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

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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, ^{1}H 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.

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Introduction

An emulsion stabilized by solid particles is known as a Pickering emulsion.[1,2] A wide range of particles, such as polystyrene latexes,[3,4,5] clay nanoparticles[6,7,8] 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.[15,16,17] It is well known that particle wettability is an important parameter in determining the nature of Pickering emulsions.[18] For hydrophilic particles adsorbed at the oil/water interface, most of the particle volume is preferentially located within the aqueous phase. This leads to a contact angle, θ, of less than 90° which produces an oil-in-water (o/w) emulsion. In contrast, for hydrophobic particles adsorbed at the oil/water interface, the particle volume resides mainly in the oil phase, θ exceeds 90° and a water-in-oil (w/o) emulsion is invariably produced.[19] Various techniques can be used to adjust the particle contact angle (θ) in order to prepare stable Pickering emulsions. For example, the surface modification of hydrophilic silica nanoparticles is often used to tune their wettability. One common approach here is surface derivatization with various commercially-available alkylsilanes.[20] However, similar results can be achieved simply by physical adsorption: recent literature examples include the adsorption of small molecule aromatic acids[21] or surfactants[22,23,24,25,26] onto silica nanoparticles.

Phase inversion of Pickering emulsions prepared using silica nanoparticles has also been investigated. For example, Binks et al. reported the catastrophic phase inversion from w/o to o/w emulsions using hydrophobic silica particles simply by changing the volume fraction of the aqueous phase. The same team also found that complementary phase inversion (i.e. from o/w to w/o) could be achieved using hydrophilic silica particles.[27] Binks et al. also reported that phase inversion could be achieved by fixing the volume fraction of the aqueous phase while increasing the silica particle concentration.[28] In a separate study, reducing the surface silanol content of silica particles caused phase inversion from an o/w emulsion to a w/o emulsion.[20] Binks et al. have also shown how these three techniques can be exploited for the phase inversion of oil-in-water emulsions where the oil droplet phase comprises a water-immiscible fragrance.[29]

Such phase inversion of Pickering emulsions has been exploited to prepare so-called double emulsions.[30] For example, gently emulsifying a w/o emulsion with a second aqueous phase can lead to a w/o/w double emulsion.[31] Alternatively, the complementary o/w/o double emulsion can be prepared by first making an o/w emulsion, followed by re-emulsification in the presence of further oil (which forms the continuous phase).[32] One important advantage of using particles instead of surfactants when preparing such double emulsions is that the former emulsifier usually prevents droplet coalescence, which otherwise eventually leads to the formation of a single emulsion on standing over long time scales.[19] Two different types of Pickering emulsifier are typically required to form double emulsions: hydrophobic particles stabilize the w/o interface and hydrophilic particles stabilize the o/w interface. For example, Binks et al. reported the successful preparation of double emulsions using two batches of silica particles with differing surface silanol contents (and hence surface wettabilities).[33]

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,[34] pharmacy,[35] separation processes,[36] and the food industry.[34,37] 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.[38] 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 ageing for one year, the external water phase remained uncoloured while the internal droplets stayed blue.[38] One technique commonly used to produce microcapsules is evaporation of a volatile oil phase within a Pickering-stabilised w/o/w double emulsion to yield hollow microspheres.[39,40] 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.[41] 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.[42] Such microcapsules may serve as potential drug delivery vehicles.[43] Polymerization of the oil phase to encapsulate the internal water droplets has also been investigated.[44,45] This approach has led to novel microcapsules comprising internal aqueous droplets loaded with stimulus-responsive nanoparticles.[46,47]

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.[48] 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.[48]

It is well known that amines react readily with aldehydes via Schiff base chemistry to form either imines or aminals.[49] This has been exploited for the modification of poly(vinyl amine) for the synthesis of primary amine-functionalized sterically-stabilized polypyrrole particles[50] and also for enhanced antibody binding in polymer-based microfluidic devices.[51] 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.

Experimental Section

Materials

Poly(ethylene imine) (PEI) (branched, MW = 10,000 by GPC; MW = 25,000 by light scattering), 1-undecanal, n-heptane, n-dodecane, isopropyl myristate, KBr (spectroscopic grade, > 99 % trace metal basis) and Nile Red dye were all purchased from Aldrich and were used as received. Methanol, ethanol, acetone and tetrahydrofuran was purchased from Fisher and were used as received. Deuterated methanol was purchased from Goss Scientific UK and was used as received. Isononyl isononanoate was kindly donated by Alliance-Boots (Nottingham, UK) and was used as received. Deionized water was used in all experiments. Cab-o-Sperse 2012A (fumed silica, provided as an aqueous dispersion at 12 % w/w solids) was kindly supplied by Cabot Corporation, (Billerica, MA, USA) and was used as received. According to the manufacturer, this sample comprises fractal aggregates of nano-sized silica particles (see TEM image in Figure S1), with a BET specific surface area of 200 m^2 g^{-1} and a primary particle diameter of 15 nm. Rhodamine 6G-labeled poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) was synthesized according to a recent literature protocol.[52]

Adsorption of PEI onto Fumed Silica Particles

PEI (0 – 2.00 g) was dissolved in deionized water (48.0 - 50.0 g). This aqueous polymer solution was then added to an aqueous dispersion of Cab-o-Sperse 2012A fumed silica (50 g, 2.0 % w/w, pH 10) and the resulting mixture was stirred for 12 h at 20 °C so as to allow physical adsorption of the cationic PEI chains onto the anionic silica particles.

