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Preparation of Graphene Dispersion and Carbon Nanoscrolls

Yuzi Xiong, Hao Chen, Encai Ou, Jiangtao Qian, Chang Peng, Yuanqin Xiong, and Weijian Xu*
Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering,
Hunan University, Changsha 410082, P. R. China

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A novel versatile approach for the bulk and facile preparation of graphene dispersion with high concentration is developed, via sonication of graphite that is intercalated by a mixture of benzene derivative and *N*-methyl-2-pyrrolidone (NMP). Subsequently, graphene nanoscrolls, a new structure between graphene and nanotubes are obtained by heat treatment of graphene sheets.

Recently, graphene as a sparkling star has attracted substantial attention throughout the scientific community because of remarkable electronic, thermal, and mechanical properties.[1–3] To date, several methods have been developed to produce this one-atom thick planar sheet.[4–8] Among them, solvent exfoliation of graphene has great potential to be used in a bulk of applications in both research and industry. And a large number of reports have developed remarkable methods to produce graphene by directly exfoliating gaphite in the liquid phase.[9–11] However, few reports have been devoted to fabrication of graphene from intercalated graphite. A large number of benzene derivatives such as benzene, *o*-xylene, toluene, *m*-xylene, and methoxybenzene can be intercalated into graphite for the preparation of graphite intercalation compounds.[12] Meanwhile the enlarged layer distance of intercalated graphite facilitates the exfoliation of graphene sheets with excellent quality, encouraging us to explore further.

Because of the specific structure, graphene can be rolled to form helical structure, which is a new type of graphene-based material. The material, called carbon nanoscrolls, has aroused considerable interest in recent years.[13–16] Current theories[17–21] and some reports[13–16] suggest that graphene and/or graphene-based materials may form through a scrolling mechanism and lead to nanotube-like nanoscrolls. Because of the special structure between graphene sheets and carbon nanotubes, carbon nanoscrolls are demonstrated that have some exciting electronic and mechanical properties, which differ from that of graphene sheets and carbon nanotubes. And the special properties of scrolled conformation, porous structure, open ends and edges making the nanoscrolls can be used in various fields such as energy storage materials, hydrogen storage material, and catalyst carriers.[15,19] Recently studies have mainly focused on theoretical calculations and molecular dynamic simulation of graphene nanoscrolls. Little research has been reported for the fabrication and characterization of graphene nanoscrolls, because there are many challenges in preparing excellent quality graphene nanoscrolls.

In this letter, graphite is processed with a mixture of benzene derivative and NMP. Subsequently the intercalated graphite was sonicated for several hours to prepare graphene dispersion. The graphene sheets were heated at 300 °C to obtain carbon nanoscrolls. TEM is used to investigate the self-scrolling process and morphologies of carbon nanoscrolls. These images exhibit the length of nanoscrolls of about a few hundred nanometers and the diameter of almost dozens of nanometers.

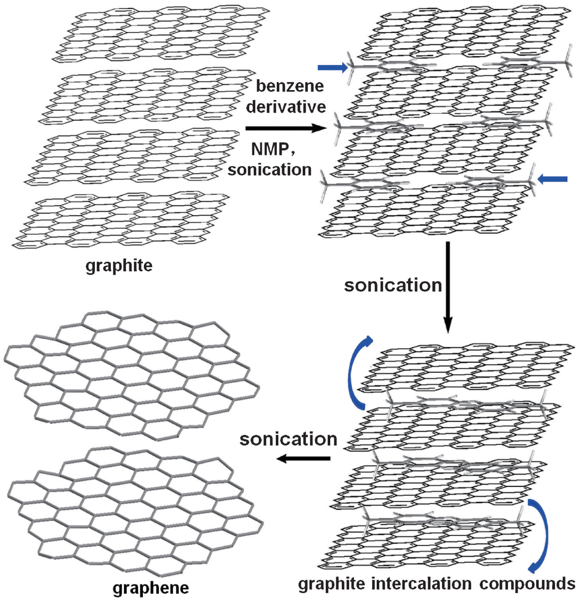

Figure 1. Preparation of intercalated graphite and graphene.

