Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2016

High performance MoS₂ membranes: effect of thermally driven phase transition on CO₂ separation efficiency.

A. Achari, Sahana S. and M. Eswaramoorthy*

Nanomaterials and Catalysis Lab, Chemistry and Physics of Materials Unit, JNCASR, Jakkur P.O, Bangalore 560064, India.

*Correspondence to: E-Mail- eswar@jncasr.ac.in

Supporting Information:

Materials and Methods Scheme S1-S2

Figures S1-S8

References (1-9)

Experimental Methods.

1. Materials and characterization techniques:

Bulk MoS_2 (< 2micron size, Sigma Aldrich), n-Butyl lithium (2.5M in hexane, Avra chemicals), Sodium Do-decylsulphate (Merck) were used without any further purification.

Rigaku diffractometer (Cu K α radiation, λ =1.54 Å) and Bruker-D8 diffractometer, (Cu K α radiation, λ =1.54 Å, step size: 0.02, current: 30 mA and voltage: 40 kV) were used to record Powder x-ray diffraction (PXRD) patterns. Field-emission scanning electron microscopy (FESEM) images were obtained by using FEI (Nova-Nano SEM-600 Netherlands) equipment. TEM measurements were performed on a TEM JEOL acceleration voltage (dc voltage) of 300 kV. Samples were prepared by placing a drop of dispersion on a TEM grid (copper grid). Electronic absorption spectra were recorded on a Perkin Elmer Lambda 750 UV-Vis-NIR Spectrometer. 1 mm path length cuvette was used for recording the spectra. XPS analysis was done in Omicron EA 125 X-ray photoelectron spectrometer with Al K $_{\alpha}$ radiation of 1486.6 eV. Raman spectra were recorded at different locations of the sample using Jobin Yvon LabRam HR spectrometer with 632 nm Ar laser.

2. Exfoliation of bulk MoS₂:

Aqueous dispersion of 1T MoS_2 was prepared by previously reported lithium intercalation method¹. Namely, 300 mg of bulk MoS_2 was dissolved in 5 mL of dry hexane, to which 2.5 M n-butyl lithium (2 mL) was added under inert atmosphere. The reaction was refluxed at 80 °C for 72 hours. Obtained product (Li_xMoS_2) was purified by washing with n-hexane several times to remove excess organic lithium and unreacted MoS_2 . The powder was dried in an oven at 60°C and dispersed in water (1mg/1mL) by sonication for 1 h. The dispersion was centrifuged repeatedly to remove LiOH and other impurities.

For membrane preparation, diluted solution of MoS_2 dispersion was vacuum filtered on AAO disc of pore size (100nm) as depicted in the following scheme.



Scheme S1: Schematic of preparation of lithium intercalated MoS₂ dispersion and vacuum filtration.

3. Gas permeation experiments:

Gas permeation measurements were carried out in a custom made permeation cell as shown in figure S1. Accurate gas flow was maintained through mass flow controllers (MKS and Hitachi). All the gases used were of high purity. Gas flow on the feed stream were kept constant at 100 sccm for individual gases and 50 sccm each for mixed gas (H_2/CO_2) permeation. On the other hand, N_2 was used as sweep gas and the flow was kept constant at 20 sccm. The pressure at both feed and permeate side of the membrane was kept constant at 1 atm.² The concentration of the gases in the permeate stream was analyzed through online gas chromatographs (Agilent 7690 A).

The permeation values were calculated according to the following equation^{3, 4}:

$$P_A = \frac{x_{PA}ft}{x_{PN2}.A.(p_F x_{FA} - p_P x_{PA})}$$

Where P_A = Permeability of gas A. $x_{FA}x_{PA}$ = Mole fraction of gas A in feed and permeate stream, x_{PN2} = mole fraction of sweep gas in the permeate stream, $p_{F}p_P$ = pressure in the feed side and permeate side respectively, A = area of the membrane, t = thickness of the membrane, f = flow rate of the sweep gas.

Separating factor was calculated according to following equation: $\alpha = \frac{P_A}{P_B}$

It was assumed that mole fraction of feed gas A in the feed side, $x_{FA}=1$. In the presence of back permeation, as the total flux of permeating gas (N₂) is very less and the flow rate of feed gas is very high (100 ml/min compared to 20 ml/min flow of sweep gas), the concentration of sweep gas in the feed stream (x_{FN2}) is very less (in the order of 10⁻²-10⁻³), and $x_{FA} \sim 1$.





Figure S1. (a, b)-Images of the permeation cell, c- Schematic diagram of the permeation cell with membrane.

Scheme S2. Schematic of the gas permeation setup. MFC- Mass flow controller, P- permeation cell, GC-Gas Chromatograph.



Figure S2. Zeta potential graph of 1T MoS₂ dispersion. Zeta potential value of -30mV to -40mV is observed, indicating its high stability. The electrostatic repulsion between the sheets is due to the negative charge on the Sulphur atom of MoS_2^5 helps in dispersion of the sheets in aqueous medium.



Figure S3. a) FESEM image of top view of MoS_2 membrane. The membrane formed is visibly uniform and completely covered, without pinholes. b) Cross-sectional FESEM image of the MoS_2 membrane. TEM images (c, d) clearly indicate well exfoliated single or few layers.



