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Preparation of Double Emulsions using Hybrid Polymer/Silica Particles: New Pickering Emulsifiers with Adjustable Surface Wettability

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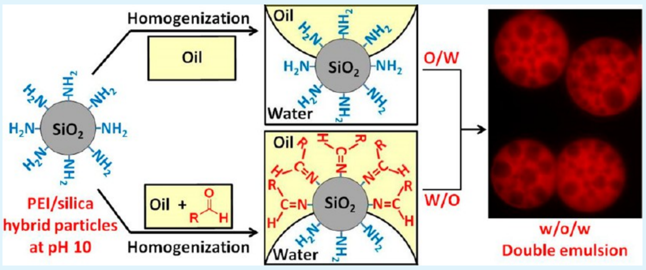
Supporting Information



ABSTRACT: A facile route for the preparation of water-in-oil-in-water (w/o/w) double emulsions is described for three model oils, namely, *n*-dodecane, isopropyl myristate, and isononyl isononanoate, using fumed silica particles coated with poly(ethylene imine) (PEI). The surface wettability of such hybrid PEI/silica particles can be systematically adjusted by (i) increasing the adsorbed amount of PEI and (ii) addition of 1-undecanal to the oil phase prior to homogenization. In the absence of this long-chain aldehyde, PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) produce o/w Pickering emulsions in all cases. In the presence of 1-undecanal, this reagent reacts with the primary and secondary amine groups on the PEI chains via Schiff base chemistry, which can render the PEI/silica hybrid particles sufficiently hydrophobic to stabilize w/o Pickering emulsions at 20 °C. Gas chromatography, ^1H NMR and X-ray photoelectron spectroscopy provide compelling experimental evidence for this in situ surface reaction, while a significant increase in the water contact angle indicates markedly greater hydrophobic character for the PEI/silica hybrid particles. However, when PEI/silica hybrid particles are prepared using a relatively low adsorbed amount of PEI (PEI/silica mass ratio = 0.075) only o/w Pickering emulsions are obtained, since the extent of surface modification achieved using this Schiff base chemistry is insufficient. Fluorescence microscopy and laser diffraction studies confirm that highly stable w/o/w double emulsions can be achieved for all three model oils. This is achieved by first homogenizing the relatively *hydrophobic* PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) with an oil containing 3% 1-undecanal to form an initial w/o emulsion, followed by further homogenization using an aqueous dispersion of relatively *hydrophilic* PEI/silica particles (PEI/silica mass ratio = 0.075). Dye release from the internal aqueous cores into the aqueous continuous phase was monitored by visible absorption spectroscopy. These studies indicate immediate loss of 12−18% dye during the high speed homogenization that is required for double emulsion formation, but no further dye release is observed at 20 °C for at least 15 days thereafter.

KEYWORDS: *Pickering emulsion, double emulsion, phase inversion, silica, poly(ethylene imine), Schiff base chemistry*

■ INTRODUCTION

Pickering emulsions are stabilized by solid particles and have been known for over a century.[1,2] A wide range of particles, such as polystyrene latexes,[3−5] clay nanoparticles,[6−8] and inorganic sols[9,10] have been reported to be effective Pickering emulsifiers. A particularly important class of Pickering emulsifiers is silica nanoparticles,[11] which have been used to form pH-responsive[12] and thermo-responsive[13,14] Pickering emulsions, as well as microcapsules known as colloidosomes.[15−17] It is well-known that the particle contact angle determines the Pickering emulsion type.[18] Thus, hydrophilic particles adsorbed at the oil/water interface are mainly located within the aqueous phase, giving a contact angle, θ, below 90° and hence an oil-in-water (o/w) emulsion. On the other hand, hydrophobic particles adsorbed at the oil/water interface reside mainly in the oil phase: in this case θ exceeds 90° so a water-in-oil (w/o) emulsion is invariably formed.[19] Various techniques have been utilized to adjust the particle contact angle (θ) so as to prepare Pickering emulsions. For example, hydrophilic silica nanoparticles can be derivatized with various commercially available alkylsilanes to tune their wettability.[20] However, physical adsorption can also be used for surface modification: for example, small molecule aromatic acids[21] or surfactants[22−26] may be adsorbed onto silica nanoparticles. Phase inversion of Pickering emulsions prepared using silica nanoparticles has also been investigated. For example, Binks and Lumsdon achieved catastrophic phase inversion of a w/o emulsion stabilized by hydrophobic silica particles by increasing the water volume

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fraction. Complementary phase inversion was also reported using a hydrophilic silica sol.[27] Binks and co-workers also found that phase inversion occurred when increasing the silica particle concentration at a fixed water volume fraction.[28] Similarly, phase inversion from an o/w emulsion to a w/o emulsion was observed on reducing the hydrophilic character of the silica particles.[20] The same team has also demonstrated that these approaches can be utilized to achieve phase inversion of o/w emulsions in which the droplets comprise a hydrophobic fragrance.[29] Such phase inversion of Pickering emulsions has been exploited to prepare so-called double emulsions.[30,31] For example, emulsification of a w/o emulsion with an aqueous solution containing cellulose under low shear can produce a w/o/w double emulsion.[32] Similarly, o/w/o double emulsions can be formed by making an o/w pre-emulsion, followed by emulsification with additional oil (plus organophilic montmorillonite).[33] Using particles rather than surfactants to stabilize double emulsions generally minimizes droplet coalescence, which is the main mechanism by which a single emulsion is generated on standing over long time scales.[19] One route for preparing double emulsions is to use two different types of Pickering emulsifier: hydrophilic particles to reinforce the o/w interface and hydrophobic particles to stabilize the w/o interface.[34] Using this approach, Binks and co-workers prepared double emulsions using two batches of silica particles with differing wettabilities.[35] In principle, double emulsions may allow controlled release of a component from the inner to the outer phase, which suggests a number of potential applications in the fields of medicine,[36] pharmacy,[37] separation processes,[38] and the food industry.[36,39] With the recent discovery that solid particles (i.e., Pickering emulsifiers) can be used to produce double emulsions with superior droplet stability, there is clearly considerable scope for their use in microencapsulation. In 2004, Arditty et al. prepared w/o/w double emulsions using *n*-octyltriethoxysilane-modified silica nanoparticles at each interface.[40] Copper sulfate was used as a colorimetric tracer to assess the ability of these double emulsions to retain encapsulated species inside the internal water droplets. After it was aged for one year, the external water phase remained uncoloured, while the internal droplets stayed blue.[40] One technique commonly used to produce microcapsules is evaporation of a volatile oil phase within a Pickering-stabilized w/o/w double emulsion to yield hollow microspheres.[41,42] For example, Lee et al. have shown that evaporation of the volatile toluene phase from w/o/w double emulsions stabilized by silica nanoparticles results in the formation of near-monodisperse 100 μm microcapsules within a microfluidic device.[43] Controlling the flow rates of the aqueous and oil phases allowed the oil volume fraction (and therefore the shell thickness) to be tuned following solvent evaporation, enabling selective microcapsule permeability.[44] Such microcapsules may serve as potential drug delivery vehicles.[45] Polymerization of the oil phase to encapsulate the internal water droplets has also been investigated.[46,47] This approach has led to novel microcapsules comprising internal aqueous droplets loaded with stimulus-responsive nanoparticles.[48,49] Recently, we have reported that a highly cationic water-soluble polyelectrolyte, poly(ethylene imine) (PEI), can be physically adsorbed onto Laponite to produce a hybrid PEI/Laponite Pickering emulsifier that is effective for a wide range of oils.[7] In all cases, o/w emulsions are obtained, since these PEI-modified synthetic clay particles are not sufficiently hydrophobic to stabilize w/o emulsions. In a subsequent study, we have shown that PEI can also be physically adsorbed onto commercial fumed silica particles to produce a versatile Pickering emulsifier for a proprietary hydrophobic aldehyde-rich fragrance.[49] Depending on the extent of PEI adsorption, either o/w or w/o Pickering emulsions can be stabilized in this latter case. Moreover, w/o/w double emulsions can be prepared using the same fumed silica particles coated using differing adsorbed amounts of PEI to tune the particle wettability.[50] It is well-known that amines react readily with aldehydes via Schiff base chemistry to form either imines or aminals.[51] This has been exploited for the modification of poly(vinyl amine) for the synthesis of primary amine-functionalized sterically stabilized polypyrrole particles[52] and also for enhanced antibody binding in polymer-based microfluidic devices.[53] Herein, we demonstrate that this facile chemistry can be exploited to tune the surface wettability of the hybrid PEI/silica emulsifier particles over a wide range, as judged by contact angle gonimetry. This is readily achieved by simply adding a model hydrophobic aldehyde (1-undecanal) to the oil phase, which leads to an in situ surface reaction with the amine groups on the PEI chains adsorbed at the silica surface. This enables the formation of either o/w or w/o Pickering emulsions depending on the initial mass of PEI adsorbed onto the fumed silica particles prior to homogenization (see Figure 1). Moreover, we show that this versatile approach allows the facile preparation of w/o/w double emulsions using a range of model oils, provided that there is sufficient 1-undecanal present in the oil phase.

