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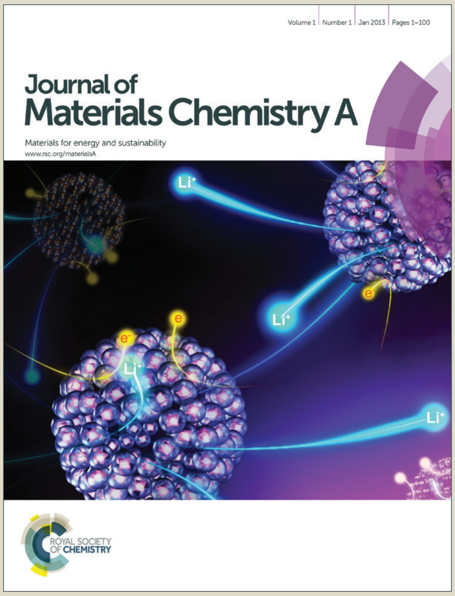

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A General Approach for Construction of Asymmetric Modification Membranes for Gated Flow Nanochannels

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Abstract: Asymmetrical distribution of specific proteins on both sides the cell membrane which is used to adjust the ion permeability, is magical inside the living creature body. These porous membrane materials with asymmetric micro/nanochannels are very common and important in both nature and artificial materials. Inspired by this, constructing of intelligent nanodevices with multifunctional properties is very urgent and significant. Here a general strategy based on simultaneously chemical polymerization reactions in both sides of anodic aluminum oxide (AAO) membrane is reported, combining with atom transfer radical polymerization (ATRP), dopamine self-polymerization (DOP-SP) and ring-opening metathesis polymerization (ROMP) technologies, to form various asymmetric membranes in the AAO nanochannels. By this method, double hydrophilic poly(3-sulfopropyl methacrylate potassium salt) @ poly(2-(methacryloyloxy)ethyl-methyla mmonium chloride) (PSPMA@PMETAC), temperature and pH double responsive poly(N-isopropylacrylamide) @poly(dimethylamino)ethyl methacrylate (PNIPAM@PDMAEMA), and hydrophilic/ hydrophobic

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poly(3-sulfopropyl methacrylate potassium salt)@ poly (hydrophobicpentadecafluorooctyl-5-norbornene-2-carboxylate) (PSPMA@PNCA-F15) polymer brushes modified asymmetrical AAO nanochannel array membranes were successfully prepared. Moreover, after *in situ* ion exchange and reduction reaction of double hydrohyphilic PSPMA@PMETAC membrane, we prepared the polymer brushes stabilized Au-Pd asymmetrically modified AAO nanochannels, showing excellent flow–through catalysis.

1. Introduction

In the recent years, the ordered porous structures inspired by nature showed extremely importance in many biological processes.[1-2] The porous membranes with smart and functional surfaces, [3] have aroused increasing interests because of their versatile applications in separation,[4] catalysis,[5] and drug delivery.[6] Among them, the environmental stimuli-responsive porous membranes with functional channels have attracted more and more attention, which can response to chemical or physical stimuli in their environments, such as temperature,[7] pH,[8] light,[9] and so on. To get these “intelligent” membranes, modification with functional molecules/ macromolecules is necessary within the pores or channels of these membranes, especially for the porous membranes with ordered straight channels and nanoscale diameters in confined geometries.[10,11]

Till now, several methods were developed to achieve above functional nanochannels, including layer-by-layer (LbL) assembly, electrochemical deposition, solution chemical modification, and so on.[10] One of the most widely utilized approaches to create the functional membranes is grafting polymer brushes onto the surface and the channels of the membranes.[12] However, most of the studies focused on the single functionality of the membranes, i.e. modifying with single chemistry. It is very difficult to selectively modify the nanochannels of the membranes with different chemical groups, which restricts the use of functional nanoporous materials in more diversified applications. There were few reports

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about the asymmetric chemical modification within the nanochannel arrays, which is still a technique challenges in nanomaterial science to prepare multi-functional membranes.

The membranes with asymmetrical chemistry of micro/nanochannels are very common and important in nature, which are built by the magical nature through self-assembled processes.[16] In the living creature body, the components of most biological nanochannels are asymmetrically distributed between membrane surfaces. In material science, the Janus nanostructures originated from liquid-liquid interface techniques with different chemical species,[14,15] such as hydrophilic/hydrophobic, polar/nonpolar, have also attracted much attention in the potential applications of novel sensors, actuators and surfactants owing to their remarkably interesting surface activities. Inspired by these materials, some asymmetric modification technologies have been developed to enhance the functionality of artificial nanochannels. However, the complex and severe preparation conditions in traditional modification approaches limited their extensive applications.

In this paper, we experimentally demonstrate a new and general method for asymmetrical modification within the nanochannels of anodic aluminum oxide (AAO) membrane.[16,17,18] The atom transfer radical polymerization (ATRP),[19] ring-opening metathesis polymerization (ROMP),[20] the self-polymerization of dopamine (DOP-SP) methods [14] were adopted to asymmetrically graft a series of functional polymer brushes, including hydrophilic poly(3-sulfopropyl methacrylate potassium salt) (PSPMA) and poly(2-(methacryloyloxy)ethyl-methylammonium chloride) (PMETAC), poly(hydrophobicpentadecafluorooctyl-5-norbornene-2-carboxylate) (PNCA-F15), double responsive poly(N-isopropylacrylamide) (PNIPAM, temperature responsive polymer brushes) and poly((dimethylamino)ethyl methacrylate) (PDMAEMA, pH responsive polymer brushes), bioactive polydopamine on the inner wall of AAO nanochannels by half-cell reactions in a sandwitch-like reactor. Moreover, the Au and Pd nanoparticle catalysts were also asymmetrically modified within the nanochannels of AAO membrane based on the double hydrophilic PSPMA@PMETAC followed by ion

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exchange and reduction reaction, showing good flow-through catalysis and permeability properties.

2. Experimental section

2.1 Chemicals

Anodic aluminum oxide (AAO) membranes with average pore diameters of 30, 130 and 180 nm were purchased from Puyuan Nano (Hefei, China). The initiators of 3–(trichlorosilyl)propyl–2–bromo–2–methyl propanoate and 2-Bromo-2-methyl-N-[2-(3,4-dihydroxyphenyl)ethyl]propionamide, anchor agent of N-(3,4-Dihydroxyphenethyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide, and monomer pentadecafluorooctyl-5-norbornene-2-carboxylate (NCA-F_{15}) were synthesized according to the literatures. [21] [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) with mass concentration of 80 w% in water, 5-norbornene-2-carboxylic acid (97 w%), Grubbs 2nd catalyst and 1H,1H-perfluoro-1-octanol (98%) were obtained from Sigma–Aldrich and used as received. 3-sulfopropyl methacrylate Potassium salt (SPMA) with mass concentration of more than 95 w% in water was obtained from TCI. 2-(dimethylamino)ethyl methacrylate(DMAEMA), N-isopropyl acrylamide (NIPAM)and Dopamine hydrochloride (98.5 w%) were obtained from J＆K Chemical Ltd, and used as received. Tetraammine Dichloropalladium(Ⅱ) with mass percent of more than 41 w% was purchased from Shanghai Dibo Chemical Co (Shanghai, China). $HAuCl_4 \cdot 4H_2O$ was purchased from Beijing Chemical Factory (Beijing, China). Other chemicals used in this work were analytical grade and used as received. Deionized water was used throughout the experiments.