The details of experiments are described in Supporting Information.[25] The possible mechanism for the intercalation of graphite and exfoliation of graphene is shown in Figure 1. The XRD patterns of graphite and graphite intercalation compounds are shown in Figures 2A and 2B. In the spectra, the layer distance of graphite is 3.333 Å. After processing with *o*-xylene, it becomes 3.375 Å, which demonstrated the enlargement of the layer distance. It is possible that benzene derivative molecules seeped into the graphite layers and lead to the enlargement of the distance of graphite layers. The weak miscibility of NMP and *o*-xylene induced the entropic excluded-volume (depletion) effects and resulted in the entrance of the toluene.[22]

After the aqueous dispersed graphene stood overnight, a delamination was observed for the separation of toluene phase and water phase as shown in Figure S1.[25] This is proof for toluene as an insert to exfoliate graphite. The aqueous dispersed graphene was used as ink to write on the floor and a drop of dispersion is shown in Figure S1.[25] We also prepared the NMP, dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF) dispersion. The concentration of NMP dispersion was up to 0.8 mg mL^{-1} which was higher than that of the other dispersion. Toluene, *m*-xylene, and methoxybenzene used as intercalating agents respectively to exfoliate graphite were also prepared and gave an excellent effort.

Raman spectroscopy has been used to probe structural characteristics of carbon materials, providing useful information on the defects (D-band) related to the vibrations of the sp^3 hybridized carbons located at 1330 cm^{-1}, and in-plane vibration

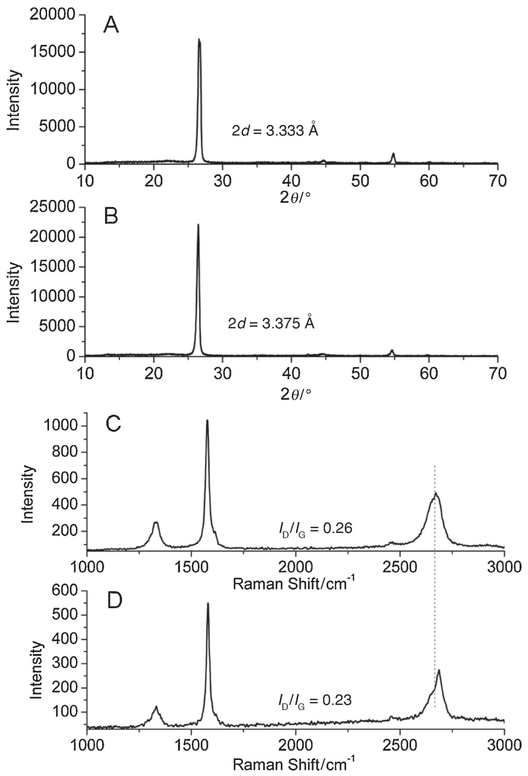

Figure 2. XRD patterns of graphite (A) and intercalated graphite (B), Raman spectra of graphene (C) and graphite (D).

of sp^2 carbon atoms (G-band) situated at 1580 cm^{-1}. The ratio of the D and G band intensities (I_D/I_G) is a useful index of the degree of structure defects.[23,24] Figures 2C and 2D show the Raman spectra of graphene and graphite. From the spectra the I_D/I_G is 0.23 for graphite and 0.26 for graphene. These values demonstrated that our process does not introduce significant structural defects on graphene plane.

The morphologies of graphene sheets were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM) as shown in Figure 3. The representative AFM height images along with height profiles for monolayer graphene sheets are shown in Figures 3A and 3B. The height profiles show the steps from the mica to an exfoliated graphene sheet, which is about 1.4 nm for the given cross-section. The damage of graphene sheets due to sonication result in the presence of graphene nanoribbon with the height about 2 nm as shown in Figure 3C. Multilayered graphene is also fabricated as shown in Figure 3D with the height of 4 nm, which demonstrated the thickness less than 5 nm. TEM image of graphene flakes deposited on a TEM grid and the well-defined edges also appeared indicating that graphene sheets are obtained (Figure 3E). High-resolution TEM (HRTEM) can be used to confirm the presence of the layers of graphene. The HRTEM image showed the edges of graphene and indicated that the graphene is made of two layers (Figure 3F). The period ripple demonstrates that there is no defect on the base-plane of graphene. We noticed that all the observed flakes have reasonable well-defined edges and appear to be of good quality with no observable holes or other damages. The measurements showed that the thickness of graphene sheets were in the range of 1–4 nm and indicated that they were mono- and/or a few layers. The exfoliated graphene sheets could be imaged clearly by SEM. Figures 4A and 4B present typical SEM images of the graphene sheets, in which the average lateral dimension of the graphene sheets was several hundred nanometers to a few micrometers.

