



Highly efficient recovery of graphene oxide by froth flotation using a common surfactant

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ABSTRACT

In this work, it is shown that graphene oxide (GO) sheets can be effectively recovered from aqueous solution by a simple froth flotation method. Small amounts of cetyltrimethylammonium bromide (CTAB) are added to assist with flocculating and driving the GO to the air–water interface, then ultrasonication is employed to form a foam that entrains the GO. The surfactant is essential in this process by firstly destabilising the GO dispersion through surface charge neutralisation, allowing the particles to aggregate. Furthermore, the hydrophobic component of the adsorbed surfactant molecules enhances adsorption of the GO at the air–water interface. Positioning the sonicator tip precisely at the air–water interface is crucial for foam formation by ensuring air bubbles are entrained into the sample. The nature of the foam can also be manipulated by altering the sonication intensity or by incorporating additional surfactant additives. At ideal GO:CTAB ratios, almost full removal (>99%) of the GO from an aqueous dispersion is achieved, with minimal overall change in the particle size distribution of the GO. It is shown that this process can also be used when GO is employed as an adsorbent for removing toxic metals and organic species from aqueous solution.

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1. Introduction

Froth flotation is an efficient and low energy separation technique that is widely used in industry for the selective removal of materials from water, being commonly employed in areas such as minerals processing [1,2] and wastewater treatment [3]. This technique involves bubbles rising through an aqueous mixture, and exploits differences in the attachment efficiencies of the materials at the air–water interface, to enable their selective separation [4,5]. Froth flotation can be used on a broad variety of materials, from molecules to colloidal particles, and is exceptional in its ability to deal with large industrial fluid volumes. The fact that bubbles are of low density and rise rapidly means that fast, low energy mixing and separation occur within a vessel [6]. Furthermore, the entrainment of materials in a concentrated froth or foam that floats on top of the aqueous subphase enables easy collection simply by skimming or spilling over of the froth, unlike separation of particulates through sedimentation. Hence froth flotation is a comparatively efficient and effective separation technique with excellent economical value

[7].

Likewise, the interest surrounding graphene oxide (GO), an atomically thin material derived from the graphite carbon lattice, has soared in recent years [8]. Unlike pristine graphene, GO has a rich composition of oxygen-containing functional groups which serve to make the material hydrophilic [9,10], hence GO has potential in aqueous applications such as adsorbents for water treatment or mineral extraction where the use of pristine graphene would be impractical. However, of paramount importance to its deployment is the efficient removal of the GO itself from water for its use as an adsorbent to be industrially viable; a method such as froth flotation to enable this would be ideal. Membrane filtration could also be a useful method for recovering GO from water, as filters with nanoscale pore sizes are commercially ubiquitous and would easily capture large GO sheets. However, filters for the industrial scale do not typically have pore sizes below 1 μm, due to significant decreases in the rate of diffusion [11]. As such it is possible that the majority of sub-micron sheets may not be captured by the membrane. Furthermore, particles with potentially large lateral dimensions like GO sheets can very quickly result in pore blocking, which may render the filter ineffective [12]. Accumulation of matter on the membrane can also eventually lead to

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fouling which can negatively impact the performance of the filter and reduce its lifespan [13]. Membrane filters therefore have the disadvantage of requiring constant upkeep, whereas froth flotation relies only on the surface chemistry.

GO sheets have been shown to exhibit surfactant-like properties and adsorb at a variety of interfaces including air–liquid [14]. This effect has been attributed to the amphiphilic character of the sheets, with the hydrophobicity being greater on their basal plane [15–18]. Therefore the entrainment of GO particles within a foam should be readily achievable. However, GO sheets in water exhibit a strong negative surface potential as a result of readily deprotonated carboxylic groups around their periphery, thus the sheets are highly stabilised against aggregation through electrostatic inter-particle repulsions [19,20]. Because of this effect, we have shown recently that clean GO sheets do not spontaneously adsorb at interfaces, and remain favourably solvated in the bulk water [14]. Therefore, GO must be rendered surface active, which can be achieved by employing a surface active ‘collector’ [14], such as a surfactant molecule, to enhance the foamability of GO and facilitate its recovery via froth flotation.

The addition of surfactants to colloidal dispersions of hydrophilic silica particles has been identified as a pathway to boosting the foamability of the particles [21–24]. The physical basis for this phenomenon is that the surfactant molecules adsorb to the surfaces of the particles, increasing their hydrophobicity such that the particles and surfactants then collectively adsorb to the air–water interface [25,26]. Foams stabilised by solid particles are known as ‘Pickering’ [27] (or ‘Ramsden’) [28] foams, and are a well established commodity in colloid science. As GO sheets are microscopic in size (and particulate in nature), foams stabilised by GO are of the Pickering variety [29]. Particle-stabilised foams show unprecedented stability due to their high desorption energy from the surfaces of the bubbles [30,31]; this effect is amplified when high aspect ratio nanosheets are used [32,33]. Therefore, utilising GO in the stabilisation of foams can be expected to offer enhanced stability to coalescence or collapse of the foam. The process of stabilising a foam however, as with emulsions, relies on the presence of a surface active or surface adsorbed component, hence the importance of surfactant inclusion in the case of GO systems.

