

Supporting Information

A General Approach for Construction of Asymmetric Modification Membranes for Gated Flow Nanochannels

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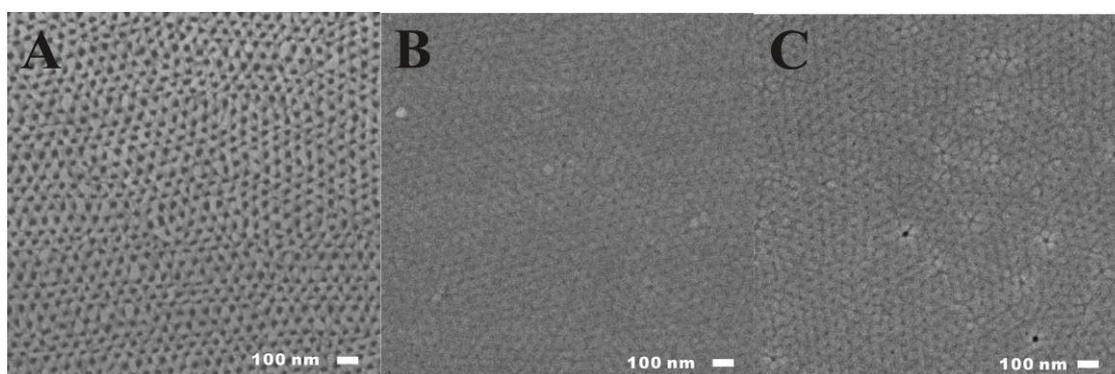


Figure S 1. FESEM images of the top surfaces of AAO membrane with the diameter of 30 nm before (A) and after asymmetric modification of PMETAC (B) and PSPMA (C) polymer brushes.

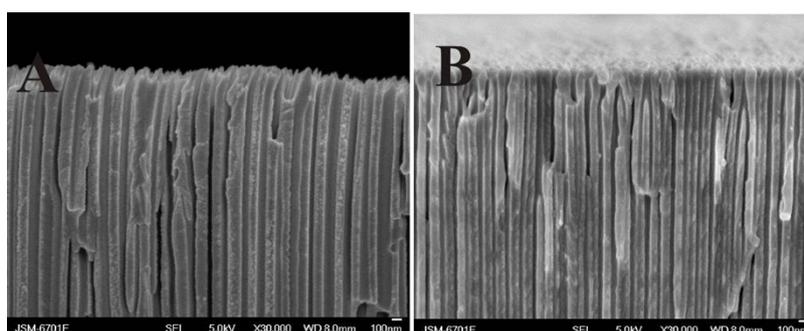


Figure S 2. Cross-sectional FESEM images of AAO membrane before (A) and after (B) modification with polymer brushes (PMETAC).

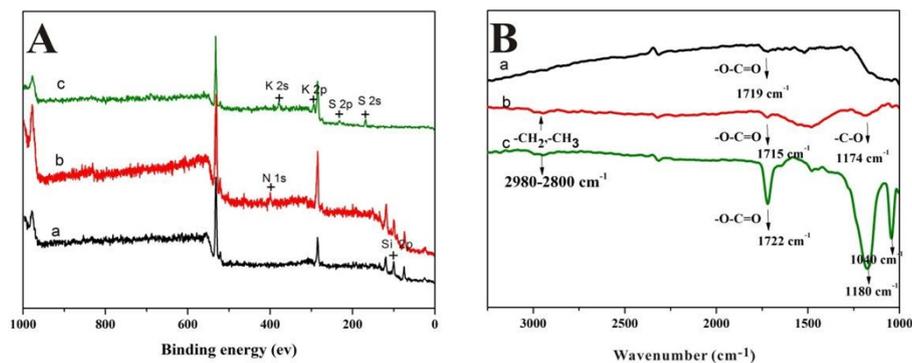


Figure S 3. (A) XPS spectra of (a) AAO-initiator membrane, (b) one side of the AAO membrane modified with PMETAC polymer brush and (c) the other side modified with PSPMA polymer brush. (B) Corresponding FT-IR spectra of same samples shown in (A).

