Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

High-Efficiency Pd Nanoparticles Loaded Porous Organic Polymers Membrane Catalytic Reactors

Yaohan Chen,[a,b] Yonggang Li,[a] Lei Dai,[a] Guorui Qin,*[a] Jing Guo,*[a] Qifeng Zhang,[a] Shenghai Li,*[a,b] Tauqir A. Sherazi,[c] and Suobo Zhang[a,b]

[a] Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

[b] University of Science and Technology of China, Hefei 230026, P. R. China.

[c] Department of Chemistry, COMSATS University Islamabad, Abbottabad Campus, Abbottabad, 22060, Pakistan.

*** Corresponding authors E-mail: grqin@ciac.ac.cn; guoqing124@ciac.ac.cn; lsh@ciac.ac.cn.**

Materials and Experiments

Materials

4,4'-diaminobiphenyl was purchased from Jilin Chinese Academy of Sciences - Yanshen Technology Co. Ltd. Phloroglucinol was purchased from Sigma-Aldrich. 4,4'-biphenol, hydroquinone, 4-nitrophenol, $Pd(OAc)_2$ and sodium borohydride ($NaBH_4$) were purchased from Innochem. 10 % palladium on activated carbon (Pd/C) catalysts were purchased from Shaanxi Kaida Chemical Engineering Co. Ltd. Ethyl acetate was purchased from Alfa Aesar. N,N-dimethylformamide (DMF), triethylamine, sodium carbonate (Na_2CO_3), hydrochloric acid (HCl) were purchased from Beijing Chemical Works. All chemicals and solvents mentioned above were used without further purification unless noted.

The preparation of polyacrylonitrile (PAN) ultrafiltration membranes was based on our previous work. The casting solution was prepared with PAN: NMP: polyethylene glycol 2000 (14: 78: 8), and the nonsolvent was deionized water. Before phase inversion, the casting solution was filtrated and degassed. The prepared PAN membranes were stored in a refrigerator at 4 °C prior to use.

Instrumentation

Fourier transform infrared spectroscopy (FT-IR) data was obtained by Bruker VERTEX 70 FT-IR spectrometer. The solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR was taken by Bruker Advance 500 MHz NMR. Nitrogen adsorption/desorption studies were obtained at 77K by Autosorb iQ from Quantachrome Instruments to measure the Brunauer-Emmett-Teller (BET) surface areas, in addition pore size distributions was calculated by non-local density functional theory (NLDFT) methods. The surface and cross-section morphology of POMs were observed by scanning electron microscopy (Merlin, Zeiss Company). The composite membrane surface elemental analysis was carried by thermo ESCALAB 280 system. The absorption concentration was measured by a UV-vis spectrometer (SHIMADZU 1800). To detect the morphology of Pd nanoparticles on POMs morphology, the Pd loaded membranes on PAN substrate was immersed in DMF to dissolve the PAN, therefore the membrane could detach from the PAN membranes. For ease detection, the detached membranes were collected and dispersed by ultrasonic in isopropanol, then observed by transmission Electron Microscope (TEM, Tecnai G2 F20 STWIN). Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed with a ThermoFisher XseriesII. For permeability test and catalytic performance, a 40 mm diameter membrane was carried at 0.1 MPa in a dead-end filtration instrument.

Experiments

Fabrication of porous organic polymer membranes

For dual diazonium reagent, 4,4'-diaminobiphenyl (0.2764 g, 1.5 mmol) was added to aqueous solution (100 mL) contained concentrated hydrochloric acid (0.7 mL), stirred 30 minutes until the solution was clear. Subsequently, the solution was cooled to 0-5 °C, and a solution of sodium nitrite (0.2139 g, 3.1 mmol) was added dropwise and stirred for another 30 minutes. Potassium iodide-starch test paper was used to detect the sodium nitrite to ensure sufficient reaction. The organic solution was an ethyl acetate solution (100 mL) containing of 0.4 mmol polyphenol (0.050 g for phloroglucinol, 0.044 g for hydroquinone and 0.074 g for 4,4'-Biphenol) and triethyl amine (5 mL). The organic was cooled to 0 °C before reaction. The POMs can be formed at the interface between the aqueous solution and the organic solution as soon as the two solutions contact.