■ RESULTS AND DISCUSSION

We have recently reported how varying the extent of PEI adsorption onto fumed silica affects the surface properties of the resulting hybrid particles.[50] The fumed silica particles used in both this earlier study and the current work have a characteristic fractal morphology and are weakly flocculated in aqueous solution. The PEI content of a 1.0% w/w aqueous silica dispersion was varied from 0% up to 1.0% w/w, with the latter value corresponding to a PEI/silica mass ratio of unity, see Figure 2. The *actual* adsorbed amount of PEI on the silica particles is readily determined by thermogravimetry; these data suggest Langmuir-type adsorption and mirror the electrophoretic behavior obtained for the hybrid particles. Figure 2 also shows how the contact angle varies with PEI/silica mass ratio for these PEI/silica hybrid particles. It is worth emphasizing that such contact angles are determined for 10 μL deionized water droplets placed on silicon wafers coated with PEI/silica hybrid particles. Thus, such *water* contact angles should not be confused with the *particle* contact angle described by Binks that dictates Pickering emulsifier performance.[19] A contact angle of 60° was determined for a wafer coated with PEI alone. Initially, the water contact angle increased from 17° for bare fumed silica particles up to 40° for a PEI/silica mass ratio of 0.20. This change in contact angle correlates with a concomitant reduction in zeta potential as the cationic PEI adsorbs onto the anionic particles and the hybrid particles become increasingly flocculated. At a PEI/silica mass ratio of 0.15, the hybrid particles are close to their isoelectric point, become highly flocculated and exhibit a maximum contact angle of 40°. Further addition of PEI results in particle redispersion and a reduction in contact angle to 18° as charge reversal leads to cationic particles. This dispersion-flocculation-redispersion process can be conveniently monitored by dynamic light scattering (see Supporting Information Figure S2) and transmission electron microscopy (TEM; see Supporting

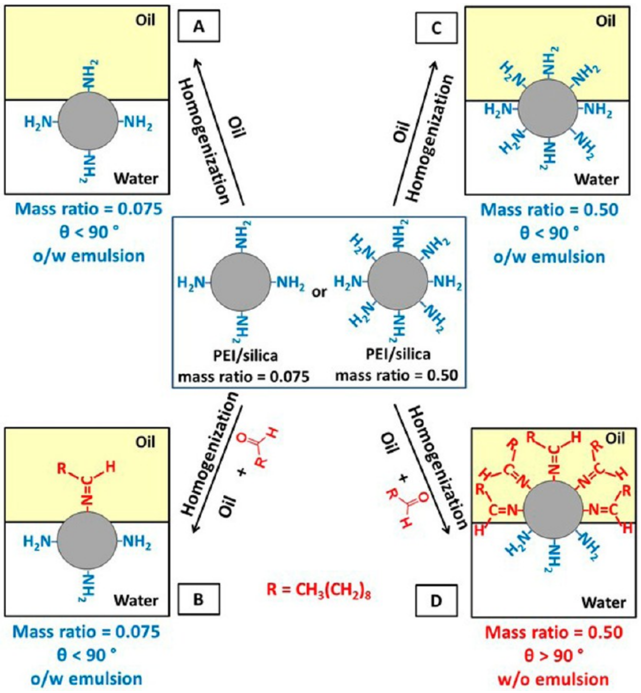


Figure 1. Schematic representation for the formation of PEI/silica stabilized Pickering emulsions. (A) PEI/silica (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075, pH 10) homogenized with pure oil resulting in an o/w Pickering emulsion; (B) PEI/silica (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075, pH 10) homogenized with oil + 1-undecanal resulting in an o/w Pickering emulsion; (C) PEI/silica (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50, pH 10) homogenized with pure oil resulting in an o/w Pickering emulsion; (D) PEI/silica (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50, pH 10) homogenized with oil + 1-undecanal resulting in a w/o Pickering emulsion. In all cases homogenization was achieved at 12 000 rpm for 2 min. N.B. For clarity, the fumed silica particles are simply shown as spheres in the above cartoon, whereas in reality they possess a more complex fractal morphology (see Figure S1 in the Supporting Information).

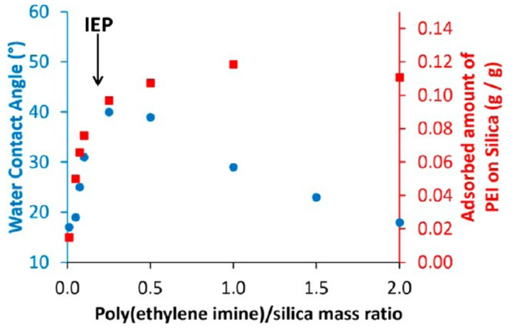
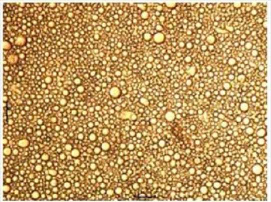
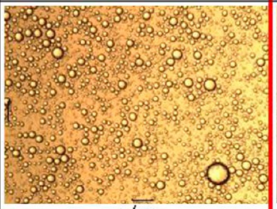
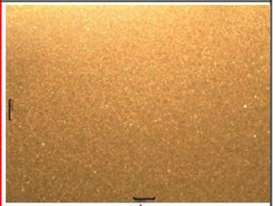
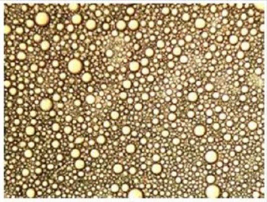
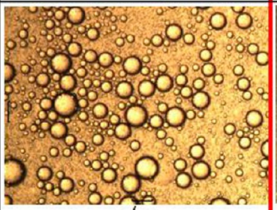
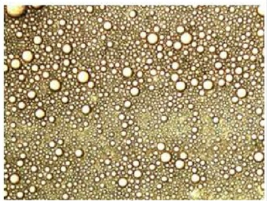
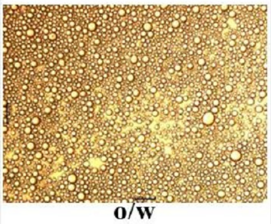
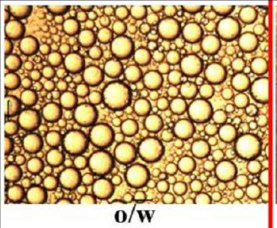


