Electronic Supporting Information

Bio-inspired CaCO$_3$ Coating for Superhydrophilic Hybrid Membranes with High Water Permeability

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**Construction of Poly(acrylic acid) Brushes on QCM Chips**

Gold-coated QCM chips (AT-cut, 5 MHz, Q-Sense) were cleaned with freshly prepared Piranha solution (concentrated H$_2$SO$_4$/H$_2$O$_2$: 70/30, v/v) at 70 °C for 15 min, rinsed with water, and subsequently dried under flowing N$_2$. Then the chips were mounted in PTFE liquid cells with one side exposed to the solution. The cells were primed with 1.0 mM ethanolic solution of disulfide initiator ((BrC(CH$_3$)$_2$COO(CH$_2$)$_{11}$S)$_2$, Sigma-Aldrich, 97%, USA) and incubated at room temperature for 12 h. Thereafter, the initiator-immobilized chips were rinsed with ethanol and dried under flowing N$_2$.

PAA brushes were prepared by surface-initiated atom transfer radical polymerization (SI-ATRP).[1] In a typical experiment, acrylic acid (1.72 mL), NaOH (1.0 g), methanol (1.0 mL), and water (9.0 mL) were added into a 25.0 mL Schlenk flask with a magnetic stir bar. After complete dissolution, pH of the solution was adjusted to 8.5-9.0 by addition of HCl or NaOH. Then CuBr$_2$ (11.2 mg) and 2,2'-bipyridine (171.8 mg) were added. The mixture was sequentially bubbled with nitrogen for 10 min, added with CuBr (71.7 mg), and bubbled with