Preparation of Oil-in-Water Pickering Emulsions

The following protocol is representative: a 5.0 ml mixture of n-dodecane (4.70 – 5.00 ml) and 1-undecanal (0 – 0.30 ml) was added to a 14 ml sample vial, followed by addition of an aqueous dispersion of PEI/silica hybrid particles (5.0 ml, 1.0 % w/w Cab-o-Sperse 2012A fumed silica, prepared using a PEI/silica mass ratio of 0.075 at pH 10). Emulsification was achieved at 20 °C using an IKA Ultra-Turrax T-18 homogenizer equipped with a 10 mm dispersing tool for 2 min at 12 000 rpm.

Preparation of Water-in-Oil Pickering Emulsions

The following protocol is representative: a 5.0 ml mixture of n-dodecane (4.70 – 5.00 ml) and 1-undecanal (0 – 0.30 ml) was added to a 14 ml sample vial, followed by addition of an aqueous dispersion of PEI/silica hybrid particles (5.0 ml, 1.0 % w/w Cab-o-Sperse 2012A fumed silica, PEI/silica mass ratio = 0.50, pH 10). Emulsification was achieved at 20 °C using an IKA Ultra-Turrax T-18 homogenizer equipped with a 10 mm dispersing tool for 2 min at 12 000 rpm.

Preparation of Double Emulsions

The following protocol is representative: n-dodecane (4.70 ml) and 1-undecanal (0.30 ml) was added to a 28 ml sample vial, followed by the addition of 5.0 ml of an aqueous dispersion of PEI/silica hybrid particles (1.0 % w/w Cab-o-Sperse 2012A fumed silica, PEI/silica mass ratio = 0.50, pH 10). Emulsification was achieved at 20 °C using an IKA Ultra-Turrax T-18 homogenizer equipped with a 10 mm dispersing tool for 2 min at 12 000 rpm. An aqueous dispersion of 10.0 ml of PEI/silica hybrid particles (1.0 % w/w Cab-o-Sperse 2012A fumed silica, PEI/silica mass ratio = 0.075, pH 10) was then added to the resulting water-in-oil emulsion (10.0 ml) and again emulsification was achieved at 20 °C using an IKA Ultra-Turrax T-18 homogenizer equipped with a 10 mm dispersing tool for 2 min at 12 000 rpm. This protocol produced 20 ml of a w/o/w double emulsion with a total oil content of 25 % v/v (i.e. 5.0 ml).

Fluorescent Labeling of Water-in-Oil-in-Water Double Emulsions

Fluorescent o/w Pickering emulsions, w/o Pickering emulsions and w/o/w double emulsions were made using the same formulations as those described above, except that Nile Red dye was first dissolved in the oil phase ([Nile Red] = 0.010 g dm^{-3}) prior to homogenization.

Alcohol Challenge

A small aliquot (0.50 ml) of an o/w Pickering emulsion or w/o/w double emulsion was transferred to a 5.0 ml vial, then excess ethanol (4.0 ml) was added and the sealed vial was shaken vigorously to break the emulsion.

Poly(2-(methacryloyloxy)ethyl phosphorylcholine) release from w/o/w double emulsions

Rhodamine-labeled PMPC[52] was dissolved in an aqueous dispersion of PEI/silica hybrid particles (1.0 % w/w Cab-o-Sperse 2012A fumed silica, PEI/silica mass ratio = 0.50, pH 10) at a concentration of 1.50 g dm^{-3}. Double emulsions were then prepared using either n-dodecane, isopropyl myristate or isononyl isononanoate as the oil phase, as reported above. The external aqueous phase was isolated after creaming of the emulsion droplets on standing and analyzed using a PC-controlled Perkin-Elmer Lambda 25 UV-visible absorption spectrophotometer. The absorbance maximum at 540 nm was recorded over time and converted into a PMPC concentration using a Beer-Lambert calibration curve (see Figure S9).

Particle Characterization

Dynamic Light Scattering

The intensity-average hydrodynamic diameter was obtained by DLS using a Malvern Zetasizer NanoZS instrument. Aqueous solutions of 0.01 % w/v dispersions were analyzed using disposable plastic cuvettes, and results were averaged over three consecutive runs. The deionized water used to dilute each dispersion was ultra-filtered through a 0.20 µm membrane to remove extraneous dust.

Aqueous Electrophoresis

Zeta potentials were determined for PEI/silica hybrid particles prepared at various PEI/silica mass ratios using a Malvern Zetasizer Nano ZS instrument. The solution pH was fixed at pH 10 in the presence of 1 mM KCl, with either dilute NaOH or HCl being used for pH adjustment as required.

Thermogravimetric Analysis

Prior to analysis, the PEI/silica hybrid particles were purified by centrifugation at 8 000 rpm for 1 h, carefully replacing the supernatant with mildly alkaline water (pH 10) each time followed by redispersion of the sedimented particles with the aid of an ultrasonic bath. This centrifugation-redispersion cycle was repeated four times to ensure that no excess non-adsorbed PEI remained in the aqueous continuous phase. The dried PEI/silica hybrid particles were heated up to 800 °C in air at a heating rate of 20 °C min^{-1} using a Perkin-Elmer Pyris-1 TGA instrument. The amount of PEI adsorbed onto the fumed silica particles was determined from the weight loss observed between 200 °C and 650 °C, which corresponded to complete pyrolysis of the organic component.

^{1}H NMR Spectroscopy

All samples were dissolved in deuterated methanol and spectra were recorded using a 250 MHz Bruker Avance DPX 250 spectrometer.