Figure 2. Water contact angle data (●) and adsorbed mass of poly(ethylene imine) per unit mass of fumed silica (■) vs target poly(ethylene imine)/silica mass ratio. Water contact angles were obtained for a 10 μL water droplet placed on the surface of silicon wafers coated with poly(ethylene imine)/silica hybrid particles prepared at various poly(ethylene imine)/silica mass ratios. The adsorbed mass of poly(ethylene imine) per unit mass of fumed silica was determined by TGA. The arrow indicates the PEI/silica mass ratio at which the isoelectric point is reached, as judged by aqueous electrophoresis. The fumed silica concentration was fixed at 1.0% w/w in each case.

Information Figure S3). Furthermore, TEM confirms that the morphology of the flocculated particles following adsorption at the oil/water interface is comparable to that of the particles prior to emulsification (see Supporting Information Figure S3).

We recently reported that phase inversion from an o/w to a w/o Pickering emulsion occurs at high PEI/silica mass ratios when using an aldehyde-rich multicomponent fragrance as an oil.[50] To examine whether this was simply due to the greater hydrophobic character of the hybrid particles displayed in Figure 2, PEI/silica particles that gave either o/w emulsions (i.e., 1.0% w/w fumed silica, PEI/silica mass ratio = 0.075, pH 10) or w/o emulsions (i.e., 1.0% w/w fumed silica, PEI/silica mass ratio = 0.50, pH 10) were homogenized in turn with a series of three model oils. However, homogenization of these two types of particles with *n*-dodecane, isopropyl myristate, and isononyl isononanoate resulted in only o/w Pickering emulsions being formed, see Table 1. It is evident that the o/w Pickering emulsions formed using the PEI/silica hybrid particles prepared at a mass ratio of 0.50 are rather larger (and less stable) than those prepared using PEI/silica hybrid particles at a mass ratio = 0.075. This is presumably because the latter PEI/silica particles are flocculated, and hence more effective Pickering emulsifiers than the former relatively well-dispersed PEI/silica particles (see TEM images in Supporting Information Figure S3). It has been previously reported that such a dispersion-flocculation-redispersion transition, which is readily achieved via adsorption of double-tailed surfactants onto particles, results in a o/w—w/o—o/w double inversion.[25] However, this is not observed for these PEI/silica hybrid particles, which suggests that some additional factor is responsible for the phase inversion that is observed when emulsifying these hybrid particles with an aldehyde-rich oil.[50] The effect of adding increasing amounts of a model hydrophobic aldehyde, 1-undecanal, to the same three oils prior to homogenization is also shown in Table 1. The 1-undecanal was selected to mimic the chemical composition of the aldehyde-rich fragrance oil used in our earlier study.[50] Addition of 3.0% v/v 1-undecanal produces a phase inversion from o/w to much finer w/o Pickering emulsion droplets of around 10 μm diameter, as measured by laser diffraction, when employing PEI/silica hybrid particles containing a relatively high PEI content (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50). However, it is emphasized that emulsions prepared using the PEI/silica particles containing a relatively low PEI content (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075) do not exhibit any phase inversion. Thus, the presence of 1-undecanal in the oil phase is a necessary but not sufficient condition for the formation of w/o emulsions. It is well-known that amines react readily with aldehydes to form imines or aminals.[51] Model reactions were carried out to determine whether 1-undecanal reacts with PEI in a similar manner. ^{1}H NMR studies of the model reaction between PEI and 1-undecanal conducted in d_5-methanol indicate a characteristic shift of the aldehyde proton signal assigned to 1-undecanal from 9.7 ppm to approximately 8.5 ppm, which is consistent with the formation of an imine bond (see Figure S4 in the Supporting Information). Table 2 shows the C/N surface atomic ratios observed for the pristine PEI and PEI/silica hybrid particles (prepared at a PEI/silica mass ratio of 0.50) deposited in turn onto planar silicon wafers and exposed to 1-undecanal/*n*-heptane solutions of varying concentration at 20 °C, as measured by X-ray photoelectron spectroscopy.[55] This surface analytical technique has a typical sampling depth of 2—

Table 1. Influence of the PEI/Silica Mass Ratio and 1-Undecanal Concentration (Present in the Oil Phase) on the Pickering Emulsion Type Produced after Homogenization of Equal Volumes of 1.0% w/w Aqueous Dispersion of PEI-Coated Fumed Silica Particles and Oil[a]

200 μm	PEI/silica mass ratio = 0.075		PEI/silica mass ratio = 0.50	
	0 % 1-undecanal	3 % 1-undecanal	0 % 1-undecanal	3 % 1-undecanal
n-dodecane	 o/w 36 ± 16 μm	 o/w 41 ± 21 μm	 o/w 57 ± 36 μm	 w/o 6 ± 3 μm
isopropyl myristate	 o/w 36 ± 33 μm	 o/w 40 ± 30 μm	 o/w 108 ± 85 μm	 w/o 5 ± 2 μm
isononyl isononanoate	 o/w 30 ± 15 μm	 o/w 36 ± 19 μm	 o/w 205 ± 136 μm	 w/o 6 ± 3 μm

[a] The three oils investigated were *n*-dodecane, isopropyl myristate, and isononyl isononanoate and the emulsification conditions were 12 000 rpm for two minutes at 20°C.

Table 2. Carbon/Nitrogen Atomic Ratios Determined by XPS for Both PEI Alone and PEI/Silica Hybrid Particles (Prepared at a PEI/Silica Mass Ratio of 0.50) as a Function of 1-Undecanal Concentration for Schiff Base Reactions Performed in *n*-Heptane at 20°C

	C/N atomic ratio[a]	
1-undecanal (%)	PEI	PEI/silica
0.0	3.8	5.4
1.0	4.6	6.2
2.0	5.1	6.9
3.0	5.9	7.1

[a] As measured by X-ray photoelectron spectroscopy.

