Electronic Supplementary Information

Janus membrane decorated via a versatile immersion-spray route: controllable stabilized oil/water emulsion separation satisfying industrial emission and purification criteria

*Weifeng Zhang, Liangxin Xu, Ruixiang Qu, Yanan Liu, Yen Wei and Lin Feng**

[†]Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China

*Corresponding author: fl@mail.tsinghua.edu.cn

Table of Contents

2. Surface Characterization of PTFE Substrate and Janus membrane

PTFE microfiltration membrane with the pore size of 0.45 μm is chosen as the substrate in this work. The surface of substrate and the as-prepared Janus membrane was observed by field emission scanning electron microscope (FESEM) as shown in Fig. S1, it is worth noting that the substrate exhibits different morphology on both sides, which owns rough surface with relatively large pores on one side and smooth surface with relatively small pores on the other side (Fig. S1a and S1b). Since the substrate was first coated with PANI by immersion method and then sprayed with SiNPs on the smooth side, so the rough side was coated with PANI polymer and the smmoth side was modified with PANI and SiNPs. From FESEM images of the Janus membrane (Fig. S1c and S1d), it is obvious that after the modification process, the pore size and porosity of rough side and smooth side have reduced compared with that of the substrate because of the aggregation of PANI polymer and SiNPs on both wires and pores.

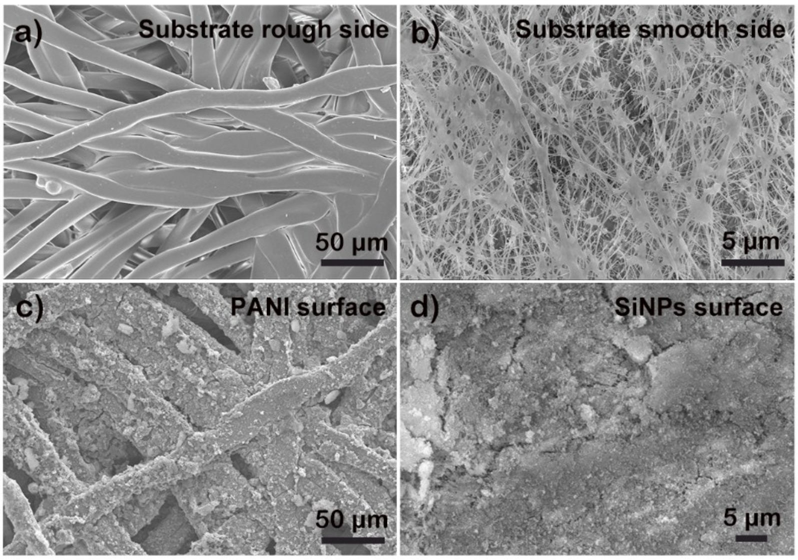

Fig. S1 FESEM images of a) PTFE substrate rough side. b) PTFE substrate smooth side. c) Janus PANI surface. d) Janus SiNPs surface.

3. Cross Section Characterization of the Janus Membrane

The cross-section SEM images of both sides were observed as shown in Fig. S2 From the FESEM images, the Janus membrane exhibits different morphology on PANI surface and SiNPs surface. Besides, modified PANI polymer and SiNPs both have a certain thickness, which further demonstrates the Janus property of the material.

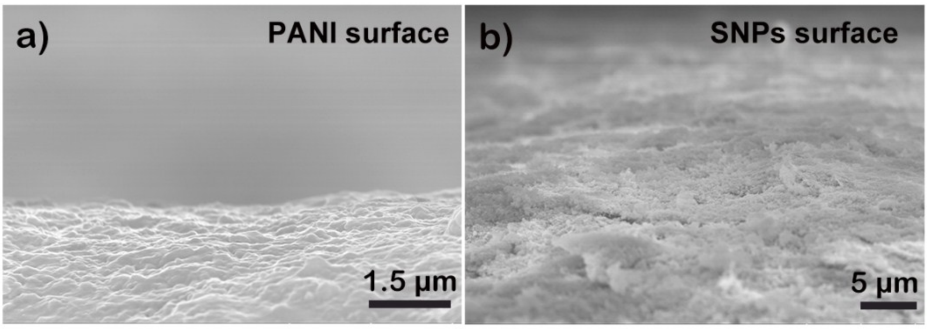

Fig. S2 Cross section FESEM image of a) PANI coated surface and b) SiNPs modified surface.

