Editor's Choice

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

Ki Youl Yoon [a], Sung Jin An [b,d], Yunshen Chen [a], Jae Ho Lee [a], Steven L. Bryant [c], Rodney S. Ruoff [b], Chun Huh [c], Keith P. Johnston [a,*]

[a] *Department of Chemical Engineering, The University of Texas at Austin, 200 E. Dean Keeton St. Stop C0400, Austin, TX 78712, United States*
[b] *Texas Material Institute, The University of Texas at Austin, 1 University Station, C2201, Austin, TX 78712, United States*
[c] *Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, 200 E. Dean Keeton St. Stop C0300, Austin, TX 78712, United States*
[d] *School of Advanced Materials & Systems Engineering, Kumoh National Institute of Technology, 61 Daehak-ro, Gumi, Gyeongsangbuk-do, South Korea*

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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 ∼1 μm 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_2 sequestration and enhanced oil recovery in deep subsurface formations, which generally contain high-salinity brines.

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_2 foam stabilization has been studied [15–18]. Although untested, G-ONs may be interesting candidates for formation and stabilization of even CO_2/water emulsions or foams, so that CO_2 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 ∼2000 m^2/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_2 foams [23] for improved oil

* Corresponding author. Fax: +1 512 471 7060.
 E-mail address: kpj@che.utexas.edu (K.P. Johnston).

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 κ^{-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 (γ) 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 μm. 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
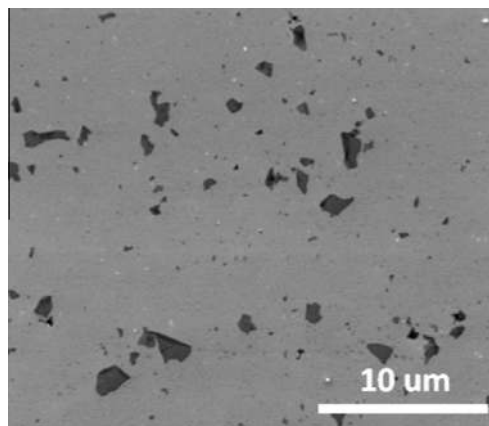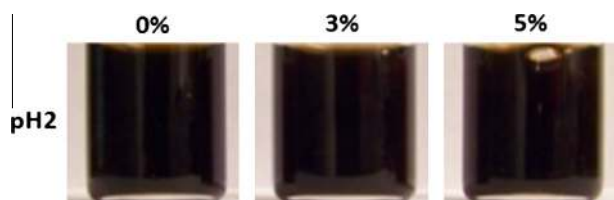

Fig. 1. Scanning electron microscopy (SEM) image of the graphene oxide nanoplatelets (G-ONs).

Fig. 2. Photographs of G-ON aqueous dispersions (0.2 wt% concentration) after 1 day at pH 2 and with 0, 3, and 5 wt% NaCl salinity. The dispersions have the same appearance, irrespective of the salt concentration or pH. The uniformly dark color means that the aqueous dispersion is stable against coalescence and/or settling.
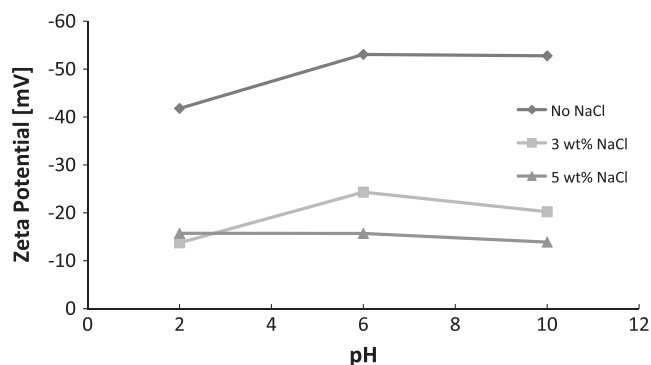
Fig. 3. Zeta potential measurement of G-ON dispersions with different NaCl concentrations at pH 2, 6, and 10.

