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Facile Polypyrrole Thin Film Coating on Polypropylene Membrane for Efficient Solar-driven Interfacial Water Evaporation

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Experimental

Materials. Pyrrole was purchased from Acros, and ferric chloride was obtained from Sigma-Aldrich. Polypropylene (76 mesh) and stainless steel (70 mesh) were purchased from McMaster. (3-aminopropyl)triethoxysilane (APTES) and *1H, 1H, 2H, 2H*-perfluorooctyltriethoxysilane (POTS) were purchased from Gelest. Deionized (DI) water with 18.2 MΩ resistivity was obtained from a Milli-Q filtration system and used for all experiment. All materials were used as received without further purification.

Polypyrrole Deposition. PPy coating was deposited onto glass slides, polystyrene, and stainless steel at a controlled thickness. Before use, the glass slides were cleaned using a freshly prepared piranha solution (mixture of H_2SO_4 (98%) and H_2O_2 (30%) with the volume ratio v/v=7/3) at room temperature for 4 hrs and rinsed with water until neutralized, while polypropylene (PP) and stainless steel substrates were rinsed with soap water and then DI water. The substrates undergoes 30s oxygen plasma etching right before the following-up procedures. The substrates were then immersed in hydrolysed APTES solution made with a mixture of water (10 mL), ethanol (90 mL), and APTES (100 μL) for 6 hrs. After being rinsed with water, the substrates were dried by nitrogen gas. The dried slides were then placed in an aqueous mixture of $FeCl_3$ (36 mmol/L, 40 mL) and pyrrole (100 μL) to start polymerization. Unbounded PPy particles on the coating were removed by excessive rinsing. Polymerization of the PPy coating was started directly on plasma oxidized polypropylene (PP) without the APTES pretreatment. Superhydrophobic modification of the coating was then conducted in a close-capped Teflon-based hydrothermal container under chemical vapor deposition of POTS. The silanization reaction was performed at 120^{o}C for 1 hr. The film was then placed under vacuum for another period of 1 hr to ensure that all unbounded silane was removed from the film.

Characterization. The thickness of the coating was measured using a stylus profilometer (KLA Tencor Instruments P6). Values reported represent an average of five different positions on the coating. The UV-vis-NIR absorption peak was acquired using UV-vis-NIR spectrophotometer (Hitachi U-4100). Scanning electron microscopy (SEM) images were acquired using an FEI Quanta 600 field emission scanning electron microscope with an acceleration voltage of 10 KV. The contact angle of water droplet on the surface was measured by the sessile drop technique and analysed via drop snake plug-in using the freely available ImageJ software package.[1] The feed water evaporation rate was evaluated by an analytical balance equipped with the simulated sunlight instrument (300 W, Cermax). The water vapor was then collected, and conductivity was measured. Coating robustness was then demonstrated by immersing the PPy-coated glass slide in 50 mL seawater (or DI water) for 7 days under mild shaking. The solutions (seawater and DI water) were then collected and mixed with 0.1 g KBr for the FTIR (Shimadzu Corp., Japan, IR Prestige 21 System) measurement transmission mode sample preparation. The surface temperature distribution under solar irradiation was measured using the IR camera (FLIR A655sc) with ±2% uncertainty of reading.

Movie S1 Water Droplet Wettability Performance on the PPy-coated Stainless Steel Mesh

This video demonstrates water motion on the hydrophilic and superhydrophobic PPy-coated stainless steel mesh. The water droplet rolls off the superhydrophobic PPy-coated mesh very readily in seconds; however, it spreads and penetrates the hydrophilic PPy-coated stainless steel mesh. The PPy-coating on the mesh is 300 nm thick.

Movie S2 Water Droplet Wettability Performance on the PPy-coated PP Mesh

This video demonstrates water motion on the hydrophobic PP mesh and superhydrophobic PPy-coated PP mesh. The water droplet rolls off the superhydrophobic PPy-coated PP mesh very readily within 0.1 s; however, it beads on the hydrophobic PP mesh. The PPy coating on the mesh is 300 nm thick. The area of mesh is 861 mm^2.