nitrogen for another 20 min. After that, the resulting brown solution was transferred, using a cannula, into a nitrogen-purged vessel containing the initiator-immobilized QCM chips. The reaction was carried out at room temperature under nitrogen atmosphere for 6 h. Finally, the chips were rinsed with extensive water, left overnight to extract the sodium ions, and dried under flowing N_2.

**Construction of Poly(acrylic acid) Brushes on Silicon Wafers**

Silicon wafers were ultrasonically rinsed with acetone, ethanol, and water for 5 min each, followed by being cleaned with Piranha solution at 70 °C for 30 min, rinsed with water, and dried under reduced pressure at 90 °C. Next, the wafers were immersed into a 10.0 mM solution (20.0 mL) of 3-(aminopropyl)triethoxysilane (APTES, Aladdin, 99%, China) in anhydrous toluene under nitrogen atmosphere for 12 h, and subsequently rinsed with toluene, acetone, and ethanol. The resulting aminated wafers (Si-NH$_2$) were placed in 18 mL of anhydrous CH_2Cl_2 (containing 0.4 mL of triethylamine), followed by dropwise addition of 6.0 mL of CH_2Cl_2 (containing 0.3 mL of 2-bromoisobutyryl bromide, BIBB, Sigma-Aldrich, 98%). The reaction mixture was incubated at 0 °C for 2 h and left at room temperature for another 12 h. After that, the wafers were rinsed with dichloromethane, acetone, and water and dried under flowing N_2. PAA brushes were prepared on the initiator-immobilized wafers by the aforementioned SI-ATRP method.
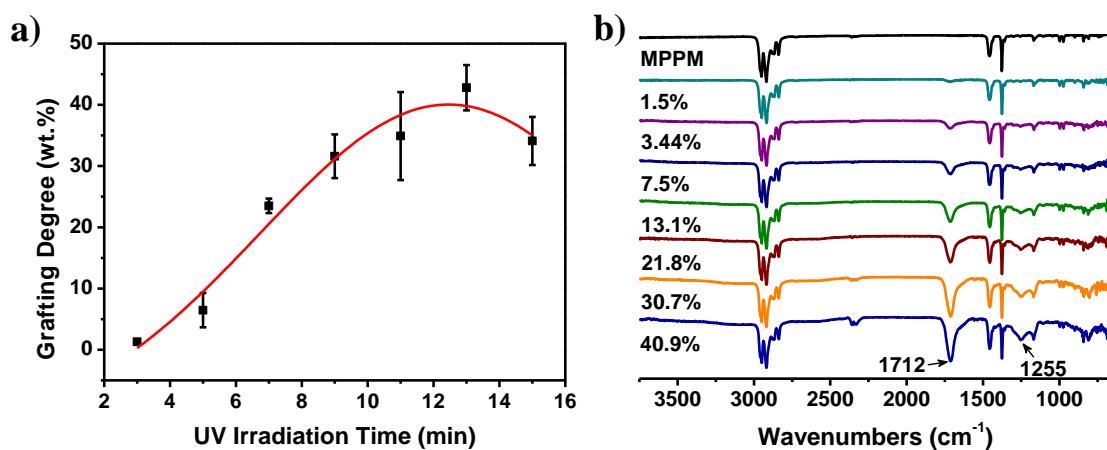
Figure S1. a) Relationship between UV irradiation time and the grafting degree of PAA on MPPM, b) ATR/FT-IR spectra of PAA-grafted MPPMs with different grafting degrees.
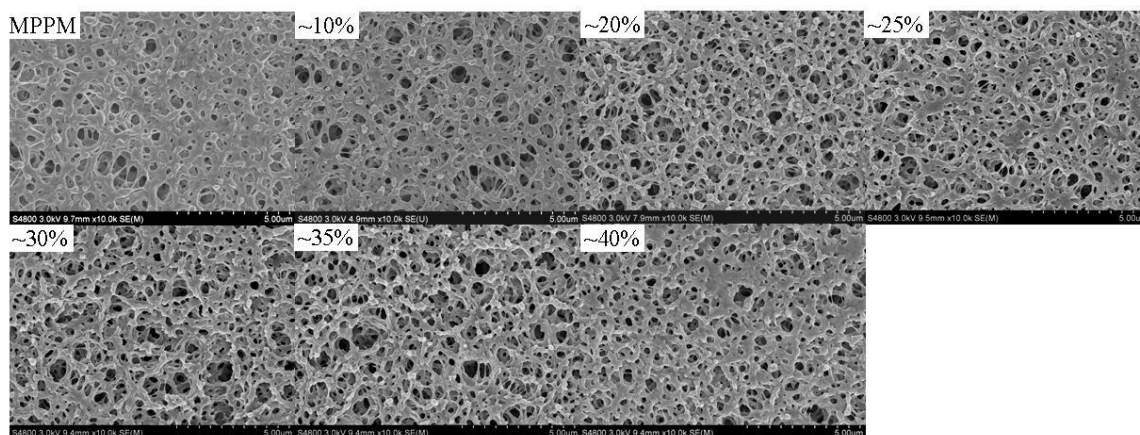

