Spraying-induced in-situ growth of $CaCO_3$ for modification of membrane for oil/water separation

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2.1 Materials

Calcium chloride ($CaCl_2$), anhydrous sodium carbonate (Na_2CO_3), alginate (SA), petroleum ether, hexane, atolin as well as 1,2-dichloroethane were bought from bought from Sinopharm Chemical Reagent Co., Ltd. (China). Anhydrous ethanol (99.5%) and sodium dodecyl carbonate (SDS) were bought from Aladdin Reagent Co., Ltd. (China). Sunflower oil was provided by supermarket.

2.2. Preparation and separation of oil-in-water emulsions

Petroleum ether, hexane, atolin, 1,2-dichloroethane and sunflower oil were mixed with water containing 50 mg/L SDS emulsifier at the ratio of 1:99. The oil/water mixtures were treated by ultrasonication for 15 min and rapid stirring for 24 h to obtain SDS-stabilized oil-in-water emulsions. In the separation experiment, the pre-wetted membrane with water was fixed on the vacuum filter device, and then various emulsions were separated under a pressure of 0.01 MPa.

The flux (J, L m^{-2} h^{-1} bar^{-1}) was determined according to the following formula:

$$J = \frac{V}{A\Delta t\, \Delta P} \qquad (1)$$

where V (L) is the volume of the emulsion, A (m^2) is the effective separation area of membrane, ΔP (bar) trans-membrane pressure, and Δt (h) represents separation time.

The separation efficiency (R) of oil/water emulsion was determined through the following formula:

$$R = (1 - \frac{C_f}{C_0}) \times 100\,\% \qquad (2)$$

where C_o and C_f are oil concentrations before and after oil-water separation, respectively, as tested by a UV-vis spectrophotometer.

2.3 Stability test

The stability of the $CaCO_3$ layer on the surface of the PVDF membrane surface was evaluated by different treatments: (1) The membrane was putted into water and stirred under 3000 rpm for at least 12 h. (2) The membrane was repeatedly bend (180°) for 100 times. The separation performance of the membranes after different treatments was measured.

2.4 Characterizations

The surface morphologies and structure of the composite membranes were studied using Scanning Electron Microscopy (SEM, TESCAN MIRA LMS, TESCAN, Czech Republic). The physical phase was analyzed by X-ray diffraction (XRD, LabX XRD-6000, Japan). The surface wettability was measured by a contact angle tester (OSA60, LAUDA Scientific, Germany). The chemical composition of membranes was analyzed by attenuated total reflectance fourier transform infrared spectra (ATR-FTIR, Nicolet560, USA) and X-ray photoelectron spectroscopy (XPS, Thermo Kalpha, USA).

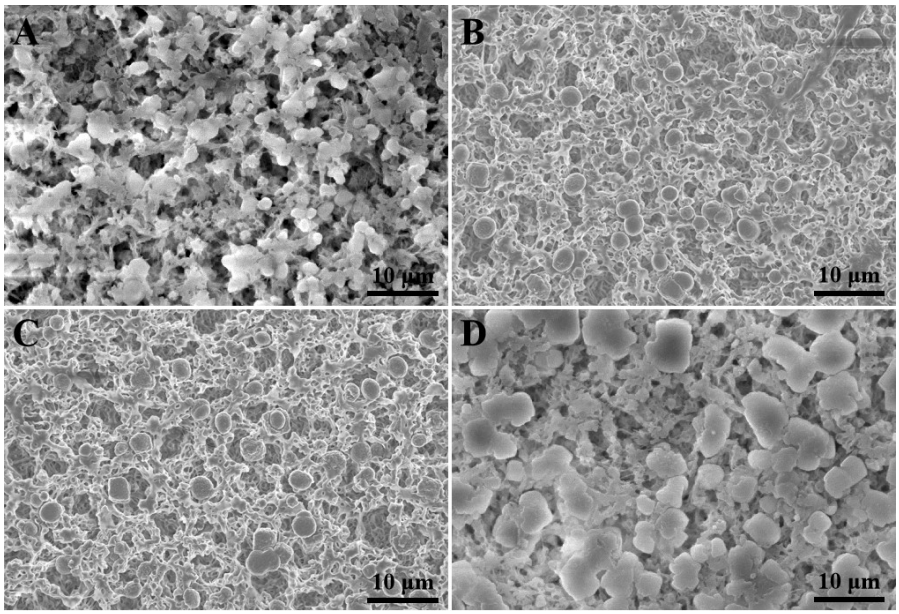

Fig. S1 SEM images of M1 (A), M3 (B), M5 (C), M9 (D)

