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ORIGINAL CONTRIBUTION

A simplified synthesis of silica Colloids with tunable hydrophobicity

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Abstract Colloidal silica nanoparticles with average diameters less than 100 nm were made using a modified Stöber method involving tetraethylorthosilicate (TEOS) and octadecyl trimethoxysilane (OTMOS) as a surface modifier. We show that the hydrophobicity of the nanoparticles could be tuned in this one-step reaction by introducing methanol as a co-solvent with ethanol and optimizing the ammonium hydroxide concentration and time elapsed between TEOS and OTMOS addition. Using this approach, silica nanoparticles could be made directly with the proper surface hydrophobicity to stabilize invert (water-in-oil) emulsions with shear-thinning rheological behavior as needed in oil drilling applications. Particle characterization data from transmission and scanning electron microscopy (TEM and SEM), Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), and contact angle measurements are presented.

Keywords Colloids · Suspensions · Silica · Nanoparticles

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Introduction

Colloidal silica nanoparticles have been widely studied and are used in a wide variety of industries: in the processing of foods and pharmaceuticals, catalysis, cosmetics, electronic devices and ceramics; they are used to aid in chemical synthesis and chromatographic separations, and can be employed as emulsion stabilizers [1–19]. One possible industrial use for silica nanoparticles is as a surfactant replacement in oil drilling fluids [20, 21]. Silica nanoparticles are interesting because they could offer a more environmentally friendly alternative to the surfactants that are commonly used and provide high thermal stability as needed under the typical conditions required for oil extraction. We were especially interested in water-in-oil emulsions, or invert emulsions, because they are widely used as drilling fluids for oil or natural gas extraction [22–24]. Our goal here was to explore the possibility of creating invert emulsions using silica nanoparticles made directly with the common Stöber method.

Silica nanoparticles obtained directly from the Stöber method are hydrophilic and do not stabilize emulsions. In 1990, Badley and coworkers [25] showed that octadecyl trimethoxysilane (OTMOS) could be added to a Stöber reaction to make hydrophobic silica nanoparticles. However, they did not demonstrate any ability to adjust the nanoparticle hydrophobicity, and furthermore, their method required a very long wait time (~5 h) between the addition of TEOS and the subsequent addition of OTMOS to the reaction. The method was essentially a post-synthesis modification of the nanoparticles, requiring the addition of OTMOS after observing significant particle growth (i.e, the formation of turbidity). Binks and coworkers have since demonstrated that silica nanoparticles with varying hydrophobicity can be obtained with different extents of post-synthesis surface modification using species like dimethyldichlorosilane [26, 27].

Here, we show that silica nanoparticles can be produced directly from a Stöber synthesis with tunable hydrophobicity by adding OTMOS to the reaction under the appropriate conditions. The ability to adjust nanoparticle hydrophobicity is especially important for making particle-stabilized emulsions, or Pickering emulsions [11–13]. In a Pickering emulsion, the nanoparticles must have intermediate hydrophobicity and partition to the oil-water interface in order to stabilize droplets and form the emulsion [12, 13, 28–30]. Using contact angle measurements, the hydrophobicity of the OTMOS-terminated silica nanoparticles was correlated with the stability of the water-in-oil emulsions made with the nanoparticles. With the appropriate level of hydrophobicity, very stable invert emulsions could be formed. Furthermore, these emulsions exhibited the shear-thinning rheological properties appropriate for oil drilling fluid applications.

Experimental section

Materials

Ethanol (EtOH, 99.9%, Fisher Scientific), methanol (MeOH, 99.9%, Fisher Scientific), ammonium hydroxide (NH$_4$OH, 28–29%, Fisher Scientific), tetraethoxysilane (TEOS, ≥98%, Sigma Aldrich), octadecyl trimethoxysilane (OTMOS, ≥97%, Sigma Aldrich), poly(1-decene) (viscosity 50 cs at 40 °C, Sigma Aldrich) and chloroform (laboratory grade, Sigma Aldrich) were used as received without further purification. Water was doubly-distilled and deionized.

