Supplementary Material (ESI) for Analytical Methods

Online monitoring of ethanol concentration using a responsive microfluidic membrane device

Supplementary Material

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Supplementary Text

Fabrication of ethanol-responsive nanogels

PNIPAM nanogels are synthesized by precipitation polymerization. In brief, monomer *N*-isopropylacrylamide (NIPAM, Sigma-Aldrich), cross-linker *N*,*N*-methylenebisacrylamide (MBA) and initiator potassium persulfate (KPS) with a molar ratio of 100:5:2 are dissolved in 320 mL pure water. The concentration of NIPAM monomer is fixed at 0.0625 mol L^{-1}. The reaction is carried out in anaerobic atmosphere in a water bath at 70 ^{o}C for 4 h. Subsequently, the dispersion solution of PNIPAM nanogels is washed by repeating centrifugation at 8000 rpm to remove the residual unreacted components. The resultant PNIPAM nanogels are freeze-dried and reserved for further preparation of the ethanol-responsive membranes.

Experiment setup for testing ethanol-responsive characteristics

To investigate the ethanol-responsive property, the microfluidic membrane device is integrated into a flow system that consists of a syringe pump, a thermocouple and a steel ruler (Fig. S1). Each part is connected with silicone tube and the whole system is settled in a constant temperature incubator.

Pressure resistance test of the microfluidic membrane device

To investigate the adhesive strength and the leakproofness of the microfluidic membrane device, a pressure resistance test is conducted by injecting dyed water into the device at different pressures (Fig. S2). The pressures are measured by using a pressure gauge. All the ports of the device are blocked except the inlet. Then, dyed water is injected into the device through the inlet

under preset pressure. As the hydraulic pressure increases from 0 to 0.05 MPa, the device remains intact without any leakage.

Effects of the capillary transport on the flow velocity of liquid column in the capillaries

The capillary transport of the fluid into the capillary tube is studied by evaluating the effect of the wettability of the inner wall of the capillary on the monitoring results. Two glass capillaries with an inner diameter of 0.4±0.01 mm are hydrophilically modified by 10% hydrofluoric acid and hydrophobically modified by chlorotrimethylsilane, respectively. The modified capillaries are inserted into pure water vertically to confirm the wettability. The water level and shape of the vapor-liquid interface in the capillary shown in Fig. S3a and S3b confirm the surface modification is successful. Then, the two capillaries are connected to a syringe pump and respectively injected with dyed water and 15% ethanol solution at a feed flow rate of 100 μL/h. The time series of movement of the liquid columns in the hydrophilically-modified capillary and hydrophobically-modified capillary are shown in Fig. S3c and S3d, respectively. The calculated flow rate of liquid is 100.6 μL/h, which is close to the feed injection rate. The flow velocity of dyed water and 15% ethanol solution is about 12.7 and 13.7 mm/min in the hydrophilic capillary, while that in hydrophobic capillary are 13.1 and 14.0 mm/min, respectively. The differences between the flow velocities in the capillaries are attributable to the difference between the inner diameters of different capillaries (0.4 mm ± 0.01mm). The results show that the wettability of capillary nearly has no effect on the flow velocity of solution in the glass capillary in our study. That is, the change in the flow velocity is due to the adjustment of ethanol-responsive membrane device.

Thermo-responsive characteristics of the microfluidic membrane device

Since the operation temperature is an important factor to influence the fermentation process and the PNIPAM is also known as a thermo-responsive material, we investigate the temperature-induced permeation flux change of dyed water in the flow system shown in Fig. S1 at the feed flow rate of 2000 μL/h.

The responsive microfluidic membranes embedded with PNIPAM nanogels show significant responsive property in response to operation temperature change across the VPTT. As operation temperatures increase from 25 °C to 40 °C, the trans-membrane water flux presented by the flow velocity of the monitoring port (v_m) increases from 3.2 mm/min to 30.5 mm/min, which is caused by the volume phase transition of PNIPAM nanogels.[S1,S2] The microfluidic membrane device is featured with a response temperature of 32.2 °C (Fig. S4). At temperature lower than 32.2 ºC, the PNIPAM nanogels in the membrane are swollen and the resistance for permeation is high, as a result the v_m value is low; while, at temperature is higher than 32.2 ºC, the PNIPAM nanogels are shrunken, and thus the v_m value exhibits a dramatic increase for the low permeation resistance.