Water Contact Angle Studies

Silicon wafers (approximately 1.0 cm^{2}) were rinsed in turn with methanol, THF, deionized water and acetone, then air-dried prior to use. Wafers were immersed in either (i) various aqueous dispersions of PEI/silica hybrid particles (1.0 % w/w Cab-o-Sperse 2012A fumed silica, 0 – 2.0 % w/w PEI, pH 10) for 2 minutes or (ii) various aqueous dispersions of PEI/silica particles (1.0 % w/w Cab-o-Sperse 2012A fumed silica, PEI/silica mass ratio = 0.075 or 0.50, pH 10) for 2 minutes. Each wafer was washed with deionized water to remove any excess PEI/silica particles and then dried using a N_2 gas stream. Each wafer prepared according to protocol (i) was analyzed directly. Each wafer prepared according to protocol (ii) was immersed in 30 ml of an n-heptane solution containing 1-undecanal (0.0 - 3.0 vol %) for 2 minutes before being washed with n-heptane to remove excess 1-undecanal and dried using a N_2 gas stream. Water contact angles were then determined for all samples using a contact angle goniometer by placing a 10 µl droplet of deionized water onto each silicon wafer at 20^{o}C. Each wafer was measured in triplicate and the mean contact angle was determined. A digital image of each water droplet was recorded using a Canon Power shot SX260 HS digital camera.

X-ray Photoelectron Spectroscopy

Silicon wafers (approximately 1.0 cm^2) were rinsed in turn with methanol, THF, deionized water and acetone, then air-dried prior to use. Wafers were immersed in either (i) an aqueous dispersion of poly(ethylene imine) (0.50 % w/w, pH 10) or (ii) an aqueous dispersion of PEI/silica particles (1.0 % w/w Cab-o-Sperse 2012A fumed silica, PEI/silica mass ratio = 0.50, pH 10) for 2 minutes. Each wafer was washed with deionized water to remove any excess PEI or PEI/silica particles and then dried using a N_2 gas stream. Each wafer prepared was immersed in 30 ml of an n-heptane solution containing 1-undecanal (0.0 – 3.0 vol %) for 2 minutes before being washed with n-heptane to remove excess 1-undecanal and dried using a N_2 gas stream. The surface compositions were then examined by XPS using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer equipped with a monochromatic Al X-ray source operating at 6.0 mA and 15 kV at a typical base pressure of 10^{-8} torr. The step size was 1.0 eV for the survey spectra (pass energy 160 eV) and 0.1 eV for the high resolution spectra (pass energy 80 eV).

Gas Chromatography

Pickering emulsions (o/w and w/o) and w/o/w double emulsions were synthesised as above using n-dodecane containing 3 % v/v 1-undecanal. Each emulsion was diluted in ethanol at a concentration of 0.5 % w/w oil in ethanol. Each sample was centrifuged at 10,000 rpm for 1 hour and the supernatant was analysed by Gas chromatography. Each sample was heated at 180 °C for 15 minutes and the peak area at 5.95 minutes, determined to be 1-undecanal, was used to calculate 1-undecanal content using a calibration plot constructed by measuring a series of samples containing known concentrations of 1-undecanal.

Transmission electron microscopy

Images were recorded using a Phillips CM100 microscope operating at 100 kV by drying a drop of dilute PEI/silica hybrid particle dispersion onto a carbon-coated copper grid.

Emulsion Characterization

Conductivity Measurements

The conductivities of the emulsions immediately after preparation were measured using a digital conductivity meter (Hanna model Primo 5). A high conductivity (typically > 10 μS cm^{-1}) indicated that the emulsion was water-continuous. All results were confirmed using the so-called "drop test", whereby one drop of the emulsion was added in turn to either pure water or pure oil, with the relative ease of dispersion in each case being assessed by visual inspection. Relatively rapid dispersion into water was taken as confirmation of an aqueous continuous phase for the emulsion, whereas relatively rapid dispersion into oil was taken as confirmation of an oil-continuous phase for the emulsion.

Optical Microscopy

A single droplet (ca. 100 μl) of either a o/w or w/o Pickering emulsion (50 % v/v) or a double emulsion (25 % v/v) was placed on a microscope slide and digital images were recorded using a Motic DMBA300 digital biological microscope equipped with a built-in camera and Motic Images Plus 2.0 ML software.

Fluorescence Microscopy

A single droplet (ca. 100 μl) of either a o/w or w/o Pickering emulsion (50 % v/v) or a double emulsion (25 % v/v) was placed on a microscope slide and viewed using an Olympus Upright Epifluorescence instrument equipped with a Hamamatsu ORCA-ER monochrome camera and Volocity software. This technique was used to view the fluorescent Nile Red dye dissolved in the oil phase for the o/w and w/o emulsions and also for the w/o/w double emulsions.

Laser Diffraction Particle Size Analysis of Emulsion Droplets

A Malvern Mastersizer 2000 laser diffraction instrument equipped with a small volume (ca. 50 ml) Hydro 2000SM sample dispersion unit, a HeNe laser operating at 633 nm, and a solid-state blue laser operating at 466 nm was used to size both the o/w Pickering emulsions and the w/o/w double emulsions. The stirring rate was adjusted to 1,000 rpm. Corrections were made for background electrical noise and laser scattering due to contaminants on the optics and within the sample. Samples were analyzed five times, and the data were averaged. A typical acquisition time was 2 min per sample after alignment and background measurements. The raw data was analyzed using the manufacturer's software. The mean droplet diameter was taken to be the mean volume-average diameter ($D_{4/3}$), which is mathematically expressed as $D_{4/3} = \Sigma D_i^4 N_i / \Sigma D_i^3 N_i$. The standard deviation for each diameter provides an indication of the width of the size distribution. After each measurement, the cell was rinsed three times with ethanol, followed by three times with deionized water. The glass walls of the cell were carefully wiped with a lens cleaning tissue to avoid cross-contamination, and the laser was aligned centrally on the detector.

