

# Nonfouling Capture–Release Substrates Based on Polymer Brushes for Separation of Water-Dispersed Oil Droplets

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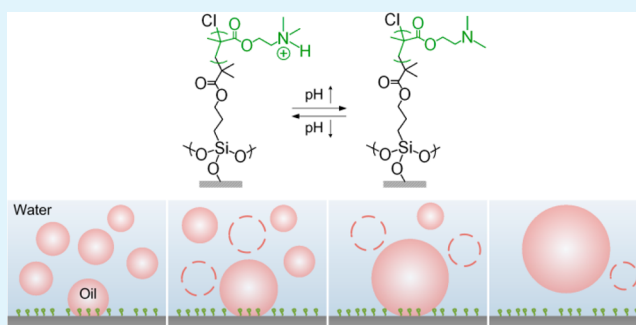
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## S Supporting Information

**ABSTRACT:** We have demonstrated capture and release of underwater–oil droplets based on fouling-resistant surfaces coated with pH-responsive polymer brushes. In response to the change of environmental pH, oil droplets were captured on the polymer brush-modified surfaces in the high adhesion state. As the droplet volume increased upon coalescence with other oil droplets in the aqueous phase, the captured droplets eventually self-released from the surfaces under the influence of buoyancy and rose to the air–water interface. The fact that the polymer brush surfaces were partially oil-wettable (high oil-in-water contact angles) enabled the adhesion but not the spreading of oil droplets. This allowed buoyancy release of oil droplets and led to fouling-resistant surfaces that could be reused for capture–release of more oil droplets. The practicality and versatility of this oil droplet capture–release system was demonstrated using monodisperse and polydisperse hydrocarbon oil compositions in purified water, tap water, and brines in which the salt concentration was as high as that of seawater.

**KEYWORDS:** responsive polymer brush, nonfouling surface, oil-in-water dispersion, oil/water separation, oil droplet capture–release



## INTRODUCTION

Oil contamination due to oil spill accidents and industrial waste discharge has long-term adverse impacts not only to mankind and the environment but also to wildlife and the ecosystems. In addition, treatments of oil-contaminated wastewater to meet regulatory limits for disposal have been a challenge for various industries in particular the oil industry. To date, a myriad of novel materials have been fabricated for oil/water separation predominantly based on absorption<sup>1–8</sup> and filtration.<sup>9–12</sup> In essence, the functionality of these materials is associated with their surface wettability which is mainly a function of surface chemical composition and/or geometrical structure.<sup>13–20</sup> Primarily for removing oil on the surface, most oil absorbent materials have a high surface area and hence demonstrate a high oil absorption capacity.<sup>1–7,21</sup> For example, CF<sub>3</sub>-modified silica aerogels can absorb crude oil up to as much as 237 times their own weight.<sup>22</sup> On the other hand, chemically coated metal mesh films demonstrate very high separation efficiencies for various oil/water mixtures.<sup>11,12</sup> For instance, polyacrylamide hydrogel-coated filters achieved more than 99% separation efficiency (determined by measuring the oil content in the water filtrate) for diesel/water and crude oil/water mixtures.<sup>12</sup> Compared to oil residing on the surface of water and oil/water mixtures, the separation of oil from oil-in-water dispersions involving minute, stable oil droplets has received relatively less attention. Separation of such oil droplets using conventional methods such as centrifugation, gravity and filtration is

remarkably challenging due to the size and the stability of the oil droplets. Nevertheless, relating to this, underwater surface wettability which involves manipulating the adhesion of oil droplets has recently emerged as a new research focus.<sup>14–19,23,24</sup> Recent progress involves the exploitation of smart materials such as temperature-responsive poly(*N*-isopropylacrylamide) hydrogels<sup>18</sup> and electrochemically switchable polypyrrole films<sup>19</sup> to gain more control over the surface wettability and adhesion of oil droplets in water.

