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Oil Emulsification Using Surface-Tunable Carbon Black Particles

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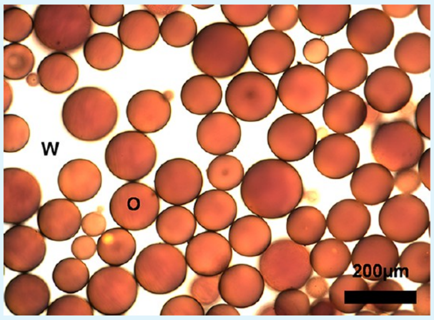

ABSTRACT: Emulsification of oil from a subsurface spill and keeping it stable in the water is an important component of the natural remediation process. Motivated by the need to find alternate dispersants for emulsifying oil following a spill, we examine particle-stabilized oil-in-water emulsions. Emulsions that remain stable for months are prepared either by adding acid or salt to carboxyl-terminated carbon black (CB) suspension in water to make the particles partially hydrophobic, adding the oil to this suspension and mixing. When naphthalene, a model potentially toxic polycyclic aromatic hydrocarbon, is added to octane and an emulsion formed, it gets adsorbed significantly by the CB particles, and its transport into the continuous water is markedly reduced. In contrast to an undesirable seawater-in-crude oil emulsion produced using a commercially used dispersant, Corexit 9500A, we demonstrate the formation of a stable crude oil-in-seawater emulsion using the CB particles (with no added acid or salt), important for natural degradation. The large specific surface area of these surface functionalized CB particles, their adsorption capability and their ability to form stable emulsions are an important combination of attributes that potentially make these particles a viable alternative or supplement to conventional dispersants for emulsifying crude oil following a spill.

KEYWORDS: *particle-stabilized emulsions, crude oil emulsification, dispersants, carbon black, cryo-SEM, oil spill remediation*

INTRODUCTION

Surfactants are commonly used to stabilize emulsions. Their ubiquity for this application rests on their effectiveness and their low cost. A practical example is the ~1.8 million gallons of surfactant (Corexit 9500A and Corexit 9527) used for the Deepwater Horizon oil spill in the Gulf of Mexico in 2010. For the subsurface application, the crude oil-in-seawater emulsion drops should be around 100 μm in diameter, and needed to stay stable in the water column for a few months for optimum consumption by bacteria. While effective, the exposure of the surfactant to the large quantity of seawater promoted its dissolution into the aqueous phase resulting in emulsion destabilization, rendering the oil less effective for natural remediation. This issue as well as the potentially negative consequences of the surfactant on the ecological chain[1] have prompted a search for alternate dispersants. Particles represent a different class of emulsion stabilizers, and they offer intriguing possibilities for this purpose. This is mainly driven by the fact that particles can adsorb almost irreversibly to liquid–liquid interfaces, allowing such emulsions to be stable even at extremely low concentrations of the dispersed phase. In addition, intrinsic surface, thermal, optical and electrical and magnetic properties of particles can be exploited to produce emulsions that have greater functionalities than surfactant stabilized ones. We exploit some of these features of particles in the work reported here.

Emulsions stabilized solely by solid particles were first observed by Ramsden[2] and Pickering.[3] Subsequent work investigated the relationship between the three phase contact angle and emulsion stability,[4,5] and the effect of particle flocculation on emulsification.[6] Commercial uses of Pickering emulsions are not common, but potential application areas that take advantage of the properties of the particles are emerging, including drug delivery,[7] novel material fabrication,[8,9] oil recovery,[10] cosmetics, food, paper, paint and personal products.[11−13] A range of particles including silica, polystyrene, iron oxide, bentonite clay, and graphene oxide[14−22] have been employed for emulsion formation. In each of these cases, the particle properties also play useful roles in determining the final characteristics of the emulsion.

Spontaneous entry of particles into liquid-fluid (termed oil−water for the remainder for this paper) interfaces is slow,[23] and mixing is used to accelerate this process. The energy ΔE required to detach a particle (we assume spherical particles for this illustration) from an oil−water interface into either bulk phase is given by

$$\Delta E = \pi R^2 \gamma_{\text{ow}} (1 - |\cos \theta|)^2 \qquad (1)$$

where R is the particle radius, γ_{ow} is the oil−water interfacial tension, and θ is the contact angle through either phase. For $R = 50$ nm, $\gamma_{\text{ow}} = 30$ mN/m, and $\theta = 90°$, eq 1 gives $\Delta E \approx 5.7 \times 10^4 kT$. Therefore, once a particle is in the interface it will not