Scanning Electron Microscopy

SEM images were obtained using a FEI inspect F FEG instrument operating at 20 kV. All samples were sputter-coated with a thin overlayer of gold prior to inspection to prevent sample charging effects.

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.[48] 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 amount of PEI added to a 1.0 % w/w aqueous dispersion of silica particles was systematically varied from zero up to 1.0 % w/w, which corresponds to a PEI/silica mass ratio of 1.0, 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 water 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 so 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 around 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 Figure S2) and transmission electron microscopy (see 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 multi-component fragrance as an oil.[48] 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 four 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 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(s) are responsible for the phase inversion that is observed when emulsifying these hybrid particles with an aldehyde-rich oil.[48] 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.[48] 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 (% 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.[49] 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.[53] This surface analytical technique has a typical sampling depth of 2-5 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 8.9 is higher than that of PEI alone (5.1). 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. Based on 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. 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 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 phase inversion from an o/w to a w/o Pickering emulsion 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 Figure S6A). 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 Figure S6B). To examine the 1-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 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 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 has 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 multi-component hydrophobic fragrance as the oil phase.[48] 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 highly 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 S7.

Previously, we found that w/o/w double emulsions prepared with the aldehyde-rich multi-component fragrance could withstand an alcohol challenge, whereby addition of excess ethanol simultaneously removes both the oil and aqueous phases.[48] 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 6d. 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, 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 Figure S8). 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 will be 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 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)[52] (Rh-PMPC) with a mean Dp of 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 Figure S9), 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 two weeks at 20°C.

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.[19,54] 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 double emulsions prepared using Pickering emulsifiers is described for three model oils (n-dodecane, isopropyl myristate or 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 relatively hydrophobic aldehyde, 1-undecanal, is added to the oil phase prior to emulsification then, provided that the adsorbed amount of PEI is sufficiently high, the complementary w/o emulsions can be obtained. This is because the 1-undecanal reacts with the primary 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 their hydrophobicity, 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. Water-in-oil-water 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). Fluorescent microscopy 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 remains of smaller PEI/silica shells within the ~ 50 μm microcapsule walls. Furthermore, 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 for 15 days thereafter.

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Supporting Information 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, 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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List of Tables

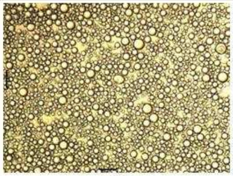
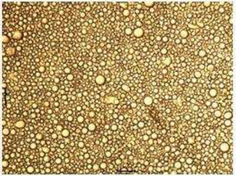
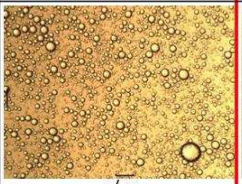
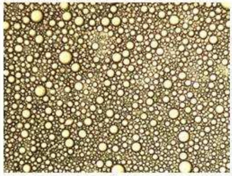
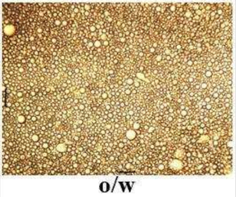
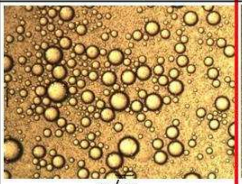
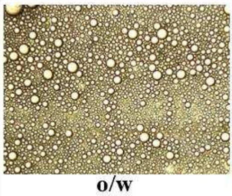
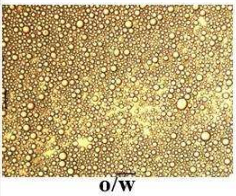
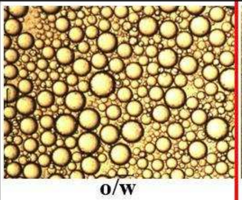
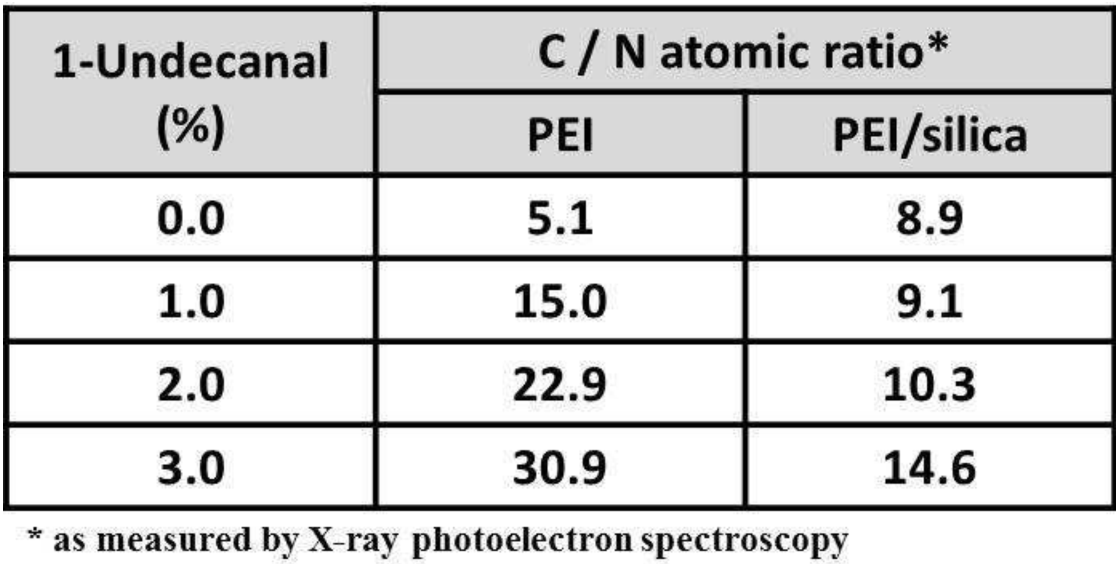
200 µm	**PEI/silica mass ratio = 0.075**		**PEI/silica mass ratio = 0.50**	
	0 % 1-undecanal	**3 % 1-undecanal**	**0 % 1-undecanal**	**3 % 1-undecanal**
***n*-dodecane**	 **o/w** **36 ± 16 µm**	 **o/w** **41 ± 21 µm**	 **o/w** **57 ± 36 µm**	 **w/o** **6 ± 3 µm**
isopropyl myristate	 **o/w** **36 ± 33 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**