Figure S4. Raman spectra of as prepared MoS₂ membrane and the membrane heated to 160 °C. The heated membrane exhibits, a reduction in intensity of $J_1 J_2 J_3$ peaks, typical of 1T-MoS₂ and increase of E^{1}_{2g} and A_{1g} peak intensities(characteristic of 2H), confirms the restoration of 2H-phase.⁶





1.6

a

Figure S5. a) Extinction spectra of 1T MoS_2 . For comparison, 2H- MoS_2 dispersion is also prepared using well established surfactant intercalation method7. Typically, 110mg of bulk MoS2 was mixed with 100mg of SDS and sonicated in 10mL of water for 8hours. The resultant solution was centrifuged at 14000rpm to remove flakes of MoS₂ to obtain a stable dispersion. Unlike lithium intercalation, there is no charge transfer between the surfactant and MoS₂. Employing surfactants for exfoliation results in 2H-MoS₂ dispersion, where electrostatic repulsion between the sheets and surfactant charge are responsible for stability. 2H-MoS₂ shows characteristic doublet peaks at 609 nm and 670 nm due to B1 and A1 excitonic transitions from K-point of brillouin zone with the energy split from spin orbit coupling of valence band.⁸ Convoluted peaks centered between 360 and 450 nm corresponds to D and C excitons from the M point in the brillouin zone. Where as in 1T phase, no such transitions are seen because of the lattice distortion.⁸. Furthermore, UV visible spectroscopy can also be used to determine the presence of mixed phase in lithium exfoliated sample.⁹ Peak at 410nm due to C exciton is a strong contribution for the 2H-phase, therefore occurrence of this transition in the 1T phase can be attributed to the contribution from the 2H-phase.⁹ We observed that, this transition at 410nm in our lithium intercalated dispersion is very less intense, indicating efficient transformation of pristine MoS₂ to 1T phase. b) Photograph of aqueous dispersion of 2H MoS₂ (left) and 1T MoS₂ (right)



Figure S6. XPS spectra of Bulk MoS₂ powder (left) and lithiated MoS₂ powder(right). Whereas bulk MoS2 shows pure 2H phase, lithiated MoS2 shows a mixture of 1T and 2H phase. It has been formerly reported that binding energies of 3d states of 1T polytype of MoS₂ appears at ~0.8-0.9eV lesser than that of 2H MoS₂⁸. The Mo 3d spectra of bulk 2H phase consists of spin orbit doublet Peaks at 228.90 and 232.53eV corresponding to Mo⁴⁺ 3d_{5/2} and Mo⁴⁺ 3d_{3/2}, while in 1T counterparts, these peaks are shifted to lower binding energies, appearing at 228.17 and 231.61eV respectively. This is because of the increased electron density on the Mo atoms after intercalation. The peak at 225.27eV is due to 2s region of Sulphur. The percentage of 1T phase (blue curve) in lithiated sample, is found to be around 60%. A small peak at 236 eV is attributed to Mo⁶⁺ 3d_{5/2} state, caused due to oxidation when exposed to air.



Figure S7. FESEM images of the as prepared (left) and heated membrane (right) at 160 °C. whereas the as prepared membrane shows tightly packed MoS_2 bundles, after heating we observe formation of irregularities in the membrane cross section. It is to be noted that the thickness of the membrane does not change significantly, confirming our hypothesis of increased inter bundler spaces after phase transformation from 1T to 2H phase.



Figure S8. Permeability data for membrane of thickness 650nm with respect to kinetic diameter of various gases.

References

- 1. A. Ambrosi, Z. Sofer and M. Pumera, *Small*, 2015, **11**, 605-612.
- H. Li, Z. Song, X. Zhang, Y. Huang, S. Li, Y. Mao, H. J. Ploehn, Y. Bao and M. Yu, *Science*, 2013, 342, 95-98.
- H. Czichos, T. Saito and L. R. Smith, Springer handbook of materials measurement methods, Springer Science & Business Media, 2006.
- 4. H. Lin, E. Van Wagner, B. D. Freeman, L. G. Toy and R. P. Gupta, *Science*, 2006, **311**, 639-642.
- 5. M. Acerce, D. Voiry and M. Chhowalla, *Nat. Nanotechnol.*, 2015, **10**, 313-318.
- 6. S. Jiménez Sandoval, D. Yang, R. F. Frindt and J. C. Irwin, *Phys. Rev. B*, 1991, 44, 3955-3962.
- 7. A. Gupta, V. Arunachalam and S. Vasudevan, J. Phys. Chem. Lett., 2015, 6, 739-744.
- 8. G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen and M. Chhowalla, *Nano Lett.*, 2011, **11**, 5111-5116.

K. C. Knirsch, N. C. Berner, H. C. Nerl, C. S. Cucinotta, Z. Gholamvand, N. McEvoy, Z. Wang,
I. Abramovic, P. Vecera, M. Halik, S. Sanvito, G. S. Duesberg, V. Nicolosi, F. Hauke, A. Hirsch,
J. N. Coleman and C. Backes, *ACS Nano*, 2015, 9, 6018-6030.