Supporting Information

Mineralized Growth of Janus Membrane with Asymmetric Wetting Property for Fast Separation of Trace of Blood

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1. The photo of experimental apparatus

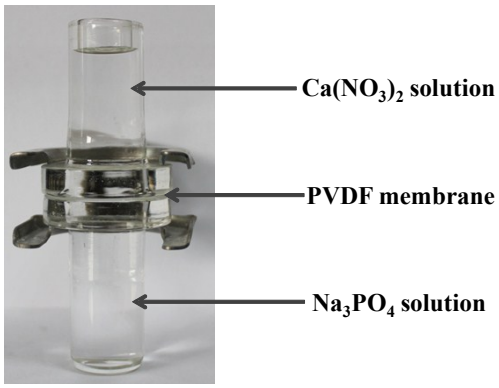

Figure S1. The photo of experimental apparatus for fabrication of asymmetric wetting membrane.

2. Morphology structure of original superhydrophobic PVDF membrane

The original superhydrophobic PVDF membranes are composed of a large amount of microspheres, and no apparent defect is observed.

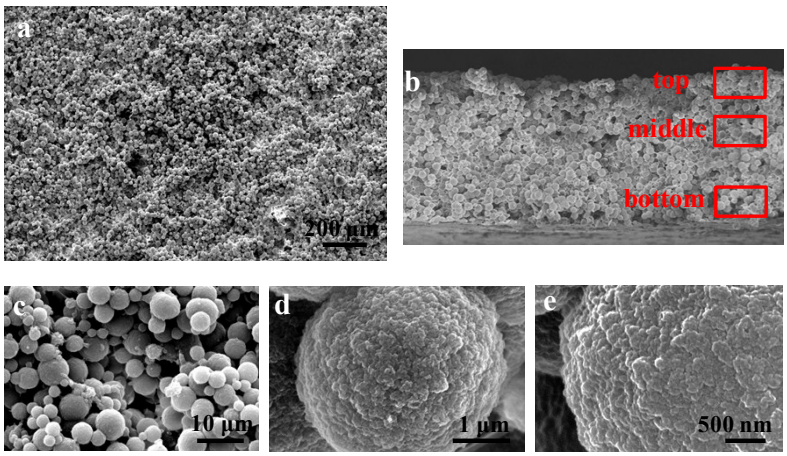

Figure S2. The morphology of the original superhydrophobic PVDF membrane. a) Top-surface SEM image. b) Cross-sectional SEM images. The inset red boxes marked with top, middle and bottom represent three different regions for cross-sectional EDX analysis in **Figure 5a**. c-e) SEM images of microspheres at different magnifications on the PVDF membrane.

3. Calcium phosphate grown on PVDF membrane with no microsphere structure

As a control experiment, typical PVDF membranes with no microsphere structure are prepared through common phase inversion process as follows: 0.5 g PVDF (solef 1015) was dissolved into 9.5 ml NMP to form a homogeneous solution under stirring. Then the solution was dropped onto the pre-cleaned glass plate and the thickness was controlled to be ~ 100 μm. The PVDF membrane was obtained after immersing the solution on the glass plate into water bath and then taken out and dried in air. After that, an as-obtained membrane was sandwiched between two vertical tubes for HAP-mineralization. The procedure is similar with that reported in the main text. The obtained mineralized PVDF membrane is shown in **Figure S3**, showing that calcium phosphate cannot grow well on the membrane surface and only few calcium phosphate aggregates (white spots) was observed on the membrane surface.

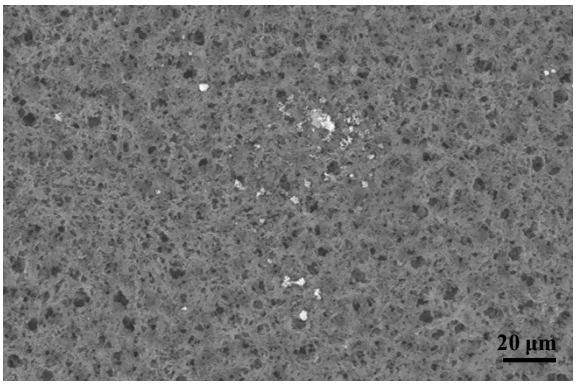

Figure S3. SEM image of PVDF membrane prepared through common phase inversion processes and then used as substrate for calcium phosphate mineralization.

4. HAP nanoplates formed on superhydrophobic PVDF membrane

Here, Na_3PO_4 (0.296 M) and $CaCl_2$ (0.493 M) were selected as reactants to prepare HAP crystals. As showed in **Figure S4**, nanoplates were observed to coat PVDF microspheres totally. This result indicates that the HAP crystalline structure is influenced by the composition of reactants.

