# Supporting Information

# Hydrophobic Meshes for Oil Spill Recovery Devices

*Da Deng,[a,b,‡] Daniel P. Prendergast,[a,‡] John MacFarlane,[a] Roberto Bagatin,[c]  Francesco Stellacci,[d,*] Philip M. Gschwend,[a,*]*

[a] Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

[b] Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI, 48202, USA

[c] Research Centre for Non-Conventional Energy – Istituto Eni Donegani Environmental Technologies, Via Fauser 4, I-28100 Novara, Italy

[d] Institute of Materials, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, CH-1015, Switzerland

‡ These authors contributed equally to this work.

* To whom all correspondence should be addressed: Francesco Stellacci [francesco.stellacci@epfl.ch] and/or Philip Gschwend [pmgschwe@mit.edu].

| TOPIC | PAGE |
|---|---|

## Optical Microscopy Images of all Coated Meshes

An inverted optical microscope was used to characterize the size and shape of the openings within three mesh sizes (uncoated opening widths of 100 μm, 220 μm, and 1500 μm) coated with a LDPE-xylene solution of 15, 30, or 60 mg/mL. For all mesh sizes, as the coating concentration increased, the size of the openings decreased, and the openings grew more jagged and irregular. Based on SEM micrographs of the 220 μm mesh (see Figure 2, main text), the jagged openings indicate a rougher coating of LDPE.
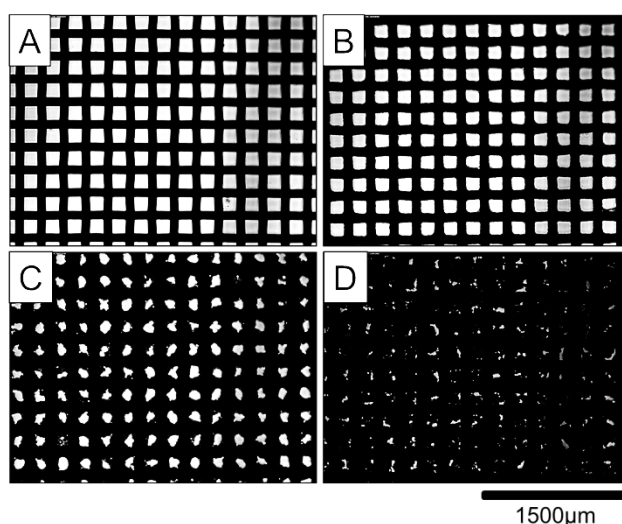


**Figure S1.** Stainless steel mesh (uncoated opening size 100 μm) as: (A) bare mesh without LDPE coating; (B) coated with low concentration LDPE solution (15 mg LDPE/mL xylene); (C) coated with medium concentration LDPE solution (30 mg LDPE/mL xylene); (D) coated with high concentration of LDPE solution (60 mg LDPE/mL xylene).

**Figure S2.** Stainless steel mesh (uncoated opening size 220 µm) as: (A) bare mesh without LDPE coating; (B) coated with low concentration LDPE solution (15 mg LDPE/mL xylene); (C) coated with medium concentration LDPE solution (30 mg LDPE/mL xylene); (D) coated with high concentration of LDPE solution (60 mg LDPE/mL xylene).
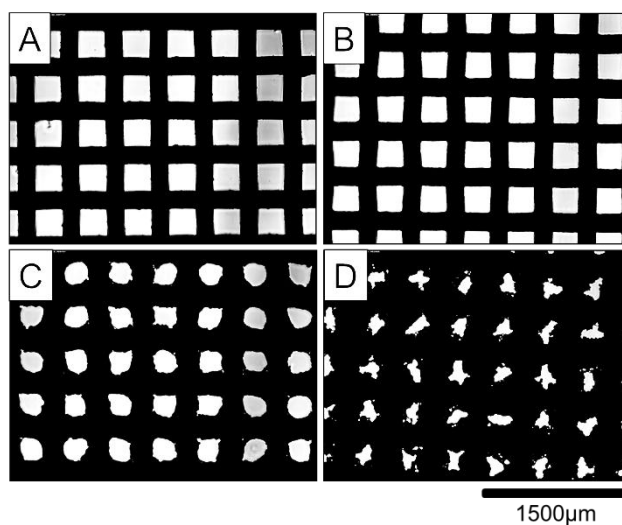