2.2 Asymmetrical modifications by ATRP techniques

All the asymmetrical modifications within the nanochannels of AAO membrane were performed in a home-made half-cell reactor as shown in Scheme 1. The asymmetrical modification was carried out in a half-cell reactor. After hydroxylation by exposure to oxygen plasma of 4 min (99 W) to each side, the AAO membrane were immersed into solution containing 0.05 % (v/v) initiator of (3–(trichlorosilyl) propyl–2–bromo–2–methyl propanoate) in dry toluene for 6 h, and then were rinsed copiously by

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ethanol. Thereafter, both sides of the initiator anchored AAO membranes were exposed under oxygen plasma for 3 s. For modification of the membrane with pore diameter of 30 nm, the monomer METAC (8g, 30.81 mmol) was dissolved into methanol/water (3.5 mL, 1/2.5 v/v) mixed solution. Bipy (0.21 g, 1.45 mmol), CuBr (0.105 g, 0.72 mmol) and $NaClO_4$ (3.85 mg, 0.03 mmol) were added successively into this solution, followed by stirring and purging with argon for 15 min. For other AAO membranes, the monomer METAC (5 mL, 19.55 mmol) was dissolved in methanol/water (6 mL, 1/2.5, v/v), followed by adding bipy (0.2312 g, 1.49 mmol) and CuBr (0.0845 g, 0.58 mmol). The monomer SPMA (1.5 g, 5.8 mmol) was dissolved in methanol/water (9 mL, 1/2.0, v/v), followed by adding bipy (0.048 g, 0.31 mmol) and CuBr (0.015 g, 0.1 mmol). To prepare the double responsive asymmetrical nanochannels membrane, NIPAM (3.78 g), PMDETA (210 μL) and CuBr (0.048g, 0.33 mmol) were dissolved in methanol/water (9 mL, 1/1, v/v); DMAEMA (1 mL), bipy (0.0608 g, 0.39 mmol) and CuBr (0.0304 g, 0.21 mmol) were dissolved in methanol/water (9 mL, 1/1, v/v). When the polymerization finished, the membranes were copiously rinsed with a mixture of methanol and water, and then dried by argon flow.

2.3 Asymmetrical modifications by ATRP and DOP-SP techniques

The AAO membranes (average pore size of 180 nm) were immersed into a solution containing 0.1% (v/v) initiator of (3–(trichlorosilyl) propyl–2–bromo–2–methyl propanoate) in dry toluene for 6 h, and then rinsed with dry toluene and ethanol copiously. Then, the initiator anchored membranes were exposed under oxygen plasma for 3 s, and the asymmetrical modification was carried out in a home-made half-cell reactor with N_2 protection. One side of the cell was poured with PSPMA monomer solution to perform ARTP reaction, while the other side was poured with Tris-HCl buffer solution containing dopamine hydrochloride (0.019 g, 0. 1 mmol) to perform dopamine self-polymerization.

2.4 Asymmetrical modifications by ATRP and ROMP techniques

2-Bromo-2-methyl-N-[2-(3,4-dihydroxyphenyl)ethyl]propionamide (0.04 g) was dissolved in

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ethanol/water (20 mL, 4/1, v/v) while N-(3,4-Dihydroxyphenethyl)bicyclo[2.2.1] hept-5-ene-2-carboxamide (0.03 g) was dissolved in ethanol/water(20 mL, 3/2, v/v) to perform asymmetrical assembly of initiators for 10 h. Then 20 mL CH_2Cl_2 solution, containing 0.03 g Grubbs 2nd catalyst, was quickly added into one side of the half-cell reactor under a N_2 atmosphere. After 20 min, the catalyst solution was extracted and reaction cell was washed by fresh CH_2Cl_2 solution quickly. Furthermore, 20 mL pre-polymerization solution of SPMA momoner was poured into one side of the cell to perform ATRP for 30 min while 20 mL CH_2Cl_2 containing 0.65 g NCA-F_{15} was poured into the other side of the cell to perform ROMP for 5 min. Finally, the membrane was copiously rinsed with ethanol and water, then dried by argon flow.

2.5 Asymmetrical modifications with polymer brushes stabilized Au and Pd NPs

Two kinds of hydrophilic polymer brushes (PSPMA and PMETAC) were firstly asymmetrically modified across the channels of the membrane as mentioned above. Then the membrane was fixed into the home made half-cell reactor. Aqueous solutions of $HAuCl_4 \cdot 4H_2O$ (5 mM) and $Pd(NH_3)_4Cl_2$ (5 mM) were simultaneously added into different side of the cell to achieve ion exchange for about 30 min, followed by reduction with $NaBH_4$ (1 mM) for 3 min, leading to a new asymmetrically catalytic array (Au-PMETAC@PSPMA-Pd). Finally, the functional membranes were rinsed with water and stored for flow–through catalysis. For loading Au and Pd NPs across the channels without polymer brushes, the same procedures were performed as mentioned above.

2.6 Flow-through catalysis and permeability tests

In order to perform organic reduction reactions, aqueous solution of 0.1 mM 4–NP with 10 mM $NaBH_4$ was forced through the functionally catalytic membranes. The membranes were placed in a homemade nanoreactor designed for fitting sample and connecting with the inlet/outlet tubes. Sample solutions were mobilized by utilizing a PHD 22/2000 syringe pump series (Harvard Apparatus, United Kindom). The products were collected and analyzed by UV–Vis spectrophotometer to determine the

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efficiency and duration of the catalytic reaction. The test for conversion vs time was performed by changing the injection rate of PHD 22/2000 syringe pump series. The same process was employed for measurements of permeability of the asymmetrical nanochannels membrane with a time interval of 3 min for collection of penetrating fluid with a stabilization time of 10 min. For test of double responsive asymmetrical nanochanels membrane, the membranes were immersed into corresponding buffer solution for 30 min before test.

2.7 Characterization

The morphologies of the sample surfaces were observed by field emission scanning electron microscopy (FESEM, JSM–6701F, Japan) at 5 kV and transmission electron microscopy (TEM), while the element information were obtained from the energy dispersive spectrometry (EDS) and the energy dispersive X–ray spectroscopy (EDX) on a TECNAI G2 TF20 apparatus (FEI, USA). The polymer brushes stabilized Au and Pd NPs across within the channels of AAO membrane were firstly scraped from the top and bottom part of the membrane and ground to fine powder in ethanol, and then transferred on a carbon–coated copper grid for TEM characterization. Chemical components of the samples were obtained by X–ray Photoelectron Spectroscopy (XPS) on an ESCALAB 250xi spectrometer (Thermon Scientific, USA) using Al Kα radiation. FT-IR was recorded on a TENSOR 27 instrument (BRUCKER) for both side of the membrane using a reflection mode. Thermal stability was determined with a thermogravimetric analyzer (TGA) (Perkin-Elmer, PET) over a temperature range of 25-1000 ℃ at a heating rate of 10 ℃/min under a N_2 atmosphere. Investigation of wetting was performed on a contact angle measurement meter (DSA100). After flow-through catalysis reaction, the products were quickly collected and then detected by UV-Vis absorption spectrophotometer with a constant time interval of 10 min, and the dates were recorded on a Specord 50 spectrophotometer (Analytik Jena, Germany).