hydration of the basal plane, as the hydroxyl functional groups are hydrogen bonding donors/acceptors and the epoxides are acceptors. Thus graphite oxide is a swellable material with roughly a monolayer of intralamellar H_2O. Thus, the stabilization is quite different than in the case of a polymeric stabilizer, which provides steric stabilization as a function of the length of extended chains [2,14]. This robust stability for wide ranges of salinity up to 5% and pH is quite unusual. For other charge-stabilized colloidal dispersions at 5% salinity, the thin double layers often lead to loss of electrostatic stabilization [30,31]. This stabilization may be due to the fact that G-ONs (i) have a high charge density at the edges favoring electrostatic repulsion; and (ii) are extremely thin thus weakening the van der Waals attraction between the platelets, which lowers the probability of platelet aggregation [9].

3.2. Properties of the emulsions

For G-ONs to serve as an emulsion stabilizer, it must adsorb at the oil/water interface, occupying a substantial interfacial area to prevent droplet coalescence. While the interfacial adsorption of colloidal particles may require energy to first form an oil/water interface, once they are adsorbed at the oil/water interface, they may provide emulsion stability [32–35]. The formation of the oil/water interface is provided by the high shear rate to overcome the Laplace pressure, which was produced by sonication. For nanoparticles with a high adsorption energy and surface coverage at the oil/water interface, emulsion droplets may be stabilized for long time periods [9].

The emulsification of oil/water using G-ON adsorbed at the interface has been achieved with simple shaking to form large oil droplets [9,35,36]. Sharif and coworkers also reported the formation of G-ONs stabilized oil/water emulsions using high power sonication to form droplets less than 5 μm with 1–5 wt% G-ONs [10]. As with the conventional Pickering emulsions, energy input is

required for droplet formation whereby the G-ON then must overcome the adsorption energy barrier and attach G-ON at the oil/water interface.

Qualitative analysis of the interfacial activity of G-ON was attempted by carrying out phase partitioning experiments, by mixing the G-ON containing water and dodecane gently. Even at low pH, G-ONs are too hydrophilic to disperse in dodecane and simply remain stable in the water phase. It is visibly evident that G-ON has a high charge density at its edges (electrical conductivities of 0.2 wt% G-ON dispersion: 725 μS/cm, 395 μS/cm, and 298 μS/cm at pH 2, 6, and 10). Therefore, the van der Waals attraction between the platelets is very small, which lowers the probability of G-ON aggregation and precipitation.

In order to determine the partition coefficient of the G-ON between water and dodecane, experiments were performed by forming emulsions with equal volumes of a 0.2 wt% of G-ON dispersion without added salt and dodecane by gentle hand shaking (low shear). The G-ON favored the lower aqueous phase and the dodecane phase was clear. Therefore, in the experiments below at high shear, it was expected that the G-ON would favor the water side of the interface and stabilize oil/water emulsions at high shear by the Bancroft rule [32].

Fig. 4 shows dodecane-in-brine emulsions, stabilized with G-ON at 0.2 wt% concentration, at different NaCl salinities and pH values. Photographs of the colors and textures of the phases of the samples are shown immediately (Fig. 4a) after sonication and 24 h later (Fig. 4b). For these emulsions, aqueous dispersions with G-ON concentration of 0.2 wt% were mixed with an equal volume of dodecane and sonicated. The ultrasound sonication produced emulsions with a droplet size range of 1–60 μm, as further described below (Figs. 5 and 6). In all cases the emulsion filled the entire volume of the vessel after sonication (Fig. 4a). A darker color was observed at pH 6 and 10 versus pH 2. In the case of G-ON, without salt, the oil-in-water emulsion filled the entire volume initially (Fig. 4a) but phase separated to a slightly smaller emulsion volume (Fig. 4b) within 24 h. A drop of the emulsion phase was added to water to confirm that it was indeed a dodecane-in-water (O/W) emulsion. The high electrical conductivities of (151.3 μS/cm, 161.5 μS/cm, and 178.5 μS/cm with no salt at pH 2, 6, and 10 indicate that water was the continuous phase for the O/W emulsion. These large conductivities indicate that the aqueous phase was the continuous phase. This curvature about oil was expected for hydrophilic G-ON with high negative surface charge, as they favored the water side over the oil side of the interface.

