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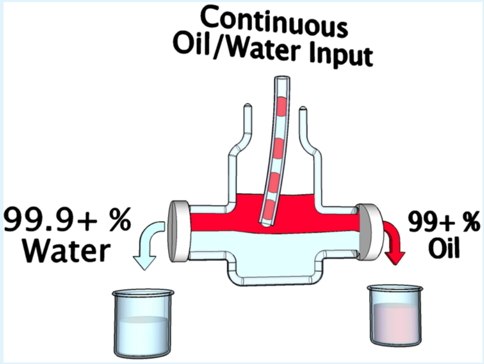
Continuous, High-Speed, and Efficient Oil/Water Separation using Meshes with Antagonistic Wetting Properties

Gary J. Dunderdale, Chihiro Urata, Tomoya Sato, Matt W. England, and Atsushi Hozumi*

National Institute of Advanced Industrial Science and Technology (AIST), 2266-98, Anagahora, Shimoshidami, Moriyama, Nagoya 463-8560, Japan

Supporting Information

ABSTRACT: We report a novel oil/water separation device, allowing continuous, high-speed, and highly efficient purification of large volumes of oily water. This device uses a pair of hydrophilic/hydrophobic polymer-brush-functionalized stainless steel meshes, which have antagonistic wetting properties, i.e., superoleophobic and superhydrophobic properties, when submerged in the opposite liquid phase. This device can purify large volumes of *n*-hexadecane/water mixture (~1000 L) in a continuous process rather than in batches, to high purities (~99.9% mol/mol) at high flow rates (~5 mL s^{-1} cm^{-2}), unlike the oil/water separation meshes reported so far.



KEYWORDS: *polymer brush, superhydrophobicity, superoleophobicity, oil/water separation, ARGET ATRP*

Pollution by industrial oily wastewater is a serious environmental concern, as many industries produce large volumes of oil-contaminated water, which must be purified before being released into the environment.[1] For example, a typical mining operation produces ~140 000 L of oily wastewater per day.[2] To address this issue, a variety of oil/water separation methods and materials have been reported. In industry, several types of mechanical devices including oil skimmers or booms[3] are used to remove oils. Alternatively, porous filtration materials such as sponges,[4,5] foams,[6,7] and textiles,[8−10] have been proposed as potentially useful in oil/water separation, but they suffer from low capacities/throughput.

Functionalized mesh membranes have recently attracted much attention because of their simplicity, high flow rates, and the low filtration pressures required.[11−15] However, these meshes can only be used in laboratory environments because of several limitations. First, the devices can only be used in a batch process to purify small volumes of oil/water mixtures (~30 mL). This is not suitable for industrial applications where large volumes of oily wastewater need to be purified at high flux rates. Second, as the mesh only filters a single phase (either oil or water), it does not purify both liquid phases simultaneously. This means that recaptured oils cannot be reused,[16] and if the oil phase is disposed of, the price is increased as it contains contaminant water. Third, because of adsorption and/or plugging by oil droplets during filtration, meshes (in particular, superhydrophobic meshes) are easy fouled by oils and hard to clean. This results in a quick decrease in flux rate and separation efficiency. Finally, preparation of conventional meshes typically relies on both complex surface texturing and the use of toxic long-chain perfluorinated compounds.[17−20]

To overcome these shortcomings, the development of a simple and effective oil/water separation system, which can purify large volumes of oil/water mixture with high efficiency and flux rate, is required. In addition, from a practical point of view and to prevent secondary pollution from toxic chemicals, the fabrication of separation meshes should not use surface roughening or perfluorination. Herein, we report for the first time a novel oil/water separation system that gives continuous, high purity and high-speed purification of large volumes of oily water. Our approach uses a pair of hydrophilic/hydrophobic polymer-brush functionalized stainless steel (SUS) meshes, with antagonistic wetting properties, to purify both the oil and water phases simultaneously.

To create these polymer brushes, a facile Activators ReGenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET-ATRP), using ascorbic acid (AA) as the reducing agent, was employed. In particular, we have developed reaction protocols that do not require the reaction solutions to be heated or purged of oxygen, as this makes the reactions extremely easy to perform. Sodium methacrylate (NaMA) was polymerized to create a hydrophilic water-selective poly(sodium methacrylate) (PNaMA) functionalized mesh,[21,22] and stearyl methacrylate (StMA) polymerized to create a hydrophobic oil-selective mesh[23] (Figure 1A).

