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Chemical reduction of graphene oxide with sodium borohydride in aqueous media

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Abstract

Reduced graphene oxide (rGO) is a very promising carbon nanomaterial for biomedical applications due to its high specific surface area, hydrophobicity, mechanical strength and biocompatibility. To evaluate the reduction of graphene oxide (GO) functional groups using sodium borohydride ($NaBH_4$) in aqueous media, GO was synthesized from graphite flakes by a modified Hummers method, chemically reduced with $NaBH_4$ using distilled water as solvent and characterized by X-ray diffraction and photoelectron spectroscopy. Most of the oxygenated groups were successfully reduced, leaving only 8.3% of oxygen and 0.3% of sodium in the final composition.
Keywords: reduced graphene oxide; carbon nanomaterials; nanocomposites; biomaterials.

Introduction

Graphene and its oxides (Fig. 1) are materials with great mechanical, thermal and electrical properties that are expanding its applications beyond electronic and chemical areas toward biomedical industry, such as drug delivery, biosensors, imaging, phototherapy, antimicrobial therapy, orthopedic, cardiovascular, dental and ophthalmological applications [1,2].

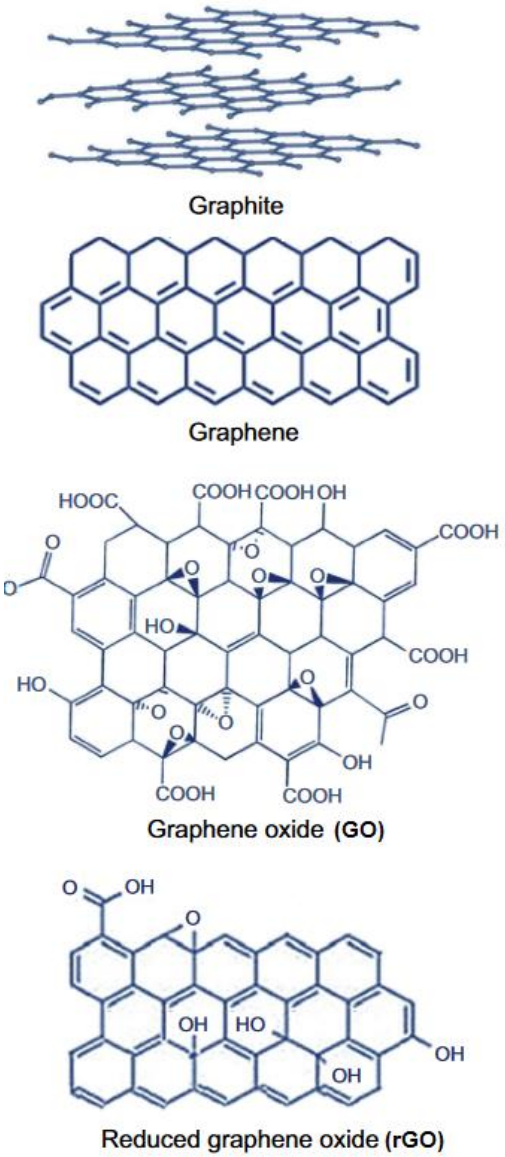

Figure 1 – Structures of graphite, graphene, GO and rGO [3].

The use of reduced graphene oxide (rGO) as a nanoscale reinforcement for oxide coatings in dental and orthopedic implants has great potential to improve their mechanical and antibacterial properties. Its reactive oxygenic groups, present on its edges and planes, can stabilize the dispersion of rGO in aqueous media, enhance the stress transfer in the composites and improve the interfacial bonding with living tissue [4].

Reduction of graphene oxide (GO) can be done by different chemical, thermal and light-driven methods [3]. The aim of this work is to evaluate the chemical reduction of GO with sodium borohydride ($NaBH_4$) in aqueous media.

Experimental Procedure

GO was synthesized by a modified Hummers method [5]. Briefly put, 1,5 g of graphite powder and 0,75 g of $NaNO_3$ were mixed with 35 mL of H_2SO_4 in a beaker and stirred for 2h in an ice bath. Then, 4,5 g of $KMnO_4$ was slowly added in three aliquots (1,5 g each) every 1h under vigorous stirring. The mixture was removed from the ice bath, heated to 35 ◦C and stirred for 30 min. Then, 69 mL of water was added, heated to 95°C and stirred for 10 min. Then, 210 mL of water and 5 mL of H_2O_2 was poured under stirring. The mixture was transferred to Falcon tubes and centrifuged for 10 minutes at 6000 rpm with HCl and then, three times with water. The solid was frozen with nitrogen and lyophilized for 3 days.