10 nm, which makes it sensitive to the Schiff base reaction between the 1-undecanal and the PEI. XPS survey spectra for both PEI alone and the PEI/silica hybrid particles are shown in Figure S5 in the Supporting Information. Inspecting Table 2, it is clear that the proprietary fumed silica particles actually contain some surface carbon atoms, since its C/N atomic ratio of 5.4 is higher than that of PEI (3.8).[56] XPS studies of the fumed silica alone confirmed this to be the case: the surface carbon content of these particles was found to be approximately 6 atom %. Nevertheless, using higher concentrations of 1-undecanal clearly results in higher C/N atomic ratios for both the PEI alone and the PEI/silica hybrid particles. This is because of the addition of the long-chain alkyl group of the 1-undecanal to the PEI chains as a result of imine/aminal formation. On the basis of the above XPS data, for PEI/silica hybrid particles comprising a sufficiently high PEI content (PEI/silica mass ratio = 0.50), the in situ reaction of the primary/secondary amine groups on the PEI chains with 1-undecanal during homogenization at 20 °C should produce a relatively hydrophobic patch on the fumed silica particles adsorbed at the oil/water interface (see Figure 1). To examine this hypothesis, water contact angle goniometry was used to characterize PEI/silica hybrid particles after being briefly exposed to up to 3.0% 1-undecanal dissolved in *n*-heptane, see Figure 3. Representative SEM images of the PEI/silica hybrid particles deposited onto silicon wafers prior to contact angle measurements are shown in Supporting Information Figure S6. The red data set corresponding to PEI/silica hybrid particles prepared with a relatively high PEI content (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50) shows an increase in water contact angle from 40° up to 114°, which indicates a transition from relatively hydrophilic to relatively hydrophobic surface character (see also the corresponding digital images recorded for 10 μL water droplets in Figure 3). In contrast, the

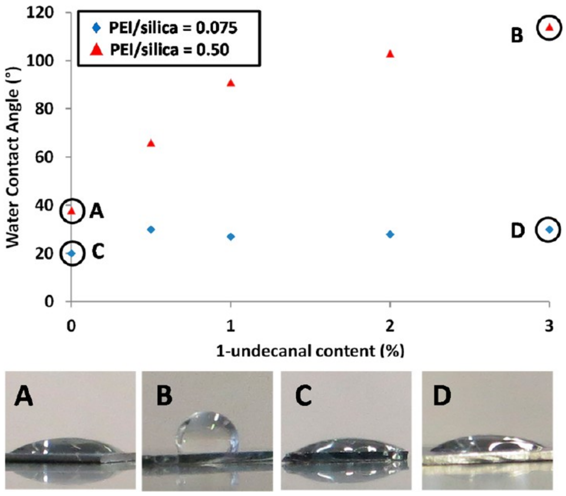
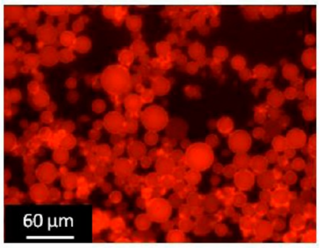
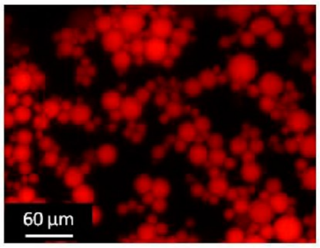
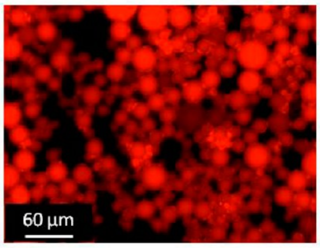
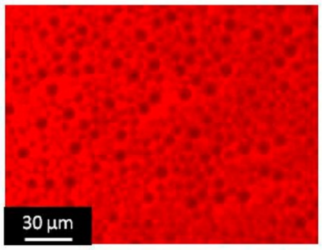
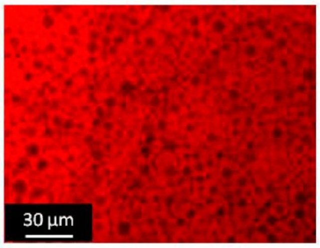
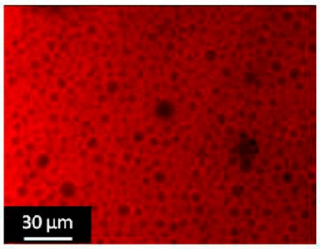
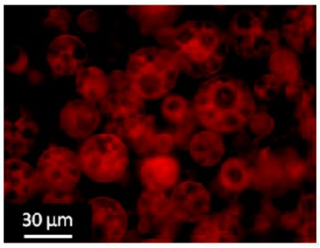
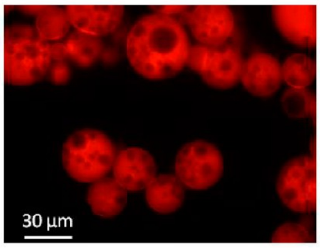
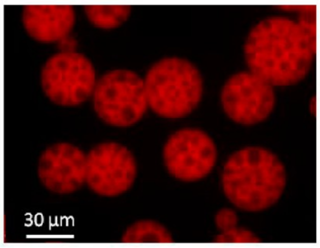


Figure 3. Contact angle of a 10 μL water droplet on (▲) poly(ethylene imine)/silica hybrid particles (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50, pH 10) and (◆) poly(ethylene imine)/silica hybrid particles (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075, pH 10) following exposure to *n*-heptane solutions containing different amounts of 1-undecanal (0–3% v/v). **A-D** show digital images of the water droplet contact angles highlighted by the labels.

blue data set shown in Figure 3 confirms that there is little or no change in water contact angle when using PEI/silica particles comprising a relatively low PEI content (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075) in the presence of 1-undecanal. Thus, these water contact angle results are fully consistent with the data presented in Table 1, which indicate that the phase inversion from an o/w to a w/o Pickering emulsion that occurs during homogenization of all three model oils is only observed in the presence of 1-undecanal when using PEI/silica hybrid particles with a relatively high PEI content. Hence variation of the adsorbed amount of PEI on the fumed silica particles enables their surface wettability to be readily controlled in the presence of 1-undecanal, which in turn dictates whether such hybrid particles can stabilize an o/w or a w/o emulsion. To further confirm this imine surface reaction, gas chromatography (GC) was used to monitor the concentration of 1-undecanal present in the oil before and after homogenization. In principle, any in situ reaction between the 1-undecanal and PEI chains (e.g., imine or aminol bond formation) that occurs during homogenization should lower the concentration of 1-undecanal remaining in the oil phase. Initially, *n*-dodecane containing 3.0% v/v 1-undecanal was dissolved in a known concentration of ethanol and analyzed by gas chromatography. Well-resolved peaks corresponding to *n*-dodecane and 1-undecanal can be observed for an optimized GC protocol (see Supporting Information Figure S7A). A linear calibration curve was constructed using a series of *n*-dodecane samples containing known concentrations of 1-undecanal and diluted with a fixed volume of ethanol (see Supporting Information Figure S7B). To examine the 1-

Table 3. Fluorescence Microscopy Studies of o/w Pickering Emulsions (50% Oil Volume Fraction), w/o Pickering Emulsions (50% Oil Volume Fraction) and w/o/w Double Emulsions (Prepared Using 25% Oil Volume Fraction)[a]

