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Magnetically-active Pickering emulsions stabilized by hybrid inorganic/organic networks†

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Magnetically-active hybrid networks (MHNs) are complex inorganic/organic composite materials that have been synthesized from the coupling of amine-functionalized iron oxide nanoparticles (amine-IONS) and pre-assembled shell crosslinked knedel-like (SCK) polymeric nanoconstructs. The intricate structure of these materials is composed of several inter-connected bundles of SCKs covalently bound to amine-IONS, which afford them magnetic responsivity. The MHNs were originally designed to sequester complex hydrocarbons from water; however, they have displayed a remarkable ability to form stable Pickering emulsions between organic solvents and water, upon mechanical stimulus. Two methods of emulsification, vortex and probe sonication, have been utilized to yield magnetically-active toluene-in-water and dodecane-in-water emulsions, which are stable for up to two months in the presence of the MHNs. A detailed study of the effect of the water-to-oil (W:O) volume ratio and the MHN concentration on the droplet size of the emulsions revealed that the smallest droplet size, and narrowest dispersity were obtained at a W:O = 3:1, for all conditions tested. Additionally, concentrations of MHNs as low as 1 mg mL⁻¹ and 1.5 mg mL⁻¹, for emulsions prepared via vortex and probe sonication, respectively, were sufficient to yield the smallest droplets and narrowest distributions. Furthermore, the oil droplets stabilized by the MHNs exhibited magnetic character, and could be manipulated with an external magnetic field.

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Introduction

The stabilization of emulsions by solid particles is a phenomenon that has been developed since the beginning of the last century and has gained increasing interest over the past decade. These emulsions, whose discovery is often attributed to Spencer U. Pickering, but which were first described by Walter Ramsden in 1903,¹ are known as Pickering emulsions.² Most of the work performed on Pickering emulsions involves the stabilization of single droplets yielding oil-in-water (o/w) or water-in-oil (w/o) emulsions. However, recent work has also yielded the stabilization of double emulsions of the oil-in-water-in-oil (o/w/o) or water-in-oil-in-water (w/o/w) types.^{3,4}

Traditionally, the stabilization of Pickering emulsions has been achieved through the use of discrete, individual particles that have varied significantly in their compositions and morphologies, including inorganic particles, such as LAPONITE[®] clay,^{5,6} silicon

oxide,^{7,8} zirconium phosphate,⁹ cadmium selenide,^{10,11} gold,¹² and iron oxide,¹³ as well as organic materials, such as bionanoparticles,¹⁴ latex beads,¹⁵ polymersomes,¹⁶ Janus nanoparticles,^{17,18} shell cross-linked micelles,¹⁹ carbonaceous microspheres,²⁰ and polysiloxane microspheres.²¹ In addition to these materials, starch-based²² and fat-based²³ particles have been investigated, with particular interest for their utilization in the food industry.

More recently, applications of the Pickering effect have transcended the mere stabilization of emulsions to give rise to a novel approach towards the synthesis of materials. This technique has been widely utilized for the construction of membranes,^{10,24} capsules,²⁵ colloidosomes,^{15,26,27} latex beads,^{5,6,17} and hybrid inorganic/organic latex beads.^{7,28} For instance, Lin *et al.* utilized tri-*n*-octylphosphine oxide (TOPO)-stabilized CdSe nanoparticles, capable of undergoing assembly at an oil-water interface, to yield ultra-thin (*ca.* 5 nm thickness) nanoparticle membranes upon assembly of the nanoparticles at a flat oil-water interface, and crosslinking of the TOPO ligands.¹¹ This process was extended to nanoparticle stabilization and crosslinking at water-in-oil emulsion interfaces to yield globular membranes capable of encapsulating oil-soluble or water-soluble compounds. The nanoparticle-crosslinked membranes displayed stability after removal from the interface, as well as elasticity and permeability, which are characteristics that could be advantageous in controlled diffusion and release applications.

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Additionally, an example that applied organic particles for colloidosome formation was developed by Thompson and co-workers, who utilized poly(glycerol monomethacrylate)-based polystyrene latex beads to stabilize oil-in-water emulsions.²⁹ Once assembled at the interface, the latex beads were crosslinked within the oil droplets with tolylene 2,4-diisocyanate-terminated poly(propylene glycol), which yielded permeable colloidosomes that were stable upon removal of the internal oil phase. The colloidosomes were loaded with a fluorescein cargo and its release was measured over time to assess the permeability of the membranes. It was found that complete release was achieved within 24 hours; therefore, the permeability of the colloidosomes was tuned by coating them with a thin layer of polypyrrole that led to improved control over the cargo release. Moreover, in the field of emulsion polymerization, Colver *et al.* employed inorganic SiO₂ nanoparticles of *ca.* 25 nm in diameter to stabilize an emulsion composed of styrene or methyl methacrylate (MMA) in water.⁷ Following the stabilization of the emulsion, potassium persulfate (KPS) was added to initiate the polymerization at 65 °C, and yield highly dispersed polystyrene (PS) or poly(methyl methacrylate) (PMMA) particles armored with a layer of SiO₂ nanoparticles on the surface of the polymeric beads.

In addition to allowing for the synthesis of unique materials, Pickering emulsions can also be used to stabilize droplets while incorporating responsiveness to an external stimulus, thereby providing a means to control the stability of the emulsion. For instance, Fujii and co-workers prepared pH-responsive emulsions, whereby shell crosslinked micelles composed of the triblock terpolymer poly(ethylene oxide)-*block*-poly(glycerol monomethacrylate)-*block*-poly(2-(diethylaminoethyl)ethyl methacrylate) were synthesized and used to stabilize 1-undecanol-in-water emulsions at pH 8–9.¹⁹ The droplets could be easily destabilized upon addition of 1 drop of a 1 M HCl solution, and readily re-stabilized after re-homogenization at pH 8–9; thus, providing control over the demulsification procedure. Additionally, magnetically-active emulsion droplets that are responsive to an external magnetic field have also been achieved.^{30–32} Of particular importance is the work of Melle and co-workers, whereby carbonyl iron particles were used to stabilize millimeter-sized droplets in decane–water emulsions.³² Alteration of an external magnetic field allowed for the manipulation of the droplets, making it possible to transverse the water–oil interface. Complete phase separation was obtained by further increasing the magnetic field; providing a means to reversibly destabilize the emulsion, as the emulsified phase was easily reproduced upon hand-shaking of the sample.

Despite the variety of materials available, and in some cases the variety of shapes of the particle stabilizers, the majority of the work performed on Pickering emulsions involves the stabilization of the droplets by single, dispersed particles. However, one of the few reports in the literature that used multi-particulate macrostructures is the work of Shen *et al.*³³ Single-walled carbon nanotube/silica (SWNT/silica) nanohybrids, whose unique structure was composed of silica particles of *ca.* 50 nm, fused to bundles of SWNTs of *ca.* 10 nm in diameter, were demonstrated to be capable of stabilizing water-in-oil emulsions,

and after functionalization with palladium on the surface of either silica or the SWNT, their application was expanded from the stabilization of droplets to the catalysis of biofuel upgrade reactions at the oil/water interface.³⁴

In this contribution, we expand on the progress made involving the stabilization of emulsions by nanohybrids of complex morphologies and the inclusion of responsivity, by reporting the use of magnetically-active hybrid inorganic/organic networks (MHNs) for the stabilization of emulsion droplets at the oil/water interface. The MHNs were obtained by covalently linking a mixture of polymeric shell crosslinked knedel-like (SCK) nanoparticles, composed of poly(acrylic acid)₉₀-*block*-polystyrene₁₄₀ (PAA₉₀-*b*-PS₁₄₀) block copolymers, and amine-functionalized IONs (amine-IONs). To the best of our knowledge, this is the first report in which a network of covalently bound organic and inorganic particles is able to stabilize oil–water emulsions. It is demonstrated that emulsions can be formed *via* different methods of emulsification, with different types of oil, and a minimal concentration of particle stabilizers. The assembly of the MHNs at the oil/water interface has been analyzed, and as is commonly observed in the synthesis of materials *via* the Pickering polymerization technique, it leads to the formation of surface-decorated materials. Additionally, the incorporated amine-IONs within the network structure provide magnetic responsivity to the stabilized droplets, possibly making them suitable for various applications, in particular, the extraction of hydrocarbons and the water purification activities performed daily in the oil and gas field.

