Electronic Supplementary Information

Ultrathin Membranes of Single-Layered MoS_2 Nanosheets for High-permeance Hydrogen Separation

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1. Materials and methods

1.1 Preparation of single-layered MoS_2 nanosheets

1 g MoS_2 powder (Alfa Aesar) was dispersed into 10 mL of 2.0 M butyllithium solution in cyclohexane (Sigma-Aldrich) in an autoclave filled with argon gas and kept at 60 °C for 2 days. The obtained intercalation intermedia was collected by filtration through 0.45 μm PTFE (polytetrafluoroethylene) filter membrane and washed with hexane (60 mL) to remove excess lithium and organic residues. Exfoliation was finished immediately after this by mild ultrasonication in 200 mL water (Millipore) for 1 hour. Excess lithium hydroxide and unexfoliated material were removed by procedures as follow. After centrifuging (20000 rpm, 30 min), the sediment was redispersed into water and centrifuged (20000 rpm, 30 min), the sediment was collected and repeated above cycle again. Finally, the sediment was redispersed into water and centrifuged (9000 rpm, 15 min), the supernatant was collected and used to prepare membranes.

1.2 Preparation of single-layered MoS_2 nanosheets membranes

The MoS_2 nanosheets membranes were prepared by vacuum filtrating MoS_2 nanosheets dispersion through anodic aluminum oxide (AAO) filters with 200 nm pores (Whatman). The thickness of membranes can be tuned by adjusting the filtered volume of the MoS_2 nanosheets dispersion. To assume compactness and density of the membranes are similar, the known amounts (0.5 to 2 mL as-prepared dispersion with concentration of *ca*. 2 mg/mL) of MoS_2 nanosheets dispersion were diluted into 250 mL water for filtration. In order to obtain the compact membranes, after the water was filtrated out completely (about 3 h), 10 mL ethanol was added and filtrated for >5 h. The thickness of MoS_2 nanosheets membrane was measured by field-emission scanning electron microscope (FE-SEM). The resulting MoS_2 membranes were stored in a vacuum oven at room temperature for 24 h to remove the residue ethanol before permeation experiment.

1.3 Sample characterization

Atomic force microscopy (AFM) was obtained on a Dimension Icon, Bruker. Scanning electron microscope images was taken on a field-emission scanning electron microscope (FE-SEM) (Hitachi S4800, Japan). Transmission electron microscopy was performed on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. X-ray diffraction (XRD) was collected on a Bruke D8. Raman spectra were collected with a Labram HR800 UV NIR Raman spectrometer employing a 532 nm laser beam.

1.4 Gas separation tests of single-layered MoS_2 nanosheets membranes

To avoid direct contact of silicone O-ring with the MoS_2 nanosheets membrane and thus damage on the ultrathin MoS_2 nanosheets membrane, aluminum tape with 1.5-cm-diameter hole sandwiched the MoS_2 nanosheets membrane on AAO support, and then high vacuum grease was used to seal the gap between aluminum tape and MoS_2 nanosheets membrane. A common filter paper was placed at the bottom of the AAO to further protect the support. The 60-nm-thick membranes were used to conduct transmembrane pressure-variable and thermal stability experiment. The test of gas permeation was performed using a fixed-volume pressure increase instrument time-lag apparatus at 35 °C and a given transmembrane pressure (the transmembrane pressure was changed from 0.02 MPa to 0.08 MPa for transmembrane pressure-variable experiment, the transmembrane pressure was fixed at 0.02 MPa for other tests), starting with an oil-free vacuum (below 10 Pa). The test order of pure gases (99.999%) is as follow: He (2.69 Å), H_2 (2.89 Å), O_2 (3.46 Å), N_2 (3.64 Å), CH_4 (3.87 Å), CO_2 (3.3 Å). The permeability coefficient, P, was calculated from the slope in the steady state region by using follow equation:

$$P = \frac{273.15 \times 10^{10}}{760} \cdot \frac{Vl}{AT\Delta p} \cdot \left(\frac{dp}{dt}\right)$$