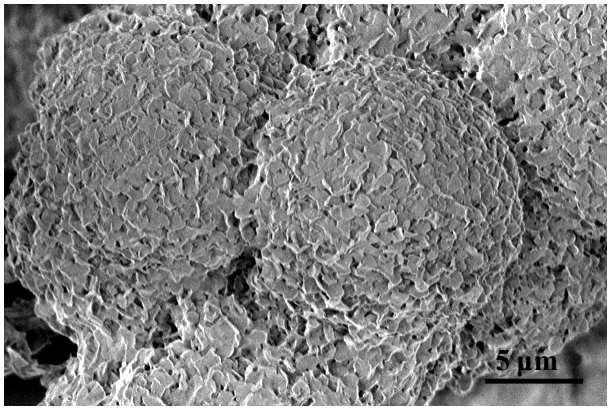

Figure S4. SEM image of PVDF microspheres coated with nanoplates, wherein Na_3PO_4 and $CaCl_2$ are used as starting reactants for HAP mineralization of the porous superhydrophobic PVDF membrane.

5. Effect of reactants concentration

The relationship between Na_3PO_4 concentration and the time of a water droplet penetrating across the HAP-mineralized porous membrane is discussed. It is noted that the molar ratios of Ca/P during mineralization processes were always maintained to be 1.67. With the increase of Na_3PO_4 concentration from 0.197, 0.296 M, to 0.592 M, the penetration time decreases sharply from 13.3, 1.2, to 1.1 s. (**Figure S5**) Obviously, to increase Na_3PO_4 concentration could increase the amount of HAP nanocrystals aggregated on the PVDF membrane. The HAP nanocrystals could further affect the wetting property of the membrane, hence the water penetration times decrease.

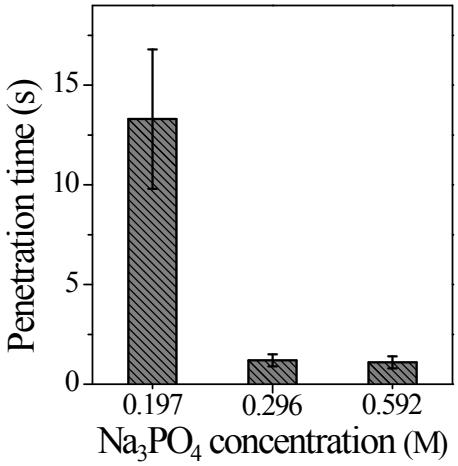

Figure S5. Time of water droplet penetrating across HAP-mineralized membrane as a function of Na_3PO_4 concentration.

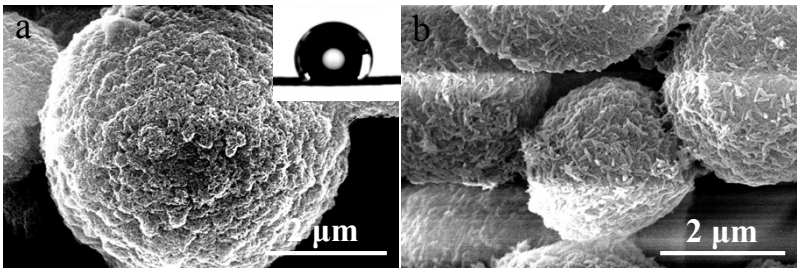

Figure S6. SEM images of top surface (a) and bottom surface (b) of PVDF membrane fabricated with 0.049 M PO_4^{3-} ions. The inset in (a) is the water contact angle, showing a single water droplet can't penetrate across the membrane.

6. Effect of reaction time

The reaction time (or diffusion time) is one of important factors to fabricate asymmetric wetting membranes with HAP gradient distribution. As showed in **Figure S1**, PO_4^{3-} ions and Ca^{2+} ions diffuse upward and downward in the membrane channels, respectively. However, there are less PO_4^{3-} ions, compared to Ca^{2+} ions, in initial time of diffusion, such that there is concentration gradient of PO_4^{3-} ions in the through-thickness direction of the membrane. With increase of reaction time, more PO_4^{3-} ions diffuse into the membrane channels and its concentration gradient becomes smaller, and finally, with more than 8.5 h, PO_4^{3-} ions distribute equally across the membrane. As a result, the whole membrane incuding both the upper and lower surfaces become hydrophilic. At this case, a water droplet spreads completely over the surface instead of penetrating through the membrane. Therefore, an appropriate the reaction time for achieving asymmetric wetting membrane in this work is determined to be 2 h. With shorter reaction time (For example 0.5 h), the obtained membrane is too hydrophobic. It takes a much longer time (more than 9 s) for a water droplet to penetrate the membrane.