Experimental section

Materials and methods

All chemicals were purchased from Aldrich Chemical Co. or VWR and used without further purification unless otherwise noted. Amine-IONs were purchased from Chemicell GmbH. Nile Red was purchased from Sigma Aldrich, and fluorescein-5-thiosemicarbazide (FITC) was purchased from Thermo Scientific. Nanopure water (18 MΩ cm) was acquired by means of a Milli-Q water filtration system, Millipore Corp. (Bedford, MA). A neodymium magnet (90 lbs pull) was purchased from magnets4less.com.

The emulsions were homogenized *via* vortexing with a G-560 Vortex Genie 2 (120 V, 0.65 A, 60 Hz, speed 6–7, Scientific Industries, Bohemia, NY) for 1 min, or probe sonication with a 150VT ultrasonic homogenizer (Biologics, Inc., 150 W, 20 kHz, 3.9 mm probe) at 30% power, 50% pulse, for 1 min. Optical microscopy was performed through a 4× or 10× objective on an Olympus IX-70 inverted microscope, equipped with a mercury arc lamp and an Olympus DP72 digital camera (Olympus, Center Valley, PA). A representative sample from the emulsified phase was transferred with a Pasteur pipette and placed on a glass-bottom, 6 well plate and further diluted with a couple of drops of nanopure water. Images were collected from various areas of the sample and the diameter of the droplets observed was measured with a CellSense software and reported in the form of a histogram analyzed with Origin 8.0 Pro (Origin Lab, Northampton, MA).

The stability of the emulsions was assessed by measuring the emulsified fraction as well as the organic solvent and water fractions, when applicable. The samples were maintained at 4 °C to prevent evaporation of the organic solvents, and monitored until the fractions were too small to measure accurately.

The type of emulsion stabilized was determined *via* confocal fluorescence microscopy carried out on a FV1000 confocal fluorescence microscope with an IX-81 inverted base (Olympus, Center Valley, PA) and PMT detectors. Nile red was dissolved in toluene or dodecane at a concentration of 10 $\mu\text{g mL}^{-1}$, while dex-FITC was utilized as a water-soluble dye at a concentration of 30 $\mu\text{g mL}^{-1}$. The samples were analyzed at an excitation wavelength = 488 nm, and emission was detected between 580 nm and 650 nm for Nile Red and between 495 nm and 545 nm for dex-FITC. The emulsions were prepared at various water-to-oil (W:O) ratios and an MHN concentration of 1 mg mL^{-1} . The MHNs were resuspended in the dex-FITC solution and further utilized in the preparation of emulsions as previously described.

Transmission electron microscopy (TEM) analysis was performed on a JEOL 1200 EX operating at 100 kV and micrographs were recorded at calibrated magnifications using a SLA-15C CCD camera. Samples for TEM were prepared as follows: 5 μL of a solution were deposited onto a formvar-coated copper grid, and after 30 s, the excess of the solution was quickly wicked away by a piece of filter paper. The samples were negatively stained with 1% phosphotungstic acid (PTA) aqueous solution. After 30 s, the excess staining solution was quickly wicked away by a piece of filter paper and the samples were left to dry overnight. Scanning Electron Microscopy (SEM) analysis was performed on a JEOL JSM-7500F operating at an acceleration voltage of 2 kV or 5 kV, and a working distance (WD) of 14.7 mm. Prior to analysis, the samples were coated with 5 nm of platinum/palladium (80%/20%).

Interfacial tension (IFT) measurements were performed with an Attension Theta optical tensiometer (Biolin Scientific, Stockholm, Sweden), and analysis was performed by fitting drops with a Young–Laplace formula using the Theta Software. First, the IFT between water and toluene or dodecane was measured as a control. Water was utilized as the drop phase and it was immersed in *ca.* 5 mL of toluene or dodecane, while five high speed images of the water drop were obtained in a period of 20 s. The IFT was calculated for each image and the process was repeated at least three times with three different water droplets. The same procedure was followed to determine the effect of the MHNs on the IFT between water and the organic solvents, at a concentration of 0.5 mg mL^{-1} .

Synthesis of MHNs

The synthesis of the MHNs was performed according to a published procedure.³⁵ Briefly, a 250 mL vial was charged with a stir bar and an aqueous solution of SCKs (12 equiv., 70 mL, 0.27 mg mL^{-1} , 20 mg, 62 μmol of available acrylic acid units). A solution of amine-IONS in nanopure water (1 equiv., 22.6 mL, 0.15 mg mL^{-1} , 3.4 mg, 5.2 μmol of ligand) was added dropwise to the reaction mixture and it was allowed to stir for *ca.* 5 min, after which a solution of 1-[3'-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide

(EDCI, 8.8 equiv., 7.5 mL, 1.8 mg mL^{-1} , 13.5 mg, 45.4 μmol) was added *via* a syringe pump at a rate of 0.25 mL min^{-1} . The reaction was allowed to stir for 24 h, followed by centrifugation at 10 000 rpm for 5 min. The brown precipitate was resuspended in 15 mL of nanopure water with the aid of sonication and vortexing, and this process was repeated twice. The supernatant was collected and centrifuged 2 more times with the aim of removing as much precipitate as possible. After centrifugation, the supernatant was collected, placed in presoaked membrane dialysis tubing (MWCO 12–14 kDa) and dialyzed against nanopure water for three days. Following dialysis, the suspension of MHNs and the supernatant were combined and lyophilized to afford 16 mg of a light brown powder in 69% yield.

Preparation of fluorescein-labelled micelles

A 100 mL round bottom flask was charged with a stir bar, and PAA₉₀-*b*-PS₁₄₀ (1 equiv., 60 mg, 3.3 μmol) was dissolved in 60 mL of THF and allowed to stir for *ca.* 15 min. Nanopure water (60 mL) was added with the aid of a syringe pump at a rate of 20 mL h^{-1} , the resulting solution was placed in presoaked dialysis membrane tubing (MWCO 12–14 kDa) and dialyzed against nanopure water for 2 days. Following characterization, the micelles were fluorescently labelled by adding fluorescein-5-thiosemicarbazide (0.05 equiv., 6.2 mg, 14.6 μmol , dissolved in 1 mL of *N,N*-dimethylformamide) to the aqueous solution, followed by stirring for 2 h. A stock solution of 1-[3'-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDCI, 0.05 equiv., 4.8 mg, 16.1 μmol) was prepared in 100 μL of nanopure water and added dropwise to the vessel. The reaction mixture was allowed to stir overnight, and placed in presoaked membrane dialysis tubing (MWCO 12–14 kDa) for 3 days. The resulting micelles were crosslinked as previously described,³⁵ purified and further employed in the synthesis of MHNs to yield FITC-functionalized MHNs. IR: ν = 3490–2460, 3095–2985, 2980–2790, 1655, 1625–1525, 1510, 1490, 1470–1420, 1415, 1370, 1350, 1310, 1300–1260, 1260–1230, 1215, 1190, 1160, 1140, 1120, 1045–975, 950, 910, 880, 845, 820, 800, 785, 765, 760–740, 730, 700, 650, 625 cm^{-1} . $D_{\text{h(N)}}(\text{DLS}) = 50 \pm 10 \text{ nm}$.

Preparation of emulsions

Toluene–water emulsions were prepared by resuspending the MHNs in nanopure water at the desired concentration (with respect to the amount of nanopure water employed), and alternating between vortex and sonication as agitation methods to obtain fully suspended particles. The W:O volume ratio was varied while maintaining a total emulsion volume of 2.5 mL. The biphasic systems were emulsified *via* vortex for 1 min, or by utilizing a probe sonicator at 30% power, and 50% pulse for 1 min. Dodecane–water emulsions were prepared by following the same preparation method but utilizing probe sonication as the method of emulsification.

Synthesis of polystyrene beads

A stock solution of 2,2'-azobis(2-methylpropionate) (AIBN) in styrene was prepared by dissolution of 1.2 mg of AIBN in 300 μL of styrene. The styrene–water emulsions were prepared at a

W : O = 10 : 1, by utilizing 1 mL of either an MHN or amine-ION aqueous suspension (0.5 mg mL^{-1} in nanopure water) and 100 μL of the styrene stock solution. Homogenization was achieved *via* vortexing, and then the reaction mixture was immersed in an oil bath at 80°C and was allowed to react for 24 hours. The brown solid layer formed after polymerization was washed with nanopure water, dried and resuspended in tetrahydrofuran (THF). Samples were drop-cast onto TEM grids and placed on carbon tape for further SEM analysis.