**Figure S3.** Stainless steel mesh (opening size 1500 µm) as: (A) bare mesh without LDPE coating; (B) coated with low concentration LDPE solution (15 mg LDPE/mL xylene); (C) coated with medium concentration LDPE solution (30 mg LDPE/mL xylene); (D) coated with high concentration of LDPE solution (60 mg LDPE/mL xylene).
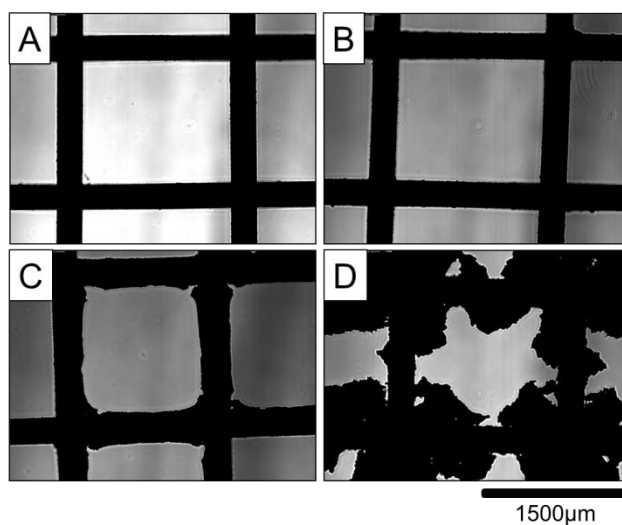
## Scanning Electron Microscopy (SEM) Micrographs

       SEM micrographs of various meshes and coating concentrations are shown in Figures S4 and S5. Some of these images also appear in the main text in Figures 2, 3, and 4.
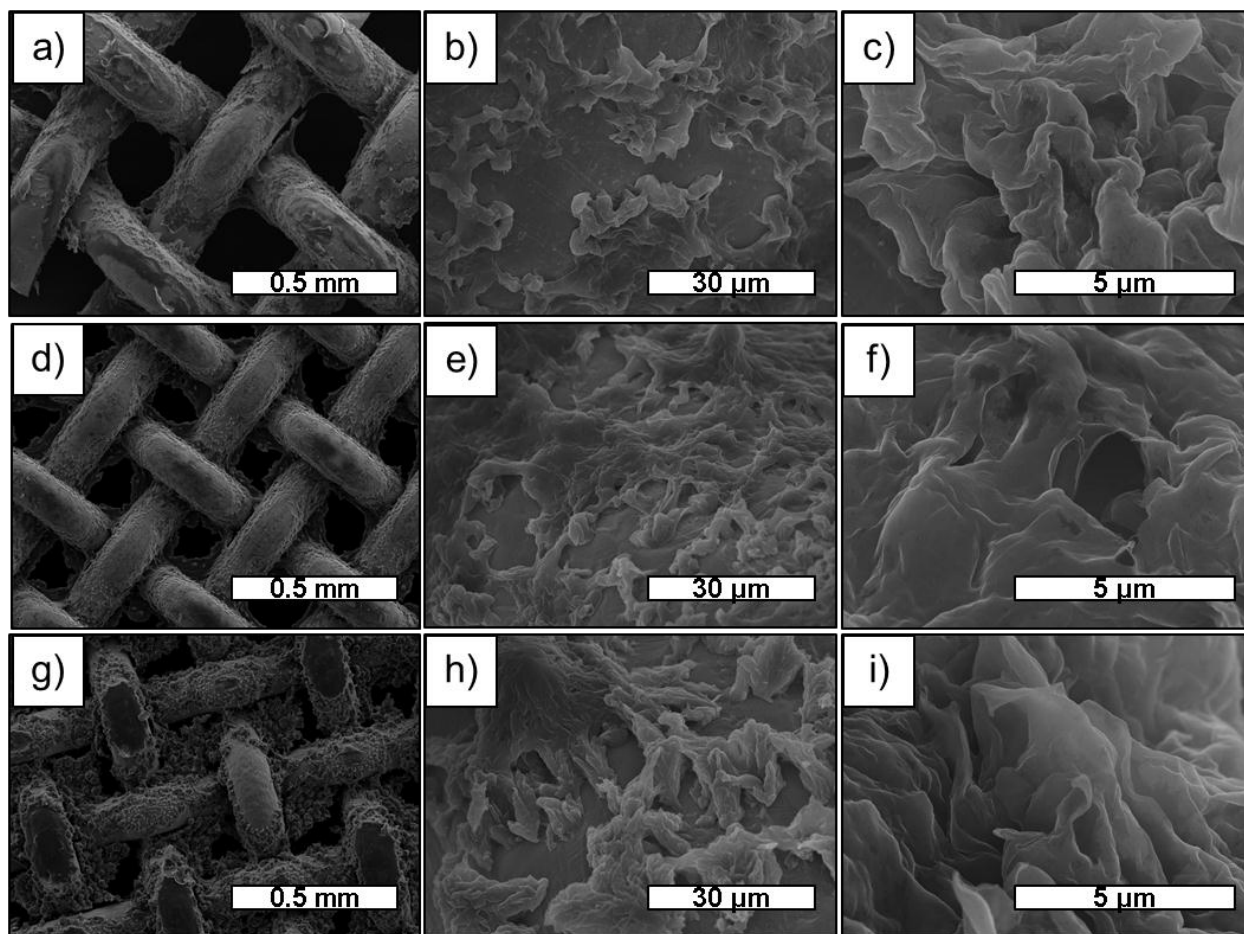


