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Foam stabilisation using surfactant exfoliated graphene

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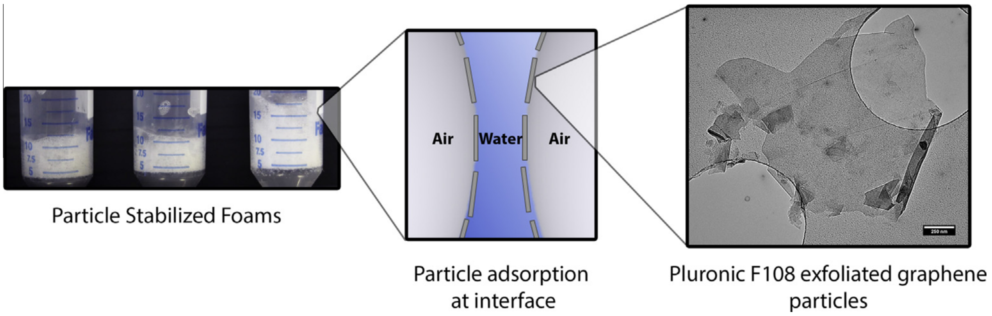
GRAPHICAL ABSTRACT



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ABSTRACT

Liquid–air foams have been stabilised using a suspension of graphene particles at very low particle loadings. The suspension was prepared through the liquid phase exfoliation of graphite in the presence of the non-ionic tri-block surfactant, Pluronic® F108. The graphene particles possess an extremely high aspect ratio, with lateral dimensions of between 0.1 and 1.3 μm as evidenced by TEM imaging. The particles were shown to exhibit a number of other properties known to favour stabilisation of foam structures. Particle surface activity was confirmed through surface tension measurements, suggesting the particles favour adsorption at the air–water interface. The evolution of bubble size distributions over time indicated the presence of particles yielded improvements to foam stability due to a reduction in disproportionation. Foam stability measurements showed a non-linear relationship between foam half-life and graphene concentration, indicative of the rate at which particles adsorb at bubble surfaces. The wettability of the graphene particles was altered upon addition of alkali metal chlorides, with the stability of the foams being enhanced according to the series $Na^+ > Li^+ > K^+ > Cs^+$. This effect is indicative of the relative hydration capacity of each salt with respect to the surfactant, which is adsorbed along the graphene plane as a result of the exfoliation process. Thus, surfactant exfoliated graphene particles exhibit a number of different features that demonstrate efficient application of high-aspect ratio particles in the customisation and enhancement of foams.

1. Introduction

The ability to produce stable aqueous foams is of great importance in a range of industrially relevant processes including mineral froth flotation, and effluent and waste-water treatment amongst others [1]. Foams can generally be described as a dispersion of air bubbles surrounded by a continuous liquid phase. However, most aqueous solutions require adsorption of surface active materials at the air–water interface in order to stabilise the bubble surface and produce persistent foams. This results in highly energetic air–water interfaces being replaced with less energetic sur-

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faces, causing a reduction in the overall free energy of the system. Materials capable of this behaviour include classic foaming agents such as surfactants, as well as solid particles which have been shown recently to be effective in stabilising foams with [2,3] and without [4,5] the aid of a surfactant.

The thermodynamic properties of particles at the air–water interface greatly improve foam stability compared to surfactants. At equilibrium, surfactant adsorption and desorption at the air–water interface occurs at relatively short timescales, with the energy of attachment usually several kT per molecule [6]. In contrast, the energy required to remove a spherical particle from the air–water interface is given by Eq. (1):

$$E = \pi r^2 \gamma (1 \pm \cos\theta) \tag{1}$$

where E is the energy of attachment, r is the particle radius, γ is the interfacial surface tension and θ is the contact angle the particle makes with the interface. Given the size of conventional particle foam stabilisers, the energy required to remove a particle from the interface is typically several orders of magnitude greater than that of a surfactant molecule. Thus, due to the effect of particle size on attachment energy, many particles can be considered irreversibly adsorbed at the interface in comparison to surfactant molecules.

The stability of bubble surfaces in foams is also affected by a combination of other properties including particle concentration and wettability. Particles stabilise the foam structure by the formation of an incompressible layer of particles at the air–water interface. Thus, efficiently stabilised foams usually require a considerable particle concentration (0.01–2% w/w), and favour particle sizes and shapes with efficient packing [1,7–9]. Additionally, the energy of attachment of particles at the air–liquid interface is highly dependent on the particle contact angle, which can be influenced by factors such as shape [10,11], surface roughness [1] and surface chemistry [12]. Particles with intermediate wettability ($40° < \theta < 90°$) have been shown to be most efficient at stabilising foams, either through adsorption at the air water interface or resisting drainage in the lamellar film. In contrast, particles with greater hydrophobicity ($\theta > 90°$) can destabilise foams through particle bridging-dewetting mechanisms. Meanwhile, hydrophilic particles ($\theta < 40°$) generally demonstrate little to no influence on foam stability, remaining dispersed within the thin film between bubbles. In some cases however, hydrophilic particles have been shown to resist drainage of the bubble film by collecting in the Plateau borders [6]. Thus, it is critical that a range of physical factors are considered when selecting particles for use as foam stabilisers.