For the G-ON stabilized emulsion with 0–5 wt% NaCl at pH 2 (Fig. 4), the emulsions were light brown, indicating scattering by the oil droplets and interfaces. Without added salt at each pH, the lower phase was brown as it contained G-ON. With added salt, an extremely thin colorless lower aqueous phase was present after 24 h. At pH 6 and 10 after 24 h, approximately 80% of the total volume was still the top emulsion phase, and the aqueous phase was colorless. Here the salt drove the G-ON out of water to the interface. The emulsion stability is enhanced by the irreversible adsorption of particles to oil/water interfaces [32].

Micrographs taken immediately after emulsion formation are presented in Figs. 5a, c and 6. Analysis of microscopy images revealed that the emulsions stabilized by G-ON consisted of oil droplets ranging from 1 to 60 μm in diameter. In the case of no added salt, the majority of the emulsion droplets were smaller than 10 μm, even 1 day later after emulsion formation (Fig. 5b and d). The droplets move during sample preparation, thus the volume fraction of droplets is not illustrative of the 1:1 by volume ratio in some cases. Emulsion droplet sizes were relatively insensitive to changes in concentration of NaCl, even though they were polydisperse with diameters ranging between 1 and 60 μm (Fig. 6). At all pH values, after the excess aqueous phase was resolved after
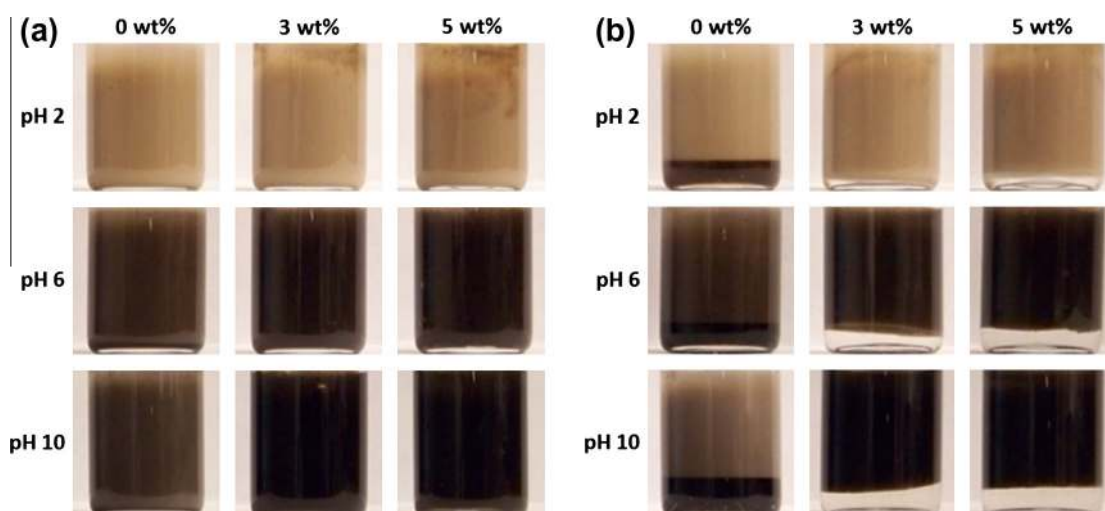
Fig. 4. Emulsions formed with equal volume fractions of dodecane and an aqueous dispersion of 0.2 wt% G-ON at pH 2, 6, and 10 with 0, 3, and 5 wt% NaCl salinity. The photos were taken (a) immediately and (b) 24 h after emulsion formation. Initially after emulsion formation, all vials appeared as a full emulsion.
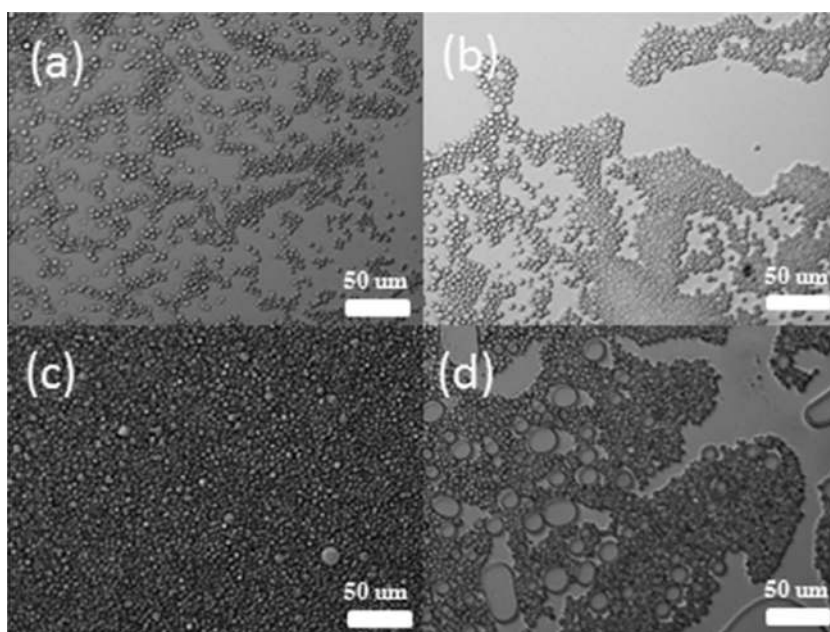
Fig. 5. Optical micrographs of emulsions without added salt at pH 6: (a) immediately after emulsion formation with 0.2 wt% G-ON, (b) 24 h later, (c) immediately after emulsion formation with 0.01 wt% G-ON, and (d) 24 h later.
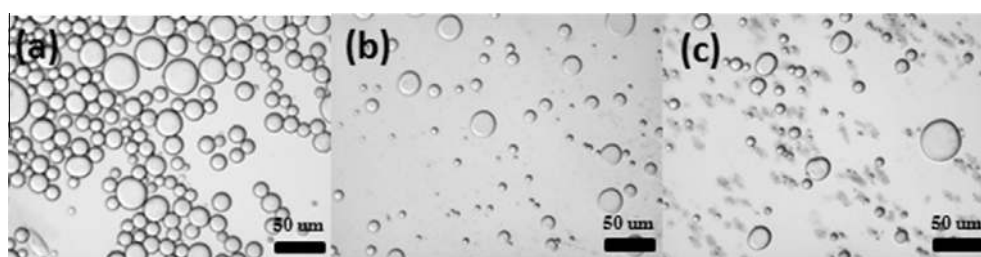
Fig. 6. Microscopy images of emulsions immediately after formation with 0.2 wt% G-ON with varying concentrations of NaCl from (a) 1%, (b) 3%, and (c) 5% at pH 2.

