Green-Reduction of Covalently Functionalized Graphene Oxide with Varying Stoichiometry

A. Pruna, D. Pullini, D. Busquets

Abstract—Graphene-based materials were prepared by chemical reduction of covalently functionalized graphene oxide with environmentally friendly agents. Two varying stoichiometry of graphene oxide (GO) induced by using different chemical preparation conditions, further covalent functionalization of the GO materials with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride / N-hydroxysuccinimide and ascorbic acid and sodium bisulfite as reducing agents were exploited in order to obtain controllable properties of the final solution-based graphene materials. The obtained materials were characterized by thermo-gravimetric analysis, Fourier transform infrared and Raman spectroscopy and X-ray diffraction. The results showed successful functionalization of the GO materials, while a comparison of the deoxygenation efficiency of the two-type functionalized graphene oxide suspensions by the different reducing agents has been made, revealing the strong dependence of their properties on the GO structure and reducing agents.

Keywords—Graphene oxide, covalent functionalization, reduction, ascorbic acid, sodium bisulfate.

I. INTRODUCTION

LATELY, the sp^2-hybridized carbon sheets known as graphene have received increased attention for a wide range of applications thanks to their excellent electronic and mechanical properties [1]. To broaden the scope of applications, new strategies are developed for increasing the dispersability of graphene materials since the strong tendency to aggregation of graphene sheets represents the main drawback of solution-processable blending of graphene into a matrix. It is well-known that graphite oxide (GO) contains many defects with epoxide, hydroxyl, carbonyl, and carboxylic acid groups, as well as double bonds on the GO sheets that can be exploited for the selective intercalation or adsorption of ions and molecules as well as for covalent modifications.

A controlled chemical functionalization is considered an appropriate approach to achieve good processability of graphene in various media and a fine tuning of its various physico-chemical properties. The chemical activity of graphene and its electronic structure have been showed to be strongly affected by the functionalization of graphene sheet edges and demonstrated potential for field-effect transistors and spintronic devices [2]-[4]. Furthermore, while the chemical reduction of GO has attracted the most interest as a route for industrial production thanks to its simple procedure and low cost [5]-[7], the toxicity driven limitations of hydrazine-based reducing agents generated the introduction of new reducing agents e.g. an environmentally friendly ascorbic acid under mild conditions [8].

In this context, the properties of graphene materials are explored by a functionalization approach of GO with varying stoichiometry by employing carbodiimide chemistry [9] while sodium bisulfite is proposed as toxicity-free reducing agent. It is demonstrated that GO and functionalized GO (fGO) have been successfully reduced and the proposed approach presents great potential for production of graphene-based composites.

II. EXPERIMENTAL

A. Materials

Graphite powder (200 mesh (99.9995%)) was purchased from Alfa Aesar. All the other reagents were of analytical grade and used as received. Analytical grade (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Aldrich. Double-distilled water was used to prepare all aqueous solutions.

B. Preparation of GO

Graphite oxide (GO) powders were synthesized from graphite by modified Hummers method as we presented in a previous work [8]. Different structure of GO was obtained by oxidizing the graphite with H_2SO_4 and $KMnO_4$ in case of GO_A and $H_2SO_4:H_3PO_4$ (6:1 v/v) and $KMnO_4$ for GO_B. The obtained GO was subjected to a drying process at 50 ºC for 24 h.

C. Preparation of fGO

EDC (1:2 w/w) and NHS (1:2 w/w) were added to the GO dispersion and subjected to sonication for 1h. Further, the reaction was performed at 80ºC under mechanical stirring for 1h. Afterwards, the resulting functionalized GO (fGO) was centrifuged, washed with deionized water and vacuum-dried.

D. Preparation of Reduced fGO (rfGO)

Dispersion of fGO were prepared by sonication for 10 min. Reducing agents were added to the dispersions (r1:fGO=10:1 w/w and r2:fGO=1:5 v/v, where r1 is ascorbic acid and r2 is

sodium bisulfite) and reacted under mechanical stirring for 6h. Temperature of 50ºC was considered for reduction. Further, rGO films were washed with distilled water and dried at 50ºC.

E. Characterization

Thermo-gravimetric analysis (TGA) was conducted with a Q50 thermal analyzer (TA Instruments) under nitrogen flow at a scanning rate of 10ºC min^{-1}. The X-ray diffraction (XRD) spectra were taken on a D2 Phaser diffractometer (Bruker) using CuKα radiation and a voltage of 30 kV. The FTIR spectra were acquired on a FTIR Spectrum BX spectrometer in ATR mode (Perkin Elmer). inVia Raman spectrophotometer (Renishaw) with a laser wavelength of 514.5nm was used to characterize the obtained materials.

