

## Graphene Solutions

A. Catheline et al.

Electronic supporting information:

Natural graphite (aldrich) and expanded graphite (Nacional de Grafite, Brazil) were used as received. NMP (Aldrich, anhydrous, ref. 328634) was distilled under reduced pressure before entering the glove box. All air sensitive procedures (preparation of  $KC_8$  and its solutions, handling of the solutions) were performed in an Innovative Technology Inc. glove box with less than one ppm  $O_2$  and moisture contents.

Preparation of the graphite intercalation compound (GIC). Graphite powder is mixed with the appropriate amount of potassium metal (using a molar ratio C/K=8) in a sealed tube. The reaction takes place at 200 °C under vacuum. After several days of reaction, when the powder acquires a homogeneous golden colour the reaction is stopped and the GIC ( $KC_8$ ) recovered.

Ref: M. Inagaki and Y. Shiuchi, *Tanso*, 1983, 114, 124

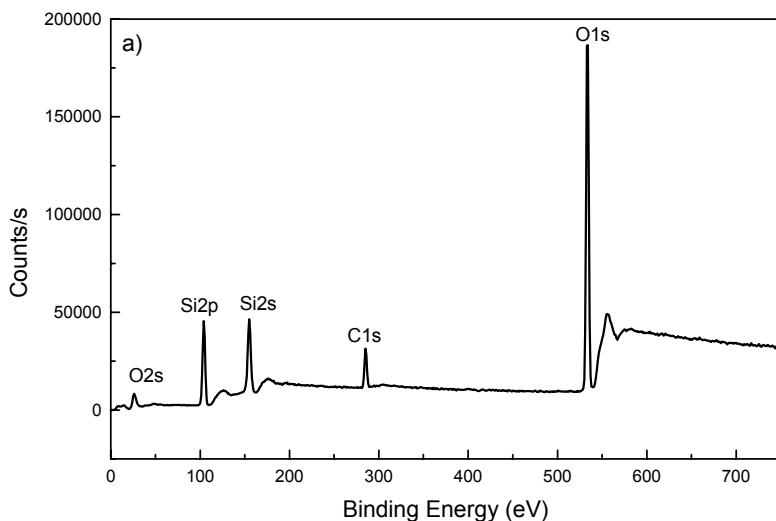
Preparation of the solution of the GIC ( $KC_8$ ) in distilled NMP. About 20 mg of  $KC_8$  is dissolved in 8 mL of distilled anhydrous NMP under inert atmosphere, at room temperature under stirring. After 24 hours, the solution is centrifuged at 4000 rpm for 60 minutes to separate the non-soluble material from the solution. The same experimental procedure was performed with the starting graphite in distilled anhydrous NMP for comparison. No material dissolved (colourless solution and no dried extract).

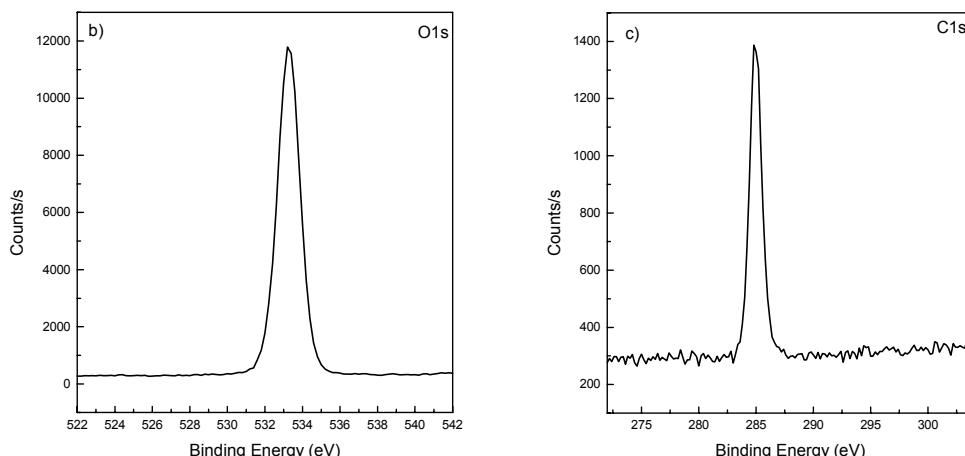
Preparation of deposits of the solutions onto substrates. Deposits of the solution were prepared onto different kind of substrates by dip-coating in the solution for 15 minutes under argon atmosphere, then washing with acetone, water and isopropanol and drying with a hot gun (still under Ar atmosphere); finally, the deposits were taken out of the gloves-box to be completely dried under vacuum at 200 °C for 48 hours.