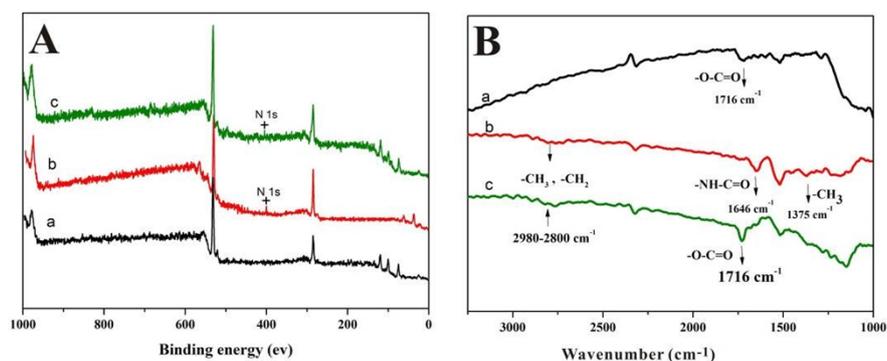


Figure S 4. (A) XPS spectra of AAO membrane before and after asymmetric modification. (a) AAO-initiator membrane, (b) PNIPAM and (c) PDMAEMA polymer brushes modified side of AAO membrane. (B) Corresponding FT-IR spectra of the same part of A.

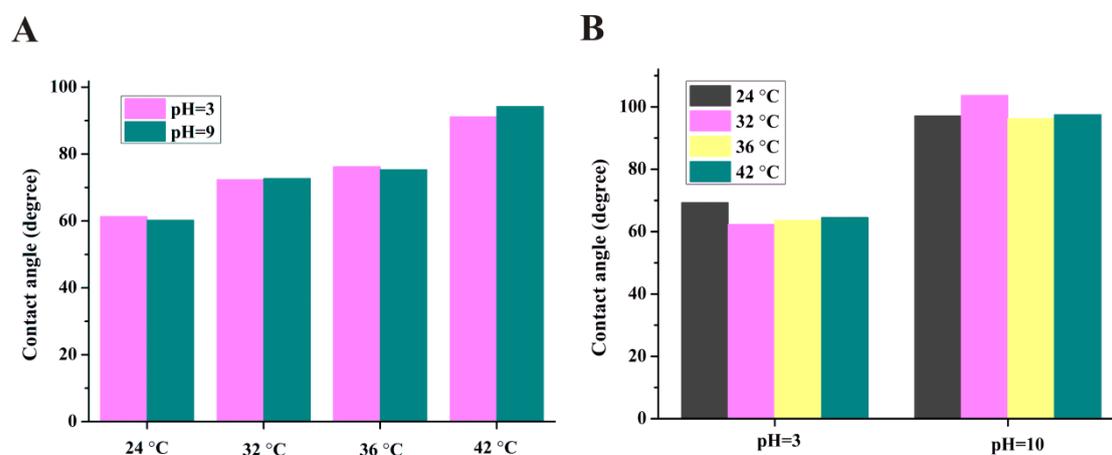


Figure S 5. (A) Contact angle changes of PDMAEMA side at different temperatures, and (B) PNIPAM side at different pHs.