Silica nanoparticle synthesis

Silica nanoparticles were prepared by hydrolysis of TEOS in methanol/ethanol mixtures, similar to the approach of Stöber [1, 2], but with the addition of OTMOS as a surface modifier. All reactions were carried out a few degrees below the boiling temperature of the mixture (i.e., 65-70 °C, depending on the solvent) for 60 min with a TEOS concentration of 0.25 M and a water/TEOS molar ratio of 38 [4]. A range of OTMOS/TEOS molar ratios, NH$_4$OH concentration and ethanol/methanol ratio were explored. The amount of modifying silane (OTMOS) and the amount of time after silica nanoparticle nucleation prior to OTMOS addition were also examined.

In a typical preparation, an alcohol solution with a volume of 23 mL is first made from a mixture of EtOH and MeOH. MeOH/EtOH volume ratios ranging from 0 to 1.5 were studied. A solution of water and NH$_4$OH (0.5–0.55 M) is then added to the alcohol mixture under vigorous stirring at room temperature. The reaction mixture is heated to the desired temperature (65–70 °C) under N$_2$ atmosphere followed by dropwise addition of 1.8 mL of TEOS, and then dropwise addition of OTMOS. OTMOS/TEOS molar ratios ranging from 0 to 1 were studied.

The resulting silica nanoparticles were precipitated by centrifugation at 10,000 rpm and 10 °C for 15 min. The supernatant was discarded and the nanoparticles were dispersed in water and EtOH with brief sonication. This washing procedure was repeated twice before dispersing the nanoparticles in EtOH at a concentration of 10 mg/mL. A typical reaction yields 500 mg of silica nanoparticles (>90% yield).

Emulsion formulation

Inverted emulsions were prepared by dispersing silica nanoparticles in ethanol and then adding poly(1-decene). Water was then added up to 30 vol% while homogenizing at 14,000 rpm for 5 min and then 20,000 rpm for another 2 min by high speed stirring with a PowerGen 125 mixer. Water must be added slowly to avoid phase separation and obtain the desired white emulsion with a creamy consistency [28–30].

The rheological properties of the emulsion were measured using a TA Instrument AR-2000 EX rheometer fitted with parallel plate fixtures. The plates were 4 cm in diameter separated by a 1 mm gap during. The viscosity measurements were carried out at 25 °C.

Characterization

Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai Biotwin TEM operated at 80 kV accelerating voltage. Nanoparticles were drop-cast onto 200 mesh carbon-coated copper grids for imaging (Electron Microsopy Science). Scanning electron microscopy (SEM) images were obtained using a Zeiss Supra 40 SEM of nanoparticles drop-cast on silicon substrates.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained with a Thermo Mattson Infinity Gold FTIR spectrometer with a Spectra-Tech Thermal ARK attenuated total reflectance module. The detector was cooled by liquid nitrogen, and spectra were taken by averaging 512 scans at a resolution of 4 cm^{-1}. A background measurement was taken before loading the sample into the ARK attenuated total reflectance module.

Thermal gravimetric analysis (TGA) was carried out under nitrogen using a Mettler Toledo TGA-1. Measurements were obtained with about 5 mg of silica nanoparticles added to a 70 alumina crucible (Mettler Toledo). Samples were heated from 30 °C to 600 °C, at rate of 10 °C/min.

Contact angle (CA) measurements were obtained using a home-built contact angle instrument equipped with camera attached to a computer for image capturing. Contact angles were calculated by a sessile drop method using Image J image analyzer software. Each DI-H$_2$O drop had a volume of 2 μL

and the measurements were performed at room temperature. For the measurements, the nanoparticle films were doctor bladed from a 10 mg/mL dispersion of nanoparticles in ethanol onto a glass slide at 78 °C (boiling point of EtOH). The reported CA is an average of ten different measurements of CA with the water drop placed on ten different locations on the nanoparticle film [31]. All measurements were carried out in a clean room.

