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A switchable mesh for on-demand oil–water separation†

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Cite this: *J. Mater. Chem. A*, 2014, 2, 15284Received 16th June 2014
Accepted 28th July 2014

DOI: 10.1039/c4ta03034f

www.rsc.org/MaterialsA

We report a switchable mesh for oil–water separation that allows handling of various oil–water mixtures in one single device. The mesh operates in oil-removing mode to permeate typical oils in oil–water mixtures, and can rapidly switch to water-removing mode to permeate water and separate viscous and sticky oils from the mixture, both with high separation efficiency.

A growing appreciation for the negative environmental and economic consequences of oil and oily wastewater spills has made the separation of oil–water mixtures a topic of heightened technological interest.¹ Porous materials displaying simultaneous hydrophobic and oleophilic wettabilities can remove oil from water *via* selective uptake and transport of oil.^{1a,2} Similar materials with selective wetting find application in technologies as diverse as self-cleaning, biocompatibility, and protein anti-adhesion.³ The removal of oil from water by hydrophobically modified, oil-selective meshes has been demonstrated several times previously.^{3,4} In these examples, oil selectively passes through the modified mesh while water does not. However, the meshes could be fouled, or even blocked, by exposure to adhesive or highly viscous oils.^{2b,5} To address these problems, porous materials with recyclable or recoverable wetting properties have been proposed.⁶ Analogously, porous materials that act in reverse, selectively isolating water from oil–water mixtures, have been developed in recent years.^{2b,7} Therefore, there are separate oil-removing and water-removing approaches to oil–water separation, and the best option will depend on the composition of the oil–water mixture and the characteristics of the oil involved. The most practical separation device should have the versatility to handle both options. Oil removal has always been accomplished by mesh surfaces that are both

hydrophobic and oleophilic, exemplified by low surface energy materials such as fluoro- and silicone-compounds, whereas water removal has always been accomplished by mesh surfaces that are hydrophilic. While for either case, the best surface materials are rough, a feature affecting wettability and allowing some of the separated liquid to be trapped in surface porosity; the mesh surface energy for the two cases is quite different. For this reason, oil and water removal by one single mesh remains a challenge. Polyelectrolyte multilayers (PEMs) fabricated *via* the layer-by-layer (LbL) assembly strategy on a wide variety of substrates, including polymers, oxides, and metals of various sizes and shapes, have emerged as efficient coatings for surface wettability manipulation.^{1c} In this communication, a switchable PEM coating applied to stainless steel meshes is described, a coating that enables on-demand separation of oil from water or *vice versa*. Switchability is achieved by fast and easy ion exchange of PEM counterions.

The sol–gel strategy affords a versatile route to micro/nano-structured surfaces. Other approaches to these rough surfaces are more laborious and sometimes limited to particular substrate geometries. The literature sol–gel procedure followed here creates a micro/nano hierarchical alumina coating on stainless steel.⁸ As indicated by the scanning electron microscopy (SEM) images of Fig. 1, after boiling in water, a coated 61 μm pore size stainless steel mesh gains a homogeneous field of approximate 20 nm “puckers” on all its surfaces (Fig. 1b and inset). At lower magnification (Fig. 1a and inset), some fractal micro-flakes are observed randomly attached to the mesh, but their attachment density is too low to hinder significantly the passage of liquids. The optical images of Fig. 1 demonstrate that the alumina-coated 61 μm mesh supports 1,2-dichloroethane oil contact angle (OCA) values of 0° and 164 \pm 4°, in air and under water, respectively. The surface is thus superoleophobic under water but superoleophilic in air, expected outcomes considering that a polished aluminum plate, with its hydrophilic, high energy oxide surface, displays a water contact angle (WCA) of \sim 80°.^{1c} Underwater, the hydrophilic coated mesh surface is not wetted by oil because replacing water

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† Electronic supplementary information (ESI) available: Experimental details, XPS, reversible switching and additional contact angle data. See DOI: 10.1039/c4ta03034f