where P is the permeability represented in Barrer (1 Barrer = 10^{-10} cm^3 (STP)·cm·cm^{-2}·s^{-1}·$cmHg^{-1}$), V (cm^3) is the downstream volume, l (cm) is the membrane thickness, A (cm^2) is the effective area of the membrane, T (K) is the measurement temperature, Δp (cmHg) is the pressure difference between the two sides, and dp/dt is the rate of pressure rise under the steady state, respectively. All gas permeation tests were performed more than three times. The effective membrane area was 1.3 cm^2. In this paper, gas permeance is given in unit of GPU (Gas Permeation Unit). 1 GPU = 10^{-6} cm^3 (STP)·cm^{-2}·s^{-1}·$cmHg^{-1}$ = 3.35×10^{-10}mol·m^{-2}·s^{-1}·Pa^{-1}. The ideal selectivity for pure gas A and B is defined as the ratio of permeances of the pure gases:

$$a = \frac{P_A}{P_B}$$

2. Supplemental figures

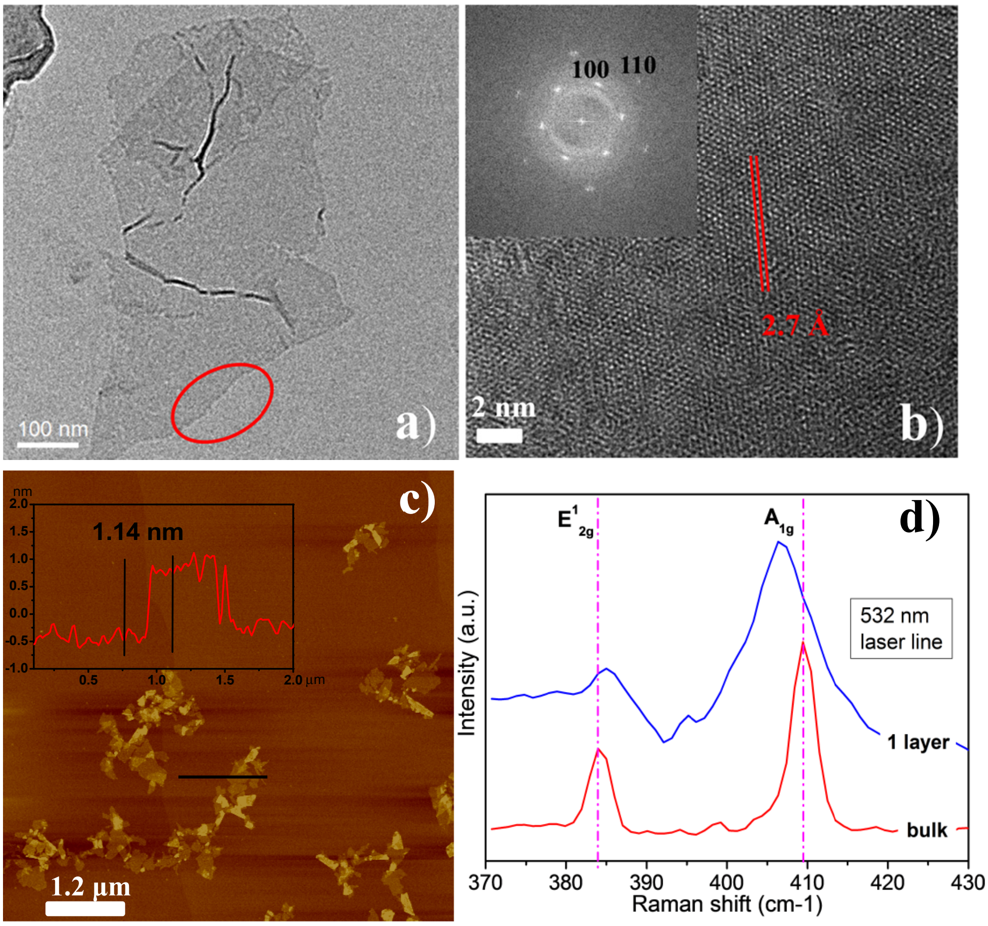