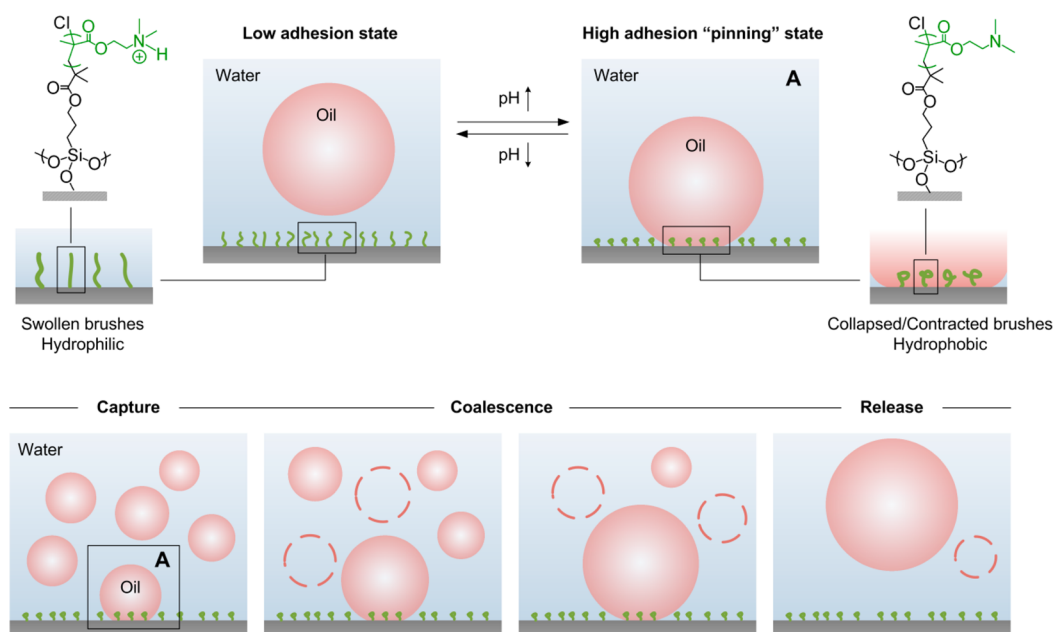
We demonstrate an underwater–oil droplet capture–coalescence–release model based on pH-responsive polymer brushes, as schematically illustrated in Scheme 1. Polymer brushes that consist of a carpet of surface-tethered polymer chains have been shown to offer environmentally switchable responsiveness, chemical stability and synthetic flexibility.<sup>25–28</sup> In response to the environmental pH, polymer brushes collapse or shrink and the surfaces become more hydrophobic, leading to the high adhesion state. The fact that the polymer brush-coated surfaces are partially oil-wettable forces the oil droplets to “pin” to the surfaces at high contact angles with large hystereses of advancing and receding contact angles (the Wenzel state). As the droplet volume increases upon coalescence with other dispersed oil droplets, the captured

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**Scheme 1. Capture, Coalescence, and Release of Underwater Oil Droplets on pH-Responsive, Nonfouling Substrates Coated with Polymer Brushes.<sup>a</sup>**



<sup>a</sup>In response to the environmental pH, dispersed oil droplets in water are “pinned” on the surfaces in the high adhesion state. The captured droplets coalesce with other oil droplets in water (indicated by dotted circles) and increase in volume. Until this stage, the surface adhesion force is greater than the buoyancy force. The captured droplets continue to grow as a result of further coalescence and eventually self-release from the surfaces under the influence of buoyancy.