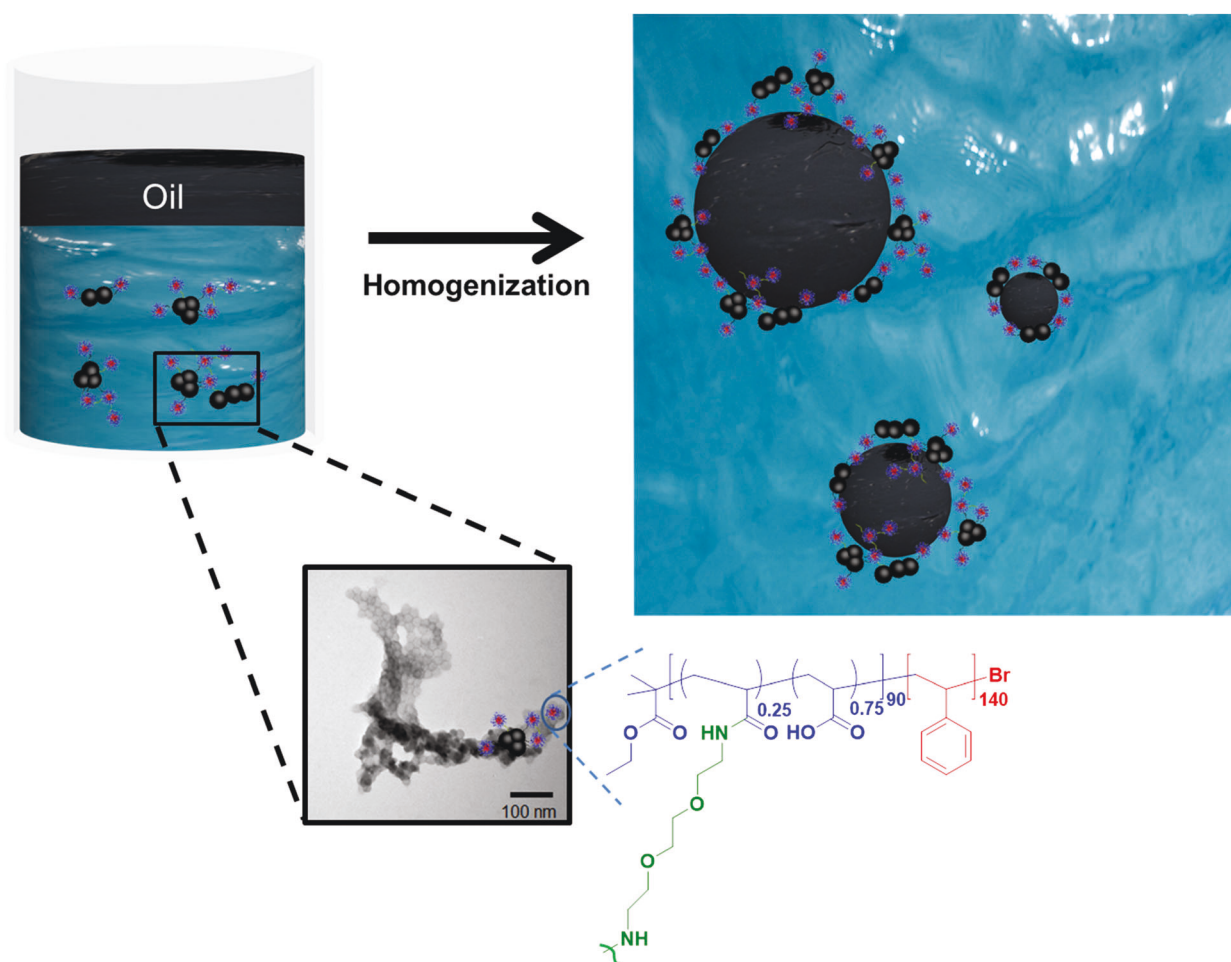
Results and discussion

Preparation of oil–water emulsions

Magnetically-active hybrid networks (MHNs) are inorganic/organic composite materials that are composed of polymeric SCK nanoparticles covalently bound to amine-IONS, which have remarkable abilities to interact with both hydrophobic and hydrophilic species.³⁵ The SCKs were synthesized from poly(acrylic acid)₉₀-*block*-polystyrene₁₄₀ block copolymers upon self-assembly in water and crosslinking reactions to afford nanostructures composed of polystyrene hydrophobic cores and crosslinked poly(acrylic acid)

hydrophilic shells (Scheme 1). These MHNs were originally synthesized for the remediation of aqueous environments contaminated with crude oil sheen, which would be facilitated by the hydrophobic–hydrophobic interaction that could take place between the crude oil molecules and the cores of the SCKs. However, our investigation into the mechanism of interaction between the MHNs and the crude oil suggested that these hybrid networks could stabilize oil–water emulsions, as they were capable of reducing the interfacial tension between toluene and water, as well as decane and water. These discoveries led us to hypothesize that the mechanism of interaction between the crude oil and the MHNs was not limited to sequestration of the hydrophobic pollutant into the core of the SCKs, but included the stabilization of oil–water emulsions *via* Pickering emulsification (Scheme 1).

In order to test this hypothesis and based on our preliminary results, two different types of organic solvents, toluene and dodecane, were selected to prepare oil–water emulsions. Dodecane has been employed in multiple literature procedures to simulate crude oil,^{36–40} therefore, it was selected as a mimic for the aliphatic components of crude oil. Additionally, toluene was selected to mimic the aromatic components of crude oil, given its lower



Scheme 1 Schematic representation of the MHNs suspended in the water phase with the inset depicting their TEM characterization (left), and their assembly at the interface between oil and water to stabilize oil-in-water emulsions (right).

health repercussions compared to other commonly-used solvents, such as benzene. Although the amphiphilic character of the MHNs allowed for their resuspension in nanopure water, toluene and dodecane; the suspensions of the MHNs in these organic solvents displayed inferior stability than the suspension in nanopure water (Fig. S1, ESI†). Consequently, the emulsions were prepared at the desired concentration of MHNs, by resuspending lyophilized networks in nanopure water, yielding a light-brown solution that created a significant contrast with the colorless organic solvents (Fig. 1). Initially, the emulsions were prepared at different W:O volume ratios, while maintaining a total volume of 2.5 mL and a $[MHN] = 0.5 \text{ mg mL}^{-1}$ (with respect to the nanopure water used as solvent). Additionally, two methods of emulsification were studied—vortexing and the commonly-used and mechanically-demanding homogenization through probe sonication.^{21,30,41–44} The former was selected because it provided a more consistent approach to the preparation of emulsions than the commonly used “hand shake method”,^{25,45–48} while requiring less mechanical power than homogenization through probe sonication.

Initial studies showed that toluene–water emulsions could be formed *via* both vortexing and probe sonication, and after emulsification, it was evident that the MHNs played a role in stabilizing the emulsions (Fig. 1). The formation of large, light-brown droplets at the interface was observed with the naked eye, and the water fraction that was previously light-brown due to the presence of the MHNs, turned colorless. In contrast to the vortex method, probe sonication resulted in emulsions that were initially cloudy through the water fraction, which could indicate the formation of a secondary emulsion. However, after *ca.* 24 hours, the cloudiness dissipated and the water fraction turned colorless as observed in the vortex case.

The formation of dodecane–water emulsions was different to the emulsification of toluene and water, as the dodecane–water

emulsions formed *via* vortexing were unstable, and coalesced into the two original oil and water phases after a few seconds (Fig. S2, ESI†). These results were surprising initially, however; interfacial tension (γ) measurements (Table S1, ESI†) revealed that the MHNs (concentration = 0.5 mg mL^{-1}) caused no significant reduction of the γ between dodecane and water, while the γ between toluene and water was reduced by *ca.* 32%. These results could explain why toluene–water emulsions can be formed by the two methods, but dodecane–water emulsions required the higher energy probe sonication method to be formed.

