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Single-step synthesis and magnetic separation of graphene and carbon nanotubes in arc discharge plasmas

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1. Details of the setup and process
2. Details on the micro-Raman, TEM, SEM, AFM, and characterization of the carbon deposits in different collection areas
3. Detailed description of the results obtained by micro-Raman, AFM and electron diffraction techniques

1. Details of the setup and process

The graphene flakes and carbon nanotubes were produced in an arc discharge setup fitted with an additional permanent magnet unit. The experimental setup (see the detailed schematic in the central inset in figure 1, and photo in fig. 1(b)) consists of an anode-cathode assembly placed in the stainless steel (non-magnetic) flanged vacuum chamber. The cathode is a carbon rod of 0.5 in. dia., and the anode is a carbon rod of 0.25 in. dia. with a hole in the centre (see inset in fig. 1) of 0.125 in. dia. filled with a mixture of carbon and Y-Ni catalyst powder (particle size of 0.1 to 1 mm in dia.) in 1:4 ratio. An enhancing/separating magnet unit DESMU (a cubic-shaped permanent magnet 5×5×5 cm) was placed to create non-uniform magnetic field in the discharge gap of about 1 cm. The magnetic field strength in the interelectrode gap was 1.2 kG. FEMM4.0 software was used to simulate a 2-dimentional topography of the magnetic field produced by the magnet; this topography is shown in figure 1c, together with the magnet and anode-cathode assembly. Helium gas was supplied through the mass flow controllers and gas valves. The gas pressure in the chamber was controlled with an electronic pressure control system. The samples were produced at the constant helium pressure of 500 Torr, arc current of about 50 A, and discharge voltage of about 30 V.

2. Details on the micro-Raman, TEM, SEM, AFM, and characterization of the carbon deposits in different collection areas.

The micro-Raman system was based on an air-cooled argon 200 mW ion laser, holographic optics, 0.5-m spectrometer and a liquid nitrogen cooled CCD detector with matrix size of 1100×330 pixels; power ~5 mW; wavelength 514 nm, which corresponds to the energy of 2.33 eV. The high-resolution scanning electron imaging was made with Hitachi Field Emission S4700 microscope; a series of Raman measurements over both scattering ranges (first and second order, which allows to study 2^{nd} order peaks) were carried out on the specimens.

TEM (JEOL JEM-1200EX) and AFM (Asylum Research MFP3D); tapping-mode (in the air) imaging was involved to provide the structural detail of the graphene sheets. The AFM tip (Olympus AC240TS silicon cantilevers, force constant k= 2 N/m, and resonance frequency f =70 kHz) was used in the analysis. To purify the arc produced soot, the following procedure was used: dispersing in 2% DOC (deoxycholic acid), sonicating (for 1 hour) and centrifuging for 2 hours at 18000 rpm and temperature of 4 °C.

SEM (model Hitachi S-4700-II FE-SEM) with the accelaration voltages ranging from 1 to 30 kV (2.5-1.5 nm resolution range, respectively) equipped with an electron back-scatter detector system. Ultra-high resolution images (1280×960) were taken with the accelaration voltages 5 kV and electron current of approx. 20 microamper.

3. Detailed description of the results obtained by micro-Raman, AFM and electron diffraction techniques.

The samples collected from the magnet sides showed the occurrence of a weak D-peak at around 1325 cm^{-1}. This D-peak is related to the amount of defects in sp^2 bonds. The G-peak (at ~ 1582 cm^{-1}) and 2D-peak at (at ~ 2650 cm^{-1}) of magnet sides samples showed promising features of a few graphene layers.[1,2] The G-peak is related to doubly degenerate E_{2g} phonon (in plane optical) mode and its intensity increases as the number of layers (sample thickness) increases. A 2D-peak (which is double of D-peak) observed in Figure 3(c) is caused by scattering of phonons with the opposite wave vectors, and it does not require defects for the activation. Its shape is sensitive to the number of layers and it becomes broader and shifts to the right as can be seen in the inset in Figure 3(c) with the number of layers increasing. FWHM, i.e. the full width at half-maximum of the samples collected from magnet top is around 60 cm^{-1} and refers to a few graphene layers[1]. The samples collected from cathode deposit showed features of other graphite-like structures with the up-shifted 2D peak (2685cm^{-1}, see caption for Figure 3), sharp and strong down-shifted G-peak (1571 cm^{-}

[1]), and very pronounced 1D-line at 1340 cm^{-1}.[3,4] A sample taken from the chamber wall showed spectra similar to that of SWNTs. These spectra feature the occurrence of a G-peak at 1581 cm^{-1} splitting of the G- line at 1557 cm^{-1},[5] a weak D-peak (which suggests a low number of defects) and a 2D peak at 2668 cm^{-1}. All the Raman data were normalized.

To study the morphology and structure of graphene samples, we have used the AFM, Raman, and electron diffraction techniques. In Figures 3a and 3b we show the 3D reconstruction and cross-section (profile) of the specimens collected at the top side of the DESMU. The AFM method clearly reveals the presence of flake-like structures with the surface size of around a micron and a height variation of 1..5 nm. One can also notice the occurrence of "bumps/wrinkles" of about ~0.5 nm which is in a good agreement with the previously reported data.[6] The SAED pattern produced in a TEM microscope from the similar specimens collected from the magnet top surface is given in Figure 3e. It reveals the pattern expected for a hexagonal close-packed crystal with the incident beam close to 0001 plane (first and second rings are indexed).

1 D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L Wirtz, *Nano Lett.* 2007, *7*, 238.

2 Z. H. Ni, H. M. Wang, J. Kasim, H. M. Fan, T. Yu, Y. H. Wu, Y. P. Feng, Z. X. Shen, *Nano Lett.* 2007, *7*, 2758.

3 T. Takamura, K. Endo, L. Fu, Y. Wu, K. J. Lee, T. Matsumoto, *Electrochimica Acta* 2007, *53*, 1055.

4 Y. Raitses, C. H. Skinner, F. Jiang, T. S. Duffy, *Journal of Nuclear Materials* 2008, *375*, 365.

5 A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, *Phys. Rev. Lett.* 2006, *97*, 187401.

6 H. C. Schniepp, J.-L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prudhomme, R. Car, D. A. Saville, I. A. Aksay, *J. Phys. Chem. B* 2006, *110*, 8535.