Figure S1. a) TEM image of a typical single-layered MoS_2 nanosheet. b) Selected area high-resolution TEM (HRTEM) image of single-layered MoS_2 nanosheet. Inset: FFT pattern of HRTEM image. The HRTEM image of the nanosheet (Figure S1 b) and the corresponding FFT pattern (inset) show the hexagonal lattice structure with a lattice spacing of 2.7 Å assigned to the (100) planes.[1] c) AFM image of MoS_2 nanosheets. d) Raman spectra of typical single-layered MoS_2 nanosheets. The peak at 384 cm^{-1} (the in-plane E^1_{2g} model arises from opposite vibration of two S atoms with respect to the Mo atom) in bulk MoS_2 blueshifts to 385 cm^{-1}, and the peak at 409 cm^{-1} (the A_{1g} model results from the out-of-plane vibration of only S atoms in opposite directions) in bulk MoS_2 redshifts to 406 cm^{-1}. The results are consist with literature report and indicate that MoS_2 has been exfoliated into single layer.[2]

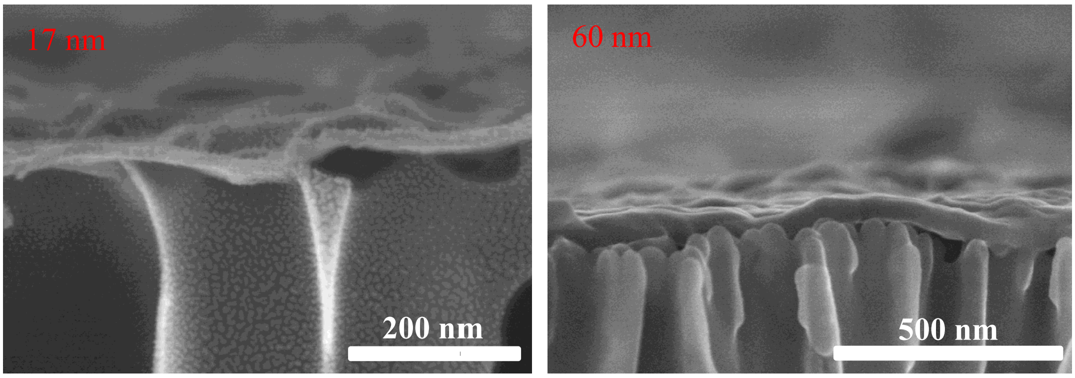
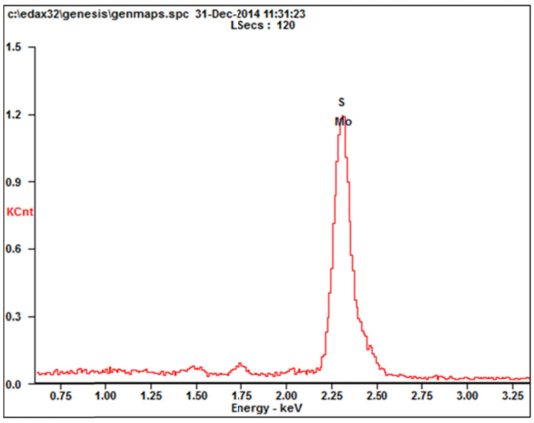


Figure S2. SEM images of 17 and 60-nm-thick MoS_2 membrane.



