

Supplementary Information

Monolayer Vermiculite Membranes for Efficient Hydrogen Isotope Separation

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Experimental Section

1. Sample Preparation

1.1 Preparation of monolayer vermiculite dispersion by ion exchange method¹

Vermiculite particles (3-10 mm diameter) were dispersed in deionized water (500 mL) and refluxed at 80°C for 1 hour. After vacuum filtration, 5 g of the resulting particles were added to a saturated sodium chloride (NaCl) solution and refluxed at 120°C for 48 hours. The product was collected via vacuum filtration, washed thrice with deionized water and ethanol, yielding sodium ion-exchanged mica (Na-Mica). Subsequently, Na-Mica was added to a 2 M lithium chloride (LiCl) aqueous solution and refluxed at 120°C for 24 hours. Following repeated washing with deionized water and ethanol, the absence of chloride ions (Cl⁻) in the filtrate was confirmed using silver nitrate (AgNO₃) solution (no AgCl precipitation observed), indicating the successful synthesis of lithium ion-exchanged mica (Li-Mica). Finally, Li-Mica was dispersed in deionized water under magnetic stirring and subjected to ultrasonic treatment for 30 minutes using a cell crusher. Centrifugation at 8000 rpm for 10 minutes removed non-exfoliated or multi-layered mica nanosheets, resulting in a light yellow dispersion of Li-Mica nanosheets.

1.2 Preparation of monolayer muscovite dispersion by ion exchange method²

Exfoliation of muscovite was achieved using cetyltrimethylammonium bromide (CTAB) following a multi-step process. First, 10 g of ground muscovite powder underwent thermal treatment at 800°C for one hour. Subsequently, 3 g of the heat-treated muscovite was added to a 5.0 M nitric acid solution and refluxed at 95°C for 5 hours. The resulting mixture was vacuum filtered and washed repeatedly with deionized water and ethanol until a neutral pH was attained, as determined by pH test paper. The acid-treated muscovite powder was then dispersed in a saturated NaCl aqueous solution, vacuum filtered, and washed thrice with deionized water and ethanol to obtain sodium ion-exchanged muscovite. For CTAB intercalation, 1.5 g of sodium ion-exchanged muscovite and 4.6 g of CTAB were dispersed in 150 mL of deionized water and stirred at 80°C for 24 hours. The mixture was filtered and washed multiple times with hot (80°C) deionized water to eliminate excess CTAB surfactant. The CTAB-intercalated muscovite was subsequently added to a 2 M lithium chloride (LiCl) aqueous solution and refluxed at 120°C for 24 hours. This mixture was repeatedly washed with deionized water and ethanol until the filtrate was free of chloride ions, as confirmed by testing with silver nitrate solution, yielding lithium ion-exchanged muscovite. Finally, the lithium ion-exchanged muscovite was dispersed in water under magnetic stirring and subjected to cell disruption ultrasonication for 30 minutes. Centrifugation at 8000 rpm for 10 minutes removed any unexfoliated or multi-layered muscovite nanosheets, resulting in a milky white nanosheet

dispersion.

1.3 Preparation of monolayer h-BN dispersion by thermal expansion method³

Commercially obtained h-BN powder with a particle size of 1-2 μm was subjected to a thermal treatment process. The powder was heated to 1263 K at a rate of 4 K min^{-1} in an air atmosphere. Upon reaching the target temperature, the sample was rapidly quenched in liquid nitrogen. To facilitate exfoliation, the heat-treated powder was dispersed in hot water and subsequently dried in an oven at 473 K for 4 hours. The dried powder underwent ultrasonication for 30 minutes using a cell crusher, followed by centrifugation at 8000 rpm for 10 minutes. This step aimed to separate exfoliated h-BN nanosheets from unexfoliated or multi-layered particles, resulting in a milky white h-BN nanosheet dispersion.

2. Structural design and preparation of single-layer vermiculite membrane device⁴

A 20 mL suspension of monolayer vermiculite flakes was introduced into a 100 mL beaker. A 20 mL aliquot of hexane was gently layered atop the aqueous phase, establishing a distinct organic-aqueous interface. Subsequently, ethanol with different volume fractions (5%, 15%, 25%, and 35%) was rapidly injected into the aqueous phase, acting as a nonsolvent. To minimize interfacial disturbance arising from hexane evaporation, the beaker was sealed with a lid. This injection initiated the assembly process, driving the vermiculite flakes to accumulate at the hexane-water interface. Over a period of approximately 12 hours, the gradual evaporation of hexane facilitated the formation of a continuous, floating film of monolayer vermiculite on the aqueous surface. For further characterization, the film was carefully transferred to a 1 cm^2 polyimide track-etched membrane (PITEM) substrate.⁵