Figure S2. Representative SEM images of PAA-grafted MPPMs with different grafting degrees.

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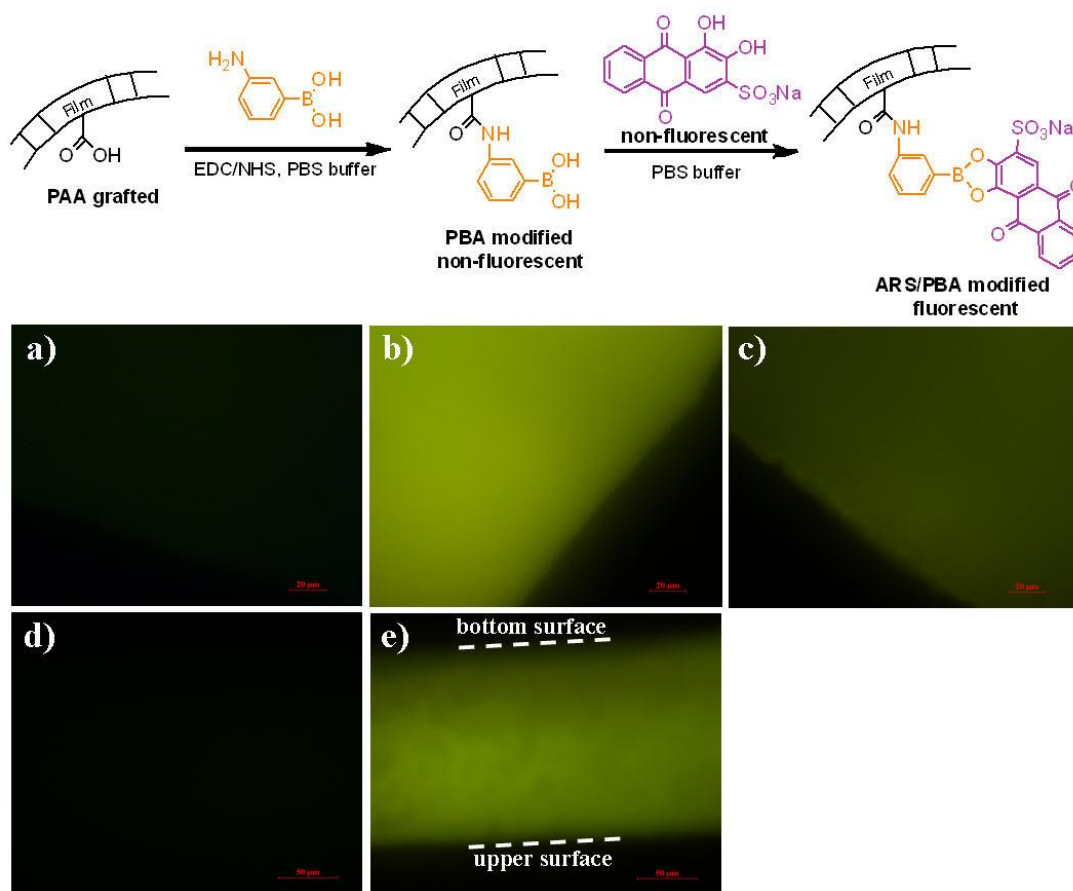
Figure S3. Fluorescence images of MPPMs (a,d) and PAA-grafted MPPMs (b,c,e) after being labeled with PBA/ARS. a,b) Top view, c) Bottom view, d,e) cross-section view. The images were captured by a fluorescence microscope (Nikon ECLIPES Ti-U, Japan). The