Aqueous processing of graphene–polymer hybrid thin film nano-composites and gels

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ABSTRACT

Research into the structure, properties and applications of graphene has moved at a tremendous pace over the past few years. This review describes one aspect of this research, that of the incorporation of graphene particles with a range of polymers to create novel hybrid materials with increased functionality such as improved conductance, increased strength and introduced biocompatibility or cytotoxicity. This review focuses on dispersing graphene in polymer matrices, both insulating and conducting. Additionally, a brief discussion of carbon based platelet production methods is given in order to provide context on the subsequent use of this family of materials such as graphene, graphene oxide (GO) and reduced graphene oxide (rGO) incorporated into polymeric thin films.

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1. Introduction

The properties and uses of graphene have been intensively studied over the past decade [1,2]. This novel material has captured the imagination of scientists and technologists alike. Graphene gained increased prominence following the award of the 2009 Nobel Prize in Physics to Geim and Novoselov for their pioneering work on elucidating structure and function and spawned a global industry in incorporating this material into applications as diverse as electronics, health, water and energy [3,4].

Graphene is a 2 dimensional form of carbon only one atom thick and linked hexagonally in a lattice. The origin of many of graphene's interesting properties is due to the unique spatial and bonding arrangement of atoms through sp2 hybridization of all of the carbon–carbon bonds across the sheet. This leads to extraordinary electron mobility [5] as well as intrinsic material strength and thermal properties. Importantly, these properties of graphene are significantly different to those of the stacked 3 dimensional form of carbon, graphite. Hence interest in exploiting graphene is high due to the relatively low cost of the bulk material as well as accessibility [6,7]. This, however, is balanced against the current challenges of scalability of production methods of the graphene. Research continues unabated though as these challenges are increasingly being met with expansion of the technology into new high volume applications.

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Over the past decade, the major theme for many researchers in materials science has been to understand the properties of graphene as well as to develop methods for its large scale production. While novel uses are regularly found, immediate goals for graphene incorporation into applications have centered on the electronics and materials industries. In these uses, the physical, mechanical and electrical properties of graphene are ideal. Functional electronics applications include supercapacitors, opto-electronic devices and displays, electrodes and high electron mobility transistors.

Current market drivers are predominantly in composites, coatings and thin films [8]. In these uses, graphene can add functionality or be used to improve mechanical properties. The physical structure of graphene in terms of the ultra-high aspect ratio due to the atomic thickness of the sheets as well as the highest known tensile strength [9] makes it a desirable load distributing and bearing component in composite materials. Graphene has a moderate surface energy (partially water wetting) making compatibilization with matrix polymeric materials somewhat challenging. However methods for the production of graphene with engineered soft matter functionality may assist in overcoming this issue [10].

Herein, methods for producing graphene will be presented; top-down methods [11] that exfoliate graphene from graphite or its variants. These top-down methods produce graphene sheets that are dispersed in a liquid making them amenable to incorporation within a polymer thin film. To achieve the ultimate incorporation into the polymer films, the graphene itself may require further functionalization. The application of graphene to create hybrid thin films and gels will be briefly discussed, giving an overview of some popular directions currently being explored in the open literature; layer-by-layer approach to functionalize a surface, in-situ vapor phase polymerization of composite thin films, and the creation of graphene based surfaces for biomedical applications.

2. Preparation of graphene

Just as the list of applications for graphene expands, the means by which to produce graphene does too. Of particular interest to graphene–polymer hybrids are the graphene production methods that yield "pristine" graphene or graphene oxide which may be subsequently reduced, be it single or multilayer, dispersed in a liquid. These methods to produce graphene dispersions are gaining increasing popularity due to their amenability for large scale production [11–13]. From a very simple view point, large 3 dimensional volumes of graphite or graphite oxide are processed in a liquid in order to "break down" the volume into individual or multilayers of graphene. When graphene oxide is employed, there exist additional processing steps to reduce the material back to graphene however there are both advantages and disadvantages to these types of approaches [14–16].