**Figure S4.** SEM micrographs of the 220 μm mesh with coating concentrations of 15 mg/mL (a, b, c) 30 mg/mL (d, e, f) and 60 mg/mL (g, h, i).
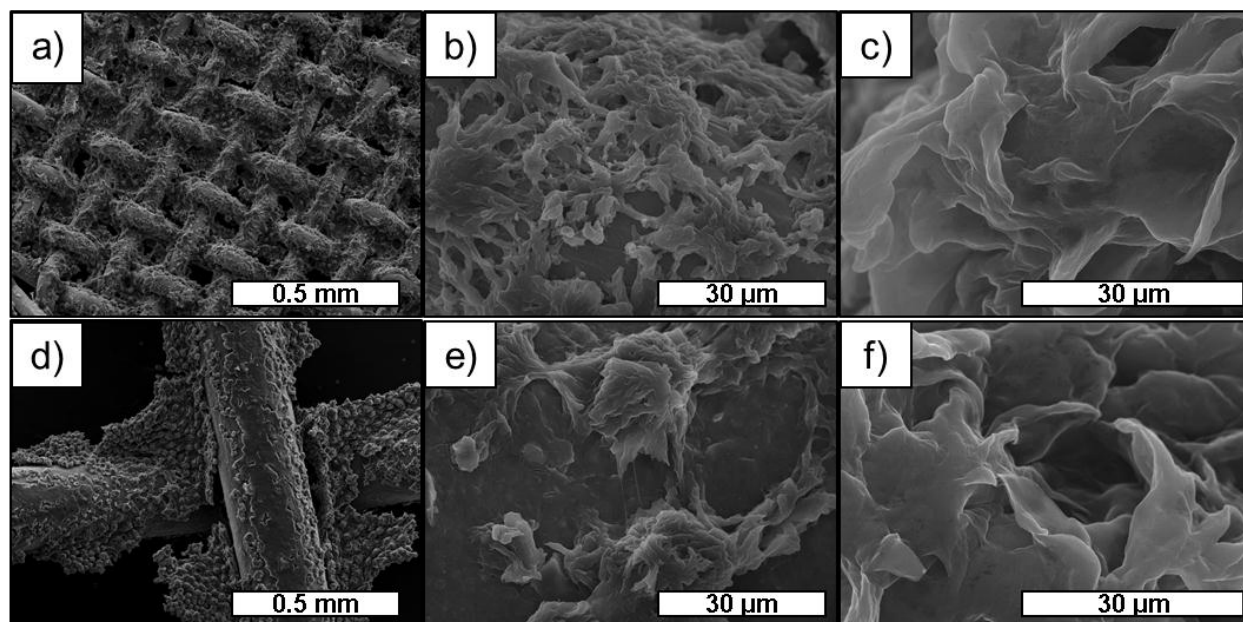
**Figure S5.** SEM micrographs of the 100 μm mesh (a, b,c) and the 1500 μm mesh (d, e, f) with a coating concentration of 60 mg/mL.