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detach spontaneously. The presence of particles at the oil−water interfaces suppresses drop−drop coalescence and enhances emulsion stability. This is because the particles can be charged, providing repulsive interactions between droplets,[24] they can bridge across neighboring emulsion drops,[25−28] they can provide steric barriers[13,29] and they can impart enhanced interfacial viscosity that retards the thinning of an intervening liquid layer as the droplets approach each other.[30,31] Stable emulsions can be formed even if there is incomplete coverage of droplet surfaces.[20,25] The interaction of particle charge with the charge on the oil−water interfaces affects the assembly of particles at these interfaces.[32−35] Interfacial particle concentrations[13,36] and their size,[13,37]shape,[38,39] and interparticle interactions[40,41] impact the stability of these emulsions.[24]

Driven by their easy availability, range of surface chemistry, biocompatibility, high specific surface area, their ability to adsorb organics, their classification as GRAS (generally regarded as safe) materials, and their fractal nature, we have used a commercially available grade of surface modified carbon black (CB) particles suspended in water to create, and examine in detail, particle-stabilized octane-in-water emulsions. The presence of the emulsifier particles in the aqueous phase is expected to promote the formation of oil-in-water emulsions. The CB particles are aggregates of 8−10 "primary" particles, each of diameter ~20 nm, fused together in a flame process. The resulting fractal particle is about 100 nm-200 nm in nominal size and has a specific surface area of approximately 200m^2/g. CB particles are used as reinforcement in rubber tires, as pigments in inks and in thermoplastics for enhanced electrical conductivity, Young's modulus and UV stability.[42,43] Carbon blacks have been used previously as an emulsifier, but their inherent hydrophobicity causes them to form water-in-oil emulsions. In this work, we take advantage of covalently linked surface groups that can be used to tune the CB hydrophilicity, to consistently form oil-in-water emulsions. We carefully examine a model system consisting of octane, water and carbon black. We use these results to guide our work on the emulsification of crude oil, a specific application studied here.

We use optical and cryogenic scanning electron microscopy to image emulsions. Their stability is monitored using centrifugation. Zeta potentials of the particles at different pH and salt concentrations provide key insights into the formation and stability of these emulsions. Since low molecular weight polycyclic aromatic hydrocarbons (PAH) in crude oil can partition into surrounding water, there is interest in finding methods to lower this transfer to reduce potential toxicity to marine organisms after an oil spill. In this context, we examine the adsorption of a model low-molecula-weight PAH, naphthalene, from the oil phase in an emulsion onto the CB particles. As a potential application of these particles, we demonstrate the successful formation of stable crude oil (taken from the Gulf of Mexico Deepwater Horizon oil spill) -in-seawater emulsions. We compare the nature and lifetimes of Corexit 9500A stabilized emulsions with those stabilized by CB and show major differences between the two.

■ MATERIALS

The *para*-amino benzoic acid (PABA)-terminated carbon black suspension in water at pH 7.5 is obtained from Cabot Corporation. PABA is covalently linked to the carbon surface, at a treatment level of 0.1−4.0 μM/m^2, adequate to make the particles hydrophilic and completely dispersible in water.[44] There are no surfactants in the CB suspension. N-octane (anhydrous, ≥99.0%), pyrene (puriss. p.a., for fluorescence, ≥99.0%), Aerosol OT (AOT, 99%) and 1N hydrochloric acid are obtained from Sigma Aldrich. Sodium chloride is obtained from Fisher Scientific. Crude Oil from the Gulf of Mexico oil spill, BP-MC 252 and Corexit 9500A are obtained through the Gulf of Mexico Research Initiative program. Corexit 9500A is a mixture of surfactants dissolved in polypropylene glycol. All materials are used as received.

■ METHODS

Preparation of Emulsions. We use a 0.015 wt % carbon black suspension for our experiments. Two routes are used to make the emulsions. In the first, 1N hydrochloric acid is added to the suspension to lower the pH to 3.3. The surface carboxylate groups get partially protonated, and the hydrophobicity of the particles increase. Emulsions are also formed by adding sodium chloride to the CB suspension. We use 0.6 M NaCl to roughly match the overall salt concentration in seawater (~3.5 wt %); the Na^+ ions salt out some of the carboxylate groups on the surface of the CB. The protonation or the binding of sodium ions to the surface carboxylate groups results in increased particle hydrophobicity and chaining of the particles in the aqueous medium, producing a noticeable rise in the aqueous suspension viscosity. Rapid aggregation of the CB particles causes a difficulty in zeta potential measurements at 0.6 M NaCl. To gain insights into the effects of salt addition through such measurements, we have used 0.15 M NaCl suspensions for some of our experiments. In experiments with seawater, the emulsification proceeds without addition of any acid or salt to the CB suspension.