Element	Wt%	At%
MoL	59.96	33.35
SK	40.04	66.65
Matrix	Correction	ZAF

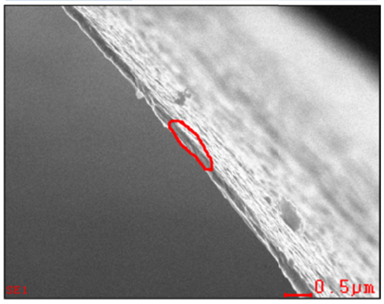


Figure S3. Energy dispersive X-ray spectroscopy (EDS) of MoS_2 nanosheets membrane. The chemical composition of the obtained nanosheets membrane was studied by energy dispersive X-ray spectroscopy (EDS). EDS analysis indicates that the as-prepared nanosheets membrane is comprised of stoichiometric MoS_2 and have no other residues.

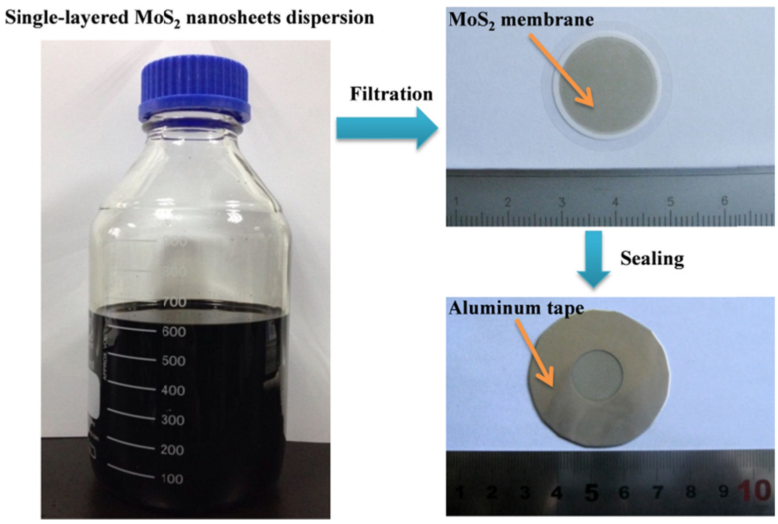


Figure S4. Fabrication process of gas separation membrane module based on MoS_2 nanosheets membrane.

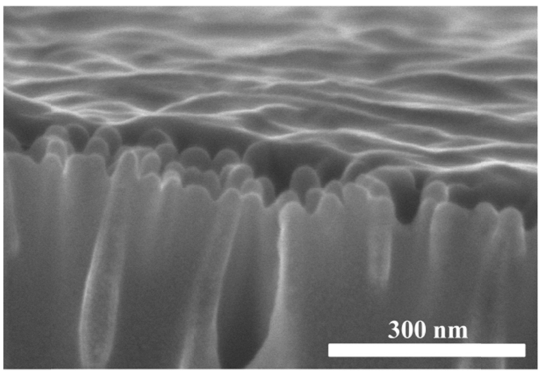


Figure S5. SEM image of top surface of 35-nm-thick MoS_2 membrane. From the SEM image, it is clearly seen that there are pits and bumps on the surface of MoS_2 nanosheets membrane. Those accidented structures are similar to those of graphene oxide membranes, called as island-like defects.[3]

Table S1. Gas permeance data of 60-nm-thick membrane single-layered MoS_2 nanosheets membranes at different transmembrane pressure.

Transmembrane pressure	He	H_2	CO_2	O_2	N_2	CH_4	H_2/CO_2
0.02MPa	1768	2446	560	678	780	884	4.4
0.04MPa	1114	1686	416	451	507	690	4.1
0.06MPa	1114	1768	448	460	519	728	4.0
0.08MPa	1152	1801	486	483	533	766	3.7

References

[1] X. R. Qin, D. Yang, R. F. Frindt, J. C. Irwin, *Ultramicroscopy* **1992**, *42-44*, 630.

[2] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, D. Baillargeat, *Adv. Funct. Mater*. **2012**, *22*, 1385.

[3] H. W. Kim, H. W. Yoon, S.-M. Yoon, B. M. Yoo, B. K. Ahn, Y. H. Cho, H. J. Shin, H. Yang, U. Paik, S. Kwon, J.-Y. Choi, H. B. Park, *Science* **2013**, *342*, 91.