For TFC membranes, firstly, the aqueous solution of diazonium reagent was poured onto the surface of the PAN ultrafiltration membrane and stood for 2 minutes. Once the surface residual solution was removed entirely, the organic solution was poured onto the PAN surface and reacted for seconds. Then, the excess solution was poured off. The membranes were put in a 0 °C environment and its surface was blown gently with a fan to remove the excess ethyl acetate. Finally, the resultant membrane was immersed in deionized water.

Fabrication of Pd NPs loaded porous organic polymer membranes

A TFC porous organic polymer membrane with 100 mm diameter prepared was loaded into a 200 mL thread bottle contained 80 mL methanol solution and 10 mg $Pd(OAc)_2$. The bottle shook in 150 rpm for 24 hours, then a 10 mL methanol solution contained 0.46 g $NaBH_4$ was added into thread bottle for shaking. After 24 hours the membrane was taken out and washed by a mass of methanol, water.

Membrane reactor for catalytic reduction reaction on 4-nitrophenol

The Pd NPs loaded POMs with 15 mm diameter were used for catalytic tests firstly. The reduction reaction was carried out with a dead-end vacuum filter. A 20 mL aqueous solution containing 4-nitrophenol and $NaBH_4$ (molar ratio= 1:60) was filtered through the Pd NPs loaded POMs assisted by a vacuum pump in room temperature. Collected the filtrate and analyzed by UV-Vis spectrometer.

To test the catalytic performance of Pd loaded POMs at high pressure, feed solutions were depended on the maximum concentration of totally reduction by dead-end device. The catalytic performance was tested by a cross-flow device and the effective area of membrane for each cell was about 15.8 cm^2.

For the comparison of the Pd loaded POPs and Pd/C catalysts by stirring with membrane reactor, a 4.5 cm diameter Pd@Mem-POP-1 was immersed in DMF to collected Pd loaded POPs. Then the collected Pd loaded POPs and Pd/C catalysts were put in a 20 mL solution contained 0.296 g 4-nitrophenol and 4.85 g $NaBH_4$ to test the catalytic performance. While a same size Pd@MEM-POP-1 was used for reduction reaction with the same condition at 22 bar.

The stability of the MRs was tested by filtering a 4-nitrophenol solution by a cross-flow device. The solution concentrations and the operating pressure were depended on different Pd loaded POMs.

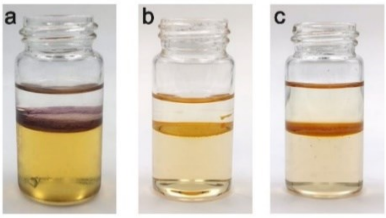

Fig. S1 Photograph of (a) Mem-POP-1, (b) Mem-POP-2 and (c) Mem-POP-3 at interface between aqueous dual diazonium reagent and different phenols in ethyl acetate.

Fig. S2 Photograph of (a) Mem-POP-1, (b) Mem-POP-2 and (c) Mem-POP-3 collected from interface.

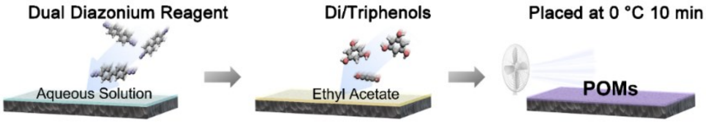

Fig. S3 Schematic of the fabrication of POP membranes.