Results and discussion

Single-step synthesis of hydrophobic ligand-terminated silica nanoparticles

Table 1 summarizes the experimental conditions that were studied and Fig. 1 shows TEM and SEM images of the silica nanoparticles obtained using different OTMOS/TEOS ratios. The nanoparticles made using the Stöber procedure without OTMOS addition are shown in Figs. 1a and b. These nanoparticles are relatively uniform in size, with an average diameter of 120 ± 8.9 nm and relatively smooth surfaces. The nanoparticles in Figs. 1c and d made with the addition of OTMOS to the Stöber reaction at an OTMOS/TEOS ratio of 0.01 were noticeably rough and smaller in diameter (94 ± 7.4 nm). We found that as proportionally more OTMOS was used in the reaction the nanoparticles became increasingly rough, although the size of the nanoparticles did not keep decreasing and there was little effect on the reaction yield (with an appropriate wait time between TEOS and

OTMOS addition, See Table 1). TEM and SEM images of these nanoparticles are shown in Figs. 1e-1j.

Scheme 1 illustrates the bonding of OTMOS to the silica surface: the siloxane functional group chemisorbs by bonding to exposed hydroxyl groups [32], leaving the hydrocarbon chain exposed to the solvent. The remaining hydroxyl groups on the surface-bound OTMOS can then react with other nearby unreacted hydroxyl groups to form a bonded network [31, 33–36]. The organic shell surrounding the nanoparticles generates the hydrophobicity. The addition of OTMOS to the reactions led to significantly rougher particles, perhaps due to the stabilization of smaller silica clusters in solution that would then add to the larger growing nanoparticles. OTMOS can bond to molecular silicate species in solution and can also poison nanoparticle growth entirely, which is why a short waiting period between TEOS and OTMOS addition of at least two minutes is needed. Effati and coworkers [3, 4] have also found that a wait time between TEOS addition and a surface modifier is needed to obtain nanoparticles from the Stöber approach. In their work, vinyl- and acrylate- surface functionalization was added to their silica nanoparticles and they found that a wait time of 5 min was needed between TEOS addition and the addition of the surface modifier [3, 4]. We found that four minutes is sufficient in the case of OTMOS to prevent any loss in reaction yield. Particles did not form when OTMOS and TEOS were added simultaneously.

Other reaction conditions found important for OTMOS functionalization included the type of alcohol and the ammonia concentration. The type of alcohol used in Stöber-type

Table 1 Summary of reaction conditions and properties of the resulting silica nanoparticles

NO.	Experimental condition						
	MeOH to EtOH Vol. ratio	NH$_4$OH (M)	OTMOS[a] to TEOS Mol. Ratio	Time between TEOS and OTMOS addition (min)	Reaction Yield (%)	Diameter (nm) [c]	Contact Angle[b]
1	1	0.5			~90	120 ± 8.9	28
2	0	0.55	0.01	2	~ 65	108 ± 45	…
3	0	0.55	0.03	4	~90	175 ± 11.9	…
4	1	0.55	0.03	4	~90	106 ± 8.9	…
5	1.5	0.5	0.05	4	~90	85.5 ± 5.3	…
6	1	0.5	0.01	4	~90	94 ± 7.4	92
7	1	0.5	0.02	4	~90	80 ± 4.5	115
8	1	0.5	0.03	4	~90	86 ± 5.4	120
9	1	0.5	0.04	4	~90	103 ± 9.6	123
10	1	0.5	0.05	4	~90	109 ± 7.8	125
11	0	0.5	0.1	4	0	No particles	…

[a] 10 vol% in CHCl$_3$ or EtOH

[b] Contact angle measurements were not performed for the samples noted with "…" since these were not tested for emulsion stabilization due to their lower reaction yields and much smaller particle size