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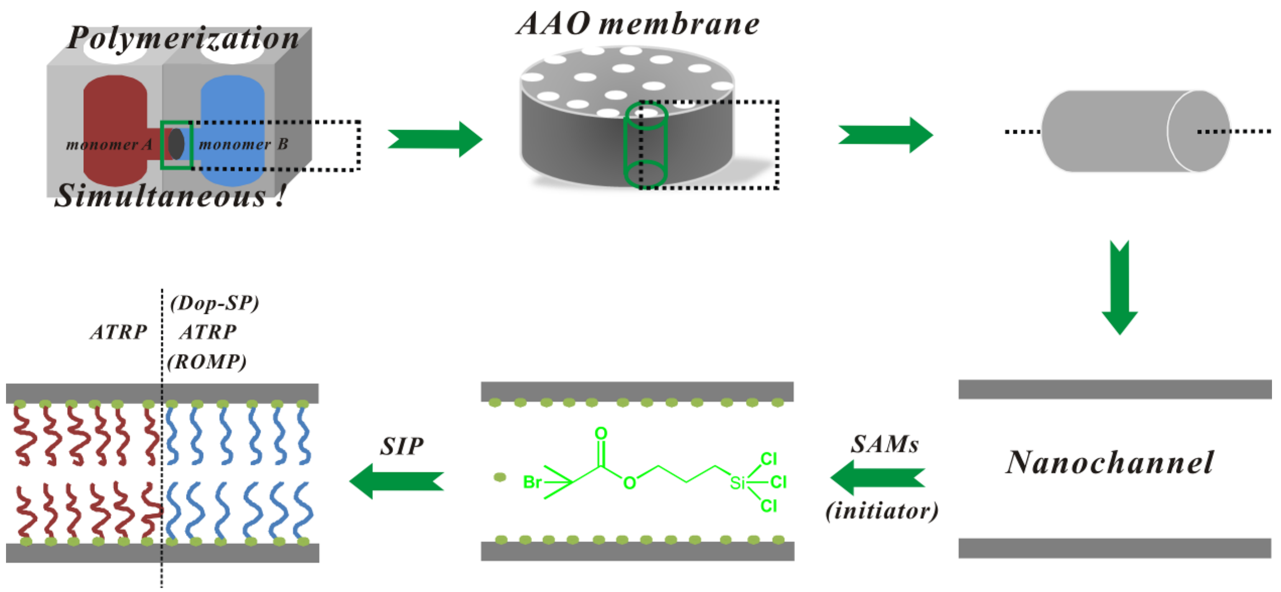

Scheme 1 Schematic illustration of the preparation processes for asymmetric modification within AAO nanochannels with polymer brushes in a half-cell reactor combining with ATRP, ROMP and Dop-SP techniques.

3. Results and Discussion

3.1 Asymmetrical modification with double hydrophilic polymer brushes

Asymmetric chemical modification with the functional polymer brushes within the nanochannels of AAO membrane was performed in a home-made half-cell reactor by *in situ* ATRP, ROMP and DOP-SP techniques, as shown in Scheme 1. One advantage of this method is that the polymer brushes can be grafted even in very small channels of the AAO membrane (30 nm). In the middle part of **Figure 1** shows the schematic illustration of the formation process of double hydrophilic polymer brushes (PMETAC and PSPMA) asymmetrically modified AAO membrane. After the polymerization modification, the wettability of both sides of the AAO membrane changed from superhydrophilicity to hydrophilicity with the contact angle changing from 0 °to 20 °, indicating the successful formation of the polymer brushes. The morphologies of AAO membranes before and after asymmetric modification with PMETAC and PSPMA polymer brushes are characterized by utilizing AFM and FESEM. In comparison with bare membrane (Fig. 1A), the diameters of the pores in each side of membrane decreased

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obviously after asymmetrical modification with PMETAC (Fig. 1B) and PSPMA (Fig. 1C). Those results are consistent with FESEM images in supporting information (Fig. S1). The double hydrophilic polymer brushes were also asymmetrically modified within the AAO nanochannels with larger pore size of about 130 nm. Compared to bare membrane (Fig. 1D), the pore diameters also decreased obviously after asymmetrical modification (Fig. 1E-F). The cross-sectional FESEM analysis before and after asymmetric modification with PMETAC and PSPMA polymer brushes was shown in Fig. S2. After the asymmetrical modification, the surface pores of the membrane were not blocked owing to the removal of initiator anchored on the top surface by oxygen plasma treatment as discussed in our previous work.[22]

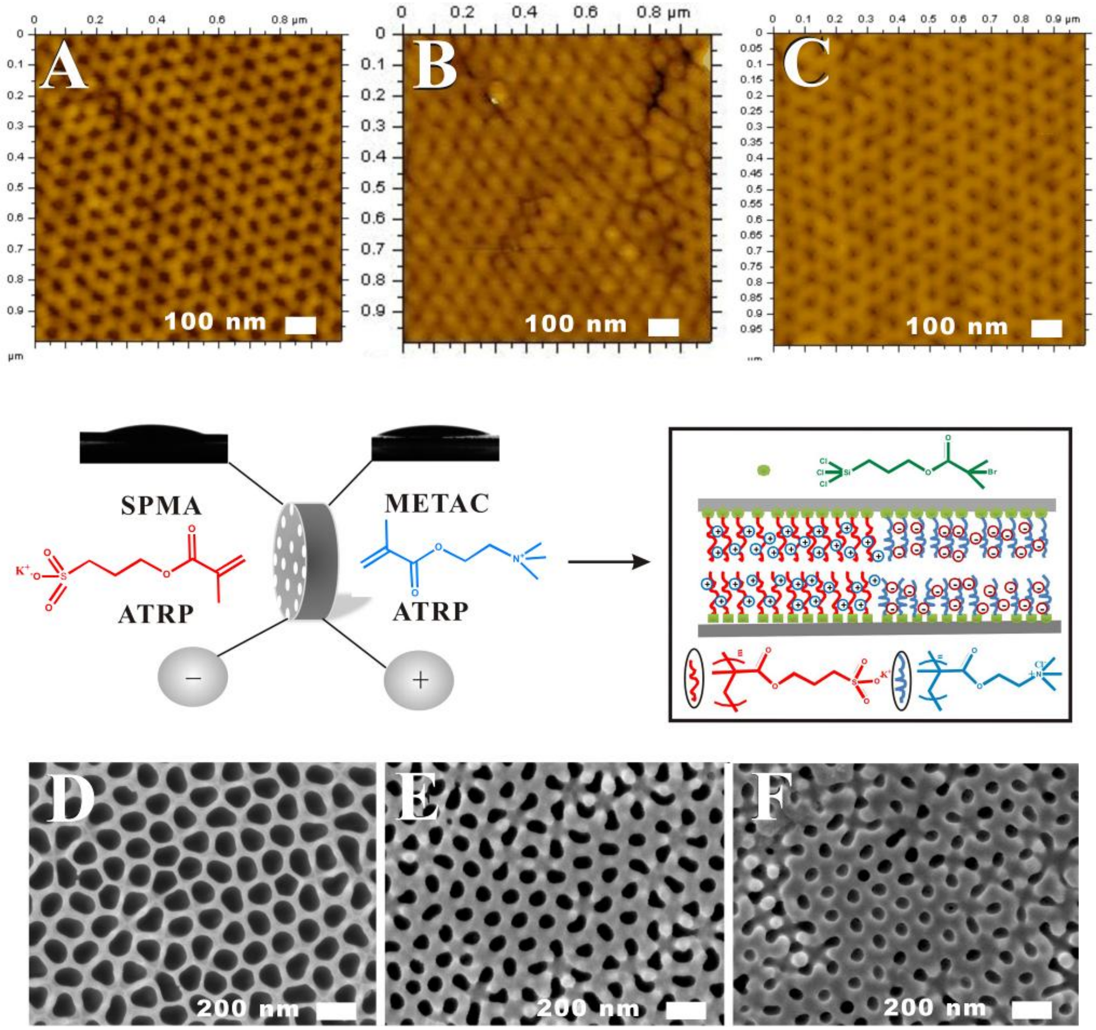

Fig. 1 AFM images of AAO membrane (pore size of 30 nm) before (A) and after modification with polymer brushes of PMETAC (B) and PSPMA (C). Schematic illustration of asymmetrical modification

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with double hydrophilic polymer brushes within AAO channels (middle). (D-F) FESEM images of AAO membrane (pore size of 130 nm) before (D) and after modification with PMETAC (E) and PSPMA (F).

