

## Supplementary Information

### **Bimetallic PdPt alloy nanoparticles decorated track-etched polyethylene terephthalate membrane for efficient H<sub>2</sub> separation**

Nishel Saini<sup>1</sup>, Sonalika Agarwal<sup>1,2\*</sup>, Kamendra Awasthi<sup>1\*\*</sup>

<sup>1</sup>*Department of Physics, Malaviya National Institute of Technology Jaipur, Rajasthan 302017,*

*INDIA*

<sup>2</sup>*Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1*

*Kagamiyama, Higashi-Hiroshima, 739-8527, Japan*

[\\*sonalika.spsl@gmail.com](mailto:sonalika.spsl@gmail.com) [\\*\\*kawasthi.phy@mnit.ac.in](mailto:kawasthi.phy@mnit.ac.in)

**Table S1.** Raman peaks of PET membranes and their corresponding bond assignments.

Peaks (cm <sup>-1</sup> )	Corresponding bonds
277	C-C stretching (aromatic), CCC bending (aromatic)
628	CCC in-plane bending
796	CH out of plane bending (aromatic)
854	C-C stretching (ring breathing), C-O stretching
1093	C-O-C anti-symmetric stretching vibration
1112	CH in-plane bending (aromatic), C-O stretching
1181	CH in-plane bending (aromatic)
1290	C-C stretching (aromatic), C-O stretching
1414	C-C stretching (aromatic)
1459	CH deformation
1612	C=C stretching (aromatic)
1727	C=O stretching
2965	Methylene groups adjacent to O- atom
3081	Aromatic C-H bonds

**Table S2.** Table representing the data from the previously reported literature used for the comparison in Robeson upper bound plot.

Membrane material	Nature of membrane	H <sub>2</sub> gas permeability	H <sub>2</sub> /CO <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	Ref.
<b>Conventional polymer</b>					
PDMS/Matrimid-5218	Surface coating	7149038	2.53	-	[1]
Silica NPs/polysulfone	MMM	32.3	1.64	28.8	[2]
PBI	Self-supported	26000	27	-	[3]
LiCl/PVDF	MMM	2.6E6	4.8	3.73	[4]
<b>Conjugate polymer</b>					
PANI/PBI	MMM	3.79	3.6	306	[5]
PANI/PBI	MMM	5.5	15.41	340	[6]
<b>Polymer blending</b>					
Polysiloxane/PVA	MMM	8400	1/118	-	[7]
PSF/PC	MMM	25.11	1.17	-	[8]
COOH functionalized polyimide/PIM-1	MMM	1245	-	128.9	[9]
PEBAX/PVA	MMM	2.63	1/7.6	-	[10]
<b>Functionalized polymer membranes</b>					
Titanium implanted PC	Surface coated	3413	4.72	-	[11]
COOH functionalized PET	Track etched	56029	2.36	-	[12]
Amine functionalized PET	Track etched	222000	4.28	4.27	[12]
UV functionalized PC	Track etched	49000	3.92	3.43	[13]
<b>Polymer crosslinking</b>					
6-FDA durene with BuDA	Self-supported	359	2.9	48.2	[14]
Matrimid with BuDA	Self-supported	245	23	273	[14]
6-FDA durene with EDA vapors	Self-supported	32.6	120	-	[15]
PEO-600 and PEO-526	Self-supported	26.3	1/6.84	8.4	[16]
PBI with TCL	Self-supported	39	22	-	[17]
P84 with BuDA	Self-	47	14	-	[18]