## Atomic Force Microscopy (AFM) Images

AFM was used to probe the most raised portions of 220 μm meshes with various coating concentrations (Figures S6, S7, and S8). These data cannot be used to estimate the overall LDPE roughness because only the uppermost, least coasted, wire surfaces could be tested with the probe. However, the increasing roughness of these surfaces (Table 3; main text) indicate that even without the formation of LDPE microstructures, an LDPE coating is present, which becomes rougher with increasing coating concentration.
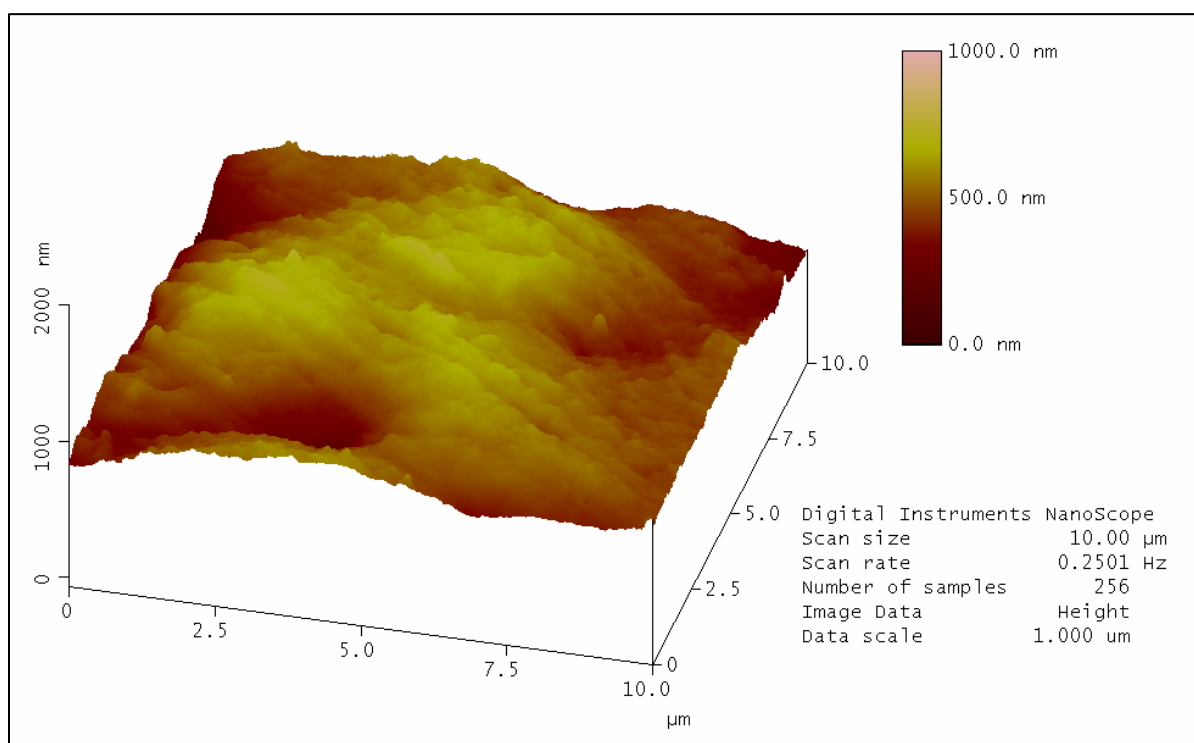