When the graphene is directly exfoliated from bulk graphite, the graphene layers that are produced have very large surface areas which are exposed to the host liquid in which it is dispersed. While this large surface area provides great advantage in certain applications, it does prove disadvantageous when trying to stabilize the graphene against re-aggregation in a dispersion. Two means to stabilize the large surface area, thus inhibiting aggregation of the graphene, are to use electrostatic and/or steric forces between neighboring graphene particles. While the use of such forces to stabilize particles (nano- or colloidal in size) in a dispersion is reasonably well understood and widely applied in practice, their use with graphene proves to be a challenge. Pure graphene is a 2 dimensional network of carbon atoms, which theoretically does not have any defects, be they physical or chemical. This means that the surface of the graphene only possesses sp2 hybridized carbon atoms, and lacks "active" sites where a charge could reside or a surfactant/polymer may strongly adsorb through electrostatic means. In practice, the presence of a non-negligible amount of defects, particularly at the edge of the graphene sheet allows for these "active" sites to be present,

facilitating a surface charge or the binding of steric stabilizers. For sufficient surface charge to occur for electrostatic stabilization the common pathway is to convert graphite to graphene oxide, exfoliate the layers, and then reduce this back to graphene. Given that the reduction process does not fully reduce the material to pure graphene, this intermediate material is commonly referred to as reduced graphene oxide (rGO). On the other hand, by using surfactant assisted direct exfoliation of graphene (labeled as SA-G), a material that is stable in an aqueous suspension is generated that is much closer to that of pure graphene however removal of the surfactant post-production can be difficult. The use of rGO or SA-G in a dispersion for the creation of graphene–polymer hybrids will greatly depend on the end application in mind where a compromise between the ease of fabricating the hybrid and the final performance and properties of the hybrid needs to be weighed.

Few methods currently exist for the large scale production of chemically unmodified or "pristine" graphene sheets. One route which shows some potential for scale up is liquid phase exfoliation of graphite in an appropriate solvent system [17]. Such a method has been demonstrated in aqueous systems in the presence of surfactants as well as in organic solvents [18,19] and ionic liquids [20,21]. In most cases, the concentration of graphene in the liquid is relatively low, typically of the order of less 100–500 ppm by mass. Liquid phase exfoliation is a simple process whereby the cohesive energy of the graphite is matched to the cohesive energy of the liquid [22,23]. Hence, there is no significant energy barrier to split the sheets apart under moderate sheer conditions imparted through sonication. Typically, the required surface tension is ~41 mJ/m^2. This optimum surface energy can be achieved simply by judicious choice of solvent of which organic exemplars include N-methylpyrrolidone (NMP) and N,N-Dimethylacetamide (DMA) [17]. Alternatively, graphene production can be performed under aqueous conditions in the presence of a surfactant to reduce the surface tension to the appropriate level for efficient exfoliation [22,24–30]. The use of surfactants also increases the stability of the suspensions as adsorption to the graphene surface provides an extra repulsive barrier against aggregation. Fig. 1 shows typical platelet graphene particles generated using surfactant assisted aqueous based exfoliation. The presence of a single layer material is confirmed by Raman spectroscopy and TEM imaging.

In organic systems and ionic liquids, the exfoliation of graphite to graphene is self-limiting as the particles are themselves surface active which thereby reduces the interfacial energy. Similarly, in aqueous systems, adsorption of surfactant molecules to the graphene–water interface depletes the surfactant from the liquid phase leading to an increase in interfacial tension; again a self-limiting process. Recently it was demonstrated that the concentration could be increased further simply by replenishing the surfactant continuously resulting in a concentration of graphene in suspension up to 20 times greater [22]. Interestingly, any surfactant may be used as long as the surface tension can be tuned to the exfoliation window at 41 mJ/m^2. Ionic surfactants such as the cationic hexadecyltrimethylammonium bromide and anionic surfactants such as sodium dodecylsulfate and sodium cholate have been extensively used [10]. Furthermore, non-ionic surfactants such as the block co-polymers of polyethylene oxide (PEO) and polypropylene oxide (PPO) have also been used [22,31]. These polymeric type surfactants are irreversibly adsorbed giving rise to highly stable suspensions, particularly at elevated ionic strength and over a range of pH however surfactant removal is hence non-trivial.

The graphene particles produced using liquid phase exfoliation typically retain the extended conjugation across the sheet. Under certain conditions such as high sonication power, defects may be introduced. Also, the edges of the graphene particles are stabilized by oxygen containing moieties so there is some small amount of negative charge of these particles in solvents with a high dielectric constant such as water. The sonication procedure also produces a range of thicknesses of the particles, however the majority of particles are single or have few layers.