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Supporting Information

Construction of graphene oxide based mixed matrix membranes with CO_2-philic sieving gas-transport channels through strong π-π interactions

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1. Materials and instruments

1.1 Materials

Benzidine purchased from Macklin, 1, 3, 5-Trihydroxybenzene, p-Phenylenediamine, sodium nitrite purchased from Sigma-Aldrich and all of them used as received. Natural graphite powder (about 45 mm) was obtained from Si-nopharm Chemical Regent and was used as received. Pebaxs$^{@}$1657 was purchased from Shanghai Rongtian Chemical Co., Ltd. Concentrated sulfuric acid (H_2SO_4, 98wt.%) phosphoric acid (H_3PO_4, 85 wt.%), hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2, 30wt.%) were made available on Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., China. Potassium permanganate ($KMnO_4$) and sodium hydroxide (Na_2CO_3) were bought from J & K. All reagents (analytical grade) were used without any purification. The Demonized (DI) water was also consistent with this study.

1.2 Instrument

ATR-FTIR: Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (4000-400 /cm) was collected on a FT-IR spectrometer in the film state.

AFM: The surface roughness test was performed on an atomic force microscope (Bruker. Dimension fast).

SEM: The morphology of the membrane was observed with a scanning electron microscope (Zeiss/Auriga FIB SEM)

XRD: X-ray diffraction (XRD) measurements were performed on a D8 ADVANCE X-ray diffractometer at 40 kV and 40 mA for Cu Ka (λ =1.5406 Å) at a scanning speed of 2^{o}/min from 5^{o} to 60^{o} by thin film mode.

The *d* space is calculated by the Bragg equation:

$$d = \frac{n\lambda}{2\sin\theta} \quad (1)$$

Where λ is the wavelength of Cu Ka radiation (1.5406 Å), θ is the angle of the reflection peak, and n is the number of energy stages.

XPS: X-ray Photoelectron Spectroscopy (XPS) was acquired on an AXIS Supra system X-ray photoelectron spectrometer. The excitation source was Al Ka, the working voltage was 30 V, and the degree of vacuum was 10^{-6} Pa.

TEM: Transmission electron microscopy (TEM) images were obtained with TSM-7500F. Transmission electron microscopy was run at 200 kV.

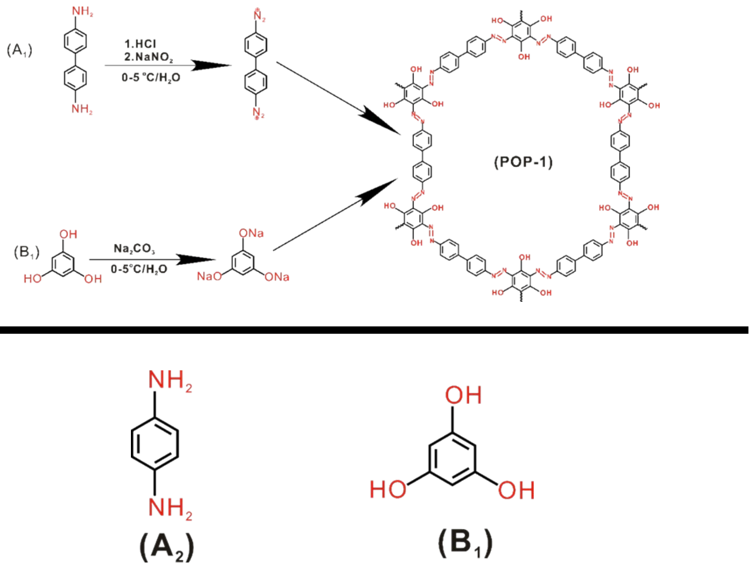
BET: Samples were treated at 120 ^{o}C for 24 h prior to measurement. The surface area was calculated based on the adsorption data using the Langmuir and Brunauer-Emmett-Teller (BET) method. The pore size distribution curve is obtained from the adsorptive branch using the non local density functional theory (NLDFT) method.

TGA: Thermo gravimetric analysis (TGA) was characterized using a STA 449 F3 Jupiter simultaneous thermal analyzer at a temperature range from room temperature to 800 °C under a N_2 atmosphere and a heating rate of 10 °C /minute.

NMR: Solid state NMR experiments were performed on an AVIII HD 400 spectrometer. The ^1H CP /MAS NMR spectra were recorded with a 4 mm double resonance MAS probe with a sample rotation rate of 8.0 kHz.

1.3 Preparation of mixed matrix membranes (MMMs)

Graphene oxide (GO) was synthesized from natural graphite powders based on an improved method.[1, 2] Firstly, 360 ml of concentrated sulfuric acid (H_2SO_4) and 40 ml of concentrated phosphoric acid (H_3PO_4) were charged into a 1000 ml three-necked flask, and then 18 g of potassium permanganate ($KMnO_4$) was added to the flask. Subsequently, 3 g of graphite powder was added to the flask, and the mixture was heated to reflux under stirring in a 50 °C oil baths under mechanical stirring for 22 hours. The above completed liquid and hydrogen peroxide (H_2O_2) alternately slowly added 1000ml beaker, and cooled with ice, and then ultrasound 1h. The supernatant was centrifuged at 1000 r/min for 5-7 min, and the precipitate was centrifuged at 7000-8000 r/min for 5-7 min. Then washing with 30wt.% HCl for 3 times, then washing with absolute ethanol for 3 times and finally washing with demonized water for 3 times, taking the precipitate into a freezer to freeze and then freeze-drying to obtain graphene oxide.



Scheme S1. Synthetic process of P-hydroxy azo-hierarchical porous organic polymers (POPs) through diazo-coupling reaction between diazonium salts and multihydroxy benzene.

Taking the preparation of POP-1 as an example, the diazo-coupling reaction was performed in two steps.[3] First, 4,4'-diaminobiphenyl (1.5 mmol) was added to a 250 ml flat-bottomed flask containing 100 ml of demonized water, and then 0.7 ml of hydrochloric acid (HCl) was added. After stirring at 0~5 °C for 15 minutes, 30 ml of aqueous sodium nitrite solution (3.1 mmol) was added and stirred for 25 minutes to completely convert the amino group to a diazonium salt. The mixture was then neutralized with Na_2CO_3 solution and then mixed with 30 ml of an aqueous solution of 1, 3, 5-trihydroxyphenol (1 mmol) and Na_2CO_3 (3 mmol) at 0-5°C. After reaction for 12 h at 0-5 °C, the solid sample was separated from the reaction solution by filtration and washed in the order of water, methanol, THF, methanol, water. Freeze in a refrigerator and freeze-dry to give a sample in a yield of 97%. Similarly, POP-2 was prepared using the corresponding monomer in a yield of 75.3%.

In this work, mixed matrix membranes (MMMs) were prepared by solution casting. In briefly, 2 ml of POP at a certain concentration and 2 ml of GO at a certain concentration are combined with stirring to form a quinone bond, thereby controlling the spacing of the graphene sheets. Then, 15 ml of Pebax@1657 the solution was in addition to the above solution and then stirred, the gas dispersed evenly, and then ultrasound, in addition to bubbles, and then poured into Teflon Petri dishes. The membrane was air-dried at ambient temperature for 24 h. In order to remove the residual solvent, the membrane was kept in a vacuum oven for 12 h. The prepared film is represented as POP-GO X-Y (where X, Y represents the mass ratio of POP to GO). Preparation of POP-1 solution: Weigh a certain mass of POP-1 powder dispersed in demonized water, the cell smashed ultrasound for 2 hours, after which the supernatant was centrifugal. Preparation GO solution: Weigh a certain amount of GO powder dispersed in demonized water until the cells pulverized ultrasound 2 hours, as long as the supernatant after centrifugation. Pebax@1657 solution preparation: 3 g of Pebax@1657 particles are dispersed in a solvent mixture of 100 g of 70% by weight ethanol and 30% by weight of water and the undissolved Pebax@1657 is removed by filtration before reacting the resulting solution for 3 h (80°C).

1.4 Gas permeation tests

The gas transmission properties of dense membranes can be explained by the dissolution-diffusion mechanism. Assuming Fick's law, the upstream pressure is much higher than the downstream pressure. The pure gas permeability (P) with the unit of Barrer (1 Barrer=10^{-10} cm^3 (STP) cm/ (cm^2s cm Hg) can be given by:

$$P = D \times S \qquad (2)$$

Where D is the average effective diffusivity in cm^2/s and S is the apparent adsorption coefficient in cm^3 (STP) /cm^3 cm Hg. The ideal selectivity of gas A to gas B is defined as the ratio of its pure gas permeability:

$$\alpha_{\frac{A}{B}} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right] \times \left[\frac{S_A}{S_B}\right] \tag{3}$$

In this study, pure gas permeability was measured using a constant volume method.[4] The gas was tested in the order of N_2 and CO_2 at 1 atm and 30°C. Gas permeability (P) is calculated from the steady rate of downstream pressure increase ($^{d_p}/_{d_t}$) by the following equation:

$$P = \frac{273 \times 10^{10}}{760} \frac{Vl}{AT\left(P_2 \times \frac{76}{14.7}\right)} \frac{d_P}{d_t} \tag{4}$$

Where V is the volume of the downstream hollow chamber (cm^3) and l is the film thickness (cm). A is the effective test area (cm^2) of the membrane, T is the operating temperature (K) and P_2 is the upstream working pressure (psi). The diffusion coefficient can be obtained by the time delay method, as shown in Equation 5, then the solubility can be simply derived from Equation 2.[5]

$$D = \frac{l^2}{6\theta} \tag{5}$$

Where θ is the diffusion time delaying from the extrapolation of the pressure over time in the steady state to the time axis.