1 day (Fig. 4b), a stable emulsion with large oil and water volume fractions still remained after 1 year (Fig. S1).

Fig. 7 shows two oil droplets in O/W emulsions stabilized with G-ON at 0.2 wt% by transmission electron microscopy (TEM). The TEM images show graphene oxide layers at the oil/water interface that stabilize the oil droplets against coalescence. Long platelets may be observed extending deeply into the aqueous phase at various angles in multilayers, particularly in the image on the right.
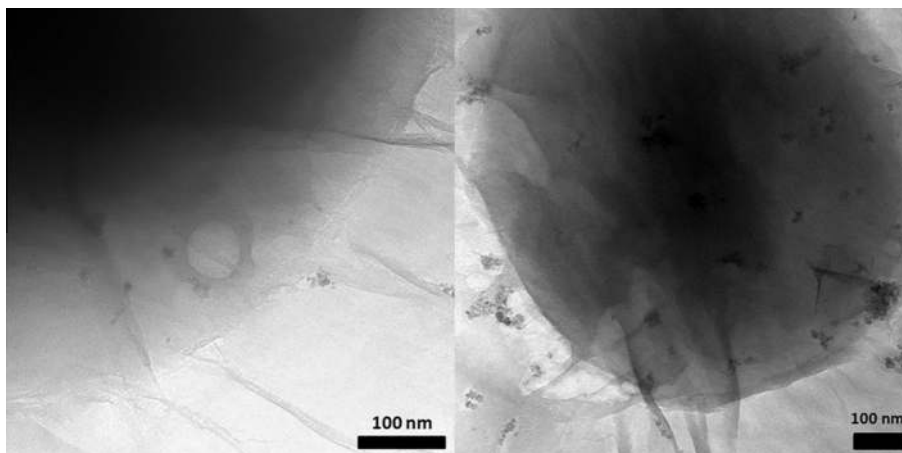
Fig. 7. TEM image of the graphene oxide nanoplatelets at the interface of oil/water emulsion at pH 6 without added salt.