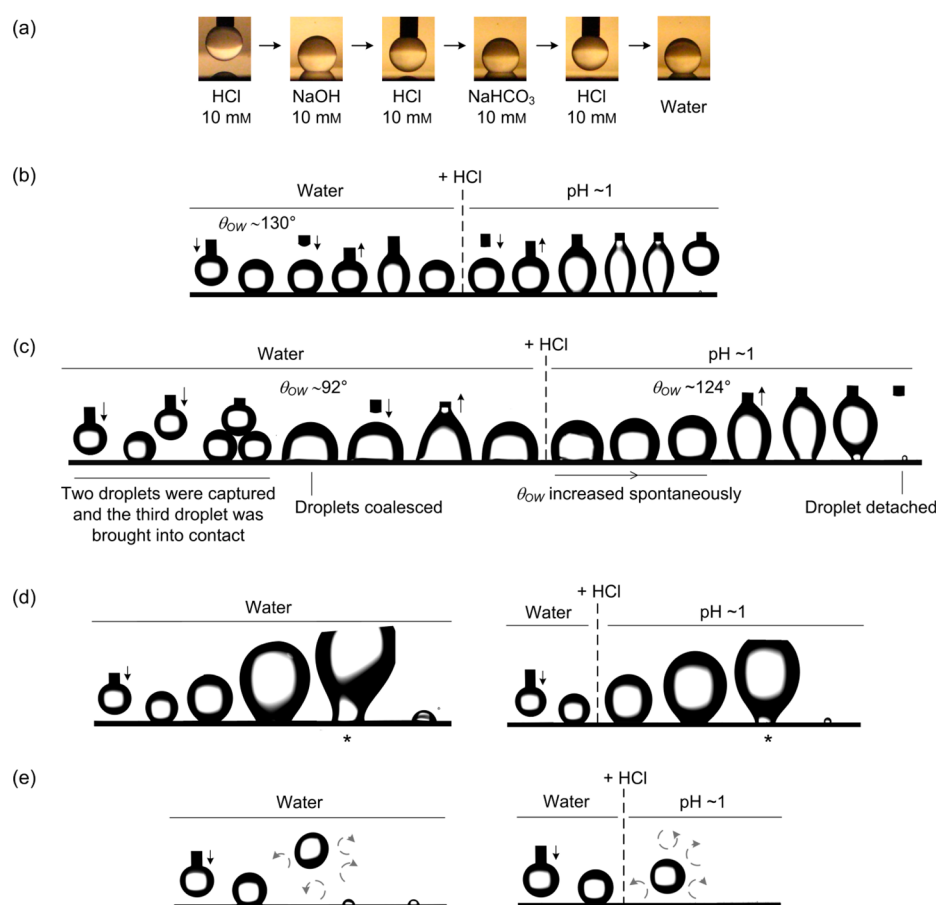
droplets eventually self-release from the coated surfaces under the influence of buoyancy and rise to the surface of water. Such a capture-coalescence-release cycle of oil droplets can recur without fouling the surfaces. Hence, the polymer brush-coated surfaces will enable the growth of minute, stably dispersed oil droplets in water into larger oil droplets which can be collected at the water surface and skimmed off via standard oil/water separation techniques such as decantation and gravimetric separation. The release of captured oil droplets can also be triggered by pH. In this case, the switch of polymer brush surfaces to the low-adhesion hydrophilic state promotes the release of captured droplets and regenerates the surfaces. This capture–release model offers advantages over oleophilic separation materials that will eventually be fouled by oil, are difficult to regenerate and require treatments for disposal.<sup>12</sup> It also offers advantages over absorption-based oil/water separation materials that require a high input of energy, such as high temperature, sonication, and combustion, for the regeneration of absorbents. The practicality and versatility of this oil capture–release system was demonstrated using monodisperse and polydisperse hydrocarbon oil compositions in purified water, tap water and brines in which the salt concentration is as high as that of seawater.

## RESULTS AND DISCUSSION

Silicon wafers were coated with the well-studied pH-responsive poly(2-(dimethylamino)ethyl methacrylate)<sup>29–32</sup> (polyDMAEMA) brushes (Scheme 1) via surface-initiated controlled/living atom transfer radical polymerization (ATRP). The desired thickness of polyDMAEMA brushes was obtained by adjusting the polymerization duration (see the Supporting Information, Figure S1). Homogeneous polyDMAEMA brushes were generated on silicon wafers, as represented by the atomic

force microscopy image of a coated surface with ellipsometric dry polymer thickness  $h_d \approx 10 \pm 2$  nm (root-mean-square surface roughness  $\approx 0.4 \pm 0.04$  nm, see Figure S2 in the Supporting Information). PolyDMAEMA is a weak polybase, which has a  $pK_a \sim 7–8$ , dependent upon the added salt concentration.<sup>33,34</sup> Below the  $pK_a$ , polyDMAEMA brushes were positively charged, swollen, and hydrophilic because of protonation of the tertiary amine moieties, whereas above the  $pK_a$ , polyDMAEMA brushes were deprotonated, collapsed, and hydrophobic. Therefore, polyDMAEMA brushes swelled in HCl solution (pH  $\sim 3$ ) with a 3- to 5-fold increase in the polymer thickness but collapsed totally in NaOH solution (pH  $\sim 11$ ) with thicknesses comparable to those obtained in the dry state (see Figure S1 in the Supporting Information).

Considering the fact that the vast majority of the world’s crude oil production is light oil (79% of the total production in 2010 had a density equal to or smaller than  $0.9 \text{ kg L}^{-1}$ ),<sup>35</sup> decane (density  $\approx 0.73 \text{ kg L}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ) was chosen as the model oil to study underwater–oil adhesion on silicon substrates coated with polyDMAEMA brushes (dry polymer thickness as determined by ellipsometry  $h_d \approx 11 \pm 1$  nm). As anticipated, in HCl solution (10 mM, pH  $\sim 2$ ), decane droplets did not adhere to the substrates when polyDMAEMA brushes were protonated (Figure 1a). On the other hand, decane droplets adhered to the substrates in NaOH solution (10 mM, pH  $\sim 12$ ),  $\text{NaHCO}_3$  solution (10 mM, pH  $\sim 9$ ) and water (pH  $\sim 6.5$ ). Adhesion of decane droplets on the substrates was reversible between the acidic and alkaline solutions or water. On the basis of these results, the adhesion of oil droplets was mainly due to the pH-responsive coatings of polyDMAEMA brushes, although there might be complex dependencies of adhesion force, surface roughness, and droplet size.<sup>36</sup> Considering the fact that polyDMAEMA is a weak poly-electrolyte, its degree of ionization is determined by charge