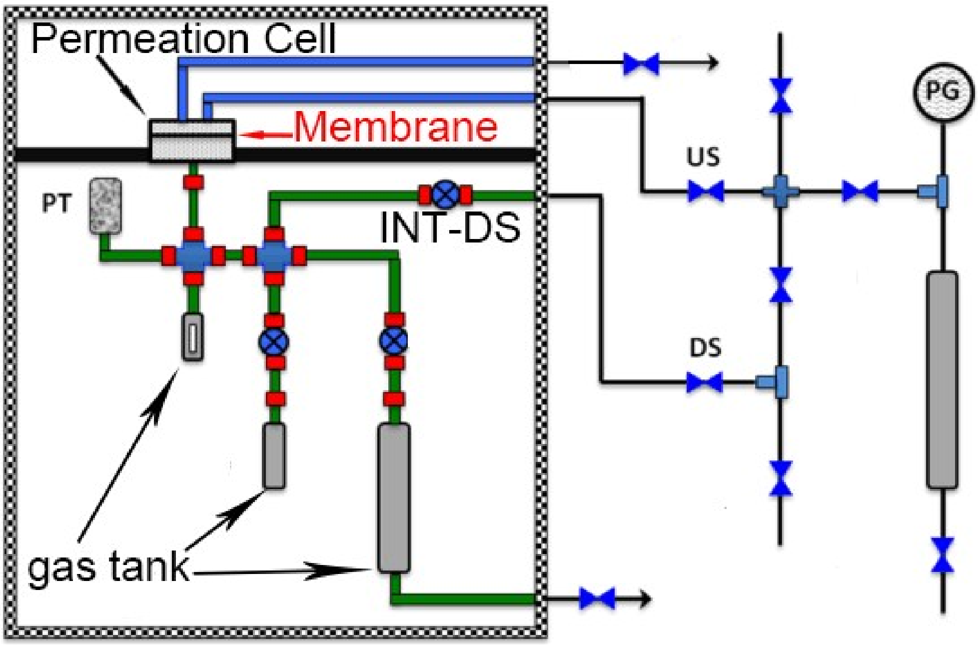


Fig. S1 Schematic diagram of dense membrane gas permeation testing apparatus

1.5 Computational Methods

For the adsorption of POPs Precursor (Pre-POPs) on a graphene monolayer, all ab initio total energy calculations were carried out based on density functional theory (DFT) within the framework of VASP (Vienna Ab initio Simulation Packages) code which uses a plane wave basis set for the electronic orbitals. [6, 7] The electronic exchange and correlation was described within the generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) functional [8]. The interaction of the valence electrons with the ionic cores was treated within the projector augmented-wave (PAW) method [9]. A large supercell was modeled with a cubic box of 9.84Å × 9.84 Å × 18.8 Å. The original distance between two graphene layers are set to 4.7 Å obtained from XRD experimental data. A Monkhorst-Pack grid was used by K-points 5 × 5 × 1. [10] The cut-off energy was employed as 450 eV. An electronic smearing was introduced within the Methfessel-Paxton scheme with $N = 0$ and σ=0.1 eV.[11] The interaction energy is defined as E_i=(E (Graphene+n×POP)-E(Graphene)-n×E(Pre-POPs))/n, where E(Graphene) and E(Pre-POPs) are the energies of graphene and POPs, n is the number of POPs.

2. General characterization of the as-prepared POPs

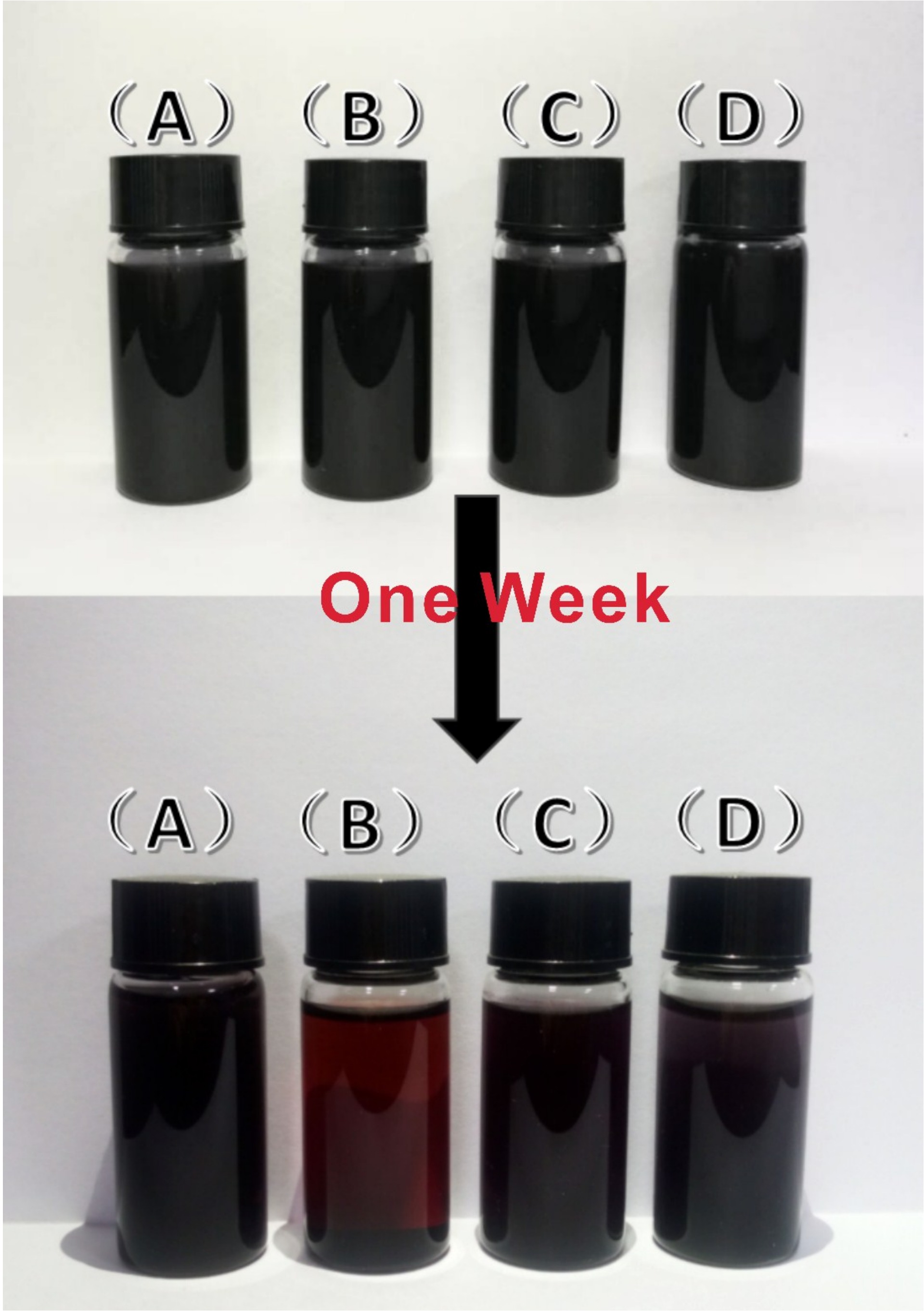


Fig. S2 Dispersity of POP-1 in common solvents. (A) represent water, (B) show N,N-dimethylformamide, (C) manifest ethylalcohol, (D) indicate water:ethylalcohol 3:7