4. pH Stability Test of the SiNPs Surfece

To further characterize the stability of the SiNPs surface, the performance of the surface toward a series of acid or alkali solutions were tested and illustrated in Fig. S3. From the digital photos, It is obvious that when different solutions were dropped on surface, all the droplets exhibited spherical shape, which means that the SiNPs surface can resist corrosive solutions in a wide range of pH values from 0 to 14, indicating the outstanding pH stability.

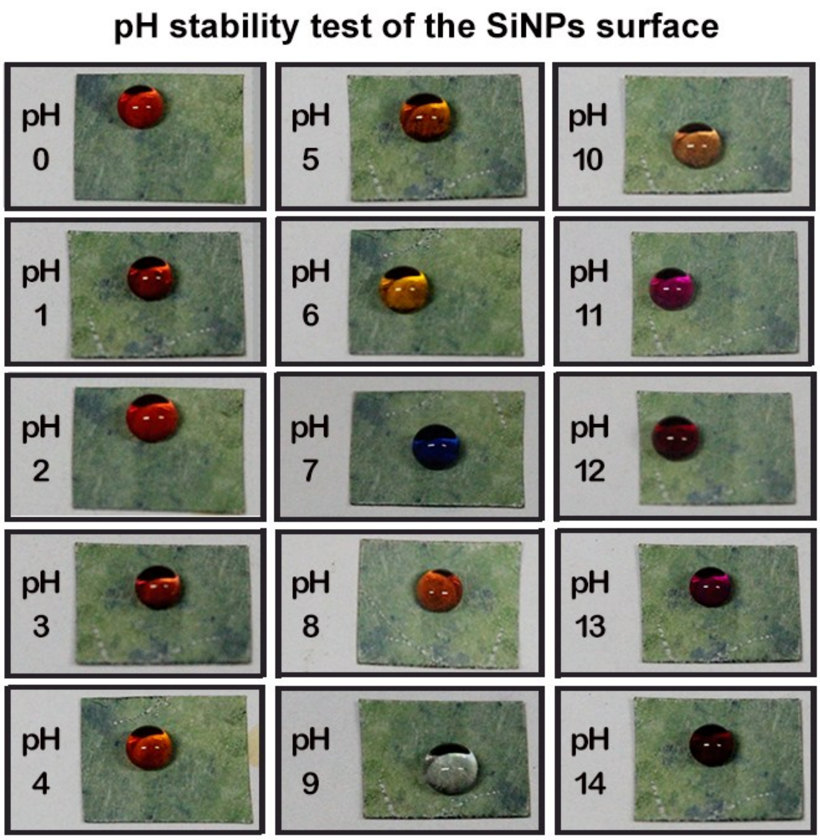

Fig. S3 Photographs of the droplet toward different pH values on the SiNPs modified surface. All the droplets exhibit spherical shape on the surface, indication the excellent pH stability of the membrane.

5. Emulsion Separation Performance of PTFE Substrate

Before the emulsion separation experiments of Janus membrane, the performance of PTFE substrate was first tested as shown in Fig. S4. From the digital photos (Fig. S4b and S4e), it is clear that the substrate cannot separate both toluene-in-water and water-in-toluene emulsions, the oil content in filtrate even reaches 982 mg L^{-1} and the efficiency is below 85%. Fig. S4a and S4d are the optical microscope images of toluene-in-water feed emulsions and water-in-toluene feed emulsions, from which numerous oil droplets or water droplets are dispersed in emulsions. While Fig. S4c and S4f are the optical images of the corresponding filtrates. The images indicate that after the emulsion separation of PTFE substrate, tiny oil droplets or water droplets still exist in the filtrates, which further demonstrates that the substrate is not able to separate both oil-in-water and water-in-oil emulsions.