	Dodecane	Isopropyl Myristate	Isononyl Isononanoate
O / W			
W / O			
W/O/W			

[a] The three oils investigated were *n*-dodecane, isopropyl myristate and isononyl isononanoate, with Nile Red dye being dissolved at a concentration of 0.010 g dm^{-3} in each oil prior to its homogenization.

undecanal concentration remaining in solution after homogenization, both the Pickering (o/w and w/o) and w/o/w double emulsions were diluted using the same concentration of ethanol and then centrifuged to remove the PEI/silica hybrid particles, thus allowing the supernatant to be analyzed by GC. The concentration of 1-undecanal remaining in an o/w Pickering emulsion prepared with PEI/silica hybrid particles comprising a relatively low PEI content (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075) was only reduced by 25%. However, analysis of the w/o Pickering emulsion prepared using PEI/silica hybrid particles with a relatively high PEI content (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50) indicated an approximate 49% reduction in the 1-undecanal concentration. This indicates that a higher degree of surface modification had been achieved, which accounts for the o/w to w/o Pickering emulsion phase inversion that is observed when a relatively high PEI/silica mass ratio is utilized. In both instances, the number of moles of reacted 1-undecanal is approximately equivalent to the total number of moles of primary and secondary amines on the PEI chains adsorbed at the silica surface (see Figure 2). Finally, a similarly large reduction (54%) in the original 1-undecanal concentration was observed when analyzing the w/o/w double emulsion by GC using the same protocol. We previously reported the formation of w/o/w double emulsions using an aldehyde-rich multicomponent hydrophobic fragrance as the oil phase.[50] However, this formulation was not properly understood at the time. With the benefit of hindsight, it seems highly likely that one or more components of the aldehyde-rich fragrance actually react in situ with the PEI chains via the same Schiff base chemistry observed for the 1-undecanal additive in the present study. To test this hypothesis, the protocol previously utilized to prepare w/o/w double emulsions with the aldehyde-rich fragrance was applied to each of the three model oils employed herein. Thus, an aqueous dispersion of PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) was homogenized with an equal volume of either *n*-dodecane, isopropyl myristate, or isononyl isononanoate containing 3.0% 1-undecanal to produce a stable w/o emulsion. It is perhaps noteworthy that, because this PEI/silica mass ratio is *above* the knee of the adsorption isotherm (see Figure 2) there is necessarily a significant excess of non-adsorbed PEI remaining within the encapsulated aqueous droplets. This w/o emulsion was then further homogenized with an equal volume of an aqueous dispersion containing PEI/silica hybrid particles (PEI/silica mass ratio = 0.075) to produce the final w/o/w emulsion. Since the adsorbed amount of PEI on these hydrophilic hybrid particles is *below* the knee of the adsorption isotherm (see Figure 2), all of the PEI chains are adsorbed onto the fumed silica particles at submonolayer coverage. Thus, there is essentially no excess PEI present in the aqueous continuous phase after formation of the double emulsion. In order to visualize the double emulsion droplets, an oil-soluble Nile Red dye was dissolved in each oil prior to homogenization to facilitate fluorescence microscopy studies. Table 3 shows digital images obtained for the o/w and w/o Pickering emulsions prepared using PEI/silica hybrid particles, as well as w/o/w double emulsions obtained for each oil. The o/w Pickering emulsions prepared at an oil volume fraction of 50% using PEI/silica hybrid particles (1.0% w/w silica, PEI/silica mass ratio = 0.075, pH 10) have a mean droplet diameter of around 60 ± 30 μm, as confirmed by laser diffraction, and the hydrophobic Nile Red dye is confined entirely within the oil droplets, as expected. Much finer w/o Pickering emulsion droplets of around 5 ± 3 μm diameter (as judged by laser diffraction) are produced under otherwise identical conditions using PEI/silica hybrid particles containing a higher PEI content (PEI/silica mass ratio = 0.50) in the presence of 3.0% 1-undecanal. In this case, the Nile Red is located exclusively within the continuous phase, as expected. Each w/o/w double emulsion was prepared using the corresponding w/o emulsion precursor shown in Table 3. In all cases, multiple aqueous droplets are observed within the larger oil droplets. Laser diffraction studies confirm that each of these w/o/w double emulsions is stable on standing for at least 5 months at 20 °C (Figure 4). Mastersizer droplet size distributions for the o/w and w/o single emulsions are shown in the Supporting Information, see Figure S8.

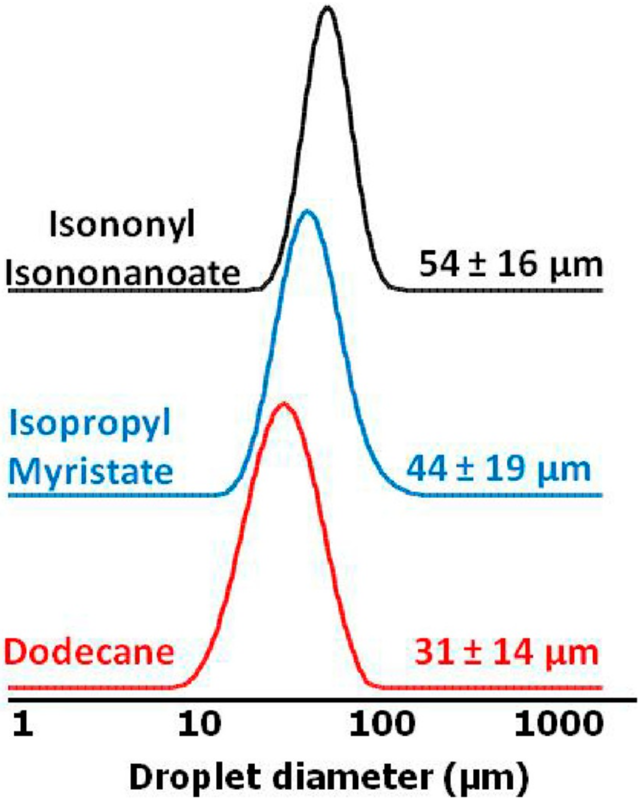


Figure 4. Mastersizer droplet size distributions obtained for w/o/w double emulsions made with *n*-dodecane, isopropyl myristate, and isononyl isononanoate. Total oil volume fraction used for double emulsion preparation = 25%.