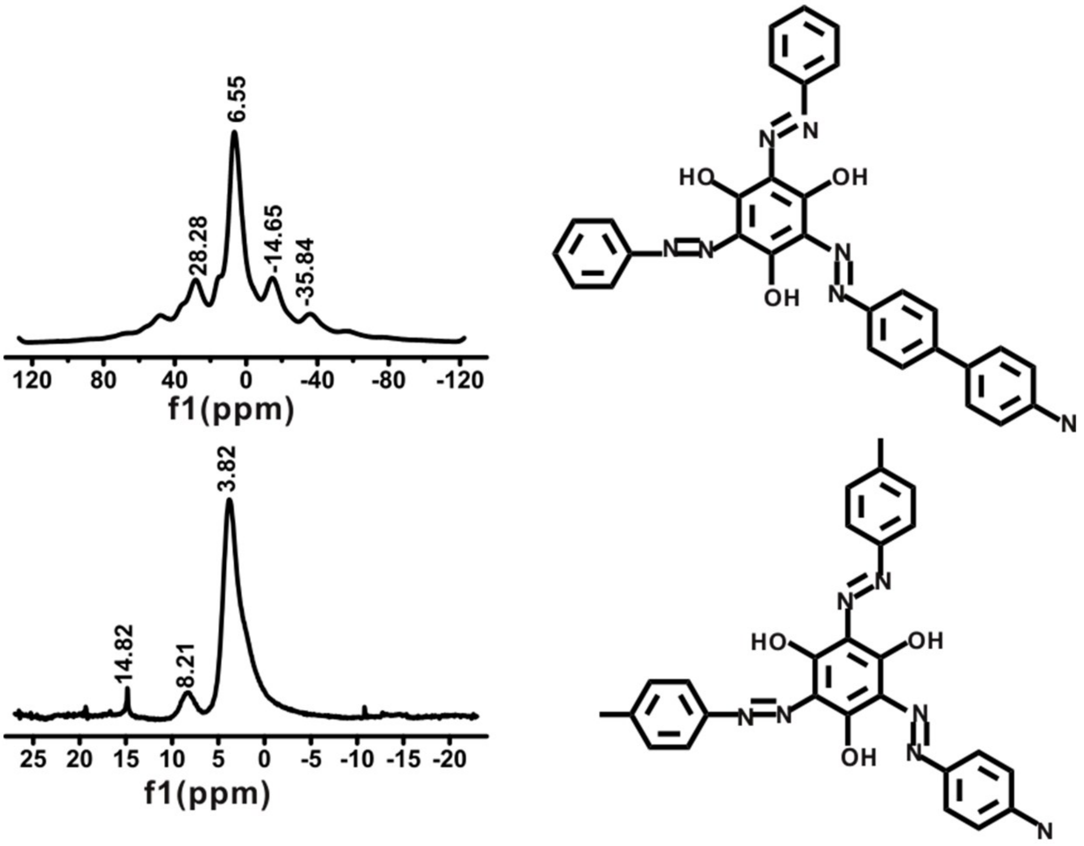


Fig. S3 Solid-state 1H-CP/MAS NMR spectra for the resultant polymers

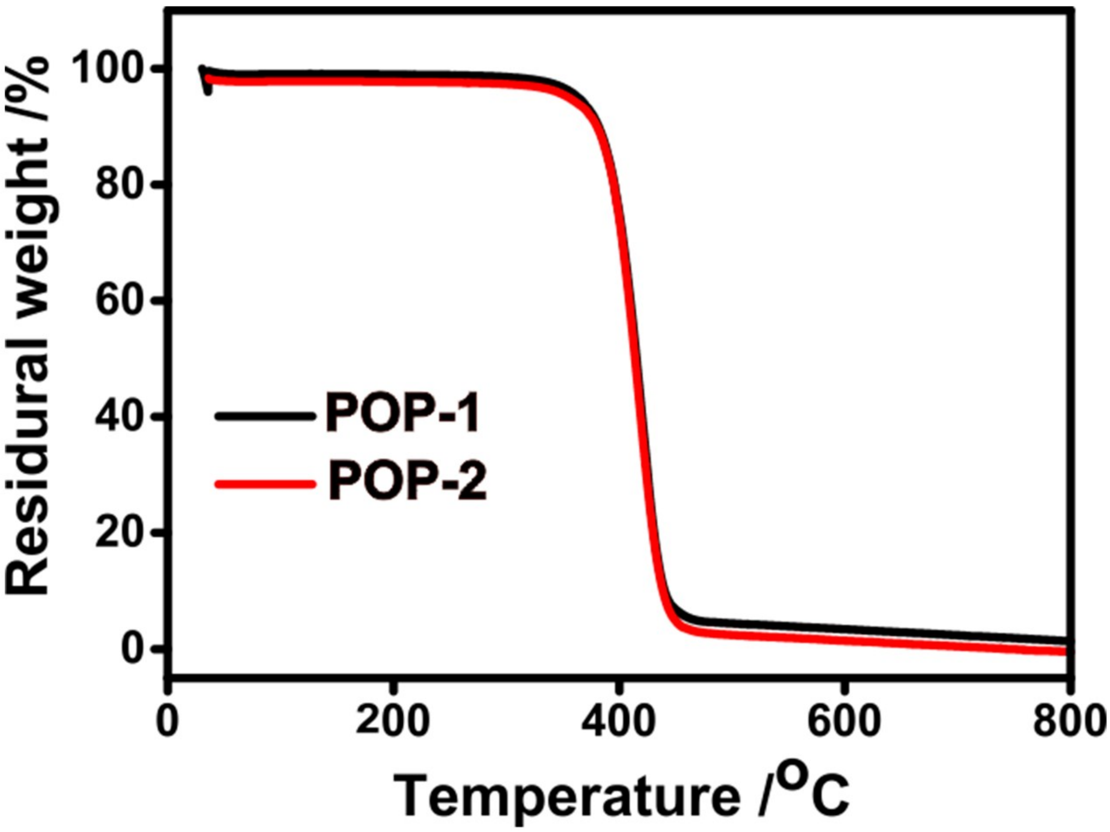


Fig. S4 Thermo gravimetric Analysis (TGA) of POPs in a nitrogen atmosphere

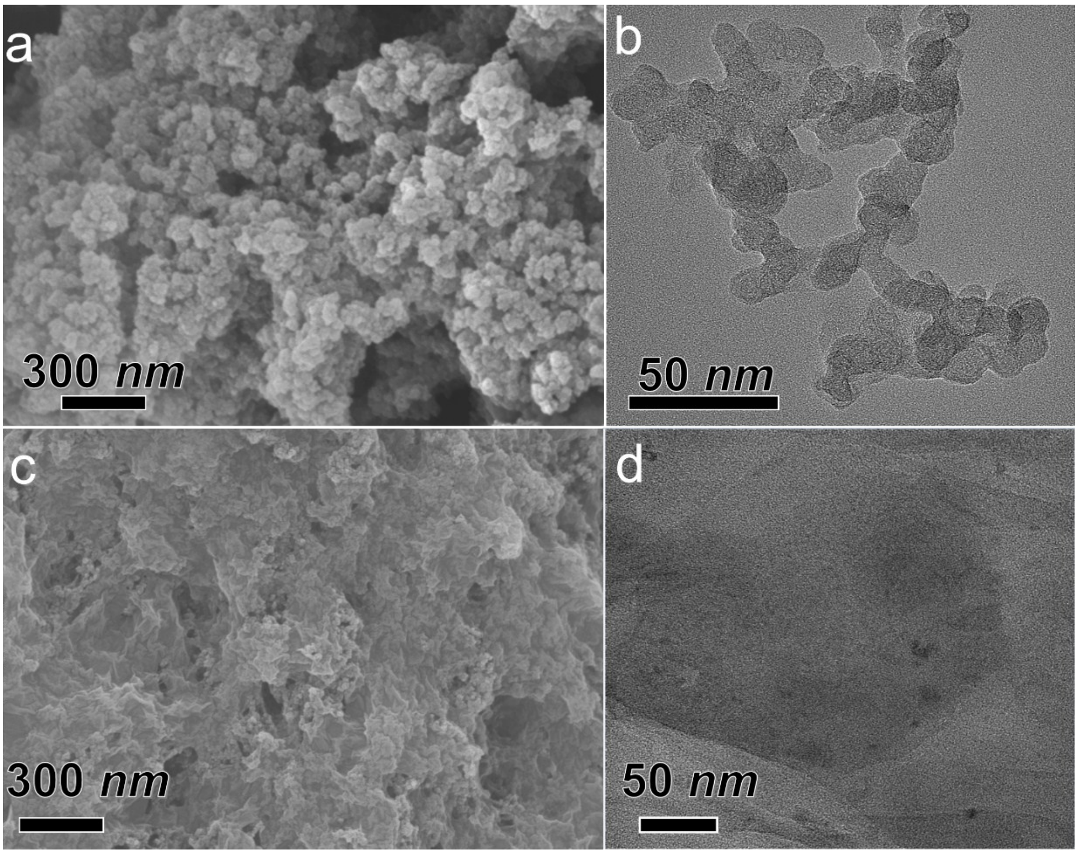


Fig. S5 SEM (left) and TEM (right) images of (a, b) POP-1 and (c, d) POP-GO