Table 1. Effect of varying the poly(ethylene imine)/silica mass ratio and 1-undecanal content added to the oil phase on the nature of Pickering emulsions obtained after homogenization of equal volumes of oil and a 1.0 % w/w aqueous dispersion of fumed silica particles at 12 000 rpm for two minutes at 20°C. The oils used were n-dodecane, isopropyl myristate and isononyl isononanoate.



1-Undecanal (%)	C / N atomic ratio*	
	PEI	PEI/silica
0.0	5.1	8.9
1.0	15.0	9.1
2.0	22.9	10.3
3.0	30.9	14.6

* as measured by X-ray photoelectron spectroscopy

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.

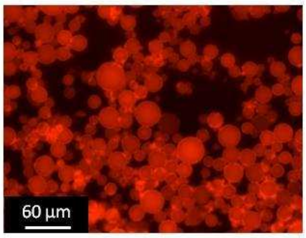
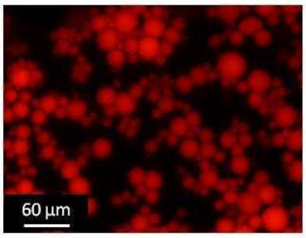
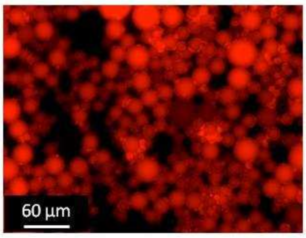
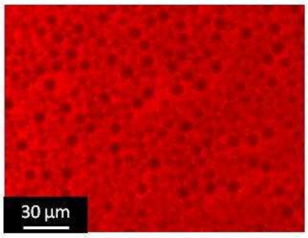
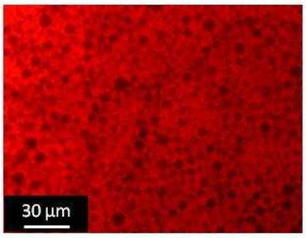
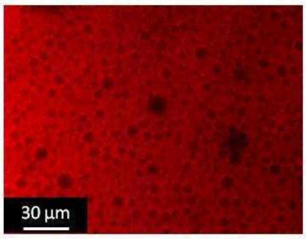
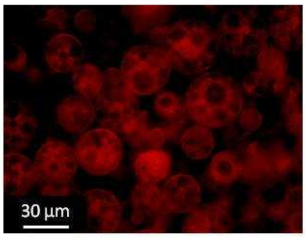
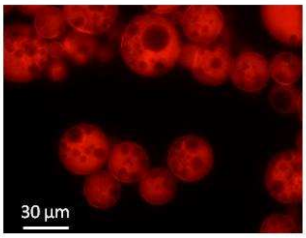
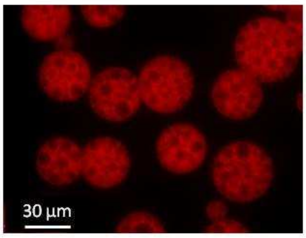
	Dodecane	Isopropyl Myristate	Isononyl Isononanoate
o / w			
w / o			
w/o/w			

Table 3. Fluorescence microscopy images obtained by dissolution of the fluorescent dye Nile Red in 3 oils prior to homogenization, for 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) with the oil droplets encapsulating multiple water droplets. The oils used were n-dodecane, isopropyl myristate and isononyl isononanoate. ([Nile Red] = 0.010 g dm^{-3})

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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 minutes. 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. (a) Water contact angle data (●) 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. **(b)** Adsorbed mass of poly(ethylene imine) per unit mass of fumed silica (■) (determined by TGA) vs. target poly(ethylene imine)/silica mass ratio. 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.