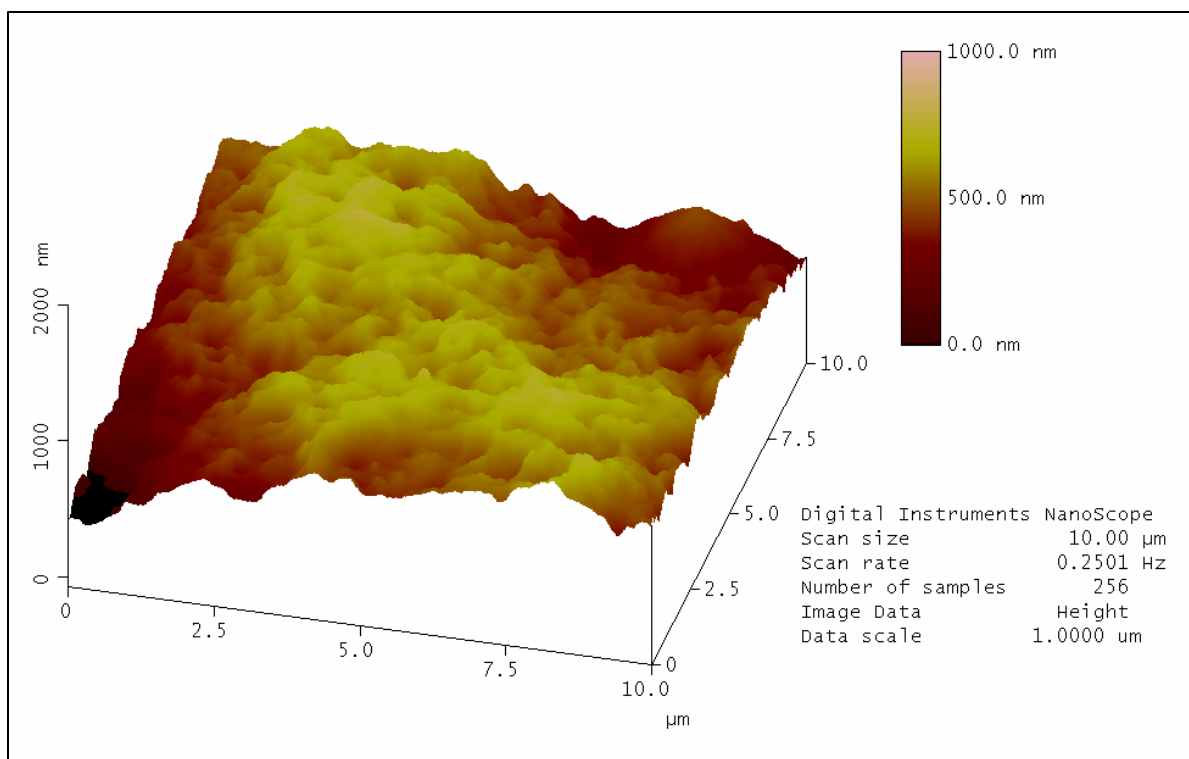**Figure S6.** AFM surface plot of a 220 μm mesh coated with a 15 mg/mL LDPE-xylene solution.

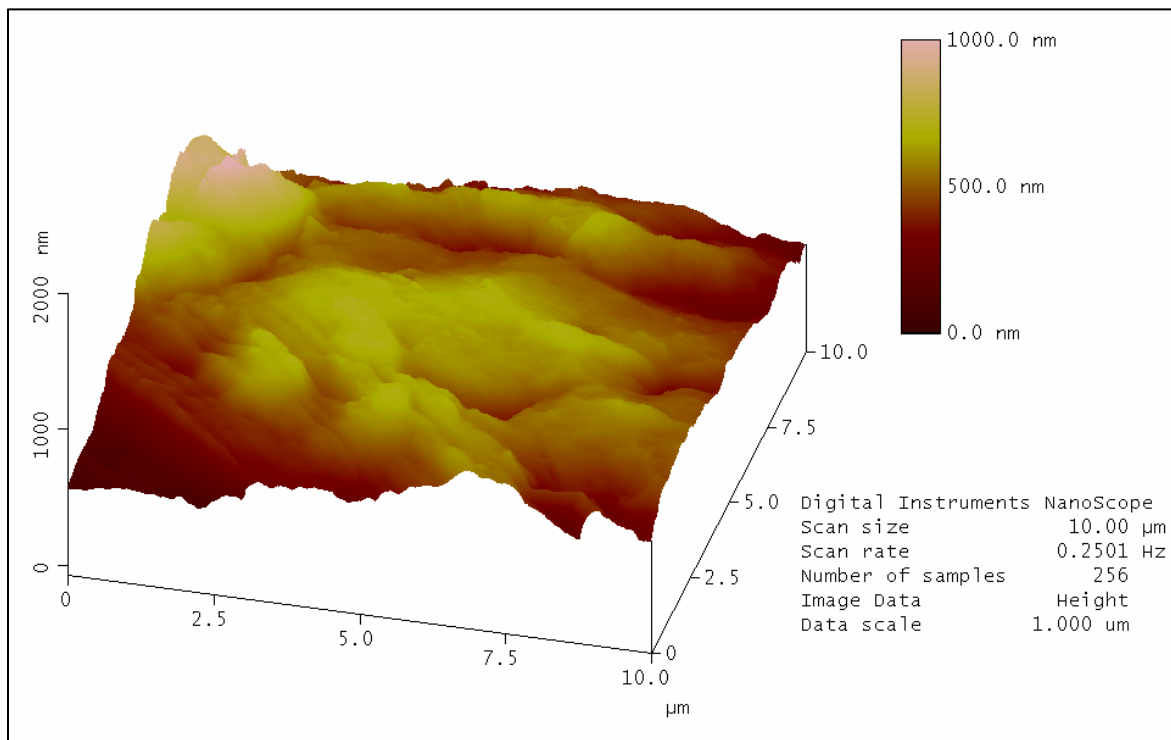**Figure S7.** AFM surface plot of a 220 μm mesh coated with a 30 mg/mL LDPE-xylene solution.