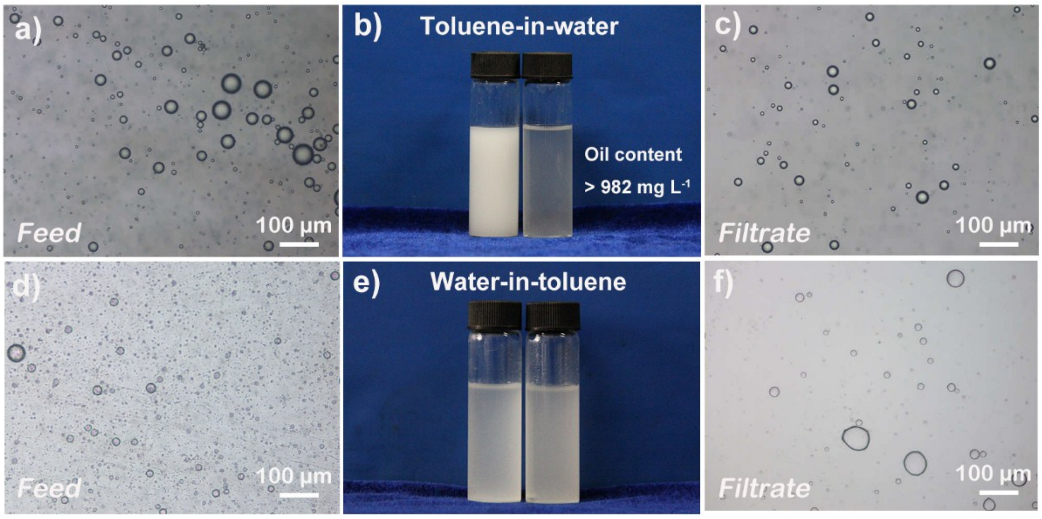

Fig. S4 The toluene-in-water and water-in-toluene emulsion separation performance of PTFE substrate and the corresponding optical microscope images. a) and d) The optical images of toluene-in-water and water-in-oil emulsions. b) and e) The digital photos of the corresponding emulsions separation performance of PTFE substrate. c) and f) The optical images of the corresponding filtrates.

6. Optical Images and Droplet Size Distribution of Oil-in-water Emulsions

It is necessary to capture the optical microscope images and measure the droplet size distribution of oil-in-water emulsions used in this work. Fig. S5 illustrates the optical images, oil droplet distributions and average droplet size of toluene in water emulsion, gasoline in water emulsion, n-hexane in water emulsion and lubrication oil in water emulsion. The oil droplet distribution and average droplet size of all the emulsions were calculated via nano measurer software. For each sample, 200-400 droplets were measured and taken average from the corresponding optical images. From the micrographs, it is obvious that numerous oil droplets dispersed in the emulsions evenly. The average droplet sizes of all the emulsions are below 10 μm. Because the pore size of the Janus membrane (<0.45 μm) is far smaller than the droplet size of the oil-in-water emulsions, the PANI surface is able to block these tiny oil droplets and separate stabilized emulsions with high efficiency.

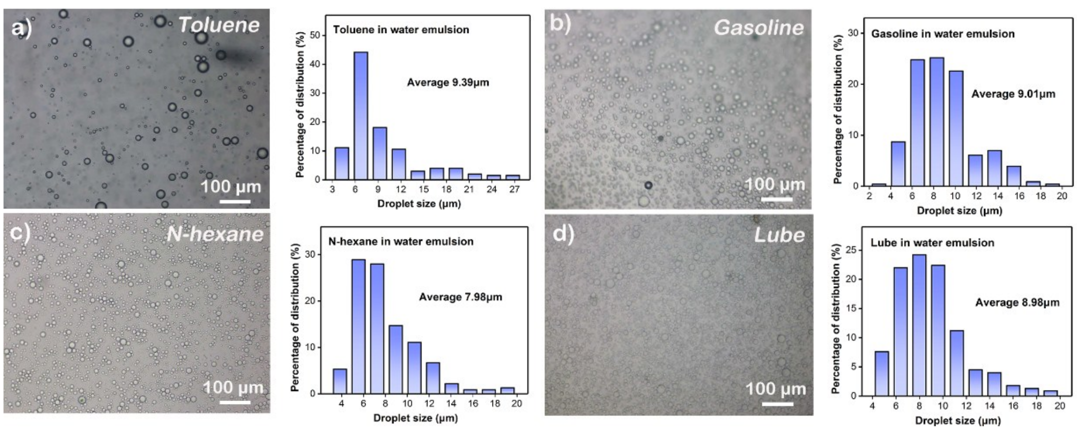

Fig. S5 The optical microscope images and the corresponding oil droplets distribution for a) Toluene in water emulsion. b) Gasoline in water emulsion. c) N-hexane in water emulsion. d) Lubrication oil in water emulsion.