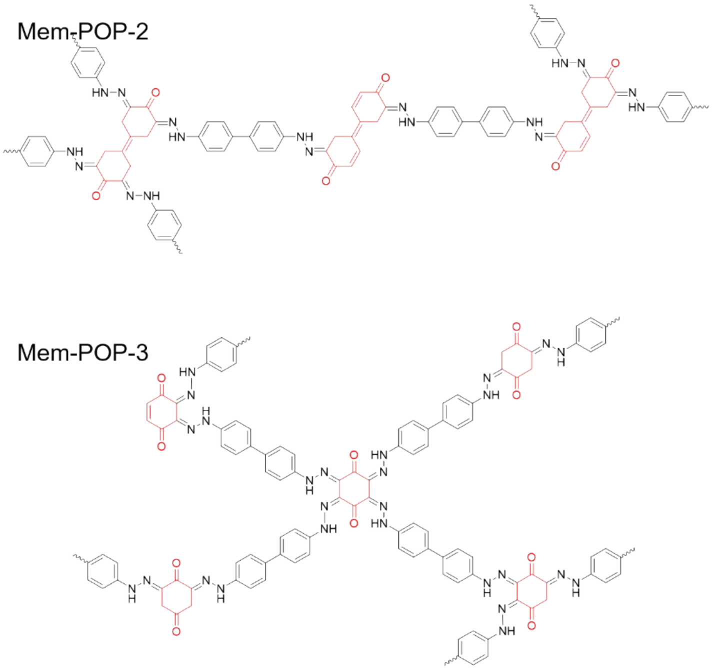

Fig. S4 Possible connect knots in Mem-POP-2 and Mem-POP-3.

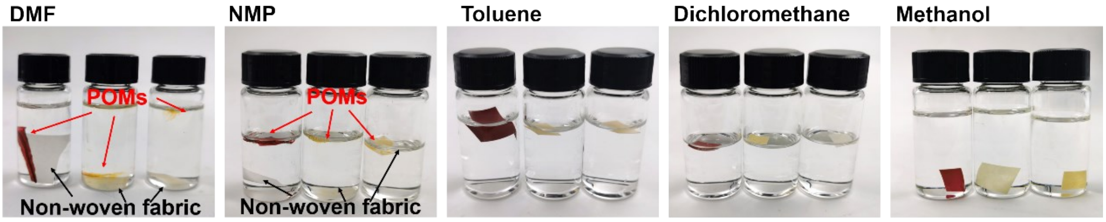

Fig. S5 Digital picture of TFC membrane immersed in solvents. The samples from left to right: Mem-POP-1, Mem-POP-2 and Mem-POP-3.

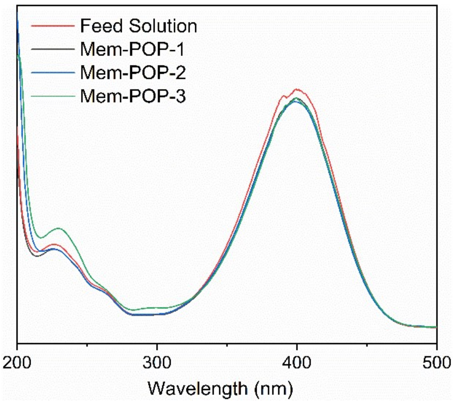

Fig. S6 UV-Vis spectra of the filtrate when pass through the pristine POMs.

Table S1 Elemental analysis of POP membranes.

Sample	C [wt.%]	H [wt.%]	N [wt.%]	O [wt.%][a)]
Mem-pop-1	62.17	4.31	14.41	19.11
Mem-pop-2	75.63	4.94	5.76	13.67
Mem-pop-3	77.56	4.99	3.97	13.48

[a)] The contents of O were obtained by 1-C wt.%-H wt.%-N wt.%.

Fig. S7 A dead-end filtration cell for evaluate the catalytic performance of MR.