**Figure S8.** AFM surface plot of a 220 μm mesh coated with a 60 mg/mL LDPE-xylene solution.

## Effect of Rinsing with Dichloromethane

A 100 μm mesh coated with a 60 mg/mL LDPE-xylene solution was used to separate 25 mL of Kuwait crude oil from seawater. Afterwards, the mesh was rinsed with dichloromethane to remove the oil. SEM micrographs of the coating before separation and after rinsing are shown in Figure S9. The solvent did not visibly erode the coating, indicating it can be reused multiple times and rinsed with nonpolar solvents to remove adhered oil.
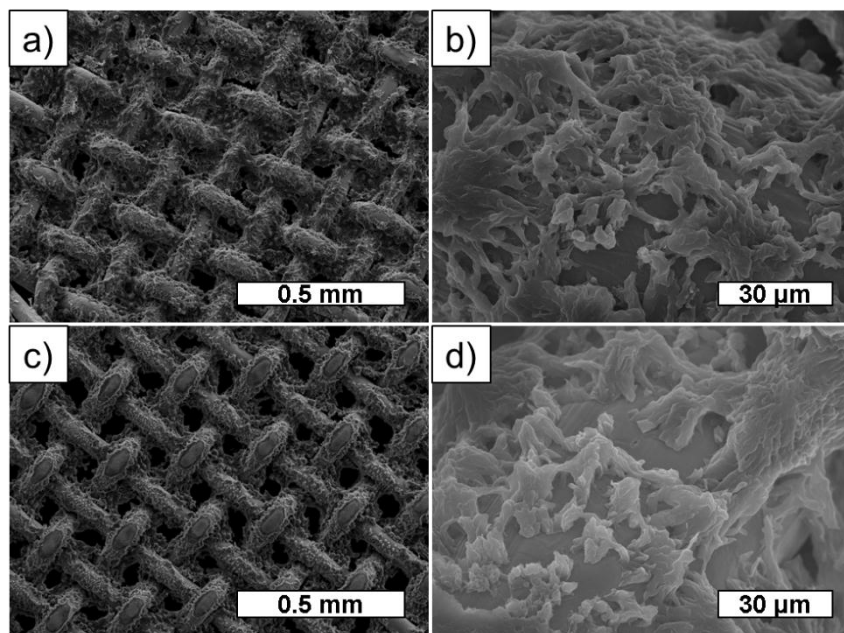


**Figure S9.** SEM micrographs of a 100 μm mesh with a 60 mg/mL LDPE-xylene coating before (a,b) and after (c,d) separating crude oil and being rinsed with dichloromethane.