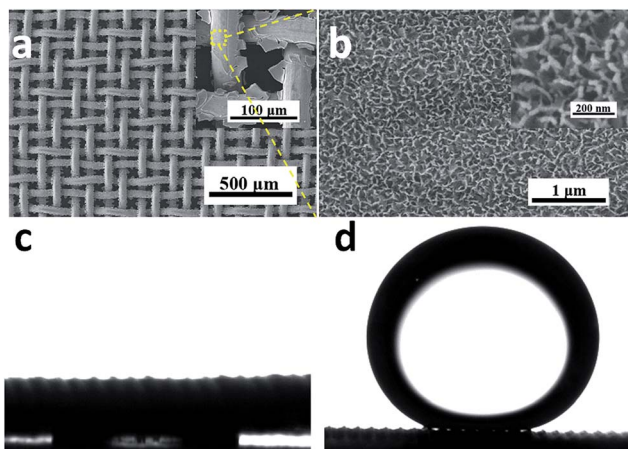


Fig. 1 (a and b) SEM images of an alumina-coated mesh of 61 μm average pore size: (a) large-area view with the inset showing a single pore; (b) high magnification image of alumina nanopuckers. (c and d) Optical images of 1,2-dichloroethane (c) completely wetting an alumina-coated mesh and (d) sitting on the same mesh under water with an OCA of 164°.

molecules by oil molecules on alumina is energetically unfavorable.^{1c} Consequently, through selective transport of water, the mesh can remove water from oil–water mixtures. Similar properties were observed previously for meshes coated with either rough hydrogels^{2b} or copper hydroxide.^{7b}

To remove oil from oily water, a mesh's surface must be superhydrophobic and superoleophilic. We previously demonstrated that the wettability of PEMs can be controlled by counterion exchange.⁹ In particular, PEMs assembled from poly(methyl sodium silicate) (PMSS) and poly(allylamine hydrochloride) (PAH) carrying the relatively low surface energy counteranion decanoate (ESI^\dagger) exhibit the desired hydrophobicity and high oleophilicity. When deposited on rough alumina-coated meshes, the WCA of $(\text{PAH}/\text{PMSS})_n$, where n is the number of bilayers, is independent of n (ESI ; Fig. S1†). Combining this finding with knowledge that defects emerge with n for PEMs grown on rough surfaces, we chose $n = 2.5$ for subsequent investigations. This PEM is so thin that it does not alter the rough alumina surface topography, as demonstrated in Fig. 2a and b. The mesh coated with the PEM carrying the decanoate counteranion, denoted as the PEM- C_{10} -mesh, is now highly hydrophobic ($\text{WCA} = 145 \pm 2^\circ$, Fig. 2c), and more importantly, superoleophilic, with a 1,2-dichloroethane OCA less than 5° (ESI ; Fig. S2†).

Diesel oil can be seen in Fig. 2e spreading on, and then permeating through a PEM- C_{10} -mesh. The deposited droplets pass through the mesh quickly, and if more droplets are deposited, the same behaviour is seen again. Oppositely, deposited water droplets do not wet or permeate the mesh. The mesh is highly suited to the separation of oil from oil–water mixtures, as seen in action in Fig. 3a and b. Diesel oil, slightly yellow and of low viscosity (about 5 cp), in a diesel–water mixture poured onto the PEM- C_{10} -mesh permeates through very rapidly into a vessel underneath, whereas the water overflows and is collected in a surrounding beaker, resulting in a clean separation.