To chemically reduce GO into rGO, a method similar to that described by Alizadeh and Soltani [6] was applied, but using distilled water instead of methanol as solvent. First, 30 mg of graphene oxide was dispersed in 20 mL of water and sonicated. The pH was adjusted to 9 by addition of Na_2CO_3 solution (5%). Then, 330 mg of $NaBH_4$ was added to the dispersion. The mixture was stirred for 5h at 60 ◦C, centrifuged with methanol and water until a neutral pH was obtained. Finally, the solid samples were dried in an oven at 100 ºC for 24h.

The obtained powders were characterized by X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS).

Results and Discussion

The XRD patterns of the synthesized materials are shown in Fig. 2. In the literature [7], the peak of GO appears around 2θ = 11°. A shift to larger angles indicates a smaller amount of oxygen in the sample. Initially, graphite has an interplanar distance of 0,337 nm (2θ = 26.4°), which increases to 0.858 nm (2θ = 10.3°) after oxidation to form GO, due to the formation of epoxy, hydroxyl and carboxyl groups. With reduction, the interlayer distance contracts back to 0,374 nm (2θ = 23.7º) due to the removal of these functional groups, returning to an XRD pattern similar to that of graphite, but with a broader peak [7].

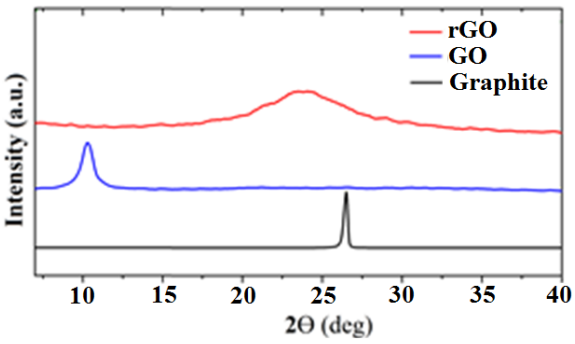

Figure 2 – XRD diffractogram of graphite, GO and rGO.

The XPS spectra are shown in Fig. 3. Five different peaks are present for GO, centered at 284.5 (C-C sp^2), 285.2 (C-C sp^3), 287.0 (C-O), 288.3 (C-OH), and 289.5 eV (COOH). Most of these peaks disappear for rGO, showing that the chemical reduction was successful in reducing most of the oxygenated functional groups, but a small amount is still present, as can be seen in Tables 1 and 2.

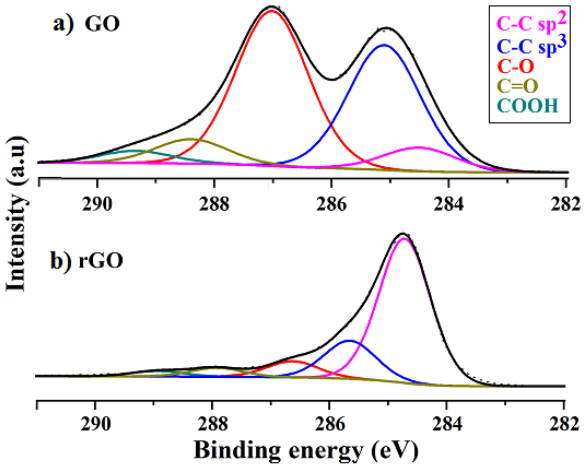

Figure 3 – XPS spectra of GO and rGO.

Table 1 – Bonding ratios (%) of GO and rGO

	GO	rGO
C-C sp^2	7.0	67.8
C-C sp^3	36.8	17.9
C-O	45.6	7.6
C=O	7.2	4.2
COOH	3.6	2.6

Table 2 – Composition (at%) of GO and rGO

	GO	rGO
C	74.6	91.6
O	25.5	8.2
Na	0.0	0.3

The final composition of rGO (Tab. 2) has a C/O ratio of 11.2, higher than the 8.6 ratio produced by Gao et al. [8] in a similar procedure.

Conclusions

Chemical reduction with $NaBH_4$ proved to be an easy and efficient method to produce rGO in aqueous media, with a high C/O ratio and almost no elemental impurities. Since $NaBH_4$ is not very good for reduction of epoxy, carboxylic acids, and alcohol groups, a future work should test if, after reduction, dehydration with sulfuric acid may reduce these oxygenated sites to obtain an even higher C/O ratio.

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