cross-section view of PAA-grafted MPPM shows that PAA chains distribute throughout the membrane, including the surface of inner membrane pores.
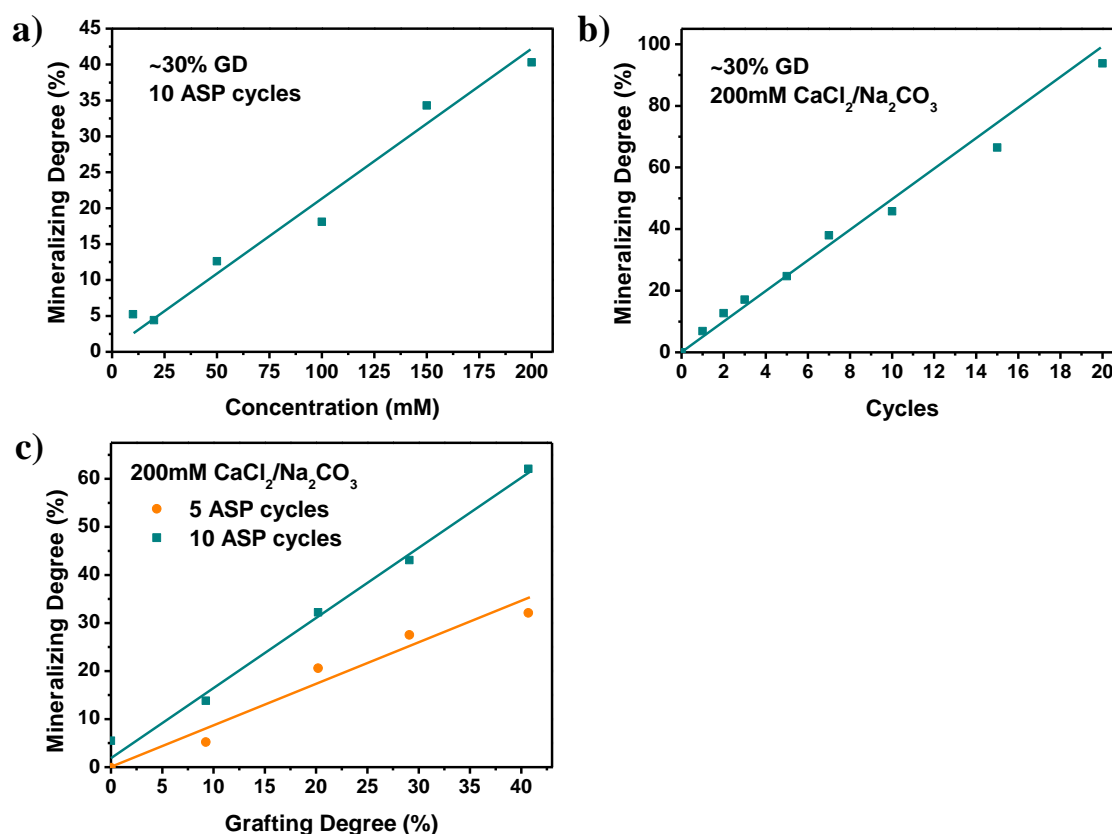
Figure S4. Dependence of the mineral-coating degree of MPPM on (a) the concentration of CaCl$_2$/Na$_2$CO$_3$ solution, (b) the number of ASP cycles, and (c) the PAA grafting degree.
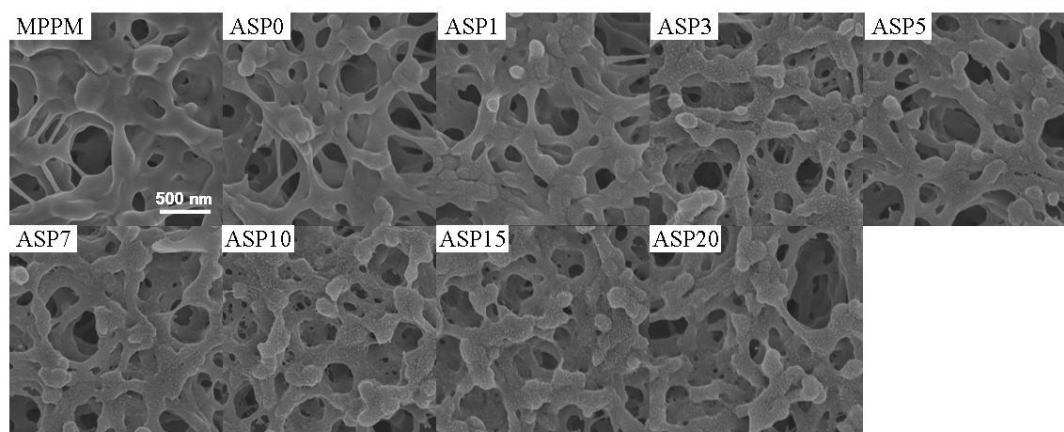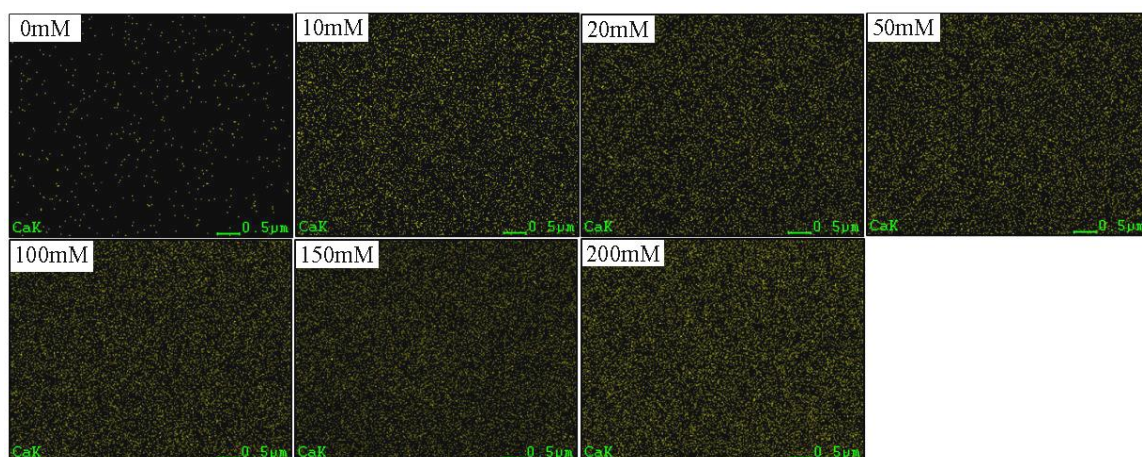