Stability of emulsions

The stability of the emulsions was studied following the preparation of samples utilizing both toluene and dodecane as the oil phases, as well as vortex and probe sonication as the methods for emulsification. For this study (Fig. 2), the W:O volume ratio was gradually varied, and an analysis was performed on samples containing higher ratios of water (W:O = 5:1, 3:1), equal ratios of water-to-oil (W:O = 1:1), and lower ratios of water-to-oil (W:O = 1:3, 1:5). Originally, the emulsions (toluene–water prepared *via* vortex or probe sonication, and dodecane–water prepared *via* probe sonication only) were formed at equal and higher ratios of water-to-oil; however, it was noticed that the toluene–water emulsions were only stable for a couple of weeks if the samples were stored under ambient conditions. This effect was attributed to the evaporation of toluene, since precipitation of the MHNs was observed after a couple of weeks, along with the disappearance of the toluene phase. Therefore, in order to prevent the evaporation of the oil phase, the samples were emulsified, stored at 4 °C and analyzed for their formation and stability over a period of time.

As mentioned before, formation of stable emulsions was observed at equal and higher ratios of water-to-oil (W:O = 1:1, 3:1 and 5:1), regardless of the type of oil or the method of

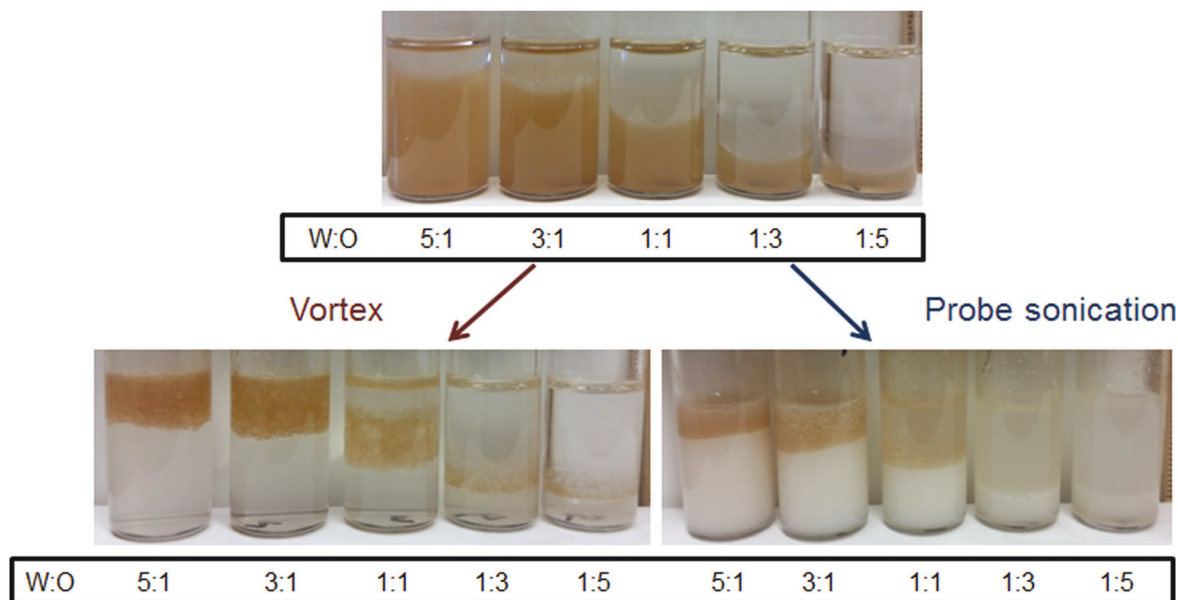


Fig. 1 Toluene–water emulsions prepared at different W:O ratios before (top) and after (bottom) emulsification *via* two different methods: vortex (left) and probe sonication (right).

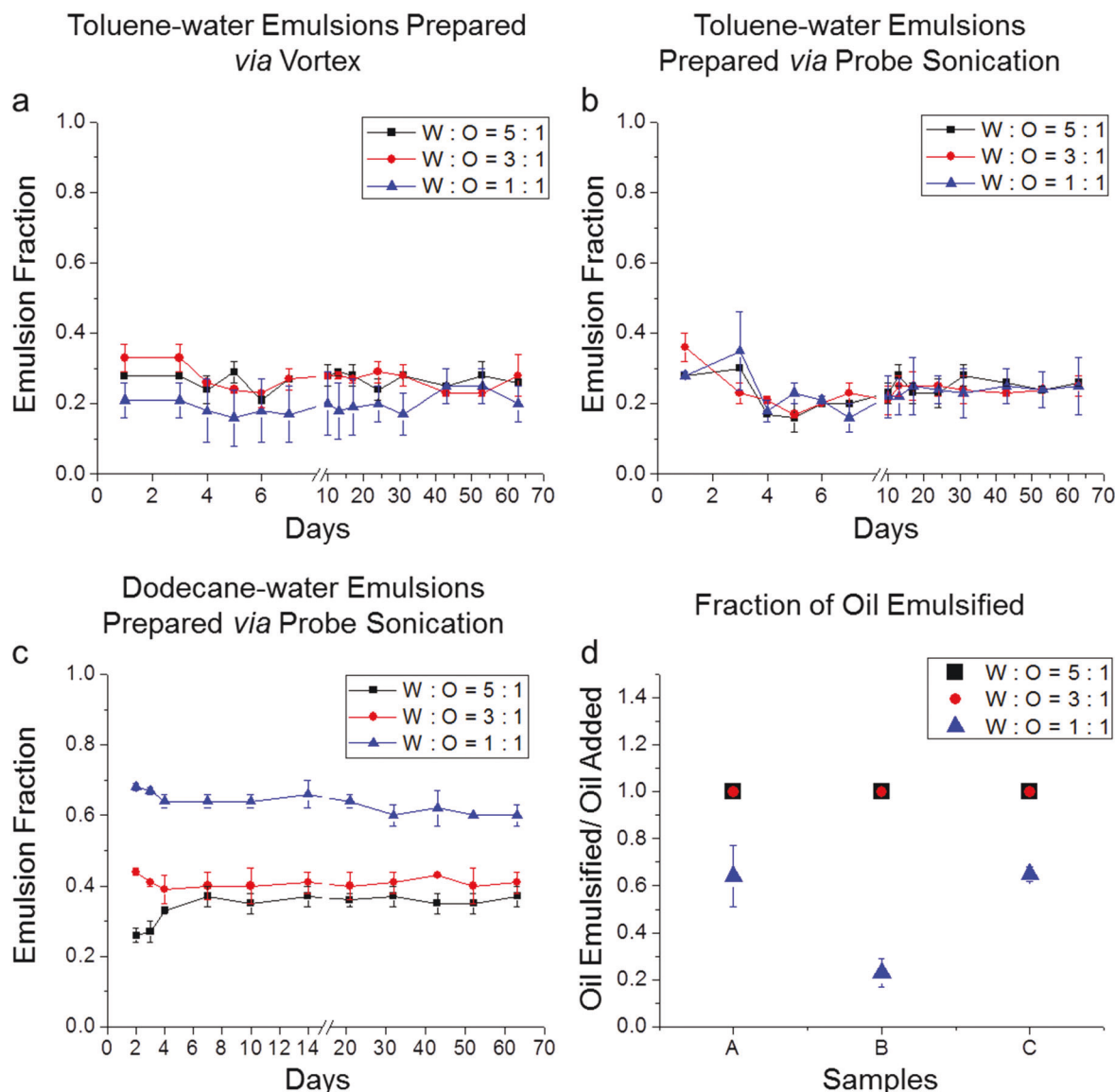


Fig. 2 Stability of toluene–water emulsions prepared *via* vortex (a) and probe sonication (b), and dodecane–water emulsions prepared *via* probe sonication (c) at different W : O ratios. Fraction of the oil emulsified at different W : O ratios (d), for toluene–water emulsions prepared *via* vortex (A) and probe sonication (B), and dodecane–water emulsions prepared *via* probe sonication (C).

emulsification employed. However, although no appreciable emulsion formation was observed at the lower ratios of water-to-oil (W:O = 1:3 and 1:5); it is worth noting that possible emulsion formation could take place upon addition of oil volume fractions ranging from 50 vol% to 75 vol%. Initially, the stability of the emulsions was assessed by monitoring the oil released due to droplet coalescence immediately after emulsion formation (Fig. 2d). The length of the oil emulsified was compared to the initial length of the volume of oil added to the samples, and the emulsified oil fraction was determined. For all samples prepared at W:O = 5:1 and 3:1, 100% of the oil added was incorporated into the emulsion. Furthermore, for the toluene–water samples prepared *via* vortex, *ca.* 60% of the oil added was emulsified; while for the same emulsions prepared *via* probe sonication *ca.* 20% of the oil was emulsified.

