



Temperature influence on the synthesis of pristine graphene oxide and graphite oxide



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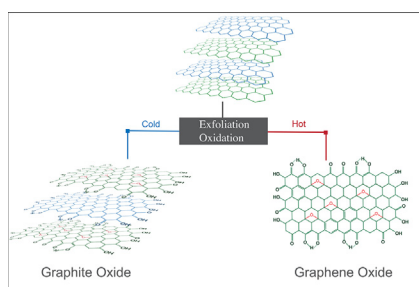
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HIGHLIGHTS

- Temperature affects the expanded graphite exfoliation during the oxidation process.
- Graphene oxide is formed at moderate temperature.
- Graphite oxide is formed at low temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Derivative oxide carbon materials, such as graphene or graphite oxides, have been recently considered to be a promising material in a wide scenarios of emerging technologies due to their physical and chemical properties, as well as, for their low production costs. Even if apparently similar, these materials exhibit different physical and chemical properties. One of the critical issue is associated with the exfoliation process and contributes to the formation of graphene oxide and graphite oxide material. Here, we show a single synthetic wet method to produce graphene or graphite oxide by applying a control of the operational temperature during the reaction. The process was optimised to obtain the pristine graphite oxide at low temperature ($T = 0\text{ }^{\circ}\text{C}$) and the pristine graphene oxide at higher temperature ($T = 30\text{ }^{\circ}\text{C}$). Finally, the peculiar features of these materials were described using spectroscopic, structural and morphological measurements.

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1. Introduction

Carbonaceous materials, such as nanotube, fullerenes, carbon fibres, are attracting attention due to their physical and chemical properties [1,2]. Recently, two oxide carbon derivatives, i.e.

graphene oxide and graphite oxide, are understudy for their similar properties. The interest in graphene oxide (GO) grew in the context of finding a more suitable and scalable method for producing pristine graphene. Nevertheless, GO exhibits, in comparison with pristine graphene, distinct features which can be employed for novel applications. Graphene oxide consists of a two-dimensional plane bonded with oxygen domains which provide an amphiphilic character with carbon atom hybridization from sp^2 and sp^3

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due to the binding of oxygen atoms into the graphene basal plane. The GO is a non-stoichiometric “molecule” because of its starting material (often expanded graphite) which influences the size of the basal plane of the final product [3–7]. Differently, graphite oxide (GtO) can be described as a “grain” of graphite where the surface is oxidized. In practice, the synthetic protocol consists of two main steps: exfoliation and oxidation. In the first step, each carbon layer is “peeling” from graphite grain by means of an exfoliating agent (often sulphuric acid). Then, the basal plane is oxidized by an oxidizing agent (commonly KMnO_4). A key issue on the wet synthesis of GO is the exfoliation step [8]. When the exfoliation step is not fully completed, a resulting GtO material is produced. This latter material has relevant properties such as an appreciable electric conductivity, which can be categorised in between graphene and graphene oxide. However, a lack of information on the behaviour of these materials causes a missing of a clear/standard synthetic procedure and mixing up the results of the characteristics of GO or GtO. Often, old literature reported the formation of graphene oxide as graphite oxide because of the little knowledge about the graphene and graphene derivatives materials around 2010. For example, under certain conditions of low number of non-exfoliated layers, GtO and GO exhibit similar spectroscopic features [9].

Essentially, three basic approaches, derived from Brodie method [5], are used as starting procedure for synthesizing GO (eventually GtO): Hummers [4], Staudenmaier [10] and Hofmann [3] methods. All of these methods produce graphene oxide by exfoliating and oxidizing of the graphite powder via chemical wet reactions. However, those procedures imply some limitations in the practical use [9,11,12]. First, the reactions involve hazardous reagents (e.g., sodium nitrate or potassium chlorate). Second, some reagents, such as sodium nitrate or fuming nitric acid, introduce heteroatoms or hole defects which affect the reactivity and the structural characteristic of GO [13,14]. Third, these methods are time-consuming (several days) with a low final yield. For these reasons, variation of Hummers-Staudenmaier-Hofmann methods have been investigated [6,15]. In the perspective of mass production of GO, Sun et al. [7] proposed a four steps protocol using a lower amount of exfoliating agent (sulphuric acid) with the positive consequence of getting high yield and quality GO. To the best of our knowledges, any clear distinction between the synthesis for graphene oxide and graphite oxide is reported and often GO dispersions consists of a mixture with GtO. Somehow, GtO is treated as undesirable product which affects the final GO yield.