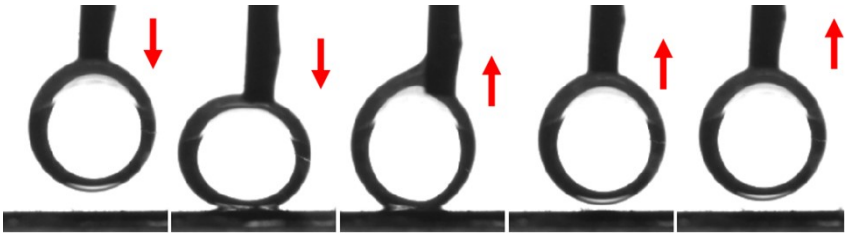

Fig. S2 Photographic images of dynamic oil adhesion on the membrane surface

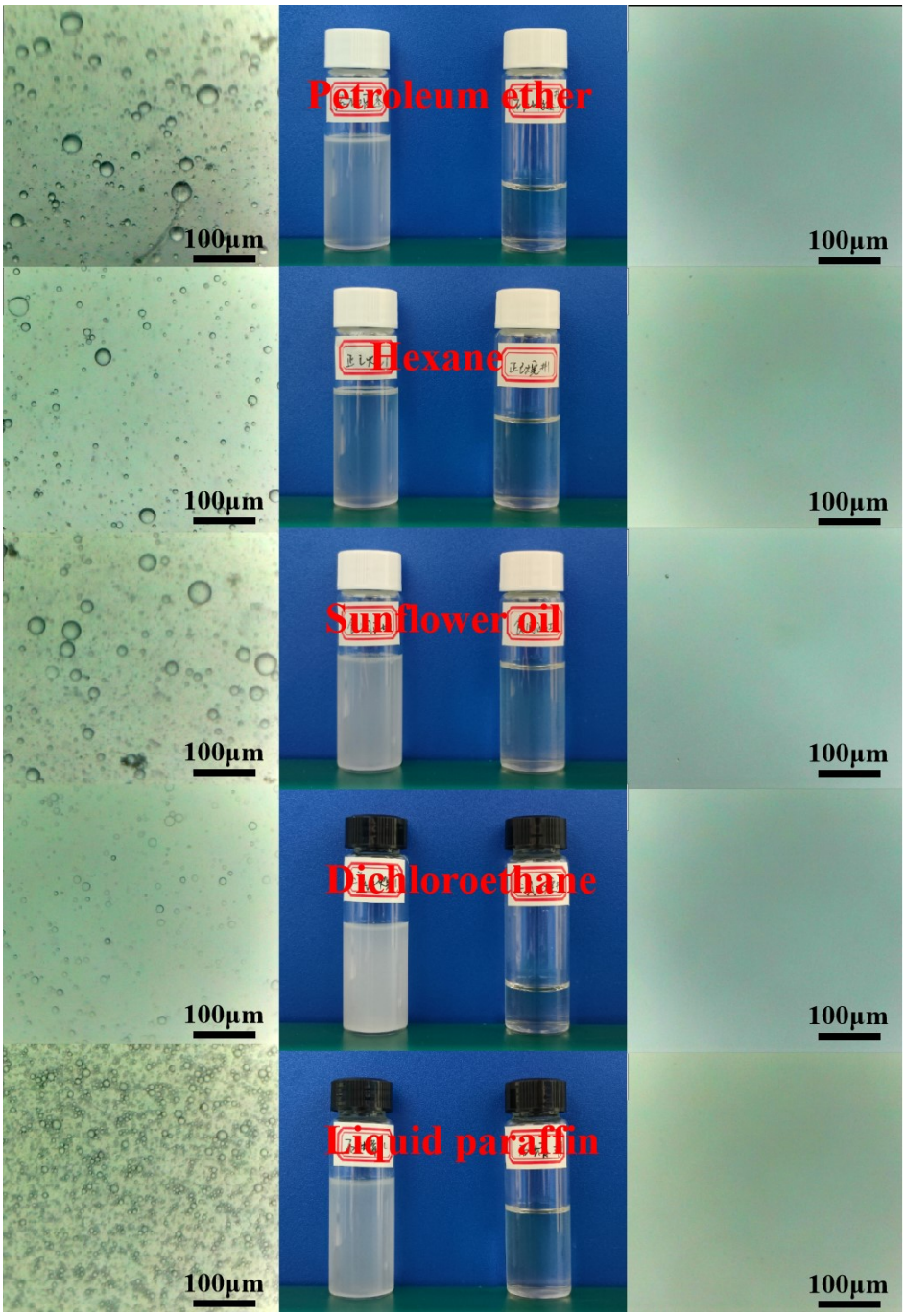

Fig. S3 Digital photos and optical microscopy photos of feed emulsions and filtrates