

Crystallite size effect on the structural modification of graphene oxides by insitu reduction and nitrogen doping.

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Graphene, the unique two dimensional carbon allotrope [1] of single-atomic thickness, has attracted great interest owing to its interesting physical and chemical properties and there is an increase in its demand in various fields of application involving electronic based devices. The electrical properties of graphene can be modulated by chemical doping. In carbon materials Nitrogen and Boron atoms are appropriate candidates for this tuning process as both elements have almost the same atomic radius and one electron more or less than carbon. Studies involving nitrogen doping of graphene have proven an enhancement in electrical properties of this material [2,3]. In this communication we report the effect of the grain size of the starting graphite material on the structural modification caused by nitrogen doping on the corresponding graphene oxides.

Graphite of three different grain sizes (10, 100 and 200 mesh) were submitted to strong oxidation with nitric acid, obtaining the corresponding graphene oxides (GO10, GO100 and GO200). Thereafter, these materials were heated to 500°C in a reactive gas mixture composed of NH₃, N₂ and H₂ whose flow rates were 10, 50 and 6 ml/min, respectively. One of the three samples was also nitrogen-doped at a higher temperature (900°C) in order to observe any changes in the structural modification. Parallel to these, all three graphene oxides were heated at 500 °C under inert nitrogen atmosphere (50 ml/min) which served as a reference when comparing with those treated with NH₃. The resulting materials were studied employing various techniques such as TEM, XPS, XRD, etc.

Fig. 1. Shows TEM images of synthesized materials which consists of ultrathin transparent graphene sheets with some wrinkled and folded features (Fig. 1a) proving that graphene oxide was truly exfoliated in the reduction process. Morphological differences can be observed when comparing GO heated under inert atmosphere (Fig. 1b) and that treated with NH₃ (Fig. 1c). In the later, the neatly and parallel lined stack of folded and scrolled edges of graphene layers show certain degree of defects with respect to the former. This effect is further emphasized at higher nitrogen doping temperature (Fig. 1d). Fig. 2 shows the XRD pattern of an original GO sample (before treatment), a GO treated under inert atmosphere and those treated with NH₃ (at 500°C and at 900°C). GO has a sharp peak at 16° corresponding to an interlayer distance of 0.67 nm. This peak completely disappears for all reduced GO and a small peak at about 26° is observed owing to the recovery of the graphite crystal structure. A significant difference can be observed when comparing GO of different crystallite sizes as this characteristic peak is smaller and broader for smaller sizes suggesting stacking thickness of resulting reduced GO is greatly dependent on the crystallite size. XPS results confirm the reduction of GO on observing the disappearance of oxygen surface groups on C 1s peak of samples before and after treatment (Fig.3). This technique also gave insights on the amount and type of nitrogen incorporated after the treatment. N 1s spectra of inert treated and NH₃ treated GO is displayed in Fig. 4. The amount of N present in the inert treated GO is insignificant whereas this specie is present in all the others ranging from 3 to 6 % being highest in the GO of larger grain size. At the same time the distribution of N as pyridinic, pyrrolic and quaternary- N is also greatly influenced by the size of the original starting graphite material. GO10 has highest proportion of pyridinic and quaternary-N while in GO200 the formation of pyrrolic- N is favoured.

References

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- [2] X. Li, H. Wang, J. T. Robinson, H. Sanchez, G. Diankov, H. Dai, *J. Am. Chem. Soc.* **131** (2009) 15939.
- [3] D-W. Wang, I. R. Gentle, G. Q. Lu, *Electrochem. Comm.* **12** (2009) 1423.

Figures

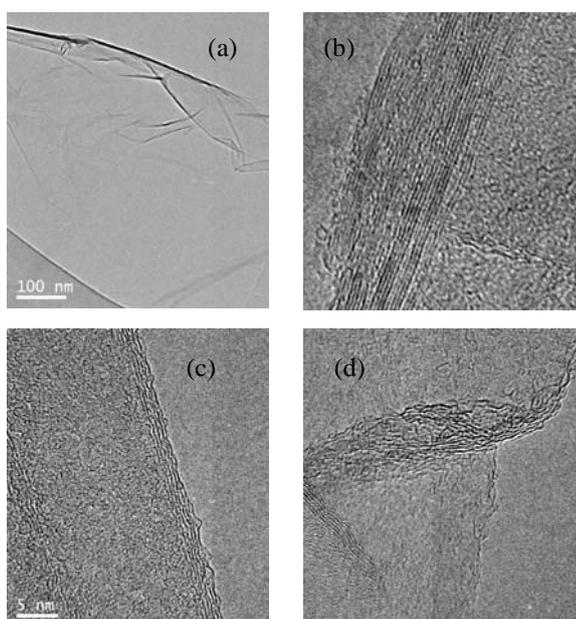


Figure 1. GO10 TEM images

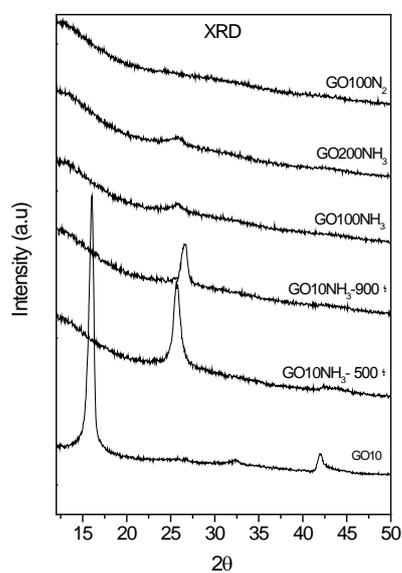


Figure 2. XRD

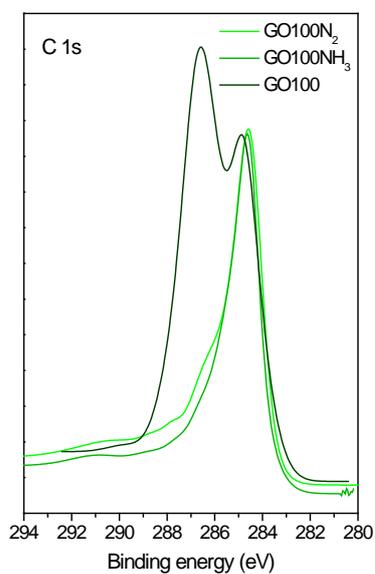


Figure 3. C 1s XPS

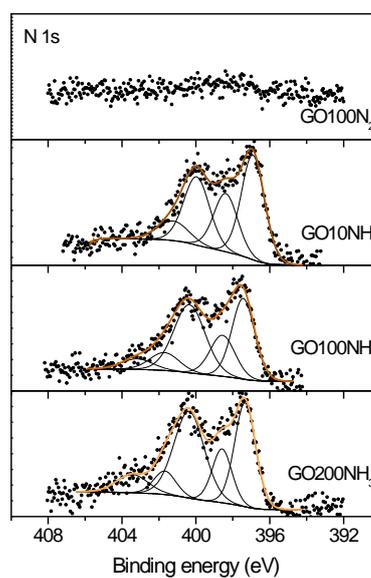


Figure 4. N 1s XPS