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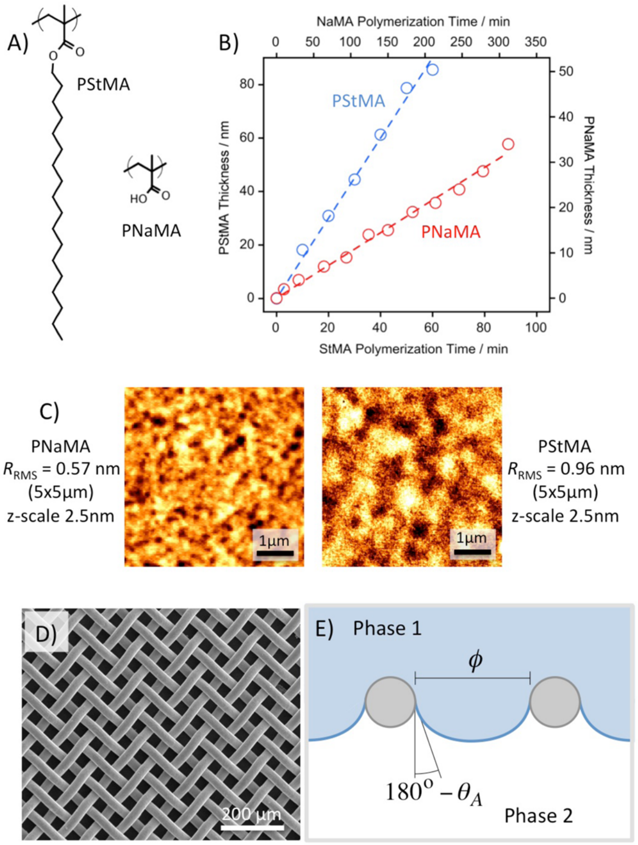

Figure 1. (A) Chemical structures of poly(sodium methacrylate) (PNaMA) and poly(stearyl methacrylate) (PStMA) brushes grown to yield hydrophilic and hydrophobic surfaces in air, respectively. (B) Kinetics of PNaMA (Red) and PStMA (Blue) brushes growth on Si substrates using ARGET-ATRP. The highly linear increase in thickness indicates a well-controlled polymerization. (C) Typical AFM images of the resulting surfaces confirmed that all samples surfaces were homogeneous and smooth. (D) Typical SEM image of the SUS mesh functionalized with polymer brushes. (E) Schematic illustration of the oil/water (phases 1/2) separation mechanism using a mesh with a pore size of ϕ, and an advancing contact angle of θ_A (phase 1 in phase 2).

Polymerization kinetics, as studied on Si reference surfaces, showed a fast and linear increase in thickness, indicating excellent retention of terminal halogen atoms on the growing polymer chains, and a well-controlled ATRP reaction (Figure 1B). This well-ordered polymerization can be achieved even though the amount of catalyst employed is reduced by around 75% compared to conventional ATRP reactions.[24,25] Polymerization of both monomers provided homogeneous coverage of substrates, and the resulting surfaces are smooth with a root-mean-squared roughness (R_{rms}) of less than 1 nm (Figure 1C).

In a similar manner, we functionalized SUS meshes with these polymer brushes to create both hydrophilic and hydrophobic meshes. The SUS mesh chosen was plain weave, with square pores around 40 μm diameter (Figure 1D). The mechanism of oil/water separation is shown in Figure 1E. For phase 1 to pass through the mesh it must advance across the mesh surface with a characteristic contact angle (advancing CA, θ_A) and displace phase 2. If θ_A is greater than 90°, there is a resistance to phase 1 passing through the mesh. This resistance, known as the inclusion pressure (P) can be calculated from the eq 1

$$P = \frac{4\gamma\cos(180^o - \theta_A)}{\phi} \tag{1}$$

where γ is the interfacial surface tension, θ_A the advancing CA of phase 1 moving across the surface in phase 2, and ϕ the size (length) of the square pore. Obviously, the resistance to a liquid passing through the pore is largest when the interfacial tension is high, the pore diameter small, and θ is small (high θ_A). Any θ_A value greater than 160° will result in 94% or more of the total possible resistance.