	supported				
<b>Metal/polymer</b>					
PdPt alloy PC	MMM	16.2	1.4	-	[19]
SiO <sub>2</sub> /PC	MMM	39.46	1.52	-	[19]
LaNi <sub>5</sub> /Polyethylene	MMM	1320	132	66	[20]
<b>CNT/polymer</b>					
MWCNT/PEBAX-1657	MMM	40.96	1/6.40	9.14	[21]
PVA-CNT/Polysiloxane	MMM	19.44	43		[22]
Pd NPs-CNT/PC	MMM	4758	7.96	4.19	[23]
<b>Graphene/polymer</b>					
GO/PDMS	MMM	313.6	1/11.7	-	[24]
GO/Polyster	Surface coating	79.7	35.3	31.5	[25]
Laser induced graphene/polysulfone	Surface coating	1.7E6	30.5	-	[26]
<b>Zeolite/polymer</b>					
pNA zeolite 4A/PC	MMM	10.8	2.34	76.6	[27]
Zeolite A/PDMS	MMM	9516	3.23	-	[28]
<b>MOF/polymer</b>					
Cu-BPY-HFS/matrimid	MMM	26.74	1.77	54.78	[29]
ZIF8/PBI	MMM	470.5	26.3	-	[30]
ZIF8/6FDA-durene	MMM	500	29	341	[31]
ZIF8/polyimide	MMM	2585	1.78	21.72	[32]
ZIF8/PD/polyimide	MMM	1858	1.75	25.45	[32]
ZIF67/PIM	MMM	4532	1/1.35	11.5	[33]
<b>PIM based</b>					
PIM-7	Self-supported	860	1/1.27	20.47	[34]
Silica NPs/PIM-1	MMM	5060	1/1.99	5.75	[35]
ZIF8/PIM-1	MMM	6680	1.06	19.1	[36]
PIM-1	Self-supported	5240	0.51	9.5	[37]
TPIM-1	Self-supported	2666	1.72	50	[38]
TPIM-2	Self-supported	655	1.51	37	[38]
<b>Thermally rearranged polymer</b>					
ZIF-8/Poly(benzoxazole-co-imide)	MMM	1206	1.273	21.3	[39]

\*here, some abbreviations are used in the above table- PDMS, poly(dimethyl siloxane); PBI, polybenzimidazole; LiCl, lithium chloride; PVDF, polyvinylidene fluoride; PANI, polyaniline; PVA, polyvinyl alcohol; PSF, polysulfone; BuDA, 1,4- butanediamine; EDA, ethylenediamine; TCL, terephthaloyl chloride;

pNA, para-nitroaniline; Cu-BPY-HFS, Cu-4,4'-bipyridine-hexafluorosilicate; PD, polydopamine TPIM, triptycene ladder polymers.