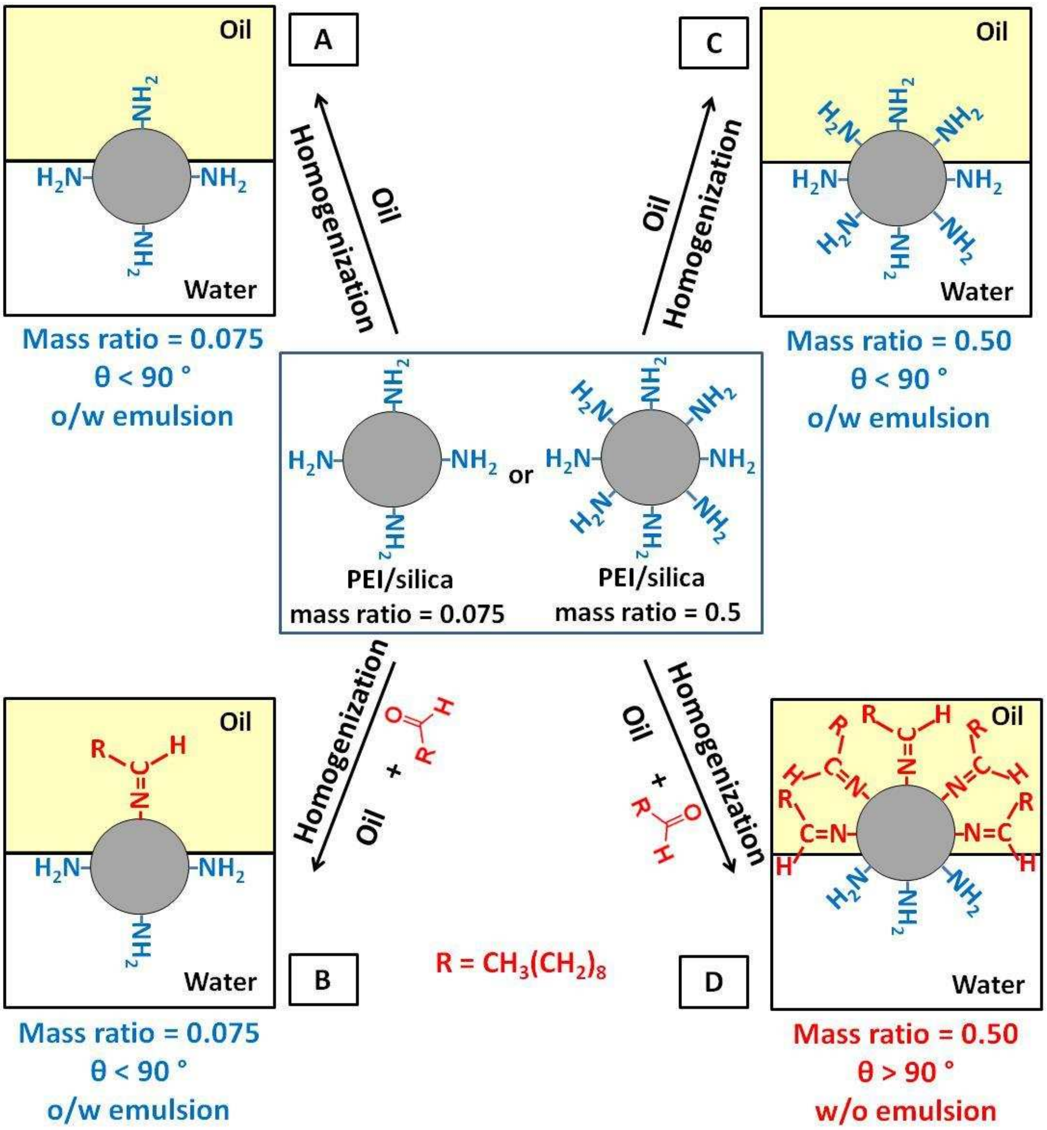
Figure 3. The contact angle of a 10 μl water droplet on (▲) poly(ethylene imine)/silica hybrid particles (1.0 % w/w fumed silica, PEI/silica mass ratio = 0.5, pH 10) and (♦) poly(ethylene imine)/silica hybrid particles (1.0 wt % fumed silica, PEI/silica mass ratio = 0.075, pH 10) following exposure to n-heptane solutions with different amounts of 1-undecanal (0 – 3 volume %). **A-D** show digital images of the water droplet contact angles highlighted by the labels.

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 %.

Figure 5. (A, B) Optical microscopy images obtained following the addition of excess ethanol to a w/o/w double emulsion made 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 %.

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.



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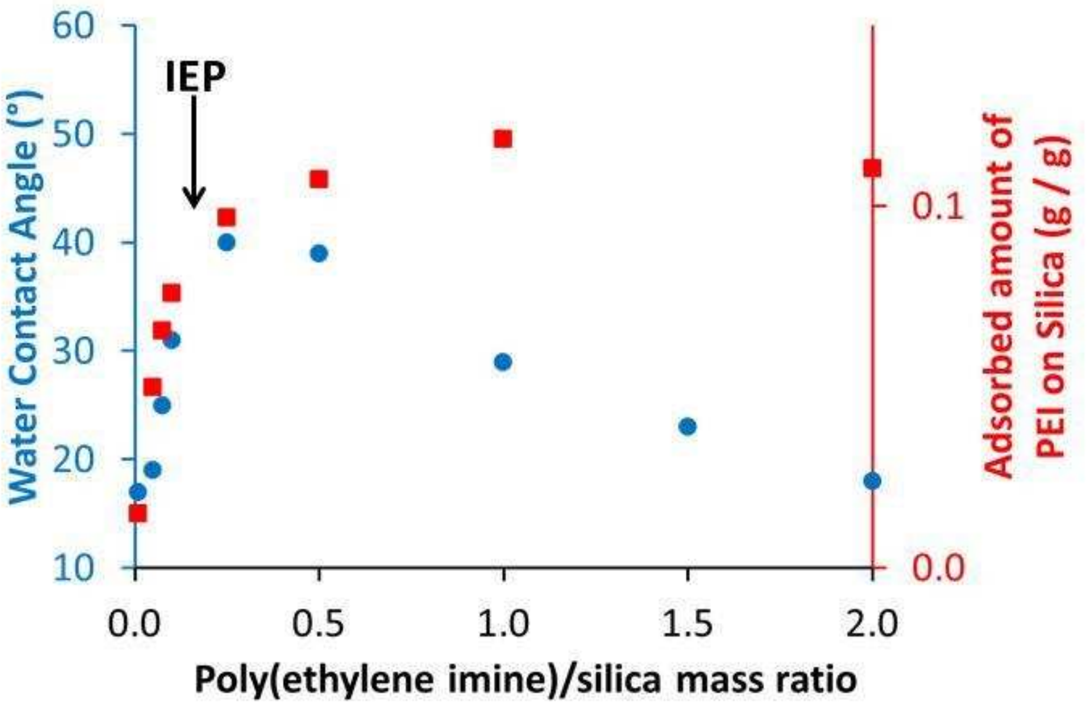