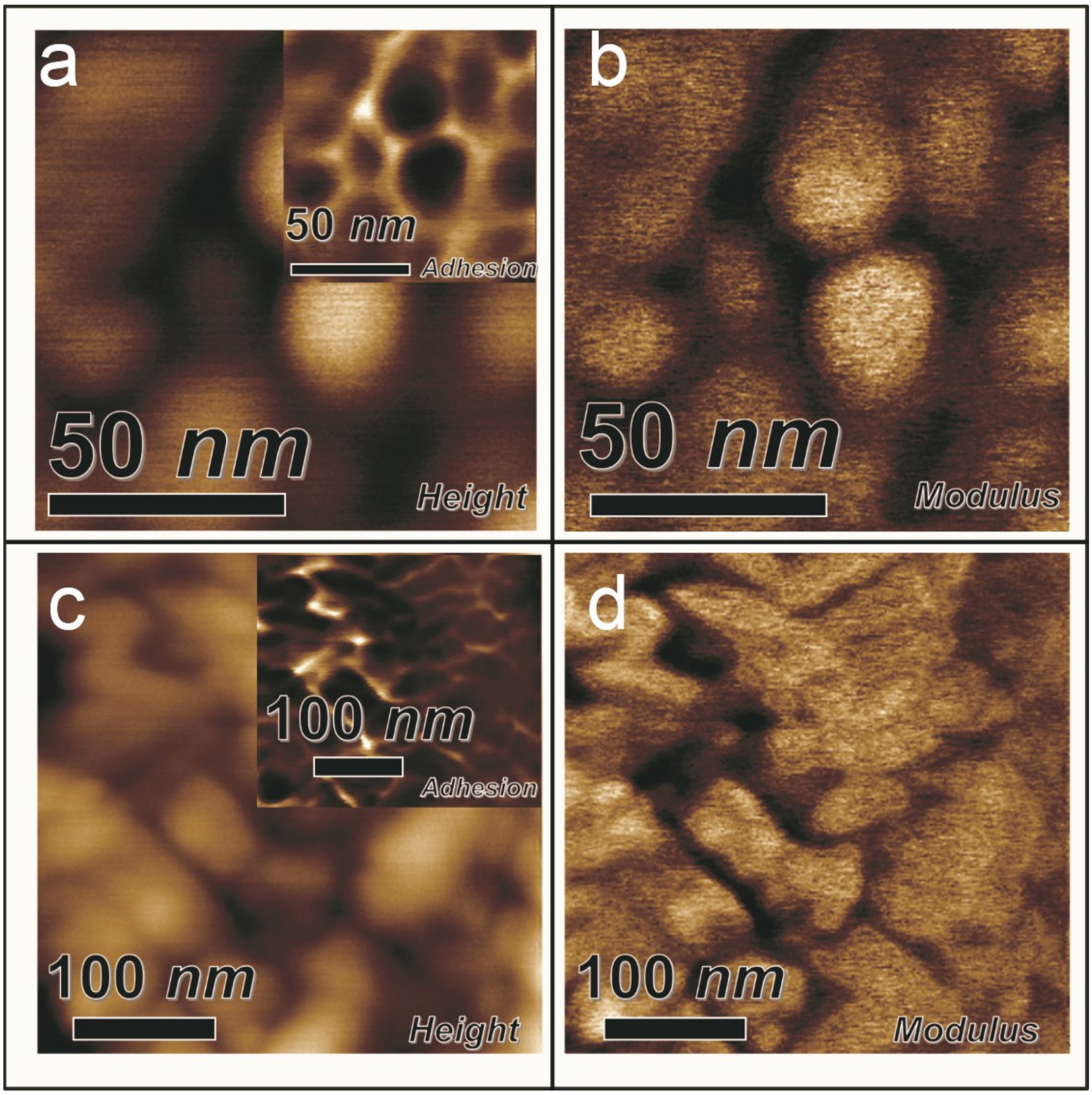


Fig. S6 AFM images in different channels of POP-2 (a, b) and graphene oxide (c, d)

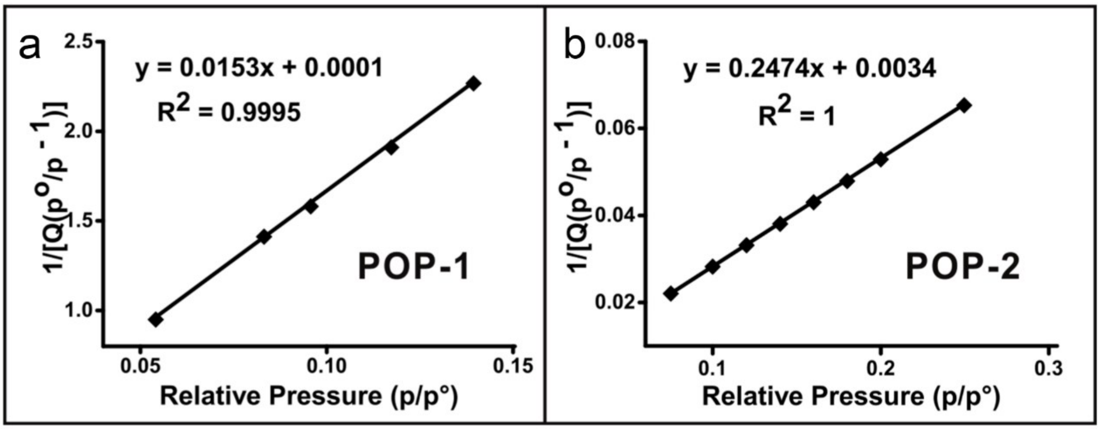


Fig. S7 BET plot from N_2 isotherms at 77 K of POPs

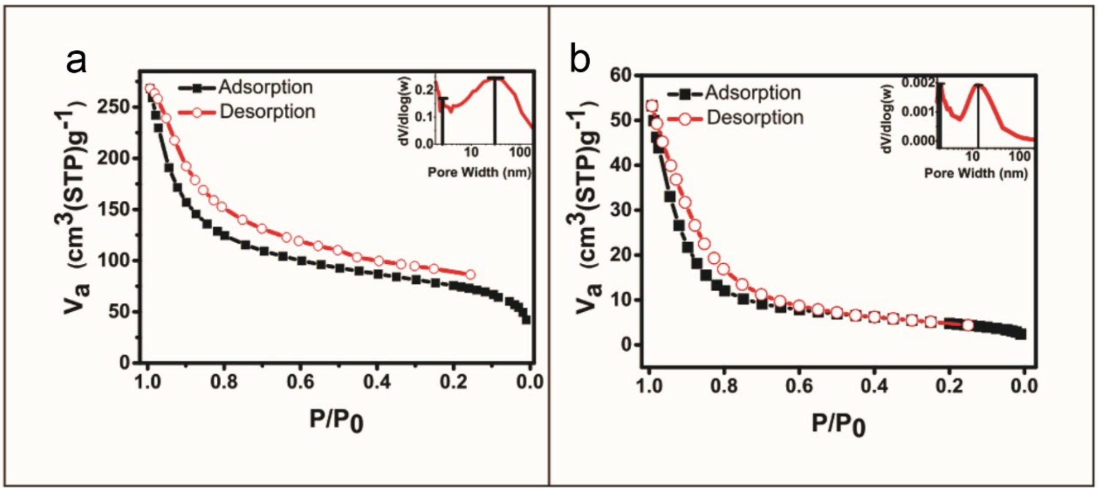


Fig. S8 Pore size distribution curve and BET plot from N_2 isotherms at 77 K of POPs (a POP-1; b POP-2)