**Figure 1.** pH-dependent capture and release of underwater decane droplets on silicon wafers coated with polyDMAEMA brushes ( $h_d \approx 11 \pm 1$  nm). (a) Adhesion of decane droplets (2  $\mu$ L each) in HCl solution (pH  $\sim$ 2), NaOH solution (pH  $\sim$ 12), NaHCO<sub>3</sub> solution (pH  $\sim$ 9), and water (pH  $\sim$ 6.5). (b, c) pH-dependent adhesion and release of decane droplets (2  $\mu$ L each). (d) Self-release of decane droplets as a function of the droplet volume. (e) Release of decane droplets under the influence of flow or turbulence introduced by a pipet. For d and e, the initial volume of decane droplets captured on the surfaces was 5  $\mu$ L. In all cases, the initial pH of water was  $\sim$ 6.5 and a diluted HCl solution (500 mM) was used in acidification. Images in each series were taken over a time scale at the same magnification with the same substrate. Last images before self-release of droplets are marked with \*.

equilibrium along the polymer.<sup>29</sup> It is only when polyDMAEMA was sufficiently or fully charged at more acidic conditions (e.g., in HCl solution at pH  $\sim$ 2) that the substrates become oil-repulsive, which explains why adhesion of decane droplets occurred even at a slightly acidic pH (i.e., in water at pH  $\sim$ 6.5). Unlike surfaces modified with an archipelago-like discontinuous coating of polymer brushes,<sup>20</sup> the adhesion of oil droplets on these substrates modified with a homogeneous coating of polyDMAEMA brushes was unaffected by the polymer chain length. Reversible pH-dependent adhesion of decane droplets in water, acidic, and alkaline solutions was reproducible on substrates coated with a thicker polyDMAEMA brush ( $h_d \approx 29 \pm 1$  nm) (see Figure S3 in the Supporting Information).

The adhesion and release of decane droplets in water on the surfaces coated with polyDMAEMA brushes was manipulated as a function of pH. As depicted in Figure 1b, a decane droplet which was captured on a substrate in water could be released from the surface upon the addition of HCl. To further illustrate that the surfaces are resistant to oil fouling, two decane droplets were deposited side by side on a surface and another decane droplet was subsequently brought into contact (Figure 1c). Upon coalescence, the droplet exhibited a reduced contact angle (oil-in-water contact angle  $\theta_{OW} \approx 92^\circ$ ) and strongly adhered to the surface. Interestingly, subsequent acidification

led to spontaneous increase in oil contact angle ( $\theta_{OW} \approx 124^\circ$ ), after which the oil droplet could be detached easily from the surface. As illustrated in Scheme 1, oil droplets will remain adhering to the surfaces as long as the surface adhesion force is larger than the buoyancy. Buoyancy is related to the weight of the displaced water, hence related to the oil droplet size. Therefore, as the droplet volume increased upon coalescence with other dispersed oil droplets, captured decane droplets ultimately self-released from the surfaces when the buoyancy force increased over a critical point (Figure 1d). Such a phenomenon occurred in both pure water and acidified water with considerably less residual oil on the surface in the latter case. It is also evident that the maximum volume of coalesced droplets that adhered to the surface before buoyancy release (indicated by \* in Figure 1d) was smaller in acidic water than in pure water. Both the amount of residual oil on the surfaces and the maximum droplet size prior to self-release suggest that surface-oil interaction forces were weaker in the acidic condition, as expected because of a higher charge density of polyDMAEMA. Consistent with this, the adhesion force (estimated based on the largest oil droplets that adhered to the surfaces before buoyancy release) is smaller in the acidic condition, as shown in Table 1. The captured decane droplets could also be released from the surfaces under the influence of

