A manufacturing perspective on graphene dispersions

David W. Johnson, Ben P. Dobson, Karl S. Coleman *

Department of Chemistry, Durham University, South Road, Durham DH1 3LE, United Kingdom

ABSTRACT

Harnessing the exceptional physical properties of graphene often requires its dispersion into aqueous or organic media. Dispersion must be achieved at a concentration and stability appropriate to the final application. However, the strong interaction between graphene sheets means it disperses poorly in all but a few high boiling organic solvents. This review presents an overview of graphene dispersion applications and a discussion of dispersion strategies: in particular the effect of shear, solvent and chemical modification on the dispersion of graphene (including graphene oxide and reduced graphene oxide). These techniques are discussed in the context of manufacturing and commercialisation.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Graphene is a true wonder material and has the potential to generate disruptive technologies. Since it was isolated in 2004 [1] a wide range of impressive properties have been reported for graphene including the following: high electron mobilities of over 200,000 $cm^2 V^{-1} s^{-1}$ at electron densities of ~2 × 10^{11} cm^{-2} [2], high thermal conductivity of ~5 × 10^3 $W m^{-1} K^{-1}$ [3], impermeability to gasses despite being one atom thick [4], ballistic transport of electrons [5,6], absorption of 2% of the light passing through it [7], and being "the strongest material ever measured" [8] with a Young's modulus of TPa. The fact that all of these properties are found within a single material has stimulated great interest in graphene. In spite of this, it is still only at the early stages of commercial development as a number of challenges need to be addressed. The first of these has been a lack of scalable synthetic routes to produce graphene in the quantities required for industrial applications. However, a number of methods for scalable graphene synthesis are now emerging [9]. The second problem relates to the difficulties in processing graphene, in particular graphene's poor colloidal stability in most common solvents [10].

For a graphene dispersion to be useful, essential criteria must be met: the graphene must disperse at a useful concentration, in a solvent appropriate to the application, and remain dispersed over a reasonable period of time. Current strategies to solve these challenges are the subject of this review.

2. What makes a good dispersion?

The parameters for creating a good dispersion are well established in the field of colloid science [11]. The free energy of any colloidal system is determined by both the interfacial area and tension. The theoretical surface area of monolayer graphene is ~2590 $m^2 g^{-1}$ [12]; consequently there are a limited range of conditions under which it can be dispersed typically involving sonication and polar aprotic solvents [13].

Maintaining a dispersion requires an energy barrier to aggregation be introduced. This can be achieved by either electrostatic or steric repulsion [14]. If the energy barrier is sufficiently high then Brownian

motion will maintain the dispersion [11]. This can be achieved by solvent selection [10,15,16], or by the modification of graphene either covalently or non-covalently [17].

From a manufacturing viewpoint the pressing challenges include the following: increasing the range of dispersing solvents to include those which are volatile and less toxic e.g. alcohols and water; improving dispersion stability as a function of concentration, time, temperature, and ionic strength; and more scalable routes to dispersion e.g. high shear mixing as opposed to sonication. In addition to these there are a series of second tier challenges which include the following: accurate characterisation, safe handling, and post-processing. The final, but crucial challenge, is dispersions must be achieved in a cost effective way.

2.1. Types of graphene used in dispersions

"Graphene" is often used to refer to a family of materials including the following: pristine graphene (G), graphene oxide (GO), and reduced graphene oxide (rGO). These materials can be further subdivided by the method of production, in particular G. However, nomenclature for graphene and its derivatives is varied with some terms being used to describe a range of materials. A formal nomenclature has been proposed by Bianco et al. but is not universally used and so care must be taken in interpreting results [18].

In the context of dispersion G is nearly always produced by solvent or surfactant assisted graphite exfoliation [13,19,20], although exceptions exist [21]. G has properties closest to those of defect free "pristine" graphene [19]; the dispersion is a mix of single to multi-layer graphene and graphite although these components can be separated [22]. GO is produced by the exfoliation of graphite oxide (GrO), which is easily achieved in water [23], however it is a very defective material with markedly different properties from G [24]. Finally, rGO is produced by the reduction of GO, generally by either chemical, or thermal methods [25,26]. The removal of the majority of oxygen functionalities from GO means rGO's properties are close to those of G, but the material remains defective [26,27]. A further related material used in dispersions are graphite nanoplatelets (GNPs) which are nanosized graphite flakes [28].

Unfortunately the dispersibility of graphene and its derivatives is almost inversely proportional to its physical properties. As a simple guide, dispersibility follows the trend GO > rGO > G. Chemical functionalisation of these materials can improve dispersibility but can also increase their defectiveness and have a negative impact on properties [29,30].

As a result there is often a compromise between the ability to process the material and its resultant physical properties. Selecting the correct graphene, and, where applicable, the correct functionalisation method requires consideration be given to the end application: a subject which has been reviewed elsewhere [9].