It is important to highlight that the difference observed between these two samples can be due to the less clear oil/emulsion boundary observed immediately after probe sonication (Fig. 1), which typically becomes more evident after the cloudiness dissipates *ca.* 24 h after homogenization. Moreover, a similar phenomenon was observed for the dodecane–water emulsions, where *ca.* 60% of the oil added was incorporated into the emulsion, but the same blurry oil/emulsion boundary was observed (Fig. S2, ESI†).

In addition to monitoring the fraction of the oil emulsified immediately after emulsion formation, the stability of the emulsions was also determined by monitoring the length of the emulsion fraction over a period of time. All samples were monitored for approximately 60 days, during which no significant reduction of the emulsified fractions was observed (Fig. 2a–c).

All in all, these data confirmed that the MHNs are capable of stabilizing oil–water emulsions which display stability for prolonged periods of time.

Characterization of emulsions *via* optical microscopy

A preliminary assessment of the emulsified samples under the initial homogenization conditions ($[MHN] = 0.5 \text{ mg mL}^{-1}$, $W:O = 3:1$) revealed the formation of droplets of varying sizes, including large droplets that could even be observed with the naked eye. Therefore, in order to avoid the bias for large particles commonly associated with dynamic light scattering measurements of polydispersed samples,^{49,50} and following previously established procedures,^{4,8,51,52} the emulsions were characterized by optical microscopy. Analysis of the dilute samples showed that highly dispersed emulsions were obtained regardless of the organic solvent or method of preparation used (Fig. 3). In fact, the difference between the droplets was so large that determining an average droplet size did not provide meaningful information. Consequently, the distribution of the droplet size for all samples was determined, and revealed highly dispersed emulsion samples, with droplets ranging from just a few micrometers to hundreds of micrometers in diameter. These results led us to focus our efforts on investigating certain parameters that could have an effect on the droplet size distribution, such as the MHN concentration and $W:O$ ratio; with the general understanding that smaller droplets lead to the formation of more stable emulsions.⁵³

Evaluation of the effect of the water-to-oil (W:O) ratio

One of the parameters that can have a significant effect on the stability of emulsions is the water-to-oil ($W:O$) ratio. Several reports have indicated that the $W:O$ ratio could determine the type of emulsion stabilized, and could even induce inversion of the emulsified phase.^{8,46,51,54} In order to study the effect of the $W:O$ ratio on the droplet size distribution of the emulsions,

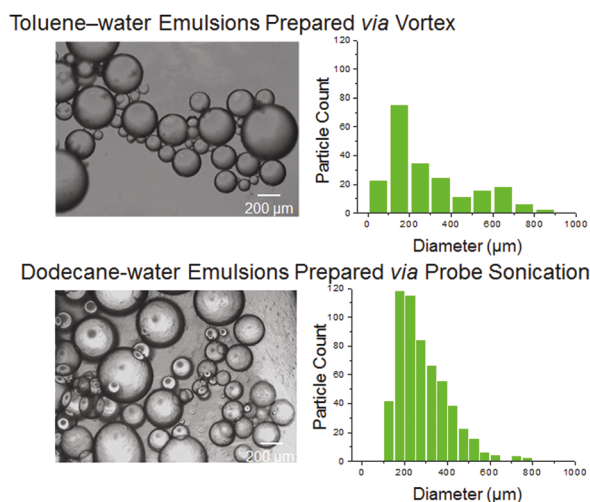


Fig. 3 Optical microscopy images and droplet size distribution of toluene–water emulsions prepared *via* vortex, and dodecane–water emulsions prepared *via* probe sonication.

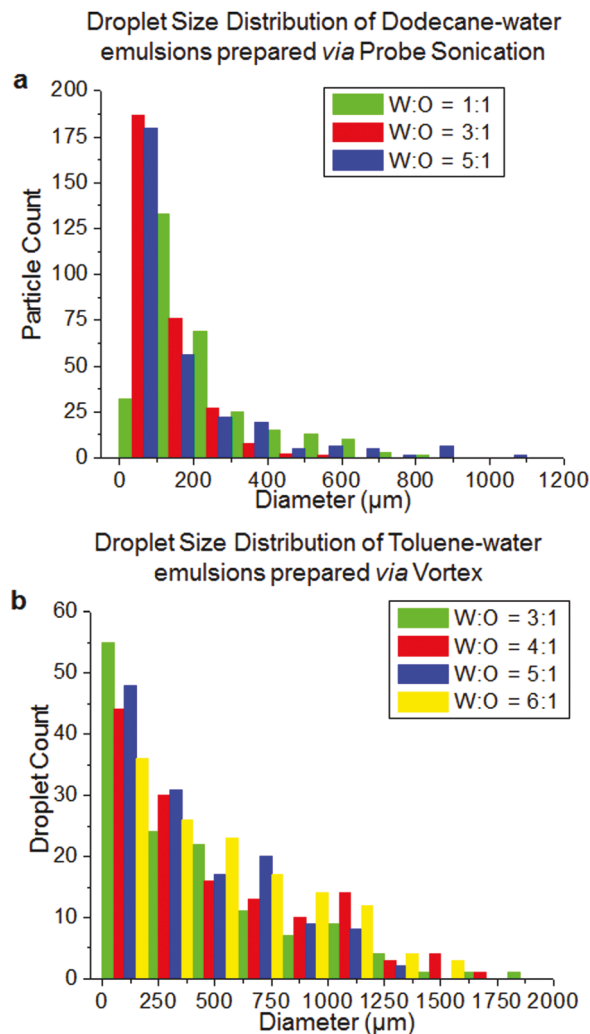


Fig. 4 Histograms of the droplet size distribution of dodecane–water emulsions prepared *via* probe sonication (a), and toluene–water emulsions prepared *via* vortex (b) at different $W:O$ ratios.

the MHN concentration and total emulsion volume were held constant (0.5 mg mL^{-1} and 2.5 mL , respectively), while the $W:O$ ratio was varied. In the case of the dodecane–water emulsions (Fig. 4a), a shift towards a smaller and narrower droplet size distribution was observed as the $W:O$ ratio was changed from 1:1 to 3:1; however, further increasing the water ratio ($W:O = 5:1$) produced emulsions with droplets of larger diameters than the 3:1 emulsions.

On the other hand, the toluene–water emulsions were less sensitive to the $W:O$ ratio than were the dodecane–water emulsions. Even though formation of the emulsions was observed at a $W:O = 1:1$ for samples prepared *via* vortex and probe sonication (Fig. S3, ESI†), the size of the droplets at this $W:O$ ratio made the characterization of these samples *via* optical microscopy difficult. The droplets formed were visibly large and had diameters on the order of millimeters, making them too large and unstable to image under the microscope. Therefore, only the samples prepared at $W:O = 3:1$, $4:1$, $5:1$ and $6:1$ were analyzed (Fig. 4b and Fig. S4, ESI†). Visually, there was a

significant difference between the droplet size of the emulsions prepared at W:O = 1:1 and 3:1, with droplets of smaller diameter observed for the emulsion with the higher water fraction. However, further increasing the W:O ratio had no significant effect on the droplet size distribution of samples prepared either *via* vortex or probe sonication. All together, these data indicate that a W:O = 3:1 might provide ideal conditions for the formation of stable dodecane–water and toluene–water emulsions, regardless of the method of emulsification.

Evaluation of the effect of the MHN concentration

Another significant parameter in the stabilization of emulsions is the concentration of the solid particles acting as stabilizers. In order to focus our studies, and based on the knowledge learned regarding the effect of the W:O ratio on the size of the droplets, a W:O ratio of 3:1 was selected to perform these experiments while the concentration of the MHNs suspended in nanopure water was varied until no significant changes were observed for the systems studied. In the case of the dodecane–water emulsions, a broad distribution was obtained at a concentration = 0.5 mg mL⁻¹, (Fig. 5a) and a significant shift towards smaller, less dispersed droplets was observed by increasing the concentration to 1 mg mL⁻¹, and even more so at 1.5 mg mL⁻¹. However, further increasing the concentration to 2 mg mL⁻¹ shifted the distribution towards larger droplets, indicating a possible saturation of the system. A more in-depth analysis was performed to determine the percentage of the droplets that fell within three size ranges: a small range from 0 to 200 µm, a medium range from 200 µm to 600 µm, and a large range from 600 µm to 1200 µm (Table 1). The results indicated that at a concentration of 0.5 mg mL⁻¹ *ca.* 28% of the droplets lay in the small range, with a significant increase to *ca.* 95% observed in this size range at 1 mg mL⁻¹. Once the concentration was increased to 1.5 mg mL⁻¹, 100% of the droplets were found in the smaller range; however, increasing the concentration to 2 mg mL⁻¹ lowered the percentage of droplets present in this range to *ca.* 96%. Although these percentages of particles within the 0–200 µm range are similar, the histograms reveal differences in the particle sizes and size distributions.