X-ray photoelectron spectroscopy. Measurements were performed with a VG 220 i.XL ESCALAB spectrometer. All spectra were taken using a Mg non-monochromatized source (1253.6 eV) at 200 W. The spot size was approximately 25 mm. The typical operating pressure was  $2 \times 10^{-7}$  Pa. The reported data for graphene deposits are extreme surface ones (no

sputtering was performed). The range of depth information is 1 to 10 nm, in agreement with the detection of the deposition surface used (HOPG and SiO<sub>2</sub>). The detection limit is of the order of 0.1 atom%. Typical binding energies were taken from The Handbook of Monochromatic XPS Spectra, The Elements and Native Oxides, B. V. Crist, Wiley, 2000.

XPS results: X-ray photoelectron spectroscopy (XPS) analysis of deposits on a Si/SiO<sub>2</sub> wafer (Figures below) repeatedly showed the absence of any detectable peak of nitrogen and potassium, implying that all solvent (NMP) and the potassium salts expected to form upon ambient air exposure of the deposits, by analogy with C<sub>60</sub><sup>1</sup> and carbon nanotubes<sup>2,3</sup> have been removed by the rinsing procedure. The carbon C1s peak, centered on 285.16 eV, is very close to the expected value of 284.5 eV for graphitic carbon (HOPG). Its rather symmetric shape together with the absence of a significant shoulder at higher binding energies confirms the deposited carbon is not at all oxidized (C1s for C-OR, C=O and COOR environments are respectively expected at 285.5, 287.8 and 288.9 eV).





**Figure 5.** XPS data of potassium-graphene salt ( $KC_8$ ) solution dip-coated over a silicon wafer, washed and dried.

References:

- 1 Stinchcombe, J.; Pénicaud A.; Bhyrappa P.; Boyd P. W. D.; Reed C. A. Buckminsterfulleride (-1) salts: synthesis, EPR and the Jahn–Teller distortion of  $C_{60}$ . *J. Am. Chem. Soc.* **1993**, *115*, 5212–7.
- 2 A. Pénicaud, L. Valat, A. Derré, P. Poulin, C. Zakri, O. Roubeau, M. Maugey, P. Miaudet, E. Anglaret, P. Petit et al., Mild dissolution of carbon nanotubes: Composite carbon nanotube fibres from polyelectrolyte solutions, *Composites Sc. Technol.* **2007**, *67*, 795–797.
- 3 Pénicaud, A.; Poulin, P.; Derré, A.; Anglaret, E.; Petit, P. Spontaneous Dissolution of a Single Wall Carbon Nanotube Salt. *J. Am. Chem. Soc.* **2005**, *127*, 8–9.

TEM measurements: TEM investigation was done using a Tecnai F20 microscope, operated at an accelerating voltage of 80kV, i.e., below the energy threshold for atoms displacement in the honeycomb carbon lattice.

Absorption spectroscopy was performed on solutions contained in sealed quartz cuvettes (Thuet, Strasbourg) with a Unicam UV4-100 absorption spectrometer from 200 to 900 nm.

### Calculation of average flake size from solution conductivity measurements

Rough average flake size is obtained as follows: n Identical square flakes of side r are assumed; from the critical  $[K^+]$  concentration, the critical [C] concentration is calculated. Taking 1.42 Å as the C-C bond distance, that concentration can be transformed into a surface which is a function of  $n.r^2$ . On the other hand, at the critical concentration, it is assumed that the volume occupied by the freely rotating n flakes is equal to the total volume of the solution and is a function of  $n.r^3$ . Using those two independent equations, a value of  $r = 8$  microns can be estimated.

Detailed calculation:

$$[K^+]_c = 10^{-3} \text{ M} \Rightarrow [C]_c = 8 \cdot 10^{-3} \text{ M}$$

In 1 l of solution, there will be a total surface  $S = 8 \cdot 10^{-3} \text{ (mol)} \times 0.026 \cdot 10^{-18} (\text{m}^2/\text{at.C}) \times 6.022 \cdot 10^{23} \text{ (at.C/mol)} = 125 \text{ m}^2$ , hence :

$$nr^2 = 125 \text{ m}^2 \quad (1)$$

The volume of a flake will be  $V_f = 4/3 \pi (r\sqrt{2}/2)^3$ . The total volume (1l) is then equal to  $nV_f$  which gives :

$$1.48 nr^3 = 10^{-3} \text{ m}^3 \quad (2)$$

combining (1) and (2), a value of  $r = 5.4 \cdot 10^{-6} \text{ m}$  is obtained.