Supporting Information

Robust superhydrophilic polylactide (PLA) membrane with TiO_2 nano-particles inlayed surface for oil/water separation

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Abstract: Instability of superwetting surface is the stumbling block of flexible polymeric membranes for continuous separation of oil/water mixture. A robust superhydrophilic surface was fabricated by nano-TiO2 inlayed on hierarchical polylactide (PLA) ultrafiltration membrane via a spin coating process. Distinctly different from most previously reported nano-particles involved polymeric membranes, both micro-/nano- architecture of PLA membrane and size matched nano particles assembly constructed the robust superhydrophilic interface mimicking coral tentacles predatory behavior. The rigid surface based on flexible polymeric membrane with hierarchical architecture showed robust superhydrophilicity and underwater superoleophobicity even after long-time water washing treatment, which was also verified by the morphology, contact angle, XPS and adhesive force in contrast to smooth membrane. The as-prepared PLA membrane showed excellent separation performance in varieties of oil/water mixtures separation with robustly high permeate flux (above 950 L/m2·h under 0.1 MPa) and oil rejection (above 99%) even after 10 cycles operation. Besides, the superhydrophilic PLA membrane exhibited outstanding anti-protein fouling property. The PLA membranes showed relatively high BSA and ink rejection, respectively, as well as the water flux recovery and continuous separation stability due to rigid interface strengthening effect. The unique interface combination strategy between functional nanoparticles and polymeric membrane provided a window of opportunity for constructing robust polymeric membrane for advanced applications e.g. oil/water separation, ion exchange and membrane catalytic reactor etc.

Experimental Procedures and Discussion

Superhydrophilic robustness to chemical corrosion of the TiO_2-PLA-1 membrane: The resistance to acid and alkali solution tests is followed: the rigid TiO_2-PLA-1 membrane with the dimension of 2 cm × 4 cm was immersing into 20 mL pH=0 HCl and 20 mL pH=13 NaOH solution at 25 ^oC with a speed of 50 r/min for 24 h. The contact angle was then recorded by OCA 20 system to evaluate the variation of superhydrophilicity after the acid or alkali damage. As shown in Figure S1 (a, b, c), the red water droplet expanded and penetrated instantaneously into the TiO_2-PLA-1 membrane surface after chemical treatment, indicating the superhydrophilicity resistant to chemical damage. Furthermore, we accurately measured the change of WCAs on the TiO_2-PLA-1 membrane after long-time chemical treatment. As exhibited in Figure S1 d and Movie S4, the pristine TiO_2-PLA-1 membrane showed the excellent superhydrophicility with the water contact angle instantaneously dropping to zero within 1 s. Although the descending rate of WCAs on the TiO_2-PLA-1 membrane surface was decreased by the chemical corrosion, the rigid superhydrophilic TiO_2-PLA-1 membrane did not lost its superhydrophilicity with WCA decreasing to ~0^o within about 2 s even after the strong acid treatment and strong alkali treatment for 24 h, respectively. Thus, we can conclude that the TiO_2-PLA-1 membrane with inlayed TiO_2 interface is well resistant to the harsh corrosion of HCl and NaOH.

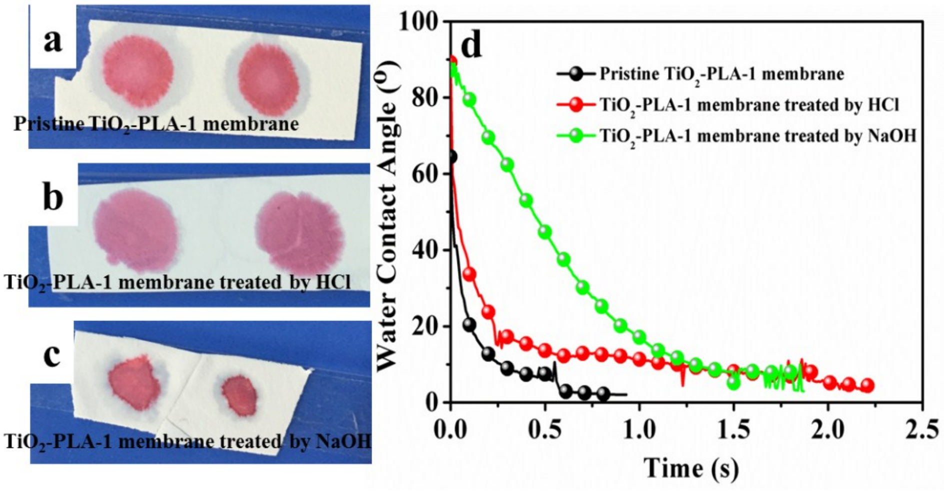

Figure s1. (a, b, c) the wettability and (d) danamic water contact angle of the rigid TiO_2-PLA-1 membrane before and after HCl and NaOH corresion, respectively

The mechanical properties of the as-prepared PLA membranes: An Instron 5567 (Wuhan, China) was used for the mechanical property measurements based on our previous studies. [1] System control and data analysis were performed using the instrument software. The standard samples with the dimension of 10 cm (length) × 1 cm (width) × 170 μm (thickness) were used to determine the mechanical properties. Four samples for each membrane were tested at a cross head speed of 5 mm/min. As shown in Figure S2, the tensile strength and elongation at break of the pristine PLA membrane is about 2 MPa and 17%, respectively. After inlayed by the nano-particles, the mechanical properties of the TiO_2-PLA-1 membrane almost have unchanged in comparison with the pristine PLA membrane.

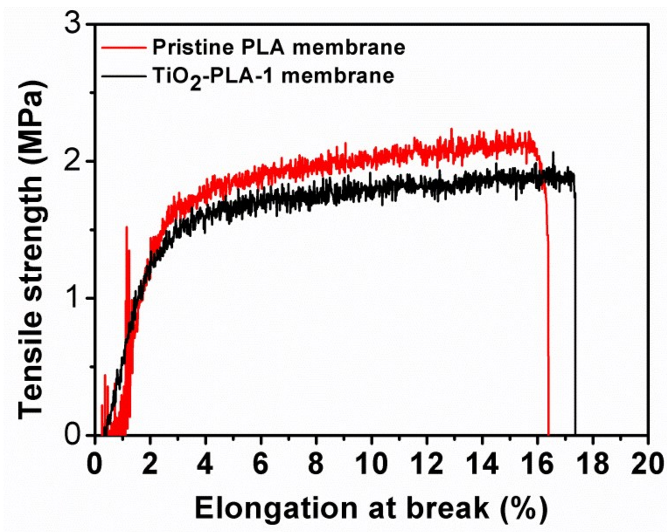

Figure S2. The stress-strain curves of pristine PLA membrane and TiO_2-PLA-1 membrane

Reference

[1] X. M. Yu, F. Liu, L. H. Wang, Z. Xiong, Y. Wang, *RSC Adv*, 2015, **57**, 8306.