The acid- or salt- mediated CB suspensions are vortexed for 10 s at 3000 rpm. N-octane at an oil:water volumetric ratio of 3:5 is then added to the suspension and vortexed at 3000 rpm for 1 min, resulting in the emulsion. At these concentrations, most of the carbon black transfers from the aqueous phase to the oil−water interfaces of the freshly formed drops. This method of forming emulsions produces droplets of a wide size distribution, ranging from a few micrometers to a few hundred micrometers. Emulsions are also prepared using seawater and with crude oil BP-MC 252 as well as with Corexit 9500A and with AOT, one of the major components of Corexit 9500A. For the Corexit 9500A experiments, the surfactant is dissolved in the oil in a 1:20 surfactant solution to oil volumetric ratio. A 10 mM AOT solution in crude oil is used for those experiments. For these latter two experiments, seawater is added to the oil containing surfactants. The CB suspension is then added, and the mixture vortexed for 1 min at 3000 rpm to form emulsions.

Emulsion Stability. When an oil-in-water emulsion is subjected to a centrifugal field, the denser aqueous phase collects at the end of the tube furthest from the axis of rotation, and the lighter emulsion-containing phase moves to the other end. During this process, the oil droplets are forced against each other, and at a critical centrifugation rate, the first few drops start to coalesce. The pressure exerted on the oil droplets at these conditions is termed the critical de-emulsification pressure and is a reasonable measure of the stability of the emulsion under forced coalescence.[45] The critical de-emulsification pressure permits a quantitative comparison of the stability of emulsions formed under different conditions. If accelerations beyond the critical value are used, additional drop−drop coalescence take place, more oil is released, and a new equilibrium is established. The critical de-emulsification pressure, $P_{\text{de-emulsification}}$ is calculated by measuring the volume of oil released at a particular centrifugal acceleration[46,47] using[48]

$$P_{\text{de-emulsification}} = \Delta\rho g_k (V_{\text{oil}} - V_{\text{released}})/A \qquad (2)$$

where $\Delta\rho$ is density difference between the aqueous and oil phases, g_k is the centrifugal acceleration, V_{oil} is the total volume of oil in the emulsion, V_{released} is volume of oil released after centrifugation, and A is the cross-sectional area of the centrifuge tube.

Emulsions are centrifuged using an International Equipment Company (IEC) clinical centrifuge for 15 min. The centrifugal acceleration is varied between 150g and 1000g. After centrifugation, the released oil is withdrawn carefully from the top of the centrifuge

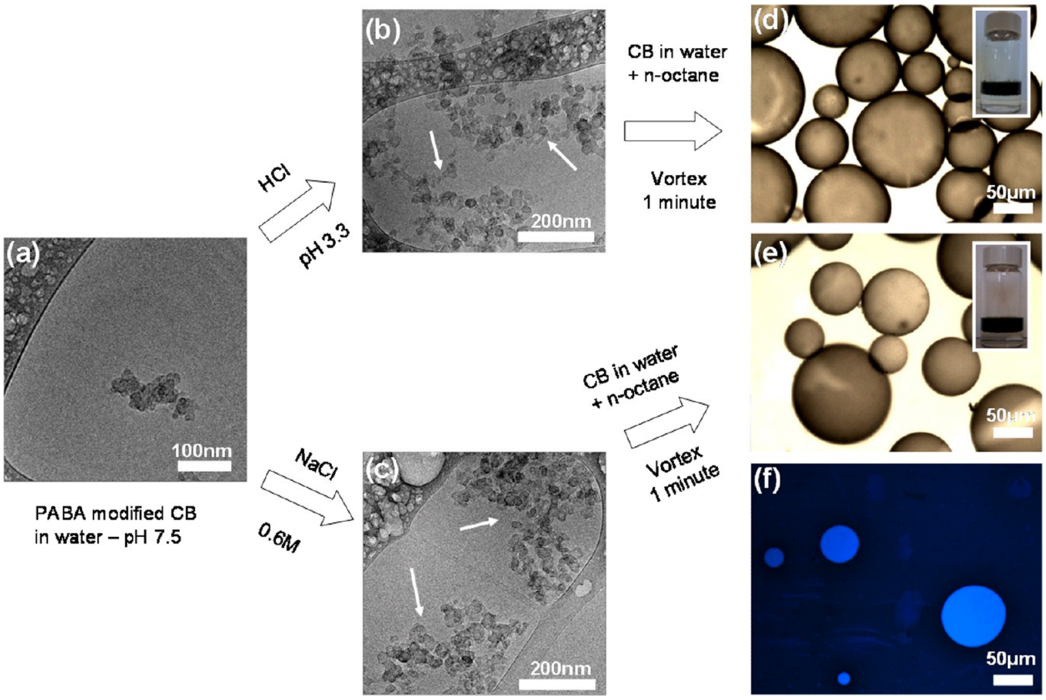

Figure 1. (a) Cryo TEM image showing a single carbon black (CB) particle of *p*-amino benzoic acid-terminated, pH 7.5, 0.015% w/w suspension CB in water. Addition of HCl or NaCl make the particles partially hydrophobic and causes particle−particle agglomeration, shown by arrows in (b, c) the cryo TEM images. Addition of octane to the acid- or salt-mediated suspension followed by vortexing results in (d, e) oil-in-water emulsions. The oil droplets are in equilibrium with excess water that is free of carbon black as shown in the insets. (f) Fluorescence image of the acid-mediated sample with pyrene-labeled octane, confirming that this is an oil-in-water emulsion.

tube with a syringe and its volume measured, from which the critical pressure for deemulsification is calculated using eq 2.