[c] The average diameters reported here was determined from TEM images of the particles. The standard deviation about the mean diameter is also given based on measurements of ten particles
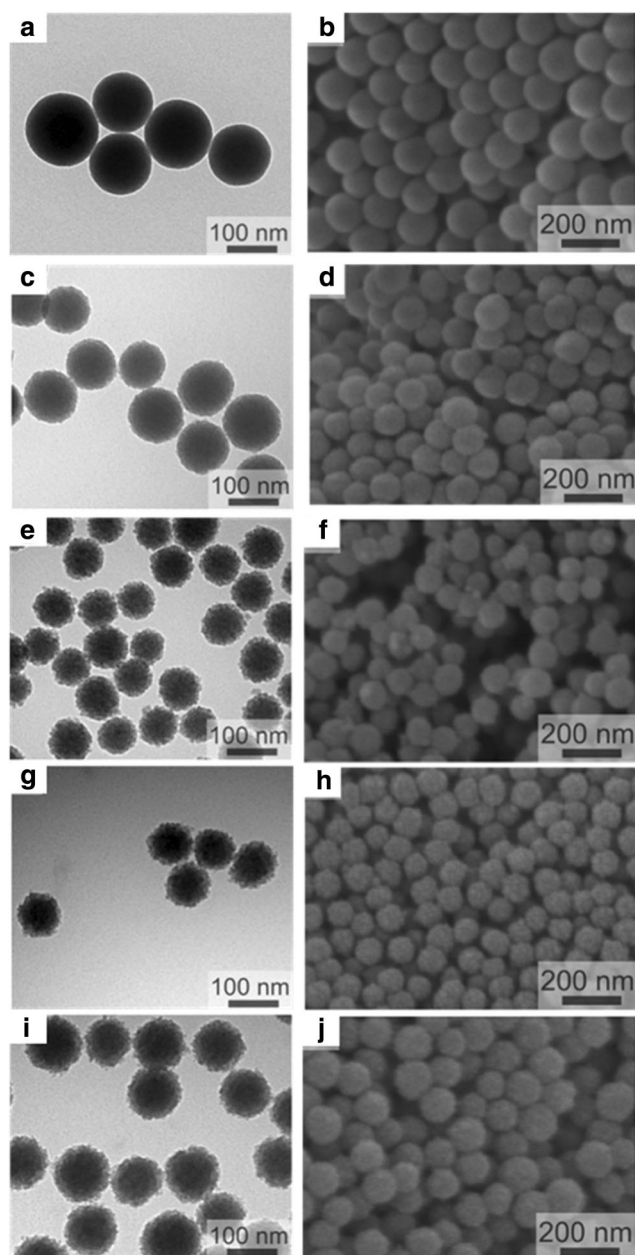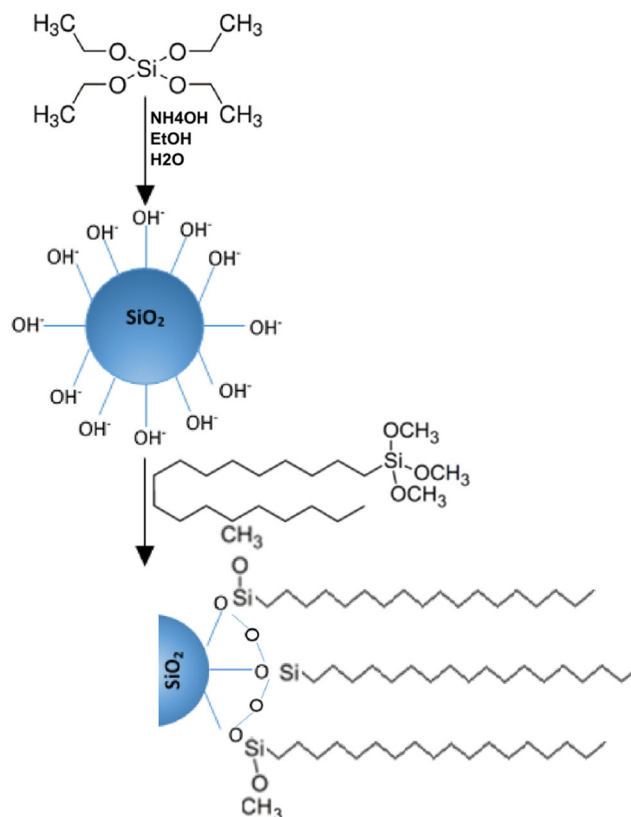
Fig. 1 (Left column) TEM and (Right column) SEM images of silica nanoparticles made with OTMOS/TEOS mole ratios and average diameters of (A,B) 0, 120 ± 8.9 nm; (C,D) 0.01, 94 ± 7.4 nm; (E,F) 0.02, 80 ± 4.5 nm; (G,H) 0.03, 86 ± 5.4 nm; (I,J) 0.04, 103 ± 9.6 nm

Scheme 1 Surface modification of silica nanoparticles with OTMOS to render them hydrophobic. TEOS is the silane source for particle growth and OTMOS is the surface modifier

106 ± 8.9 nm to 86 ± 5.4 nm (Table 1), which is also consistent with other work [3, 4].