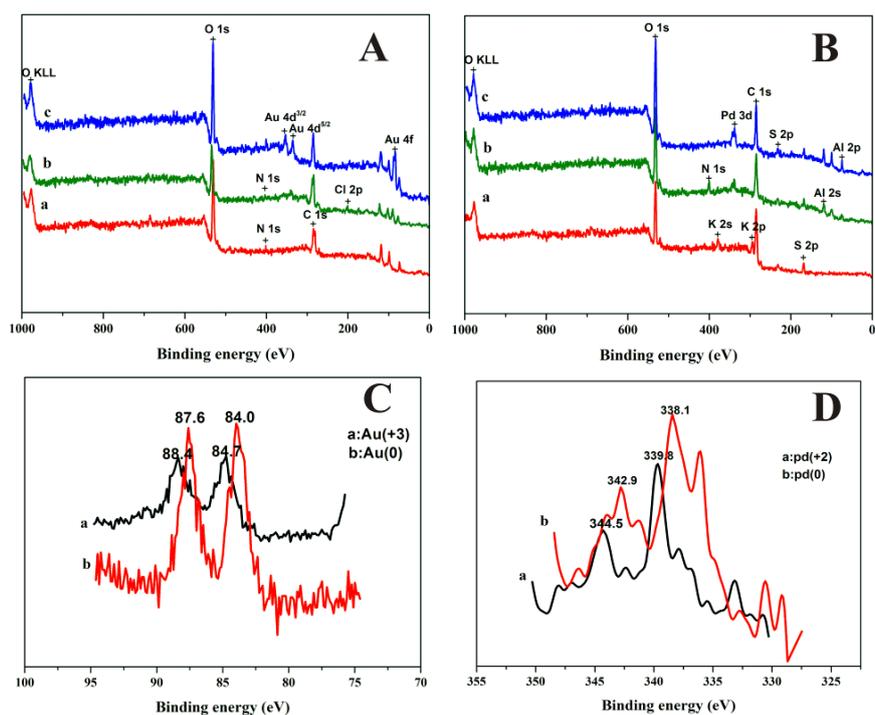


Figure S 6. (A) XPS survey spectra of (a) AAO-PMETAC, (b) AAO-PMETAC-Au(+3) and (c) AAO-PMETAC-Au(0) of one side of asymmetric AAO catalytic membrane. (B) XPS survey spectra of (a) AAO-PSPMA, (b) AAO-PSPMA-Pd(+2) and (c) AAO-PSPMA-Pd(+0) of the other side of asymmetric AAO catalytic membrane. (C) XPS spectra of AAO-PMETAC-Au(0) in the Au (4f) level regions before (curve a) and after (curve b) reduction reaction. (D) XPS spectra of AAO-PSPMA-Pd(0) in the Pd(3d) level regions before (curve a) and after (curve b) reduction reaction of asymmetric AAO catalytic membrane.

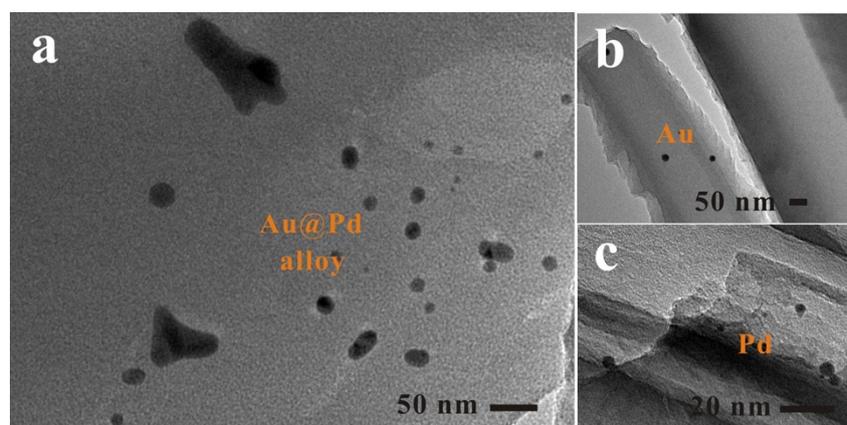


Figure S 7. TEM images of Au and Pd loaded bare AAO membrane without polymer brushes.

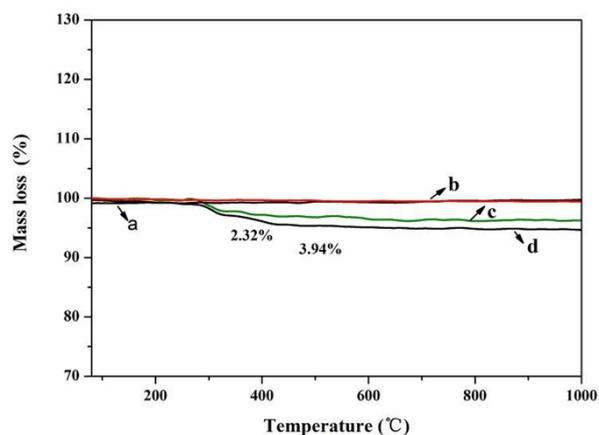


Figure S 8. TG curves of (a) bare AAO membranes, (b) AAO-initiator membranes, (c) AAO-PMETAC-Au@PSPMA-Pd membrane, and (d) AAO-PMETAC@PSPMA membrane.