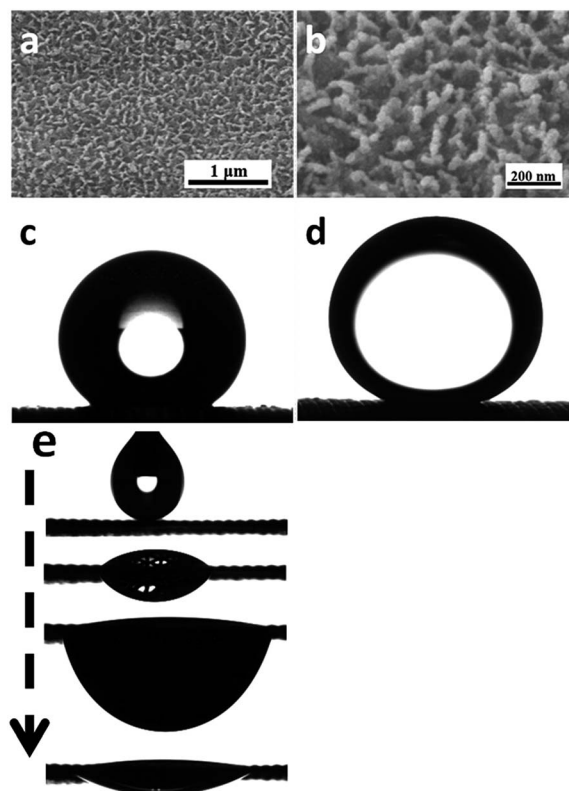


Fig. 2 (a and b) Low and high magnification SEM images of the PEM- C_{10} -mesh surface. (c) Optical image of the WCA for the PEM- C_{10} -mesh in air. (d) Optical image of the 1,2-dichloroethane OCA for the PEM-Cl-mesh underwater. (e) Spreading and permeation of diesel oil for the PEM- C_{10} -mesh.

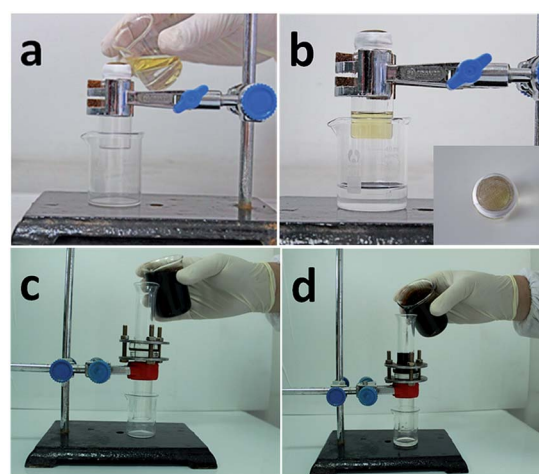


Fig. 3 Photographs of oil–water separation in the filtration-type device. (a and b) For PEM- C_{10} -mesh mounted on top of a glass bottle, the diesel–water mixture poised above the device before separation (a) and after separation (b); the oil permeate is in the bottle and the water retentate is in the surrounding beaker. The inset shows the mesh. (c and d) For the PEM-Cl-mesh placed in between two glass tubes, crude oil–water separation recorded analogously to (a) and (b); now, the water permeate is in the surrounding beaker and the oil retentate is in the tube above the mesh.

The PEM-C₁₀-mesh, while effectively separating low viscosity oils from oily water, is easily contaminated, and even blocked, by high viscosity oils. The same problems arise with sticky oil, and in both instances, the degraded mesh then itself becomes a potential source of secondary oil pollution, a common issue inherent to oil-removing meshes. Practical applications demand meshes that resist oil contamination and that are easily rejuvenated. A water-removing mesh, on the other hand, by permeating water and retaining the oil, achieves these properties when handling oily water containing viscous or sticky oils. The PEM coating on the mesh allows a convenient switch of the same mesh from oil-removing to water-removing. The latter requires higher surface energy as well as underwater superoleophobicity, features sought by exchanging decanoate counterions by chloride counterions in the PEM. We previously demonstrated the tuning of PEM wetting by counterion exchange.^{9b} Here, the PEM-C₁₀-mesh is simply immersed in 1 M aqueous sodium chloride for 5 min; chloride counterions are thereby introduced into the PEM's outermost layer (ESI; Fig. S3†). Fig. 2d shows that PEMs carrying the high surface energy Cl⁻ display reasonable hydrophilicity, with a WCA of 35° in air (ESI; Fig. S4†), and superoleophobicity, with a 1,2-dichloroethane OCA of 159° underwater. The underwater Cassie model rationalizes these behaviors.^{7b} The now chloride-exchanged mesh, designated the PEM-Cl-mesh, has the right characteristics to separate water from oil–water mixtures and potential to resist oil contamination. This is demonstrated with a mixture of water and crude oil, densely black and of high viscosity (about 1200 cp or greater), in Fig. 3c and d. Water is seen to quickly permeate the mesh, leaving the highly viscous oil to be collected separately. The lack of color in the permeate documents the quality of this separation, showing similar separation efficacy as that achieved by other water-removing meshes.^{2b,7b} The PEM-Cl-mesh can be switched back to a PEM-C₁₀-mesh by treating the mesh with a sodium decanoate solution briefly. Because the ion exchange is very rapid,¹⁰ the switch in between the two meshes (Fig. S5, ESI†) may be realized *in situ* simply by passing a salt solution through the mesh.