Figure S5. SEM images of the mineral-coated MPPMs prepared from different number of ASP cycles (~30 wt.% PAA-grafted MPPMs, 200 mM CaCl$_2$/Na$_2$CO$_3$ solution). When the cycle number is more than 15, large particles (size > 5 μm) will form on the membrane surface and block the membrane pore.
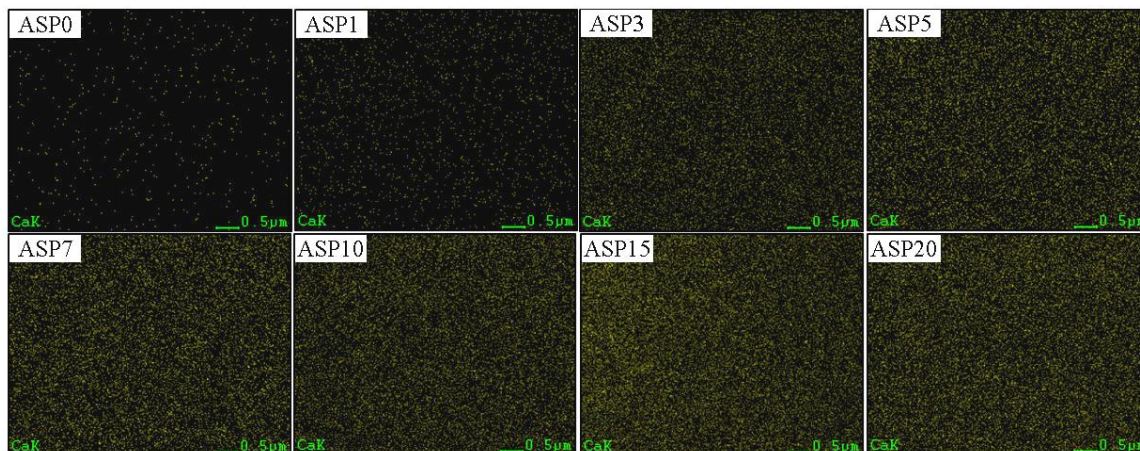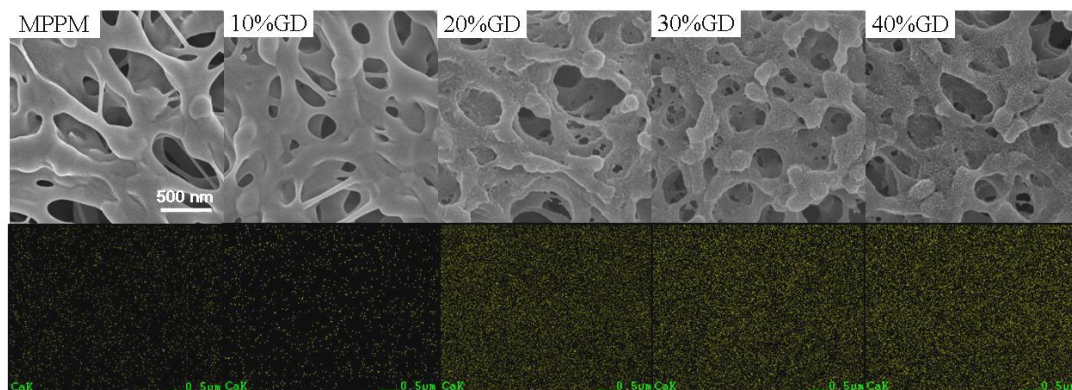
Figure S6. Distribution of calcium element (yellow point) on the mineral-coated MPPMs prepared from different number of ASP cycles (~30 wt.% PAA-grafted MPPMs, 200 mM $CaCl_2$/Na_2CO_3 solution).
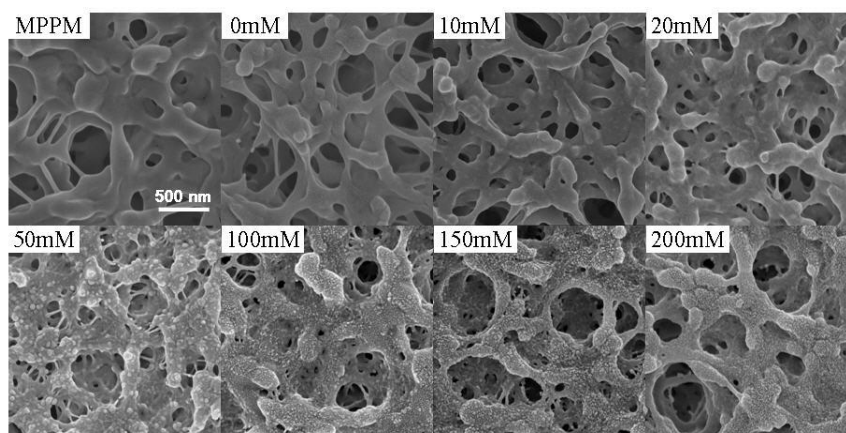