One material that holds great potential as a foam stabiliser is graphene [13]. Graphene has gained tremendous interest over the past decade due to its unique structure, characterised by a single monolayer of sp^2 bonded carbon atoms arranged in a planar, hexagonal lattice [14,15]. This 2-dimensional structure is responsible for an assortment of exceptional material properties [16–18], which could enhance the performance of a wide variety of technologies including particle stabilised foams. For instance, graphene is an ideal candidate for imparting foam stability due to its extremely high surface area to volume ratio, which may enable effective foam stabilisation at low loadings in comparison to conventional stabilising particles [19]. Pristine graphene has also been shown to exhibit effective gas barrier properties [20], which could assist in preventing foam deterioration caused by disproportionation.

Although there are many methods used to produce graphene [21], ultrasonic exfoliation of graphite is particularly suited to preparing graphene for use in stabilising wet foams. The process is capable of forming highly concentrated, aqueous dispersions of graphene using continuous surfactant addition, which promotes exfoliation of the graphite in the liquid phase [22–25]. Surfactant adsorbs onto the graphene surface, preventing reaggregation of the graphene by imparting electrostatic and steric interactions specific to the surfactant. Thus, using an appropriate surfactant during the exfoliation process enables particle surface interactions, and therefore particle wettability, to be tailored to particular foaming applications.

Although foams have been stabilised previously using high-aspect ratio particles [19], surfactant exfoliated graphene particles exhibit even higher aspect ratios, approaching that of two dimensional materials [26]. Consequently, investigating foams stabilised using surfactant exfoliated graphene provides an opportunity to study the stability mechanisms employed by planar particle geometries at low particle loadings. Despite intense interest in graphene within a broad range of research areas however, the authors are unaware of any studies using graphene as a foam stabilising species. Here, foams stabilised using low concentrations of liquid phase exfoliated pristine graphene particles are demonstrated. Both the foam and the graphene particles under investigation were prepared using the non-ionic surfactant, Pluronic F108. Unlike conventional stabilising particles, the graphene particles provide stability by resisting drainage and disproportionation of the foams even at very low concentrations. This is achieved through the high surface area and low gas permeability properties exhibited by the graphene sheets, in addition to favourable surface interactions arising from the adsorbed surfactant.

2. Materials

In this study, synthetic graphite powder with a nominal particle size of less than 20 μm was used as received from Sigma Aldrich. The poloxamer Pluronic® F108 (M_n ~14.6 kDa, $HO(C_2H_4O)_{141}(C_3H_6O)_{44}(C_2H_4O)_{141}H$) and LiCl, NaCl, KCl and CsCl were also obtained from Sigma Aldrich. All solutions were prepared using ultra-pure water with a pH of 6.8 and resistivity of 18.2 MΩ cm.

3. Methods

3.1. Preparation of stock graphene suspensions

Stock graphene suspensions were prepared *via* the method of ultrasonic exfoliation of graphite, with continuous surfactant addition [22]. In a typical experiment, a 10% w/w solution of Pluronic F108 (180 mL) was added at a rate of approximately one drop per second to a 2% w/w suspension (196 mL) of graphite powder in water under ultrasonication for 90 min. In total, 10 batches of the suspension were prepared. The suspensions were then centrifuged at 2500 rpm for 20 min to sediment larger, non-exfoliated graphite particles. The suspensions were then combined and further concentrated by heating the solutions at 70 °C while stirring, evaporating the suspensions down to a total volume of 500 mL. The solutions were then sonicated for a further 20 min at 70 W. The resulting suspension was dialysed against water for a minimum of 48 h to remove unadsorbed surfactant from the stock suspension.

3.2. Characterisation of graphene suspensions

The graphene concentration of the stock suspension was obtained using the method described by Lotya et al. [25]. Samples of the suspension were diluted by a factor of 100 and the visible light spectra measured using UV–Visible spectroscopy. Applying the Beer-Lambert Law to the absorption intensity of the samples at a wavelength of 660 nm and applying an extinction coefficient [27], ε, of 54.22 L g^{-1} cm^{-1}, yielded an average stock graphene concentration of 0.54 mg/mL.