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A thermo-responsive membrane with cross-linked smart gates via "grafting-to" method

Supplementary Material

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Experimental Section

Materials: Poly(ethylene terephthalate) (PET) track-etched membranes with average pore sizes of 4 μm and 5 μm (Tsinghua University) were used as porous substrate membranes. *N*-isopropylacrylamide (NIPAM; Kohjin) was purified by recrystallization twice in hexane and acetone (50/50, v/v) and dried *in vacuo* at room temperature. Glycidyl methacrylate (GMA; Acros Organics) with purity of 97% was used as comonomer in NIPAM solution. 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (V_{50}) and benzophenone (BP) were

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initiators during the fabrication of microspheres and membrane with carboxyl groups, respectively. Bovine serum albumin (BSA) was used as hydrophobic model molecules during the adsorption experiment at high temperature. Acrylic acid (AAc), 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (EDC·HCl; 99%), ethylenediamine (EDA), *N,N′*-methylenebisacrylamide (MBA) and tetramethylethylenediamine (TEMED) were used as received without further purification. Deionized water with resistivity higher than 18.0 MΩ (Milli-Q, Millipore) was used throughout all the experiments.

Preparation and characterizations of microspheres: The functionalized poly(*N*-isopropylacrylamide-*co*-glycidyl methacrylate) (PNG) microspheres were synthesized by precipitation polymerization in two steps. In the first step, the poly(*N*-isopropylacrylamide) (PNIPAM) microsphere seeds were formed by free radical polymerization of NIPAM monomers. Specifically, monomer NIPAM (0.118 M) and crosslinker MBA ([MBA]/[NIPAM] = 3 wt%) were dissolved into deionized water. After bubbling nitrogen for 30 min, the solution was heated to 70 ^{o}C and V_{50} ([V_{50}]/[NIPAM] = 2.25 wt%) was added to initiate the polymerization. The polymerization was lasted for 20 min to form the PNIPAM microsphere seeds. Subsequently, the shell rich with epoxy groups surrounding the PNIPAM seeds were fabricated by copolymerizing NIPAM and GMA. A certain amount of GMA was added to the solution, and the reaction was continued for 6 h at the nitrogen atmosphere. The resultant PNG microspheres were washed for 5 times (20 min each time) at 8000 rpm by centrifugation (Biofuge Primo R, Sorvall) to remove the unreacted monomers, initiator and crosslinker. After purification, the PNG microsphere suspension

was obtained. A series of PNG microspheres were fabricated by adjusting the molar ratio of GMA to NIPAM in order to find out the optimum volume swelling/shrinking ratio.

The morphology and size of the dried PNG microspheres were observed by Scanning Electron Microscope (SEM; JSM-5900LV, JEOL) under an accelerating voltage of 20 kV. A drop of diluted PNG microsphere suspension was dripped on the sample holder, and the PNG microspheres were dried rapidly in air. After gilt, the PNG microsphere sample was subjected to SEM observation.

The temperature-dependent hydrodynamic diameters of PNG microspheres in water were measured by Dynamic Light Scattering (DLS) technique using a Zetasizer Nano analyzer (Zen3690, Malvern) equipped with a He-Ne light source (λ = 633 nm). The PNG microsphere suspension was highly diluted before the measurement. The test temperatures range from 22 ^{o}C to 40 ^{o}C. At every test temperature, the hydrodynamic diameters of PNG microspheres were measured after equilibrium for 20 min.

Preparation of thermo-responsive membranes with grafted PNG microspheres The PET substrate membrane was cut into pieces of 6 cm×6 cm, and then immersed in acetone solution containing photo-initiator BP (0.5 M) under ultrasonic vibration for 10 s. After being soaked for 1 h in dark and dried *in vacuo* at 30 ^{o}C for 2 h, the membrane was immersed in 20 vol% AAc aqueous solution under ultrasonic vibration. Subsequently, a UV lamp with an illuminance spectrum of 250~450 nm (250 W) was employed to initiate the polymerization of AAc monomers on the PET membrane under the nitrogen atmosphere [S1]. After irradiation for 1h, the membrane was rinsed with deionized water for 24 h, and dried at least 8

h at 50 °C. The resultant membrane with carboxyl groups was weighed by electronic balance (Mettler Toledo).