Figure S7. SEM images of the mineral-coated MPPMs prepared from different concentration of $CaCl_2$/Na_2CO_3 solution (~30wt.% PAA-grafted MPPMs, 10 ASP cycles).

Figure S8. Distribution of calcium element (yellow point) on the mineral-coated MPPMs prepared from different concentration of $CaCl_2/Na_2CO_3$ solution (~30 wt.% PAA-grafted MPPMs, 10 ASP cycles).

Figure S9. SEM images and corresponding calcium element (yellow point) distribution of the mineral-coated MPPMs prepared from PAA-grafted MPPMs with different grafting degree (200 mM $CaCl_2/Na_2CO_3$ solution, 10 ASP cycles).

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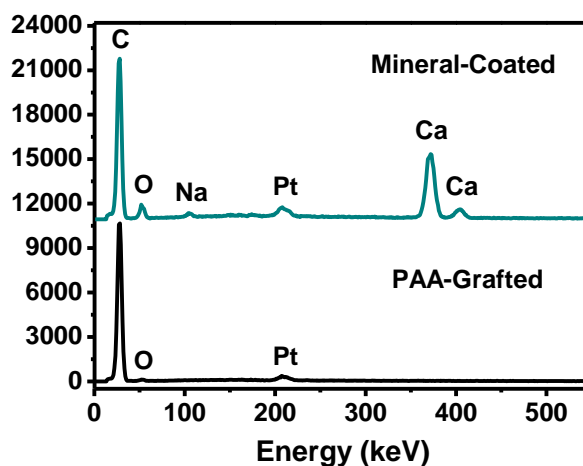
Figure S10. EDX spectra of PAA-grafted MPPM (~30 wt.% GD_{PAA}) before and after being mineral-coated (10 ASP cycles, 200 mM $CaCl_2/Na_2CO_3$ solution).
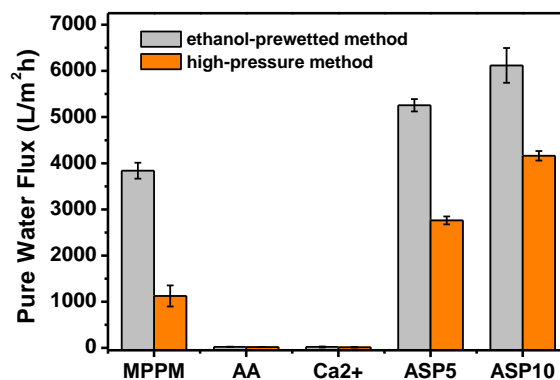

