

## Editor's Choice

## Graphene oxide nanoplatelet dispersions in concentrated NaCl and stabilization of oil/water emulsions

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## ARTICLE INFO

## Article history:

Received 22 December 2012

Accepted 12 March 2013

Available online 4 April 2013

## Keywords:

Graphene oxide nanoplatelets

Stable dispersions

Oil-in-water emulsions

High salt

## ABSTRACT

Stable dispersions of graphene oxide nanoplatelets were formed in water at pH 2–10 even with 5 wt% NaCl. For these conditions, oil-in-water emulsions stabilized with graphene oxide nanoplatelets remained partially stable for 1 year. The droplet sizes were as small as  $\sim 1 \mu\text{m}$  with a low nanoplatelet concentration of 0.2 wt%. The emulsions were stable even for nanoplatelet concentrations down to 0.001 wt%. The stabilities of the emulsions even at high salinity may be attributed to the high anion density at the graphene oxide nanoplatelet edges which protrude into the water phase. Furthermore, the graphene oxide nanoplatelets are shown to adsorb on the surfaces of the oil droplets. The conceptual picture of graphene oxide nanoplatelets adsorbed to a greater extent on the water side of the oil/water interface, along with the high density of anions on their edges, cause the oil/water interface to curve about the oil phase, resulting in oil-in-water emulsion droplets. The dispersion stability with a very small amount of graphene oxide-based stabilizer, offers an intriguing opportunity for applications including CO<sub>2</sub> sequestration and enhanced oil recovery in deep subsurface formations, which generally contain high-salinity brines.

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## 1. Introduction

Nanoplatelets of graphene or graphene oxide (G-O) are drawing considerable interest for potential applications, because of their extremely large surface area per mass and their unique properties including very high electrical and thermal conductivities and promising mechanical properties. Research activities are extensive for graphene oxide, e.g., in durable polymer composites with high elasticity [1], as nano-scale sensors that can be deployed in highly confined spaces [2], or as catalytic supports in facilitating oxidation and hydration reactions [3,4]. As a pathway to distribute such nanoplatelets uniformly in polymer phases, stable aqueous dispersions have been successfully designed [5–8]. Graphene oxide nanoplatelets (G-ONs) have also been shown to stabilize oil-in-water emulsions [9,10].

G-ONs disperse well in water and are thus hydrophilic [2,11–13]. G-ONs dispersed in high salinity brines are shown here to be highly stable against aggregation or settling. However, as G-ONs have an edge-to-center distribution of hydrophilic and

hydrophobic properties, they are amphiphilic and can adsorb to oil/water interfaces and lower the interfacial energy [14]. Solid-stabilized foams and emulsions can exhibit longer stabilities than surfactant-stabilized foams/emulsions, and the use of various solid particles for CO<sub>2</sub> foam stabilization has been studied [15–18]. Although untested, G-ONs may be interesting candidates for formation and stabilization of even CO<sub>2</sub>/water emulsions or foams, so that CO<sub>2</sub> could be perhaps securely stored in deep subsurface formations. Generally, plate-like particles have been shown to produce highly stable foams and emulsions due to the steric hindrance provided by the adsorbed particles at the oil–water interface [19,20]. Similarly, since G-ONs can cover an extremely large interfacial area for a given mass, theoretically about  $\sim 2000 \text{ m}^2/\text{g}$  [2,11], they may be expected to be highly efficient stabilizers at low concentrations. Not only do the G-ONs stabilize emulsions, they also offer the potential for multifunctionality in upstream oil industry applications. They might be used for electrical sensing, to increase the effective viscosity of the oil-displacing fluids, and/or to deliver certain chemicals at downhole locations or even into reservoir formations. Similar use of nanoparticles for potential oilfield applications is an active research area, e.g., for silica nanosphere-stabilized oil/water emulsions [21,22] and CO<sub>2</sub> foams [23] for improved oil

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displacement, and for delivery of superparamagnetic nanoparticles deep into reservoirs for improved oil detection [24].

We report here: (1) dispersion of G-ONs in water over a wide range of pH and salinity up to 5 wt% NaCl, (2) stabilization of oil-in-water emulsions with G-ON at various concentrations as low as 0.001 wt%, and (3) stabilization of emulsions in high salinity brines, even up to 5 wt% NaCl. The G-ON-stabilized Pickering emulsions remained partially stable for 1 year. The emulsion stability at high salinity is believed to be due to the high anion density at the G-ON edges, which are most likely in the water phase and provide electrostatic stabilization, and to the steric separation of the oil droplets. A key consideration for subsurface applications is that aqueous dispersions of G-ONs are stable and that G-ONs stabilize emulsions at high salinity conditions that generally prevail in deep aquifers and in oil reservoirs.

## 2. Experimental

### 2.1. Preparation of graphene oxide nanoplatelets (G-ONs)

Graphite oxide was synthesized by the modified Hummer's method [25]. One gram of natural graphite (Bay Carbon, SP-1) was first mixed with 50 ml concentrated  $H_2SO_4$  in a flask, which was then cooled to 0 °C in an ice bath, followed by the addition of 5 g of  $KMnO_4$  over a 30-min duration. The mixture was then heated and stirred at 35 °C for 2 h. An ice bath was subsequently used to cool down the solution to 3–4 °C; and 23 ml of de-ionized water was slowly added into the flask while stirring to minimize heating. The temperature in the ice bath was monitored and controlled to be no higher than 7 °C, by adding water, and ice if needed. Once the temperature was stabilized, more DI water (270 ml) was added to dilute the suspension, by stirring at 300 rpm.  $H_2O_2$  (30 wt% in water) was added in drops to remove excessive  $KMnO_4$ . The final suspension was filtered and washed by HCl (10% in water) five times, which was suction-dried for 12 h in the glass filter. Further drying was done in vacuum at room temperature for 1 day.