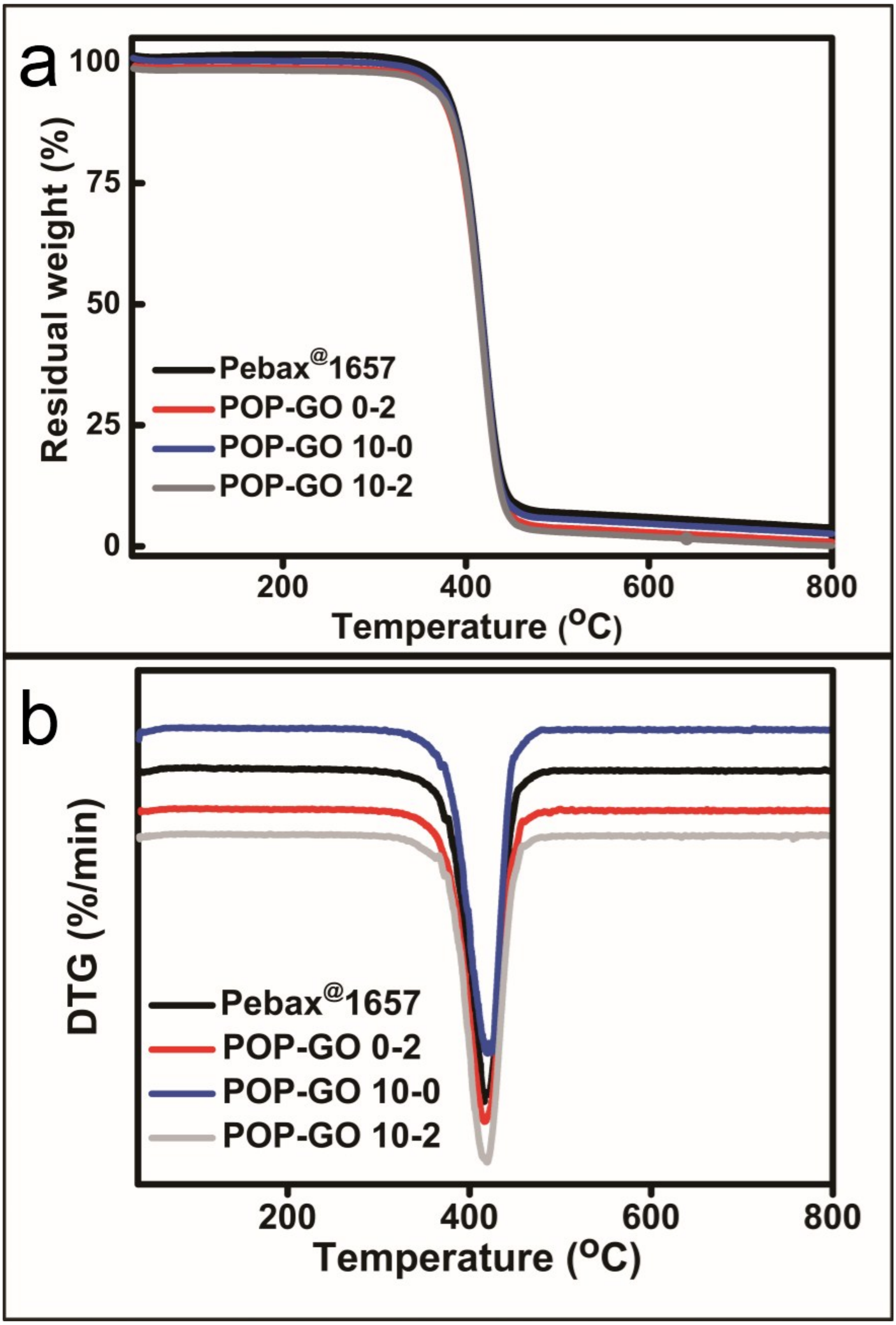


Fig. S9 TGA (a) and DTG (b) of different mass concentrations of POP-GO

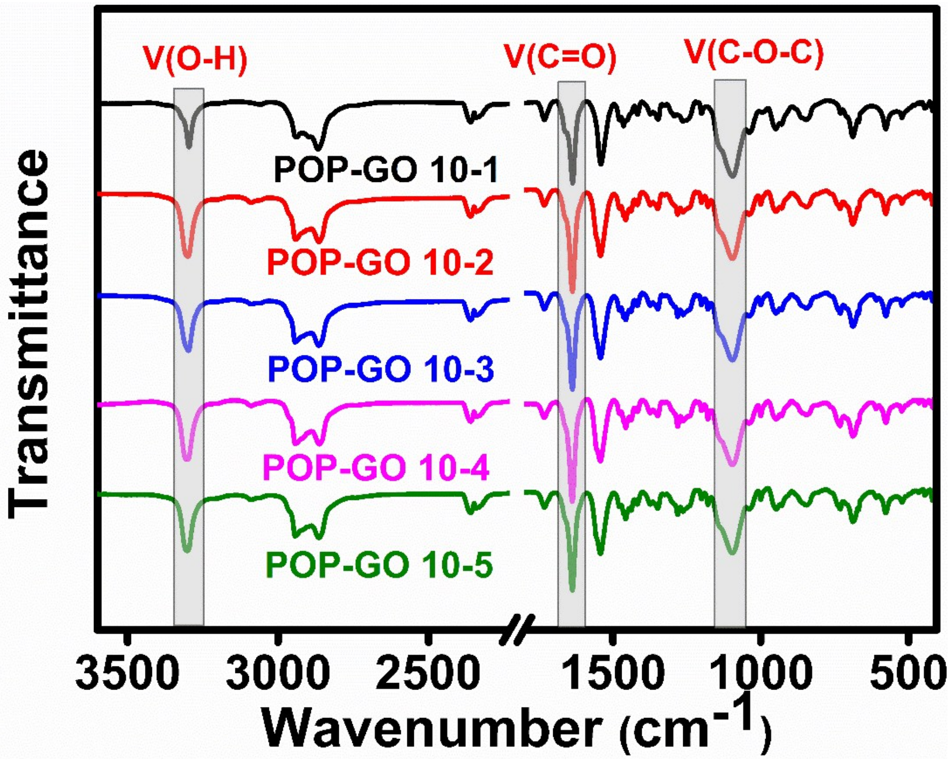


Fig. S10 ATR-FTIR spectra of POP-GO with different mass concentration ratios

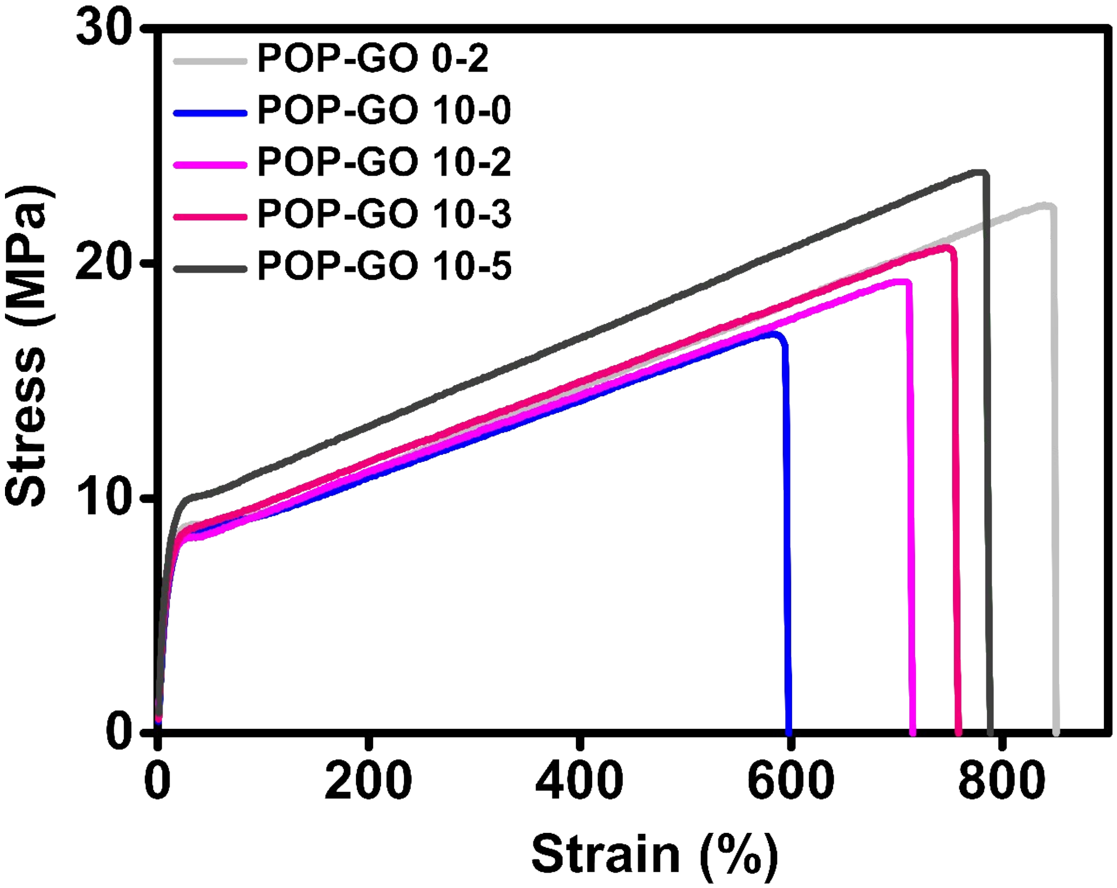
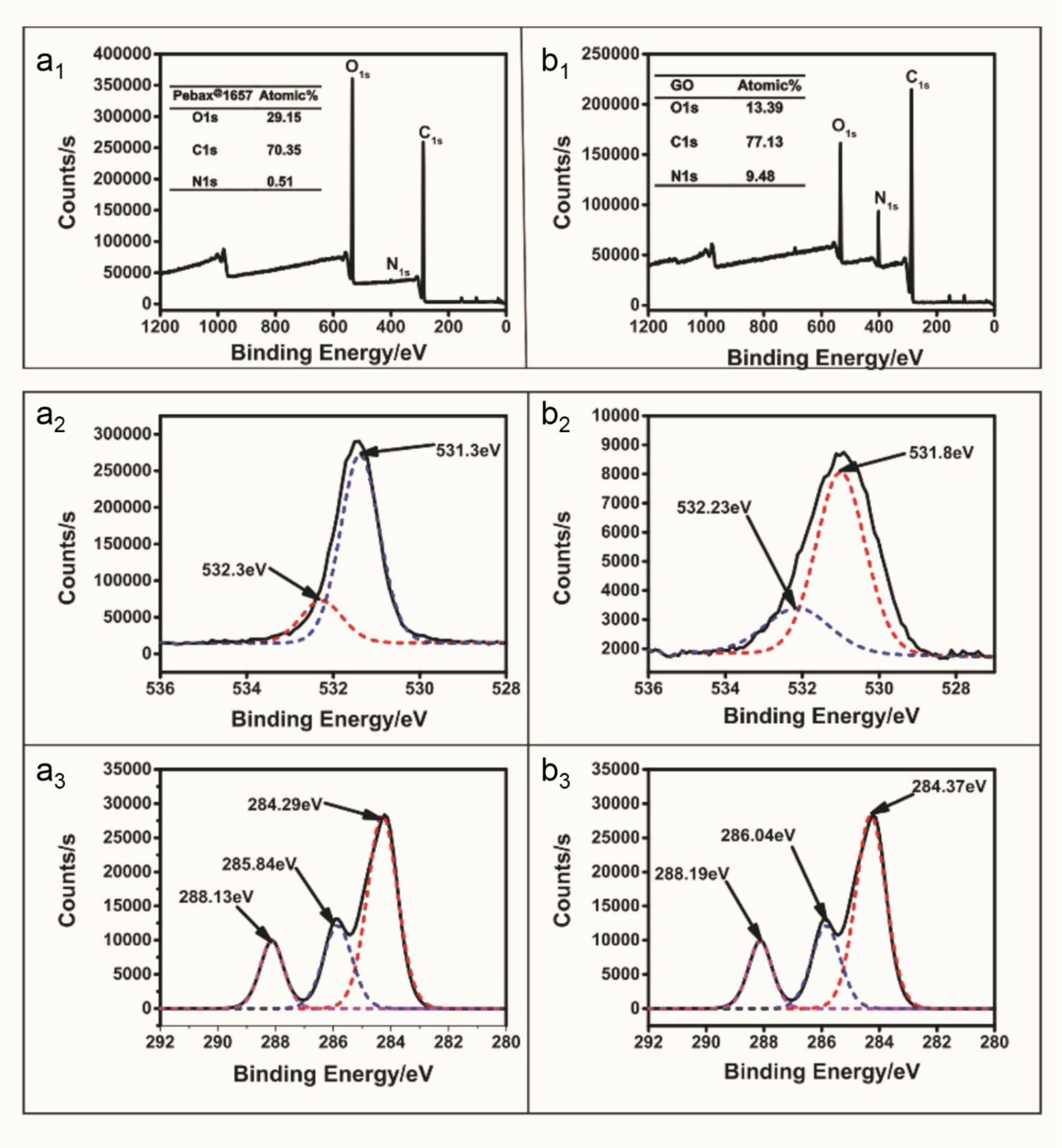
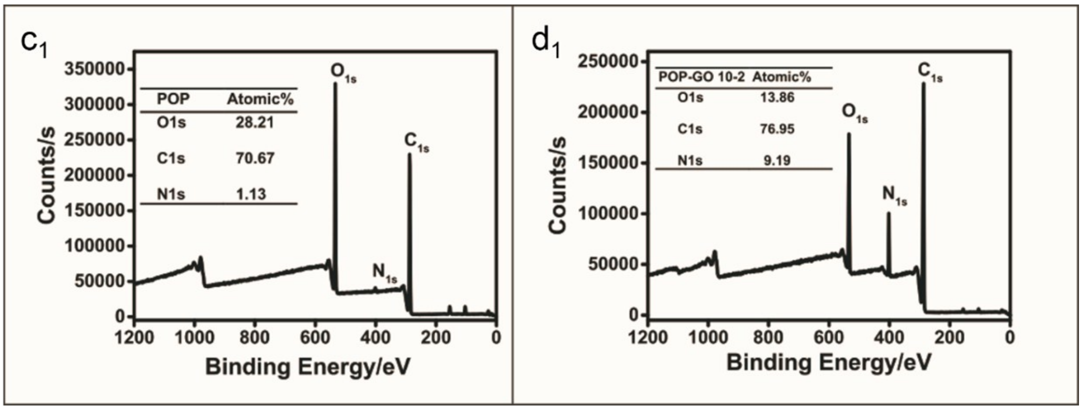