To confirm the chemical compositions of the polymer brushes asymmetrically modified AAO membranes, XPS and FT-IR were used for analysis (Fig. S3). After the polymerization reactions, the signal of N 1s was detected, which could be attributed to successful grafting of PMETAC on one side of the membrane **(**Fig. S3A(b)). The appearance of K 2s peak and S 2s peak were indicative of the successful modification of PSPMA on the other side of the membrane **(**Fig. S3A(c)**)**. The appearance of -C═O stretch vibration peak at 1722-1730 cm^{-1} showed the successful assembly of initiator onto the membrane (Fig. S3B(a)). Both side of the membrane detected the signal of -C═O stretch vibration peak, which could be attributed to the ester group of PMETAC and PSPMA **(**Fig. S3B(b-c)). All the results above showed that asymmetrical modifications of double hydrophilic polymer brushes of PMETAC and PSPMA were successfully modified within the AAO nanochannels.

3.2 Asymmetrical modification with double responsive polymer brushes

As a general method to achieve the asymmetric modification in nanochannels, it was used to prepare pH and temperature double responsive AAO membranes as shown in Fig 2. One side of the AAO nanochannel membrane was grafted from a temperature responsive polymer of PNIPAM, while the other side of the nanochannel membrane was modified with a pH-responsive polymer brush of PDMAEMA by the ATRP techniques, leading to a double responsive asymmetrical membrane. As shown in Fig. 2A**,** one side of the AAO membrane is temperature responsive owing to grafting from PNIPAM, whose polymer chain could swell or collapse below or above the lower critical solution temperature (LCST). On the other side, the membrane was pH responsive owing to grafting from PDMAEMA, whose polymer chains would stretch below the pKa as shown in Fig. 2B.

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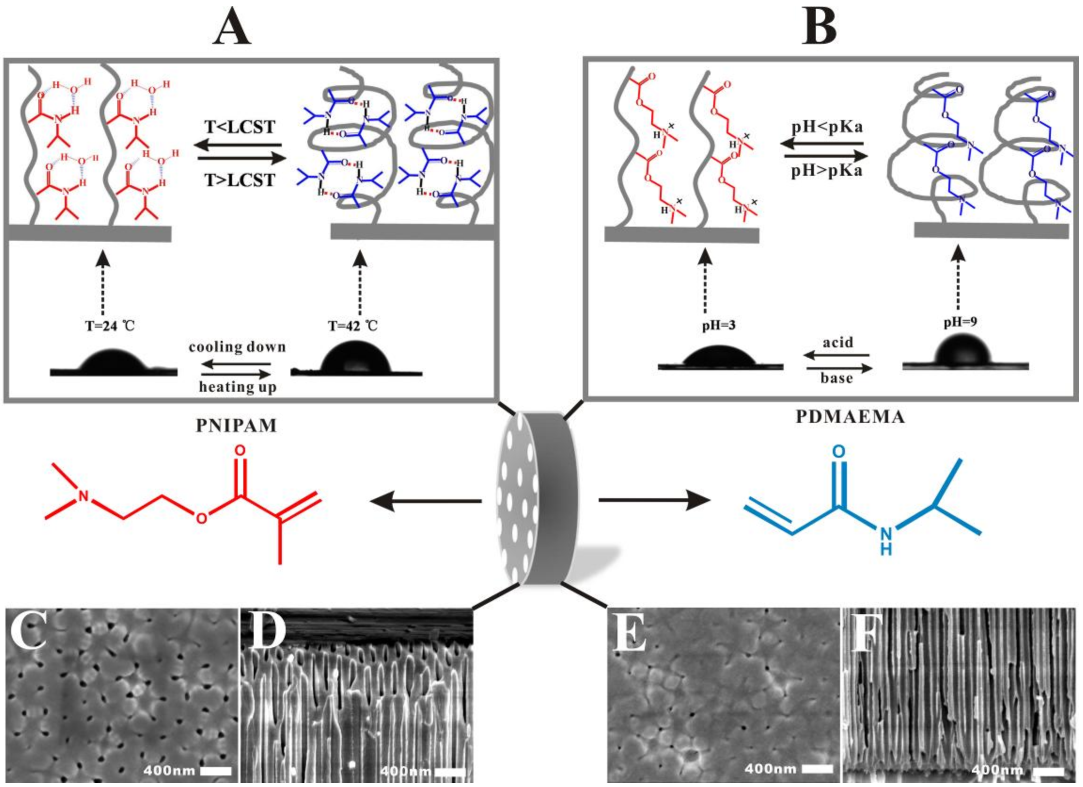

Fig. 2 Wettability and schematic diagrams of the temperature responsive PNIPAM polymer brushes (A) and pH responsive PDMAEMA polymer brush modified AAO membranes. Top view and cross-sectional FESEM images of PNIPAM (C, D) and PDMAEMA (E, F) polymer brushes modified AAO membranes.

Fig. 2C-F shows the top surfaces and cross-sectional FESEM images the AAO membranes after asymmetrically chemical modification with PDMAEMA and PNIPAM. It is clear that the pore size of the membrane decreased a lot after modification with the polymer brushes (Fig. 2(C, E)). From the cross-sectional images, we can see that the polymer brushes layer covered all the inner surface of the AAO nanochannels resulting in the decrease of the pore diameters as shown in Figure 2 (D, F). The XPS and FT-IR measurements also confirmed the successful modification of the polymer brushes in the AAO nanochannels as shown in Fig S4 .

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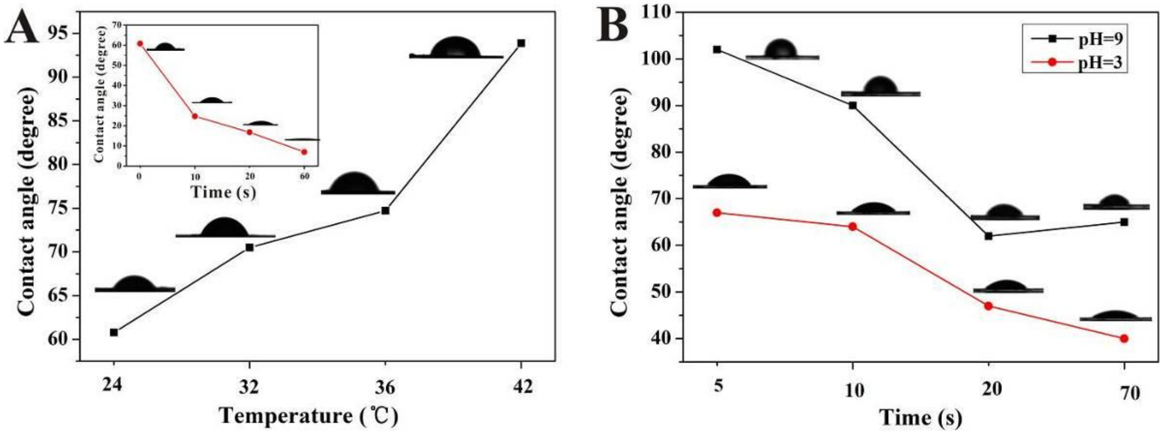

Fig. 3 Wettability of the temperature and pH double responsive AAO membranes: (A) contact angle change *VS* temperature for the temperature responsive side of AAO grafting with PNIPAM polymer brushes (the inset is contact angle change *VS* time at 24 ℃), (B) contact angle change *VS* time for the other pH responsive side grafting with PDMAEMA polymer brushes.