OTMOS surface termination of silica nanoparticles confirmed by ATR-FTIR spectroscopy and TGA.

Figure 2a shows ATR-FTIR spectra for silica nanoparticles produced with and without the addition of OTMOS. Peaks between 2975 and 2840 cm^{-1}, corresponding to C–H methyl and methylene stretching vibrations [37], are observed for the OTMOS-functionalized nanoparticles, but are not present in the spectra of nanoparticles made without OTMOS. There is also a difference between the nanoparticles made with and without OTMOS in the spectral region in which methyl groups give rise to asymmetric and symmetric deformations at 1465–1440 cm^{-1} and 1390–1370 cm^{-1}, respectively. Bands at 3580–3200 cm^{-1}, corresponding to O–H vibrations, are present on all of the nanoparticles, indicating that adsorbed water and silanol O–H groups are present [37].

Figure 2b also shows TGA data for the silica nanoparticles. There are two weight loss events corresponding to the evaporation of absorbed moisture and trapped solvent below 200 °C and then silanol dehydration and pyrolysis of the organic surface modifier above 200 °C. There are two things to notice from the data. The nanoparticles made with the highest

reactions is known to affect particle size [1, 3, 4], and higher concentrations of methanol led to smaller nanoparticles (See Table 1, Fig. 1). Increased solvent polarity speeds the hydrolysis and condensation reactions, which enhances particle nucleation and growth and gives rise to smaller particles [1, 4, 32]. The best results were obtained with equimolar mixtures of EtOH and MeOH. Excessive amounts of MeOH led to aggregation. A decrease in NH$_4$OH concentration from 0.55 M to 0.5 M also led to reduced particle size, from
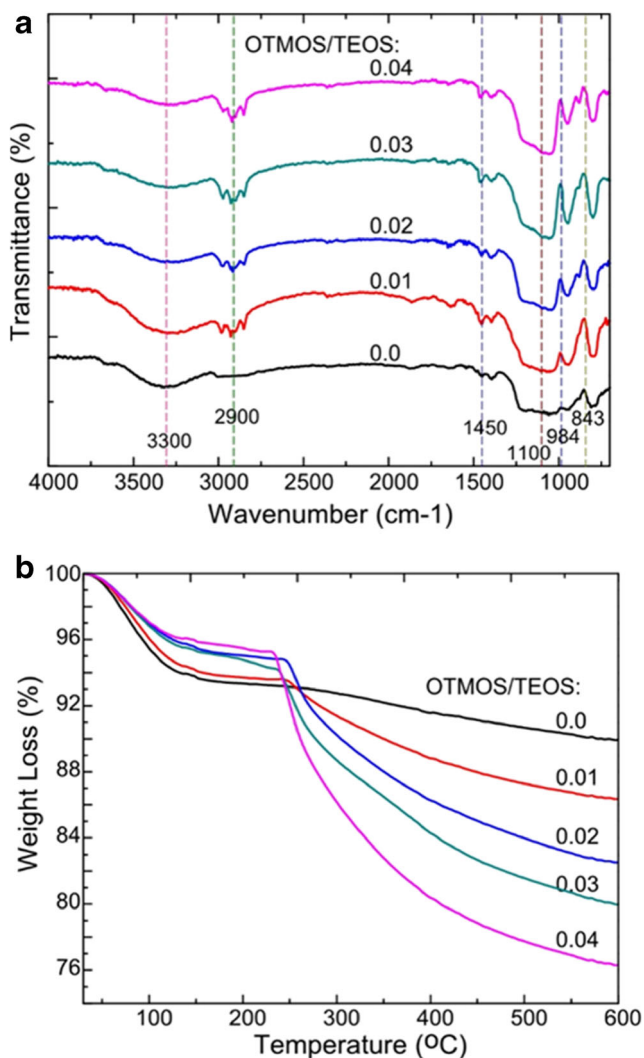
Fig. 2 (A) ATR-FTIR spectra and (B) TGA data for silica nanoparticles made with varying OTMOS/TEOS mole ratios, corresponding to the samples 6 to 9 listed in Table 1