Cryogenic Scanning Electron Microscopy (cryo-SEM). Approximately 5 μL of the emulsion is placed on a cylindrical sample holder. Both are then plunged into liquid nitrogen, rapidly solidifying the emulsion. The sample is fractured with a flat-edge cold knife at −130 °C, then warmed to −95 °C for a few minutes to sublime some of the residual octane and water. Sublimation enhances surface topological details. The sample is then cooled back to −130 °C, sputtered with a gold−palladium composite, then moved from the preparation chamber to the imaging stage. A Hitachi S-4800 field-emission SEM operated at 3 kV and 20 μA is used for imaging. The sample is maintained at −130 °C during imaging. All of the processes starting from the fracturing to the imaging take place under a high vacuum.

Additional Characterization. A ZEISS Axioplan 2 Imaging System is used for fluorescence microscopy. A Nikon Eclipse E 600 and a Fisher Scientific Micromaster are used for brightfield optical microscopy. A Malvern Zetasizer is employed for zeta potential measurements. Samples for cryogenic transmission electron microscopy (cryo-TEM) are prepared in a controlled environment vitrification system manufactured at the Technion. The CB suspension is vortexed for 10 s after addition of either acid or salt, transferred to a holey carbon TEM grid after 1 min and then vitrified in liquid ethane. Vitrified samples are transferred to a Gatan 626DH cryo holder maintained at −175 °C, and imaged using a JEOL JEM 2100 transmission electron microscope operating at 200 kV.

Napthalene Adsorption. A 600 ppm naphthalene solution is formed in octane, and used for forming the emulsion. The samples are allowed to stand for 72hrs at 25 °C (based on kinetic studies[49] adsorption equilibrium is established in this time frame). The emulsion is then destabilized by centrifuging at 5000g for 15 min. A clear octane phase forms at the top, a clear aqueous phase forms at the bottom, and a thin layer of CB is sandwiched between these two phases. A small volume of octane is withdrawn from the top, diluted 30 times and then analyzed using a Shimadzu QP2010S GC-MS to determine naphthalene concentration. A control experiment without carbon black is also performed. In this case droplets form immediately upon vortexing, but separate into an oil phase and water phase as soon as the mixing stops. These samples are vortexed 5 times over a 72 h period, to ensure naphthalene transport away from the octane is complete, prior to measuring the concentration.

■ RESULTS AND DISCUSSION

Figure 1 outlines the processes used to create the emulsions. A cryo-TEM image of a 0.015% w/w CB suspension is shown in Figure 1a. Individual CB particles are observed, as is expected from a stable aqueous suspension of hydrophilic particles (the average interparticle distance is of the order of 2 μm for this suspension, so we do not see more than one particle in these cryo-TEM images at the magnification needed to see one particle, but this is a typical image seen in various portions of the TEM grid). Upon the addition of HCl or NaCl, particles start agglomerating. Cryo-TEM images of such agglomerated particles are shown in images b and c in Figure 1. We do not observe any unagglomerated particles in the acid or salt mediated cases, suggesting that changing the CB surfaces from hydrophilic to partially hydrophobic drives agglomeration, and is consistent with an observed increase in suspension viscosity. Upon addition of octane and vortexing, shear induced in the system generates new oil−water interfaces, drives the CB into these interfaces, and stabilizes the emulsion. The bottom aqueous phase looks clear and is in equilibrium with the top emulsion phase. Examination of this bottom phase by optical microscopy revealed a carbon black concentration that is about 5 orders of magnitude lower than that in the original suspension, suggesting that most of the CB is at the octane-water interfaces. Optical micrographs of the emulsion droplets are shown in images d and e in Figure 1. A few drops of water disperse immediately when added to this emulsion, while drops of octane "bead" up. When the octane is labeled with pyrene, and the emulsion imaged in fluorescence mode, the droplets are clearly visible (Figure 1f). These experiments confirm that we have produced octane-in-water emulsions.