Previously, we found that w/o/w double emulsions prepared with the aldehyde-rich multicomponent fragrance could withstand an alcohol challenge, whereby addition of excess ethanol simultaneously removes both the oil and aqueous phases.[50] In contrast, a conventional o/w Pickering emulsion is invariably destroyed under such conditions.[4,5,7] Figures 5a and 5b show optical images obtained for w/o/w double emulsions following an alcohol challenge, with many intact spherical microcapsule-like structures being readily identified. The corresponding scanning electron microscopy images are shown in Figure 5c and 5d. Here the microcapsule-like structures have partially collapsed under the ultrahigh vacuum conditions required for SEM studies. Close inspection of Figure 5d provides some evidence for the original double emulsion, since this ca. 50 μm diameter microcapsule contains multiple approximately spherical domains within its interior. Moreover,

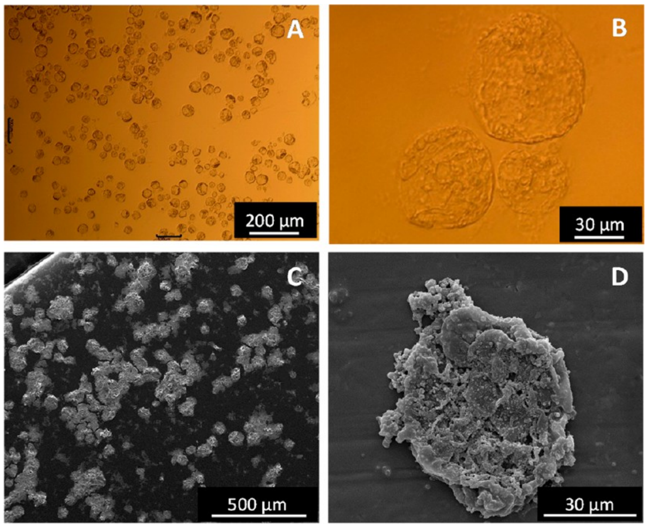


Figure 5. (A, B) Optical microscopy images obtained following the addition of excess ethanol to a w/o/w double emulsion prepared with *n*-dodecane. (C, D) Scanning electron microscopy images obtained following the same alcohol challenge followed by drying at 20 °C of w/o/w double emulsions made with *n*-dodecane. In each case the oil volume fraction was 25%.

such microcapsules appear to be somewhat more robust under ultrahigh vacuum conditions than the covalently cross-linked colloidosomes prepared from o/w emulsions, which tend to form flattened 2D "pancake" structures.[4,5] In a control experiment, an o/w Pickering emulsion prepared using an aqueous dispersion of PEI/silica hybrid particles (1.0% w/w silica, PEI/silica mass ratio = 0.075, pH 10) for the homogenization of *n*-dodecane did not survive an alcohol challenge (see SEM images shown in Supporting Information Figure S9). It is perhaps surprising that the original superstructure of the w/o/w emulsion droplets is preserved when subjected to excess ethanol to remove both the oil and aqueous phases. Further work is warranted to understand this observation. In principle, these w/o/w double emulsions can be used to encapsulate water-soluble actives, because the inner aqueous droplets are surrounded by a hydrophobic barrier of oil. However, the internal aqueous droplets are likely to sediment within the gradually creaming oil droplet phase owing to the difference in density between these two fluids. This could result in direct contact between the internal and external aqueous phase, thus providing a mechanism for premature release of the payload. To examine this possibility, a rhodamine-labeled water-soluble polymer, poly(2-(methacryloyloxy)ethyl phosphorylcholine)[54] (Rh-PMPC; mean DP = 100), was used as a model fluorescent dye. This highly hydrophilic polymer was selected because its zwitterionic character should minimize its interaction with the cationic PEI and anionic silica components of the hybrid Pickering emulsifier. The Rh-PMPC was dissolved in the aqueous dispersion of PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) prior to preparing the initial w/o Pickering emulsion using each of the three model oils in turn. After formation of the w/o/w double emulsion, the external aqueous phase was isolated following creaming and monitored by visible absorption spectroscopy. Using a linear calibration plot constructed for Rh-PMPC in water (see Supporting Information Figure S10), the absorbance (λ_{max} = 540 nm) of the external aqueous phase of the w/o/w emulsion can be converted into a Rh-PMPC concentration, and hence the extent of release of this water-soluble polymer can be monitored. Figure 6 shows that there is no *increase* in the release of Rh-PMPC for all three oils over a 15-day period. However, approximately 12–18% Rh-PMPC is released into the external aqueous phase immediately after w/o/w emulsion formation. Presumably, this is because some of the original w/o Pickering emulsion droplets break up during homogenization of the w/o/w double emulsion. Nevertheless, the majority (~80%) of the water-soluble pay-load is retained within the internal aqueous cores for at least 2 weeks at 20 °C.

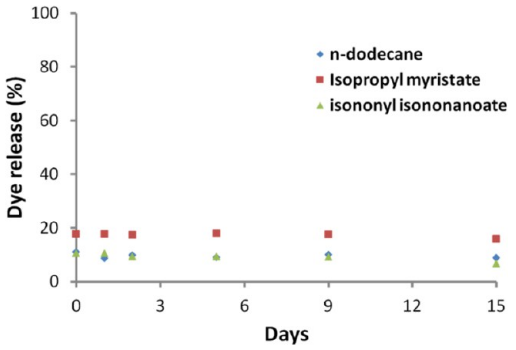


Figure 6. Dye release profiles obtained for a model polymeric dye, rhodamine-labeled poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC), from the internal aqueous phase to the aqueous continuous phase of the w/o/w double emulsions prepared using *n*-dodecane, isopropyl myristate or isononyl isononanoate.

Finally, it is noteworthy that the long-term stability of *surfactant-stabilized* double emulsions is typically rather poor, with gradual phase separation to produce a single emulsion normally being observed.[19,57] The Pickering double emulsions described herein are expected to exhibit superior long-term stability, not least because the hybrid emulsifier particles are much more strongly adsorbed at the oil/water interface.

CONCLUSIONS

A versatile route to w/o/w double emulsions prepared using Pickering emulsifiers is described for three model oils (*n*-dodecane, isopropyl myristate, and isononyl isononanoate) using fumed silica particles coated with poly(ethylene imine) (PEI). Such PEI/silica hybrid particles are normally relatively hydrophilic and only stabilize o/w emulsions, regardless of the adsorbed amount of PEI. However, if a hydrophobic aldehyde, 1-undecanal, is added to the oil phase prior to emulsification then, provided that the adsorbed amount of PEI is sufficiently high, then w/o emulsions can be obtained provided that the adsorbed amount of PEI is sufficiently high. This is because the 1-undecanal reacts with the primary and secondary amine groups on the PEI chains at the surface of the silica particles via Schiff base chemistry. Evidence for such an *in situ* surface reaction was obtained from ^{1}H NMR, XPS and gas chromatography studies, which reveal imine bond formation for model reactions conducted on PEI and 1-undecanal in both the presence and absence of silica. This interfacial reaction significantly increases the hydrophobicity of PEI/silica particles, as judged by contact angle goniometry measurements. For example, the water contact angle of the PEI/silica particles increases from 40° to 114° after exposure to 3% 1-undecanal. This *in situ* Schiff base chemistry was exploited to produce stable w/o/w double emulsions for each of the three oils. Such double emulsions were produced by first using relatively hydrophobic PEI/silica hybrid particles (1.0% w/w fumed silica, PEI/silica mass ratio = 0.50; 3.0% 1-undecanal dissolved in the oil phase) to prepare w/o emulsions, followed by further homogenization with an aqueous dispersion of relatively hydrophilic PEI/silica particles (1.0% w/w fumed silica, PEI/silica mass ratio = 0.075). Fluorescence microscopy studies confirmed the formation of w/o/w double emulsions, which were sized by laser diffraction. Following an alcohol challenge, scanning electron microscopy studies of the dried PEI/silica residues indicate the presence of smaller PEI/silica shells within the ~50 μm microcapsule walls. Finally, aqueous dye release studies from the internal aqueous cores into the aqueous continuous phase indicate some immediate loss during double emulsion formation, but no further release at 20 °C was observed thereafter for 15 days.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental section, transmission electron images of the fumed silica, further DLS data and transmission electron microscopy images for the PEI/silica hybrid particles, ^{1}H NMR spectra obtained before and after the Schiff base model reaction between PEI and 1-undecanal, XPS survey spectra of pristine PEI and PEI/silica hybrid particles, scanning electron microscopy images of particles adsorbed on silicon wafers, gas chromatography traces, Mastersizer droplet size distributions for o/w and w/o Pickering emulsions, scanning electron microscopy images of Pickering emulsions after an alcohol challenge and a linear Beer–Lambert calibration plot for rhodamine-labeled PMPC in water. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Pickering, S. U. Emulsions. *J. Chem. Soc.* **1907**, *91*, 2001–2021.

