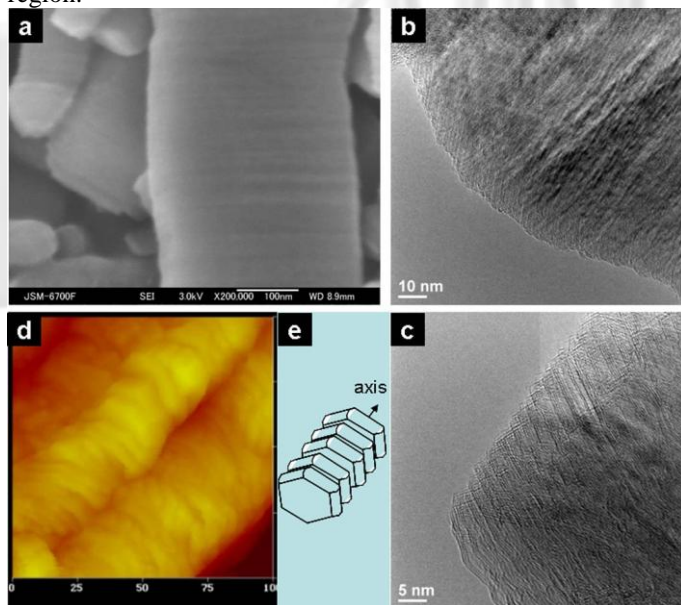
1 g of GPCNF was suspended in 100 ml concentrated sulphuric acid with the assistant of 1 hour ultrasonication. Then, 1-5 g potassium permanganate (KMnO<sub>4</sub>) was slowly added into the solution. The reaction mixture was stirred at room temperature for 1 h and then heated to 55–70 oC for an additional 1 h. After that, 100ml water was added slowly into the solution within the ice water bath. Caution: the temperature of the solution will increase to 100 oC! While the temperature cool down to room temperature (about 2 h), 400 ml water and 20 ml 30% H<sub>2</sub>O<sub>2</sub> was added. The obtained solution was separated using centrifuge at the speed of 4800 rpm. And the remained slurry was washed with distilled water and then centrifuged for 5 times until the pH value close to 7. Some slurry was dried and denoted as GPCNF-O

Exfoliation of oxidized GPCNF was achieved though ultrasonic dispersion 3 hours. The obtained solution was condensed to about 1 g/100ml. Some solution was centrifuged to obtain oxidized graphene discs (GD-O).

The samples were characterized by STM, TEM, SEM and XRD. Instrument settings and sample preparation details are given elsewhere<sup>[3]</sup>.

## Results and Discussion

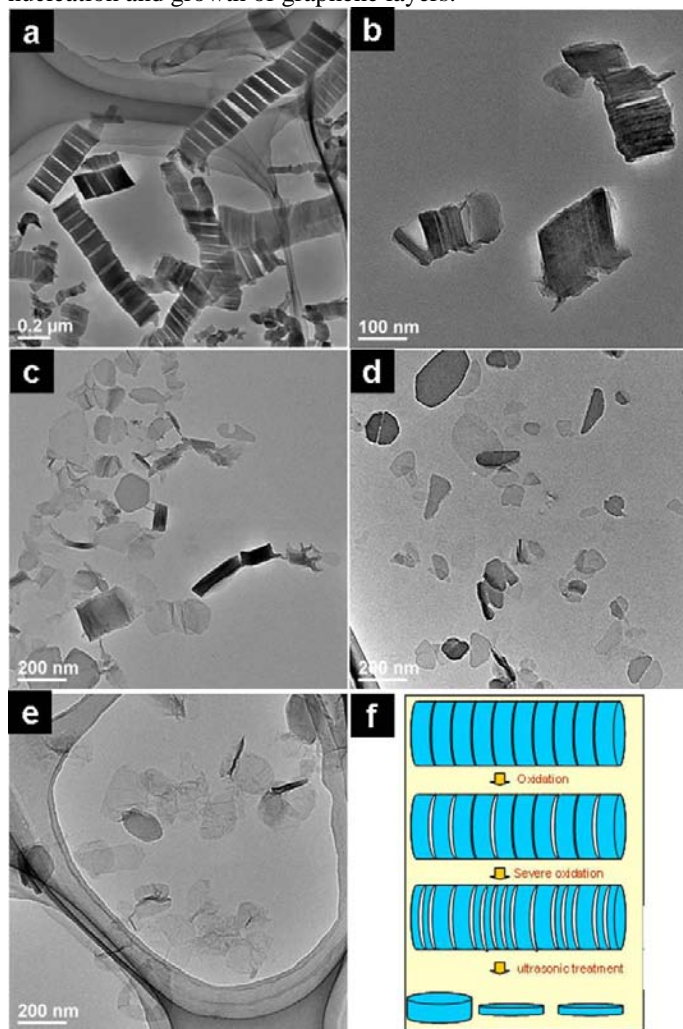
The PCNFs used in this work were prepared by the decomposition of carbon monoxide over iron metal particles operated at 600 °C, which is characterized by graphene sheet alignment perpendicular to the fiber axis. The pristine PCNF has a BET surface area of 80 m<sup>2</sup>/g and a diameter of 80-300 nm with a polygonal cross section, according to N<sub>2</sub> adsorption and SEM observation, respectively. The pristine PCNF has very high carbon content with the elemental composition of 99.8% C and 0.2% H. XRD pattern reveal that the pristine PCNF exhibit a high degree of graphitization with the interlayer distance (d<sub>002</sub>) of ca. 0.336 nm, comparable to the natural graphite. However, the high resolution TEM images showed that the graphene layer orientation is not strictly straight, some dislocation and tortuosity exhibit in the local region.



