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Influence of the reduction strategy in the synthesis of reduced graphene oxide

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ABSTRACT

In this work, a comparative study of the different graphene oxide reduction strategies to produce reduced graphene oxide are discussed. Firstly, the optimization of the well-known oxidation route reported in literature (Improved Hummers Method) to obtain graphite oxide was carried out. Subsequently, different sets of reduced graphene oxide powders were synthesized through three different reduction routes: chemical, thermal and multiphase methods in order to obtain the most effective reduction strategy. Samples were analyzed by Raman spectroscopy, SEM, FTIR, elemental analysis, X-ray Diffraction and TGA. It was demonstrated that multiphase reduction method, e.g. combination of more than one reduction route, specifically, thermal and chemical ones, allowed to enhance the effectiveness for the removal of the oxygen functional groups. A mild thermal treatment followed by a chemical reduction of graphene oxide using ascorbic acid as reducing agent, showed that the 47% of oxygen functional groups was reduced. This manuscript demonstrates that the amount of oxygen functional groups in the reduced graphene oxide structure is highly dependent on the reduction strategy. These amount of oxygen functional groups could directly affect the use of reduced graphene oxide in the different potential applications proposed in bibliography.

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1. Introduction

Graphene is a two-dimensional (2D) carbon allotrope with a honey-comb lattice shape in which each carbon atom forms one vertex [1]. Since its discovery in 2004, graphene has been attracted the attention of researchers due to its extraordinary properties and its potential applications [2]. The large variety of methods to synthesize graphene, such as mechanical exfoliation process and cleavage [3], chemical vapor deposition (CVD) [4] or chemical reduction of graphene oxide [5], can be grouped in two different approaches: Bottom-Up or Top Down. Bottom-Up approach consists on the synthesis of graphene starting with carbon atoms or molecules and build up to graphene deposited over a substrate. On the other hand, in the Top Down approach, a pattern generated on a large scale (graphite) is reduced to graphene [6]. Graphite is the most known raw material used in the Top Down approach to synthesize reduced graphene oxide or powder graphene. Graphite oxide is obtained by treating graphite with strong oxidizing agents [7]. This material can be defined as a set of functionalized sheets of

graphene formed by different oxygen functional groups, such as epoxides, hydroxides and carboxyl. The incorporation of oxygen groups into graphite makes its structure more hydrophobic, making possible the separation of its layers in aqueous solution by sonication [8,9] to obtain graphene oxide. In literature, several methods have been reported how synthesize graphite oxide such as Brodie [10], Staudenmaier [11] and Hummers Method [7] and its variations (Modified and Improved Hummers method) [12]. This material is considered an intermediate for the manufacture of reduced graphene oxide, which can be defined as a homogenous material with structural defects, resulting from the elimination of a large portion of oxygen functional groups from the graphene oxide structure [13]. In general, reduced graphene oxide structure is similar to that of graphite oxide but it is not completely homogenous like graphene due to the occurrence of remaining functional groups [14]. Reduced graphene oxide can be obtained by removing the oxygen functional groups from graphite oxide following different strategies [15]: thermal reduction [16,17], photo reduction [18], electrochemical reduction [19], microwave reduction [20], solvothermal reduction [21], chemical reduction [5,22,23] by using a wide variety of reducing agents (hydroiodic acid, ascorbic acid, hydrazine, NaBH₄ or some metal hydrides

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[15]) and multiphase reduction [24–26]. Fig. 1 summarizes the advantages and disadvantages of the most important reduction techniques listed above.

In this work, the structure and chemistry of different reduced graphene oxide samples prepared through different graphene–reduction strategies such as chemical, thermal and multiphase techniques, were compared. Graphene oxide can be reduced by using several reducing agents. In this work, hydrazine and ascorbic acid have been selected as the reducing agents. Hydrazine (N_2H_4) is a colourless flammable liquid with an ammonia-like odor, highly toxic and dangerously unstable unless handled in a solution [27] but it is a powerful and a convenient reductant because the by-products yielded in the reduction process are typically nitrogen gas and water. On the other hand, ascorbic acid or vitamin C, is a natural organic compound with antioxidant properties that owns both innocuous nature and environmentally friendly characteristics. It is a white solid that dissolves well in water to give mildly acidic solutions [28]. Ascorbic acid has been proposed recently as a potential agent to be used for graphene oxide reduction [29,30]. Chemical reduction technique involves the use of a liquid media, which can difficult the industrial production of reduced graphene oxide. However, other reduction procedures do not require this liquid media such as thermal reduction of graphene oxide. Even though, this procedure presents the disadvantage of the occurrence of a violent expansion of the material, which could damage the structure of the resulting material. A combination of both chemical and thermal reduction techniques was performed. The resulting products were compared to those separately obtained with each of the above-mentioned techniques.