Furthermore, individual G-ON and aggregated G-ONs are observable on the oil droplets (Fig. 7). In the case of rods, entanglement of the rods has been shown to increase emulsion stability [19]. The emulsion stability may also be attributed to the electrostatic repulsion between the oil droplets coated with the highly charged G-ON's. Furthermore, when the size of G-ON was larger than the emulsion droplets, highly wrinkled sheets were observed by Sharif and coworker [10]. In Fig. 7, some of the G-ON may have spanned adjoining oil droplets, while keeping them separate.

For extremely low G-ON concentrations, down to 0.001 wt%, emulsions of dodecane and water (1:1 volume ratio could still be formed at pH 6 by probe sonication. Photographs of the emulsions taken 24 h after their formation (Fig. 8 and Fig. S2) revealed the colors and phases of the emulsions. The ability to form and stabilize emulsions with a very small amount of G-ON may offer opportunities for applications including CO_2 sequestration in deep subsurface formations and enhanced oil recovery from reservoirs, which generally contains high-salinity brines.

3.3. Interfacial tension measurement of G-ON dispersion

G-ON may be expected to be amphiphilic from structural considerations as it has an edge-to-center variation of hydrophilicity.
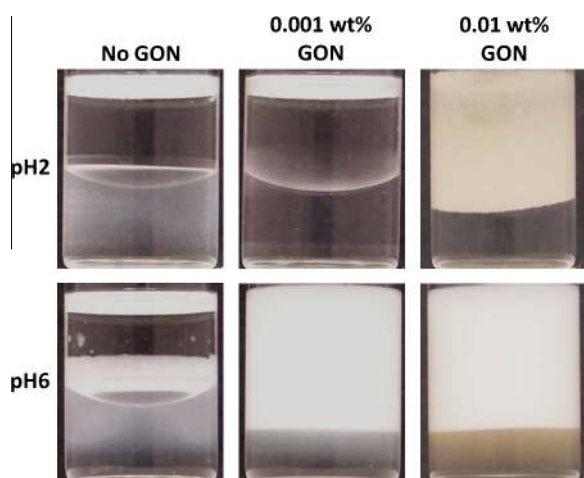
The edge carboxylate groups are hydrophilic, whereas the sp^2 carbon on the center surfaces is partially hydrophobic. G-ON has been shown to lower the interfacial tension between water and oil [9,14]. Consequently, adsorbed G-ON at an oil/water interface has the potential to stabilize an emulsion droplet, as was shown in Figs. 5 and 6. A. Therefore, the compact G-ONs at the interface in oil-in-water emulsions interact with each other by van der Waals attractions, electrostatic interactions, and hydrogen bonding [37]. The earlier studies [1,9,29,35,37] indicate that the edge of G-ON is still hydrophilic with high concentration of carboxylates while the basal plane is partially hydrophobic. Just as with the robust stability of the aqueous G-ON dispersions above, the long-term stability of the oil-in-water emulsions for wide ranges of salinity and pH is remarkable, in view of the fact that at high salinities, the electrostatic repulsion will diminish significantly. One possible mechanism is that the oil interacts more strongly with the partially hydrophobic center of the basal G-ON, while the hydrophilic edge from carboxylate group still residing in the water phase [37] and providing sufficient electrostatic repulsion with highly negative charge density. In view of its monolayer thinness and its high elasticity, a slight bending of the platelet, concave to water, will allow a majority of anionic charges from the carboxylate group still remain in the water side of the oil/water interface of the emulsion droplets.

