1. PRF# 56455-ND5
2. Project Title: Rejuvenating Conjugated Polymer Membranes for Oily Water Treatment
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ACS PRF impact: This grant provides support the PIs and students to pursue the study of the oily water treatment and the regeneration of membranes (self-cleaning). The support by ACS PRF has enabled us to work on elucidating the switchable adhesion of oils on polymeric membranes and utilizing these properties for oily water treatment and regeneration of membrane materials. This has been a very important support.

Report: There is a growing demand for the protection and reuse of water resources through oily wastewater treatment. Oleophilic/hydrophobic or underwater oleophobic properties were utilized to separate water from water/oil mixture via absorption or filtration. However, typical oil absorbents gradually lose their wetting capability or reach the limit in absorbing capacity due to fouling or saturation. Materials with special wettability capable of *in situ* switching their wettability would enable controlled trap and release of oils toward continuous oil/water separation.

Conjugated polymers can change their mechanical and electrical properties when electrochemically "doped" (i.e., undergoing a reduction and oxidization process). Polypyrrole dodecylbenzenesulfonate (PPy(DBS)), as a conjugated polymer, exhibits a large difference in surface energy under reduction or oxidation via the application of low voltages. The PPy(DBS) surface turns into an oxidized state upon application of an oxidative voltage (e.g., 0.1 V), in which doped DBS^- molecules bond to the PPy chains via polar sulfonic acid groups, while dodecyl chains protrude out from the polymer chains, constituting the surface layer. Since the dodecyl groups are hydrophobic (or oleophilic), the oxidized PPy(DBS) surface exhibits a state of underwater-oleophilicity and high adhesion to oils. The PPy(DBS) surface turns into a reduced state upon application of a reductive voltage (e.g., –0.9 V). The DBS^- molecules reorient within the reduced PPy(DBS), exposing the hydrophilic (or oleophobic) sulfonic acid groups at the outermost surface. This change reduces the interfacial tension between the PPy(DBS) surface and aqueous medium, causing the reduced polymer surface to be more underwater-oleophobic. Furthermore, a minute amount of DBS^- molecules are desorbed from the PPy(DBS) matrix during reduction, and therefore, a portion of desorbed DBS^- molecules, which are near the droplet boundary, accumulate at the interface between the organic droplet and the aqueous electrolyte. The accumulated DBS^- molecules, acting as surfactants, result in a decrease of interfacial tension between the organic droplet and aqueous electrolyte.

This project utilizes this known knowledge to explore a new membrane-based oil/water separation technique using an *in situ* cleaned membrane with tunable wetting properties of PPy(DBS) (**Fig. 1**). This project. The continuous absorption and release of dichloromethylene (DCM) is demonstrated via in situ switch of underwater wettability (*i.e.,* affinity for organic liquid in an aqueous environment) of a CNT-embedded PPy(DBS) mesh. We first grow CNTs on the stainless steel mesh surface, and subsequently electropolymerize PPy(DBS) on CNT surfaces, creating a cauliflower-shaped morphology of the PPy(DBS) surface. We oxidize or reduce PPy(DBS) meshes (with and without CNT embedment) in 0.1M $NaNO_3$ to absorb and subsequently *in situ* release DCM, while simultaneously regenerating the polymer surface. We then prove that the CNT embedment enhances the surface wettability and longevity of the PPy(DBS) mesh. Lastly, we show a proof-of-concept oil collection and surface recovery of the polymer surface via in situ underwater wettability switch.

Fig. 1 shows the mechanism of absorption of DCM and release of once-absorbed DCM using the PPy(DBS) mesh, and *in situ* regeneration of the PPy(DBS)
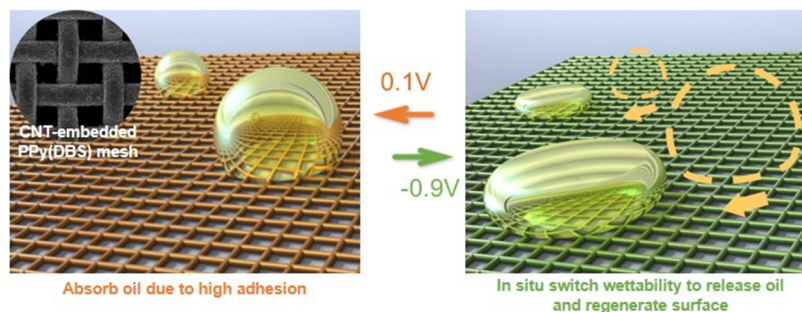
Fig. 1. Schematic illustration of the mechanism of oil absorption and release using a PPy(DBS) mesh via *in situ* wettability switch. Oxidized PPy(DBS) surface shows strong affinity to oils, adhering the oils on the polymer surface (left). Upon reduction, PPy(DBS) surface *in situ* switches underwater wettability, allowing oils to be released from the mesh via rolling off or permeating through the pores (right). This wettability switch is attributed to the reorientation and desorption of DBS^- molecules.