7. The Flux of Stabilized Oil-in-water Emulsions and Long Term Operation

Because the speed of the emulsion separation process is important for real applications, the fluxes of the PANI surface towards oil-in-water emulsions were tested and displayed in Fig. S6. The flux of the emulsions is all above 1300 L/m^{2}h. For gasoline in water emulsion, the flux even reaches to 1800 L/m^{2}h. Since the emulsions used in this work are stable and the separation performances are excellent, so the fluxes of the PANI surface are relatively high compared with other works (Table S1). Moreover, the long term operation tests of the PANI surface was also conducted as shown in Fig. S6b, toluene in water emulsion was chosen as the sample. It is obvious that with the increasing of separation times, the flux decreases gradually because of the aggregation of oil droplets. But after washing the membrane with water, ethanol and drying, the flux can return to the original state, indicating the stability of the membrane.

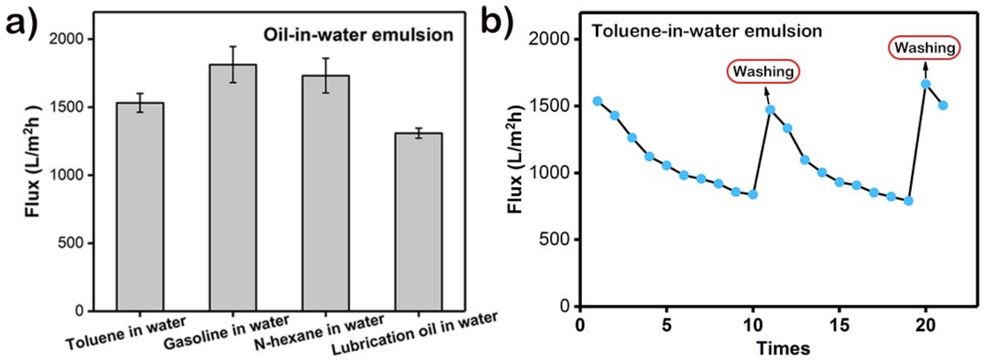

Fig. S6 a) Flux of different water-in-oil emulsions. b) Long term operation tests of the PANI surface.

8. Stability Test of PANI Coated Layer

The stability test of the PANI coating layer was conducted. The Janus membrane first separated oil-in-water emulsions for 30 times (After each separation cycle, the mesh was washed with ethanol and water), then FESEM images were captured as shown in Fig. S7. It is clear that the PANI polymer is still wrapped on the membrane and the water contact angle is 0°, demonstrating that the PANI coated on the surface is very stable.

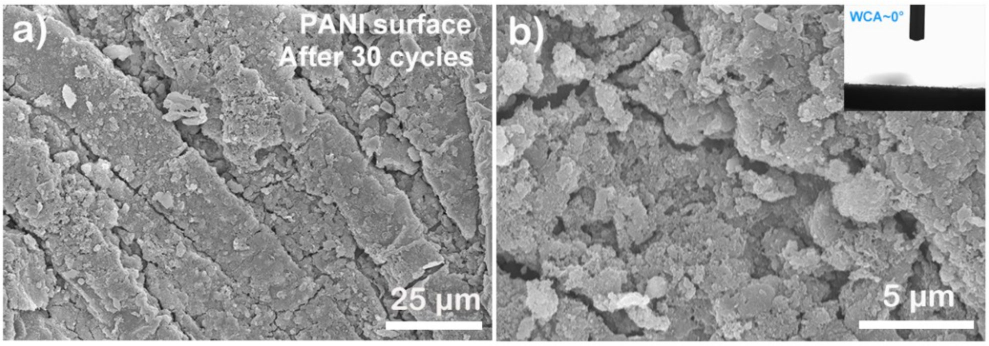

Fig. S7 a) FESEM image of the PANI surface after 30 cycles of emulsion separation. b) High-magnification image of the surface, the inset is the corresponding water contact angle.