Table 1. Calculated Adhesion force

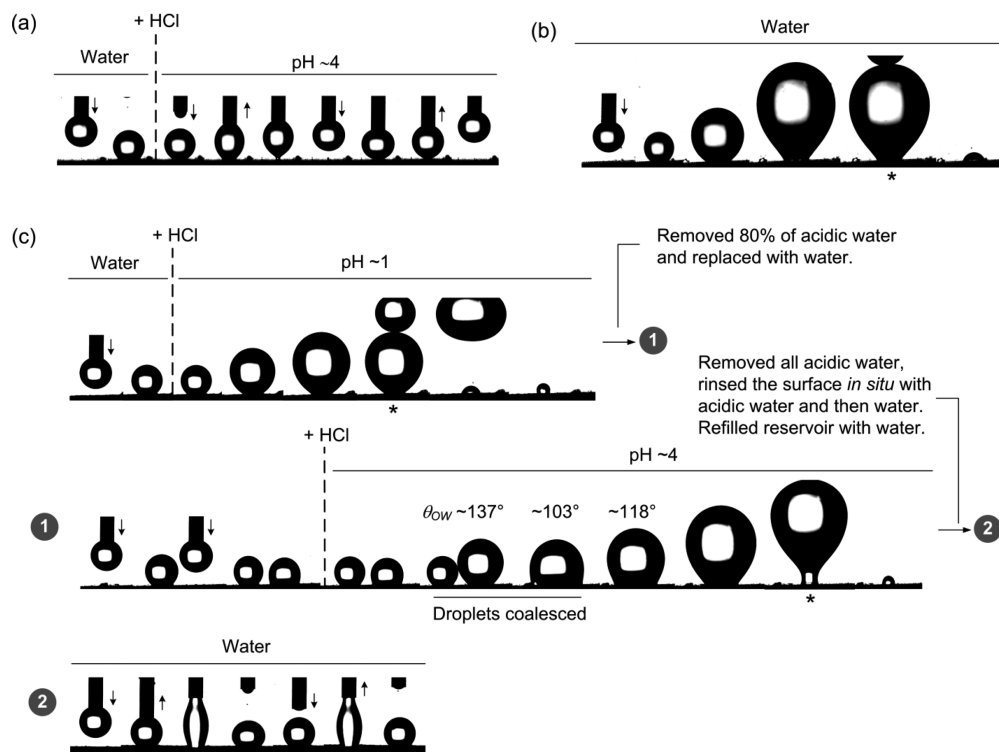
oil-in-water	$\gamma_{ow}^a$ (N m <sup>-1</sup> )	$\theta_{ow}^b$ (°)	$R^c$ (mm)	$f_A^d$ ( $\mu$ N)
decane in purified water	0.0512	75.9	2.54	508.1
decane in acidified purified water	0.0512	99.8	2.25	300.2
SS-D80 in tap water	0.0253	129.6	1.99	57.4
SS-D80 in acidified tap water	0.0253	143.4	1.45	22.8
SS-D80 in NaCl 600 mM <sup>e</sup>	0.0236	126.8	1.86	55.3
SS-D80 in acidified NaCl 600 mM (HCl 20 mM)	0.0236	152.1	0.88	7.6
SS-D80 in acidified NaCl 600 mM (HCl 51 mM)	0.0236	155.6	1.17	7.8

<sup>a</sup>Oil-in-water interfacial tension. <sup>b</sup>Oil-in-water contact angle. <sup>c</sup>Radius of an oil droplet. <sup>d</sup>Adhesion force calculated according to Liu et al.<sup>39</sup> based on the largest oil droplets that adhered to the surfaces before buoyancy release.  $f_A = \pi RW$ , where  $W = \gamma_{ow}(1 + \cos \theta_{ow})$ . See the Supporting Information for details. <sup>e</sup>NaCl 600 mM was prepared using tap water

flow, leaving no oil residue at all in the case of acidified water (Figure 1e). It should be highlighted that the polymer brush surface allowed oil droplets to be captured in response to the change of environmental pH. The polymer brush surfaces, which exhibited high oil-in-water contact angles, enabled the adhesion but not the spreading of oil droplets. This allowed buoyancy release of oil droplets and led to fouling-resistant surfaces which could be reused for capture-release of more oil droplets. Such a capture-release of oil droplets was not observed on silicon substrates coated with hydrophobic monolayers such as propyltrimethoxysilane, phenyltrimethoxysilane, octadecyltrimethoxysilane, and perfluorooctyltrichlor-

osilane (see Figure S4 in the Supporting Information). On these monolayer surfaces, oil droplets either did not adhere to the surfaces or spread across the surfaces.

