



Graphene oxide and graphene flakes as stabilizers and dispersing aids[☆]



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ABSTRACT

Various uses of graphene oxide and graphene as Pickering stabilizers in emulsification, emulsion polymerization, and suspension polymerization applications are discussed. The use of such stabilizers in composites, graphite dispersions, foams, aerogels, and porous materials is reviewed. Other advanced material applications of these Pickering stabilizers are presented for select applications, including electro-rheological fluids, opto-rheological fluids, particles for supercapacitors, phase change materials, catalysis, and stabilizers.

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1. Early basis for graphene (graphite) as a Pickering stabilizer

In his recent book [1], Bon points out that the origins of using particulates as emulsion (foam) stabilizers may be traced to British industrialists in the late 19th century seeking to improve mineral flotation processing [2,3]. Of particular interest, the Bessel patent [6] addresses applying their improved processing to the processing of graphite, now known to be a low cost source of graphene. We may infer, therefore, that colloidal graphene as a Pickering stabilizer is a technology nearly 140 years old, since the surface layers of the Bessel graphite were composed of graphene.

Several excellent reviews on Pickering emulsions have appeared [4–8], and a more recent comprehensive review is that of Chevalier and Bolzinger [9]. The large number of increasing applications has yielded specialized reviews utilizing Pickering emulsions in stimuli-responsive materials [10], Janus particles [11], and to the topic of this review, the use of graphene and graphene oxide as Pickering stabilizers in the design and synthesis of polymer/graphene composites [12]. Park and Lee have provided a recent review of particles at interfaces and the associated energetics, with a particular emphasis on anisotropic particles [13]. Anisotropy, of course, distinguishes G (graphene), GO (graphene oxide), and rGO (reduced graphene oxide) adsorption to interfaces from spherical nanoparticles and microparticles. Two-dimensional particles usually align themselves parallel to a fluid–fluid interface.

The Gibbs free energy needed to displace a uniform spherical particle from an oil/water interface into the water phase has been estimated as [5,6]

$$\Delta G = \pi r^2 \gamma_{ow} (1 - \cos\theta)^2$$

[☆] This paper was edited by Professor Nicholas Abbott.
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where r is the particle radius, γ_{ow} is the interfacial tension (Gibbs interfacial free energy), and θ is the contact angle (defined as the angle between the oil/water interface and [increasing to] a tangent to the particle surface passing through the triple phase contact line at the water–oil interface). The corresponding energy for transfer of a graphene or graphene oxide flake at the interface of oil and water into water is

$$\Delta G = -\alpha(\gamma_{so} - \gamma_{sw} - \gamma_{ow}) = \alpha\gamma_{ow}(1 - \cos\theta)$$

where α is the flake projected area inserted at the oil/water interface and it is assumed that the flake lies in the oil/water interface whether the interface is curved or flat. We expect that usually the contact angle will nominally be 90° , so that this equation simplifies to $\alpha\gamma_{ow}$. However, some applications discussed in the sequel involve flakes 60 nm thick, so it is likely in such cases that a contact angle less than 90° will be found, as edges are more hydrophilic than basal planes of GO (graphene oxide), rGO (reduced graphene oxide), or G (graphene). The surrounding sheaths of spherical particles or graphene nanosheets provide robust steric stabilization against particle–particle collisions and against mechanical deformation.

2. Availability of graphene, graphene oxide, and other graphenic stabilizers

Securing graphene dispersions in solvents and in aqueous phases is reviewed by Sun in this issue [14] and recently by Texter [15]. Using graphene flakes and platelets as Pickering emulsion stabilizers has been less characterized than the use of GO and rGO flakes, but applications are increasing. The chemical production of GO flakes is also reviewed in this issue [16], and other approaches widely used are referred to in the sequel as modified Hummers methods [17,18]. The now ready availability of relatively low cost reduced GO and rGO, and

decreasingly expensive graphene dispersions suggests that Pickering emulsion formulation will become increasingly considered as a source of emulsions for new material applications. In addition, other application areas are developing based on the use of so called graphene quantum dots and carbon dots. Reviews of G, GO, and rGO, and their functionalization [19,20] are available.

Often the presence of a surfactant or a polymeric dispersing aid in a particular application is unwanted. A claim has been made that the use of a water soluble surfactant, binol, is useful for stabilizing GO single sheets or few sheet flakes in water during chemical reduction to rGO, and that binol can be completely removed by some sequence of solvent washing steps/treatments [21]. While this same possibility is true for many, many surfactants, the difficulty and expense of such surfactant removal is usually considered impractical on a cost basis. Binol is structurally very similar to many naphthalene-based surfactants. The questionable conclusion of complete removal of binol was simply a measured contact angle for water on an rGO film that was still less than 90°.

Graphene quantum dots, Qdots (GQDs), compose an exciting new class of nanocarbon stabilizers. Initial efforts may be traced to the use of variously substituted pyrenes where it was established that such amphiphiles exhibited strong binding to carbon nanotubes and to graphene because of pi-pi overlap. Earlier in this special issue Li and co-workers describe the synthesis of model GQDs [22]. While their studies were focused on profound structure-property relationships, one can easily see that choosing peripheral substituents that are solvent loving, such as oligomeric ethylene oxide for aqueous applications, would result in GQDs that would exhibit strong attraction for graphenic surfaces as well as strong attraction for the solvent. The number and type of GQDs are also reviewed herein, where Kellarakis covers recent GQD preparations and applications [23].