III. RESULTS AND DISCUSSION

The thermal stability of GO materials as a function of oxidation conditions was studied by TGA as shown in Fig. 1. While graphite showed thermal stability up to 650ºC, both GO materials proved thermally unstable and showed stepwise weight losses. The observed weight losses were assigned to inter-lamellar water and to the decomposition of the labile and more stable oxygen functional groups. The varying trend of mass loss observed for the two GO materials suggested less content of oxygen functional groups in GO_B with respect to GO_A.
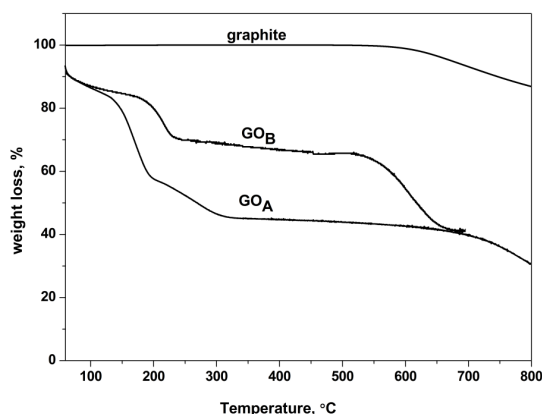

Fig. 1 TGA plots for GO materials as function of oxidation conditions

Upon oxidation of graphite, it was found that the GO materials could be easily dispersed in water as depicted in optical image in Fig. 2 (a). Subjected to reduction, the reduced GO (rGO) aqueous dispersions changed color from brown to black – see representative image in Fig. 2 (b). Higher hydrophilicity was observed for rGO_B material than rGO_A, which could be explained by the presence of a higher amount of residual oxygen resulted from a spatial hindrance of reducing agent towards the functional groups of the less expanded GOB.

The functionalized GO (fGO) dispersions subjected to reaction with ascorbic acid and sodium bisulfite turned black –

see Fig. 2 (c) - thus confirming the successful ability of the proposed agents towards the removal of oxygen functional groups from the two materials. For representation, only the GO_A counterparts are imaged. At the end of chemical reduction procedure, both dispersions exhibited good homogeneity and the materials appeared well dispersed. No noticeable optical difference was observed between the dispersions obtained by using the two reducing agents.
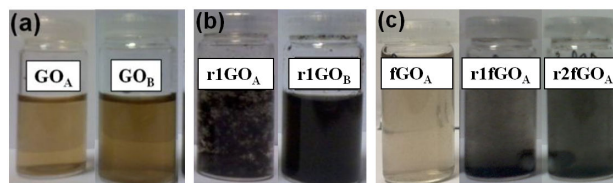

Fig. 2 Optical images of aqueous dispersions of: (a) GO as function of oxidation conditions, (b) GO upon reduction with ascorbic acid and (c) GO_A upon functionalization and reduction with ascorbic acid (r1) and sodium bisulfite (r2)

XRD was further performed in order to estimate the degree of reduction and it was found that they came into agreement with earlier results. Fig. 3 depicts the spectra obtained for the GO as function of oxidation conditions and effect of reduction with ascorbic acid on GO_A and functionalized GO_A (fGO_A). The varying expansion of graphite obtained in the two oxidation conditions is confirmed by the down-shift of the typical (002) diffraction peak of graphite from 26.5 degrees to 10.5 and 11.5, respectively which correspond to interlayer spacings of 0.83nm and 0.68nm, respectively. Upon the reduction with ascorbic acid, a partial recovery of sp2 lattice was observed for both GO and fGO materials by the up-shift of peak position. The slight difference in the angular value for (002) peak suggests less reduction ability in the case of fGO material.
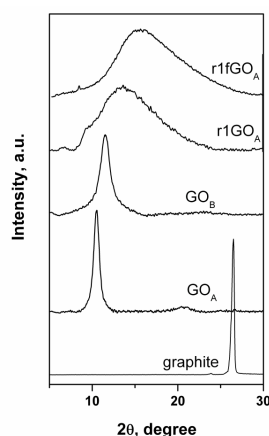

Fig. 3 XRD patterns of GO as function of oxidation conditions and effect of reduction with ascorbic acid on GO_A and fGO_A.