According to eq 1, it is θ_A submerged in oil or water, and not static CA in air (θ_S), which determines if a liquid can pass through the mesh. Also, it highlights that the phase in which the surface is submerged (either air, water, or oil) is important. So in fact, there are three different situations with three different θ_A values, which are important in determining the ability of a surface to act in an oil/water separation device. We measured these θ_A's on planar polymer brushes in the situations relevant to oil/water separation, as shown in Figure 2. Normally in oil/water separation, the mesh surface shows selectivity to either water or oil, being either superhydrophobic or superoleophobic. In contrast, our polymer brush surfaces show neither superhydrophobicity nor superoleophobicity in air. If the first liquid to wet the PNaMA-functionalized mesh is n-hexadecane, because of the small θ_A (6°), it can pass through the mesh, whereas if the first liquid to wet the PStMA mesh is water, due to the relatively low θ_A (103°), it would give only a slight resistance to water passing and not work effectively in oil/water separation. These θ_A values would result in low selectivity and poor oil/water separation and do not seem to meet the demands required for oil/water separation.

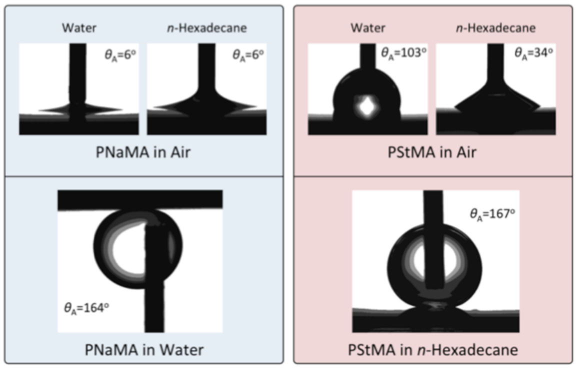

Figure 2. θ_A values of of water and n-hexadecane on PNaMA (left) and PStMA (right) brush surfaces grown on Si surfaces. PNaMA and PStMA surfaces show neither superhydrophobic nor superoleophobic behavior in air. But, when these surfaces are submerged in a liquid, PNaMA exhibits superoleophobicity (n-hexadecane droplet in water), and PStMA superhydrophobicity (water droplet submerged in n-hexadecane).

However, this problem is easily overcome by priming the PNaMA and PStMA meshes with a drop of water and n-hexadecane, respectively, before the oil/water mixture is added. Then, the θ_A values of n-hexadecane on PNaMA underwater (θ_A = 164°), and θ_A of water on PStMA mesh submerged in n-hexadecane (θ_A = 167°) (Figure 2 bottom) offer significant resistance to the passage of n-hexadecane and water, respectively. As far as we are aware, this simple method of priming meshes with a drop of liquid has never been reported

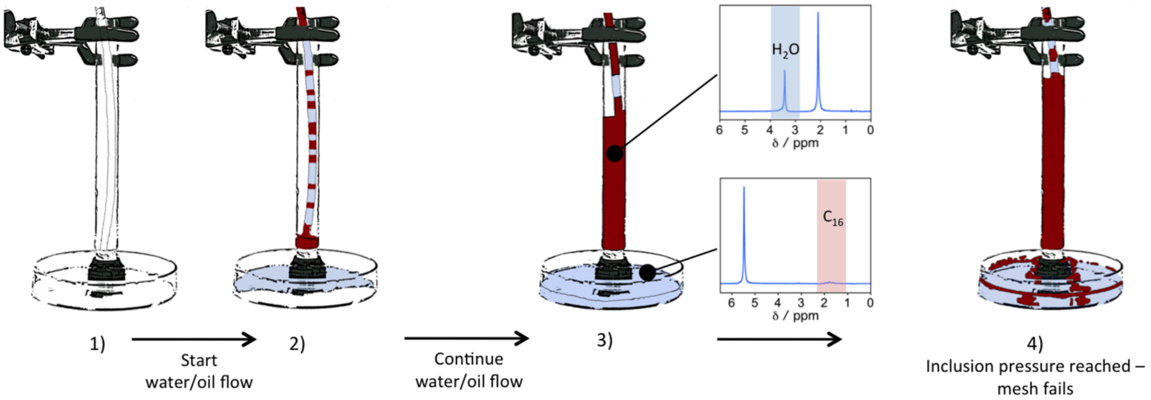

Figure 3. Oil/water separation using a single SUS mesh functionalized with hydrophilic PNaMA brush. (1) Initially, the mesh is dry and is primed with a drop of water; (2) then, a mixture of oil/water (50:50% v/v) is pumped to the mesh, water passes through the mesh, and oil is prevented from passing; (3) as the flow of oil/water continues, oil accumulates above the mesh; (4) eventually, this accumulated height of oil exceeds the inclusion pressure and the mesh fails, allowing oil to flow into the purified water. Insets in 3 show NMR analysis of the liquid phases above and below the mesh.