9. Optical Images and Droplet Size Distribution of Water-in-oil Emulsions

Similarly, Fig. S8 shows the optical images, water droplet distributions and average droplet size of water in toluene emulsion, water in gasoline emulsion, water in n-hexane emulsion and water in lubrication oil emulsion. The water droplet distribution and average droplet size of all the emulsions were calculated via nano measurer software. For each sample, 200-400 droplets were measured and taken average from the corresponding optical images. From the micrographs, it is clear that tiny water droplets dispersed in the emulsions evenly. The average droplet sizes of all the emulsions are below 9 μm. Since the pore size of the Janus membrane (<0.45 μm) is far smaller than the droplet size of the water-in-oil emulsions, the SiNPs surface can block these tiny water droplets and separate stabilized emulsions with high efficiency.

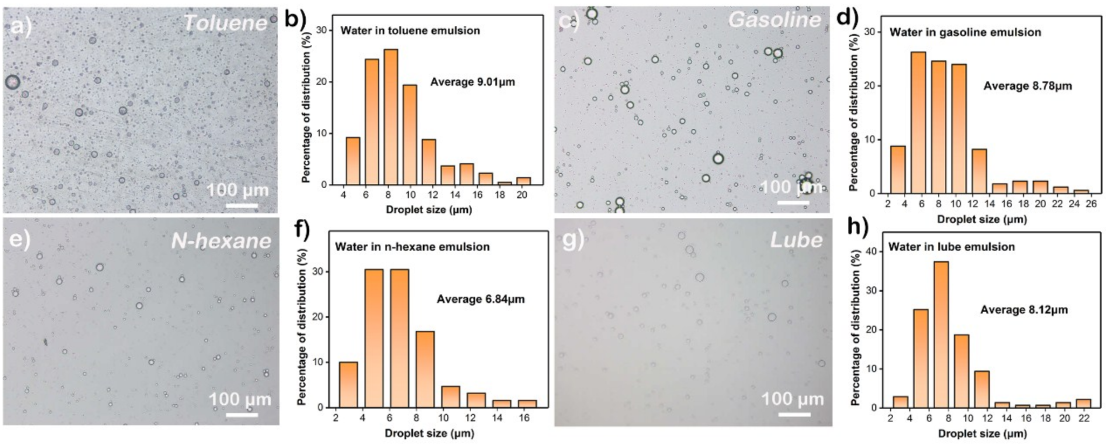

Fig. S8 The optical microscope images and the corresponding water droplets distribution for a) Water in toluene emulsion. b) Water in gasoline emulsion. c) Water in n-hexane emulsion. d) Water in lubrication oil emulsion.

10. The Flux of Stabilized Water-in-oil Emulsions and Long Term Operation

The fluxes of the SiNPs surface towards water-in-oil emulsions were tested and displayed in Fig. S9. From the chart, the flux of the emulsions is all above 1100 L/m^2h. Because the emulsions used in this work are stable and the separation performances are good, the fluxes of the SiNPs surface are relatively high compared with other works (Table S1). Moreover, the long term operation tests of the SiNPs surface was also conducted as shown in Fig. S9b, water in toluene emulsion was chosen as the sample. It is obvious that with the increasing of separation times, the flux decreases gradually because of the aggregation of oil phase and water droplets. But after washing the membrane with water, ethanol and drying, the flux is able to return to the original state, indicating the stability of the membrane.

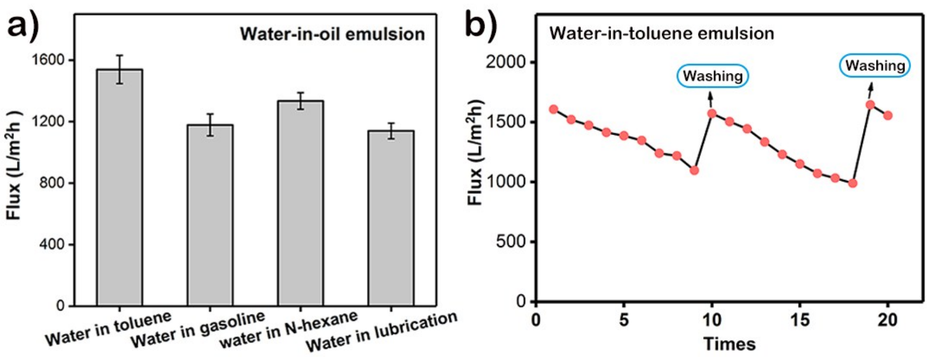

Fig. S9 a) Flux of different water-in-oil emulsions. b) Long term operation tests of the SiNPs surface.