The wettability of the double responsive asymmetric AAO membrane was also investigated by changing the environmental temperature and pH. For the temperature sensitive PNIPAM, the lower critical solution temperature is about 32 ℃.[23] The PNIPAM polymer brushes swell below LCST, while collapse above LCST leading to the contact angle changes on the surface. As shown in Fig. 3A, the contact angles increased from 61 ° to 94 ° with the rising of the temperature from 24 ℃ to 42 ℃. For pH responsive side as shown in Fig. 3B, the contact angle switched from 101 ° to 67 ° with the pH changing from 9 to 3. The possible mechanism is that the pH responsive PDMAEMA has a pKa of 7.5, and the polymer brush is hydrophobic in basic environments with a big water contact angle due to the deprotonation of amine groups, while hydrophilic in acidic environments with a smaller water contact angle.[24] Interesting, the contact angle is time-varying for the pH responsive PDMAEMA at the first minute (Fig. 3B). The contact angles of PDMAEMA side at different temperatures, and PNIPAM side at different pH were also tested (Fig. S5). These results further proved that asymmetric modification was successfully performed.

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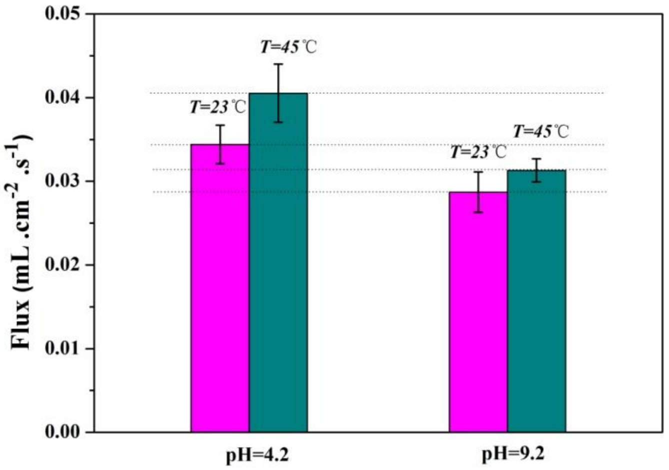

Fig. 4 Flux measurements for the pH and temperature double responsive asymmetrical AAO membranes at 23 ℃ (below the LCST of PNIPAM) and 45 ℃ (above the LCST of PNIPAM); pH=4.2 (below the pKa of PDMAEMA) and pH=9.2 (above the pKa of PDMAEMA). The injection rate is 1 mL/min; the effective area of the membrane is 0.3846 cm^2.

Furthermore, to prove above results, the permeability of the double responsive membrane was also investigated by water flux tests. As shown in Fig. 4, the flux increased obviously with the rising of the temperature from 23 ℃ to 45 ℃ in each buffer solution system, which could be attributed to the changes of conformation of PNIPAM polymer brush from swollen to collapse within the AAO channels. Similarly, the flux decreased with the rising of the pH value from 4.2 to 9.2 because of the state of the PDMAEMA polymer brush switching from hydrophilic state to hydrophobic.

3.3 Asymmetrical modification by ATRP and DOP-SP techniques

Besides ATRP technique, we also showed a sample asymmetrical modification approach within the channels of AAO arrays combining with dopamine self-polymerization technique.[25] PSPMA was grafted from one side of membrane by ATRP while the other side of the membrane was assembled with poly-dopamine (Pdop) in a Tris-HCl buffer solution as shown in Fig. 5. Different from the assembly of

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initiator used above, only one side of the membrane was contacted with the solution, while the other side was exposed to air. PSPMA polymer brush was grafted from the middle of the nanochannels to one side of the top surface of the AAO membrane with a hydrophilic monomer of 3-sulfopropyl methacrylate potassium salt by ATRP technique, while the other part of the nanochannels membrane was modified with dopamine by a process of autoxidation polymerization in a Tris-HCl buffer solution (pH=8.5).

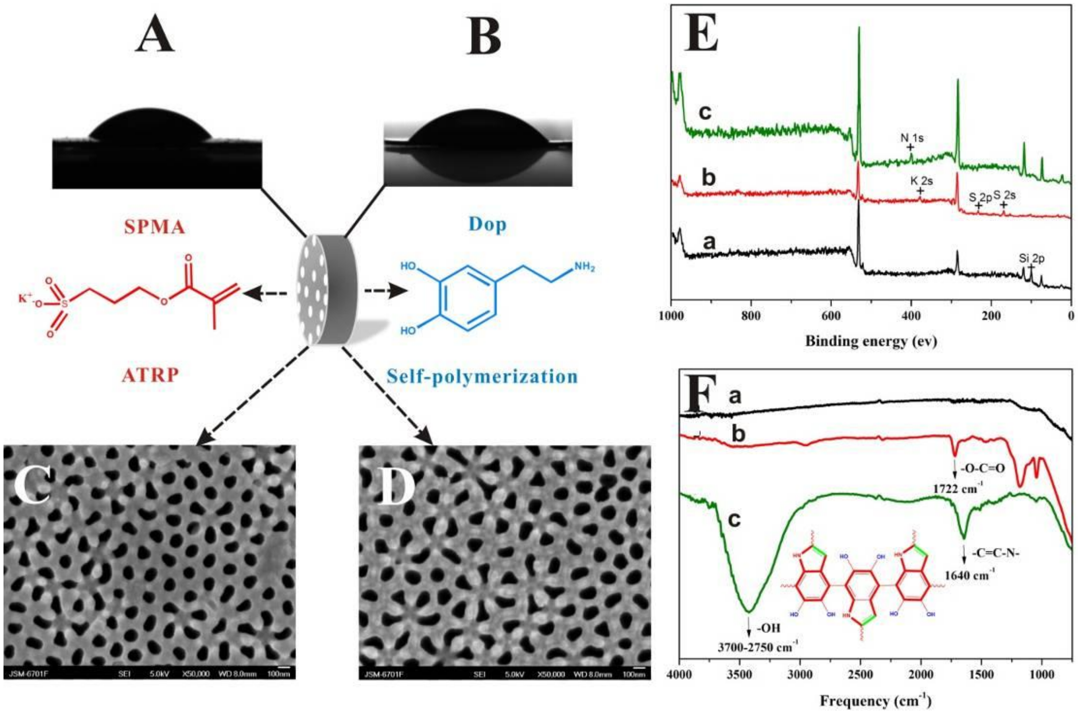

Fig. 5 Wettability and top surface view for the AAO membrane asymmetrically modified with PSPMA (A,C) and poly-dopamine (B,D) polymer brushes. (E,F) The corresponding XPS and FT-IR spectrums of the bare AAO (a), the side of PSPMA modified AAO (b), and the other side of poly-dopamine modified AAO membranes.

After asymmetrical modification, both sides of the membrane were hydrophilic (Fig. 5A-B), and the pore diameters decreased obviously (Fig. 5C-D). XPS and FT-IR were also employed to confirm the chemical composition of the polymer brushes. As shown in Fig. 5E, successful modification of PSPMA was proved by the appearance of K 2s and S 2s signals and the appearance of N 1s peak for Pdop on the other side of the membrane. Interestingly, the dopamine autoxidation polymerization on one part of membrane was not affected by the existence of chlorosilane initiator anchored on the channels of AAO array owing to strong binding force between dopamine and Al substrate. As shown in Fig. 5F, the sharp absorption peak at 1722 cm^{-1} from -C=O stretch in the ester group of PSPMA, a wide absorption peak at 3700-2750 cm^{-1}assigning to –OH stretch vibration and an absorption peak at 1640 cm^{-1} from backbone vibration of –N-C=C peak of Pdop, also show the successful asymmetric modification of PSPMA and Pdop.