before, but its advantages are clear—smooth, nonperfluorinated materials can be used in oil/water separation devices.

As shown in Figure 3, we incorporated a PNaMA-functionalized mesh into an oil/water separation device to highlight the problems encountered when a single mesh rather than an antagonistic pair is used. The mesh was positioned at the bottom of the glass tube and primed with a drop of water. An *n*-hexadecane/water (50:50% v/v) mixture was then pumped into the device continuously at a rate of 100 mL min^{-1} (Figure 3(2)). Water (blue color) passed through the mesh and was collected below, whereas *n*-hexadecane could not pass through the mesh due to the high θ_A (164°), and so accumulated in the tube. With further pumping, water continued to pass through the mesh and *n*-hexadecane accumulated above the mesh (Figure 3(3)). We compared the performance of our PNaMA meshes to literature reports using NMR analysis. The purity of filtered water was found to be 100.00 ± 0.006% mol/mol, consistent with other reported functionalized meshes,[26−28] even though the mesh is non-perfluorinated and not nanostructured. On the other hand, the oil phase which remained above the mesh was very low purity, containing a large amount of water (7.9% mol/mol). This low purity is because the oil phase does not pass through a mesh filter, and so is not purified. This is a serious limitation of conventional oil/water separation meshes reported so far—they can selectively purify only one of the two phases (usually water).

Continuing pumping of *n*-hexadecane/water into the device, *n*-hexadecane continues to accumulate above the mesh. With increasing height of *n*-hexadecane, the pressure forcing *n*-hexadecane through the mesh increases, and eventually becomes comparable to the inclusion pressure eq 1. At this point, *n*-hexadecane is forced through the PNaMA-modified mesh (Figure 3(4)), resulting in contamination of the previously purified water. This is the second problem of conventional oil/water meshes reported so far: they are only able to purify a small amount (batch) of oil/water mixture before the inclusion pressure is reached.

To overcome these two problems, we constructed an apparatus which uses two antagonistic meshes—one hydrophilic PNaMA mesh, and one hydrophobic PStMA mesh (Figure 4A). Again, these meshes were first primed with a drop of water for the PNaMA mesh and *n*-hexadecane for the PStMA mesh.