2.2. Dispersion of graphene

Several solvents have been identified as being particularly good at dispersing graphene in particular: NMP, DMSO and DMF [15]. Ionic liquids (ILs) have shown some promising results, however as they are not widely used in industry they are beyond the scope of this review and interested readers are directed to a recent review [31]. Generally research into G dispersion is combined with its exfoliation from graphite; while exfoliation and dispersion are distinct phenomena they are related.

Solvent interactions with graphene have been rationalised in terms of both surface energies and Hansen solubility parameters [15,19]. However, as highlighted in a recent review, there are problems with both these approaches [32]. Despite this, work in this area has produced useful results in identifying and predicting good G solvents. Recent molecular dynamics simulations support what has been found experimentally, namely that:

$$NMP \approx DMSO > DMF > GBL > H_2O$$

for G dispersion [33]. The mechanism of this dispersion is attributed to a layer of confined solvent near the G surface which prevents aggregation of G sheets *via* sterics.

The dispersion of G into solvents is most commonly achieved by sonication, which creates shear stresses and cavitation in the solvent [34]. This has the effect of breaking apart graphite and exfoliating the sheets into individual G flakes. The dispersion concentration is known to be linked to both the sonication time and power (Fig. 1) [16]. By far the most widely used solvent for dispersing graphene is NMP, where sonication of graphite can yield stable G dispersions in the range of 0.01–2 mg ml^{-1} [16,19]. G, which has been isolated from its parent graphite can be redispersed to concentrations of up to 63 mg ml^{-1} (falling to 33 mg ml^{-1} over 200 h) [16].

The extreme conditions of sonication even allows for the dispersion of G in to poor, low boiling point solvents including the following: acetone, chloroform, IPA, and cyclohexanone although a 48 h sonication time is required [35]. However, long sonication times are generally undesirable as it can reduce sheet size and introduces defects which undermine graphene's properties [35–37].

Alternatives to sonication exist, recently both Liu et al. and Paton et al. used a high shear mixer to produce G dispersion in NMP of 0.27 mg ml^{-1} and 0.07 mg ml^{-1} respectively [38,39]. Paton et al. noted that non-turbulent local shear rates of $>10 \times 10^4$ s^{-1} were necessary for exfoliation. From an industrial perspective high shear mixing is a promising technique as it is a more mature technology than ultrasonication.

It has also been demonstrated that ball milling with organic solvents can be used to disperse graphene [40]. Tested solvents included NMP, TMU, DMF, THF, acetone, ethanol, and formamide with concentrations of 88, 88, 97, 76, 66, 10.32 and 3.67 μg ml^{-1} found respectively.
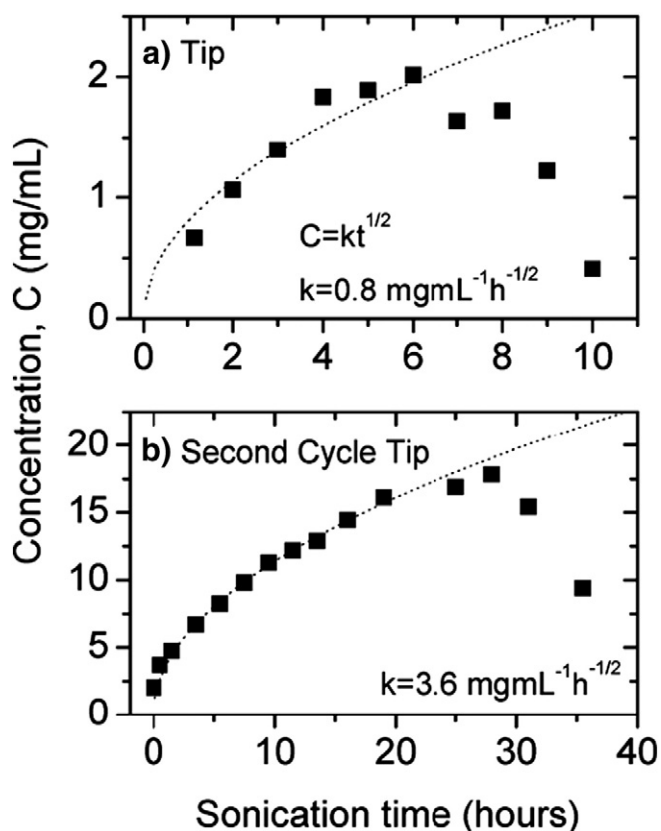

Fig. 1. (a) Exfoliated graphene concentration as a function of sonication time of graphite in NMP. (b) Concentration of graphene redispersed after isolation from graphite. Note that on isolating the graphene from graphite that the total concentration of graphene dispersion increases dramatically.
Reprinted with permission from Porwal et al. [16].