OTMOS/TEOS ratio had the lowest amount of weight loss below 200 °C. This is because the samples were the most hydrophobic and adsorbed the least amount of water. On the other hand, the total weight loss was proportional to the amount of OTMOS used in the reaction, indicating that higher OTMOS/TEOS ratios led to more adsorbed organic surface species.

Silica nanoparticle wettability, invert emulsion stability and shear-thinning behavior

Contact angle measurements (Fig. 3) confirmed that the silica nanoparticles made with higher OTMOS/TEOS ratios were significantly more hydrophobic. Nanoparticles made without any OTMOS addition are hydrophilic as expected, exhibiting a contact angle 28^0 and increasing OTMOS/TEOS ratios led to silica nanoparticles with increasing hydrophobicity.
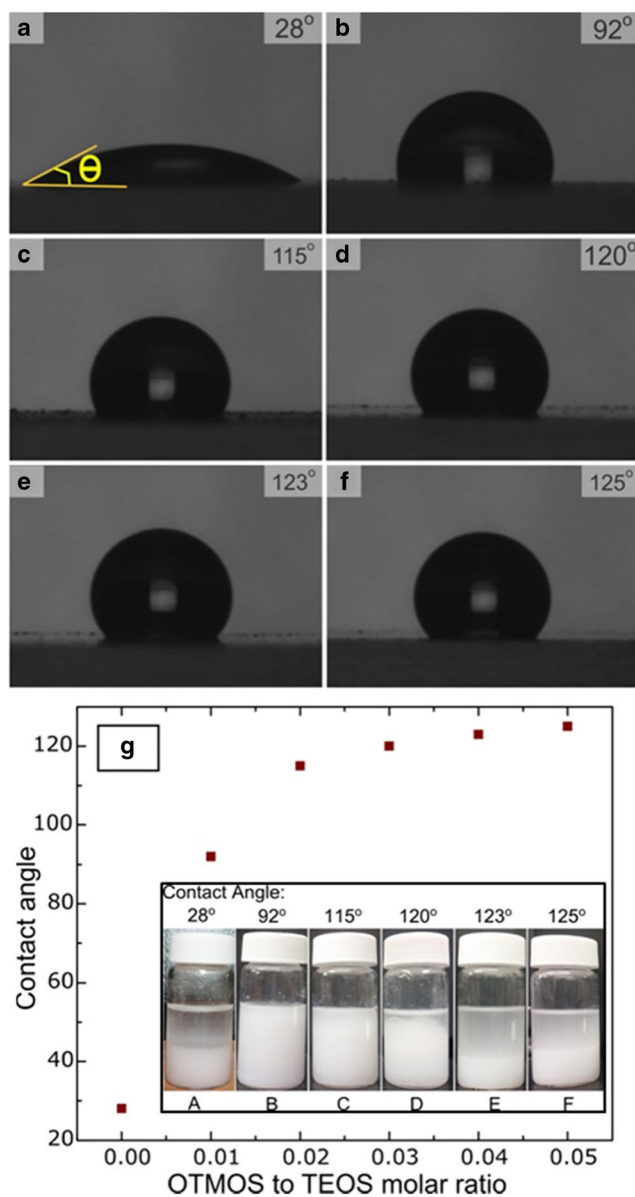

Fig. 3 Water contact angle measurements obtained from glass slides coated with a layer of silica nanoparticles made with OTMOS/TEOS mole ratios of (A) 0.0, (B) 0.01, (C) 0.02, (D) 0.03, (E) 0.04, (F) 0.05. (G) Plot of the average contact angles obtained from the silica nanoparticles in (A)-(F). The inset shows a photograph of invert emulsions made with 2 wt% of the silica nanoparticles

Nanoparticles made with an OTMOS/TEOS ratio of 0.01 exhibited a contact angle of 92^0 (Fig. 3b). The nanoparticles made with more OTMOS were more hydrophobic. Figures 3c-f show the contact angle measurements made for nanoparticles made with increasing OTMOS/TEOS ratios and these data are plotted in Fig. 3g.

