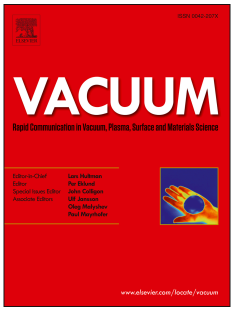

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X-RAY PHOTOELECTRON SPECTROSCOPY OF REDUCED GRAPHENE OXIDE PREPARED BY A NOVEL GREEN METHOD

Simona Rella[1], Maria Rosaria Acocella[2], Silvia Colella[3,6], Carola Esposito Corcione[4], Antonella Giuri[4], Gaetano Guerra[2], Andrea Listorti[5,6], Aurora Rizzo[6], Cosimino Malitesta[1*]

1. Laboratorio di Chimica Analitica, Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento (DiSTeBA), via Monteroni, km 1, 73100 Lecce, Italy
2. Dipartimento di Chimica e Biologia e Unità di Ricerca INSTM, Università di Salerno, Fisciano (SA), Italy
3. Dipartimento di Matematica e Fisica "E. De Giorgi", Università del Salento, Via per Arnesano, 73100 Lecce, Italy
4. Department of Engineering for Innovation, University of Salento, via per Monteroni, km 1,73100, Lecce, Italy
5. Center for Bio-Molecular Nanotechnology - Fondazione Istituto Italiano di Tecnologia IIT, Via Barsanti, 73010 Arnesano (Lecce), Italy
6. Istituto di Nanotecnologia CNR-Nanotec, Distretto Tecnologico via Arnesano 16, 73100 Lecce, Italy

*cosimino.malitesta@unisalento.it

Abstract

This work is focused on the surface characterization of reduced graphene oxide (rGO) obtained through reduction of graphite oxide. The reduction was performed using a green method (based on UV irradiation under N_2) with low environmental impact, free of additional functionalization reagents, simple and low-cost.

X-ray photoelectron spectroscopy (XPS) was applied for chemical characterization of surface C species showing a significant reduction of oxygen-containing functional groups from the surface of rGO.

Keywords: XPS; graphene oxide; green method; UV irradiation

Graphene is a 2-D single layer of sp^2-bonded carbon atoms characterized by high specific surface area, Young's modulus, thermal stability, mobility of charge carriers and plus fascinating transport phenomena such as the quantum Hall effect[1]. Graphene was first isolated from graphite by Geim and co-workers at Manchester University [2]. Up to now, several methods have been developed to prepare graphene.

The conventional method for preparing graphene is based mainly on preparing the precursor, graphite oxide, and then reducing graphite oxide by different approaches to remove a large portion of oxygen-containing functional groups such as carboxyl, epoxide and hydroxyl groups [3]. Researchers have proposed many methods to reduce graphite oxide [4], such as chemical vapor deposition (CVD), mechanical exfoliation, aerosol pyrolysis, solvothermal synthesis, epitaxial growth, electrochemical reduction, hydrothermal reduction, and thermal exfoliation and chemical reduction with various reducing agents (i.e.

hydrazine, sodium borohydride, hydroquinone and ,more recently, green reducing methods employing Vitamin C, fructose, UV irradiation [5,6]).

A very important parameter used to characterize the degree of oxidation in graphene is the sp^2 carbon fraction. Since the π-electrons from the sp^2 carbon largely determine the optical and electrical properties of carbon-based materials, the fraction of sp^2 bonding can provide insight into the structure–property relationships [7,8]. To modulate the electronic and optical properties of graphene via controlled deoxidation, a proper understanding of the role of the individual functional group in determining these properties is required [9].

The structural and compositional properties of these graphene materials are investigated by characterization methods commonly applied in materials science. These include, for example, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy, Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR).

The high specific area of the material has promoted an extensive use of XPS in its characterization (see e.g. [3,5,6,10–18]) also with the aim to evidence (surface) contamination originating from preparation process and possibly resulting in considerable negative effects on electronic and optical properties.

Previous studies reported the use of XPS in the characterization of reduced graphene oxide. In particular, a detailed analysis of C 1s core level spectra allowed to reveal the content and nature of carbon bonds attached to oxygen groups (C sp^2, C sp^3, C-OH – hydroxyl, C-O-C – epoxy, >C-O – carbonyl, COOH – carboxyl, C(O)OC – ester, etc.).

In this work, XPS is used to investigate the reduction of graphite oxide (GO) by a novel green method which conjugates the application of UV irradiation of an aqueous dispersion of GO [5] with the use of an inert atmosphere (made of N_2), which proved to favor GO reduction [8,19].

A scheme of photoreduction of graphite oxide is shown in Figure 1.