**Fig. 1** SEM (a), TEM (b, c) and STM images of graphitized platelet carbon nanofibers.

To improve the order of graphite crystalline structure, the pristine PCNF was further heat-treated in argon atmosphere at 2800 °C. The GPCNF has similar XRD crystal structure but different microscopic morphologies compared to its parent CNF. As shown in Figure1, SEM, TEM and STM images confirmed that the GPCNF in general consist of nano-sized plate units, as illustrated with a model of hexagonal-type plate stacking. Such plate unit has a mean thickness of ca. 3 nm

consisting of several graphene sheets. Meanwhile, rod-like structure with concentrically laminated loop ends was also widely observed on the raised edge, especially for these fibers which have the faceted and curved shape. Formation of plate or rod shaped units is mostly due to rearrangement and reorganization as a result of graphitization, and also possibly due to the inheriting of the primal embryo in the as-prepared PCNFs, as a reflection of the periodical repetition of temporal nucleation and growth of graphene layers.



**Fig. 2** TEM images of isolated graphene discs oxidized at R of 1 (a), 2(b), 3 (c), 5 (d) and 6 (e).

The GPCNFs were suspended in concentrated sulphuric acid followed by treatment with  $\text{KMnO}_4$  according to the Hammer method. The oxidized product was ultrasonically exfoliated for 1 hour. We found that the plate-shaped units were easily isolated from the bulk GPCNFs, and the degree of cutting depended strongly on the mass ratio of oxidized agent  $\text{KMnO}_4/\text{GPCNF}$  ( $R_{\text{K/GP}}$ ). As shown in Figure 2, while the  $R_{\text{K/GP}}$  of 1, the GPCNFs are still integrity even though a lot of kerfs are homogeneously distributed as a result of oxidization cutting. Increasing the R ratio to 2 causes the GPCNF break into small segments, which still contain tens of plate-shaped

structural units. These segments could be further cut into smaller ones if R increases to 3. Notably, the relative larger diameter units are almost isolated from the bulk GPCNFs, with small-diameter segments remaining in successive iterations. That means the rate of cutting is dependent on the diameter of GPCNF. Further increasing the R to 5, we found that almost all the structure units are isolated and even some disc-typed graphene sheets are separated from the structure units. It is evident that the thickness of these segments successive cut into thin ones as the R ratios increase. However, further increasing the R to 7-10 could severely disrupt the corruption of GPCNFs due to the excessive oxidation.

The structure of GPCNFs with different levels of oxidation was investigated by XRD. The samples oxidized at  $R=1$  and 2 have a relatively broad peak at  $2\theta$  values of  $\sim 26^\circ$  (a  $d_{002}$  spacing of 3.4 nm), contributed by the graphitic structure. With the increase of R to 3-5, this peak greatly weakened but a new shape peak at  $\sim 10.5^\circ$  present, corresponding to d value of 0.8 nm, which is very similar to that of graphitic oxide. However, further increasing the R to 7, the peaks at  $\sim 26$  and 10 both almost disappeared, indicating severe oxidation result in the strongly disruption of both graphitic structure and its oxides.

The oxidation of GPCNF is very similar to that of graphite, in which oxidation of graphite causes the introduction of epoxy and hydroxyl groups into the graphene layers, as well as the introduction of carboxylic groups mainly located on the edges of the layers. Simultaneously, carbon hydrolyzation occurred and the  $\text{sp}^2$  bonds changed to  $\text{sp}^3$  bonds. At the same time,  $\text{H}_2\text{O}$  and  $\text{SO}_4^{2-}$  ions could insert themselves into the graphene layer, inducing an increase in the interlayer spacing. The layers between plate units have relative weaker van der Waals forces compared with that between graphene layers in one unit, resulting in the stepwise cutting of GPCNFs: first separation of the plate units and second exfoliation of the graphene sheets.

## Conclusions

In this work, a simple solution-based oxidative method has been used for transversal cutting of PCNFs to separate very uniform graphene discs. The diameter of discs is in accordance with the diameter of the parent PCNF, which can be controlled by catalyst size and temperature during the PCNF growth process. The thickness of graphenes discs strongly depended on the oxidative conditions.

## References

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