To stabilize an emulsion, the nanoparticles must partition to the fluid interface as shown in Fig. 4. The nanoparticles with partial hydrophobicity and a contact angle of 90° were found to yield the most stable invert emulsions. These emulsions were stable for days. The water droplet size provides another
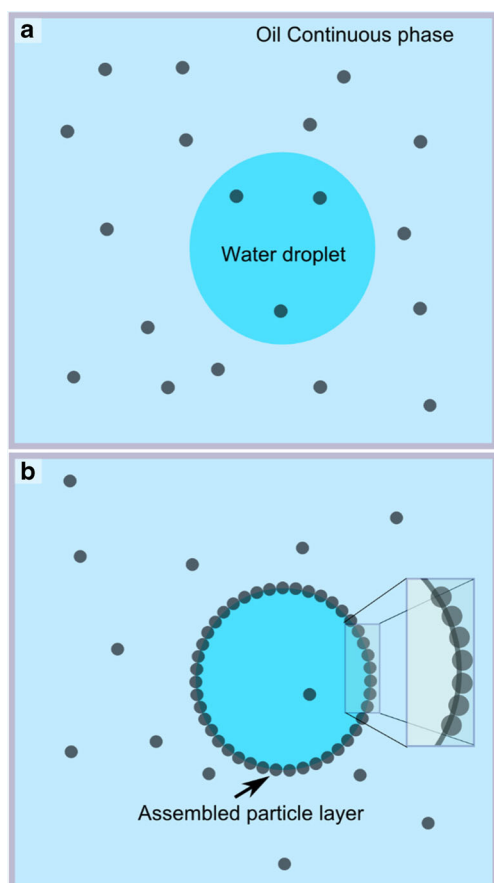
Fig. 4 Emulsion stabilization requires that nanoparticles partition to the oil-water interface [26, 38, 39]. If the nanoparticles are too hydrophilic or too hydrophobic, they disperse in the continuous phase as in (A). With intermediate water-oil wettability, or contact angles near 90°, the particles segregate to the oil-water interface as shown in (B) and stabilize the emulsion. Such a particle-stabilized emulsion is called a Pickering emulsion

Fig. 5 Optical microscopy images of invert emulsions with (A,C) 1 wt% and (B,D) 2 wt% silica nanoparticles made with 0.01 or 0.02 mol ratio of OTMOS/TEOS, respectively. Images were taken after dilution with poly 1-decene (oil phase) by a factor of 20. (E) A flow curve of an invert emulsion stabilized with 2 wt% silica nanoparticles made with an OTMOS/TEOS mole ratio of 0.01 and a contact angle of 92° (Sample B from Fig. 3)

measure of emulsion stability. Figures 5a-d shows optical microscopy images of the water droplets in invert emulsions made with the nanoparticles that had contact angles of 90° and 115°. Table 2 summarizes the sizes of the water droplets that were measured. The nanoparticles with 90° contact angle gave a finer dispersed phase than the nanoparticles with 115° contact angle, which is consistent with their greater stability.