(2) Ramsden, W. Separation of Solids in the Surface-Layers of Solutions and "Suspensions" (Observations on Surface-Membranes, Bubbles, Emulsions, and Mechanical Coagulation). Preliminary Account. *Proc. R. Soc. London.* **1903**, *72*, 156–164.

(3) Binks, B. P.; Lumsdon, S. O. Pickering Emulsions Stabilized by Monodisperse Latex Particles: Effects of Particle Size. *Langmuir* **2001**, *17*, 4540–4547.

(4) Thompson, K. L.; Armes, S. P.; Howse, J. R.; Ebbens, S.; Ahmad, I.; Zaidi, J. H.; York, D. W.; Burdis, J. A. Covalently Cross-Linked Colloidosomes. *Macromolecules* **2010**, *43*, 10466–10474.

(5) Walsh, A.; Thompson, K. L.; Armes, S. P.; York, D. W. Polyamine-Functional Sterically Stabilized Latexes for Covalently Cross-Linkable Colloidosomes. *Langmuir* **2010**, *26*, 18039–18048.

(6) Cauvin, S.; Colver, P. J.; Bon, S. A. F. Pickering Stabilized Miniemulsion Polymerization: Preparation of Clay Armored Latexes. *Macromolecules* **2005**, *38*, 7887–7889.

(7) Williams, M.; Armes, S. P.; York, D. W. Clay-Based Colloidosomes. *Langmuir* **2012**, *28*, 1142–1148.

(8) Cui, Y.; van Duijneveldt, J. S. Microcapsules Composed of Cross-Linked Organoclay. *Langmuir* **2012**, *28*, 1753–1757.

(9) Chen, T.; Colver, P. J.; Bon, S. A. F. Organic-Inorganic Hybrid Hollow Spheres Prepared from TiO_2-Stabilized Pickering Emulsion Polymerization. *Adv. Mater.* **2007**, *19*, 2286–2289.

(10) Chen, W.; Liu, X.; Liu, Y.; Kim, H.-I. Synthesis of Microcapsules with Polystyrene/ZnO Hybrid Shell by Pickering Emulsion Polymerization. *Colloid Poly. Sci.* **2010**, *288*, 1393–1399.

(11) Binks, B. P.; Lumsdon, S. O. Stability of Oil-In-Water Emulsions Stabilised by Silica Particles. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3007–3016.

(12) Fujii, S.; Armes, S. P.; Binks, B. P.; Murakami, R. Stimulus-Responsive Particulate Emulsifiers Based on Lightly Cross-Linked Poly(4-vinylpyridine)-Silica Nanocomposite Microgels. *Langmuir* **2006**, *22*, 6818–6825.

(13) Binks, B. P.; Murakami, R.; Armes, S. P.; Fujii, S. Temperature-Induced Inversion of Nanoparticle-Stabilized Emulsions. *Angew. Chem., Int. Ed.* **2005**, *44*, 4795–4798.

(14) Ngai, T.; Auweter, H.; Behrens, S. H. Environmental Responsiveness of Microgel Particles and Particle-Stabilized Emulsions. *Macromolecules* **2006**, *39*, 8171–8177.

(15) Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. Colloidosomes: Selectively Permeable Capsules Composed of Colloidal Particles. *Science* **2002**, *298*, 1006–1009.

(16) Fielding, L. A.; Armes, S. P. Preparation of Pickering Emulsions and Colloidosomes Using Either a Glycerol-Functionalised Silica Sol or Core-Shell Polymer/Silica Nanocomposite Particles. *J. Mater. Chem.* **2012**, *22*, 11235–11244.

(17) Bon, S. A. F.; Chen, T. Pickering Stabilization as a Tool in the Fabrication of Complex Nanopatterned Silica Microcapsules. *Langmuir* **2007**, *23*, 9527–9530.

(18) Finkle, P.; Draper, H. D.; Hildebrand, J. H. The Theory of Emulsification. *J. Am. Chem. Soc.* **1923**, *45*, 2780–2788.

(19) Binks, B. P. Particles as Surfactants—Similarities and Differences. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21–41.

(20) Binks, B. P.; Lumsdon, S. O. Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions. *Langmuir* **2000**, *16*, 8622–8631.

(21) Li, J.; Stoever, H. D. H. Doubly pH-Responsive Pickering Emulsions. *Langmuir* **2008**, *24*, 13237–13240.

(22) Midmore, B. R. Synergy Between Silica and Polyoxyethylene Surfactants in the Formation of O/W Emulsions. *Colloids Surf., A* **1998**, *145*, 133–143.

(23) Binks, B. P.; Rodrigues, J. A.; Frith, W. J. Synergistic Interaction in Emulsions Stabilized by a Mixture of Silica Nanoparticles and Cationic Surfactant. *Langmuir* **2007**, *23*, 3626–3636.

(24) Cui, Z. G.; Yang, L. L.; Cui, Y. Z.; Binks, B. P. Effects of Surfactant Structure on the Phase Inversion of Emulsions Stabilized by Mixtures of Silica Nanoparticles and Cationic Surfactant. *Langmuir* **2010**, *26*, 4717–4724.

(25) Binks, B. P.; Isa, L.; Tyowua, A. T. Direct Measurement of Contact Angles of Silica Particles in Relation to Double Inversion of Pickering Emulsions. *Langmuir* **2013**, *29*, 4923–4927.

(26) Jiang, J.; Zhu, Y.; Cui, Z.; Binks, B. P. Switchable Pickering Emulsions Stabilized by Silica Nanoparticles Hydrophobized In Situ with a Switchable Surfactant. *Angew. Chem., Int. Ed.* **2013**, *52*, 12373–12376.

(27) Binks, B. P.; Lumsdon, S. O. Catastrophic Phase Inversion of Water-In-Oil Emulsions Stabilized by Hydrophobic Silica. *Langmuir* **2000**, *16*, 2539–2547.

(28) Binks, B. P.; Philip, J.; Rodrigues, J. A. Inversion of Silica-Stabilized Emulsions Induced by Particle Concentration. *Langmuir* **2005**, *21*, 3296–3302.

(29) Binks, B. P.; Fletcher, P. D. I.; Holt, B. L.; Beaussoubre, P.; Wong, K. Phase Inversion of Particle-Stabilised Perfume Oil–Water

Emulsions: Experiment and Theory. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11954−11966.

(30) Garti, N. Double Emulsions—Scope, Limitations and New Achievements. *Colloids Surf., A* **1997**, *123*, 233−246.