Fig. S11 stress–strain curves of POP, GO and POP-GO membranes of involving comparison


a1
Pebax®1657 Atomic%
O1s 29.15
C1s 70.35
N1s 0.51
O_{1s}
C_{1s}
N_{1s}
b1
GO Atomic%
O1s 13.39
C1s 77.13
N1s 9.48
C_{1s}
O_{1s}
N_{1s}
a2
531.3eV
532.3eV
b2
531.8eV
532.23eV
a3
284.29eV
285.84eV
288.13eV
b3
284.37eV
286.04eV
288.19eV
Counts/s
Binding Energy/eV


c1
POP Atomic%
O1s 28.21
C1s 70.67
N1s 1.13
O_{1s}
C_{1s}
N_{1s}
d1
POP-GO 10-2 Atomic%
O1s 13.86
C1s 76.95
N1s 9.19
C_{1s}
O_{1s}
N_{1s}
Counts/s
Binding Energy/eV

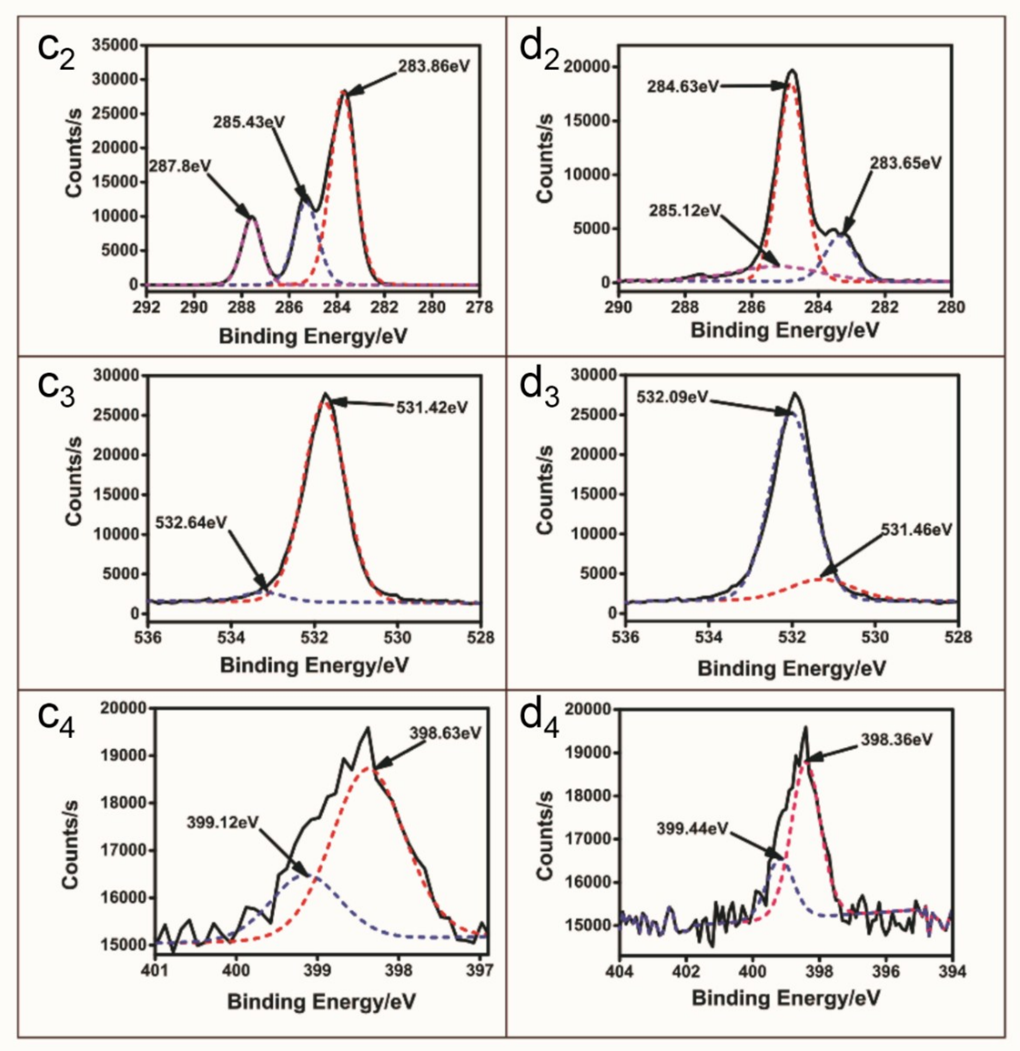


Fig. S12 XPS analysis on (a) Pebax@1657, (b) Graphene oxide, (c) POP-1, and (d) POP-GO 10-2