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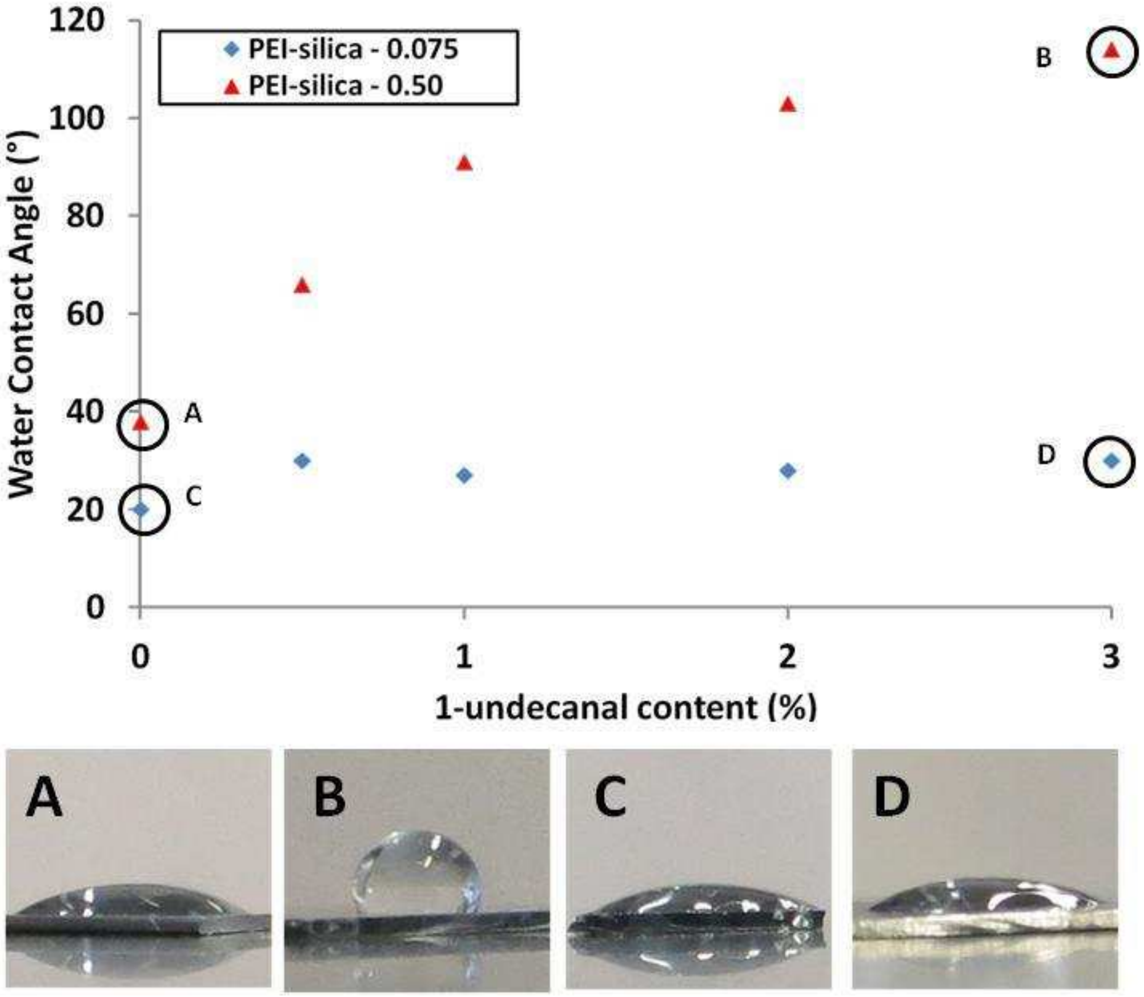

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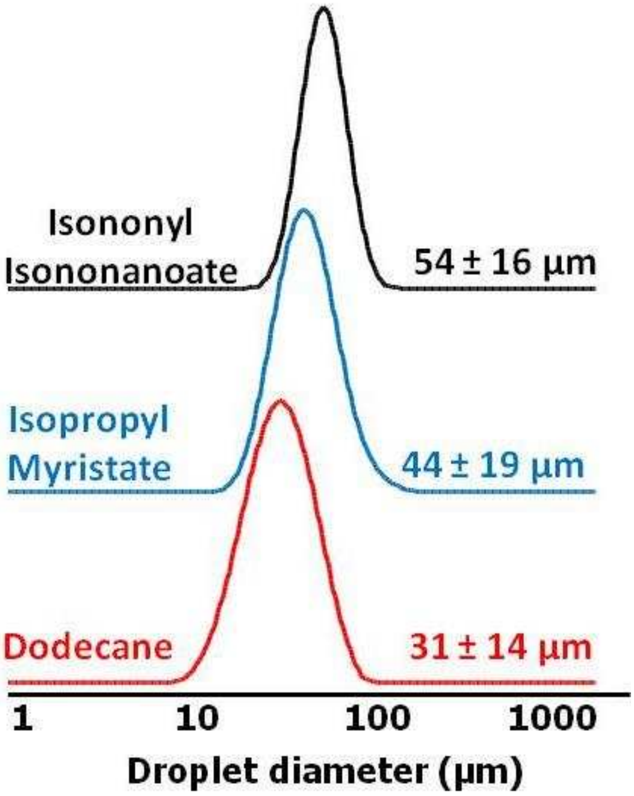