To assess the quality of separation more quantitatively, oil–water (30/70 v/v) mixtures were prepared by mixing *n*-hexadecane, diesel oil, rapeseed oil, hexane, petroleum ether, and 1,2-dichloroethane, respectively with water and each mixture was separated by both oil-removing (PEM-C₁₀-mesh) and water-removing (PEM-Cl-mesh) approaches, and the purity of the permeate was examined by gas chromatography. The separation efficiency was calculated following a literature procedure,¹¹ and the results are displayed in Fig. 4. All are successfully separated through both meshes, with the purity of separated oil or water above 99.5%, and in some cases, nearly 100%. In addition, the PEM-Cl-mesh is easily rejuvenated after each test by just a gentle water rinse. Fig. 4 proves that both the PEM-C₁₀-mesh and the PEM-Cl-mesh are highly effective and potential candidates for oil–water separation in industrial applications. This affords additional flexibility in handling different oily waste waters. A typical oil–water mixture can be separated with either a PEM-C₁₀-mesh or a PEM-Cl-mesh with high efficiency, and in case the water is salty (such as seawater), the PEM-Cl-mesh,

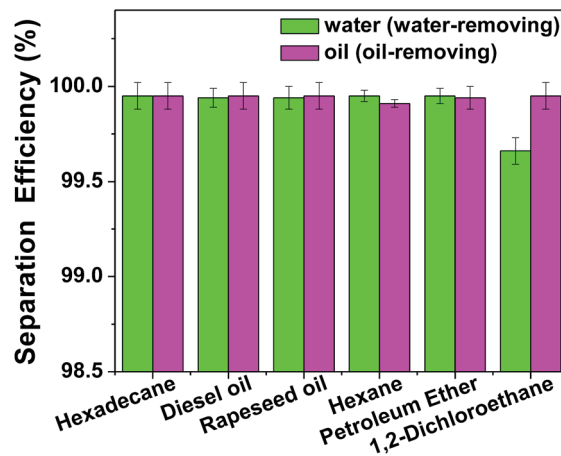


Fig. 4 Separation efficiency expressed as permeate purity for the PEM-C₁₀-mesh (oil-removing) and the PEM-Cl-mesh (water-removing) tested against various oil–water mixtures.

operating in the water-removing mode, is quite suitable regardless of the viscosity of the oil. Moreover, the PEM coatings are robust and stable under typical operation conditions, including in the seawater environment.^{1c}

Conclusion

In summary, after nanoscale roughening of a stainless steel mesh by a sol–gel process, a subsequent PEM coating offers convenient control over wetting and permeation by the components of oil–water mixtures. Most significantly, designed and constructed appropriately, these meshes can selectively separate either oil or water from their mixtures. The liquid isolated from such a mixture is determined according to the surface energy endowed by the PEM counterions, and these counterions are easily ion exchanged, affording switchable separation and facile mesh rejuvenation. In simple tests of oil–water separation for various oils, meshes were found to be highly efficient, with the liquid collected from the mesh at purity above 99.5%. The ease of preparation, high separation efficiency, robustness, low cost, and flexible properties of the meshes suggest numerous applications in the treatment of oily wastes.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21174145). Z. S. thanks the NSFC Fund for Creative Research Groups (50921062) for support.

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