Ethanol concentration monitoring of real fermentation broths

To confirm the availability of the microfluidic membrane device in a real fermentation broth with complex composition, a simple fermentation process is conducted. 25 g glucose is dissolved in 250 mL pure water as the substrate. Then, 2 g yeast extract, 1.25 g $(NH_4)_2SO_4$, 0.375 g KH_2PO_4, 0.555 g $MgSO_4$ and 0.0375 g $CaCl_2$ are dissolved in the substrate to obtained the initial fermentation broth. Meanwhile, 12.5 g glucose and 7.5 g dry yeast (Angel Yeast) are added into 250 mL pure water and activated in a shaker bath (SHA-BA, Changzhou Guanjun) at 35 °C for 20 min. The activated yeast suspensions and the initial fermentation broth are mixed in a conical flask and the pH value of the mixture is adjusted to 4.0-5.0 by $NH_3 \cdot H_2O$. All the containers are

sterilized at 120 °C for 30 min before use. Afterward, the open conical flask is placed in the shaker bath at 35 °C for the aerobic breeding of the yeast. Four hours later, the conical flask is sealed by a rubber plug with an inserted and plugged PE tube and the anaerobic metabolism of the yeast begins. The samples of the fermentation broth are drawn every 12 h and 20 g of glucose are added every 24 h by an injection syringe through a PE tube. The fermentation process is lasted for more than 48 h. The ethanol concentrations of the samples are detected by the microfluidic membrane device in the flowing system shown in Fig. S1† at 30 °C. The $v_{m\text{-}0.4}$ values of samples at different fermentation time are recorded and the ethanol concentrations are obtained.

Supplementary References

[S1] F. Luo, R. Xie, Z. Liu, X. J. Ju, W. Wang, S. Lin and L. Y. Chu, *Scientific Reports*, **2015**, 5, 14708.

[S2] R. Pelton, *Advances in Colloid and Interface Science*, **2000**, 85, 1-33.

Supplementary Figures

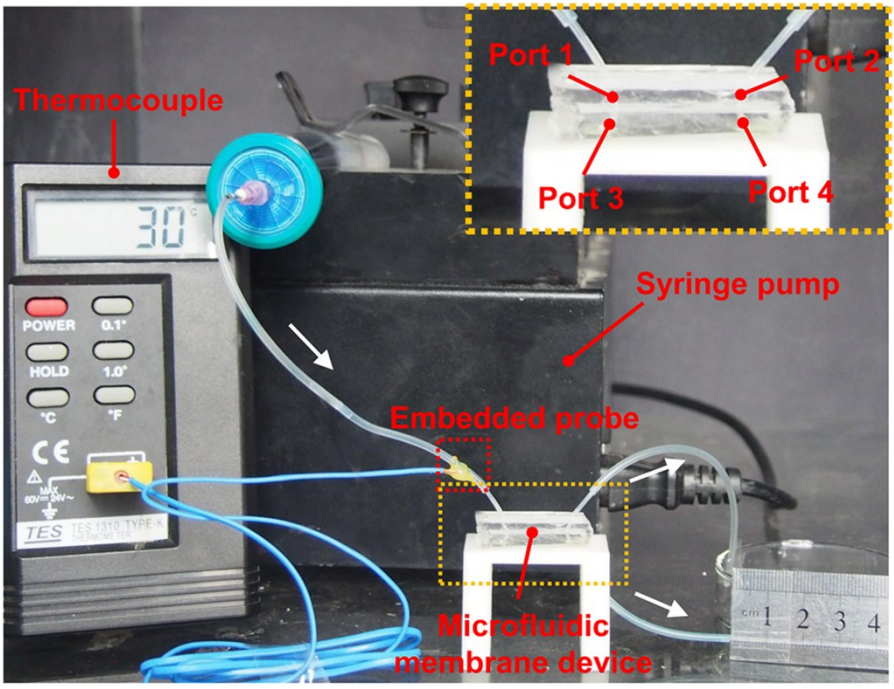

Fig. S1 Experimental setup for testing the ethanol-responsive characteristics.