Figure 1

The mechanism of UV photoreduction of graphite oxide has been the subject of several papers (see e.g . ref. 20)

GO samples were prepared by Hummers' oxidation method [21], starting from a high-surface-area graphite, HSAG. 120 mL of concentrated sulfuric acid and 2.5 g of sodium nitrate were introduced into a 2000 mL three-neck round bottomed flask immersed into an ice bath and 5 g of graphite were added, under nitrogen, with magnetic stirring. After obtaining an uniform dispersion of graphite powders, 15 g of potassium permanganate were added very slowly to minimize the risk of explosion. The reaction mixture was thus heated to 35 °C and stirred for 24 h. The resulting dark green slurry was first poured into a copious amount of deionized water, and then centrifuged at 10000 rpm for 15 min with a Hermle Z 323 K centrifuge. The isolated GO powder was first washed twice with 100 mL of a 5 wt. % HCl aqueous solution and subsequently extensively washed with deionized water. Finally, it was dried at 60 °C for 24 h. Further information about GO are reported in previous papers [21,22].

GO was dispersed in water (0,1 mg/ml) by magnetic stirring for 30 minutes followed by sonication for 1 hour. Few milliliters of GO/water dispersion were degased by N_2 and placed into a UV oven (3D systems, 50/60 Hz) for 48 h under a nitrogen atmosphere. Reduced graphene oxide (rGO) undergoes to complete exfoliation, as proved by XRD data (not reported), resulting in a graphene material.

For XPS measurements, the samples were dried and anchored by copper adhesive tape to the bar of the unit sample holder and then introduced into the analysis chamber through a transfer probe.

X-ray photoelectron spectroscopy (XPS) measurements of graphite oxide (GO) and reduced graphene oxide (rGO) were performed with a Kratos Axis Ultra electron spectrometer using monochromatic Al Kα source (1486.6 eV) operated at 225 W (15kV, 15mA). Instrumental resolution (FWHM) at a pass energy of 20 eV as evaluated on the Ag 3d 5/2 was 0.60 eV and on standard PET is 1.0 eV.

Survey scan spectra were recorded using pass energy of 160 eV and a 1eV step. Narrow scans of C 1s and O 1s were acquired using a pass energy of 20 eV and a 0.1 eV step. The hybrid lens mode was used for all measurements. In each case the area of analysis was about 700 µm *300 µm. During the acquisition a system of neutralization of the charge has been used. Base pressure in the analysis chamber was 2.5×10^{-9} torr.

No degradation was observed under X-ray irradiation. Processing of the spectra, including fitting of high resolution spectra, was accomplished with CasaXPS Release 2.3.16 software. The binding energy (BE) scale was referenced to the C 1s line of graphitic carbon/C sp^2, set at 284.50 eV [23].

Fitting of C 1s signal was performed by subtracting Shirley background and using three components. A GL(30) lineshape (a combination of Gaussian 70% and Lorentzian 30%) was employed for a C-O component, including hydroxyl, epoxide, etc., and a C=O component. In addition, a graphitic carbon/C sp^2 component was fitted with Voigt line shape exhibiting a higher binding energy tail [24]. In particular, asymmetry was defined by a function LA(α, β, m), where α and β define the spread of the tail on either side of the Lorentzian component and the parameter m specifies the width of the Gaussian used to convolute the Lorentzian curve. While FWHM of GL components were free parameters in fitting procedure, LA parameters and relevant FWHM of graphitic carbon/C sp^2 component were fixed.

Assignment of peaks was based on literature [5,6,14,18].

Figure 2 (A) shows C1s XP spectrum of graphite oxide. It clearly indicates a considerable degree of oxidation in agreement with literature data [5,6,14,18]. The high binding energy component could include a carboxylic contribute as it is wider than other components. After reduction, the peak for the graphitic carbon/C sp^2 component becomes largely dominant (see Fig. 2 (B)) . Although the C1s XPS spectrum of reduced graphene oxide still exhibits oxygen functional groups, their intensities are much smaller than those in graphite oxide (Figure 2). This shows that most of oxygen-containing functional groups were removed upon the reduction.

Figure 2

The relative concentrations of surface functional groups obtained from fitting of the C 1s XPS regions are summarized in Table 1, along with fitting parameters.

Table 1

An evaluation of oxidation degree of analyzed materials can be obtained by rationing the area of graphitic carbon/C sp^2 component and the sum of areas of oxygenated components (Table 2).

Table 2

It is evident the significant removal of oxygenated groups upon reduction. In particular, as expected, reduction proved efficient in N_2 atmosphere.

Table 3 compares our results with findings reported in other graphite oxide reduction studies.

Table 3

In comparison to previous methods (Table 3), the proposed one (much more efficient than methods Nos. 2-6,8-10,12) is quite comparable in efficiency to those employing reductants, in solution such as hydrazine and NaBH4 (see Nos. 11 and 13),and plasma assisted reduction (see No. 7). However, the present approach seems superior because it is low cost, easy to apply and has a low environmental impact. In fact, it not required the use of toxic reducing agents or complex and expensive instrumentation (like plasma reactor). This improvement can facilitate the large-scale production of graphene from graphite oxide for a number of applications.

In conclusion, we successfully prepared reduced graphene oxide with a green method, as proved by XPS analysis. The proposed method appears better than previous ones in term of degree of reduction or of easy application. The realization of counter electrodes in composite polymeric material containing this graphene for solar cells is under investigation.

Acknowledgements

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Figure captions

Figure 1 : Scheme of photoreduction of graphite oxide to produce reduced graphene oxide. Irradiation results also in exfoliation of graphite matrix.