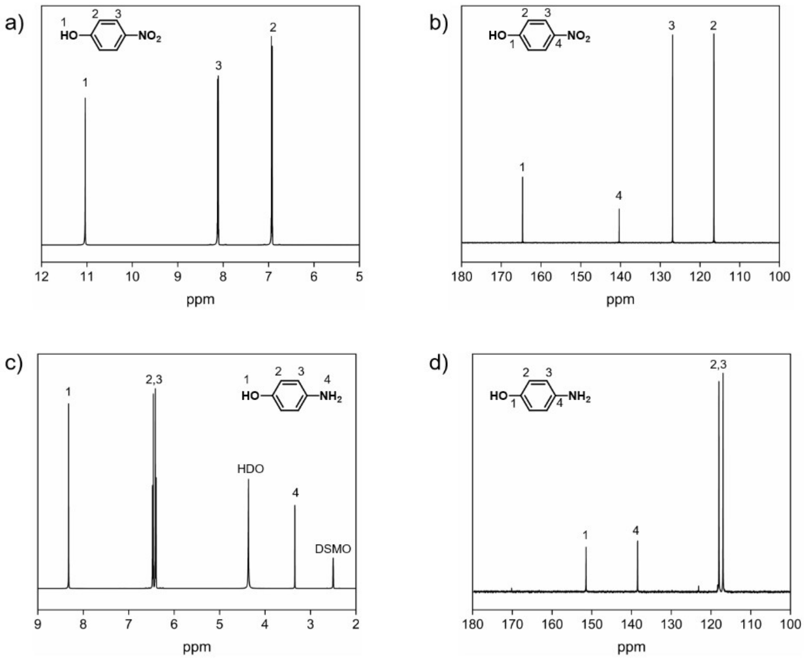

Fig. S8 a) ^{1}H-NMR and b) ^{13}C-NMR spectrum (500 MHz) of 4-nitrophenols in DMSO-d$_6$ at 25 °C. c) ^{1}H-NMR and d) ^{13}C-NMR of 4-aminophenols obtained from the filtrate. The crude products were obtained from the filtrate and removed the water in vacuum.

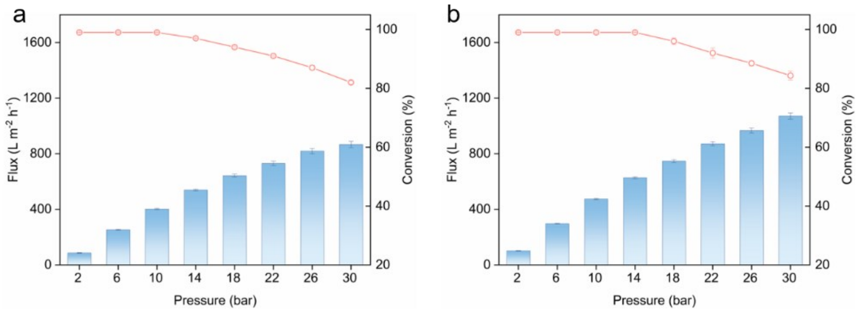

Fig. S9 Flux and conversion of (a) Pd@Mem-POP-2 and (b) Pd@Mem-POP-3 when treated 4-nitrophenol solution at different pressure. 4-nitrophenol concentration of feed solution was depended on the maximum concentration that can be completely reacted in the dead-end device. Pd@Mem-POP-2: 25 mmol L^{-1}; Pd@Mem-POP-3: 55 mmol L^{-1}.

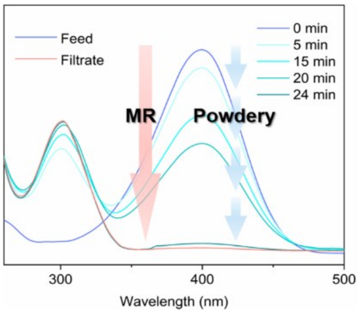

Fig. S10 UV-spectra of the reduction of 4-nitrophenol via Pd@Mem-POP-1 and Pd NPs loaded powdery POPs. The powdery POPs were collected from a same area Pd@Mem-POP-1 TFC membrane by immersing in DMF to detach.

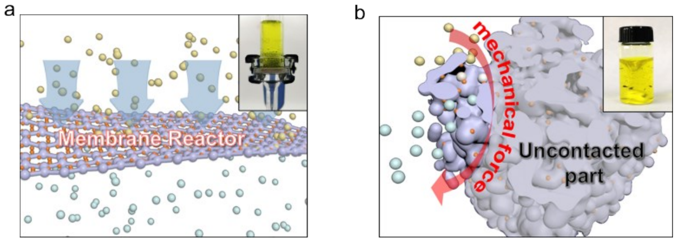

Fig. S11 (a) Image of MR for 4-nitrophenol reduction. Inset: Digital photo of a dead-end filter of MR. (b) Image of Pd NPs loaded powdery POPs for 4-nitrophenol reduction. Inset: Digital photo of an agitation system.