A similar phenomenon was observed for the toluene–water emulsions prepared *via* probe sonication, but the effect was less prominent (Fig. S5b, ESI†). Increasing the concentration from 0.5 to 1 to 1.5 mg mL⁻¹ shifted the distribution towards smaller droplets, and further increasing the concentration to 2 mg mL⁻¹ reverted the trend, yielding emulsions of larger droplets than those formed at 1.5 mg mL⁻¹. Moreover, the quantitation of the droplet distribution showed that at a concentration of 0.5 mg mL⁻¹ *ca.* 33% of the droplets lay in the small range, with an observed increase to *ca.* 38% at 1 mg mL⁻¹, and *ca.* 45% at 1.5 mg mL⁻¹; while only *ca.* 24% of the droplets lay within this range at a concentration of 2 mg mL⁻¹. These results were slightly different to those observed for toluene–water emulsions prepared *via* vortex. A shift in the distribution towards a lower size range was observed after increasing the concentration from 0.5 mg mL⁻¹ to 1 mg mL⁻¹, while further increasing the concentration to 1.5 mg mL⁻¹ and 2 mg mL⁻¹ yielded

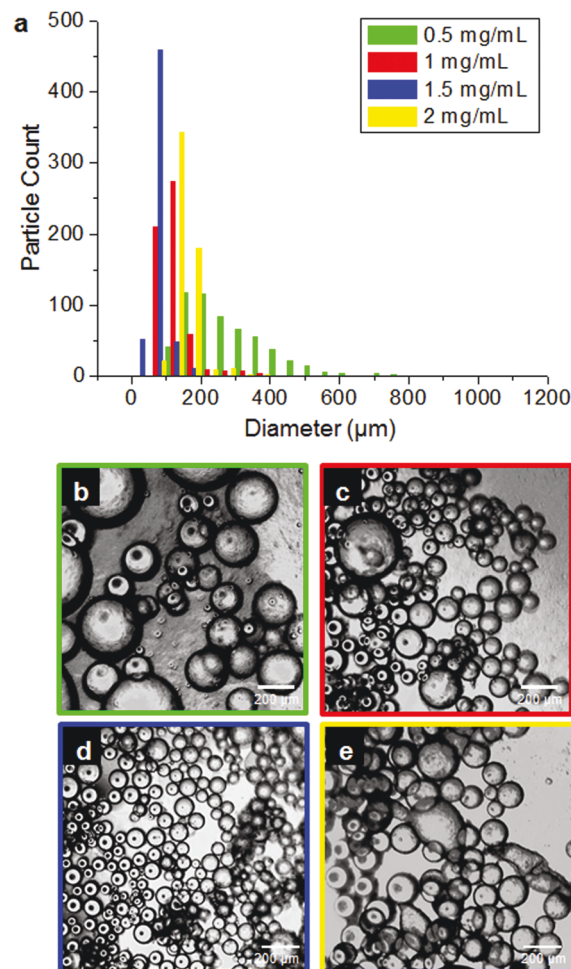


Fig. 5 Histograms of the droplet size distribution (a) and optical microscopy images (b–e) of dodecane–water emulsions prepared at a W:O = 3:1, and varying concentrations of MHNs (optical microscopy images are color coded on the borders following the legend on (a)).

Table 1 Distribution of the droplet size of emulsions stabilized at a water-to-oil ratio = 3:1 and different MHNs concentrations and methods of emulsification

Organic solvent	Method	Size range (µm)	Concentration of MHNs (mg mL ⁻¹)			
			0.5 (%)	1 (%)	1.5 (%)	2 (%)
Toluene	Vortex	0–200	47	69	40	28
		200–600	40	22	59	69
		600–1200	13	9	1	3
	Probe sonication	0–200	33	38	45	24
		200–600	57	59	55	73
		600–1200	10	3	0	3
Dodecane	Probe sonication	0–200	28	95	100	96
		200–600	70	5	0	4
		600–1200	2	0.0	0	0.0

distributions similar to those obtained at 0.5 mg mL⁻¹ (Fig. S5a, ESI†). Additionally, at a concentration of 0.5 mg mL⁻¹ *ca.* 47% of the droplets lay in the small size range discussed previously; while at a concentration of 1 mg mL⁻¹ *ca.* 69% of the droplets

lay in this range. Additionally, a reduction of the percentage of droplets present in the small range was observed as the concentration of MHNs was further increased, while the percentage of the droplets present in the middle range increased.

In order to understand the discrepancy of these results, a detailed TEM study of the MHNs before and after probe sonication was performed. This study was done with the aim of analyzing the effect of probe sonication on the morphology of the MHNs. As described before, the MHN system was originally designed for the sequestration of hydrophobic pollutants from aqueous environments, and exhibited a network-like morphology composed of multiple SCKs bound to amine-IONS.³⁵ The configuration and arrangement of the two components of the networks cannot be controlled; therefore the synthesis of the MHNs yields structures of different sizes, compositions and topologies. The TEM micrographs of the MHNs before probe sonication exhibited similar structures (Fig. 6a–d), where most of the SCKs appeared to be linked to clusters of SCKs and amine-IONS or to other SCKs, with few singular SCK nanoparticles observed in the samples. In addition, the TEM analysis after probe sonication also revealed network-like structures of various sizes and compositions, which are characteristic of the MHNs (Fig. 6e–h). However, we also observed smaller MHN clusters that appeared to be composed of fewer SCKs and amine-IONS than those observed prior to probe sonication. Moreover, fiber-like structures and singular SCKs surrounded by what appeared to be polymeric residue (Fig. 6g and h) were also observed. It is hypothesized that these structures correspond to loose strands of block copolymer resulting from the break-down of some of the SCK nanoparticles; however, it is difficult to determine with certainty whether the strands are in fact block copolymers, or artifacts commonly present in stained TEM grids.⁵⁵ Nevertheless, the micrographs also showed the presence of well-defined network structures, indicating that the MHN morphology is retained, even if some fragmentation of the structures occurred.

To corroborate the previously stated hypothesis that the MHNs underwent fragmentation under probe sonication, recovery of the MHNs *via* magnetic action before and after probe sonication was performed. The results indicated (Fig. S6, ESI†) that only *ca.* 51% of the MHNs could be recovered from the water *via* magnetic action after probe sonication, compared to the *ca.* 84% recovery of a control sample of MHNs that was not subjected to probe sonication. This difference corresponded to *ca.* 33% decrease in the recovery efficiency of the MHNs, and indicated that the method of probe sonication led to the disconnection of some of the MHN network structure into either individual SCKs or polymer fibers, which were no longer covalently bound to the amine-IONS and, thus, remained in the water upon separation *via* magnetic action. The effects of probe sonication on the morphologies of the MHNs and SCKs are not surprising, since scission of covalent bonds in polymer fibers,⁵⁶ and molecular bottlebrushes⁵⁷ has been widely reported in the field of mechanochemistry. Additionally, the fractionation of non-crosslinked and crosslinked polymer micelles as a consequence of sonication has also been previously observed by our group, as well as others.^{58–62}

In general, these observations could explain why a slightly higher MHN concentration is required to produce less dispersed emulsions *via* probe sonication than *via* vortex. The dissociation of the SCK nanoparticles into polymer strands would reduce the concentration of particles present in the solution, and thereby reduce the concentration of particle stabilizers capable of yielding stable emulsions. As a consequence, larger concentrations of MHNs would be required to achieve the same results by probe sonication as were observed when emulsions were prepared *via* vortex.