## Persistent Wetting of Meshes by Oil

A 100 μm mesh coated with a 60 mg/mL LDPE-xylene solution was used to separate olive oil from water. The oil persistently wetted the mesh, filling the interstitial spaces of the mesh and covering all but the most raised potions of the woven wires. This lowered the water contact angle of the mesh from 127±2° to 108±2°, reflecting both a decrease in the fraction of air in contact with the water droplet, and a smoother surface. Thus, meshes that have been brought in contact with oil act much more like smooth, continuous LDPE surfaces than rough LDPE with micro-scale openings. Predictions of mesh performance, especially breakthrough depth, should take this changed behavior into account.
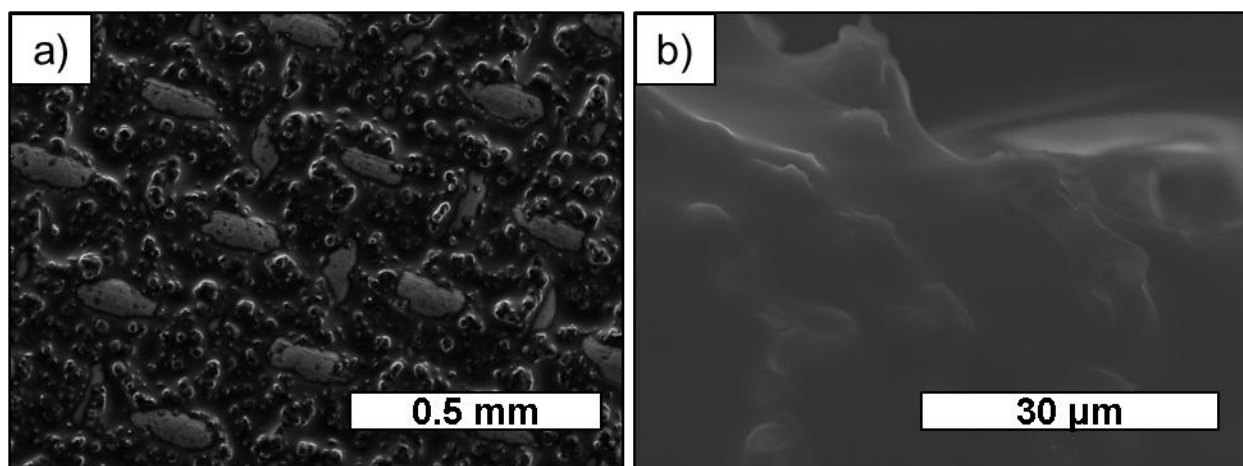


**Figure S10.** Olive oil wetting a 100 μm mesh coated with a 60 mg/mL LDPE-xylene solution. The oil fills the interstitial spaces of the mesh (a), making the surface much smoother (b).

## Differential Scanning Calorimetry (DSC) Analysis

DSC was used to evaluate the crystallinity of the LDPE coatings on a series of 220 μm meshes with various coating concentrations. The enthalpy of fusion of each sample was measured directly using the following temperature program for each run:

1) Heat from 50.0°C to 80.0°C at 20.0°C/min

2) Hold for 1.0 min at 80.0°C

3) Heat from 80.0°C to 160.0°C at 20.0°C/min

4) Hold for 1.0 min at 160.0°C

5) Cool from 160.0°C to 80.0°C at 20.0°C/min

The percent crystallinity values were calculated using a value of 290 J/g used for fully crystalline LDPE.[1] The values in Table S1 are the average of three runs, with experimental errors reported. The masses measured were quite low, due to the low mass ratio of the LDPE coating to the steel substrate. The two measured samples are mostly amorphous (~80%), and have approximately equal crystallinity. Figure S11 shows the melting curves of the 30 and 60 mg/mL LDPE coatings. No melting curve could be observed for the 15 mg/mL mesh due to the small sample mass.

