

MORPHOSTRUCTURAL STUDY OF SOME GRAPHENE-BASED AEROGELS FOR SENSORS FABRICATION

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Abstract

This paper presents a detailed study of the feature-rich essential properties of the family of two-dimensional graphene flakes, as well as the preparation and properties of graphene-based aerogels. The usefulness of Raman spectroscopy, a versatile tool used to identify and characterize the chemical and physical properties of these graphene flakes and their composites is clearly stated. Furthermore, strategies for the preparation of bulk graphene-based aerogels are also discussed. The properties of nanocomposites were analyzed using XRD and SEM combined with micro Raman spectroscopy, which provides structural and optical information.

Introduction

Although the X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) spectra can give important information about the composition and structure of graphene aerogels, the Raman spectra can give complementary information that can be correlated with the electrical conductivity of the structure. The Raman spectrum of graphene shows a relative simple structure characterized by two main bands designated as the G and 2D bands (a third band, the D band, can be observed when defects are present in the carbon network). The usefulness of Raman analysis lies in its ability to differentiate between single, double and triple layered graphene. The ratio between the intensities of the specific peaks of graphene – 2D and G was determined. According to the literature, if the ratio is around 2 or above, the recorded spectrum corresponds to a monolayer graphene [1]. The 2D band is always a strong band in graphene even if the D band is not present and the graphene has no defects. This band is also used to determine the thickness of the graphene layer. In contrast to the G-band position method, the method used to determine the thickness of the graphene layers based on the 2D band depends not only on the position of the band but also on the shape of the band [2]. In the case of a double-layered graphene, the interaction of the planes divides the π and π^* electronic bands in four structures of parabolic bands (π_1 , π_2 , π_1^* , π_2^*). The spatial groups theory explains the fact that the laser light excites the electrons as pairs (π_1 , π_1^* și π_2 , π_2^*) between the four band structures. This gives the maximum 2D dispersivity for the bilayer graphene that can be characterised by four Lorentzian maxima. For the multilayered graphene, the splitting of the electronic bands becomes more complex and more dispersive leading to further widening of the 2D bands [3].

Experimental

The graphene oxide (GO) was prepared using a modified Hümmer method. Briefly, the graphite (supplied by Alfa Aesar, average particle size of 44 μm) was oxidized with H_2O_2 and KMnO_4 in the presence of H_2SO_4 and H_3PO_4 . After oxidation, the resulting mixture was filtered through a polyester filter. The mixture was then destabilized by the addition of acetone, was separated by centrifugation, and washed with a 30% HCl solution followed by redispersion in water. The process was repeated 5 times without HCl addition until the absence of chlorine ions that were detected by adding a AgNO_3 solution. The GO concentration was determined using gravimetric analysis by evaporating in vacuum (< 10 mBar) 5 mL of suspension at 60 °C for 16

hrs. The suspension was then diluted until the resulting concentration was 2 mg/mL. The precursor used in the aerogels synthesis was a blend of GO1 synthesised according to the above method having a concentration of 0.9 mg/mL, and a Quattro-Type graphene suspension whose concentration was increased to 0.75 mg/ml by centrifugation at 24.000 RPM and redispersed in water [4].

Next, the suspension was frozen at -196°C then lyophilised using a freeze drier built by the INCEMC collective by modifying the GSL-1500X (MIT Corporation) oven (patent pending invention). The freeze drying took place at a pressure lower than 1 Torr using a vapour trap cooled with liquid nitrogen. The second stage consisted of heating the graphene to 300°C in vacuum and maintaining it for 60 minutes at that temperature. The heating speed was $4^{\circ}\text{C}/\text{min}$ and the forced cooling was done under a stream of cold air to room temperature.

Preparation of the aerogel for the Raman study

The graphene aerogel was pressed on mirror polished silicone substrates cleaned by sonication in alcohol and distilled water. The excess material was extracted several times using adhesive tape until the semi-transparent graphene sheets could be observed [5]. The optical images of the exfoliated graphene flakes were obtained using the 50x and 100x objectives of the Olympus optical microscope. The diffraction spectrum was obtained with the X'Pert Pro MPD diffractometer using the Cu (K- α) line and the Raman spectra of the exfoliated graphene were collected using the microRaman system (Olympus BX-51 optical microscope and Andor Shamrock 500i Spectrometer, $\lambda_{\text{ex}}=514\text{ nm}$).