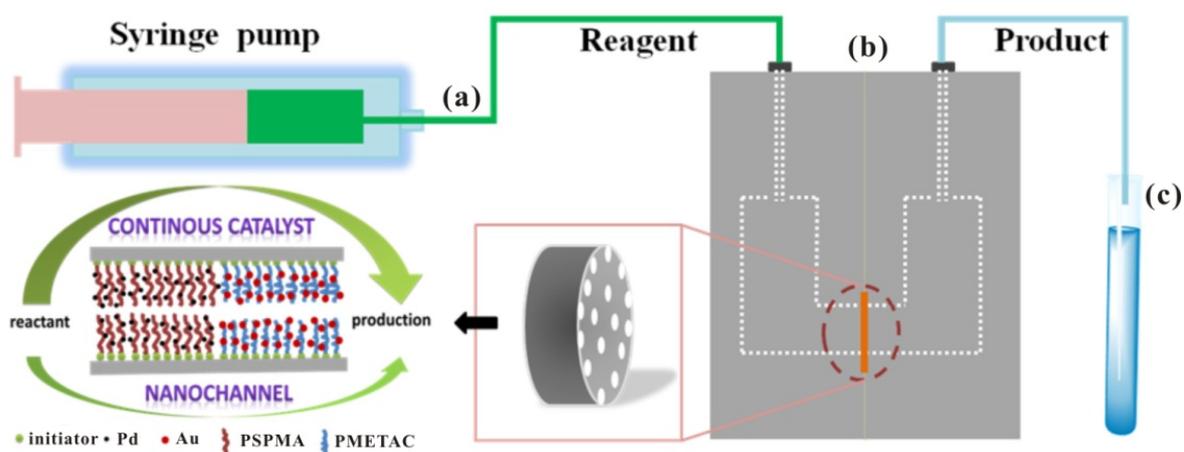


Figure S 9. Schematic diagram showing the process of (a) injection using a PHD 22/2000 syringe pump series ($E=250V$, $I=0.50A$), (b) catalyst using a homemade reaction cell, (c) detection using a UV spectrophotometer. The AAO membrane was magnified in Schematic diagram and effective membrane area is 0.3846 cm^2 .

Flow-through catalysis:

Equation (1) for calculation of water volume flow:

$$J = \frac{V \times 0.1}{3 \times 0.1225 \pi \times 60 \times 1000} \left[\frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \right] \quad (1)$$

For a solution flowing through a catalytic membrane, first-order kinetics is described by

Equation (2):

$$-\frac{dCx}{dx} = -\frac{dCx}{dx} \frac{dt}{dx} = \frac{kCx}{v} \quad (2)$$

Where C_x is the concentration of 4-NP at a distance x into the membrane, t is time, k (s^{-1}) is the first-order rate constant, and v is the linear velocity of the solution in the membrane. Integration of eq 1 across the length, l , of the membrane followed by rearrangement yields

Equation (3):

$$C_t = C_0 \exp\left(-\frac{kl}{v}\right) \quad (3)$$

Where C_0 and C_t are the concentrations of 4-NP entering and exiting the membrane, respectively.

Permeability tests

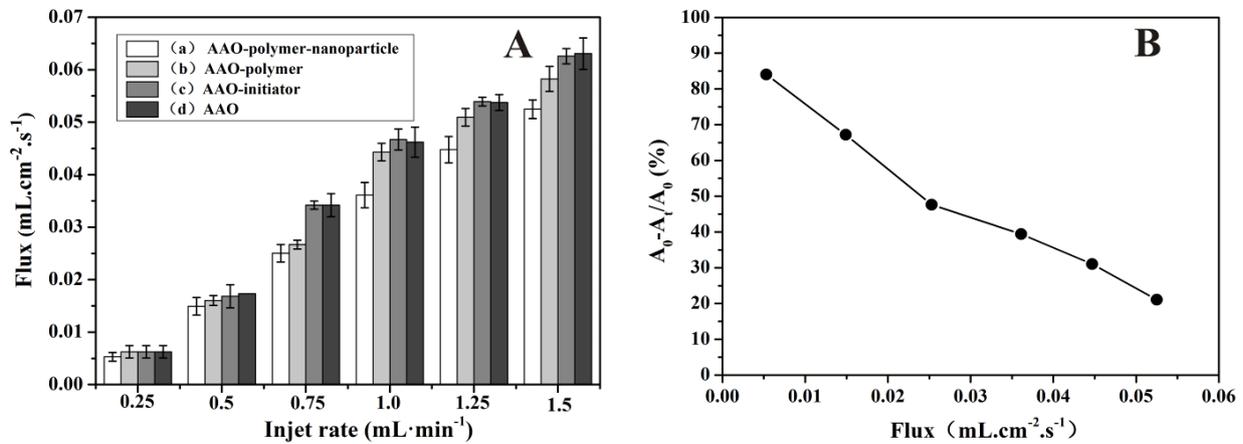


Figure S 10. (A) Histogram of flux V s injection rate of (a) Au-PMETAC@PSPMA-Pd (b) PMETAC|PSPMA (c) AAO-initiator and (d) bare AAO membranes. (B) Catalytic efficiency curve under different fluxes.

The permeability of the polymer brushes asymmetrically modified AAO nanochannels array was also investigated. After checking leakage, the solution in reactor chamber was

sampled at a fixed time interval of 3 min while 2 min was needed to keep equilibrium before the testing. Flux (J) was calculated from the following relation:

$$J = \frac{V}{A_m \cdot t} \left[\frac{mL}{cm^2 \cdot s} \right] \quad (1)$$

where V is the volume of penetrating fluid collected during 3 min, A_m is the effective membrane area (0.3846 cm²), t is the collection time of penetrating fluid, detailed formula for calculation of flux to water was provided in supporting information. As shown in Fig. 10A, the flux obviously increased with rise of the injection rate. The flux decreased after grafting asymmetrical polymer brushes PMETAC and PSPMA, compared to that of the bare and initiator anchored membranes. Furthermore, the flux became smaller after loading Au and Pd nanoparticles, which may be resulted from the blocking effect of nanoparticles.

