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Editorial Overview

Colloidal graphene—Scalable processing for advanced materials☆

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ABSTRACT

A context for the burgeoning emergence of colloidal graphene in various states of oxidation is provided for a collection of detailed reviews and perspectives on the exfoliation, synthesis, and use of colloidal graphene as a functional material in diverse advanced materials. Methods of generation cover orders of magnitude in scale, from bench top to manufacturing, and special attention is given to overlap with extant dispersion technology. Syntheses range from redox manipulations of coal extracts and graphite to multistep synthesis of polycyclic aromatic hydrocarbons. The advanced materials discussed include diverse sensing materials, including an introduction to optoelectronic devices, and numerous energy materials. Challenges for refining our understanding of basic properties of graphene on various length scales are presented.

1. Introduction

This inaugural issue on colloidal graphene comes at a time when there are only a few less than 50 papers containing the phrase "colloidal graphene" indexed in databases, but already there are some thousands of papers exploring the properties and applications of colloidal graphene. We expect that this topic will be addressed by many monographs in the future, as our prowess in forming and manipulating graphene dispersions and solutions improves. The solutions and dispersions of graphene we term "colloidal graphene" include graphene quantum dot (GQD) solutions and dispersions, whether emanating from polycyclic aromatic syntheses or from fragments of reduced graphene oxide (rGO) or graphene (G), as well as dispersions and suspensions of rGO and G of micron and hundreds of microns (and larger) largest dimension, but where the smallest dimensions are of nanometer scale. A key path to rGO and realizing the commercial potential of colloidal graphene (in applications) is to produce rGO in various states by reduction of GO solutions and dispersions.

This issue covers some major colloidal graphene topics, including how to form colloidal graphene and how to apply colloidal graphene in diverse application areas. In summarizing these topics below, we also mention some areas not covered in depth in this issue, as well as some supplementary references on topics covered. Among the almost 50 extant "colloidal graphene" papers alluded to above, all were published after 2009, and they address GQDs (synthesis, characterization, and applications) [1–14], dispersing graphene [15–23], composites and catalysts [24–29], sensing [30–33], alignment and interfacing of nanosheets [5,25,34], drug delivery [35], separation processing [36–41] (8), and characterization [42–44] (2). Of course, *de facto* colloidal graphene is used whenever graphene is introduced into a liquid multiphase fluid and is reduced to nanometer scale in at least one dimension.

2. Top-down dispersion of graphene

Producing dispersions of graphene has evolved significantly over the past 10 years (or so). Very dilute dispersions in various solvents have been made, and many different kinds of stabilizers have been evaluated in preparing aqueous and other solvent-based dispersions. The review by Wei and Sun [45] discusses exfoliation methods and results using ultrasonication, shear-based homogenization, and supercritical fluid methods. They introduce yield as a measure of dispersion efficiency, a long overdue practice in view of the number of reports that discard 98% or more of the graphene sample used in dispersion attempts. Shear-based exfoliation is predicted to scale to higher throughput, although this achievement is still theoretical. A so-called high-power sonication method was recently claimed as offering significant throughput advances, but again most of the graphene is centrifuged to sediment [46]. Such approaches simply are not practical for high volume applications [47]. Chen and co-workers [48] claimed a "universal exfoliation principle" in using a 50:1 weight ratio of imidazole to graphene to produce 0.1% (w/w) graphene dispersions, apparently unaware of the imidazolium-based dispersions of Ager and co-workers [49] achieved earlier at 50-fold higher graphene in water (5% w/w) using only a 0.5:1 weight ratio of stabilize to graphene. Zhong and her co-workers [50] review very successful electrochemical exfoliation efforts, focusing on cathodic processes that do not oxidize the exfoliated sheets. They

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also discuss electrochemical methods to functionalize graphene for advanced composite applications. These methods are predicted to become more competitive as they are optimized through electrochemical engineering.

Other top-down exfoliation approaches include dry [51,52] and wet ball milling (small media milling) [53–58]. Such milling processes provide the highest volume dispersion approaches used worldwide in manufacturing, and must be considered serious contenders in efforts to make graphene dispersions available on the multi-kilogram scale at low cost. The next most prevalent method of dispersion on large scales is pressurized homogenization and is the preferred method for emulsion technologies. An initial application using this technology was recently reported by Ding and co-workers [59]. Another significant approach involves producing intercalated graphite followed by microwave irradiation, and such methods are becoming more prevalent [60–62]. An American company, XG Sciences [63], uses acid intercalation followed by microwave irradiation to make highly expanded graphite, highly suitable for subsequent liquid dispersion treatments. Such materials are available for about $160/kg.

Mention also must be made of the top-down synthesis of graphene quantum dots. These chemistries, such as oxidative scission of pitch-based carbon fibers to produce GQDs are discussed later in this issue by Kelarakis [64], and hydrothermal cutting and microwave assisted cutting, which are discussed later in this issue by Ge and co-workers [65]. Limitations of these top-down methods are discussed by Li and co-workers [66].