## References

- [1] S. Shishatskiy, C. Nistor, M. Popa, S. P. Nunes, and K. V. Peinemann, "Polyimide Asymmetric Membranes for Hydrogen Separation: Influence of Formation Conditions on Gas Transport Properties," *Adv. Eng. Mater.*, vol. 8, no. 5, pp. 390–397, May 2006, doi: 10.1002/ADEM.200600024.
- [2] J. Ahn, W.-J. Chung, I. Pinnau, and M. D. Guiver, "Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation," *J. Memb. Sci.*, vol. 314, no. 1–2, pp. 123–133, Apr. 2008, doi: 10.1016/J.MEMSCI.2008.01.031.
- [3] S. C. Kumbharkar, Y. Liu, and K. Li, "High performance polybenzimidazole based asymmetric hollow fibre membranes for H<sub>2</sub>/CO<sub>2</sub> separation," *J. Memb. Sci.*, vol. 375, no. 1–2, pp. 231–240, Jun. 2011, doi: 10.1016/J.MEMSCI.2011.03.049.
- [4] P. Pal, S. P. Chaurasia, S. Upadhyaya, R. Kumar, and S. Sridhar, "Development of hydrogen selective microporous PVDF membrane," *Int. J. Hydrogen Energy*, vol. 45, no. 34, pp. 16965–16975, Jul. 2020, doi: 10.1016/J.IJHYDENE.2019.08.112.
- [5] V. Giel, J. Kredatusová, M. Trchová, J. Brus, J. Žitka, and J. Peter, "Polyaniline/polybenzimidazole blends: Characterisation of its physico-chemical properties and gas separation behaviour," *Eur. Polym. J.*, vol. 77, pp. 98–113, Apr. 2016, doi: 10.1016/j.eurpolymj.2016.02.008.
- [6] V. Giel, Z. Morávková, J. Peter, and M. Trchová, "Thermally treated polyaniline/polybenzimidazole blend membranes: Structural changes and gas transport properties," *J. Memb. Sci.*, vol. 537, no. March, pp. 315–322, Sep. 2017, doi: 10.1016/j.memsci.2017.04.062.
- [7] W. Salim, V. Vakharia, K. K. Chen, M. Gasda, and W. S. W. Ho, "Oxidatively stable borate-containing membranes for H<sub>2</sub> purification for fuel cells," *J. Memb. Sci.*, vol. 562, pp. 9–17, Sep. 2018, doi: 10.1016/j.memsci.2018.05.020.
- [8] N. K. Acharya, V. Kulshrestha, K. Awasthi, A. K. Jain, M. Singh, and Y. K. Vijay, "Hydrogen separation in doped and blend polymer membranes," *Int. J. Hydrogen Energy*, vol. 33, no. 1, pp. 327–331, Jan. 2008, doi: 10.1016/j.ijhydene.2007.07.030.
- [9] M. Huang *et al.*, "In-situ generation of polymer molecular sieves in polymer membranes for highly selective gas separation," *J. Memb. Sci.*, vol. 630, p. 119302, Jul. 2021, doi: 10.1016/j.memsci.2021.119302.
- [10] K. C. Wong, P. S. Goh, and A. F. Ismail, "Enhancing hydrogen gas separation performance of thin film composite membrane through facilely blended polyvinyl alcohol and PEBAX," *Int. J. Hydrogen Energy*, vol. 46, no. 37, pp. 19737–19748, May 2020, doi: 10.1016/j.ijhydene.2020.09.079.
- [11] N. K. Acharya *et al.*, "Gas permeation study of Ti-coated, track-etched polymeric membranes,"