Dong and co-workers reported GQDs prepared by oxidizing carbon black in aqueous nitric acid, collecting a supernatant solution/suspension after centrifugation [24], and then converting GQDs isolated from such supernatant into GQD “surfactants” by thermal reduction. The starting materials “nGQDs” had an average diameter of about 11.5 ± 1.6 nm, an average thickness (determined by AFM) of 1.4 ± 0.3 nm, and an oxygen for about every six-ring in the nGQD; such moieties might be described as GO-dots [51]. These starting nGQDs were then subjected to varying amounts of thermal reduction in dimethylformamide (DMF) to produce rGQD by heating in DMF suspension for 1 to 7 days. These GQDs had to be sonicated to disperse in water; applications in emulsification are discussed in a later section [25].

An interesting application to the stabilization of graphene in water using GQDs comes from He and co-workers [26]. Their GQDs were prepared by a process reminiscent of GO via a modified Hummers method, with NaClO₃ digestion following the strong acid oxidation. Centrifugation was used to isolate a smaller size fraction, and this material was reduced by slow addition of ammonia. Dialysis was then used to separate a small molecular weight fraction of (8 kDa–14 kDa), and the GQD fragments were filtered through a nominally 20 nm filter to remove large fragments [26]. Unfortunately molecular structure and pK_a aspects were not characterized further, although UV/Vis spectra and XPS spectra were provided. A number frequency particle size distribution from analysis of TEM is illustrated in Fig. 1, where a number frequency average of about 4 nm was obtained. AFM analyses suggested these GQDs were less than 2 nm thick, and the authors concluded this corresponded to less than 2–3 graphenic layers. The larger GQD cores synthesized by Li and co-workers were about 3 nm in diameter, so this approach of He and co-workers is potentially highly significant. While they relied on un-reduced oxygen containing defects for amphiphilicity, such sites could provide simple attachment points for other solvent-loving groups.

Guo and co-workers have reported 10 nm GQDs made by thermal reduction of GO dots, useful for Pickering emulsification and capping or stabilizing nano Au@GQD composite nanoparticles [27]. Cho and

co-workers prepared luminescent GQDs of varying amphiphilicity by grafting varying amounts of hexylamine to epoxy groups [28]. Grafting amounts of hexylamine of 25%, 50%, and 75% by weight relative to the starting GQD produced amphiphilic QCDs. Applications of these GQDs to Pickering emulsification and dispersions of graphene and graphite are discussed in the sequel.

3. Emulsions

Huang and co-workers showed that GO flakes exhibited preferential surface segregation at the air/water interface by depositing aqueous GO films from aqueous methanol [29]. Brewster angle microscopy (Fig. 2) provided vivid imagery of GO flake compression as the Langmuir trough pressure was increased from a gas phase behavior of randomly oriented non-touching flakes, to randomly close-packed flakes, to randomly close-packed with small interstitial areas, and to randomly close-packed with very little interstitial area. These last two close-packed arrangements required bending of contacting sheets along contact lines, and at the most closely packed state a surface pressure of about 35 mN/m was measured [29]. This surface pressure corresponds to a surface tension at the air/water interface of about 37 mN/m, and this surface tension may be taken as an approximation to the upper GO surface energy of these flakes. This energy is consistent with a fairly hydrophobic GO basal plane, but about 8 mN/m higher than benzene and toluene surface tensions at 25 °C. Hydroxyl, ether, and carboxyl groups emanating from the basal plane might account for such a higher surface energy. This surface energy is comparable to that of many oxygen-free polymers (polyvinylidene fluoride, 32 mN/m; polystyrene, 34–38 mN/m) and oxygen-containing polymers (polyethylmethacrylate, 32–34 mN/m; nylons, 34–39 mN/m; cellulose acetate, 38–41 mN/m) [30]. Contact angle analysis of GO films as a function of thermal reduction temperature yielded 49–51 mN/m for GO surface energy and values ranging from 36 to 40 mN/m for thermally reduced GO and rGO, having about 87% sp² carbon [31]. An estimate of about 47 mN/m [15,32] for the surface energy of graphene suggests that there remains considerable uncertainty to our knowledge of these surface energies. This apparent discrepancy for GO might be found in the influence of bending and mechanical stresses not included in the modeling of the GO compression reported by Huang and co-workers [29].

Sun and co-workers studied the kinetics of GO adsorption and tiling at the toluene/water interface in a series of elegant pendant drop experiments [33]. Diffusion to the interface is rate determining. When the adsorbed amount of GO is in the interfacial “gas” domain, interactions between sheets are minimal. By decreasing the volume of toluene in a given droplet, the adsorbed GO sheets reached a “jammed” state. When the toluene phase volume was decreased further, the jammed

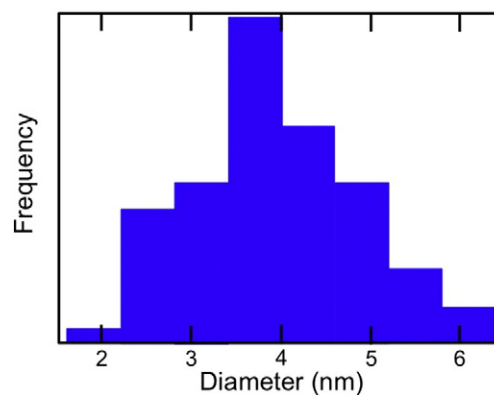


Fig. 1. GQD size distribution determined by AFM analysis of GQD stabilizers prepared by He and co-workers. Adapted with permission from Ref. [26]; ©2015 by the American Chemical Society.

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