Results and discussion

The XRD diffractogram, the SEM and optical images of the GO sample dried at 30°C for 20 hrs in vacuum at 10 mBar are shown in figure 1.

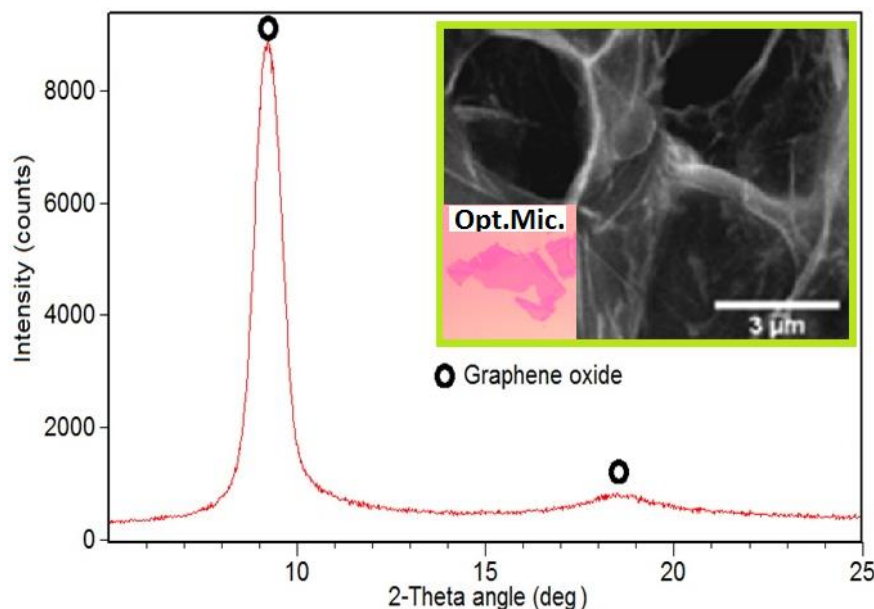
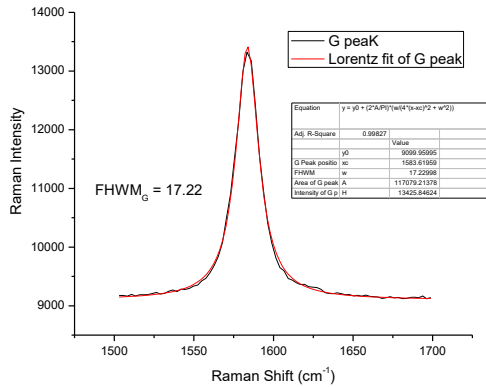


Figure 1. XRD diffractogram and the SEM/Optical image (inset) of the graphene aerogel

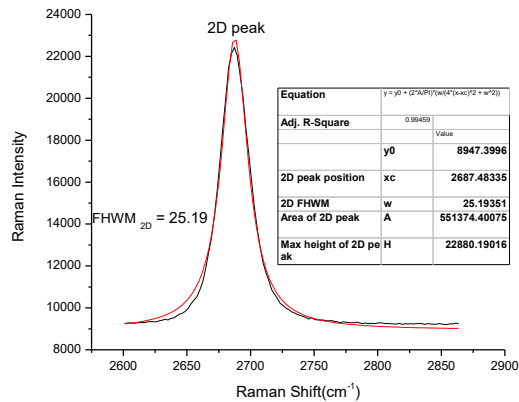
The XRD diffractogram shows that the obtained product is pure graphene oxide without traces of graphite.