- Vacuum*, vol. 81, no. 3, pp. 389–393, Oct. 2006, doi: 10.1016/j.vacuum.2006.03.027.
- [12] Kamakshi, R. Kumar, V. K. Saraswat, M. Kumar, and K. Awasthi, "Palladium nanoparticle binding in functionalized track etched PET membrane for hydrogen gas separation," *Int. J. Hydrogen Energy*, vol. 42, no. 25, pp. 16186–16194, Jun. 2017, doi: 10.1016/j.ijhydene.2017.05.040.
- [13] R. Kumar, Kamakshi, S. Shisodia, M. Kumar, and K. Awasthi, "Effect of UV irradiation on PC membrane and use of Pd nanoparticles with/without PVP for H<sub>2</sub> selectivity enhancement over CO<sub>2</sub> and N<sub>2</sub> gases," *Int. J. Hydrogen Energy*, vol. 43, no. 47, pp. 21690–21698, Nov. 2018, doi: 10.1016/j.ijhydene.2018.06.094.
- [14] L. Shao, L. Liu, S. X. Cheng, Y. D. Huang, and J. Ma, "Comparison of diamino cross-linking in different polyimide solutions and membranes by precipitation observation and gas transport," *J. Memb. Sci.*, vol. 312, no. 1–2, pp. 174–185, Apr. 2008, doi: 10.1016/J.MEMSCI.2007.12.060.
- [15] L. Shao, C. H. Lau, and T. S. Chung, "A novel strategy for surface modification of polyimide membranes by vapor-phase ethylenediamine (EDA) for hydrogen purification," *Int. J. Hydrogen Energy*, vol. 34, no. 20, pp. 8716–8722, Oct. 2009, doi: 10.1016/j.ijhydene.2009.07.115.
- [16] L. Shao, S. Quan, X. Q. Cheng, X. J. Chang, H. G. Sun, and R. G. Wang, "Developing cross-linked poly(ethylene oxide) membrane by the novel reaction system for H<sub>2</sub> purification," *Int. J. Hydrogen Energy*, vol. 38, no. 12, pp. 5122–5132, Apr. 2013, doi: 10.1016/j.ijhydene.2013.02.050.
- [17] L. Zhu, M. T. Swihart, and H. Lin, "Tightening polybenzimidazole (PBI) nanostructure via chemical cross-linking for membrane H<sub>2</sub>/CO<sub>2</sub> separation," *J. Mater. Chem. A*, vol. 5, no. 37, pp. 19914–19923, Sep. 2017, doi: 10.1039/c7ta03874g.
- [18] M. Omidvar, C. M. Stafford, and H. Lin, "Thermally stable cross-linked P84 with superior membrane H<sub>2</sub>/CO<sub>2</sub> separation properties at 100 °C," *J. Memb. Sci.*, vol. 575, pp. 118–125, Apr. 2019, doi: 10.1016/j.memsci.2019.01.003.
- [19] A. K. Patel and N. K. Acharya, "Metal coated and nanofiller doped polycarbonate membrane for hydrogen transport," *Int. J. Hydrogen Energy*, vol. 43, no. 47, pp. 21675–21682, Nov. 2018, doi: 10.1016/j.ijhydene.2018.03.205.
- [20] D. V. Strugova *et al.*, "Novel process for preparation of metal-polymer composite membranes for hydrogen separation," *Int. J. Hydrogen Energy*, vol. 43, no. 27, pp. 12146–12152, Jul. 2018, doi: 10.1016/j.ijhydene.2018.04.183.
- [21] R. S. Murali, S. Sridhar, T. Sankarshana, and Y. V. L. Ravikumar, "Gas Permeation Behavior of Pebax-1657 Nanocomposite Membrane Incorporated with Multiwalled Carbon Nanotubes," *Ind. Eng. Chem. Res.*, vol. 49, no. 14, pp. 6530–6538, Jul. 2010, doi: 10.1021/IE9016495.
- [22] Y. Zhao, B. T. Jung, L. Ansaloni, and W. S. W. Ho, "Multiwalled carbon nanotube mixed matrix membranes containing amines for high pressure CO<sub>2</sub>/H<sub>2</sub> separation," *J. Memb. Sci.*, vol. 459, pp. 233–243, Jun. 2014, doi: 10.1016/j.memsci.2014.02.022.
- [23] R. Kumar, Kamakshi, M. Kumar, and K. Awasthi, "Functionalized Pd-decorated and aligned MWCNTs in polycarbonate as a selective membrane for hydrogen separation," *Int. J. Hydrogen Energy*, vol. 41, no. 48, pp. 23057–23066, Dec. 2016, doi: 10.1016/j.ijhydene.2016.09.008.
- [24] F. U. Nigiz and N. D. Hilmioglu, "Enhanced hydrogen purification by graphene - Poly(Dimethyl siloxane) membrane," *Int. J. Hydrogen Energy*, vol. 45, no. 5, pp. 3549–3557, Jan. 2020, doi:

- 10.1016/j.ijhydene.2018.12.215.
- [25] A. F. M. Ibrahim, F. Banihashemi, and Y. S. Lin, "Graphene oxide membranes with narrow inter-sheet galleries for enhanced hydrogen separation," *Chem. Commun.*, vol. 55, no. 21, pp. 3077–3080, Mar. 2019, doi: 10.1039/c8cc10283j.
- [26] N. K. Mishra, N. Patil, M. Anas, X. Zhao, B. A. Wilhite, and M. J. Green, "Highly selective laser-induced graphene (LIG)/polysulfone composite membrane for hydrogen purification," *Appl. Mater. Today*, vol. 22, p. 100971, Mar. 2021, doi: 10.1016/j.apmt.2021.100971.
- [27] D. Şen, H. Kalipçılar, and L. Yılmaz, "Development of polycarbonate based zeolite 4A filled mixed matrix gas separation membranes," *J. Memb. Sci.*, vol. 303, no. 1–2, pp. 194–203, Oct. 2007, doi: 10.1016/j.memsci.2007.07.010.
- [28] M. Rezakazemi, K. Shahidi, and T. Mohammadi, "Hydrogen separation and purification using crosslinkable PDMS/zeolite A nanoparticles mixed matrix membranes," *Int. J. Hydrogen Energy*, vol. 37, no. 19, pp. 14576–14589, Oct. 2012, doi: 10.1016/j.ijhydene.2012.06.104.
- [29] Y. Zhang, I. H. Musselman, J. P. Ferraris, and K. J. Balkus, "Gas permeability properties of Matrimid® membranes containing the metal-organic framework Cu-BPY-HFS," *J. Memb. Sci.*, vol. 313, no. 1–2, pp. 170–181, Apr. 2008, doi: 10.1016/j.memsci.2008.01.005.
- [30] T. Yang and T. S. Chung, "High performance ZIF-8/PBI nano-composite membranes for high temperature hydrogen separation consisting of carbon monoxide and water vapor," *Int. J. Hydrogen Energy*, vol. 38, no. 1, pp. 229–239, Jan. 2013, doi: 10.1016/j.ijhydene.2012.10.045.
- [31] S. N. Wijenayake *et al.*, "Composite membranes with a highly selective polymer skin for hydrogen separation," *Sep. Purif. Technol.*, vol. 135, no. 1, pp. 190–198, Oct. 2014, doi: 10.1016/j.seppur.2014.08.015.
- [32] Z. Wang, D. Wang, S. Zhang, L. Hu, and J. Jin, "Interfacial Design of Mixed Matrix Membranes for Improved Gas Separation Performance," *Adv. Mater.*, vol. 28, no. 17, pp. 3399–3405, May 2016, doi: 10.1002/adma.201504982.
- [33] X. Wu *et al.*, "Nanoporous ZIF-67 embedded polymers of intrinsic microporosity membranes with enhanced gas separation performance," *J. Memb. Sci.*, vol. 548, pp. 309–318, Feb. 2018, doi: 10.1016/j.memsci.2017.11.038.
- [34] B. S. Ghanem, N. B. McKeown, P. M. Budd, and D. Fritsch, "Polymers of intrinsic microporosity derived from bis(phenazyl) monomers," *Macromolecules*, vol. 41, no. 5, pp. 1640–1646, Mar. 2008, doi: 10.1021/ma071846r.
- [35] J. Ahn *et al.*, "Gas transport behavior of mixed-matrix membranes composed of silica nanoparticles in a polymer of intrinsic microporosity (PIM-1)," *J. Memb. Sci.*, vol. 346, no. 2, pp. 280–287, Jan. 2010, doi: 10.1016/j.memsci.2009.09.047.
- [36] A. F. Bushell *et al.*, "Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8," *J. Memb. Sci.*, vol. 427, pp. 48–62, Jan. 2013, doi: 10.1016/j.memsci.2012.09.035.
- [37] C. G. Bezzu *et al.*, "A spirobifluorene-based polymer of intrinsic microporosity with improved performance for gas separation," *Adv. Mater.*, vol. 24, no. 44, pp. 5930–5933, Nov. 2012, doi: 10.1002/adma.201202393.

- [38] B. S. Ghanem, R. Swaidan, X. Ma, E. Litwiller, and I. Pinnau, "Energy-efficient hydrogen separation by AB-type ladder-polymer molecular sieves," *Adv. Mater.*, vol. 26, no. 39, pp. 6696–6700, Oct. 2014, doi: 10.1002/adma.201401328.
- [39] J. S. Kim, S. J. Moon, H. H. Wang, S. Kim, and Y. M. Lee, "Mixed matrix membranes with a thermally rearranged polymer and ZIF-8 for hydrogen separation," *J. Memb. Sci.*, vol. 582, pp. 381–390, Jul. 2019, doi: 10.1016/J.MEMSCI.2019.04.029.