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High yield, solid exfoliation and liquid dispersion of graphite driven by a donor-acceptor interaction

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ABSTRACT

Graphene derived from readily available graphite is viewed as the most effective route for large-scale production, due to the low cost of the raw material. However, the difficulty in achieving complete exfoliation, as well as the intrinsic insolubility of graphite, remains a key challenge. Herein, we describe a single-step approach to effectively disrupt and cleave the network of $\pi-\pi$ interactions, induce the exfoliation of graphite and disperse the resulting exfoliated material in organic solvents, all driven by electron rich (graphene) donor-acceptor interactions. This is achieved through the addition of specially synthesised non-polar, branched, electron-deficient aromatic acceptor molecules. Minimal energy input through mild manual grinding of graphite with the tailored acceptor induces donor-acceptor interactions that preferentially affect the $\pi-\pi$ system in graphite resulting in solid phase exfoliation. Graphite exfoliation and dispersion formation is further improved after mild bath sonication (30 min) of the acceptor-graphite composite in a solvent leading to 1250% increment in yield in NMP solvent for instance. The use of electron acceptors allows high concentration dispersions, not only in high boiling point solvents, whose surface energy generally matches that of graphene but also in a low boiling point solvent with mediocre properties.

1. Introduction

Graphene is a two dimensional crystalline nanomaterial consisting of a single atomic layer of carbon atoms bonded in a hexagonal lattice similar to a honeycomb. It has attracted significant attention due to its superior mechanical and electronic properties, including the highest intrinsic electron mobility known (about 100 times that of silicon), its extremely high charge carrier mobility (up to 20,000 $cm^2\ V^{-1}\ s^{-1}$, close to the Dirac point), and its ability to exhibit ballistic charge transport [1–3].

In recent years, research in this field has been geared towards increasing the quality and yield of graphene to ensure readiness in practical applications. The top-down approach of graphene synthesis from readily available and inexpensive graphite is seen as the most promising route. However, the difficulty in exfoliating graphite and its intrinsic insolubility have limited its large scale processing for industrial development. To overcome the van der Waals interactions in graphite, exfoliation by physical means, such as ultrasonication and ball milling, are widely applied. Moreover, while exfoliation and dispersion in water have been adequately solved through the addition of assistants such as surfactants, the use of organic solvents needs to be further explored, especially for applications where residual water is undesirable, for example in electronic devices [4].

The direct liquid phase exfoliation of bulk graphite powder in an appropriate organic solvent is a known scalable technique that could be used for applications such as functional coatings, conducting inks, composites, batteries, supercapacitors and top down approaches to electronics [5–13]. In this approach, solvents possessing matching surface energies with graphite, such as *N*-methylpyrrollidone (NMP), are used to exfoliate graphite via a simple sonication process. However, one major drawback is the low yield, typically around 0.01 mg/mL [10], and, for enhanced yield, longer sonication times are required, in the order of 460 h for high boiling point solvents [14] and 48 h for low boiling point ones [15]. A significant disadvantage of prolonged sonication is that it leads to

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partial destruction of the graphene sheets, and is impractical for large-scale applications. Increasing the yield in graphene, while reducing sonication times still remains a key challenge for mass production.

Due to the intrinsic insolubility of graphite, a consequence of the extensive network of interlayer $\pi-\pi$ interactions, the exfoliation and dispersion processes are limited to solvents whose surface tension best match the surface energy of graphite. However, these often have high boiling points, rendering further downstream processing more complex and economically non-viable. The prospect of extending liquid phase exfoliation to non-polar low boiling point solvents, such as chloroform, which has relatively poor matching surface energy will offer significant versatility by expanding the range of solvents available for exfoliation and enable development of new applications.

With the objective to increase the yield and enable the scaling up of graphene production, a number of groups have explored liquid phase exfoliation combined with the use of intercalants [16,17]. As van der Waals force is inversely proportional to r^6, where r is the distance between the molecules, its magnitude tends to zero for interlayer distances greater than 0.5 nm. Intuitively, the rationale behind the addition of intercalants is that, since the molecular attractive forces between adjacent layers of graphite are relatively weak, they are susceptible to further weakening, or can even be completely overcome, by increasing the distance between the layers [18]. However, the reported shifts in the interlayer distances, as evidenced by X-ray powder diffraction (XRD) were too small to conclude that intercalation had effectively occurred [15,16,19–23] and extensive sonication was still required to achieve exfoliation.