Movie S3 Surface Temperature Distribution of PP and PPy-coated PP Mesh

This video demonstrates the temperature distribution map of PP mesh (left) and PPy-coated PP mesh (right) under solar irradiation. All experiments were conducted in a dark room. The light was turned on after 10 s and held for 30 min at illumination power of 1000 W/m^2. The temperature of the membrane gradually increased and remained at equilibrium. The light was then shut off for cooling. The PP mesh does not show distinguishable temperature change under illumination and cooling; however, the temperature of PPy-coated PP mesh increases to ~50°C during solar heating then effectively maintains heat, allowing the mesh to cool slowly to room temperature.

PPy coating on Glass Slide

PPy coating is tightly and uniformly coated on the glass slide. The corresponding scanning electron microscope image (**Fig. S1**) shows that coating on the flat glass is smooth in the micrometer scale with few aggregated PPy particles. By zooming in at the position at high magnification indicated by the red square, it is apparent the smooth PPy coating is composed of the compacted stacked nanoparticles with nanometer-scale roughness. Each PPy particle is roughly 50 nm in diameter.

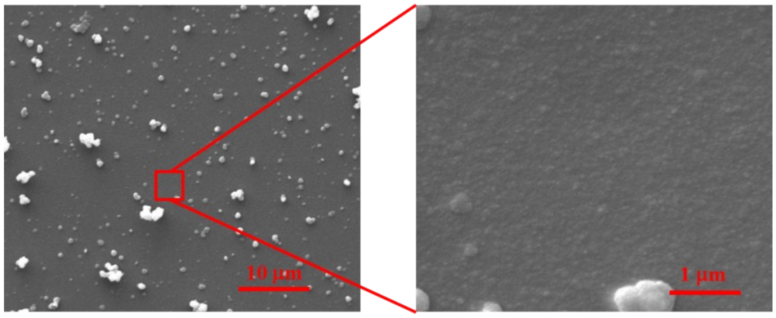

Figure S1. The morphology of the PPy coating. SEM images of PPy coating (12-hr dipping time) on the glass slide. The low magnification image (left) shows the coating to be smooth with submicron particles, while at high magnification, (right), the image shows that the coating is composed of small stacked PPy nanoparticles. The particle is roughly 50 nm in diameter.

PPy coating on Stainless Steel Mesh

PPy coating tightly and uniformly coated the stainless steel mesh wires. The corresponding scanning electron microscope image (**Fig. S2**) shows that PPy on the mesh is smooth at the micrometer scale. At high magnification, by zooming in at the position of the red square, the image shows the smooth PPy coating to be composed of compacted ellipsoid-like particles packed with nanometer-scale roughness. Each ellipsoid-like particle is around 50 nm in diameter and 150 nm in length.

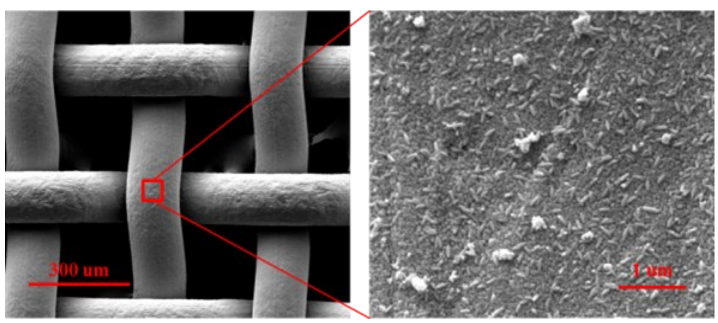

Figure S2. The morphology of the PPy coating. SEM images of PPy coating (12-hr dipping time) on the stainless steel mesh. The low magnification image (left) shows the coating to be smooth, while at high magnification (right) the image shows that the coating is composed of the stacked ellipsoid-like PPy particles. The particles are roughly 50 nm in diameter and 150 nm in length.

After this post-vapor treatment, the PPy coating becomes hydrophobic on the flat surface and superhydrophobic on the mesh due to the introduction of micro-scale roughness. The water droplet easily rolls off the square centimeter-sized mesh surface within 1 s, while the droplet spreads on the mesh (**Fig. S3 and the demo video can be found in Movie S1**).