surface. Under oxidation, the PPy(DBS) mesh can 'absorb' oils by adhering the oils on the PPy(DBS) surface, and under reduction, previously attached oil droplets roll off from or permeate through the mesh. Based on this principle, controlled absorption and release of DCM are demonstrated. First, an oxidized PPy(DBS) mesh (in NaNO$_3$ electrolyte) is dipped in and out of DCM (dyed with purple), where the mesh absorbs DCM. Then, the mesh is moved to a new location within electrolyte without losing DCM, followed by PPy(DBS) reduction. Reduced PPy(DBS) surface *in situ* switches its wettability, allowing DCM to be fully released from the mesh. While the DCM is released, the PPy(DBS) surface is simultaneously *in situ* regenerated. After completing this oil absorption and release cycle with simultaneous regeneration of the PPy(DBS) surface, the PPy(DBS) mesh is oxidized again, ready for another cycle of absorption and release (*i.e.,* consecutive process). Together, this process demonstrates the continuous absorption and release of oils, while regenerating the PPy(DBS) surface via *in situ* wettability switch.

Finally, PPy(DBS) meshes are used to demonstrate the absorption and transport of DCM in 0.1M NaNO$_3$ environment from one vial to another, and show the release of DCM droplets from the mesh while simultaneously regenerating PPy(DBS) surfaces, as the first step toward continuous oil/water separation. The experiment is performed using the setup shown in **Fig. 2a**. First, an oxidized PPy(DBS) mesh is dipped in and out of the left vial filled with DCM dyed in purple. DCM is absorbed on the mesh and transferred to the right vial. PPy(DBS) is then reduced, allowing DCM to be released from the mesh and reclaimed into the right vial, while simultaneously regenerating PPy(DBS) (see **Fig. 2b**). In addition, the DCM transfer rate is nearly linear as depicted in **Fig. 2c**, indicating that the amount of DCM transferred during each cycle is nearly identical. This suggests that the adhesion between oxidized PPy(DBS) surface and DCM is still strong enough to maintain the absorption capacity, though retention force slightly decreases after redox cycles.

In summary, the controlled absorption, transport, and release of oils are demonstrated using CNT-embedded PPy(DBS) meshes via in situ wettability switch as well as the regeneration of PPy(DBS) surfaces. PPy(DBS) mesh is used to absorb oils when oxidized owing to its high affinity to oils, and is used to release the absorbed oils when reduced via switching its oil affinity *in situ* from high to low with -0.9V, while simultaneously regenerating the polymer surface. The embedment of CNTs creates the cauliflower-shaped morphology, enhancing *in situ* underwater wettability switch, as characterized by 138% higher retention force and 16% shorter switch time after 250 redox cycles. A rolled CNT-embedded PPy(DBS) mesh is used to demonstrate a continuous absorption and transport of DCM with 16 times heavier than the weight of a mesh in 50 redox cycles. Upon further study of optimizing the material and morphology, this approach is promising for the development of highly efficient, continuous, and automatic oil/water separation.

The central theme of this project is to utilize a tunable and recyclable PPy(DBS) membrane, facilitating the separation regardless of the density ratio of the oil/water mixtures. Therefore, this technology enables the separation of a wide range of mixtures with organic solvents and aqueous liquids, unlike existing gravity-driven separation methods. This project will therefore pave the way for developing environmentally friendly and energy efficient oil/water separation techniques.
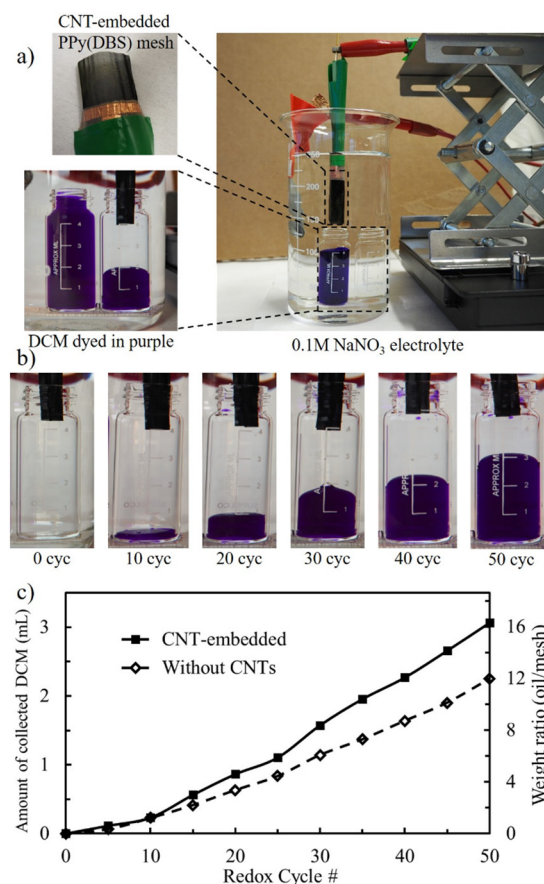

Fig. 2. Absorption, transport and release of DCM using a PPy(DBS) mesh. a) oil collection setup with the PPy(DBS) mesh. b) DCM transport for 50 continuous redox cycles using CNT-embedded PPy(DBS) mesh. c) Amount of DCM collected using the PPy(DBS) mesh (2 cm x 3 cm) with and without CNT embedment after 50 redox cycles. Second y axis shows the weight ratio between the transported DCM and the PPy(DBS) mesh.