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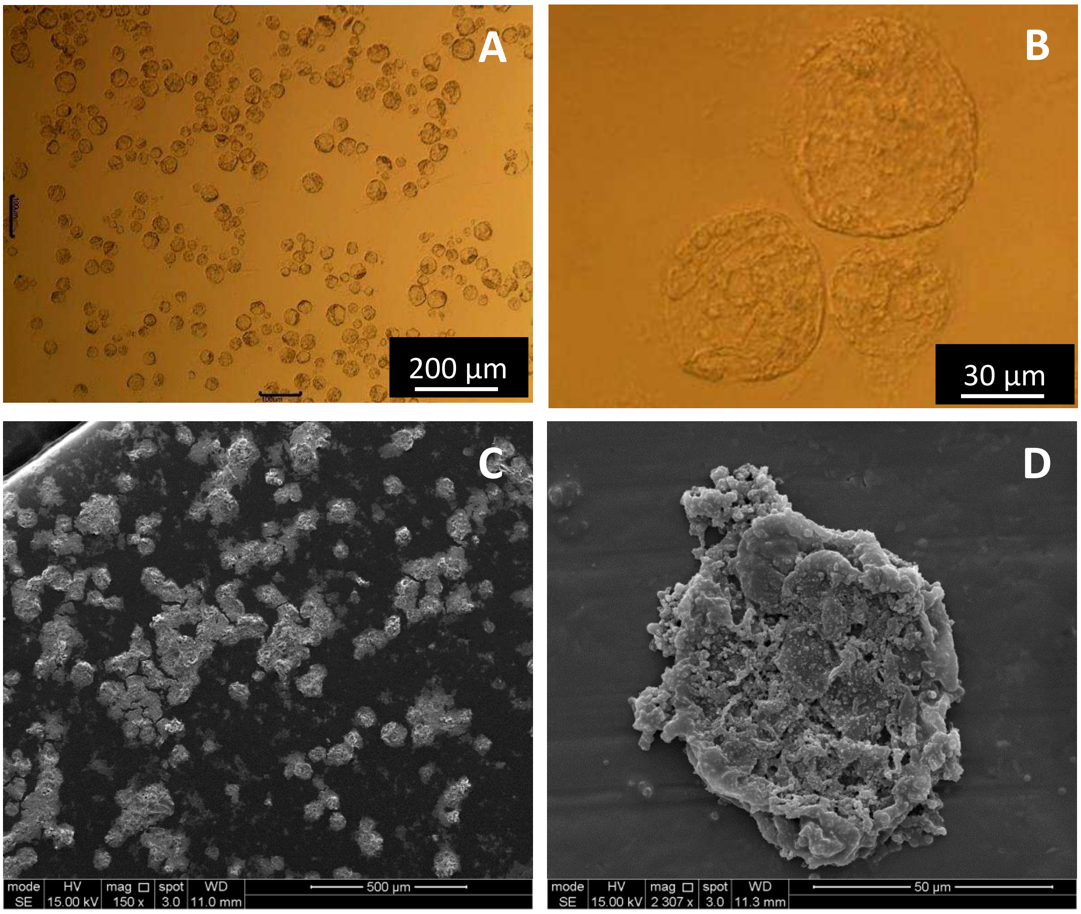

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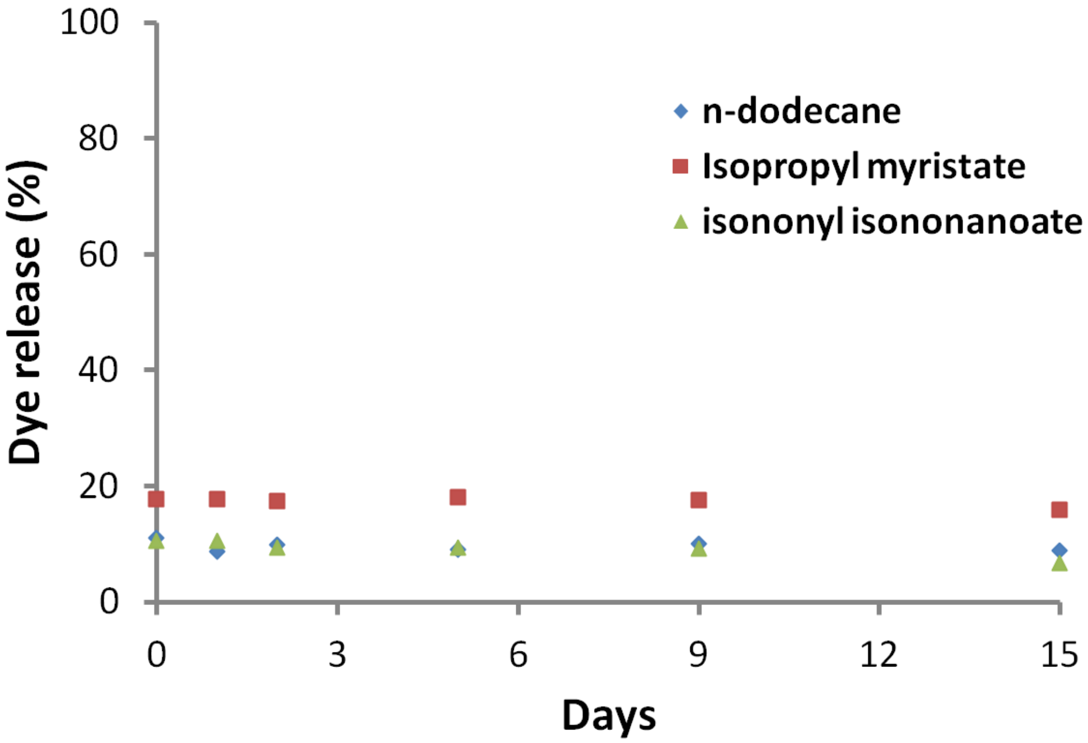

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TOC Graphical Abstract for ACS Applied Materials and Interfaces manuscript:

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

Mark Williams, Nicholas J. Warren, Steven P. Armes,* Pierre Verstraete and Johan Smets