Hagen-Poiseuille (HP) equation was used to investigate the polymer brushes structure of swelling state in confined nanochannels: [1]

$$J = \frac{Q}{A_m} = \frac{n\pi(D/2)^4 \Delta P}{8\eta L} \quad (2)$$

where Q is the volumetric flow rate from test, A_m is the effective external area (0.3846m²), J is the flux, n is the number of pores per unit area of membrane (~10⁹), D is the average pore diameter, η is the fluid viscosity, ΔP is the pressure difference across the membranes, and L is the average length of the pores (~60 μm). The calculation results (Table S1), which indicated that the average pore diameters obviously decreased after asymmetrically grafting from polymer brushes, compared to bare AAO membrane. The pore diameters decreased further while Au and Pd NPs were asymmetrically loaded onto the channels, which may be resulted from the cooperative effect both of polymer brushes and stabilized nanoparticles. However, with the increase of the injection rate, the calculation results engender deviation. We speculate that this may result from the theoretical hypothesis in Hagen-Poiseuille equation.[2]

The flux injection rate also affected the catalytic efficiency of the Au-PMETAC@PSPMA-Pd membrane. The reaction was thought as a pseudo-first-order with an average rate constant (k) of $\sim 5.9 \text{ s}^{-1}$ because NaBH_4 was in large excess compared to 4-nitrophenol. The residence time decreased with the rise of flux rate. The residence time was 0.2 s with a flux of 0.0149 $\text{mL}/(\text{cm}^2 \text{ s})$ and a linear velocity of only 0.03 cm/s assuming a 50% porosity. As shown in Fig. 10B, catalytic efficiency decreased with the increase of the flow rate. The maximum flux rate of through the membrane was limited to about 0.0524 $\text{mL}/(\text{cm}^2 \cdot \text{s})$ to avoid the fracture of the AAO membrane. The reaction rate constant (k) was calculated according to the kinetics formula of the a catalytic membrane in previous report.^[3] The reaction rate constants (k) ranging from 5.75 to 5.52 s^{-1} for a catalytic efficiency membrane, conformed well to the first-order reaction kinetic model (Table S2).

Table S1. Pore diameter estimated by the Hagen-Poiseuille (HP) equation in different membrane pressure.

V^a (mL/min)	ΔP^b (Pa)	pore diameter			
		d_1^c	d_2^d	d_3^e	d_4^f
0.25	0.01379	174.8 nm	182.4 nm	182.4 nm	182.4 nm
0.5	0.04830	172.0 nm	178.2 nm	181.3 nm	182.6 nm
0.75	0.12412	149.2 nm	151.0 nm	161.5 nm	161.5 nm
1.0	0.22065	145.7 nm	149.5 nm	155.3 nm	155.3 nm

^aInjection rate of the PHD 2000 INFUSION PUMP($E=250\text{V}$, $I=0.50\text{A}$). ^bPressure difference across the membrane. ^cPore diameter of the AAO-PMETAC-Au@PSPMA-Pd membrane. ^dPore diameter of the AAO-PMETAC@PSPMA membrane. ^ePore diameter of the AAO-initiator membrane. ^fPore diameter of the bare AAO membrane.

Table S2. Rate constant k calculated by first-order kinetics equation of catalytic membrane and average velocity of nanochannel assuming a 50% porosity.

J^a (mL cm ⁻² s ⁻¹)	0.0053	0.0149	0.0253	0.0361	0.0447	0.0525
k^b (s ⁻¹)	5.75	5.54	6.18	6.04	6.22	5.52
V^c (cm s ⁻¹)	0.0106	0.0298	0.0501	0.0722	0.0895	0.1050

^aFlux determined in the permeability experiments. ^bRate constant k calculated by first-order kinetics equation of catalytic membrane and average velocity of nanochannel assuming a 50% porosity. ^cAverage linear velocity in the nanochannel of the membrane.

References

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- [2] (a) V. Smuleac, D. A. Butterfield and D. Bhattacharyya, *Chem. Mater.*, 2004, **16**, 2762;
 (b) K. J. Kim and P. V. Stevens, *J. Membr. Sci.*, 1997, **123**, 303.
- [3] D. M. Dotzauer, J. Dai, L. Sun and M. L. Bruening, *Nano Lett.*, 2006, **6**, 2268.