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A comparative study on different aqueous-phase graphite exfoliation methods for few-layer graphene production and its application in alumina matrix composites

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ABSTRACT

Four different methods (attrition milling, shear mixing, low-power bath sonication and tip sonication) used for the aqueous-phase, surfactant-assisted exfoliation of graphite were compared. Few-layer graphene (FLG) concentration, yield and production rate were measured for each method at different production times and the quality of the as produced FLG was determined using Raman spectroscopy and X-ray diffraction. It was inferred from the results that a combined method comprising tip sonication and shear exfoliation would offer the best balance between quality and quantity of FLG for relatively short processing times (<6 h). FLG dispersions produced with this method were used to fabricate 1 wt.% FLG/Al_2O_3 nanocomposites by ball milling and extrusion, followed by pressure-less sintering. The influence of the FLG addition on the microstructure and mechanical properties was studied, with observed increases of 26.4% and 67.6% in flexural strength and fracture toughness, respectively, and a 25.3% decrease in average grain size.

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1. Introduction

Since it was first isolated in 2004 [1], graphene has been one of the most researched and promising materials [2], due to its extraordinary mechanical [3], electronic [4] and thermal properties [5]. These properties give graphene and its related materials an enormous potential in many fields [6], among which is that of composite materials [7]. The use of graphene in the manufacturing of composites requires a simple, efficient, cost-effective and ultimately scalable production method, which should allow to obtain good quality graphene in high concentrations and large quantities, avoiding the introduction of structural defects. Metals [8], polymers [9] and ceramics [10] can improve their mechanical, electrical and thermal properties with the addition of graphene as second phase filler, and these composites can then be applied in many different fields which include supercapacitors [11], batteries [12], transparent conductors [13] or sensors [14]. While metal matrix and, specially, polymer matrix composites have been widely stud-

ied and reviewed [15–18], graphene/ceramic composites are still developing and comparatively less accounted for [19–21].

Three main questions must be answered when fabricating these composites: How to produce good quality graphene in adequate quantities, how to homogeneously disperse the graphene in the ceramic matrix, and how to keep the graphitic structure during sintering. As an answer for the first question, researchers have tried both bottom-up [22,23] and top-down [24,25] approaches. Bottom-up methods like chemical vapor deposition (CVD) allow for the production of pristine, defect-free graphene with great control over the thickness of the layers produced, which enables high yields of monolayer graphene. On the down side, these methods require harsh conditions and produce low quantities of graphene, a fact that greatly limits their use on scalable applications such as the production of composites. On the other hand, top-down methods are comparatively more cost-effective and do not require extreme conditions, but they tend to produce not only monolayer graphene, but a mixture of graphene flakes with different number of monolayers, known as few-layer graphene (FLG). While the exceptional mechanical, electrical or thermal properties of graphene are reduced as the number of monolayers per flake increases in FLG, tending toward those of graphite [26,27], if that number of monolayers is kept below 10, these properties are still considered useful for composite production and FLG can be readily used as a second phase filler.

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One of the most used methods for production of FLG is the oxidation of graphite, followed by its exfoliation and subsequent reduction to obtain reduced graphene oxide (rGO). While this technique allows for the production of relatively large quantities of FLG, the strong acids and hard oxidants used during the process introduce basal plane defects on the graphene structure that cannot be totally recovered during reduction, affecting the properties of the as produced FLG [28]. An alternative to this method is the direct assisted exfoliation of graphite, which produces a mixture of graphene flakes with a high yield of mono-, bi- and trilayer graphene, and therefore could be a desirable and scalable way to produce FLG for composite production. The objective in this case is, simply, to overcome the Van de Waals forces that keep the individual graphene layers together by π-π bonding in graphite, usually with the help of ultrasonication [25,29], mechanical shear force [30], milling [31] or even electrochemical processes [32]. The mere application of energy to the medium containing the graphite is not enough for an efficient exfoliation, as the exfoliated layers tend to restack if not prevented by an adequate surface energy in the medium or the presence of species adsorbing onto the graphene layers causing steric or electrostatic stabilization of the FLG. Solvents with surface tension close to that of graphene (∼41 mN/m) make for good media for the direct exfoliation of graphite [25]. Unfortunately, the known solvents that meet this condition are harmful, expensive and have high boiling points, which makes it difficult to evaporate them when processing the FLG [33]. A desirable, much cheaper, environmentally friendly alternative would be the use of water as medium for the direct exfoliation of graphite. It can be attained with the assist of surfactants such as sodium dodecyl sulfate (SDS) [34], an anionic surfactant that adsorbs its hydrophobic tail onto the surface of graphene or FLG, causing electrostatic repulsion and stabilizing the exfoliated FLG against reaggregation [35]. A setback for this surfactant-assisted aqueous-phase exfoliation of graphite is the relatively low concentration of FLG that can be obtained, so, to further facilitate and optimize the direct exfoliation of graphite in the presence of SDS, a surface tension – reducing agent, such as ethanol, can be added so that the surface tension in the medium can be set near the aforementioned value of 41 mN/m, enhancing the exfoliation procedure and allowing for higher concentrations of FLG [36].