Figure 2 : Fitted C 1s XP spectrum of graphite oxide (A) and reduced graphene oxide (B) after UV reduction (48h in N_2 atmosphere)

Table captions

Table 1: Results of fitting of C 1s XPS regions of graphite oxide before and after treatment

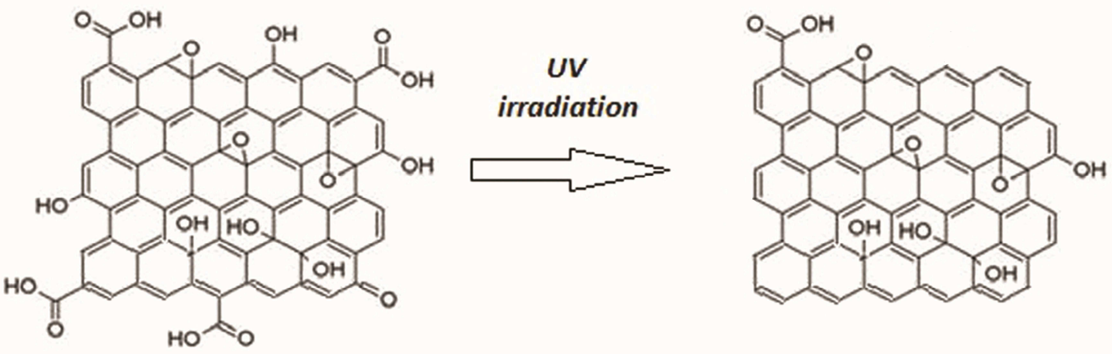
Table 2 : Degree of oxidation

Table 3 : Summary of C sp2 component/ oxygenated components ratios of rGO prepared by different approaches. (*) estimated from Fig.6 (b) [5]

	GO				r-GO UV oven for 48 h in N_2 atmosphere			
Assignment	BE [eV]	Lineshape	FWHM	Surface group distribution [%]	BE [eV]	Lineshape	FWHM	Surface group distribution [%]
C sp^2	284.50	LA(1.3,3,3)	1.00	69.01	284.50	LA(1.3,3,3)	1.00	83.76
C-O	286.74	GL(30)	1.18	17.75	286.54	GL(30)	1.21	8.01
C=O	288.19	GL(30)	2.27	13.24	288.34	GL(30)	2.07	8.23

Ratio	GO	r-GO
		UV oven for 48h in N_2 atmosphere
(Graphitic component)/(Oxygenated Components)	2.22	5.15

No.	REDUCTION METHOD	RATIO	REF.
1	UV irradiation 48h in N_2 atmosphere	5.15	Present work
2	UV irradiation	1.39(*)	[5]
3	Thermal reduction oven – 220°C – air	2.13	[18]
4	Solvothermal reduction H_2O – 100°C – 24h	0.90	[25]
5	Solvothermal reduction DMF – 150°C – 1h	1.98	
6	Thermal annealing in Ar/H_2 atmosphere [150°C]	2.57	[26]
7	Plasma-assisted reduction in Ar/H_2 atmosphere [150°C]	5.02	
8	Microwave-irradiation process in hydrogen plasma	3.75	[27]
9	γ-ray irradiation in alcohol/water	4.21	[28]
10	Reduction agent: $NaBH_4$ – 1h	2.58	[29]
11	Reduction agent: $NaBH_4$ – 48h	5.8	
12	Reduction agent: N_2H_4 – 1h	2.78	
13	Reduction agent: N_2H_4 – 48h	5.8	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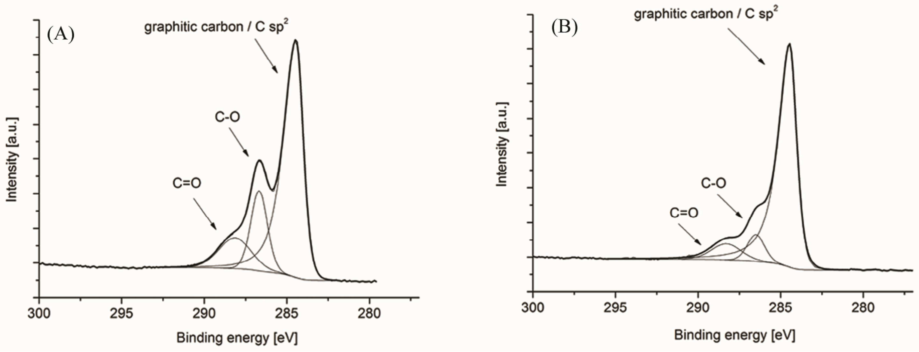
irradiation
OH
HO
O
Graphite oxide
Reduced Graphene oxide


(A)
graphitic carbon / C sp^2
C-O
C=O
Intensity [a.u.]
300
295
290
285
280
Binding energy [eV]
(B)
graphitic carbon / C sp^2
C-O
C=O
Intensity [a.u.]
300
295
290
285
280
Binding energy [eV]

Highlights:

- Surface characterization of graphene obtained through reduction of graphite oxide
- Reduction by a green method
- Chemical characterization by X-ray photoelectron spectroscopy