A Few Layer Graphene Material Prepared by Thermal Reduction of GO

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Abstract

Graphene shows a wide range of application due to its electrical, optical and mechanical properties and several methods of preparation have been developed in the last ten years. However, to prepare large graphene quantities with a relatively small number of defects is still a challenge. Physical and chemical exfoliation of graphite has been mentioned as an appropriate method to prepare graphene or few layer graphene materials for many applications, such as nanocomposites, sensors and electronic devices [1]. The aim of this work is to show the results concerning to preparation of few layer graphene material by thermal reduction of graphite oxide (GO). The energic oxidation of graphite using modified Staudenmaier methodology resulted in GO [2]. Two different types of graphite were evalueted: graphite flake (FK) and graphite nanosheets (GNS). It was also evaluated different times of oxidation (24, 48, 72 and 96h) and different reduction temperature of GO (600, 700 and 1000ºC). The samples were characterized by XRD, Raman spectroscopy and TEM. The Figure 1a shows the XRD patterns of GNS and FK. It is possible to observe the interlayer spacing along the c-axis ($d\text{-}_{002}$) at 25º and ($d\text{-}_{004}$) at 55º as sharp peaks for FK. The less intense peak at 25º and absence of peak at 55º indicates that GNS sample is exfoliated. The formation of GO is indicated by the increase of the interlayer spacing along the c-axis (d_{002}) due the insertion of various oxygen-containing functional groups in the graphite structure. The Fig. 2a shows the XRD patterns of GO prepared from GNS oxidation during 96h. The formation of GO was confirmed by peak at 11.3° corresponding to the d-spacing of 0.81nm. When the GNS graphite is oxidized, the delocalized electronic structure is disrupted, i.e. in the sp^2 bonding networks of the graphite. Therefore is very important restoring the π-network by reduction reaction, so that the electrical conductivity is restored again. A manner to restore the π -network is by the thermal reduction. Therefore the GO was submitted to different thermal treatments. Figure 2a shows the XRD patterns to GO samples oxidized during 96h and GO that had different thermal treatment (GO6, GO7 and GO10; these were heated at 600, 700 and 1000 °C, respectively). According to Fig. 2a it can be seen that the increases in the reduction temperature decreases the intensity of the peaks characteristic of GO at 11°. GO6 and GO7 showed a smaller peak of starting material, GNS, about 24°. It shows that the heating restore the organization of graphitic structure, but it was not verified for higher temperatures. Figure 2b shows the Raman results for GO thermally reduced. The main Raman features of graphene and graphite are the G band (~1580 cm^{-1}), the D band (~1350 cm^{-1}) and the 2D band (~2670 cm^{-1}). The the D band is related to crystal defects. The G band originates from in-plane vibration of sp^2 carbon atoms and the 2D band corresponds to the second order overtone of the D band. For single layer graphene (SLG) the 2D band is a sharp and symmetric peak while it becomes broader when grapheme thickness increases from SLG to few layer graphene[3]. The Figure 2b shows that a sp^2 carbon network was restored, but with many defects. No peak is observed in the 2D band region indicating that amount of graphene, if it is presence, is very small relative to amount of sp^3 carbon. On the other hand, best results were obtained with GO prepared from FK. The Fig. 3 shows as example the results when FK was oxidized during 24 or 72h and the resulting GO was reduced at temperature of 600, 700 e 100°C. The X-ray diffraction spectrum shows the peak relative to the d-spacing at 25° and no GO characteristic peak at 11°, Fig. 3a and 3b. The less intense and broader peaks observed for SFK24H7, SFK24H6, SFK72H7 and SFK72H6 Indicate a great exfoliation. The interlayer distances (d_{002}) between graphenes and the crystal size (C) were estimated using Bragg's Law and Scherrer's Equation, respectively and it was estimated that the crystal has 10-15 stacked graphene sheets. It can be seen in the Raman spectra that the graphite structure was recovered and the defects are similar to those existing at starting graphite, FK, Fig. 3a and 3b. The band 2D of SFK24H6 and SFK72H6 indicates that a stacking of few layer of graphene was obtained. The TEM image supports these results, Fig. 4.

