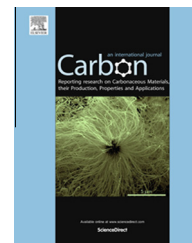


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# Few-layer graphene by assisted-exfoliation of graphite with layered silicate

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## ABSTRACT

Few-layer graphene has been achieved in liquid dispersion from graphite by the assistance of titanasilicate JDF-L1, using ultrasound and methanol as dispersive media. After a sedimentation step, both the dispersed and the sedimented phases were collected and then the titanasilicate was removed by alkaline hydrothermal dissolution from the mixed materials to obtain few-layer graphene (FLG) and sedimented material, respectively. The production of smaller particles was confirmed by means of N<sub>2</sub> adsorption and zeta-potential measurements, so that the BET specific surface area increased from 20 m<sup>2</sup>/g of the raw graphite to 333 ± 22 m<sup>2</sup>/g in FLG. Raman spectroscopy shows a decrease in the ratio of intensities of the peaks G and 2D from 3.8 in the raw material to 2.5 in FLG. Particles as fine as 1.3 nm, corresponding to 4-layered FLG, were observed by AFM, while high-resolution TEM showed defect-free regions of graphene.

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## 1. Introduction

Since graphene was firstly isolated in 2004 [1], it has become one of the most studied materials due to its exceptional mechanical, thermal and electronic properties. This interest has induced the necessity for new scalable preparation routes, since the already existent methods are too expensive and achieve low yields. One of the most common syntheses is based on an oxidation–reduction process, but the preparation of graphene oxide yields to an increase in structural defects and the process is not environmentally friendly due to the use of highly oxidative materials and inorganic acids [2].

Among all the procedures present in literature, the most promising are based on the exfoliation of graphite in liquid media by means of ultrasound treatment. It has been shown that the final material has low defect concentration, but the

yields are still very low. Different organic solvents have been used following such procedure, obtaining the best results for those that have similar surface tension to graphite, such as *o*-dichlorobenzene [3], *N*-methylpyrrolidone [4] or benzylamine [5]. However, these are expensive solvents and require special handling. Other researchers have tried this procedure assisted by surfactant molecules, such as sodium cholate [6], polyvinylpyrrolidone [7], cetyltrimethylammonium bromide [8], gum Arabic [9] and sodium dodecylbenzene sulfonate [10], which allowed the use of water as solvent, or organic salts in organic solvents [11]. In all these cases the exfoliation of graphite into graphene has increased its yield compared to the previously commented.

In this work, we show an exfoliation process from graphite powder into nanographite, or hereafter few-layer graphene (FLG), by the use of porous layered titanasilicate JDF-L1

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[12,13] as exfoliation assistant and methanol as solvent. Thin graphene-like particles were stuck on the external surface of the sheet-like JDF-L1 particles so that the supernatant of the dispersion was constituted in a material with textural and structural features far superior to those of the initial graphite. JDF-L1 has been mainly applied in gas separation embedded in a polymeric matrix membrane [14,15], as a biocide by exchanging with Ag, Zn or Cu ions [16], and crystallized on glass fibers as a hydrogen adsorbent [17]. A few layered materials such as sepiolite [18,19], magadiite [20] and montmorillonite [21] have been used to obtain graphene-like materials after impregnating them with certain organic compounds and successive carbonization in  $N_2$  atmosphere. However, these are much more complex processes than the one proposed here, where no organic molecules are decomposed. In addition, the chosen solvent used was methanol, which removal is much easier since its boiling temperature and vapor pressure are much lower than those of water or the other organic solvents previously commented. Besides, JDF-L1 is inexpensively prepared, without the use of any organic molecule, it has no pollutant behavior and it is easily removed by alkaline hydrothermal dissolution to obtain the final material. Overall, the new process proposed here is scalable and chemically friendly.