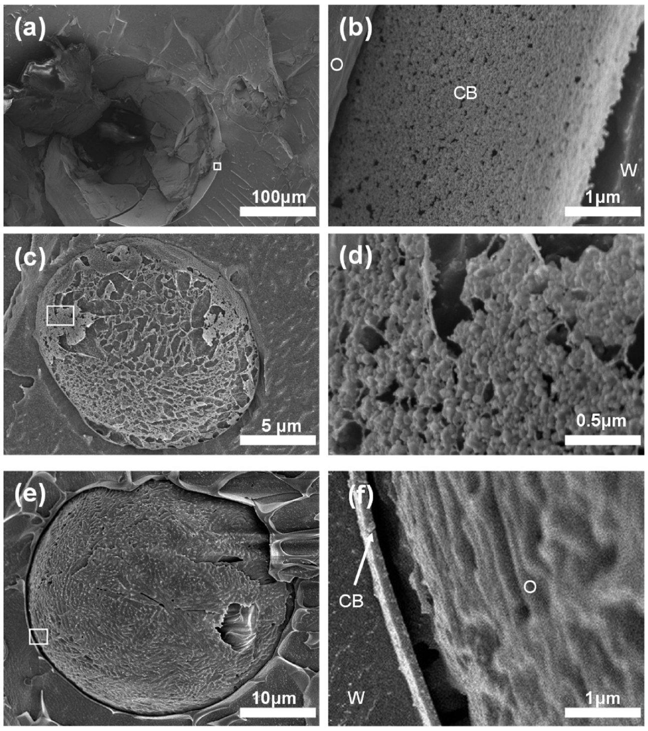

Figure 2. Cryo-SEM images of an octane-in water emulsion stabilized by carbon black at different conditions. (a, b) pH 3.3, 0.015 wt % CB; (c, d) pH 3.3, 0.0075 wt % CB. At this CB concentration, the surface of the oil drop is not covered completely by particles. (e, f) 0.6 M NaCl, 0.015 wt % CB.

Cryo-SEM provides a more detailed insight into the structure of the particle aggregates and their positioning at the oil−water interfaces. Figure 2a shows an image of an octane droplet in an emulsion prepared after addition of acid to a 0.015%w/w CB suspension. Multiple layers of CB consisting of closely packed particle aggregates are present at the interface, more evident in the higher magnification image of the interface in Figure 2b. The aggregation of particles upon addition of acid implies that the entities that reside at the oil−water interfaces are not individual carbon black particles but rather clusters of a few. We see evidence of these in our cryo-TEM images. Such clusters are harder to displace from oil−water interfaces than individual CB particles because the displacement energy scales with the square of the particle size, and provide additional stability for the emulsions. Emulsions have also been formed at 0.0075% w/w CB, shown in images c and d in Figure 2. We observe incomplete coverage of the droplet surface, but the emulsions are stable. We propose that the increased interfacial shear viscosity produced by the presence of a connected network of particles at the surface prevents thinning of the intervening water layer as droplets approach each other, and is responsible for suppressing coalescence. Images e and f in Figure 2 show a typical CB-stabilized octane droplet from an emulsion prepared by addition of NaCl. While its features in these images show similarities to those formed using addition of acid, there are significant differences related to the hydrophobic−hydrophilic balance of the particles that are explored next.

The coefficients of thermal expansion of octane and water are 0.001 $^{\circ}C^{1-}$ and 0.0002 $^{\circ}C^{1-}$respectively.[50] During rapid sample solidification, the octane shrinks in volume more than the water, creating a gap at the octane-water interfaces. These gaps are a consequence of the cooling process, and they are often observed in rapidly solidified oil-in-water emulsions.[51,52] Quite remarkably, for an emulsion prepared in the presence of 0.15 M NaCl, (Figure 3a, b) the CB particles stay with the solidified aqueous phase. In contrast, for an emulsion prepared by the addition of acid, the particles stay with the octane (Figure 3d, e). If a major portion of the particle is within the aqueous phase as it spans the oil−water interface, it stays with the solidified water after freezing. Conversely, if most of the particle is in the octane, it is pulled into the solidified octane upon freezing. The hydrophilic/hydrophobic balance of the particles dictates particle location, and thus determines which phase they preferentially adhere to. To the best of our knowledge, this is the first report of the use of cryo-SEM to connect particle location to its hydrophilic/hydrophobic balance. Figure 3c, f illustrate this concept.

Because many of the features observed in these emulsions are related to the hydrophilic/hydrophobic balance of the CB particles, which in turn are related to the residual charge on the particle surface, we measured zeta potentials for the particles under different conditions, and report them in Figure 3g. The zeta potential of the particles in the unmodified CB suspension is −60 mV. When the pH is lowered to 3.3, the zeta potential is −15 mV, indicating protonation of some surface carboxylate groups on the CB particles. At 0.15 M NaCl, the zeta potential changes to −42 mV, caused by salting of some carboxylate groups. The isoelectric point of the CB particles is 2.9 for no salt, shifts upward to 3.5 for 0.01 M NaCl and 4.0 for 0.15 M NaCl, indicating specific binding of sodium ions. The salt-modified particles carry substantially more charge than those modified by a change in pH, and are thus more hydrophilic. As further support, we note that the solubility of sodium benzoate in water is ∼4 M at 20 °C, whereas that of benzoic acid in water is 0.02 M at 20 °C.[53] These measurements are consistent with the observation that more hydrophilic particles stay with the aqueous phase upon freezing.