As observed visually, a uniform and stable suspension of 0.2 wt% G-ONs in water was obtained by sonication (VWR B2500A-MT) for 2 h at room temperature.

### 2.2. Pickering emulsion preparation

The G-ON aqueous dispersion (0.2 wt%) was used for the emulsion preparation. 1 ml of dodecane (Alfa Aesar, Purity: 99+%) was added to 1 ml of the G-ON dispersion in a glass flask. The system was emulsified using a probe sonicator (Branson Sonifier 250) for 1 min. in the pulse mode (power: 4–5, duty cycle: 20–30%). To study the effects of salinity on emulsification, brines of 1, 3, or 5 wt% of NaCl were used. The dodecane–water emulsions were kept for a year to study the stability against phase separation, by measuring the changes in emulsion volume with time.

### 2.3. Characterization

Zeta potential was measured with a Brookhaven ZetaPALS instrument at 25 °C. Measurements were conducted in 10 mM KCl (Debye length  $\kappa^{-1} = 3$  nm) and the zeta potential was determined with the Smoluchowski model ( $\kappa a \gg 1$ ). Transmission electron microscopy (TEM) was used to observe the surface of oil-in-water emulsion. The experiments were performed on a FEI TECNAI G2 F20 X-TWIN TEM using a high-angle annular dark field detector. The samples were prepared using a “flash-freezing” technique, in which 400 mesh carbon-coated copper TEM grids (Ted Pella, carbon Type-B) were cooled using liquid nitrogen and then dropped

O/W emulsions stabilized with G-ONs [26]. Scanning electron microscopy (SEM; Zeiss Supra 40 VP field-emission SEM operated at an accelerating voltage of 30 kV) was used to observe the morphology of graphene oxide nanoplatelets (G-ONs). The interfacial tension ( $\gamma$ ) was measured from axisymmetric drop shape analysis of a pendant water droplet containing a known concentration of nanoplatelets in equilibrium with an excess oil phase, as described previously [27]. The average was taken of at least 5 measurements that were acquired every 10 s. The pendant drop was illuminated with a monochromatic light source, consisting with an optical rail for alignment, a CCD video camera (Sony, XC73CE), and a computer, and the digital images were recorded. The coordinates of the profiles were then analyzed through a computer program embedded in a software package CAM200 (KSV Ltd., Finland) according to the Laplace equation [27]. For the emulsions, the images were analyzed to determine the droplet size using NIH Image J.

## 3. Results and discussion

### 3.1. Aqueous dispersion of G-ON

Fig. 1 shows an SEM image of G-ONs. While each G-ON is only a monolayer-thick, its areal dimension is fairly large with a wide size distribution, after the exfoliation of the graphene oxide sheets. The particle length varied from less than 100 nm to a few  $\mu$ m. The areal dimension of the G-ON was in the range up to several microns. Fig. 2 shows the aqueous dispersions of G-ON for different NaCl salinity and pH. The uniform dark appearance of the samples indicates that the dispersions are stable and homogeneous. The interior surfaces are sparsely charged but the edges are known to be highly charged [9,14]. The aqueous stability of the resulting G-ON dispersions are due to dense negative charges at their edges and the small inter-platelet attraction [28].

The zeta potential values for the G-ON dispersions were  $-41.8$ ,  $-53.1$ , and  $-52.8$  mV with no salt at pH 2, 6, and 10, respectively (Fig. 3). At pH 2, these values were more negative than reported previously [9], which may be attributed to the smaller plate size and greater fraction of edge sites. In addition, even after adding up to 5 wt% NaCl, the zeta potential of G-ON dispersions were about  $-15$  mV at pH 2, 6, and 10. The maintenance of a moderate zeta potential without salt reflects the high charge density at the nanoplatelet edges [28,29].

The electrostatic repulsion by the negatively charged groups at the edges of the G-ONs contributes to the stable dispersion of G-ON in water. The dispersibility in water is also influenced by

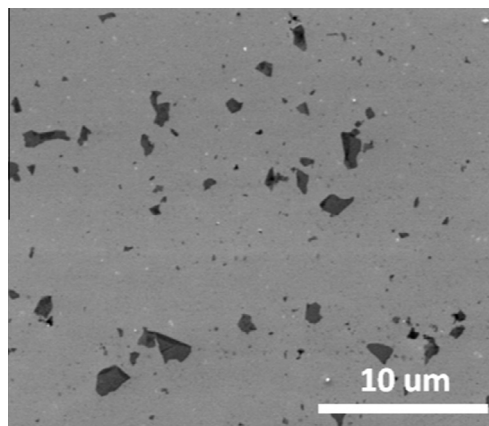


Fig. 1. Scanning electron microscopy (SEM) image of the graphene oxide nanoplatelets (G-ONs).

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