## 2. Experimental section

### 2.1. Exfoliation process

400 mg of 5  $\mu\text{m}$  milled graphite GR5 (supplied by Richard Anton KG) and 1.6 g of sheet-like crystals of JDF-L1 ( $0.1 \times 3 \times 3 \mu\text{m}$ ) previously synthesized [22] were dispersed in 150 mL of methanol (Scharlau, HPLC grade, 99.99 wt%), see Fig. 1. This dispersion was stirred at room temperature for 2 h. Subsequently an ultrasound (US) bath treatment (P Selecta Ultrasons 50/60 Hz) was carried out for another 2 h maintaining the temperature of the bath below 35  $^\circ\text{C}$ . It is worth mentioning that the ultrasound time was short as compared to others: e.g. 100 h when commercial graphite was treated with gum Arabic [9].

To allow the separation of larger particles from smaller ones a sedimentation step took place. Two sedimentation times (1 h and 2 h) were tested, obtaining the best results when the process was carried out for 1 h. After this period of time the supernatant was separated by means of a glass pipette from the sedimented particles and both materials

were dried in a convention oven at 70  $^\circ\text{C}$  for 2 h, obtaining 50 mg from the supernatant fraction. To ensure that the exfoliation in smaller particles taking place was due only to JDF-L1 assistance, a control sample was prepared. This consisted in the dispersion of raw graphite in methanol performing all the previous procedure without the layered silicate.

Since the final material must not have JDF-L1 a process to completely remove it was carried out. Due to the limited amount of material obtained in the supernatant phase, up to 5 supernatants (i.e. about 250 mg) obtained in the same conditions were collected and subsequently dispersed in an aqueous solution (30 mL) of 0.1 wt% of NaOH (Scharlau, pellets, extra pure). After stirring for 2 min, this dispersion was transferred to a 35 mL Teflon-lined autoclave and maintained for 24 h at 180  $^\circ\text{C}$  in a rotatory oven at 15 rpm speed. Then, the product was washed with water (20 mL) and centrifuged at 5000 rpm for 20 min. This was repeated 5–6 times, so that no inorganic remain (due to possible traces of NaOH and JDF-L1) was observed by thermogravimetry analysis (TGA). This material was dried in an oven for 2 h at 70  $^\circ\text{C}$ , obtaining 180 mg of few-layer graphene (FLG), thus the yield was of about 9%. To show up that the exfoliation process only took place on the supernatant fraction, the same process was carried out on the sedimented fraction and the obtained product was also characterized (sedimented material). In addition, to ensure that this treatment with NaOH did not produce any change in the graphitic structure, it was carried out on a control sample too. Finally, NaOH was used to remove the titanossilicate because it is a cheap reactant in which the silicate is soluble under high pH hydrothermal conditions.

### 2.2. Characterization

Supernatant and sedimented materials, FLG product and the different control samples were characterized by zeta-potential measurements,  $N_2$  adsorption, TGA, XRD, SEM, TEM, Raman, UV-vis spectroscopy and AFM.

Zeta-potential measurements were performed on a Brookhaven Instruments 90 Plus equipment, employing the Smoluchowski equation. The samples were dispersed in water using an ultrasound bath for 15 min and all the measurements were conducted at 25  $^\circ\text{C}$ .

All the materials were characterized by  $N_2$  adsorption to quantify the external surface area which in this case indicates a reduction in the number of layers present in the graphitic materials. The measurements were carried out in Tristar

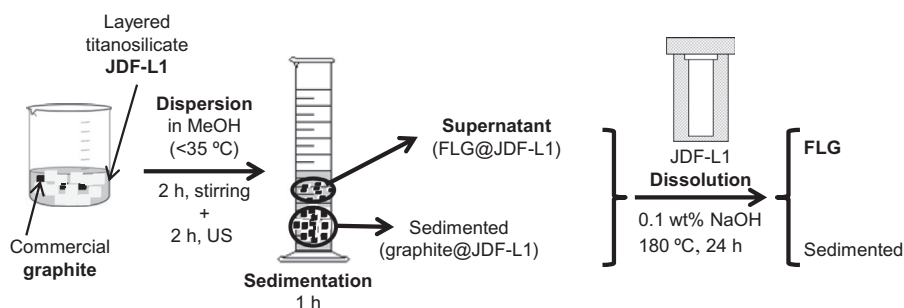


Fig. 1 – Representation of the exfoliation process; FLG corresponds to few-layer graphene.

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