11. Stability Test of SiNPs Coated Layer

The stability test of the SiNPs layer was conducted. The Janus membrane first separated water-in-oil emulsions for 30 times (After each separation cycle, the mesh was washed with ethanol and water), then FESEM images were captured as shown in Fig. S10. It is clear that although some of the nanoparticles were washed by water and ethanol, most of the SiNPs are still coated on the surface and the water contact angle is 137.5°, demonstrating that the SiNPs layer is relatively stable. Besides, the surface can still separate water-in-oil emulsions with high efficiencies. What's more, after a simple re-spray coating procedure, the WCA of the surface can return to 152.6° (Fig. S10b).

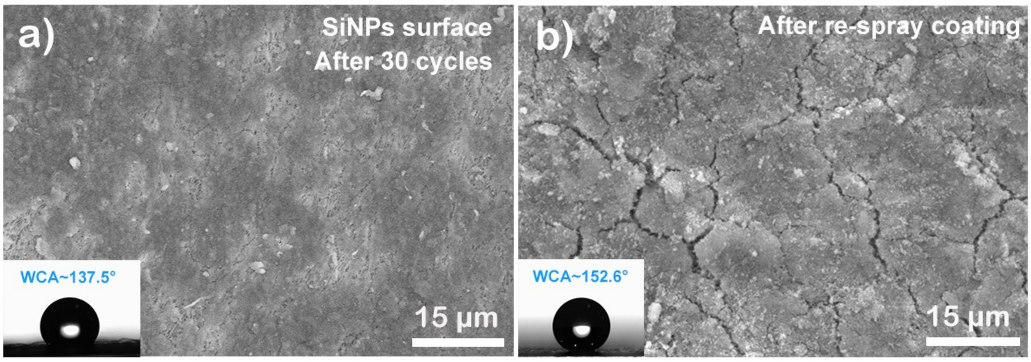

Fig. S10 a) FESEM image of the SiNPs surface after 30 cycles of emulsion separation. b) Image of the SiNPs surface after re-spray coating process. Insets are the corresponding water contact angles.

12. Comparison of the Janus Membrane with Other filtration Materials

Compared with a series of excellent oil/water emulsion separation materials with single wettability or Janus emulsion separation materials (Table S1), the as-prepared Janus membrane have relatively high flux, higher separation efficiency and better performance which meets the industrial emission standards. Besides, the fabrication route is also a facile method.

Table S1. Comparison of the Janus membrane in this work with other filtration materials reported previously.

Filtration materials	Methods	Substrate	Separation efficiency	Flux (L/m^3 h)	Reference
Hydrogel coated filter paper	Aldol condensation reaction coating	Cellulose paper	99.0% (gasoline)	~63 (O/W)	[28]
PDA-PEA coated membrane	Co-deposition method	PP membrane	98.0% (n-hexane)	<120 (O/W)	[29]
Graphene oxide membrane	Sol-gel fabrication method	Non-woven fabric	91.5% (toluene)	About 592 (O/W)	[30]
Chitosan-polyacrylamide sponge	Blending of polymer solution	Free standing	> 93% (toluene)	NA	[31]
Janus Polymer/CNT hybrid membrane	Dispensing and photografting	Free standing	NA	~6000 (O/W); ~7000(W/O)	[24]
Janus graphene oxide sponge	Fluorine and oxygen functionalization	R-GO sponge	NA	NA	[25]
Bio-based polycocolloid foam	In situ polymerization	Free standing	About 97% (hexane)	>500	[32]
Tungsten oxide coated mesh	Hydrothermal	Copper mesh	> 200 mg L^{-1} (gasoline)	NA	[33]
$Cu(OH)_2$ covered mesh	Immersion method	Copper mesh	> 100 mg L^{-1} (gasoline)	NA	[34]
Co_3O_4 nano-needle mesh	Hydrothermal	Steel mesh	About 60 mg L^{-1} (gasoline)	~1500 at 5kPa (O/W)	[35]
PANI-SiNPs Janus membrane	Immersion-spray method	PTFE membrane	> 99.7%, < 30 mg L^{-1} (gasoline)	~1800 (O/W); ~1500(W/O)	**This work**