In order to study the difference between MR and traditional heterogeneous catalysis in-depth, a 4.5 cm diameter Pd@Mem-POP-1 on PAN support was detached and collected for an agitating catalytic system, while a same area Pd@Mem-POP-1 was used for MR at the pressure of 22 bar. 10 % palladium on activated carbon (Pd/C) catalysts with same content of palladium were also used to compare. All conditions of the catalytic reaction were the same and the catalytic performance was compared by the reaction time required for 99 % conversion. As illustrated in Fig. S6, once the solution flowed through the Pd@Mem-POP-1, the resultant filtrate was the totally reduced product 4-aminophenol, which only needed 40 seconds, however, it took 24 minutes and 26 minutes for Pd loaded powdery polymers and Pd/C catalysts respectively for reduction by stirring. The reason for this discrepancy is that the solution must contact fully with the membrane when filtration (Fig. S11a), but may not penetrate into the deeper powdery polymer in a short time although under vigorous stirring conditions (Fig. S11b). The substrates were evenly distributed and flowed into MR, which meant that all Pd NPs in MR had equal chance to react with 4-nitrophenol. As a comparison, due to the minor diameter of the pores, the diffusion limitation cannot be fully overcome by stirring. Therefore, the solution cannot permeate the deep porous frameworks of polymer, which lead to a low catalytic efficiency.

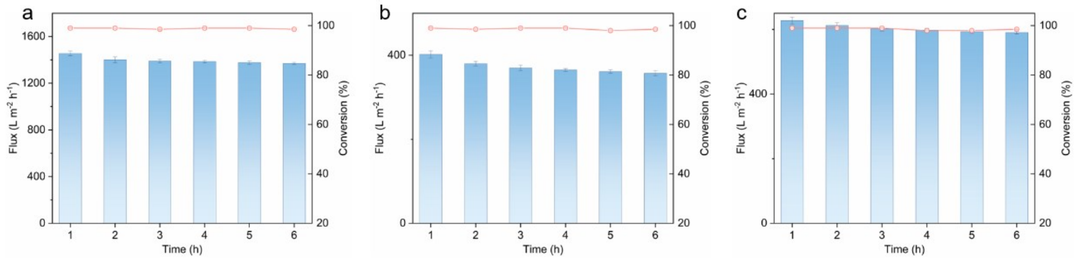

Fig. S12 Flux and conversion of (a) Pd@Mem-POP-1, (b) Pd@Mem-POP-2 and (c) Pd@Mem-POP-3 when treated 4-nitrophenol solution at different pressure. 4-nitrophenol concentration of feed solution was depended on the maximum concentration that can be completely reacted in the dead-end device. Pd@Mem-POP-1: 104 mmol L^{-1}, 22 bar; Pd@Mem-POP-2: 25 mmol L^{-1}, 10 bar; Pd@Mem-POP-3: 55 mmol L^{-1}, 14 bar.

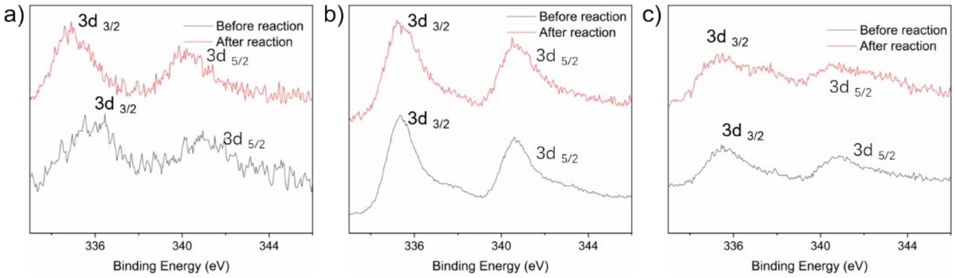

Fig. S13 X-ray photoelectron spectroscopy of a) Pd@Mem-POP-1, b) Pd@Mem-POP-2 and c) Pd@Mem-POP-3. Black curve: before catalysis; Red curve: after catalysis.