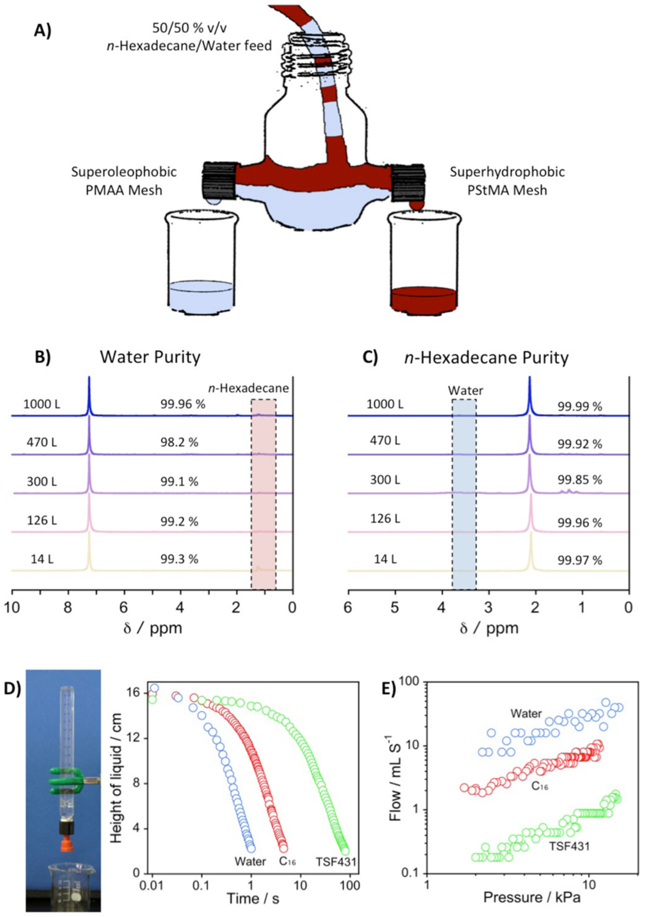

Figure 4. Oil/water separation system using two antagonistic polymer brush-functionalized meshes. (A) An ∼50:50% v/v mixture of *n*-hexadecane/water was continuously pumped into the separation apparatus. NMR analysis of (B) water and (C) *n*-hexadecane confirmed that highly purified liquid phases were achieved, even after 1000 L had passed through the apparatus. (D) Drain speeds of water (blue), *n*-hexadecane (red), and TSF431 silicon oil (green) through functionalized meshes in the experimental configuration shown in the photo. (E) Flow rates of those liquids at different pressures.

When a 50:50% v/v mixture of *n*-hexadecane/water was pumped into this apparatus, water flowed through the PNaMA mesh, and *n*-hexadecane through the PStMA mesh, and a buildup of either component prevented. Oil/water mixtures of high and low oil volume fraction were also tested (90:10% and 10:90% v/v) and passed through the meshes easily without any significant buildup of either component. Although the minor volume liquid flowed through the respective mesh periodically after enough was pumped into the cell to create physical contact with the appropriate mesh (see Movie S1, Movie S2, and Movie S3). Although this does not affect the performance, it could be avoided by designing a separation apparatus that accounts for differences in liquid density and places meshes at the correct height for contact with either oil or water.

NMR analysis of filtrates showed high quality purification (99−100% ± 0.4% mol/mol) of both *n*-hexadecane and water, and this high selectivity was maintained when more viscous oils such as a metal cutting lubricant (silicon oil TSF431, 100 cSt) was separated from water (see Supporting Information). We continued the flow of *n*-hexadecane/water mixture into the separation apparatus for up to 1 week (a total oil/water mixture of 1000 L) and periodically took samples of filtrates. At all times high purity separation was observed (Figure 4B, C). This is in marked contrast to the single functionalized meshes reported so far, which can purify only one of the phases and separate only small amounts of oil/water mixtures. As a comparison, the single mesh shown in Figure 3 failed after only ∼14 mL of mixture had flowed into the apparatus.

Consistent with this high-quality purification, the measured drain rates of water through PNaMA meshes and *n*-hexadecane through PStMA meshes were found to be high (Figures 4D, E). Depending on the pressure at which the liquid is run through the mesh, flow rates of >2 mL s^{-1} can be obtained using a mesh of 1 cm diameter. This is important in industrial applications where large volumes of mixtures need to be purified quickly. Although, more viscous oils (TSF431, 100 cSt) flowed through the meshes more slowly, they still flowed at reasonable rates at low pressures, in contrast to alternative purification mechanisms such as ultrafiltration.

In conclusion, we have highlighted that polymer brush-functionalized meshes can function highly effectively as oil/water separation meshes, even though they are smooth, nonperfluorinated, and exhibit neither superhydrophobicity nor superoleophobicity in air. As discussed, it is the advancing contact angles of water and oil submerged in the opposite liquid phase which determines the performance of oil/water separation. Using a pair of antagonistic meshes rather than just a single mesh, prevents the buildup of either oil or water above the mesh, and also simultaneously purifies both phases to high purity (99−100 ± 0.4%). This allows our reported oil/water separation device to run continuously, and separate large volumes of oily water (∼1000 L) at high flow rates (∼5 mL s^{-1} cm^{-2}). We hope that this type of technology will be useful in the treatment of contaminated water (or oil) in industrially relevant situations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06207.

Details of polymer brush synthesis and further information on the calculation of purity by NMR A (PDF)

Time-lapse movie of continuous oil/water separation (MPG)

Time-lapse movie of oil/water separation using 90:10 v/v water:*n*-hexadecane (MPG)

Time-lapse movie of oil/water separation using 10:90 v/v water:*n*-hexadecane (MPG)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: a.hozumi@aist.go.jp.

Notes

The authors declare no competing financial interest.

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