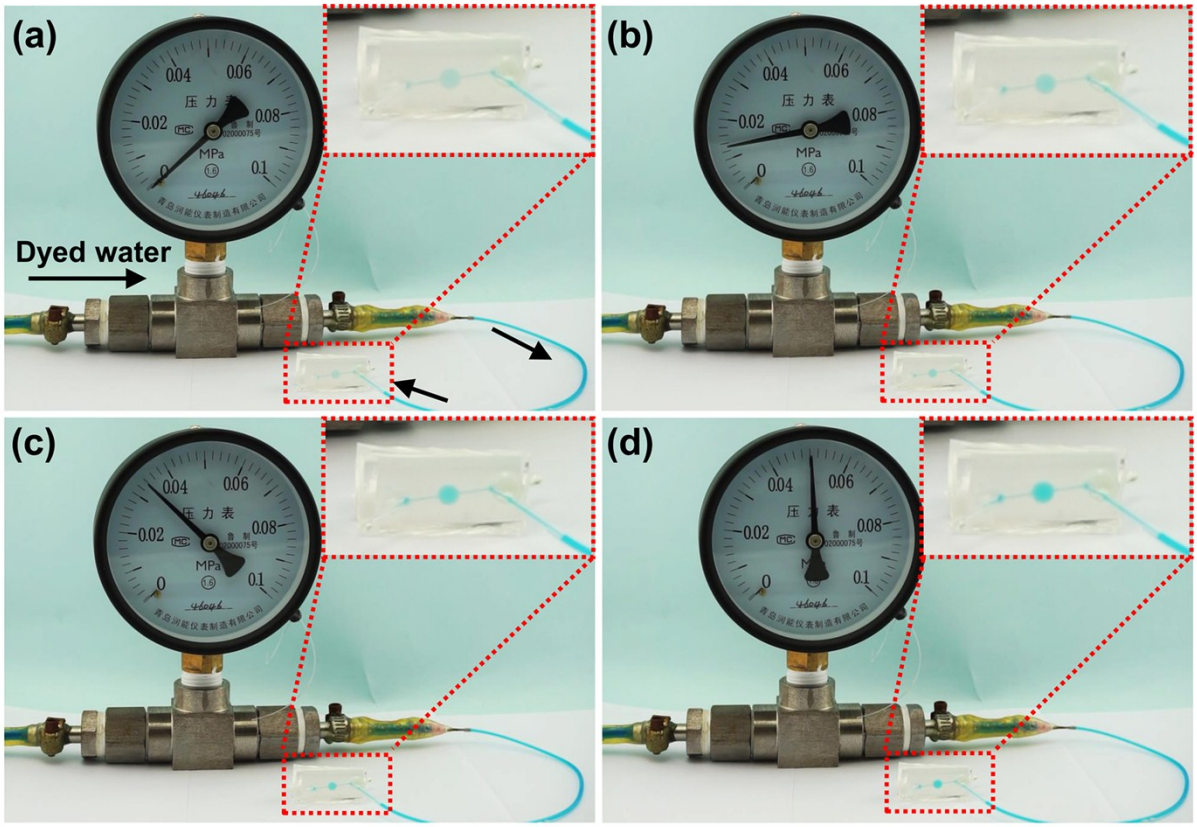

Fig. S2 Pressure resistance test of the microfluidic membrane device.