The practicality and versatility of polyDMAEMA brushes-coated substrates in capture, coalescence and release of oil droplets was demonstrated using ShellSol D80 (SS-D80) oil and nonpurified tap water. SS-D80 is a commercially available cocktail of aliphatic hydrocarbons with a low content of aromatics (density  $\approx 0.82$  kg L<sup>-1</sup> at 15 °C). In a similar way to the decane/water system, the adhesion and release of SS-D80 oil droplets on polyDMAEMA brushes-coated substrates ( $h_d \approx 16 \pm 1$  nm) in tap water was fully controllable via pH. An SS-D80 oil droplet that was captured on a substrate in water could be released upon acidification (Figure 2a). Increase in volume upon coalescence with other oil droplets in water eventually led to self-release of SS-D80 oil droplets from the surfaces in both water (Figure 2b) and acidified water (Figure 2c). In the latter case, dilution of acidified water and rinsing the substrate using acidic water successfully restored the surface adhesive attributes for capturing oil droplets. Comparing panel b and c in Figure 2, weaker surface-oil interaction forces were observed in the acidic conditions as indicated by a smaller maximum droplet size before self-release and a smaller amount of residual oil on the surfaces. This agrees with the calculated adhesion forces of SS-D80 oil droplets in tap water and acidified tap water, as shown in Table 1. These results clearly show that underwater-oil adhesion on substrates coated with polyDMAEMA brushes remained pH-responsive in nonpurified tap water containing oil with a polydisperse aliphatics composition. In addition, the



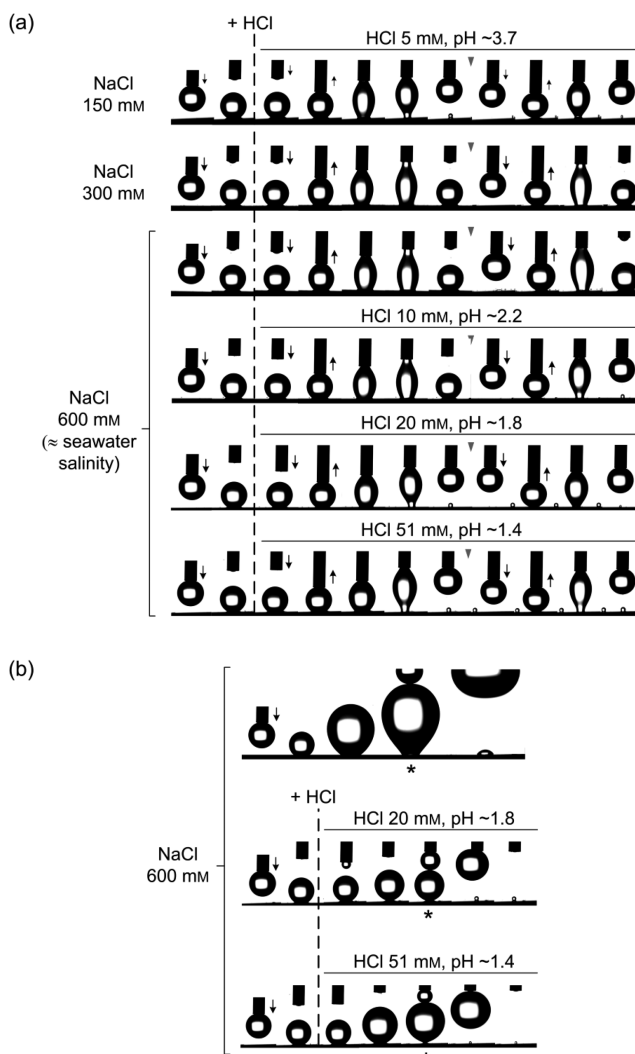
**Figure 2.** pH-dependent capture and release of SS-D80 oil droplets in nonpurified tap water on silicon wafers coated with polyDMAEMA brushes ( $h_d \approx 16 \pm 1$  nm). (a) pH-responsive adhesion and release of an oil droplet. (b) Self-release of an oil droplet in water under the influence of buoyancy. (c) Self-release of oil droplets in acidified water as a function of the droplet volume. In all cases, the initial volume of oil droplets captured on the surfaces was 2  $\mu$ L. The initial pH of water was  $\sim 6.5$  and a diluted HCl solution (500 mM) was used in acidification. Images in each series were acquired over a time scale at the same magnification with the same substrate. Last images before self-release of droplets are marked with \*.

coated substrates were robust and reusable and can be regenerated.