2. Materials and methods

2.1. Materials

Graphite powder (<20 μm) was supplied by SIGMA-ALDRICH (Spain). Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4), chlorhydric acid (HCl), hydrogen peroxide (H_2O_2) and ethanol

($\text{CH}_3\text{CH}_2\text{OH}$) with a purity grade of 99%, 96%, 37%, 99.5% and 99.5%, respectively, were supplied by PANREAC (Spain). Monohydrate hydrazine with a purity grade of 98% was supplied by SIGMA-ALDRICH (Spain) and ascorbic acid with a purity grade of 99% was supplied by VWR (Spain).

2.2. Methods

2.2.1. Synthesis of graphite oxide (GrO)

Graphite oxide was synthesized following the Improved Hummers Method with slightly modifications [7]. A mixture of 15 g of graphite and 45 g of KMnO_4 (oxidizer agent) was slowly added to 400 mL of H_2SO_4 under constant agitation. The mixture was maintained at 50 °C for 3 h. Then, the mixture was added to a beaker containing a mixture of 400 g of flake ice and 3 mL of H_2O_2 to stop the oxidation reaction. The mixture was filtered under vacuum; then, it was washed with 200 mL of deionized water, HCl and $\text{CH}_3\text{CH}_2\text{OH}$. Finally, the compact cake was dried at 100 °C overnight.

2.2.2. Synthesis of graphene oxide (GO)

Graphene oxide synthesis was carried out by graphite oxide exfoliation. Thus, a mixture of 800 mg of graphite oxide and 800 mL of deionized water was introduced in a cooling jacketed reactor to maintain the solution at room temperature. The mixture was sonicated (50% amplitude and a complete cycle) for 2 h in order to separate the graphene sheets of graphite oxide to obtain graphene oxide [31]. The final mixture was centrifuged and the obtained solid was dried overnight at 80 °C.

2.2.3. Synthesis of reduced graphene oxide: reduction strategies

2.2.3.1. Chemical reduction. Chemical reduction of graphene oxide was carried out using two different oxidizing agents: hydrazine and ascorbic acid. As commented above, hydrazine was selected because of its powerful reduction capacity but it is a very toxic product, which is also detrimental for the environment. For this reason, an alternative reducer agent, ascorbic acid, was proposed. This agent is innocuous and environmentally friendly.

THERMAL REDUCTION	CHEMICAL REDUCTION	SOLVOTHERMAL REDUCTION	ELECTRO-CHEMICAL REDUCTION	PHOTO REDUCTION	MICROWAVE REDUCTION	MULTISTEP REDUCTION
ADVANTAGES	ADVANTAGES	ADVANTAGES	ADVANTAGES	ADVANTAGES	ADVANTAGES	ADVANTAGES
- High reduction degree - Environmentally friendly - Non-expensive	- High reduction degree - Non Expensive - High amount of reduction agents	- Quick - Effective	- Removal of oxygen groups facilitated by electrolytes - Longer RGO sheets	- Under U.V. irradiation, easily oxygen reduction - More removal of epoxy groups	- Quick reduction	- Very high reduction degree - Combination of best reduction techniques
DISADVANTAGES	DISADVANTAGES	DISADVANTAGES	DISADVANTAGES	DISADVANTAGES	DISADVANTAGES	DISADVANTAGES
- Small and wrinkly RGO sheets - Release of CO_2 causes structural damage	- Non environmentally friendly	- Extreme thickness causes the breaking of RGO sheets	- More defective RGO sheets	- Complex equipment	- High cost equipment	- High time consuming

Fig. 1. Advantages and disadvantages of reduction strategies used in the production of reduced graphene oxide.

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