7. Effect of PVDF membrane thickness

Three PVDF membranes with thicknesses of 50 μm, 100 μm, 500 μm are chosen for forming HAP-mineralized asymmetric wetting membranes as shown in Figure S7. The water-penetration tests showed that both the membranes with thicknesses of 50 μm and 100 μm could allow the penetration of a water droplet (13 μL) across the membrane within a short time, 1.0 s and 1.2 s, respectively. As for the membrane with thickness of 500 μm, a water droplet can penetrate into the membrane but cannot pass through the membrane as shown in **Figure S8**. This is because that the thicker membrane has thicker hydrophilic zone. The water droplet is more inclined to spread in the direction of parallel to the membrane.

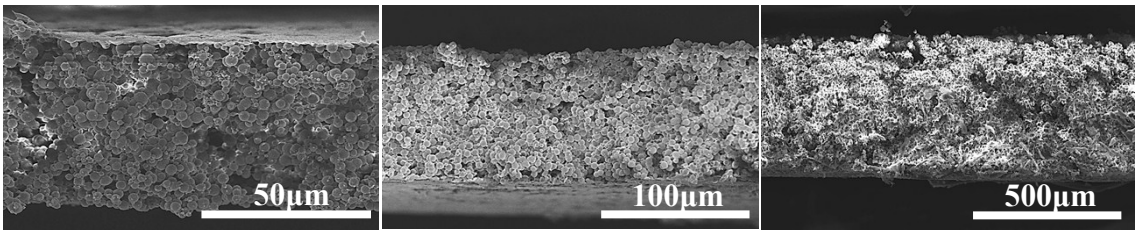

Figure S7. SEM images of the asymmetric membranes with three kinds of thicknesses: a, 50μm; b, 100μm; c, 500μm

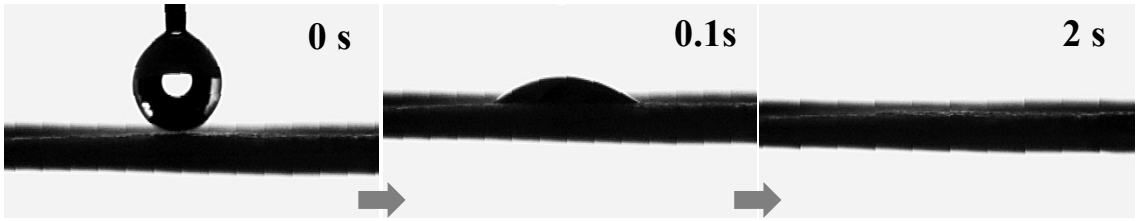

Figure S8. Dynamic contact angles of a water droplet penetrating into the membrane with thickness of 500 μm.

8. Effect of ascorbic acid in blood on the glucose electro-oxidation current

To prove the current generated from glucose while not ascorbic acid (AsA), three buffered aqueous solutions (pH=7) namely 0.1 mM AsA, 6 mM glucose + 0.1 mM AsA, and 15 mM glucose + 0.1 mM AsA, respectively, are prepared and their electro-oxidation currents are measured. As shown in **Figure S9**, the current generated from the solution of 6 mM glucose + 0.1mM AsA is much higher than that of 0.1 mM AsA solution. With the addition of more glucose in solution (15 mM glucose + 0.1 mM AsA), the current increases further. It indicates that the electro-oxidation current is mainly generated from glucose in plasma.

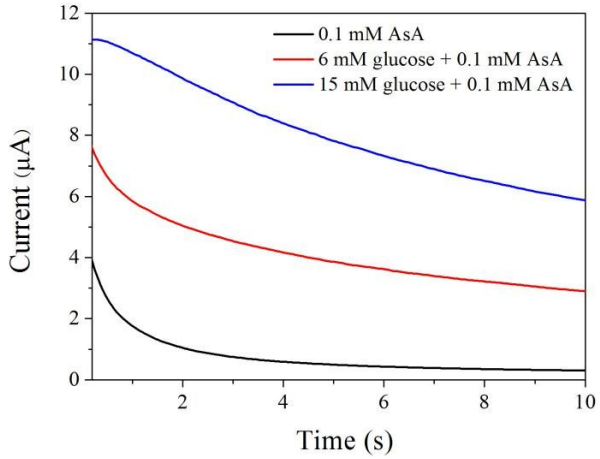

Figure S9. Amperometric current-time curves of three different samples.

9. Effect of membrane separation on glucose concentration in blood

Two buffered aqueous solutions (pH=7) containing 5.9 mM and 13.4 mM glucose, respectively are prepared and the glucose concentrations after membrane separation are measured by a glucose/lactate analyzer (YSI 2300-Stat, U.S.). The glucose concentrations after separation are 6.0 mM and 12.7 mM (three times measurements for each sample), respectively. This result shows that the membrane has little impact on glucose concentration during plasma separation.