In this work, the aqueous-phase exfoliation of graphite has been studied, using sodium dodecyl sulphate (SDS) as dispersant, and ethanol to modify the system's surface tension, keeping it at 41.0 mN/m. In these conditions, the FLG yield, concentration and quality were measured for each of the exfoliation methods used, namely bath sonication, probe sonication, shear exfoliation and attrition milling. Different times of application were studied, with the objective of comparing all the methods to select the one that is best for the production of FLG dispersions for ceramic composite production. The quality of the FLG sheets was determined by the number of graphene monolayers per flake, the lateral size of the FLG and the type of defects in the graphene structure. 1 wt.% FLG/Alumina (Al_2O_3) nanocomposites were then fabricated and characterized to check if the FLG suspensions prepared with the selected method are indeed adequate for the manufacturing of ceramic composites and to study the effect that the addition of this FLG has on the composite properties. Pressure-less sintering was selected to consolidate the composite as this technique is readily scalable, free of restraints on the size and shape of pieces and more cost-effective than pressure-assisted sintering methods such as spark plasma sintering or hot pressing. Using pressure-less sintering, Kamali and co-workers produced 1 wt.% electrochemically exfoliated graphene nanosheets/Al_2O_3 composites and measured a 45% increase in fracture toughness over monolithic alumina [37]. Liu and co-workers used commercially available graphene nanosheets produced via rapid thermal expansion of intercalated graphite to fabricate Al_2O_3 nanocomposites, achieving improvements over alumina of 60% and 70% in flexural strength and fracture toughness for an optimal graphene nanosheets content of 0.75 vol.% [38]. Kim and co-workers used ultrasonication of electrochemically expanded graphite to produce FLG dispersions and synthesize Al_2O_3 nanocomposites with a maximum improvement of 48% in fracture toughness and 28% in flexural strength at a loading of 0.25 vol.% of FLG [39]. A potential drawback of pressure-less sintering for FLG-reinforced ceramic composites could be that thermal damage may be induced during high temperature sintering, so FLG integrity and distribution had to be assessed after sintering.

2. Materials & methods

2.1. Initial aqueous-phase – graphite mixtures preparation

FLG dispersions were prepared from aqueous-phase graphite suspensions. The graphite used is a waste product of the machinery industry, as this would allow for the valorization of an industrial waste product. The as-received graphite was washed with acetone and HCl to eliminate traces of oil used in the cutting tools and traces of iron remaining from those same tools. After filtration and rinsing with mili-Q water to reach neutral pH, the graphite was dried overnight in an 80 °C oven and sieved to select the desired particle size, taking the fraction with particle size between 125 μm and 250 μm.

The aqueous-phase was prepared by mixing mili-Q water with a 15 wt.% of ethanol (96 vol.%, Panreac) and 0.065 wt.% (2.6 mM) of Sodium Dodecyl Sulphate (SDS) (>99% purity, Fluka). The mixture was mechanically stirred for 10 min and then its surface tension was measured using the stallagmometer method to ensure that it was ∼41.0 mN/m. The previously washed and sieved graphite was then mixed with the prepared aqueous-phase, prior to performing the surfactant-assisted, aqueous-phase exfoliations detailed in Section 2.2. The initial graphite concentration in the suspensions was 100 g/l in every sample.

2.2. FLG suspensions preparation

The graphite mixtures prepared following the procedure detailed in Section 2.1 were then subjected to bath sonication, tip sonication, shear exfoliation or attrition milling to obtain FLG suspensions. Each particular exfoliation procedure was performed as detailed in the following subsections.

2.2.1. Bath sonication

16 plastic tubes with 1 g of graphite and 10 ml of aqueous-phase each were placed on a plastic rack and into a Branson 3510E-MH Low power sonication bath (100 W, 42 kHz). The bath was filled with cold water that was renewed frequently to avoid heating up the graphite suspensions. Sonication was continually performed and pairs of tubes were removed as samples at times of 0.25, 0.5, 1, 2, 4, 6, 10 and 14 h. The samples were then centrifuged at 1500 r.p.m for 30 min to eliminate large agglomerates and unexfoliated graphite, and the top 80% of the supernatant was collected.

2.2.2. Tip sonication

40 g of graphite were mixed with 400 ml of aqueous phase in a plastic bottle. The bottle was placed in a flowing cold water bath to avoid heating up the suspensions during sonication. Tip sonication was applied with an Ikasonic U-200-S Control Probe sonicator (300 W/cm², 24 kHz), using a 7 mm diameter tip sonotool. Samples were obtained at 0.25, 0.5, 1, 2, 4, 6, 10 and 14 h of sonication. Each sample was then centrifuged at 1500 r.p.m. for 30 min and the top 80% of the supernatant was collected.