We compare the stability of the acid- and salt-mediated emulsions using centrifugation, and report results in Table 1. The key observation is that the salt-containing emulsions have a higher critical deemulsification pressure than those stabilized using the acid. The zeta potential measurements revealed that the salt-mediated particles have more charge than those formed by addition of acid, and are therefore more hydrophilic. We propose that these particles are able to bridge octane drops across an intervening water layer, and suppress drop−drop coalescence. We show evidence of particle bridging in panels a and b in Figure 4, and have observed many such particle-bridged drops in our salt-containing samples. Particle bridging is unlikely if the CB is too hydrophobic, and we have not observed any "bridged" drops for the acid-mediated samples. If left unperturbed, both types of emulsions are stable against coalescence for months. The volume of the emulsion phase does not change over this time period.

Given the high specific surface area of CB particles and nonspecific binding capability of carbon, we have examined the absorption of naphthalene as a model polycyclic aromatic hydrocarbon from octane-in-water emulsions stabilized by CB

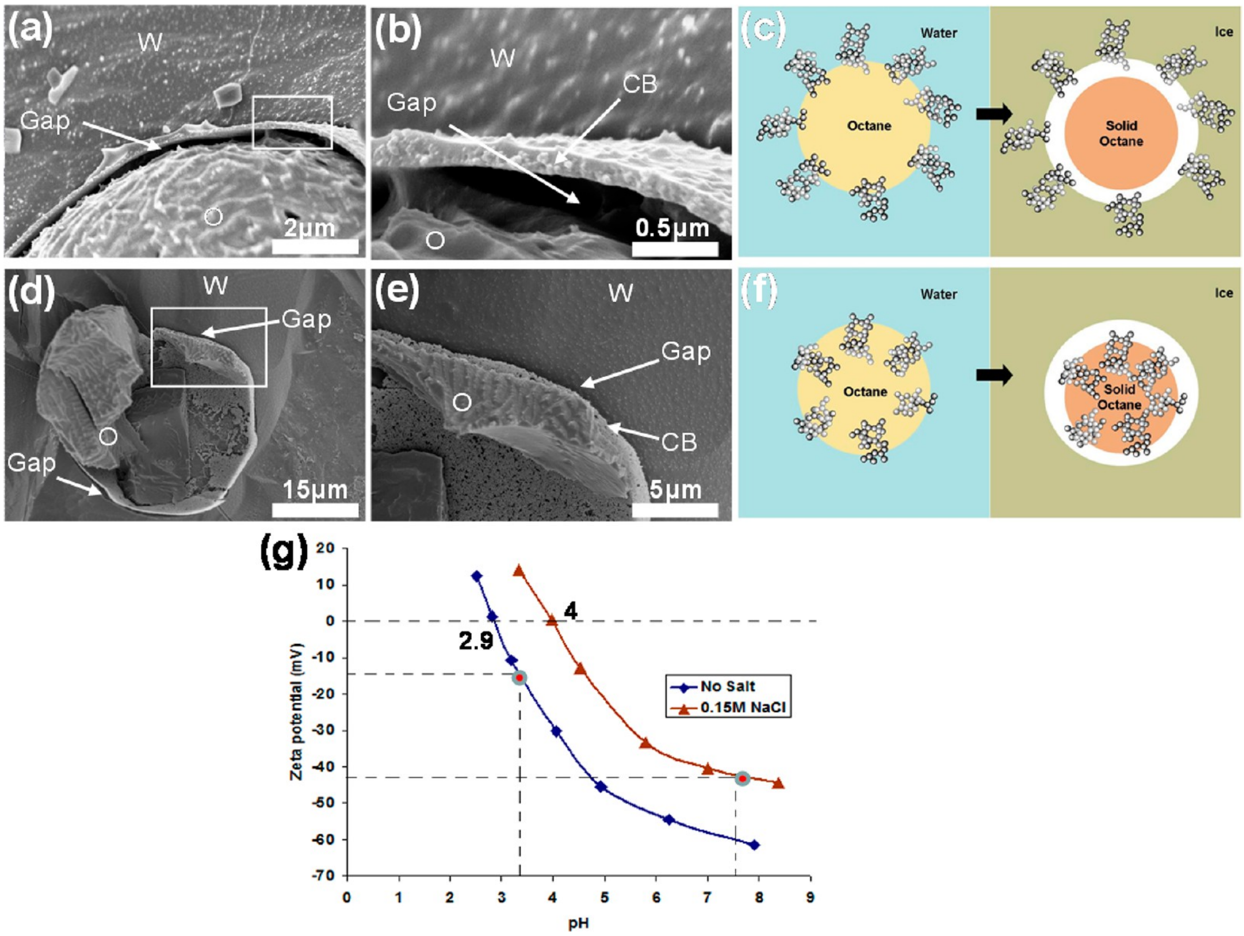

Figure 3. (a, b) Cryo-SEM image of an octane-in-water emulsion stabilized by carbon black for pH 7.5, NaCl 0.15M, showing CB particles staying with aqueous phase. (c) Model illustrating the location of most carbon black particles with the water phase. (d, e) Cryo-SEM image of a octane-in-water emulsion stabilized by carbon black at pH 3.3 showing CB staying with octane. (f) Model showing the location of most carbon black particles with the octane. (g) Zeta potentials of CB particles suspended in water or a 0.15 M NaCl solution. The red dot marked zeta potentials correspond to conditions used in the experiments.