References

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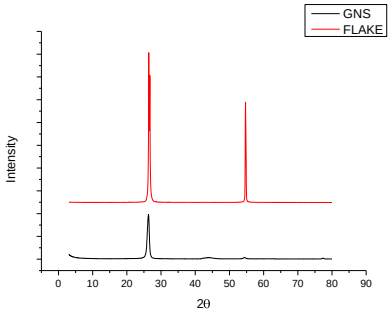
[3] Z. Ni, Y. Wang, T. Yu, Z. Shen. Nano Res, **1** (2008), 273.

Figures

(a)



(b)

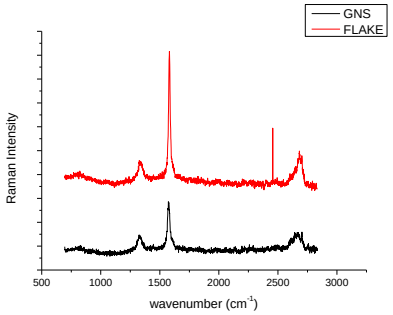
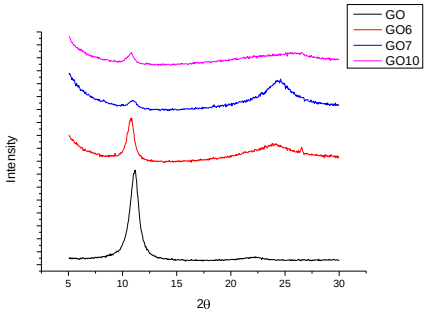


Figure 1: a) XRD patterns and b) Raman spectra of starting graphite material

(a)



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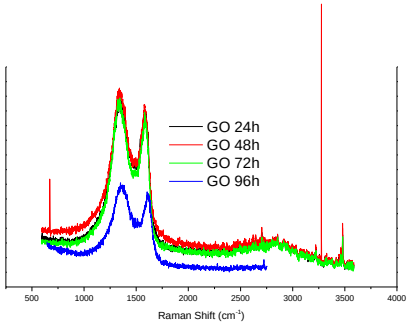
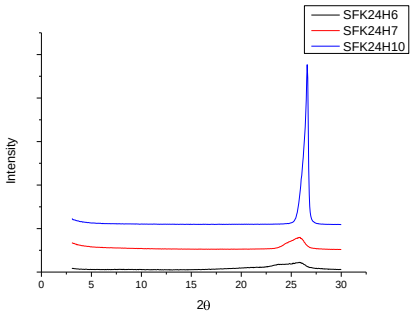
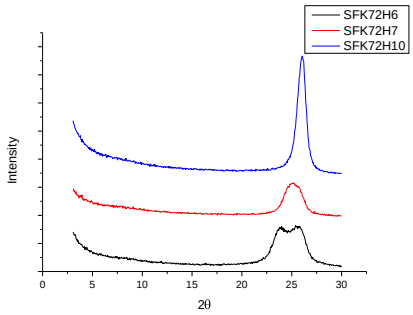


Figure 2: a) XRD patterns of GO and GO reduced at different temperatures, b) Raman spectra of GO oxidized at different times and reduced at 1000°C

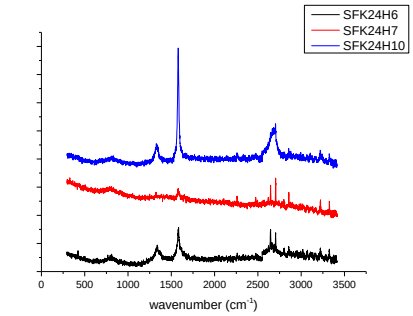
(a)



(b)



(c)



(d)

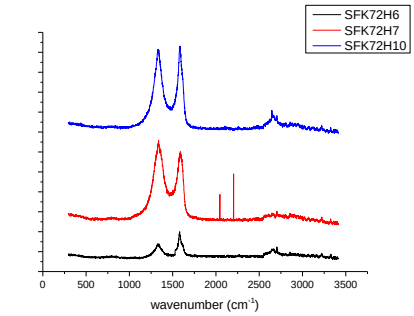


Figure 3: a) and b) XRD patterns, c) and d) Raman spectra of FK oxidized during 24h and 72h and reduced at different temperatures

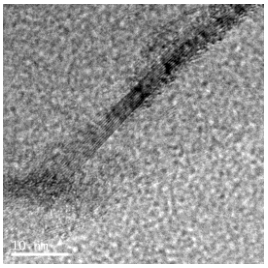


Figure 4: TEM of FK oxidized during 24h and reduced at temperature of 700°C