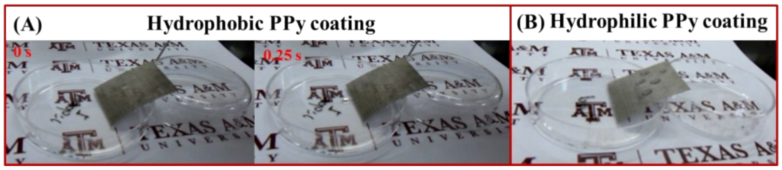

Figure S3. Water wetting behaviour of PPy coating. (A) The water droplet rolls off the surface easily within 1s. (B) The hydrophilic PPy coating lets the water droplet spread on the mesh. The polymerization time for PPy coating is 12 hrs and mesh size is 25 mm×25 mm. A video of both droplet roll off properties is shown **in Movie S1.**

Polypropylene Mesh

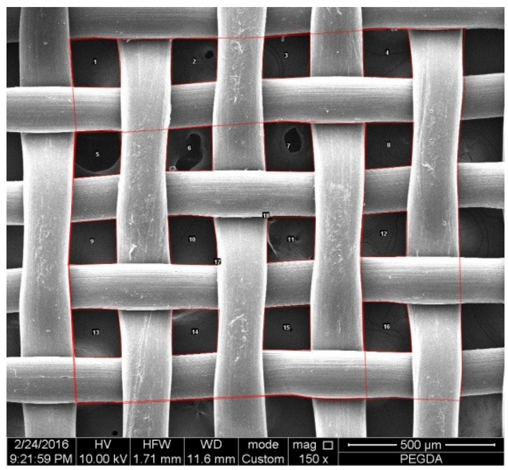

Figure S4. The morphology of PP mesh. SEM image of PP mesh as received. It has a pore size of 24% (standard deviation 6%) and wire diameter of 161 μm in diameter.

Adhesion Robustness of PPy Coating on the Glass

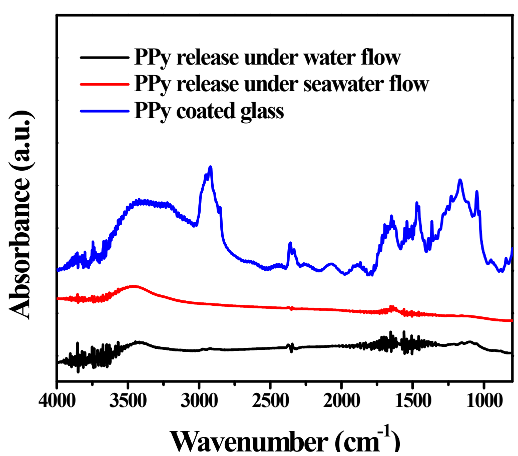

Figure S5. FTIR spectra of PPy coating on glass and released PPy from the coating under water and seawater continuous flow.

The FTIR spectrum of polypyrrole is shown in Figure S5 (blue-color spectrum). The peaks at 1551 cm^{-1} and 1468 cm^{-1} can be attributed to C-N and C-C asymmetric and symmetric ring-stretching, respectively. The N-H and C-H stretching vibration of polypyrrole appeared at 3429 cm^{-1} and 2928 cm^{-1}.[2] PPy-coated glass slides (~300 nm coating on glass slides with the dimension of 25 cm×25 cm×75 cm) were immersed in 50 mL water and seawater under mild shaking for 7 days. The solutions (seawater and DI water) were then collected and mixed with 0.1 g KBr. Any detached and degraded PPy is able to be mixed with KBr and will present in the FTIR spectra. None of those two spectra, however, show the existence of PPy. The peak near 3500 cm^{-1} is representative of water, meaning little extent of water existed due to relative high humidity.

Reference

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2. S. A. Waghuley, S. M. Yenorkar, S. S. Yawale and S. P. Yawale, *Sensors and Actuators B: Chemical*, 2008, **128**, 366-373.