Fig. 4 shows the typical FTIR spectra of GO before and after reduction and functionalization, respectively. The spectra in Fig. 4 (a) confirmed the different composition of the GO

materials. Besides the presence of a peak indicative of unoxidized graphitic domains at 1602cm^{-1} [10], oxygen groups were indicated in GO_A by the presence of peaks at 1720, 1484, 1290, 1158, 1042 and 982cm^{-1} [8], [11]. The GO_B presents weaker bands than GO_A, along with a more intense peak at 1517cm^{-1} [8]. The reduction of both GO materials with the two green reducing agents was confirmed by FTIR spectra depicted in Fig. 4 (b). For exemplification, only the reduction of GO_A is depicted. The partial removal of decorating oxygen groups in rGO_A is revealed by the disappearance of band of adsorbed water, weakening of bands corresponding to oxygen-groups together with an increased peak intensity of C=C stretching at 1602cm^{-1} that suggests the recovery of sp^2 lattice. Upon functionalization of carboxylic groups (see the case for GO_A in Fig. 4 (c)), a new band appears at 1575cm^{-1} which is attributed to the transformation of γ(C=O) of —COOH to —COO— together with a peak at 1625cm^{-1} (the amide C=O stretching) while peak of GO at 1720cm^{-1} (stretching vibrational modes of the carbonyl groups) [12] disappears. Correspondingly, the spectra of reduced fGO_A materials show weaker bands for oxygen-containing groups along with the peaks relative to the covalent functionalization with NHS.
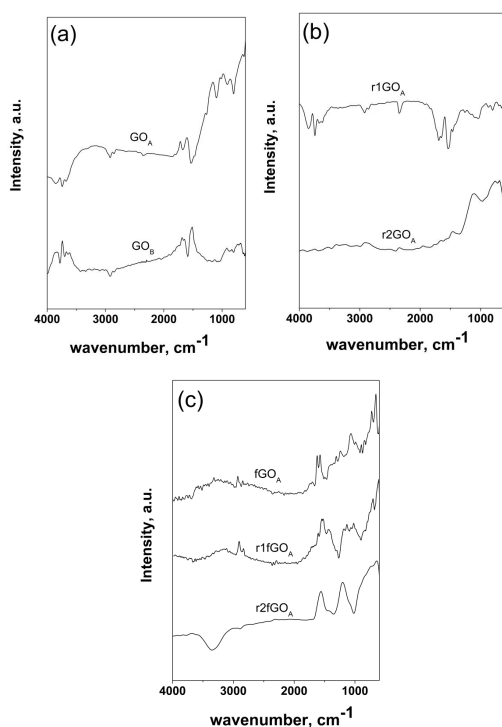

Fig. 4 FT-IR spectra of (a) GO as function of oxidation conditions, (b) GO_A upon reduction and (c) fGO_A before and after reduction (ascorbic acid (r1) and sodium bisulfate (r2))

Raman spectroscopy was further used to characterize the obtained graphene materials. For exemplification, the spectra of GO_A are depicted in Fig. 5. All materials showed the two main Raman features arising from the first-order scattering of the E_{2g} phonon of sp^2 C atoms and the breathing mode of k-point photons of A_{1g} symmetry, respectively [13]. The effect of the functionalization approaches on the Raman characteristics shows that both D and G bands undergo significant changes. Specifically, the I_D/I_G ratio increases upon functionalization procedure reflecting the increase in disorder [14]. The increased I_D/I_G ratio observed after reduction with both agents is indicative of defects obtained upon removal of oxygen functionalities, while ascorbic acid proves to be more efficient in this regard than sodium bisulfite.
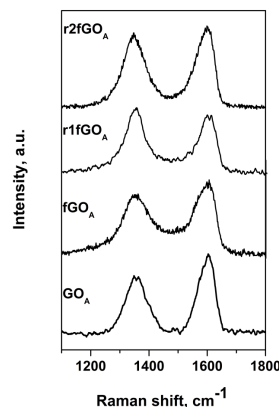

Fig. 5 Raman spectra of GO upon functionalization (a) graphene materials upon reduction with ascorbic acid (b) and sodium bisulfite (c) as depending on functionalization

So far, various reducing agents have been reported for the reduction of GO, including hydrazine and ascorbic acid. Here we demonstrate that sodium hydrosulfite can be used to reduce GO; the short time required for the reducing process could be the best advantage of such a reducing agent. Nevertheless, several factors could improve its reduction efficiency, such as the proportioning of reducing agent, use of catalysers or the reduction temperature [15]. Therefore, we believe that the reduction of GO using sodium bisulfite presents great potential and further study is ongoing.

IV. Conclusions

Successful preparation of GO nanosheets with varying structure is reported. Covalent functionalization was successfully achieved by employing simple carbodiimide chemistry. Chemical reduction of both GO and functionalized GO is proposed by employing environmentally friendly agents. A new route for the reduction of GO and functionalized GO is presented by employing sodium bisulfite at moderate temperature. Although sodium bisulfite showed lower efficiency, it can be improved by adjusting the reduction parameters. The approach followed in this study could provide great potential for composite applications.

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