3. Top-down and bottom-up dispersion of graphene oxide and reduced graphene oxide

If we consider the chemical and physical conversion of graphite to suspensions of single-sheet or few-sheet graphene oxide, then it is appropriate to term GO production a “top-down” process. The production of reduced graphene oxide, rGO, from single-sheet or few-sheet GO may be thought of as a “sideways” or bottom-up process. It is probably most appropriate to think of these materials as being less “top-down” than exfoliation of graphene from graphite or aggregated graphene, but not as “bottom-up” as certain graphene quantum dot syntheses.

The syntheses and functionalization of GO and rGO are concisely reviewed by Park and Ruoff in this issue [67]. They stress the importance of controlling, identifying, and quantifying the functional groups introduced into GO in its synthesis, use, and conversion to rGO. Professor Ruoff and his co-workers have been singularly responsible for initiating and developing GO and its reduction to rGO as a facile and high volume route to make dispersions of rGO readily available. Other related reviews are also available [68,69]. GO dispersions are also finding a myriad of new uses as a relatively low cost and ultrathin tabular material [70–72], and their use as stabilizers in emulsion and dispersion technology is reviewed at the end of this issue [73]. A key factor pointed out by Park and Ruoff is that useful functionalization of GO often can be done prior to the chemical reduction that produces rGO, and many functionalization chemistries are more easily done in polar solvents with GO than with rGO in much less polar environments (although, of course, some chemistries are more facile in nonpolar milieu). It is important that aggregation prior to functionalization be avoided.

Powell and Beall [74] provide an alternative approach to obtaining GO and rGO from humic acid extracted from low-grade coal and related materials. We may expect that the number of sources of useful carbon for generating GO and rGO to grow as our knowledge of how to convert biomass and other polymers to graphitic carbon grows [75].

4. Bottom-up dispersion of graphene (graphene quantum dots)

Bottom-up syntheses of graphene quantum dots, GQDs, starting, for example, from bromoiodoaniline, are discussed in this issue by Li and co-workers [76], showcasing their extensive contributions to this field. Various bottom-up chemistries and approaches are discussed, and this general synthetic approach includes the synthesis of polycyclic aromatic hydrocarbons [77]. A key factor illustrated by Li and co-workers [76] is the inclusion of suitable functionalization to provide solubility in a desired solvent system. Another key aspect discussed involves careful characterization of the associated optical properties of GQDs. This factor is also stressed in the review of Kelarakis [64] in this issue, where GQDs are more broadly reviewed, and various additional organic synthetic routes are discussed, in addition to the ring opening of fullerenes as a source of GQDs. These exciting new materials are important in imaging, sensing, catalysis, and energy conversion. Later in this issue, Ge and co-workers [65] present progress made in using GQDs in various optoelectronic devices. Other recent reviews of GQD applications include formulating composites [78] and luminescent applications [79].

5. Modeling graphene stabilization and dispersion

Monte Carlo and molecular dynamics studies of complex fluid systems involving surfactant and polymer solutions as well as multiphase fluids and dispersions are increasing in scope and complexity [80–82]. Modeling graphene dispersion, graphene interactions with solvent, and adsorption of surfactant on graphene are discussed in this issue by Yang and co-workers [83]. They discuss molecular dynamics-based studies of graphene-solvent interactions, surfactant adsorption, and surfactant-based graphene exfoliation and dispersion. A particularly noteworthy aspect discussed, based on studies from Blankschtein and co-workers [84], is that the DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory fails to account for salt effects in the near field for graphene sheet interactions when stabilized by surfactant.

Very recent molecular dynamics studies of graphene include the examination of aggregate structures of CTAB (cetyltrimethyl ammonium bromide) on graphene and conclude that such surfactant stabilized platelets of varying thickness could be separated by density gradient centrifugation [85]. These simulations and other modeling methods are also being applied to composite formation and prediction of mechanical properties [86]. Simulations of an epoxy/graphene composite showed that elastic modulus increased with the degree of graphene dispersion or exfoliation, and that experimental results fit a model of incomplete exfoliation.

6. Manufacturing

Colloidal graphene in the marketplace is in its infancy, but finding suppliers is not too difficult. A perspective on this topic including commercialization may be found later in this issue [87]. When one investigates how to secure colloidal graphene from vendors, we find there exist a variety of start-up enterprises in addition to established chemical suppliers. A listing of such suppliers is given in Table 1. Included are suppliers for graphene oxide (G), reduced graphene oxide (rGO), and exfoliated graphene (G). Many of the products available are in the very dilute regime, suitable mainly for prototype development, physicochemical research and development, and perhaps conductive inks. Some sources are offering dispersions/pastes in the 1% to 24% by weight range, so practicality is being addressed for kg level manufacturing.

7. Sensors and electronic devices

Graphene, like carbon nanotubes, is highly susceptible to having its transport properties modified by perturbations to its delocalized electronic π system, whether covalently or physically. A very important class of sensing is electrochemical sensing since electronic coupling provides direct access to probing electron mobility, conductivity, and related properties. Sensors in this class have been very thoroughly discussed by Hu and his co-workers [97] in this issue. They focus on advances in the application of graphene electrochemical sensors to disease diagnosis biomarkers (molecules), drugs (molecules), and food