In this work, we develop and explore a recovery method for GO from aqueous solution by capturing the sheets within a foam network. Cetyltrimethylammonium bromide (CTAB) surfactant is incorporated to facilitate this process, and the synergistic effects of the two components are investigated to understand the key factors driving foam formation. Previous work has reported the separation of carbon nanoribbons by froth flotation [34]; however, the focus was on statistical analysis and modeling of the separation. Our work focuses on the fundamental physical chemistry of the foaming phenomenon for GO nanosheets, and optimising the recovery process such that maximal capture is achieved in the most efficient way. CTAB has been used as an aid for GO synthetic procedures [35,36]. Other studies on foam preparation using two-dimensional carbon nanomaterials involve high energy and low yielding techniques such as freeze drying [37,38], chemical vapour deposition [39] and electrochemistry [40], therefore a facile and thermodynamically driven foaming process may improve the feasibility of GO use at larger scales.

2. Experimental

Graphene oxide was synthesised from graphite flakes (Sigma, +100 mesh) according to the improved Hummers' method of Marcano et al. [41] Changes to the procedure include an incremental addition of the potassium permanganate prior to heating the mixture, and purification by dialysis for 1 week (cellulose dialysis

tubing, 14 kDa molecular weight cutoff, Sigma) after an initial 3 cycles of centrifugation (4000 rpm), in which redispersion of the GO in ultrapure water was undertaken. The product was kept and characterised in aqueous suspension at all times.

Flotation and foaming of the GO was achieved by ultrasonication using a Branson 450 Digital Sonifier (20 kHz frequency, 400 W max power). A specified concentration of cetyltrimethylammonium bromide (ChemSupply, ≥95%) was added to the GO dispersion then mixed initially by gentle shaking. For froth flotation, the tip of the ultrasonic probe was then positioned precisely at the air–liquid interface of each sample. Sonication amplitudes were then varied between 10%, 30% and 50% of the maximum amplitude for the microtip used, corresponding to energy inputs of 0.79, 2.55 and 4.05 W/cm³ for this instrument (see [Supplementary Data](#) for calculations), and the total sonication time kept constant at 30 s. Characterisation of the resultant foams by light microscopy imaging was conducted using a Kozo XJP-300 polarizing microscope with a 4× magnification microscope objective lens and an attached CCD camera (Flea3, Point Grey, Richmond, BC, Canada). Foam material was moved by spatula onto a glass slide after which a cover slip was gently mounted to create an even plane of focus for imaging. Cocamidopropyl betaine (CAPB) was obtained from Aussie Soap Supplies as a 35% solution in water by mass.

Zeta potentials of GO/CTAB systems were measured by phase analysis light scattering using a Brookhaven Nanobrook Omni. Data points were averaged from 5 measurements for each sample with each measurement comprising 20 phase cycles at 25 °C. The palladium electrode was immersed carefully to ensure no bubbles were created and cuvettes were made from polystyrene with pathlengths of 1.0 cm. Zeta potentials, ζ , were determined according to the Smoluchowski approximation:

$$u_E = \frac{v_E}{E} = \frac{\zeta \epsilon}{\eta}$$

where u_E is the electrophoretic mobility, v_E is the electrophoretic velocity, E is the electric field strength, ϵ is the permittivity and η is the viscosity of the medium.

Atomic force microscopy characterisation of the GO before and after being subjected to the flotation process was performed using a JPK NanoWizard 3. Samples were prepared by spin coating a small aliquot (< 5 μ L) of diluted GO dispersion (0.1 mg/mL) onto a freshly cleaved mica disk (ProSciTech) for 1 min (2000 rpm). Images were 50 μ m² in area and obtained in tapping mode with a set-point value around 0.6 V and a line rate of less than 0.5 Hz. Cantilevers were Bruker NCHV model with nominal spring constants of 20–80 N/m and resonant frequencies around 320 kHz. The images were refined using the JPK data processing software, however analysis of individual sheet lateral dimensions were performed using Gwyddion software [42]. Post-flotation GO was purified of surfactant by initially redispersing the foam in 1 M HCl and centrifuging at 8000 rpm for 15 min. The GO was then washed twice in a 50/50 mixture of water and ethanol with further centrifugation to remove as much CTAB as possible. Final redispersion of the GO was in ultrapure water only.

Quantification of cadmium chloride (BDH Chemicals, ≥99.5%) removal was performed using atomic absorption spectroscopy (AAS) on a GBC Scientific Equipment XplorAA with an air–acetylene flame ionisation detector. The instrument was fitted with a Cadmium element lamp and analysis was performed at a wavelength of 228.8 nm with a slit width of 0.5 nm. Caffeine (Sigma, ≥99.5%) removal was monitored by UV–visible spectrophotometry on a Cary 60 instrument from Agilent Technologies in 1 cm path-length quartz cuvettes across the wavelength range 200–350 nm. All samples were prepared by adding the specific

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