Determination of the type of emulsions stabilized by the MHNs *via* confocal microscopy

In order to determine whether oil-in-water (o/w) or water-in-oil (w/o) emulsions were stabilized by the MHNs, a series of control studies was performed *via* confocal microscopy. The organic

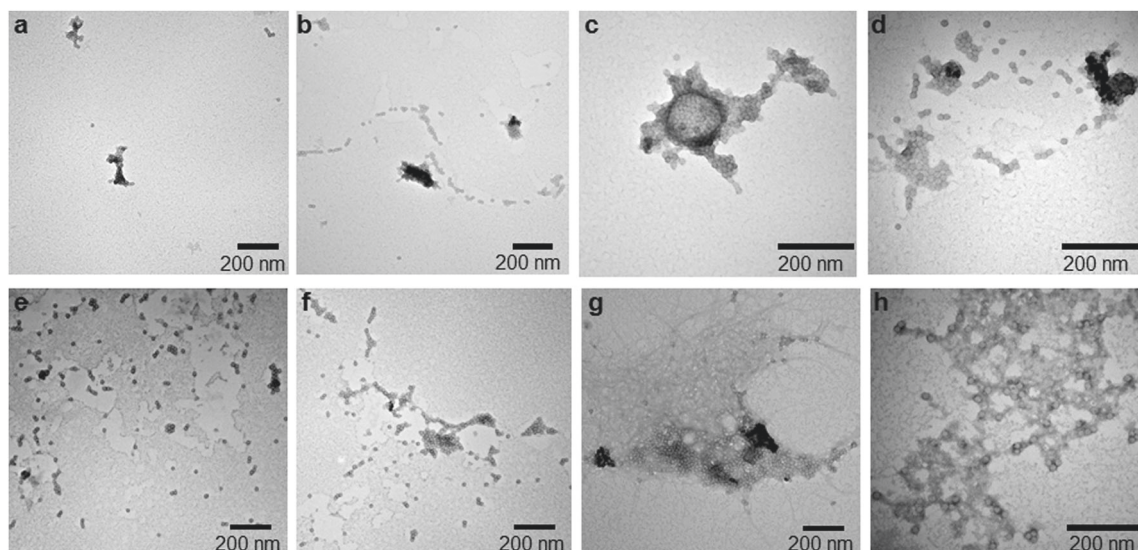


Fig. 6 Transmission electron micrographs of a suspension of MHNs (0.5 mg mL^{-1}) before (a–d) and after (e–h) probe sonication.

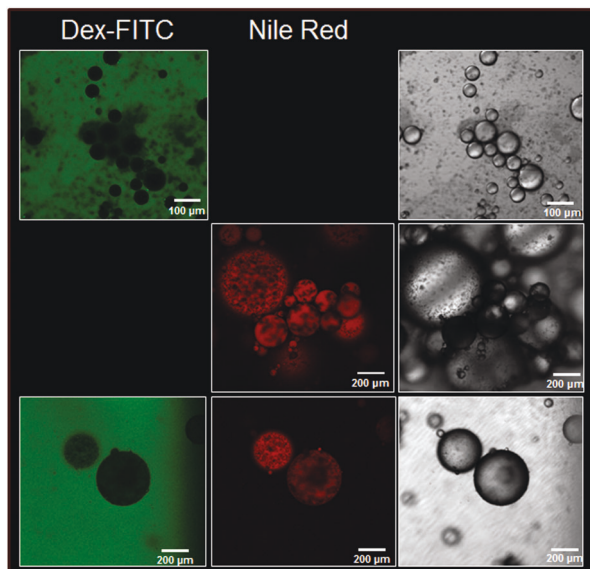


Fig. 7 Confocal laser micrographs depicting the type of toluene–water emulsions formed *via* vortexing at a [MHN] = 1 mg mL^{−1} and a W : O = 3 : 1, for samples containing dex-FITC in the aqueous phase only (upper row), Nile red in the organic phase only (middle row), and both dex-FITC and Nile red in the aqueous and organic phases, respectively (bottom row).

dye Nile red was dissolved in either toluene or dodecane in order to identify the oil phase in the emulsion sample, while the water-soluble dye dex-FITC was incorporated to identify the water phase. In the case of the toluene–water emulsions prepared *via* vortex, three different emulsion samples were prepared at a [MHN] = 1 mg mL^{−1} and a W : O = 3 : 1, and analyzed (Fig. 7). The first sample was prepared by utilizing an aqueous dex-FITC solution as the water fraction without dye being present in the toluene fraction. The confocal micrographs obtained showed green fluorescence in the background, indicating a continuous phase composed of water. The second sample was prepared by utilizing a solution of Nile red in toluene as the oil fraction, with no fluorescent dye present in the water fraction. In this case, red fluorescence was identified within the emulsion droplets, while no fluorescence was observed in the background, indicating that the droplets were composed of toluene. Lastly, an emulsion sample containing both dex-FITC in the water phase, and Nile red in the oil phase was analyzed. As expected, the micrographs showed red droplets surrounded by a green background, corroborating the findings that toluene-in-water (o/w) emulsions were stabilized by the MHNs. Moreover, this same experiment was performed at the same MHN concentration and different W : O ratios (5 : 1 and 1 : 1, Fig. S7, ESI†), and no differences were observed, indicating the formation of o/w emulsions even at varying W : O ratios. The same results were observed for toluene–water emulsions and dodecane–water emulsions prepared *via* probe sonication, at the same concentration and different W : O ratios.

Assembly of the networks at the oil/water interface

To determine whether the MHNs assembled at the interface between oil and water, an emulsion of styrene and water was

prepared *via* vortex at a W : O = 10 : 1, and AIBN was dissolved in styrene prior to emulsification to initiate the polymerization of styrene upon stabilization of the oil droplets by the MHNs. The solid sample obtained after polymerization was resuspended in THF and analyzed *via* scanning electron microscopy (SEM). The SEM results showed the formation of multiple PS beads of circular, as well as irregular shapes (Fig. 8a and b); which corresponded to the shapes of the droplets observed *via* optical microscopy under all conditions studied. Additionally, inspection of the PS beads at higher magnification revealed the presence of smaller nanostructures, which imparted texture to the surface of the beads. These nanostructures corresponded in size and shape to the SCKs that compose the network structure of the MHNs, and were not observed when PS beads were synthesized from the emulsion polymerization of styrene droplets stabilized solely by amine-IONS (Fig. 8c and Fig. S8, ESI†). In contrast, the amine-ION-stabilized beads showed a much smoother surface than those stabilized by the MHNs.

Additionally, confocal microscopy was also employed to assess the surface coverage of the droplets by the hybrid networks. To do so, MHNs were prepared by utilizing micellar structures prepared from PAA₉₀-*b*-PS₁₄₀ that were functionalized with fluorescein-5-thiosemicarbazide (FITC), and which were cross-linked to generate FITC-functionalized SCKs. These fluorescently-labelled SCKs were further employed in the synthesis of the MHNs to yield FITC-functionalized MHNs (FITC-MHNs), which were utilized to prepare a toluene–water emulsion *via* vortex at a W : O = 3 : 1, and [FITC-MHN] = 1 mg mL^{−1}. The emulsion droplets were characterized both by optical microscopy (Fig. 8d) and confocal microscopy (Fig. 8e) upon excitation of the sample with a 488 nm laser. The data showed droplets of various sizes which are characteristic of the emulsions stabilized by the MHNs (Fig. 8d). Moreover, the droplets appeared to be decorated with irregular species of different sizes and morphologies, which coincide with our previous characterization of the MHNs. Furthermore, the confocal image (Fig. 8e) showed that the irregular structures present on the surface of the droplets exhibited green fluorescence, and covered the majority of the droplet's surface, although some areas of the surface remained uncovered. Additionally, given that the droplets appeared to be present at different positions along the Z axis, the sample was further analyzed by collecting multiple confocal images while progressively moving the focal point along the Z axis (Fig. S9, ESI†). The data showed the evolution of the surface coverage, which began from the bottom of the sample (Z = 0–16 μm) and displayed droplets covered with green fluorescence from the FITC-MHNs, to the formation of green “haloes” at higher Z coordinates (Z = 64–208 μm), which were a consequence of the arrangement of the FITC-MHNs at the oil/water interface. Unfortunately the large diameter of some of the droplets made it impossible to completely image the larger droplets from bottom to top; as the top of the droplet was out of the focal range of the instrument.