Figure S11. Pure water flux of a series of MPPMs measured by ethanol-prewetted method (gray columns) and high-pressure method (orange columns). MPPM: nascent MPPMs; AA: PAA-grafted MPPMs with ~30 wt.% GD_{PAA}; Ca2+: Ca^{2+}-treated MPPMs fabricated by immersing PAA-grafted MPPMs (~30 wt.% GD_{PAA}) in 200 mM $CaCl_2$ solution for 5 min, then rinsing with water, and dring under reduced pressure; ASP5 or ASP10: mineral-coated MPPMs prepared from 5 or 10 ASP cycles (~30 wt.% PAA-grafted MPPMs, 200 mM $CaCl_2/Na_2CO_3$ solution).
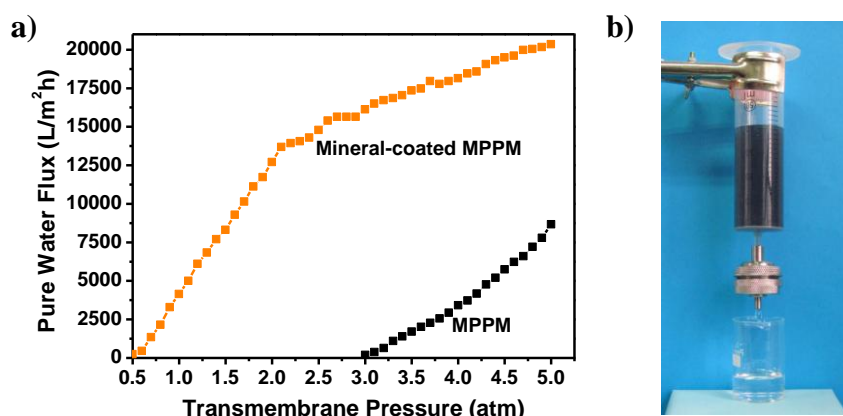
Figure S12. a) Dependence of the pure water flux on the trans-membrane pressure. Dry membranes were directly mounted in a dead-end filtration cell. Then the flux was measured by stepwise increasing the trans-membrane pressure in intervals of 0.01 MPa at a waiting time of 1 min for each point. b) Demonstration of filtration under ultralow trans-membrane pressure. A dry mineral-coated MPPM was mounted in a dead-end cell equipped with a syringe. 50 mL of carbon black particles suspension was poured into the syringe. Water permeated through the membrane under the drive of gravity while the carbon was rejected by the membrane.
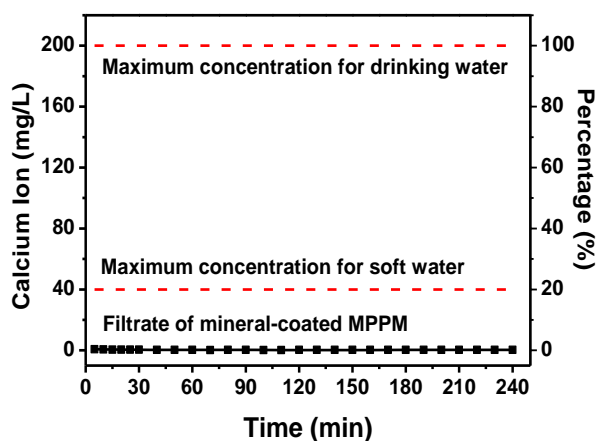
Figure S13. The concentration of calcium ion in the filtrate during water permeability measurement. The filtrate was firstly acidified with HNO_3 and then the calcium content was measured by an atomic adsorption spectrometer (PerkinElmer AA800, USA). The results were much lower than the maximum Ca^{2+} concentrations recommended by World Health Organization for soft water and safe drinking water (Guidelines for Drinking-water Quality, WHO).
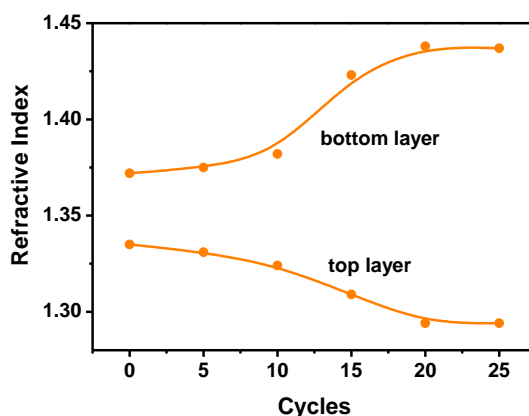
Figure S14. Relationship between refractive index of the top/bottom layer of PAA brushes and the number of ASP cycles. Refractive indexes were evaluated by fitting the ellipsometric data with a simple graded layer model. The refractive index of the top layer of PAA brushes declined while that of the bottom layer increased, indicating a denser layer was forming near the bottom surface during ASP. In other words, the PAA brushes collapsed gradually.

Calculation of the mass of water solidified by PAA brushes: Wet mass change of the whole PAA brush layer (Δm_{tatal}, Fig. 5b, black line) and mass loading of the mineral coating (Δm_{CaCO3}, Fig. 5b, cyan line) can be obtained from QCM data. Deducting Δm_{CaCO3} from Δm_{total} gives information about the water in PAA brush (Δm_{water}). This information is composed of two components, namely, the mass change of PAA brush solidified water ($\Delta m_{brush\ solidified\ water}$) and the water loss due to its space occupied by $CaCO_3$ ($\Delta m_{water\ excluded\ by\ CaCO3}$). $\Delta m_{brush\ solidified\ water}$ directly reflects the thickness change of PAA and can be calculated by the following equations, assuming the density of water and $CaCO_3$ is 1.0 g/cm^3 and 2.9 g/cm^3, respectively.

$$\Delta m_{total} = \Delta m_{water} + \Delta m_{CaCO_3}$$

$$\Delta m_{brush\,solidified\,water} = \Delta m_{water} - \Delta m_{water\,excluded\,by\,CaCO_3}$$

$$= \Delta m_{water} - \frac{\rho_{water}}{\rho_{CaCO_3}} \cdot \Delta m_{CaCO_3}$$

Reference

[1] R. Dong, S. Krishnan, B. A. Baird, M. Lindau and C. K. Ober, *Biomacromolecules*, 2007, **8**, 3082.