The effects of salt (NaCl) addition on this oil capture-release process were investigated using SS-D80 oil and nonpurified tap water. It is well-known that salt influences the properties of weak polyelectrolytes in solutions by disrupting the hydration layer surrounding the polymers and introducing a charge screening layer.<sup>32,37,38</sup> As a result, even in the acidic condition (pH 3), polyDMAEMA brushes shrank in NaCl solutions as a function of the salt concentration from  $\sim 125$  nm (no salt) to  $\sim 85$  nm (500 mM NaCl).<sup>32</sup> Similarly, pH-sensitive poly(acrylic acid) brushes grafted on spherical substrates swelled to a markedly lesser extent in 1 M KCl solution than in 1 mM KCl solution.<sup>37</sup> As shown in Figure 3a, pH-dependent adhesion and release of SS-D80 oil droplets were unaffected in a diluted NaCl solution (150 mM) wherein oil droplets adhering to the surfaces could be released upon acidification when polyDMAEMA brushes were protonated and hydrophilic. However, in more concentrated NaCl solutions (300 mM and above), more acidity was required to release oil droplets from the surfaces. In 600 mM NaCl solutions ( $\approx$  seawater salinity), SS-D80 oil droplets adhering to the substrates could only be released from the surfaces when the final HCl concentration reached 20 mM and above. The pH-responsive adhesion and release of SS-D80 oil droplets in 600 mM NaCl solution (20 mM HCl) was reversible for at least eight cycles based on two substrates. In more-concentrated NaCl solutions containing low  $H^+$  concentrations (e.g., 600 mM NaCl and 5 mM HCl), oil droplets adhered firmly to the surfaces and it was impossible to release the droplets from the substrates. Increasing the  $H^+$  concentration (e.g., 600 mM NaCl and 20 mM HCl) promoted ion exchange and hence protonation of the tertiary amine groups along polyDMAEMA chains, resulting in more hydrophilic surfaces and hence enabling oil droplets to be released. Essentially, like in decane/water and SS-D80/water systems, polyDMAEMA brushes-coated surfaces were resistant to oil fouling in NaCl solutions, i.e., oil droplets in 600 mM NaCl solution did not spread across the surfaces as the droplet volume increased but self-released from the surfaces when buoyancy became predominant (Figure 3b). Similar to both decane/water (Figure 1d) and SS-D80/water (Figure 2c) systems as discussed previously, weaker surface–oil interaction forces were observed in acidified NaCl solutions (Figure 3b) based on the droplet size before self-release and the amount of oil residue on the surfaces. This is also indicated by the calculated adhesion force for SS-80 oil droplets in acidified and nonacidified 600 mM NaCl solutions (Table 1).

## CONCLUSIONS

We have demonstrated the capture, coalescence, and release of light hydrocarbon oil droplets in water and brine solutions using fouling-resistant surfaces coated with pH-responsive polymer brushes. The polymer brush surface allowed oil droplets to be captured in response to the change of environmental pH. Oil droplets did not spread across the polymer brush surface upon volume increase but eventually self-released from the surfaces under the influence of buoyancy. The surfaces were resistant to oil fouling, which allowed them to be reused for capture-release of more oil droplets. The pH-responsiveness of the surfaces enabled the surfaces to be regenerated. We foresee that this capture-release model can be applied to small water-dispersed oil droplets, which will allow the droplets to be separated from bulk water and be collected at



**Figure 3.** pH-dependent capture and release of SS-D80 oil droplets in NaCl solutions on silicon wafers coated with polyDMAEMA brushes ( $h_d \approx 16 \pm 1$  nm). (a) Adhesion and release of oil droplets as a function of NaCl and  $H^+$  concentrations. Inverted blue triangles in the images indicate the same or new oil droplets were used to determine adhesion in the same solutions. (b) Self-release of oil droplets from the coated surfaces as a function of the droplet volume. In all cases, the initial volume of oil droplets captured on the surfaces was  $2 \mu\text{L}$ . NaCl solutions with initial pH  $\sim 8$  were prepared using nonpurified tap water and acidified using HCl solutions (0.5–5 M). Images in each series were acquired over a time scale at the same magnification with the same substrate. Last images before self-release of droplets are marked with \*.

the surface of water. Separation of such oil droplets from the water phase is a challenging task in the oilfield but as yet has received relatively less attention. This work has focused on a model system using a planar surface which can be studied in detail. In a real world application, a packed-bed system could be used in which oil/water dispersions will flow through a column, interacting with a much larger surface area. Potential key applications of this approach are in the separation of residual oil droplets from brine effluents produced by conventional oil/water separator facilities and in the cleanup of oil-in-seawater spillages.