3.4 Asymmetrical modification by ATRP and ROMP techniques

Superhydrophobic materials have attracted significant attention owing to their extraordinary surface properties, such as self-cleaning, [26] anti-fouling. [27] Recently, a wetting conversion material resulted from AAO nanochannels membrane was developed by assemble of Pdop onto the surface of the membrane modified by fluorosilane.[28] However, there were scarcely reports focused on developing of asymmetric wettability membranes, which is an important challenge in development of new multi-functional membrane devices in material science. In this part, we introduced an easy approach for construction of asymmetric wettability nanochnnels membrane from ATRP and ring-opening metathesis polymerization techniques, by which both of the initiator and polymerization were performed asymmetrically.

As shown in Figure 6 A-B, one side of the AAO nanochannels membrane grafted from PSPMA by ATRP showed a water contact angle of 21 ° while the other side grafted from PNCA-F$_{15}$ by ROMP with the contact angle of 133 °. The morphologies of the polymer brushes modified AAO membranes are shown in Fig. 6C-D. XPS and FT-IR were also employed to confirm the successful modification of PSPMA and PNCA-F$_{15}$ (Fig. 6E). The appearance of the strong F 1s peak and C-O, C-F signals demonstrated that PNCA-F$_{15}$ has been successfully grafted on one side of the membrane, while the appearance of K 2s peak and S 2s peaks was indicative of successful modification of PSPMA on the

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other side of the membrane. Fig. 6F showed that polymerization mechanism of ring-opening metathesis polymerization (ROMP) in this experiment.

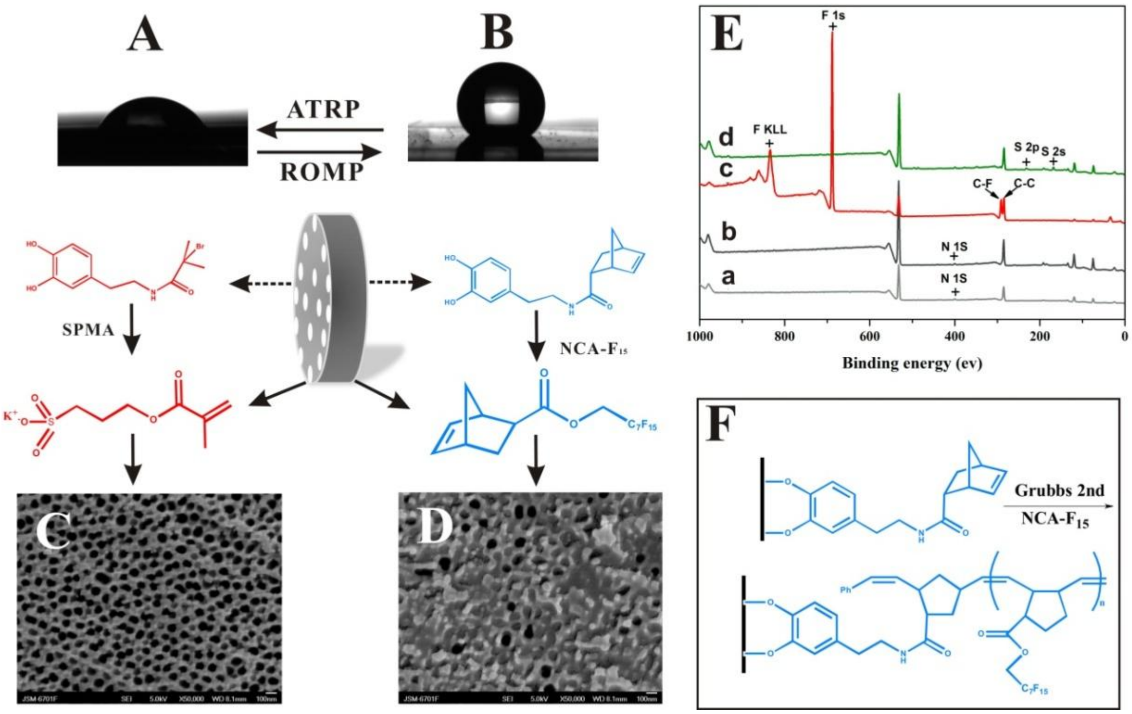

Fig. 6 Contact angle and top surface view for the AAO membrane asymmetrically modified with PSPMA (A,C) and PNCA-F$_{15}$ (B,D) polymer brushes. (E) XPS spectrums of bare AAO (a), initiator modified AAO (b), the side of PNCA-F$_{15}$ modified AAO (c), and the other side of PSPMA modified AAO membranes (d). (F) The polymerization mechanism of NCA-F$_{15}$ ring-opening metathesis polymerization (ROMP).

3.5 Asymmetrical modification with Au and Pd NPs

3.5.1 Preparation of polymer brushes stabilized Au, Pd NPs

Even though many works based on the functional catalytic membranes were reported,[29] especially for ordered 1D nanochannel arrays reactors, [30] constructing of the asymmetrical catalytic channels array for selective catalysis, has scarcely been focused on. In this part, the noble metallic nanoparticles of Au and Pd were asymmetrically loaded within the AAO nanochannels by *in situ* ion exchange and reduction

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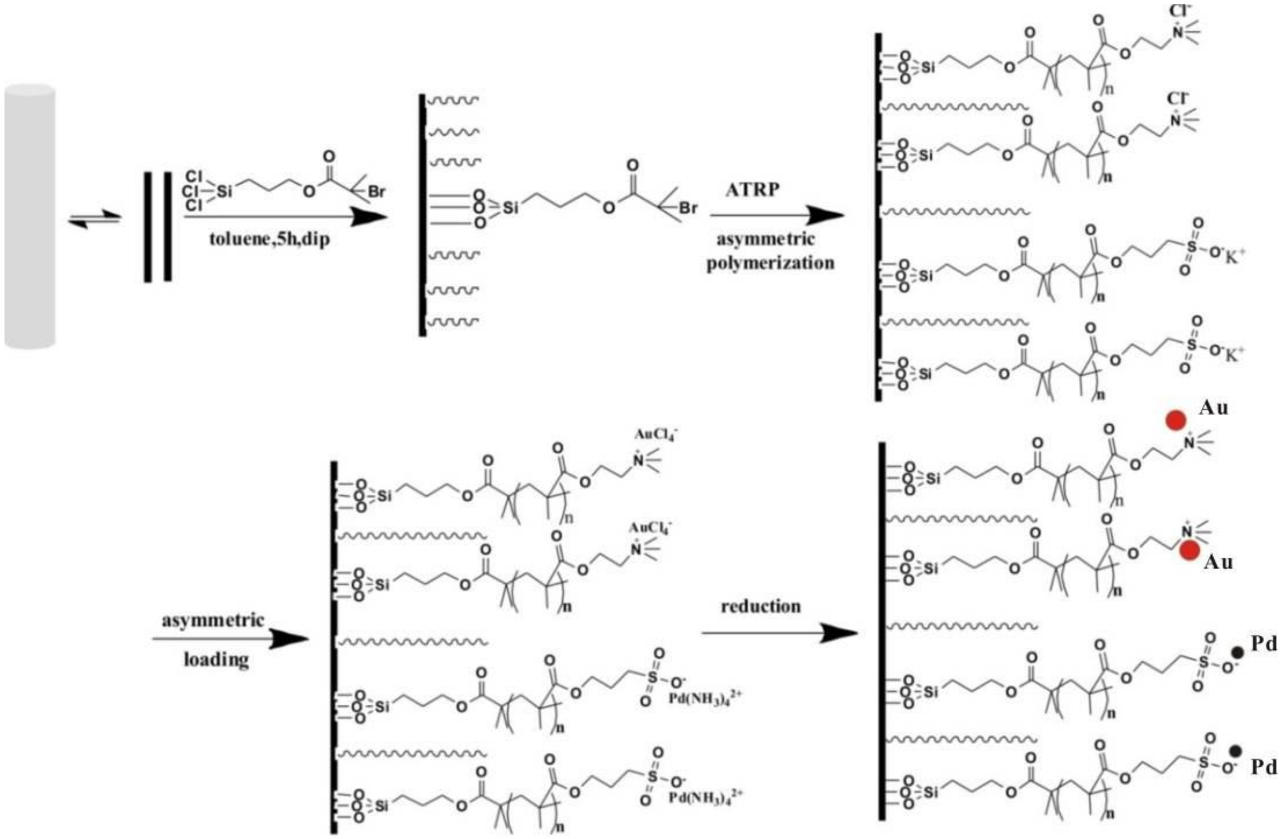
strategies, based on double hydrophilic asymmetrical membrane (PSPMA@PMETAC). As shown in Scheme 2, the double hydrophilic polymer brushes were firstly asymmetrically grafted on the inner wall of the channels. Thus, the PMETAC brushes have lots of ammonium cationic sites paired with counter Cl^{-} anion, while the PSPMA brushes have lots of sulfonic anion sites paired with counter K^{+} loading on the surface of the AAO nanochannels. By subsequently exchanging of Cl^{-} anion with $AuCl_4^{-}$ and K^{+} cation with $Pd(NH_3)_4^{2+}$, and following reduction reaction by $NaBH_4$, Au and Pd NPs were stabilized by the polymer brushes on the inner wall of AAO nanochannnels.