The pH-dependent equilibrium interfacial tension at the dodecane/water interface, for 0.2 wt% G-ONs dispersed in water, was investigated with a pendant water droplet as shown in Fig. 9. The interfacial tension increases with pH, and decreases with salinity. The interfacial tension of the bare dodecane/water interface
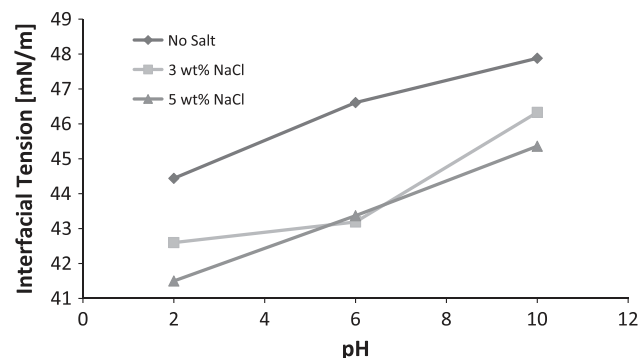

Fig. 8. Emulsions formed with equal volume fractions of dodecane and an aqueous dispersion (without added salt) without any G-ON, or with 0.01 wt%, and 0.001 wt% of G-ONs at pH 2 and 6 without salt. The photos were taken 24 h after emulsion formation.

Fig. 9. Interfacial tension measurement of 0.2 wt% G-ON at the dodecane–water interface with and without salt at pH 2, 6, and 10.

was 52.8 mN/m [38]. The interfacial tension at the dodecane/water interface decreased from 47.8 mN/m at pH 10 to 44.4 mN/m pH 2 without added NaCl salt. After adding 5 wt% NaCl salt to the G-ON dispersion, the dodecane/water interfacial tension was reduced by about 3 mN/m at each pH. As expected, the salt drove the highly hydrophilic G-ON from the aqueous phase towards the interface. This reduction in interfacial tension with G-ON by about 10 mN/m was large compared to the case of spherical silica nanoparticles, which have relatively uniform surface hydrophilicities [22]. Thus, the variation in hydrophilicity from the center to the edges in G-ON is beneficial for adding amphiphilicity, as reflected in the lowering of the interfacial tension. Once the large G-ON adsorbed onto the interfaces, they formed relatively rigid shells that provided steric hindrance and electrostatic repulsion, which provided long-term stability of the emulsion [19].

4. Conclusions

Graphene oxide nanoplatelet (G-ON) dispersions are shown to be stable in water with up to 5 wt% NaCl over a wide range of pH from 2 to 10, in contrast with previous work at lower salinities. The remarkable stability at such high salinity may be attributed to the combination of the strong electrostatic repulsion rendered by the charged edges and the weak van der Waals attraction from the extremely thin plates. Normally to achieve such robust colloidal stability for a wide range of salinity and pH, polymer chain adsorption on particle surface is required to generate configurational entropic repulsion [2]: The robust stability of G-ON dispersions without any additional surface coating, along with the very large surface area per mass for coverage of the oil/water interface make G-ON a very attractive material for various oilfield applications.

Oil-in-water Pickering emulsions with droplet sizes down to ~1 μm were formed using aqueous dispersions of G-ON with concentrations as low as 0.2 wt% without any addition of surfactants. The adsorption of G-ON at the oil/water interfaces (as shown by TEM and deduced from reductions in interfacial tension) stabilized the oil droplets in water, again over a wide range of pH from 2 to 10, and high salinities up to 5 wt% NaCl. These results show that the combined effects of strong electrostatic repulsion and weak van der Waals attraction provide not only the robust dispersion stability but also high emulsion stability [9]. The stability of emulsions even at such high salinity is due to the high carboxylic anion charge density at the G-ON edges, which appear to extend into the water phase, with slight bending of the highly elastic plates covering the oil droplet. The emulsions were partially stable for 1 year. The stonger inter-platelet repulsion at the water (hydrophilic) side of the interface relative to the oil (lipophilic) side contributed to the curvature about oil, along with the effects of attractive forces. The ability to stabilize emulsions with very low G-ON mass is of interest for various oilfield applications, such as delivering chemicals to downhole target locations, increasing the effective viscosity of oil-displacing fluids, and sensing reservoir geometry.

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