**Table S1: Crystallinity of coated 220 μm mesh.**

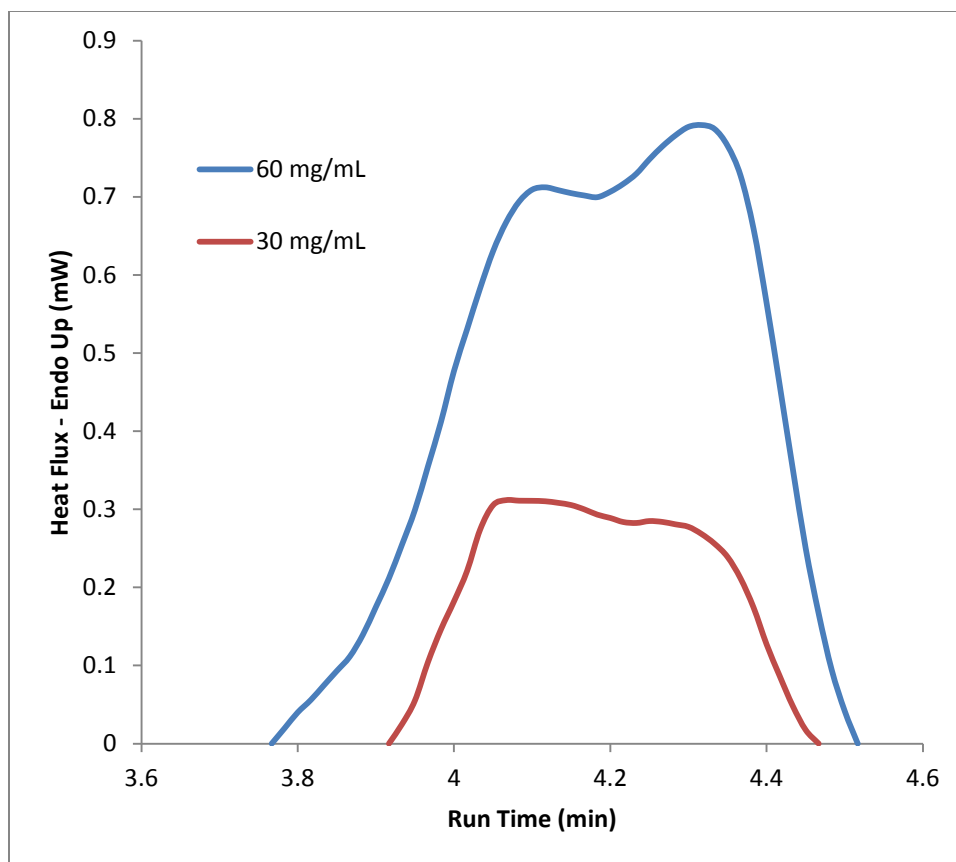| Coating Concentration (mg/mL) | Mass of LDPE Tested (μg) | Enthalpy of Fusion (J/g) | % Crystallinity |
|---|---|---|---|
| 15 ± 1 | 85 ± 3 | BDL | N/A |
| 30 ± 2 | 130 ± 4 | 55 ± 6 | 19 ± 2% |
| 60 ± 4 | 344 ± 10 | 61 ± 7 | 21 ± 3% |

**Figure S11:** Baseline-subtracted melting peaks for the medium mesh with various coatings. The mass ratios of LDPE to SS for the 60, 30, and 15 mg/mL coatings were 0.017, 0.0069, and 0.0037, respectively.

**Feasibility Experiments**

The LDPE coated meshes were initially evaluated for use in oil-water separations using proof of concept testing. First, a 1500 μm mesh was coated in a 60 mg/mL LDPE-xylene solution as described in the main text. It was then folded into boat-like shape and its separation ability tested by both "bottom–up" and "top-down" methods. The "bottom-up" method tested the ability of the mesh to recover oil from a layer atop a pool of water. The hydrophobicity of the coated boat was clearly demonstrated by its ability to float on a water surface without sinking. When the boat was put atop a floating layer of oil, the oleophilic nature of the boat allowed the oil to percolate through the mesh and accumulate inside. At the same time, the hydrophobic nature of the coated mesh prevented the water from entering, achieving effective oil-water separation. As compared with the original oil-water system, all visible oil was completely removed, and the oil was pipetted into another container without forming a visible layer of water. This test exhibited the ability of the LDPE-coated mesh to draw oil through it *via* capillary action, even upwards against gravity. Thus, oil-water separations may not need to be driven by hydrostatic pressure; depending on the mesh characteristics and desired oil flux, the oleophilic LDPE coating alone can drive the separation.

In contrast, the top-down method is more similar to a filtering process. A non-emulsified mixture of canola oil and water was slowly poured into a LDPE-coated mesh boat identical to the one used in the bottom-up test. The oil passed through the oleophilic boat, while the water was retained inside, where it could be easily collected. The resultant oil and water fractions were clearly separated from one another. The LDPE coated mesh was able to allow the percolation of oil without the concomitant passage of water, despite the presence of both.

**Description of Experimental Video**

       A video of the bench-scale oil collection unit has been provided as part of the supporting information. It depicts the separation of canola oil (0.5 cm thick yellow layer) from water (dyed blue with copper (II) sulfate) in a beaker. Prior to the video, a test tube with "windows" cut into the sides and covered with the 220 μm mesh with a 60 mg/mL coating was lowered into the beaker and brought into contact with the oil and water. At the start of the video, oil was allowed to accumulate in the bottom of the test tube, below the mesh. A peristaltic pump was then used to remove the collected oil into a nearby collection vial. Although the video did not exactly mimic the experiments used to determine the oil permeate flux (in this case, the oil was allowed to collect in the bottom of the test tube before pumping), the video clearly shows continuous *in situ* separation of oil and water.

**References**

(1) Wunderlich, B; In *Thermal Analysis*, 1st ed.; Academic Press: New York, **1990**; p 780.