(31) Binks, B. P.; Dyab, A. K. F.; Fletcher, P. D. I. Novel Emulsions of Ionic Liquids Stabilised Solely by Silica Nanoparticles. *Chem. Commun.*. **2003**, *20*, 2540−2541.

(32) Oza, K. P.; Frank, S. G. Multiple Emulsions Stabilized by Colloidal Microcrystalline Cellulose. *J. Dispersion Sci. Technol.* **1989**, *10*, 163−185.

(33) Sekine, T.; Yoshida, K.; Matsuzaki, F.; Yanaki, T.; Yamaguchi, M. A Novel Method for Preparing Oil-In-Water-In-Oil Type Multiple Emulsions using Organophilic Montmorillonite Clay Mineral. *J. Surfactants Deterg.* **1999**, *2*, 309−315.

(34) Zou, S.; Wang, C.; Gao, Q.; Tong, Z. Surfactant-Free Multiple Pickering Emulsions Stabilized by Combining Hydrophobic and Hydrophilic Nanoparticles. *J. Dispersion Sci. Technol.* **2013**, *34*, 173−181.

(35) Barthel, H.; Binks, B. P.; Dyab, A.; Fletcher, P. Multiple Emulsions. U.S. Patent US 07722891, May 25, 2010.

(36) Nakashima, T.; Shimizu, M.; Kukizaki, M. Particle Control of Emulsion by Membrane Emulsification and its Applications. *Adv. Drug Delivery Rev.* **2000**, *45*, 47−56.

(37) Florence, A. T.; Haq, M. E.; Johnson, J. R. Interfacial Properties of Polymethyl Alpha-Cyanoacrylate and Polybutyl Alpha-Cyanoacrylate. *J. Pharm. Pharmacol.* **1976**, *28*, 539−543.

(38) Stroeve, P.; Varanasi, P. P. Transport Processes in Liquid Membranes—Double Emulsion Separation Systems. *Sep. Purif. Methods* **1982**, *11*, 29−69.

(39) Muschiolik, G. Multiple Emulsions for Food Use. *Current Curr. Opin. Colloid Interface Sci.* **2007**, *12*, 213−220.

(40) Arditty, S.; Schmitt, V.; Giermanska-Kahn, J.; Leal-Calderon, F. Materials Based on Solid-Stabilized Emulsions. *J. Colloid Interface Sci.* **2004**, *275*, 659−664.

(41) Fujii, S.; Okada, M.; Sawa, H.; Furuzono, T.; Nakamura, Y. Hydroxyapatite Nanoparticles as Particulate Emulsifier: Fabrication of Hydroxyapatite-Coated Biodegradable Microspheres. *Langmuir* **2009**, *25*, 9759−9766.

(42) Miguel, A. S.; Scrimgeour, J.; Curtis, J. E.; Behrens, S. H. Smart Colloidosomes with a Dissolution Trigger. *Soft Matter* **2010**, *6*, 3163−3166.

(43) Utada, A. S.; Lorenceau, E.; Link, D. R.; Kaplan, P. D.; Stone, H. A.; Weitz, D. A. Monodisperse Double Emulsions Generated From a Microcapillary Device. *Science* **2005**, *308*, 537−541.

(44) Lee, D.; Weitz, D. A. Double Emulsion-Templated Nanoparticle Colloidosomes with Selective Permeability. *Adv. Mater.* **2008**, *20*, 3498−3503.

(45) Maeda, H.; Okada, M.; Fujii, S.; Nakamura, Y.; Furuzono, T. Pickering-Type Water-in-Oil-in-Water Multiple Emulsions toward Multihollow Nanocomposite Microspheres. *Langmuir* **2010**, *26*, 13727−13731.

(46) Gao, Q.; Wang, C.; Liu, H.; Chen, Y.; Tong, Z. Dual NanoComposite Multihollow Polymer Microspheres Prepared by Suspension Polymerization Based on a Multiple Pickering Emulsion. *Polym. Chem.* **2010**, *1*, 75−77.

(47) Zhang, J.; Ge, X.; Wang, M.; Yang, J.; Wu, Q.; Wu, M.; Liu, N.; Jin, Z. Hybrid Hollow Microspheres Templated From Double Pickering Emulsions. *Chem. Commun.* **2010**, *46*, 4318−4320.

(48) Ning, Y.; Wang, C.; Ngai, T.; Yang, Y.; Tong, Z. Hollow Magnetic Janus Microspheres Templated from Double Pickering Emulsions. *RSC Adv.* **2012**, *2*, 5510−5512.

(49) Dyab, A. K. F. Macroporous Polymer Beads and Monoliths From Pickering Simple, Double, and Triple Emulsions. *Macromol. Chem. Phys.* **2012**, *213*, 1815−1832.

(50) Williams, M.; Armes, S. P.; Verstraete, P.; Smets, J. Double Emulsions and Colloidosomes-in-Colloidosomes Using Silica-Based Pickering Emulsifiers. *Langmuir* **2014**, *30*, 2703−2711.

(51) DiFlavio, J.-L.; Pelton, R.; Leduc, M.; Champ, S.; Essig, M.; Frechen, T. The Role of Mild TEMPO-NaBr-NaClO Oxidation On The Wet Adhesion of Regenerated Cellulose Membranes with Polyvinylamine. *Cellulose* **2007**, *14*, 257−268.

(52) Morgan, M.; Fielding, L. A.; Armes, S. P. Synthesis and Characterisation of Sterically Stabilised Polypyrrole Particles Using a Chemically Reactive Poly(Vinyl Amine)-Based Stabiliser. *Colloid Polym. Sci.* **2013**, *291*, 77−86.

(53) Bai, Y.; Koh, C. G.; Boreman, M.; Juang, Y.-J.; Tang, I. C.; Lee, L. J.; Yang, S.-T. Surface Modification for Enhancing Antibody Binding on Polymer-Based Microfluidic Device for Enzyme-Linked Immunosorbent Assay. *Langmuir* **2006**, *22*, 9458−9467.

(54) Madsen, J.; Warren, N. J.; Armes, S. P.; Lewis, A. L. Synthesis of Rhodamine 6G-Based Compounds for the ATRP Synthesis of Fluorescently Labeled Biocompatible Polymers. *Biomacromolecules* **2011**, *12*, 2225−2234.

(55) Schmid, A.; Fujii, S.; Armes, S. P.; Leite, C. A. P.; Galembeck, F.; Minami, H.; Saito, N.; Okubo, M. Polystyrene-Silica Colloidal Nanocomposite Particles Prepared by Alcoholic Dispersion Polymerization. *Chem. Mater.* **2007**, *19*, 2435−2445.

(56) The C/N atomic ratio of 3.8 for PEI is significantly higher than the theoretical atomic ratio of 2.0. This is because the bare silicon wafer contains carbon at 10 atom % as a surface contaminant. Presumably, the PEI layer is either relatively thin compared to the XPS sampling depth, or is relatively non-uniform (patchy). Either scenario would lead to an anomalously high value for PEI alone, but it is emphasized that this minor discrepancy does not affect the conclusions of this study.

(57) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions Stabilised Solely by Colloidal Particles. *Adv. Colloid Interface Sci.* **2003**, *100*, 503−546.