## EXPERIMENTAL SECTION

**Materials.** 2-(Dimethylamino)ethyl methacrylate (DMAEMA), propyltrimethoxysilane, phenyltrimethoxysilane, octadecyltrimethoxysilane, and 1H, 1H, 2H, 2H-perfluorooctyl-trichlorosilane were purchased from Sigma-Aldrich. A sample of ShellSol D80 oil (ShellSol is a trademark of Shell Chemicals) was kindly provided by Schlumberger Gould Research. ATRP initiator, (3-trimethoxysilyl)propyl-2-bromo-2-methylpropionate **1**, was supplied by Gelest Inc. All chemicals and solvents were of analytical grades and used as received unless otherwise stated. Cu(I)Cl was kept under vacuum until needed. Triethylamine was distilled from KOH and stored over molecular sieves (3 Å grade). Purified water with a resistivity of 18.2 MΩ cm was obtained from a Millipore Synergy system. Anhydrous toluene was withdrawn from a PureSolv solvent purification system (Innovative Technology). Silicon wafers (diameter 100 mm, orientation <100>, one side polished) were purchased from Compant Technology and cleaned in an air plasma with a forward power of 100 W (Emitech K1050X plasma asher) for 10 min.

**Polymerization and Characterization.** A piece of plasma-oxidized silicon wafer was immersed in a solution of ATRP initiator **1** (3 μL), anhydrous toluene (50 mL), and triethylamine (3 μL) for 18 h to generate an initiator-terminated self-assembled layer. The wafer was rinsed with toluene, sonicated in acetone (1 min), rinsed with absolute ethanol and dried under a stream of nitrogen gas. Subsequently, polyDMAEMA brushes were synthesized on initiator-coated surfaces via surface-initiated ATRP according to the published protocol and formulation.<sup>20</sup> All steps were carried out at room temperature (~20 °C). Polymer thickness was determined via an  $\alpha$ -SE spectroscopic ellipsometer (J. A. Woollam) at an incident angle of 70°. For measurement of wet polymer thickness, substrates were placed in a custom-built liquid cell fitted with quartz windows normal to the laser beam path. A silicon substrate/Cauchy film model was used and fitted between 400 and 900 nm. Surface topography and root-mean-square roughness of dry substrates were determined via atomic force microscopy which was performed on a Dimension 3100 microscope (Veeco Instruments) using the tapping mode. Olympus OMCL-AC series silicon probes with a resonance frequency of 300 kHz and a spring constant of 42 N m<sup>-1</sup> were used. Images were processed using the NanoScope software (Veeco Instruments).

**Coating of Hydrophobic Monolayers.** A silicon wafer was immersed in a solution containing anhydrous toluene (50 mL), triethylamine (3 μL) and propyltrimethoxysilane (10 μL), phenyltrimethoxysilane (15 μL), octadecyltrimethoxysilane (10 μL) or perfluorooctyl-trichlorosilane (120 μL) for 18 h at room temperature. Substrates were rinsed with toluene, sonicated successively in toluene and acetone (1 min each) and rinsed with absolute ethanol before drying under a stream of nitrogen gas. For perfluorooctyltrichlorosilane, the wafer was sonicated additionally in isopropyl alcohol and hexane.<sup>20</sup>

**Capture, Coalescence, and Release of Oil Droplets in Water.** Tests were carried out on a FTA1000 contact angle instrument (First Ten Ångströms) with an adjustable sample stage at room temperature. Typically, a substrate was placed in a glass cuvette containing water or NaCl solution and an oil droplet was formed at the tip of a needle (22 G, blunt tip, outer diameter 0.711 mm and inner diameter 0.483 mm) above the substrate. The droplet was slowly approached to the substrate until they came into contact, after which the needle was slowly lifted from the surface. An oil droplet was captured if it remained on the surface. To increase the volume of a droplet adhering on a surface, a droplet was formed at the needle tip and the droplets were brought into contact for them to coalesce. This process was repeated until the desired volume was achieved. In all steps, extra care was taken to avoid squeezing the droplets toward the substrates. The pH of the water phase was adjusted via addition of HCl solution (prepared using purified water) in a dropwise manner without disturbing the substrates.

## ASSOCIATED CONTENT

### Supporting Information

Thicknesses of polyDMAEMA brushes coated on silicon wafers in dry, HCl solution and NaOH solution as a function of ATRP duration (Figure S1). AFM images (3D, 2D and cross-sectional view) of a dry silicon substrate grafted with polyDMAEMA brush (Figure S2). pH-dependent underwater capture and release of decane droplets on a silicon wafer coated with polyDMAEMA brush ( $h_d \approx 29 \pm 1$  nm) (Figure S3). Water droplets in air and decane droplets in water on silicon wafers modified with hydrophobic monolayers (Figure S4). Calculation of adhesion force. 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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