13. The Versatile Janus Material Fabrication Method Applied on Other Substrates

It is worth noting that the immersion-spray coating route used in this work is a versatile method which is able to impart various substrates with Janus wettability as shown in Fig. S5, PVDF membrane with pore size of 0.8 μm, nylon membrane with pore size of 0.45 μm and PTFE membrane with pore size of 0.22 μm can all be changed to Janus materials.

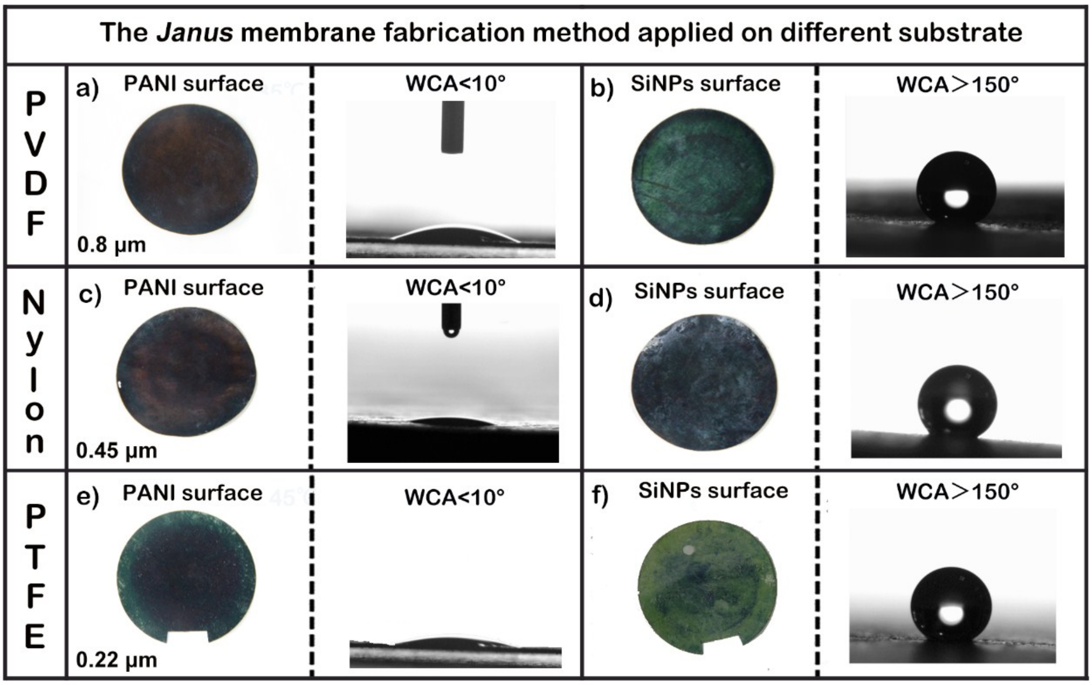

Fig. S11 The Janus membrane fabrication method applied on different substrate and the corresponding water contact angles for a) and b) PVDF microfiltration membrane with the pore size of 0.8 μm. b) Nylon microfiltration membrane with the pore size of 0.45 μm. c) PTFE microfiltration membrane with the pore size of 0.22 μm. This route is able to impart all these substrates with Janus wettability.

14. Wetting Behavior and Low Adhesive Performance of the Janus Membrane

The as-prepared Janus membrane exhibits excellent antifouling property and low adhesive performance on both sides as shown in Movie S1 and S2. PANI modified surface is able to block oil droplets completely and the droplets can not adhere to it, while water is not able to penetrate and adhere to the SiNPs coated surface at all, exhibiting excellent self-cleaning property.

Movie S1. Underwater superoleophobic wetting behavior and low adhesive performance of the PANI coated surface.

Movie S2. Superhydrophobic wetting behavior and low adhesive performance of the SiNPs coated surface.