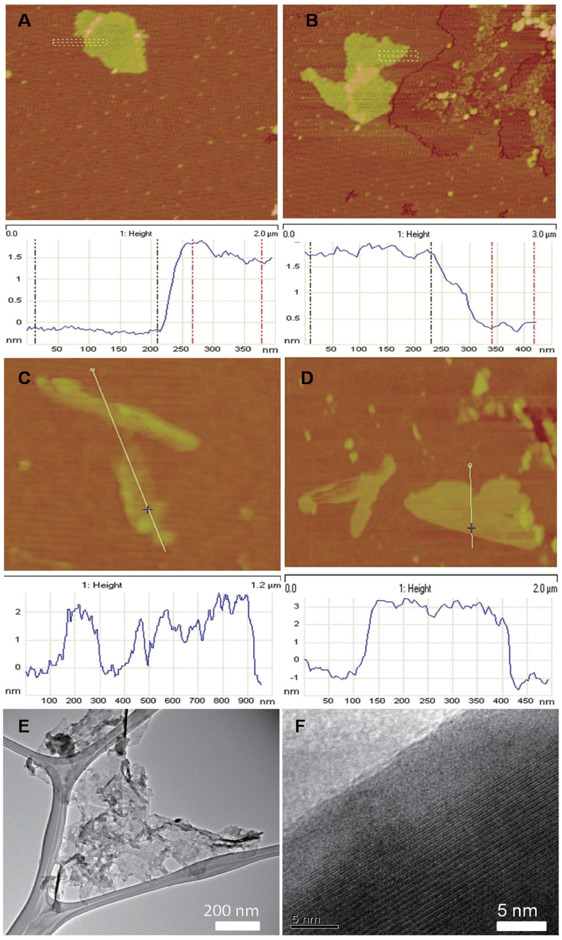

Figure 3. AFM images of monolayer graphene (A, B), graphene nanoribbon (C), and multilayer graphene (D). TEM images of graphene (E) and HRTEM of graphene (F).

The carbon nanoscrolls are characterized by SEM as shown in Figures 4C–4I. From Figures 4A and 4B, the graphene sheets were stretched out on the silicon wafer very well. When the graphene sheets were heated to 300 °C and maintained at this temperature for 1 h the smallish graphene sheets are rolled (Figure 4C), however, some of the biggish sheets are rolling as shown in Figure 4C (insert image) and Figure 4D (the arrow shows the scrolling direction of graphene sheets). While the sample is maintained at 300 °C for 2 h, more nanoscrolls are observed and all the bigger graphene sheets are rolling (Figure 4E). The graphene sheets heated to 300 °C for 3 h are also investigated by SEM as shown in Figure 4F. In this image, graphene sheets cannot be observed but replaced with carbon nanoscrolls. And some of the nanoscrolls that labeled as 1, 2, and 3 in this image were magnified in Figures 4G, 4H, and 4I. It indicates the incompletely rolled nanoscrolls, the excellent carbon nanoscrolls, and a graphene sheets with one corner rolled which possibly ascribes to the large sheet with a few layers. These images exhibit the length of nanoscrolls of about several