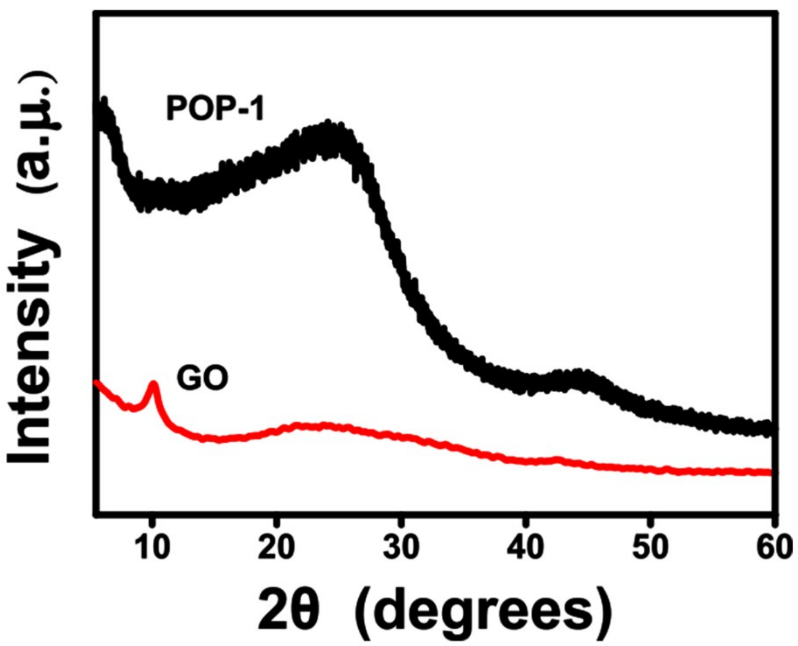


Fig. S13 Powder XRD of Graphene Oxide and POP-1

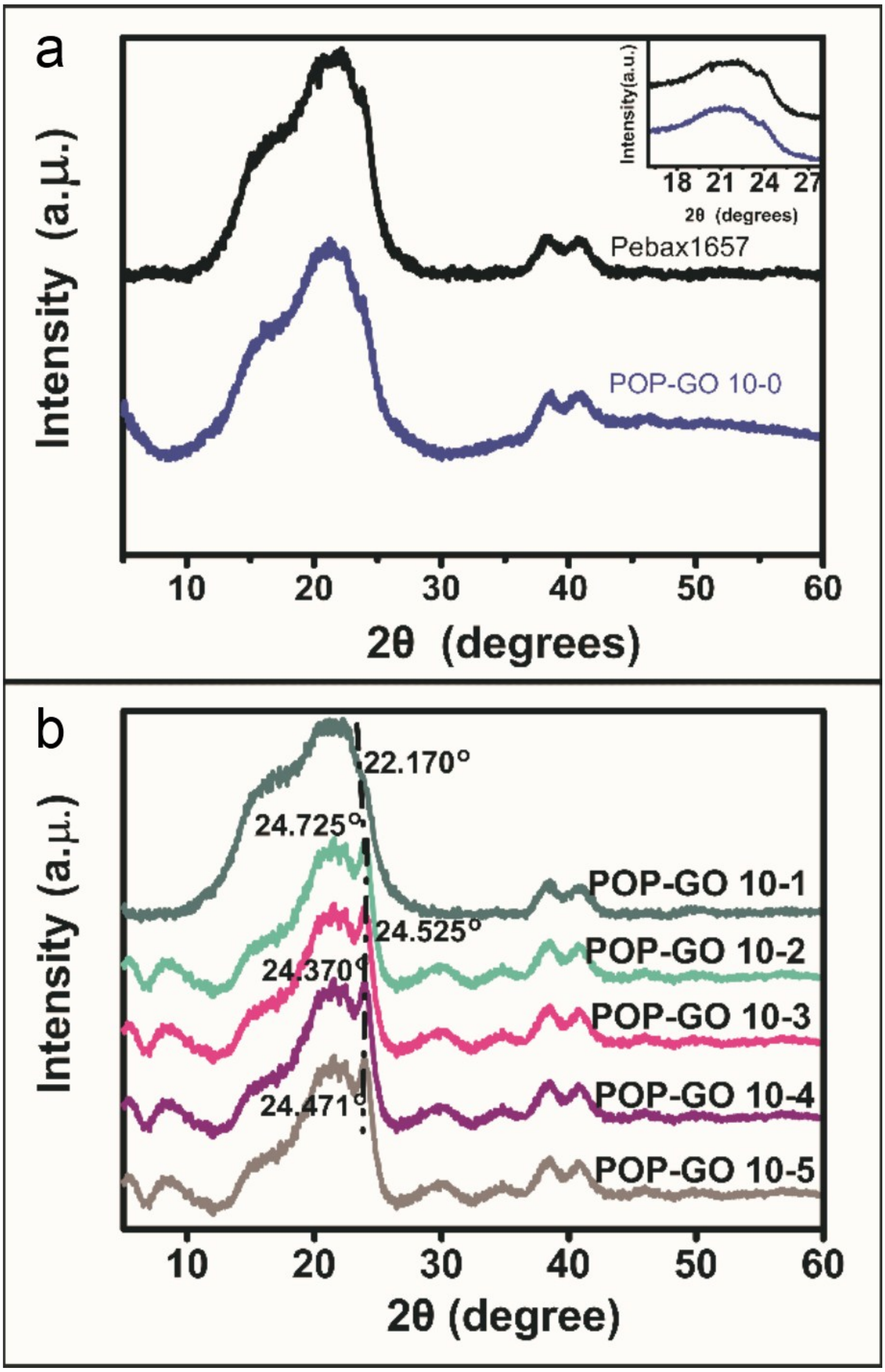


Fig. S14 XRD of POP-GO with different GO mass concentration ratios

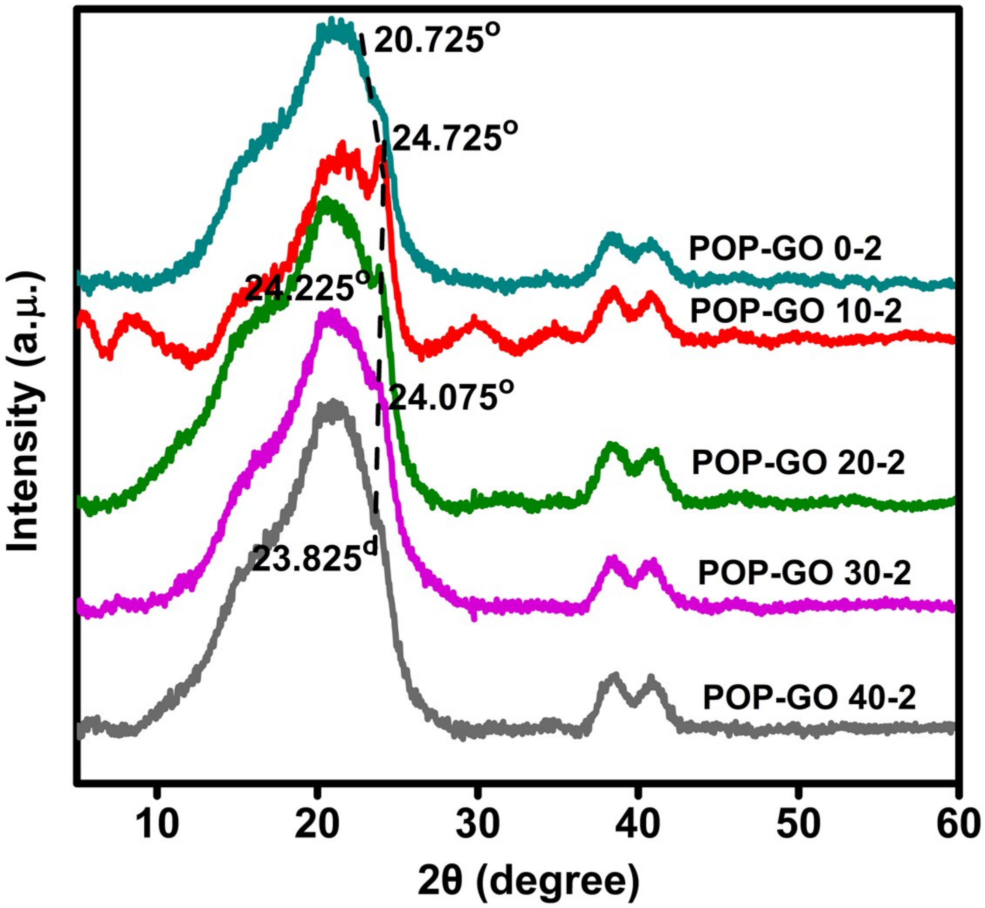


Fig. S15 XRD of POP-GO with different POP mass concentration ratios

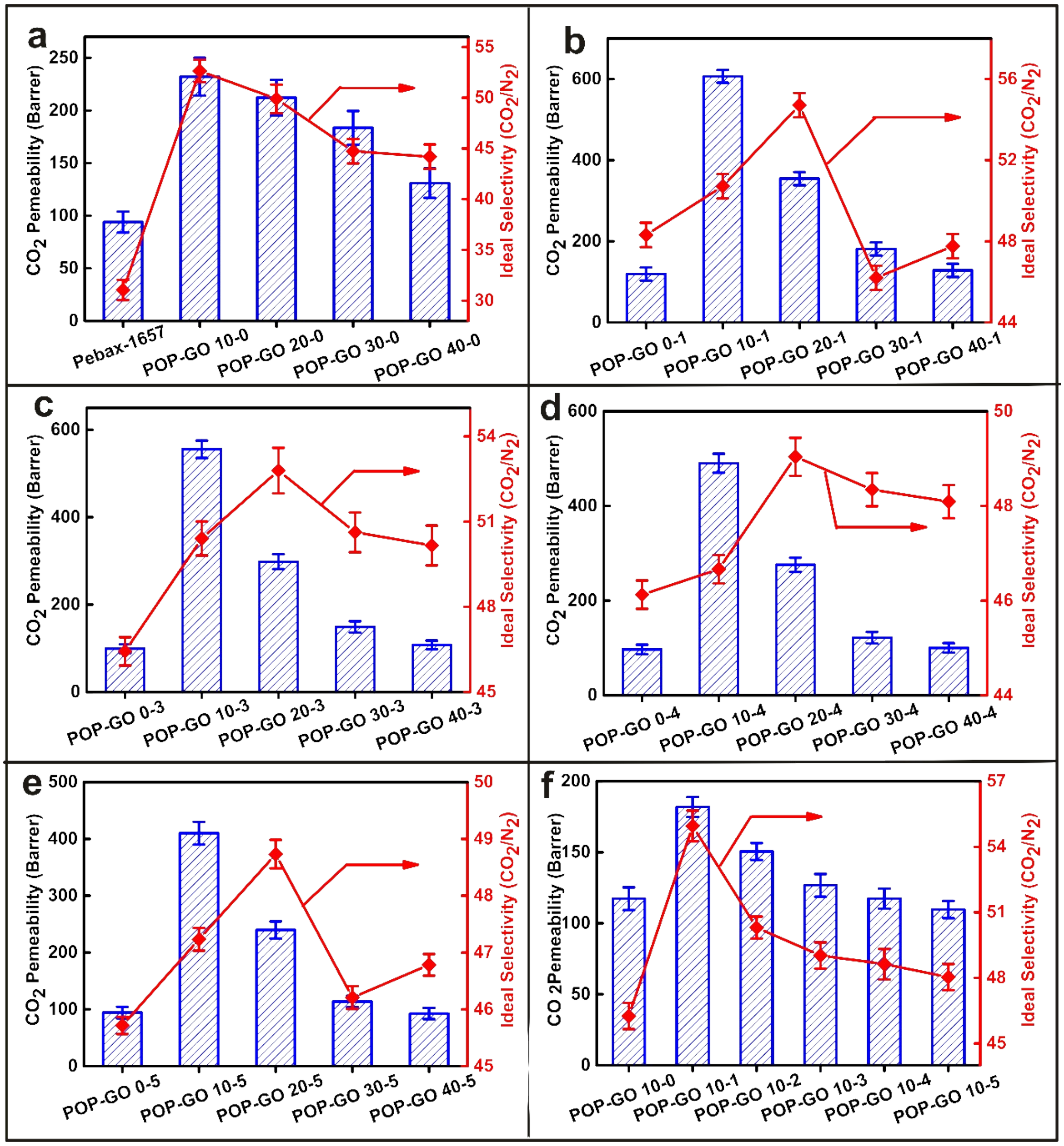


Fig. S16 (a-e) Gas permeability and selectivity vary with different graphene oxide concentration (Where POP represents POP-1), (f) Gas permeability and selectivity of POP-GO 10-Y membranes (Where POP represents POP-2).

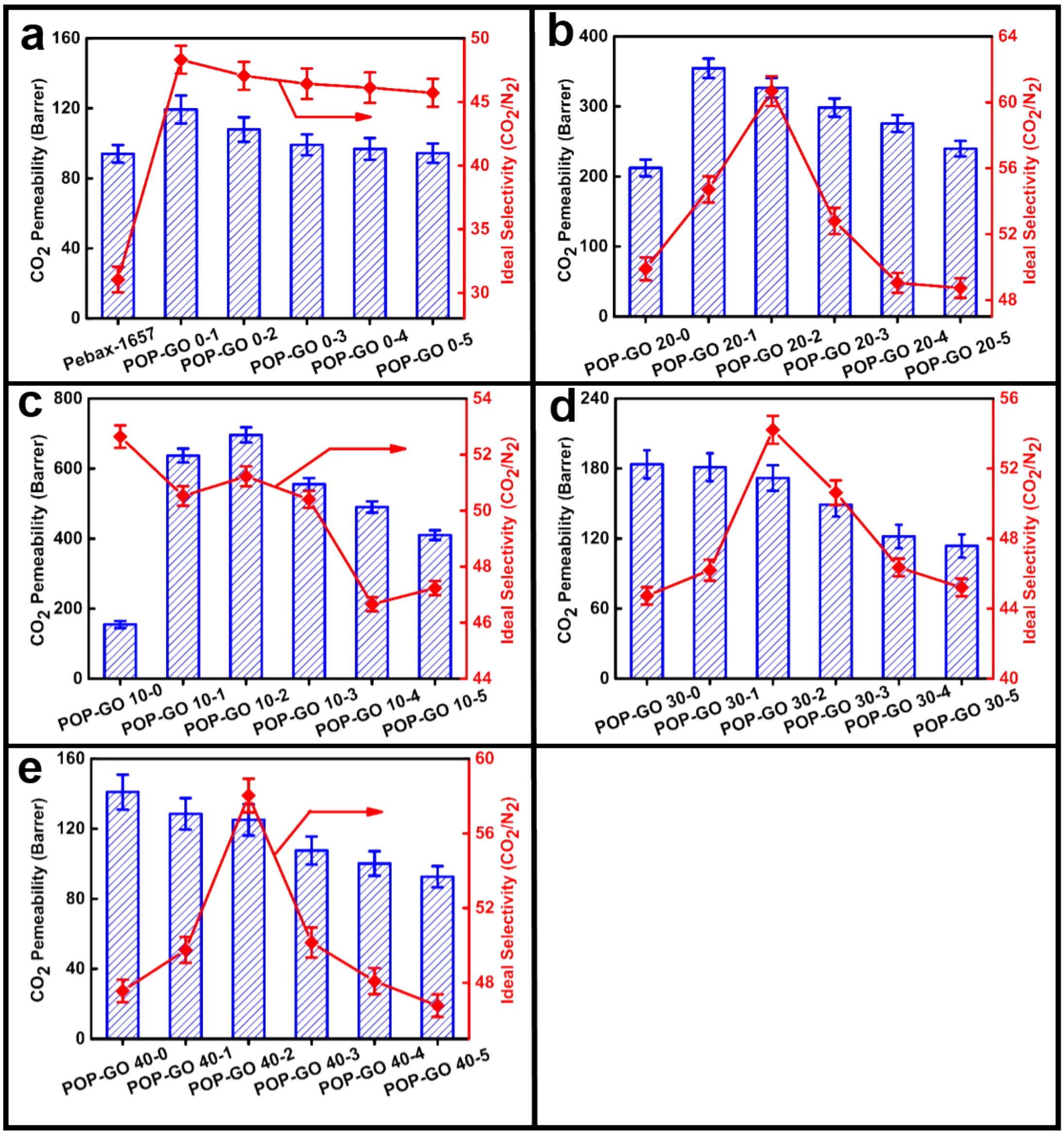


Fig. S17 Gas permeability and selectivity vary with different POP-1 concentration

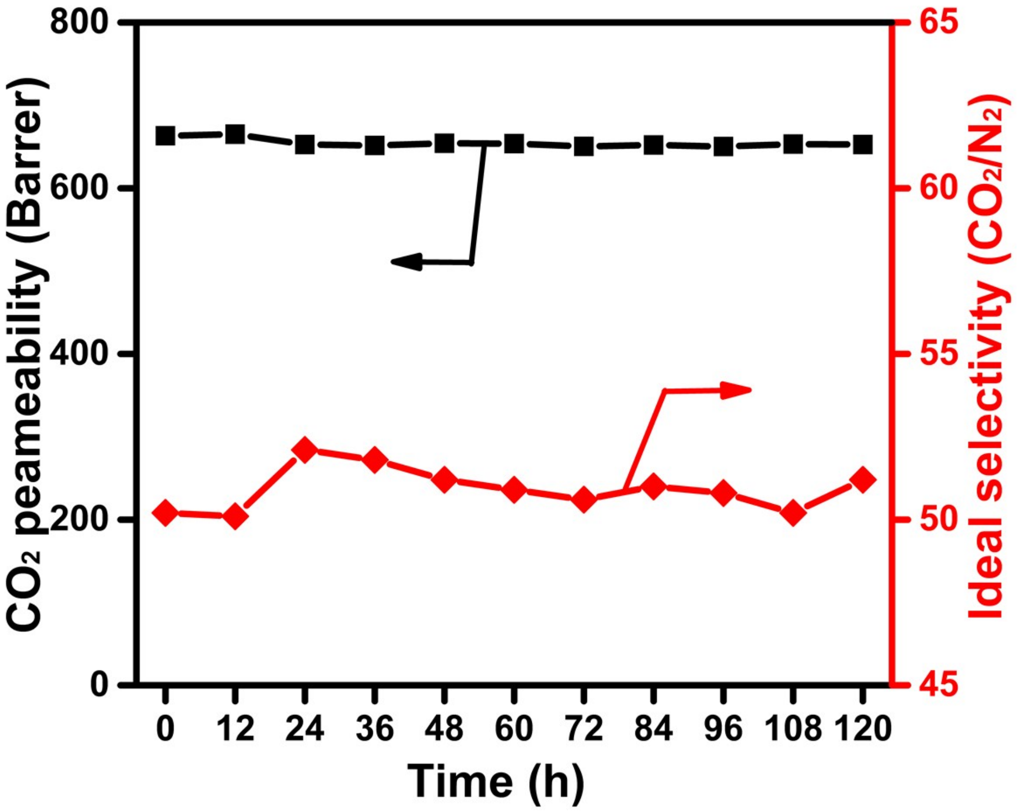


Fig. S18 Long-term stability of POP-GO 10-2 membrane for CO_2/N_2 separation

Reference and Notes:

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