Table 1. Critical De-emulsification Pressure for Different Emulsions[a]

emulsion type	critical de-emulsification pressure (kPa)
0.6 M NaCl (0.015 wt % CB)	4.6
pH 3.3 (0.015 wt % CB)	2.2
0.0075 wt % CB (pH 3.3)	1.4

[a] Repeated experiments show a variability of ~5% in the critical deemulsification pressure.

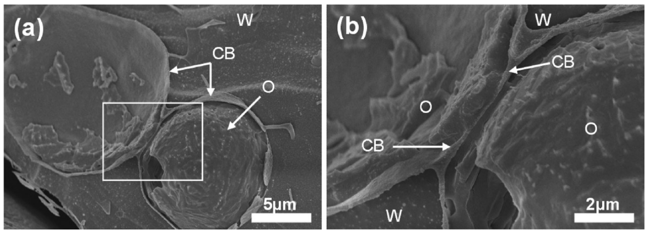

Figure 4. (a, b) Two octane drops bridged by CB particles in a sample prepared using 0.015 wt % CB and 0.6 M NaCl.

Table 2. Napthalene Adsorption ubder Different Conditions[a]

experiment	napthalene conc. in octane (ppm)	napthalene adsorbed (by mass) (%)
pH 3.3, 0.015 wt % CB	426	27.7
pH 3.3, 0.0075 wt % CB	567	3.8
0.6 M NaCl, 0.015 wt % CB	575	2.4
control	589	NA

[a] The reduced concentration of naphthalene in octane compared to the control case indicates that the CB particles adsorb naphthalene from the octane. The last column is obtained by doing a mass balance for the naphthalene.

on to the surface of the particles and report results in Table 2. The concentration of naphthalene in oil is reduced dramatically from the control case with no carbon black. More naphthalene is adsorbed for the acid-mediated case than the salt mediated emulsions as a consequence of the greater hydrophobicity of the acid-mediated emulsions.

The successful formation of octane-in-water emulsions indicates that these particles have potential for use in crude oil emulsification in the event of a spill. To that end, we use crude oil from the Gulf of Mexico Oil Spill, BP-MC-252, to form emulsions. Figure 5a shows emulsions formed with 10 vol % oil using an acid-mediated CB suspension, whereas Figure 5b shows an emulsion formed using a 0.6 M NaCl mediated

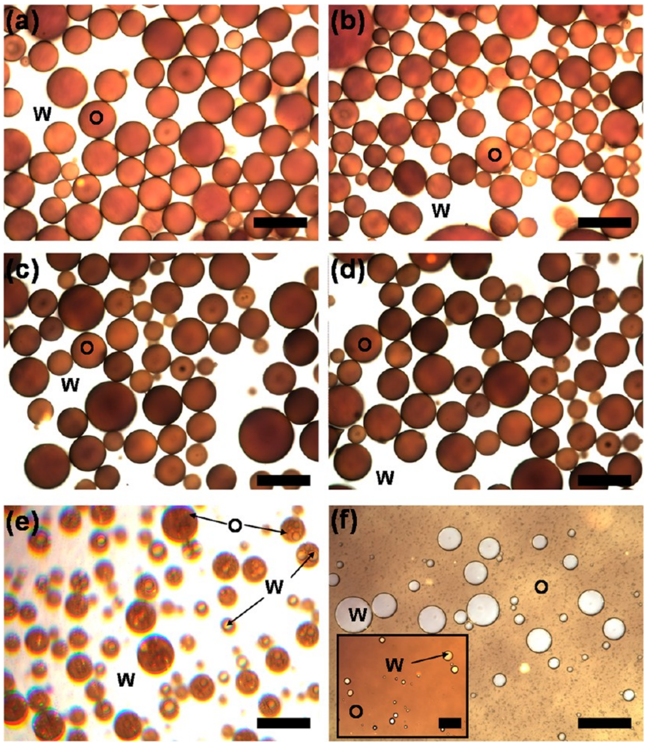

Figure 5. Oil-in water emulsions formed with 10 vol% BP-MC 252 crude oil, 0.015 wt % CB and DI water. Optical micrographs showing oil droplets in water for (a) pH 3.3, (b) 0.6 M NaCl (W-water, O-oil). Optical micrographs of a 0.015 wt % CB in seawater mixed with BP-MC 252 crude oil, resulting in an oil-in-water emulsion: (c) image taken immediately after mixing, (d) image taken 1 h after mixing, showing stable crude oil droplets in seawater. (e) Vortexing BP-MC 252 crude oil (10 vol%) containing Corexit 9500A (1:20 dispersant to oil ratio) with seawater (Narragansett bay) results in a water-in-oil-in-water (W/O/W) double emulsion. (f) The double emulsion in e transforms within an hour to a film of oil containing water drops, in equilibrium with water below. The inset in f shows a water- in-crude oil emulsion formed using 10 mM AOT. Scale bars are 200 μm.