Scheme 2 Schematic illustration of the preparation processes for polymer brushes stabilized Au, Pd asymmetrical catalytic membrane (Au-PMETAC@PSPMA-Pd).

The morphologies and compositions of the Au, Pd asymmetrically modified AAO membranes were characterized by FESEM, TEM, EDS, and XPS. In order to confirm the distribution of Au and Pd NPs on the surface of the AAO nanochannels, the EDS and FESEM analysis were carefully performed on

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different areas of the cross-section of AAO membrane without the pretreatment of gold spray. Three regions with the same area were chosen for the EDS tests: bright region on AAO-PMETAC-Au(0) side, the middle region, and the dark region on AAO-PSPMA-Pd(0) side, marked as 1, 2 and 3, as shown in Figure 7. The appearances of Au peak in region 1 and Pd peak in region 3 showed the successfully asymmetric modification of Au and Pd NPs in the different part of AAO nanochannels, with the Au and Pd NP sizes of about 20 and 5 nm. The signals of Au and Pd in region 2 also provided that Au and Pd NPs were successfully modified through all the part of the AAO nanochannels. It was further characterized by XPS in Fig. S6. The appearance of Au 4f and Pd 3d signals indicates the successfully loading of metallic nanoparticles into the nanochannel membranes. And the signals of Au 4f and Pd 3d peak show the complete reduction from Au^{3+} and Pd^{2+} to elemental metals.

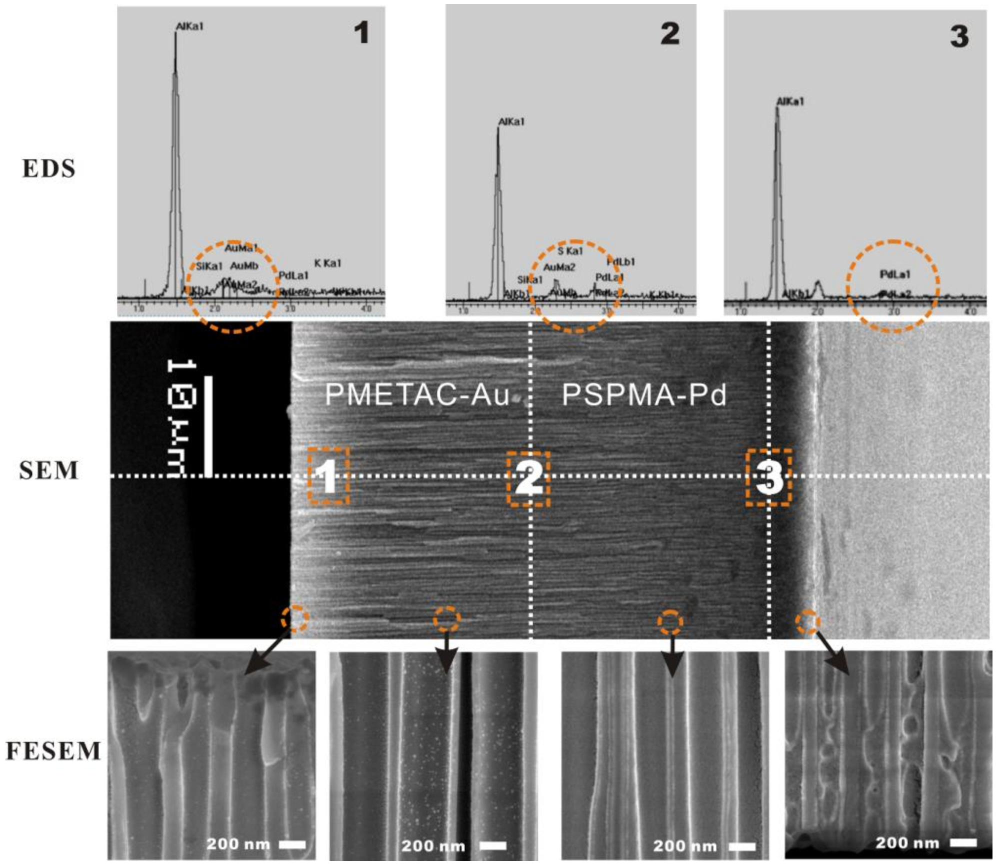

Fig. 7 Energy dispersive spectrometry analysis and FESEM images of Au-PMETAC and Pd-PSPMA-asymmetrically modified AAO membrane.

Journal of Materials Chemistry A Accepted Manuscript

Fig. 8 shows the TEM images and EDX spectrums of the polymer brushes and polymer brushes stabilized Au and Pd NPs asymmetrically modified AAO channels. For TEM tests, the samples were scraped from the top and bottom parts of the membrane and ground to fine powder. As shown in Fig. 8A, the thickness of the PMETAC polymer brushes was about 25 nm, while the thickness of the PSPMA polymer brushes was about 50 nm (Fig. 8B). The size of PMETAC polymer brushes Au NPs was about 15-20 nm (Fig. 8C), and the PSPMA polymer brushes Pd NPs have smaller size of about 5 nm (Fig. 8D). EDX spectrums of the Au and Pd NPs loaded AAO are shown in Fig. 8E-F. Only small amount of nanoparticles were loaded on the channels of the pores without the stabilization of polymer brushes (Fig. S7). TG measurements including bare AAO, AAO-initiator, AAO-PSPMA@PMETAC and Au-PMETAC@PSPMA-Pd, were also carried out correspondingly (Fig. S8).