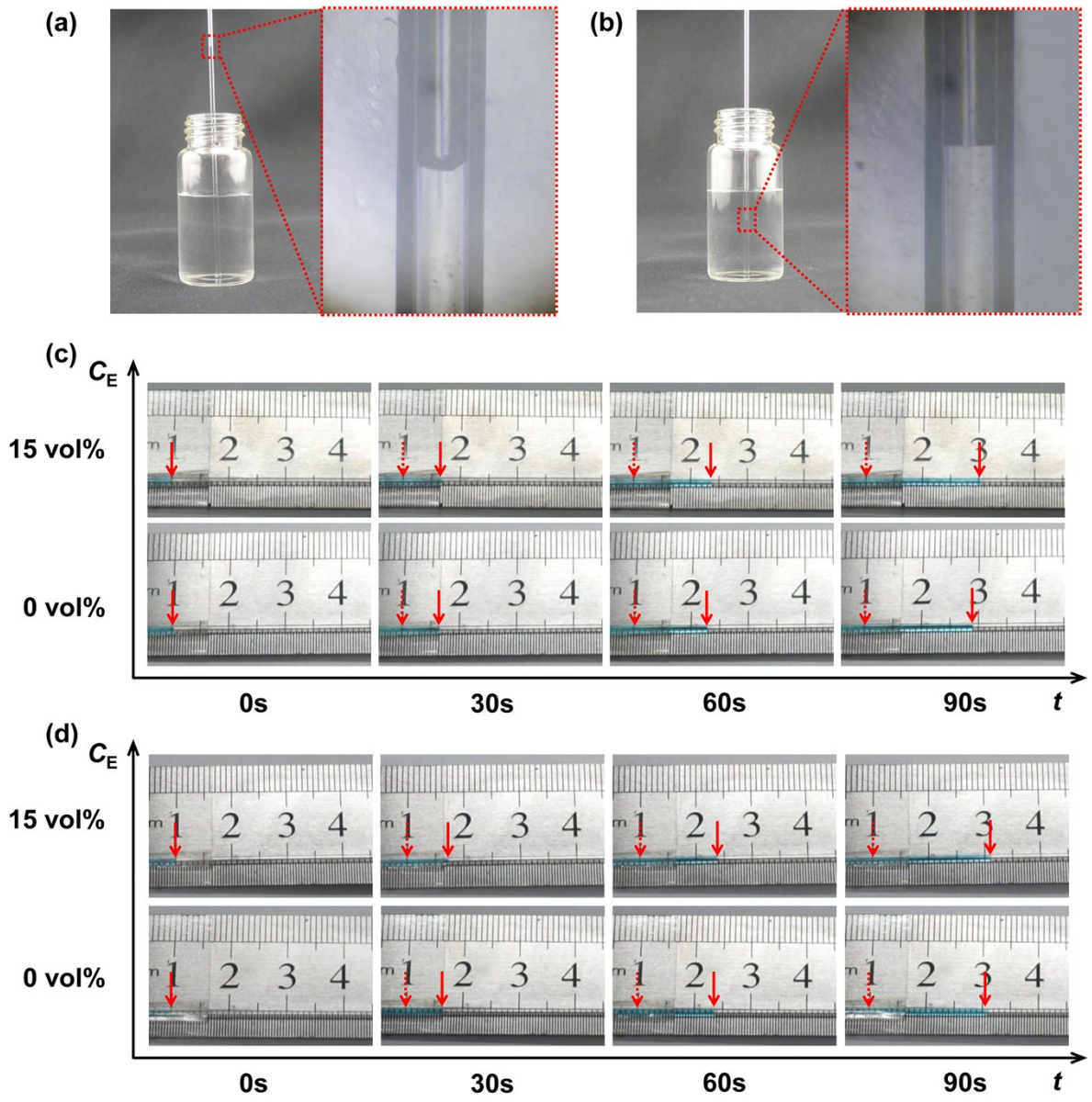

Fig. S3 Effect of the wettability of the capillary on the movement of liquid column. Digital photographs and microscope images of hydrophilically modified (a) and hydrophobically modified (b) capillaries, and time series of movement of the liquid columns of dyed water and 15% ethanol solution in the hydrophilic capillary (c) and hydrophobic capillary (d) driven by the syringe pump at a flow rate of 100 μL/h.

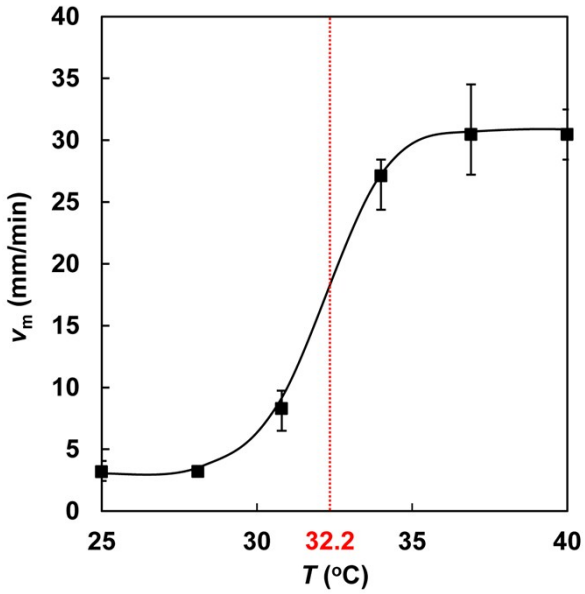

Fig. S4 Thermo-responsive water flux of the microfluidic membrane device.