suspension. Both are crude-oil-in water single emulsions. They have been left in our laboratory for 6 months and have not shown any phase separation or changes to the volume of the emulsion phase over this time period.

Emulsions prepared by using 0.015 wt % CB, seawater from Narragansett Bay and 10 vol % crude oil result in crude oil-in-water emulsions, shown in images c and d in Figure 5. Although we show an image taken after 1 h, this emulsion stays stable in a vial for several months. As a comparison, we use Corexit 9500A to form an emulsion with 10 vol % crude oil and 90 vol % seawater. An optical micrograph of the resulting emulsion, taken right after vortexing, is shown in Figure 5e. These are water-in-crude oil-in-water double emulsions. This double emulsion destabilizes in about an hour in a vial. Interestingly, the “top” phase at this point consists of a layer of oil with water drops dispersed within it, or a water-in-oil emulsion, shown in Figure 5f. This is a key difference between the CB- and Corexit 9500A-stabilized crude oil/seawater emulsions.

Crude oil contains asphaltenes and resins.[10,54−56] We propose that the interaction of these components with Corexit 9500A[57,58] promotes the formation of water-in-crude-oil-in-water double emulsions when first mixed. The double emulsion then destabilizes rapidly to form the water-in-oil emulsion. We confirm this using a series of experiments. First, when octane with Corexit 9500A is vortexed with seawater, no emulsion is produced. When crude oil without any added surfactant is vortexed with seawater, the emulsion is unstable, and the oil separates from the water; but we observe a few water drops dispersed within oil. When AOT, a major component of Corexit 9500A[59] is added to octane and vortexed with seawater, an emulsion is not produced. However, when AOT is added to the crude oil and the solution vortexed with seawater, a water-in-oil emulsion results, shown in the inset in Figure 5f. These results support our hypothesis that components of crude oil and Corexit 9500A interact to form water-in-oil emulsions. We note that for an oil spill remediation application, the presence of water droplets in the crude oil is undesirable because of the reduced calorific content, decreased ability to burn the oil, the reduction in bioremediation efficiency, the additional volume for removal,[56] and the increased viscosity.[56,60]

Our experiments provide strong evidence that this CB suspension has potential for use as an alternative dispersant for subsurface oil spills. The detailed examination of octane-in-water emulsions and the successful formation of these emulsions with added NaCl provided key insights into the conditions necessary to form crude oil-in-seawater emulsions. The principle of in situ tuning of surface properties of particles to enhance their ability to form emulsions, in combination with the ability to exploit intrinsic particle properties, is a powerful strategy for making advanced materials that is being explored in our laboratory and elsewhere.

■ CONCLUSIONS

We demonstrate the formation of octane-in-water emulsions using carboxyl terminated carbon black particles. These emulsions are prepared either by dropping the pH, which makes the particles more hydrophobic by protonating surface carboxylate groups, or by adding NaCl, which imparts hydrophobicity due to specific adsorption and binding of the sodium ions to the particles. These two routes vary the hydrophilic/hydrophobic balance on the carbon black particles in different ways and by different amounts. We use cryo-SEM to characterize these emulsions, and examine particle configurations at the oil−water interfaces. The difference in thermal expansion coefficients for octane and water creates gaps between the oil and water phases upon rapid cooling and solidification, and provide insights into the hydrophobic/hydrophilic balance of the particles. The acid-modified particles are anchored deeply in the octane. Conversely, the more hydrophilic particles mediated by salt stay with the aqueous phase upon solidification. The critical de-emulsification pressure is higher for the salt-mediated particles than those where acid is added. Particle bridging in these salt-mediated emulsions is responsible for greater stability. We show evidence of significant adsorption of a model cyclic hydrocarbon, naphthalene, on to the surface of the CB particles. The formation of stable crude oil-in-seawater emulsions using these CB particles, without any supplementary acid or salt addition, has been demonstrated. In contrast, we observe unstable water-in-crude oil-in-water double emulsions when we use a commercial surfactant Corexit 9500A. Our study has broad implications for the development of particle-based dispersants that have specific application for emulsifying oil and keeping them stable in water columns in the event of an oil spill. The strategy of tuning surface properties of particles prior to forming emulsions has applications in the synthesis of materials with novel combinations of properties.

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Notes

The authors declare no competing financial interest.

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