Finally, the rheological properties of the most stable emulsion were tested. In order to be used as oil drilling fluids, the emulsions must exhibit shear-thinning rheology. Figure 5e shows a flow curve for the invert emulsion stabilized with 2 wt% of the nanoparticles made with 0.01 OTMOS/TEOS mole ratio. The data shown are representative of the tests carried out on three samples. The viscosity drops as the shear rate increases, indicating that the fluid exhibits shear-thinning behavior as appropriate for drilling fluids [22, 23]. The observed shear-thinning rheological properties are consistent with the hydrophobicity determined from contact angle measurements and the observed invert emulsion stability.
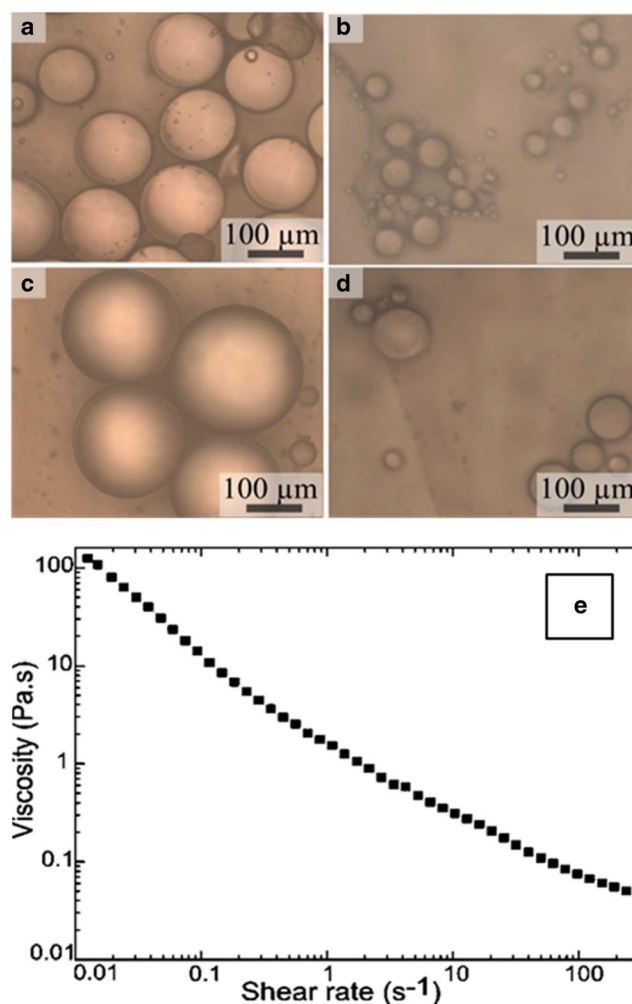
Conclusions

Researchers have been interested in finding a replacement for surfactants used to stabilize invert emulsions (water-in-oil) in

Table 2 Average water droplet size in various invert emulsions stabilized by silica nanoparticles

Emulsions (30/70 W/O ratio)[b]	Diameter (μm)	Emulsion status
1 wt% of 0.01[c] OTMOS-silica NPs	100–200	Stable for days
2 wt% of 0.01 OTMOS-silica NPs	~60	Stable for weeks
1 wt% of 0.02 OTMOS-silica NPs	~200	Stable for days
2 wt% of 0.02 OTMOS-silica NPs	~100	Stable for days

[b] The nanoparticle content reported here is on the basis of oil

[c] OTMOS to TEOS molar ratio

oil drilling fluid applications and silica nanoparticles provide an interesting alternative, since they do not degrade at the high temperatures and pressures needed for these applications and have surfaces that can be modified chemically to tune wettability and optimize emulsion stability [20, 21]. There are methods known to generate silica nanoparticles with tunable hydrophobicity, but these routes require multiple synthetic steps [25–27]. Here, we report a straightforward single-step synthetic route to silica nanoparticles with tunable hydrophobicity, as needed to stabilize invert emulsions with shear-thinning rheological properties required for oil drilling applications. The method employs a simplified one-step St ber-type reaction can be used to make silica nanoparticles with tunable hydrophobicity by adjusting the amount of an organic surface modifier, OTMOS, used in the reaction. The key is to let particle growth begin prior to OTMOS addition and to adjust the other various reaction conditions like the amount of alcohol and concentration of base to ensure a high yield of nanoparticles is still obtained. TGA and contact angle measurements show that the hydrophobicity of the nanoparticles is increased systematically with increasing OTMOS/TEOS ratios used in the reaction. The silica nanoparticles with the appropriate—i.e., intermediate—hydrophobicity could then be used to stabilize invert emulsions. The silica nanoparticles with contact angles of ~90° yielded emulsions that were stable for weeks and exhibited shear-thinning rheological behavior, as desired for oil drilling applications. The nanoparticles with slightly more hydrophilicity or hydrophobicity did not stabilize emulsions to any significant extent and the ability to tune the surface hydrophobicity was found to be important for stabilizing the nanoparticle emulsions.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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