A composite membrane was fabricated for hydrogen isotope separation. This membrane comprised a porous polyimide track-etched membrane (PITEM, it4ipS.A.) substrate coated with a single layer of vermiculite flakes. The PITEM, with its uniform pore diameter, provided mechanical support for the vermiculite layer and facilitated ion transport. The PITEM's chemical stability and adhesion properties further enhanced the composite structure. However, due to the PITEM's non-proton-conducting nature, a large-area vermiculite membrane was separately prepared via a modified Langmuir-Blodgett (L-B) method using Nafion 117 (DuPont, USA) as the substrate. This vermiculite membrane was then incorporated into an electrochemical pump coupled with a mass spectrometer to evaluate its hydrogen/deuterium separation performance.

A composite membrane electrode assembly was fabricated using a Nafion 117 membrane as the substrate. A single layer of vermiculite membrane was deposited onto the Nafion substrate, followed by platinum sputtering on the vermiculite surface for 30 seconds using a 108AUTO ion

sputtering instrument. This platinum layer serves both as a catalyst for the hydrogen oxidation reaction and to enhance membrane conductivity. Subsequently, the vermiculite membrane was sandwiched between two carbon cloth layers, each loaded with a platinum catalyst, using a Nafion solution as both an adhesive and binder. This assembly was hot-pressed at 120°C and 0.5 MPa to ensure good contact and adhesion. The resulting device was then affixed to the center of a circular copper sheet (3 cm diameter) with a central hole (approximately 1 mm diameter) for gas permeation. The copper sheet acts as both a current collector and structural support. After air-drying the adhesive for 24 hours, a conductive silver paste was applied to establish an electrical connection between the carbon cloth and the copper sheet. Finally, the conductive paste was allowed to dry for 24 hours, completing the fabrication of the vermiculite membrane device.

3. Hydrogen Isotope Separation test

A Chenhua CHI 760E electrochemical workstation was employed to control the experimental conditions and drive the electrochemical hydrogen-deuterium (H/D) separation process. Separation efficacy was evaluated using a Leybold Phoenix Quadro helium leak detector equipped with a mass spectrometer. The vermiculite membrane device was secured within the leak detector's sealed chamber, situated between two flanges. Electrical connections were established between the device's electrodes and the electrochemical workstation, enabling the application of a controlled voltage. A pre-mixed 1:1 H/D gas mixture, regulated by a Horiba Stec S4832 mass flow meter, filled the chamber above the membrane. At the anode, the H/D mixture underwent oxidation, producing protons and deuterium nuclei. Driven by the applied voltage, these species permeated the vermiculite layer and reached a secondary carbon cloth layer acting as the cathode. Here, reduction occurred, yielding hydrogen and deuterium gas, which subsequently passed through perforations in a copper sheet into a lower chamber for analysis by the mass spectrometer.⁶

4. Characterization

The material's crystal structure was analyzed via X-ray diffraction (XRD) using a Rigaku SmartLab diffractometer (Rigaku, Japan) with CuK α radiation ($\lambda = 0.15406$ nm). Surface and cross-sectional morphologies of the nanosheets and films, respectively, were imaged using a Regulus8100 scanning electron microscope (SEM, Hitachi) equipped with an SU8010 energy-dispersive X-ray spectroscopy (EDS) detector (Hitachi). Further morphological analysis was conducted using a JEM-F200 transmission electron microscope (TEM, JEOL, Japan). The thickness and morphological characteristics of the two-dimensional vermiculite flakes were determined using a DimensionIcon atomic force microscope (AFM, Bruker, USA).