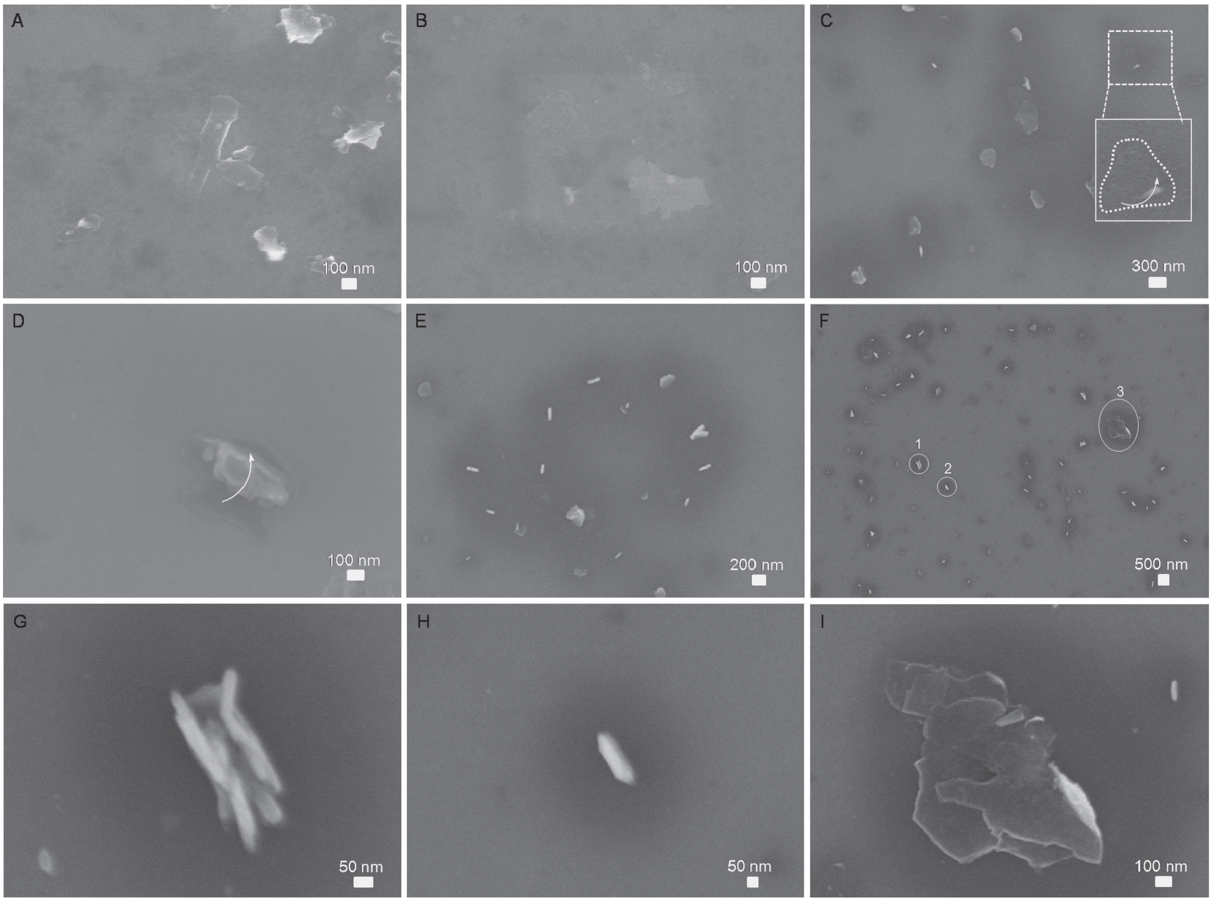

Figure 4. TEM images of graphene sheets (A, B) and carbon nanoscrolls (C, D, E, F, G, H, and I).

hundred nanometers and the diameter of almost dozens of nanometers.

Here benzene derivative and NMP mixed solution is used to intercalate graphite, then the graphite intercalation compounds are sonicated in various solvents to produce graphene dispersion. AFM and TEM show graphene sheets with excellent quality and the layers less than 5. The graphene sheets are heated to 300 °C to obtain graphene nanoscrolls. The self-scrolling process and morphologies of graphene nanoscrolls are observed by SEM. The special properties of scrolled conformation, porous structure, and open ends and edges made the nanoscrolls significantly valuable for their applications in various fields such as energy storage, hydrogen storage, catalystcarrier, solar cells, and nanoelectronic devices.

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25 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.