In attempts to delve into the nature of the interlayer van der Waals' interactions, various studies have focused on the adsorption of organic molecules on graphite. Several model compounds have been used to investigate the factors contributing to enhanced adsorption: an extension on $\pi-\pi$ interactions by using polyaromatic hydrocarbons, likened to a graphene sub-unit [24], or the ability of the interacting molecules to host excess charge density coming from the graphitic sheets [25]. In this perspective, the use of solvents with strong electron withdrawing or donating functional groups, to exfoliate and stabilize graphene through donor-acceptor interactions, has been explored. Donor-acceptor interactions are intermolecular interactions between π-electron rich (donor) and π-electron deficient (acceptor) molecules that have the potential to control the sorption of organic compounds on surfaces. It is noteworthy that, even in these systems, exfoliation and dispersion have been mainly ascribed to matching surface energies rather than molecular-level electronic interactions, between the graphitic layers and aromatic molecules, induced by the presence of electron-withdrawing groups in hyper-conjugated aromatic systems. This is probably related to the fact that exfoliation is an entropy driven process, involving disruptions of the $\pi-\pi$ interactions that lead to a greater degree of disorder, and has thus energetic consequences: the overall reaction must be endothermic to satisfy the Gibbs free energy equation ($\Delta G = \Delta H\text{-}T\Delta S$). In general, weak electron acceptors or donors do not match the energetic cost associated with such interlayer graphitic cleavage and are qualified as poor additives.

Alternatively, there have been several reports of non-covalent solid phase functionalization of graphite, similarly relying on the principles of molecular adsorption (triazine, triphenyl), with the main complementary technique being intensive ball milling [26–28]. While substantial yields are sometimes reported, a significant disadvantage is the generation of smaller graphene sheets as a result of the shear forces involved. In addition, not all exfoliated graphite was dispersible in organic solvents. In the case of triazine derivatives, only DMF was shown to effectively disperse the exfoliated graphite. While with the triphenylene system the authors reported enhanced dispersion of solid phase exfoliated graphite in DMF, methanol and THF, but were unable to obtain stable dispersions in non-polar chloroform [28]. The limitation of graphite dispersion in organic solvents is due to the polar nature of both additives, which explains the high attainable dispersions in water.

Amemori et al. [29] and Gharib et al. [30] reported a significant change in the solubility behaviour of selected polymeric systems bearing pyrene side groups, when branched electron-deficient acceptors were intercalated to facilitate the cleavage of the $\pi-\pi$ interactions. The authors explained the increase in solubility by the occurrence of a mechanism involving donor-acceptor electronic coupling with the $\pi-\pi$ network. It was also found that the modification of acceptors with branched alkyl chains was crucial for the successful disruption of $\pi-\pi$ interactions between pyrene groups.

In the work presented here, a similar approach is used: the complete layer-by-layer delamination of graphite may be likened to a solubilisation process, whereby the van der Waals' interactions are first disrupted, then the single layers are isolated in solvation spheres. The concept is to use tailored organic molecules, designated as acceptors A1 and A2 (Fig. 1), as intermediates to interact with the graphitic sheets and assist with the weakening of the interlayer by mobilising part of the electron density. The subsequent step would then be the propping open of the graphite to generate individual graphene sheets through the synergetic action of the solvent. In these systems, it has been demonstrated that the introduction of branched electron-deficient acceptors, A1 and A2 (Fig. 1), followed by mild sonication can induce exfoliation and dispersion of graphite [31].

The results reported here show that the interactions of the acceptors with graphite are not solvent dependent, and exfoliation into single and few-layered graphene occurs mostly in the solid phase after manual grinding. Stable dispersions of graphene are obtained following mild bath sonication and centrifuge in a solvent. Furthermore, to date, the best reported solvent for the liquid phase exfoliation of graphite is NMP, a chemical that is currently on the European Candidate List of substances of high concerns due to its toxicity [32,33]. In this respect, there is a need to explore alternative solvents that meet environmental and safety standards. To the best of our knowledge, it is the first time that experimental data on the use of dihydrolevoglucosenone (DHLG), a bio-based solvent, in the exfoliation of graphite and dispersion of graphene are reported. The data of initial investigations show that DHLG is a very promising candidate as a dipolar aprotic solvent, and can be explored as green alternative to toxic NMP [34].

2. Experimental

2.1. Materials

Synthetic graphite, 2-ethylhexylamine, pyromellitic dianhydride (PMDA), naphthalene-1,4,5,8- tetracarboxylic acid dianhydride and organic solvents, N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), chloroform, dichloromethane, acetone, anisole, 1,2 dichlorobenzene, cyclohexanone, hexane, toluene, isopropanol and dimethylsulphoxide were used as received from Sigma Aldrich. Dihydrolevoglucosenone (DHLG) was obtained from Circa Group Pty Ltd (Australia).

2.2. Synthesis of acceptors

A1 and **A2** were synthesised (Supplementary Information S1 and S2) according to methods reported elsewhere [29]. In the optimisation experiments, it was found that the branched alkyl chain was