Nevertheless, the combination of the SEM and confocal microscopy data showed that the MHNs can assemble at the oil/water interface to stabilize the emulsions, covering a significant portion of the droplets formed, despite the irregular size and

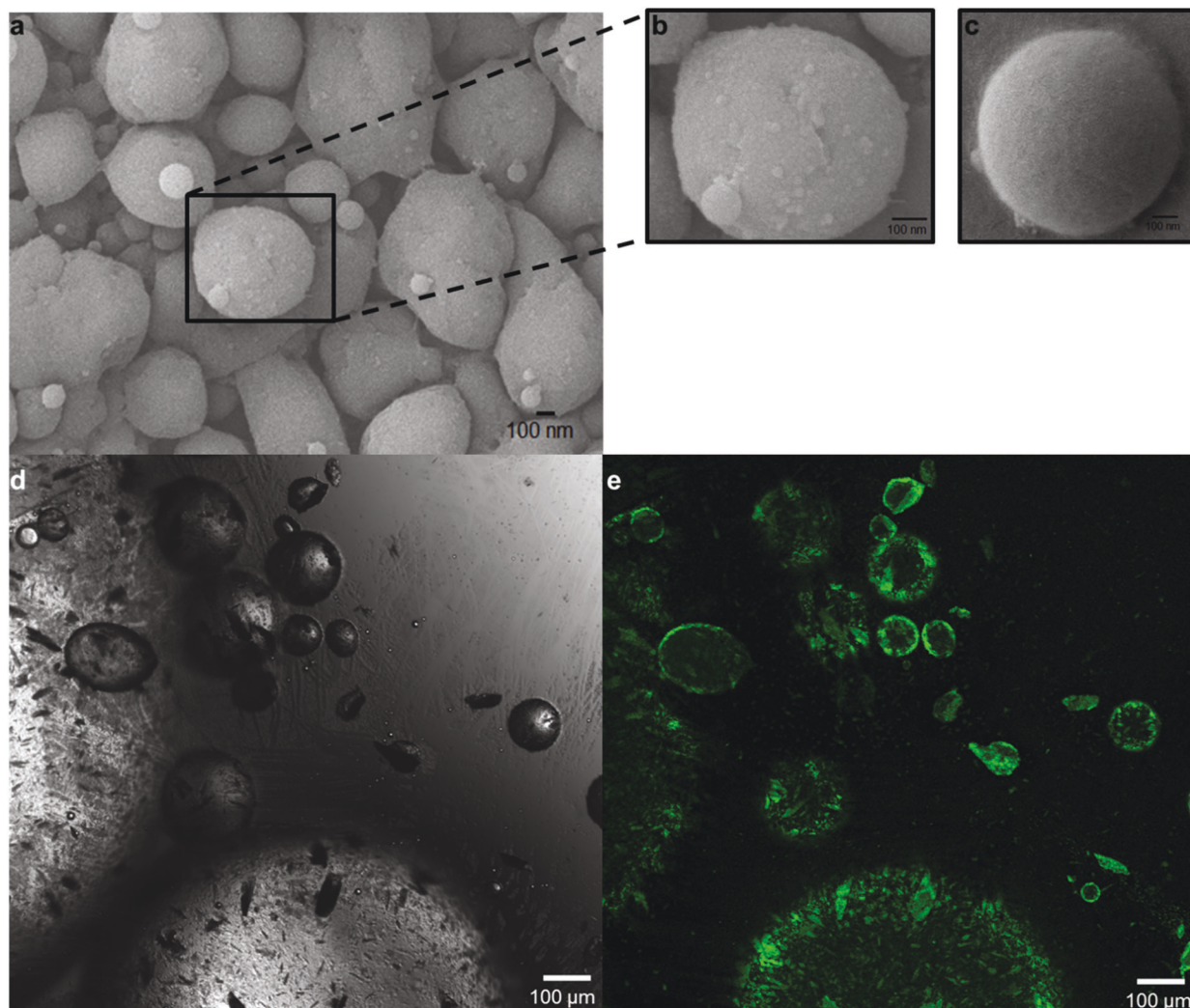


Fig. 8 Scanning electron micrographs of polystyrene beads synthesized from the emulsion polymerization of styrene droplets stabilized in water by the MHNs (a and b), or by the amine-IONs (c). Optical micrograph (d) and confocal laser micrograph (e) of a toluene–water emulsion formed *via* vortex at a [FITC-MHN] = 1 mg mL^{−1} and W : O = 3 : 1, stabilized by FITC-MHNs.

shapes that are characteristic of the MHNs. Moreover, the unique capability of the MHNs to stabilize emulsion of hydrophobic monomers in water, and withstand polymerization, can give rise to the synthesis of materials with morphologies that may be unattainable *via* the conventional methods employed for assembly of polymeric materials.

Magnetic responsivity of emulsions

One of the most interesting features of the emulsions stabilized by the MHNs is their responsivity to an applied magnetic field. This feature is attributed to the presence of magnetically-active IONs within the network structure of the MHNs, which in turn, stabilize the oil droplets formed. A qualitative assessment with a neodymium magnet (90 lbs pull) allowed us to identify the magnetic response of the droplets, which were not only attracted to the magnet, but were also magnetically manipulated to transverse the interfacial barrier between the oil and water phases (see the video of Fig. S10 in the ESI†). It was also noticed

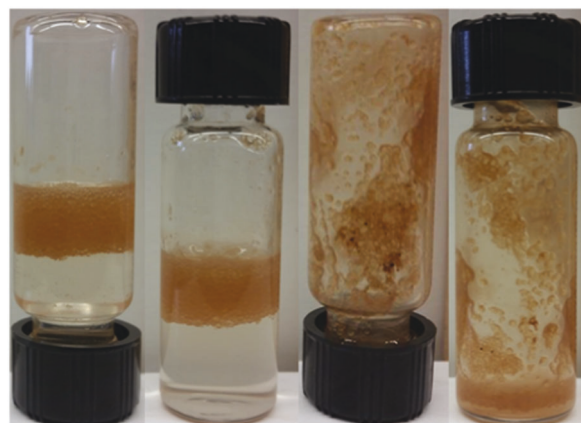


Fig. 9 Pictographic representation of a toluene–water emulsion before (left) and after (right) separation of the emulsion fraction *via* magnetic action.

that upon removal of the applied magnetic field, the droplets returned to their original state, without disrupting the stability of the emulsion. Moreover, we have exploited this characteristic of the emulsions to separate the emulsified oil phase from the water phase *via* magnetic action (Fig. 9). The toluene droplets were manipulated with a magnet while the water phase present in the sample was decanted, allowing the toluene droplets to remain inside the vial, thus separating the two phases. We have identified that the magnetic responsivity of these emulsions could be further exploited in applications related to the process of extraction of hydrocarbons, and the consequential water purification activities that are routinely performed in the oil and gas field.

Conclusions

We have explored the use of intricate, inorganic/organic composite networks, known as MHNs, as particle stabilizers for oil–water emulsions. Although the stabilization of Pickering emulsions has been traditionally achieved by the utilization of dispersed particles of different shapes and compositions, the use of network-like structures to stabilize emulsions has not been fully explored in the literature. The MHNs, which are composed of multiple polymeric nanoparticles bound to each other and to iron oxide nanoparticles, have displayed the ability to stabilize toluene–water and dodecane–water emulsions for at least 2 months. The emulsions stabilized can be homogenized by mechanical stimuli, such as vortexing or probe sonication; and in all cases oil droplets were stabilized in a continuous aqueous phase, yielding o/w emulsions.

To further understand the role of MHNs as particle stabilizers, the effects of the W:O ratio and MHN concentration on the droplet size distribution were analyzed. Although the emulsions displayed a high dispersity in the size of the droplets stabilized, the data showed that a W:O = 3 : 1 yielded the smallest droplets with the least dispersion observed, regardless of the type of oil and method of homogenization utilized. Moreover, the MHNs showed the remarkable ability to stabilize emulsions at extremely low concentrations. It was found that the emulsions homogenized *via* vortex at an MHN concentration of 1 mg mL^{−1} yielded the smallest droplets. These same results were observed for emulsions homogenized *via* probe sonication at a slightly higher concentration of 1.5 mg mL^{−1}.

Additionally, the magnetic character incorporated into the MHNs by the amine-IONS present within the network structure, led to the formation of magnetically-active emulsion droplets which were easily manipulated by an external magnetic field, providing a facile method of separation for the emulsified oil phase and the aqueous phase. This particular characteristic of the emulsions stabilized by such intricate network structures provides a pathway for their application not only towards the extraction of hydrocarbons *via* enhanced oil recovery, or after the implementation of the steam-assisted gravity drainage technology in oil sands, but also towards the remediation of the produced water that results from the constant efforts to provide clean and affordable energy to the growing global

population. Each of these systems has the possibility for broad application in fields where emulsions are commonly employed, such as the beauty industry.

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