The G (figure 2a) and 2D (figure 2b) bands of the monolayer graphene with the calculated width at half maximum gives information regarding the number of atomic planes and the density of defects in the carbon atoms plane. The G band around 1585 cm^{-1} in the

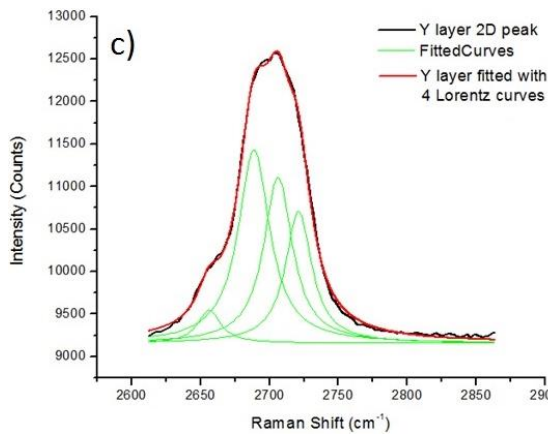
graphene spectra is a sharp band and corresponds to the in-plane vibration of the sp^2 hybridized carbon atom that make the graphene sheet. The position of the G band is very sensitive to the number of the layers in the sample [6]. In the case of our samples, in the areas with multiple layers, the G peak shifts to the left from 1584 cm^{-1} (mono-layer) to 1581 cm^{-1} (multi-layer). The 2D vibration is symmetrical having the width reduced to the half of the height ($\sim 25\text{ cm}^{-1}$) and is the best indicator for the monolayer graphene obtained from the aerogel on the silicone substrate. However, the signature of the monolayer graphene is given by the intensity of the 2D band (around 2700 cm^{-1} , value that depends on the excitation wavelength of the laser) that is at least twice the intensity of the G band (around 1560 cm^{-1}) [7], (figure 2-a, b).



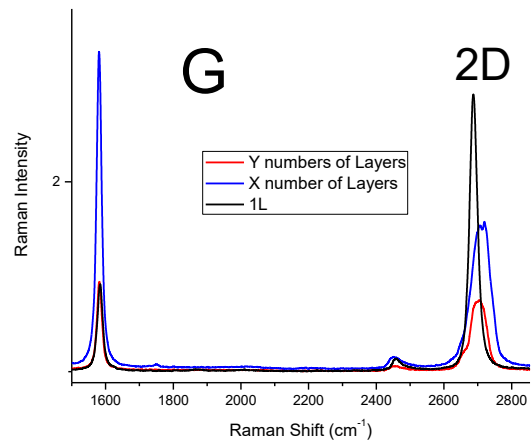
a) Lorentzian deconvolution of G peak for 1 layer graphene



b) Lorentzian deconvolution of 2D peak for 1 layer graphene



c) Deconvolutions of the 2D band in the sample with different number of layers



d) Raman Shift for different numbers of graphene layers

Figure 2. Raman spectra collected from different areas of the aerogel sample

Based on the above, we suggest that the carbon atom planes were not everywhere fully separated in the sample as it was previously mentioned in literature [8]. This aspect is better seen in the detailed images of the G and 2D bands shown in figure 2c. It can be observed that by adding successive layers of graphene, the 2D band is divided into several overlapping modes and the peak's symmetry decreases with increasing graphene layers in the sample.

The single layer graphene shows a symmetric peak and can be fitted with a single Lorentzian function due to the band structure with a single electron (π) and to the conduction

band (π^*). The full width at half maximum (FWHM) of a single layer is $\sim 26.3 \text{ cm}^{-1}$ [9], close to the value obtained for our samples (25.2 cm^{-1}) (figure 2b).

To determine the exact number of sheets in case of multilayered graphene, more complementary analyses on the same area are necessary such as imaging the area using AFM or STM.

Conclusion

The physicochemical analysis shows that the graphene oxide was successfully synthesized and the graphene aerogel had between one and several graphene layers and that between some of them there is a good electrical bond. The size of the porous mass cells is around $3 \mu\text{m}$ due to the fast freezing of the dispersion medium preventing the growth of massive ice crystals. Thus, the synthesis method of the aerogel led to a 3D material having probably a good electrical conductivity allowing the charge transfer to the silver nanoparticles that will decorate the aerogel in order to build sensors for H_2S detection.

Acknowledgements

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