The present paper is focused on the description of an alternative production method for graphene or graphite oxides, based on the four steps described in the Sun approach [7]. This approach has the advantage of producing high GO/GtO yield and allows a scale up production. Here, a single protocol is reported to synthesized both GO or GtO by only changing the operational temperature during the reaction. Our results provide experimental evidences concerning the difference of physical chemical properties of the final product of synthesis (GO and GtO) by taking advantage of handy techniques.

2. Experimental

2.1. Chemicals

The following chemicals were used as received: KMnO_4 (Sigma–Aldrich), H_2SO_4 (98%, Sigma–Aldrich), HCl (37%, Sigma–Aldrich), ECOPHIT 50 (size 40–50 μm , SGL GROUP).

2.2. Graphene oxide synthesis

The production of graphene oxide was carried out using a modification of the Sun protocol, described in our previous work

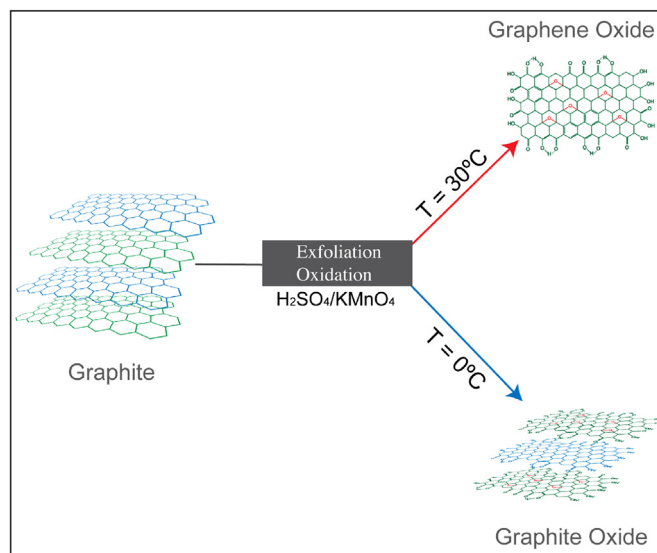


Fig. 1. Reaction scheme for the synthesis of graphene oxide and graphite oxide.

[16]. Briefly, expanded graphite (2.5 g) and KMnO_4 (7 g) were introduced into a 500 mL beaker and stirred until homogeneity. The beaker was placed in an ice-bath and 50 mL of concentrated sulphuric acid (98%) were added slowly¹ with continuous stirring with magnetic stir bars until a paste (green-petrol colour) was obtained. The beaker was placed into a water bath at about 30 °C for 30 min to produce a spontaneous volumetric expansion. Next, the hydrolysis of the material was obtained adding 200 mL of distilled water very slowly in order to prevent an uncontrolled temperature increase. Then, the green-brownish liquid was placed in a water bath at 80 °C for 1 h to obtain a darker suspension. The warm suspension was paper filtered (2 μm pore size) and washed with 500 mL distilled water, 500 mL HCl 0.15 M (to remove Mn^{2+}) and finally with 500 mL distilled water. The presence of sulfate ions in the GO dispersions was checked by a BaSO_4 spot test. The solid samples were prepared by drying in an oven at 80 °C overnight.

2.3. Graphite oxide synthesis

The synthesis of graphite oxide dispersion was carried out by means of lowering the operational temperature for the synthesis of graphene oxide. In practise, all the reagents were pre-cooled for about 2 h in an ice-bath. Then, the method follows each synthetic step described above except for maintaining the temperature as low as an ice-bath temperature during the entire synthesis process. For this reason some differences were encountered. First, the colour of the mixture were dark/black in all steps. Next, the volumetric expansion was suppressed [8], and, finally, the product appears as a powder-like instead of flaky material. The solid samples were prepared by drying in an oven at 80 °C overnight.

A scheme for the synthesis of graphene oxide and graphite oxide is shown in Fig. 1.

The direct observation of the two raw materials showed some peculiar difference: GO sample is a flake-like material that cannot be easily powdered when is treated with pestle and mortar and pasty material is obtained (may be due to the adsorption of

¹ The temperature is kept below 55 °C to prevent accidental explosion due to the presence of Mn_2O_7 in a solution of sulphuric acid.

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