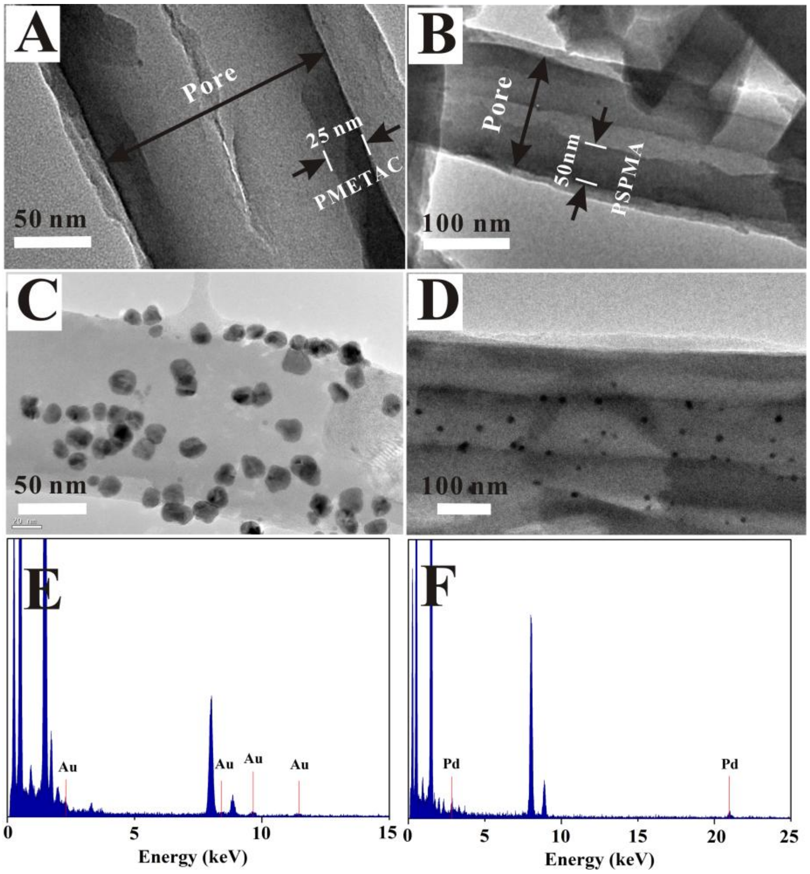

Fig. 8 TEM images of PMETAC polymer brush modified AAO (A), PSPMA polymer brush modified

Journal of Materials Chemistry A Accepted Manuscript

AAO (B), PMETAC stabilized Au loaded AAO (C) and PSPMA stabilized Pd loaded AAO (D). (E,F) EDX spectrums of polymer brushes stabilized Au NPs and Pd NPs loaded AAO membranes.

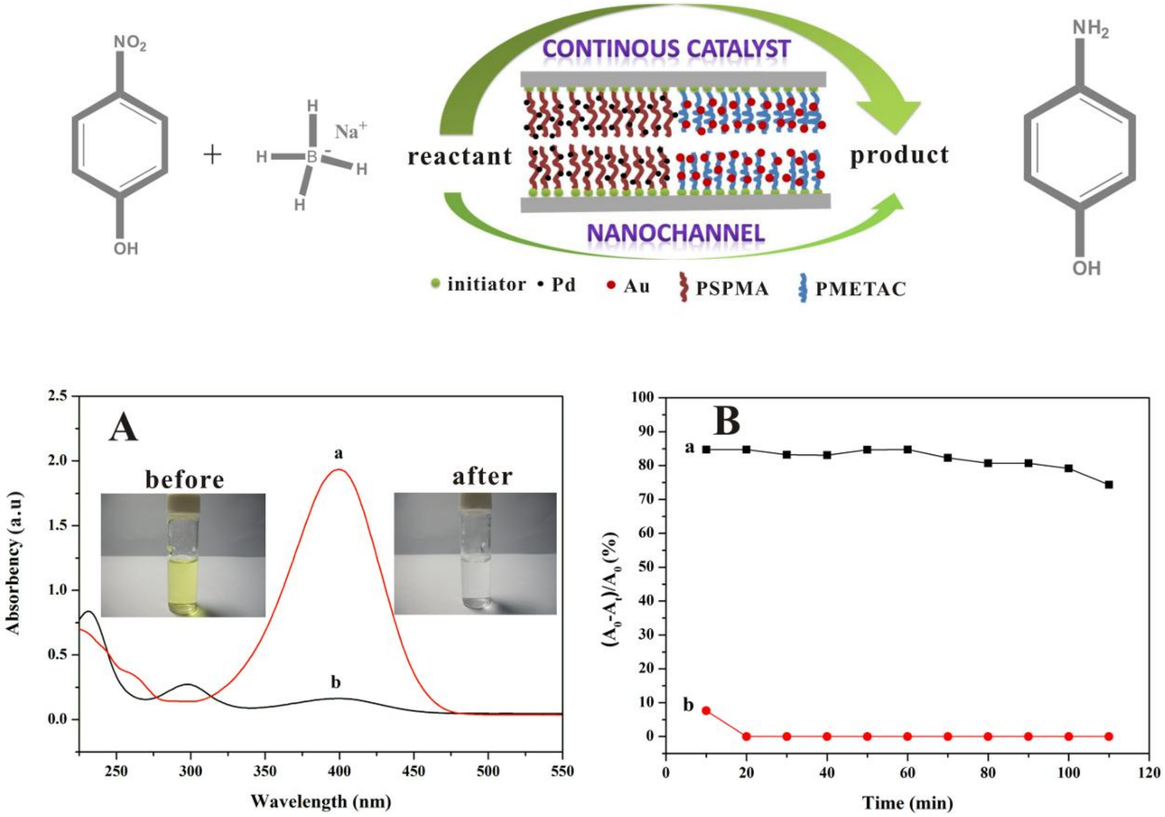

Fig. 9 Schematic illustration of the flow-through catalysis process with Au and Pd asymmetrically modified AAO membrane. (A) UV-Vis absorption spectra of 0.1 mM 4-NP and 10 mM $NaBH_4$ reaction solution before (a) and after (b) passing through the catalytic membrane. (B) Plots of the conversion percentage of 4-NP *VS* time with Au-PMETAC@PSPMA-Pd catalytic membrane (a), and AAO membranes without polymer brushes but loading of Au-Pd nanoparticles (b). The reactions were performed with an injection flow rate of 0.5 mL/min.

3.5.2 Flow-through Catalysis

In our previous work, the polymer brushes stabilized catalytic metal NPs showed high catalytic activity.[31] Here, a simple and representative organic reaction system of 4-nitrophenol (4-NP) and $NaBH_4$

Journal of Materials Chemistry A Accepted Manuscript

was used to investigate the catalytic efficiency of polymer brushes stabilized Au, Pd asymmetrically modified through-hole AAO membrane by a flow-through method (Fig. S9). In this flow–through catalysis process, the color of solution quickly changed from glassy yellow to colorless because the 4-nitrophenol was reduced to 4-aminophenol in the presence of Au-Pd catalysts and excess $NaBH_{4,}$ which was monitored by UV-vis absorption spectroscopy as shown in Fig. 9 A. Figure 9 B shows the kinetics curves of the conversion percentage of 4-NP with the reaction time for PMETAC-Au@PSPMA-Pd catalyst membranes. The catalytic efficiency of the membrane decreases only slightly in the first 110 min, while only less than 10 % conversion efficiency for the Au-Pd loaded bare AAO membrane without polymer brushes (Fig. S10) was obtained. The results showed that polymer brushes can work as an effectively stabilized template for metallic nanoparticles, which ensures the successfully construction of asymmetric Au, Pd loaded AAO membrane for high flow-through catalysis.

4. Conclusion

In conclusion, we experimentally demonstrate a general approach for asymmetric chemical modification within AAO nanochannel arrays by simultaneous polymerization strategies in a half cell reactor, combining with ATRP, DOP-SP, and ROMP techniques to form double hydrophilic, double stimuli-responsive (temperature and pH), and hydrophilic/ hydrophobic polymer brushes. After *in situ* ion exchange and reduction reaction, the polymer brushes stabilized Au, Pd catalysts on the inner surface of AAO nanochannels were generated, showing high flow–through catalytic property in reduction of 4–nitrophenol. Moreover, this simple approach could promote the development of asymmetric chemical modification with various functional molecules in nanochannel array membranes, which have promising applications in organic charged-molecule separations, oil-water separation, and asymmetric organic catalytic reactions.

Acknowledgments

Journal of Materials Chemistry A Accepted Manuscript

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Supporting Information More information of FESEM images, XPS spectra, FT-IR spectra, TG curves, permeability tests, etc.

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