The membrane with carboxyl groups was aminated by EDA after being activated by EDC·HCl. EDC·HCl (2 wt%) was dissolved into TEMED buffer solution at pH 4.7. After ultrasonic vibration for 10 s, the membrane with carboxyl groups was immersed in the EDC·HCl solution for 1 h at 4 °C [S2]. Subsequently, 2 mL EDA was added and then the membrane was treated with ultrasonic vibration for 10 s again. The amination process was continued for 24 h at 4 °C. The resultant membrane with amino groups was rinsed with water, dried and weighed.

Finally, the membrane with amino groups was immersed in the PNG microsphere suspension, and treated with ultrasonic vibration to make sure the microspheres suspension well-dispersed in the membrane pores. Later, the membrane and PNG microsphere suspension were heated to 70 °C and reacted for 24 h. The PNG microspheres were immobilized on the PET membrane by the chemical reaction between the epoxy groups on PNG microspheres and the amino groups on membrane. The resultant membrane immobilized with PNG microspheres was washed with a large amount of deionized water for 24 h, dried for 12 h at 50 °C, and weighed by electronic balance.

Characterizations of thermo-responsive membranes with grafted PNG microspheres

The grafting degree of PNG microspheres on the membrane is calculated by the grafting yield (Y) which is defined as the mass increase percentage of membrane immobilized with PNG microspheres in comparison with the membrane with amino groups (Eq. S1).

$$Y = \frac{W_{PNG} - W_{NH_2}}{W_{NH_2}} \times 100\% \quad \text{(S1)}$$

where Y stands for the grafting yield of membrane with PNG microspheres [%], W_{NH2} and W_{PNG} are the masses of membrane before and after immobilization of PNG microspheres respectively [g].

The microscopic configurations of membranes with grafted PNG microspheres were characterized by employing SEM (JSM-5900LV, JEOL) and Atomic Force Microscope (AFM; SPA400, Seiko). The membrane specimen was freeze-dried for 24 h to maintain the microscopic configuration before AFM observation. The tapping mode and Si_3N_4 cantilevers were employed to obtain dynamic atomic force microscopy images. To observe the SEM cross-sectional view, the membrane specimens were immersed in liquid nitrogen in advance, fractured and stuck to the sample holder. After being gilt, the membrane specimens were subjected to SEM observation of cross-section and surface views.

The hydraulic permeability through the membranes with grafted PNG microspheres at different temperatures was studied by measuring the water flux under a constant pressure. The investigated membranes were immersed in deionized water overnight in advance. The test membrane was placed in a microfiltration apparatus in which the temperatures of the membrane and feed water were controlled by a thermostatic unit. The temperature range was changed from 22 ^{o}C to 40 ^{o}C. At the predetermined temperature, the membrane was stabilized for 5 min to ensure the equilibration of volume phase transition of the grafted PNG microspheres, and then compressed nitrogen gas was introduced to achieve the trans-membrane pressure of 0.04 MPa. The volume of deionized water permeating across the membrane and the corresponding time were recorded. The water flux (J) in the unit of

mL·cm^{-2}·min^{-1} at the predetermined temperature was calculated by Eq. (S2):

$$J = \frac{V}{S \cdot t} \tag{S2}$$

where, V represents the volume of deionized water permeating across the membrane at the predetermined temperature [mL], t is the corresponding permeation time [min], and S is the effective membrane area for filtration [cm^2] calculated by the effective diameter for filtration (39 mm). The water flux was measured for three times at each test temperature to obtain the average value. The thermo-responsive coefficient (J_{40}/J_{25}) is defined as the ratio of the measured water flux of membrane at 40 ^{o}C to that at 25 ^{o}C. The higher the J_{40}/J_{25} value is, the better the thermo-responsive performance of membranes.

Both the reversibility and stability of thermo-responsive performance and dynamic adsorption of BSA molecules of membranes with grafted PNG microspheres were also carried out in the same microfiltration apparatus mentioned above. During the repeatability experiment, the measurements of water flux through membranes were operated at 22 ^{o}C and 40 ^{o}C alternately for 5 cycles under 0.04 MPa. During the dynamic adsorption experiment, the feed BSA aqueous solution (0.6 mg mL^{-1}) was heated to 40 ^{o}C and permeated through the membrane under 0.01 MPa. After a certain interval, the 3 mL filtrate solution was collected and its absorbance was measured by the UV-vis Spectrometer (UV-1700, Shimadzu) at a wavelength of 281 nm. The BSA concentration in the filtrate solution was calculated by the BSA calibration curve. Finally, the amount of BSA adsorbed on the membrane per unit area (Q_m) at different time was obtained.

References

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