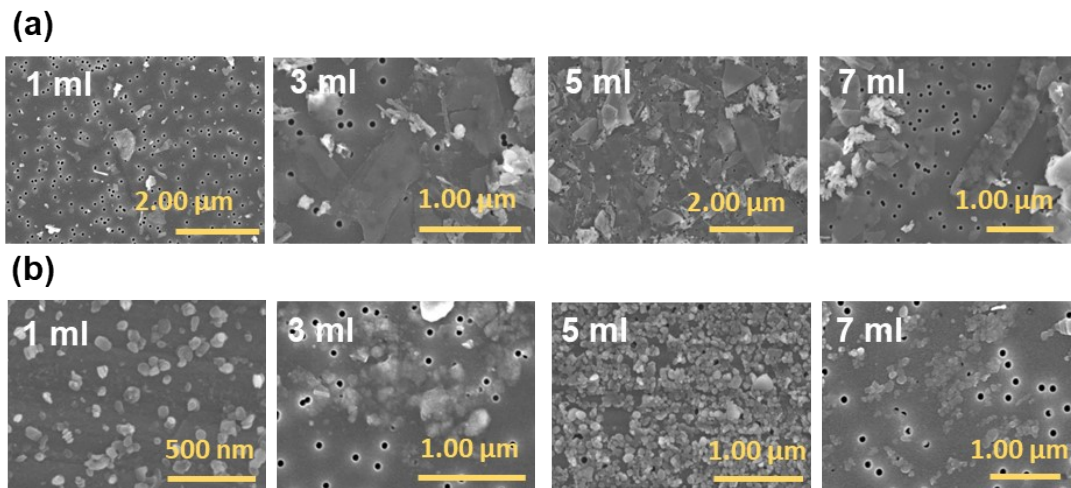


Figure S1. (a, b) SEM images of monolayer muscovite and h-BN membrane, all samples were prepared using the same method, with the variable being ethanol content. The ethanol content from was 1, 3, 5, and 7 mL, respectively.

Content/%	K	Na	Li	Mg	Fe	Al	Si
Vermiculite	4.88	2.78	0.14	22.60	4.83	10.75	54.02
Na-Vermiculite	2.65	6.14	0.27	23.91	4.70	9.58	52.76
Li-Vermiculite	3.35	2.87	4.32	24.05	4.71	10.26	50.44

Table S1. Changes in element content of vermiculite during ion exchange

The two-step ion exchange method, utilizing Na⁺ and Li⁺, effectively expands the interlayer spacing of vermiculite, facilitating the exfoliation of individual vermiculite sheets. The efficacy of ion exchange was confirmed through elemental analysis using inductively coupled plasma atomic emission spectrometry (ICP-OES). As detailed in Table S1, the original interlayer cation (K⁺) significantly decreased with the progression of ion exchange, while the concentrations of the exchanged ions (Na⁺ and Li⁺) increased accordingly.

I (A cm ⁻²)	flow rates of H ₂ (mbar·l/s)			flow rates of D ₂ (mbar·l/s)			flow rates of HD(mbar·l/s)			Separation
	environment	permeate	[H ₂]	environment	permeate	[D ₂]	environment	permeate	[HD]	Ratio
0.006	2.96E-04	5.68E-04	2.72E-04	4.78E-05	5.73E-05	9.50E-06	5.01E-05	9.81E-05	4.80E-05	8.84
	4.25E-05	4.62E-05	3.70E-06	2.48E-05	2.48E-05	0.00E+00	4.02E-06	4.90E-06	8.80E-07	9.41
	2.30E-05	2.83E-05	5.30E-06	0.00E+00	5.05E-07	5.05E-07	0.00E+00	4.46E-07	4.46E-07	7.59
0.008	2.96E-04	6.73E-04	3.77E-04	7.03E-05	8.10E-05	1.07E-05	4.81E-05	1.17E-04	6.89E-05	9.11
	5.87E-05	8.45E-04	7.86E-04	5.43E-06	5.83E-05	5.29E-05	7.77E-06	1.48E-04	1.40E-04	6.96
	5.12E-05	5.80E-05	6.80E-06	2.13E-05	2.13E-05	0.00E+00	6.03E-06	8.32E-06	2.29E-06	6.94
0.010	1.46E-04	6.30E-04	4.84E-04	1.27E-04	1.32E-04	5.00E-06	8.66E-06	1.07E-04	9.83E-05	9.84
	6.38E-05	5.87E-04	5.23E-04	1.85E-05	5.40E-05	3.55E-05	6.42E-06	1.06E-04	9.96E-05	6.72
	1.25E-05	1.49E-05	2.40E-06	7.26E-07	1.01E-06	2.84E-07	0.00E+00	7.90E-08	7.90E-08	7.54
0.012	2.59E-04	1.00E-03	7.41E-04	3.26E-05	8.30E-05	5.04E-05	4.56E-05	1.84E-04	1.38E-04	6.77
	2.78E-05	3.10E-05	3.20E-06	2.50E-06	2.91E-06	4.10E-07	0.00E+00	2.30E-08	2.30E-08	7.62
	1.49E-05	1.71E-05	2.20E-06	1.58E-06	1.82E-06	2.40E-07	1.42E-08	8.70E-08	7.28E-08	8.09
0.014	3.42E-04	1.11E-03	7.68E-04	3.26E-05	8.26E-05	5.00E-05	6.01E-05	2.12E-04	1.52E-04	6.70
	3.50E-05	5.50E-05	2.00E-05	0.00E+00	2.65E-06	2.65E-06	4.50E-09	4.50E-09	2.27E-05	7.54
	1.32E-04	7.17E-04	5.85E-04	6.67E-05	1.04E-04	3.73E-05	6.42E-06	1.15E-04	1.09E-04	6.98

Table S2. Changes in gas flow rates of H₂, HD, and D₂ in the mass spectrometer before and after the reaction

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