

Electronic Supplementary Information for

Fabrication of hybrid membranes by incorporating acid-base pairs functionalized hollow mesoporous silica for enhanced proton conductivity

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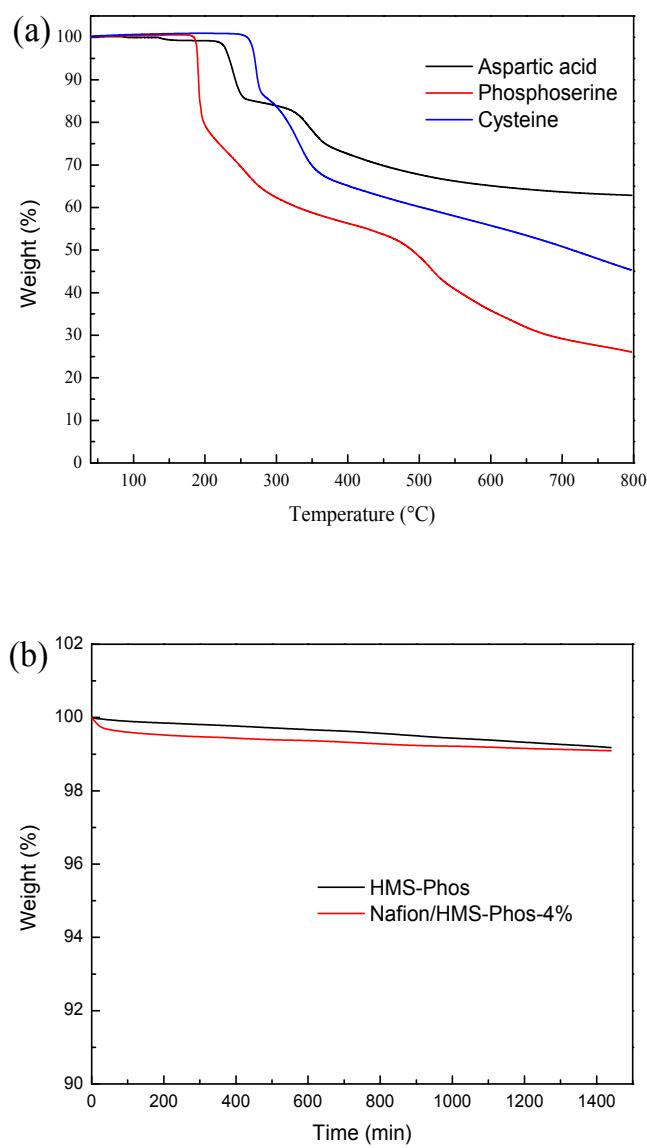


Fig. S1 TGA thermograms of (a) three kinds of amino acids; (b) HMS-Phos particles and Nafion/HMS-Phos-4% hybrid membrane.

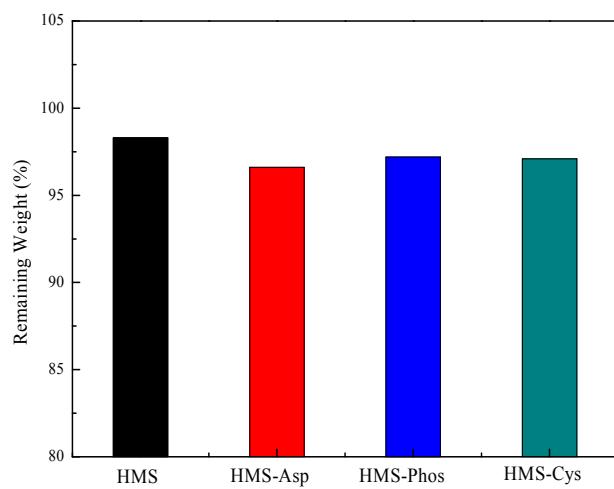


Fig. S2 The chemical stability of HMS and amino acid functionalized HMS under Fenton's test.

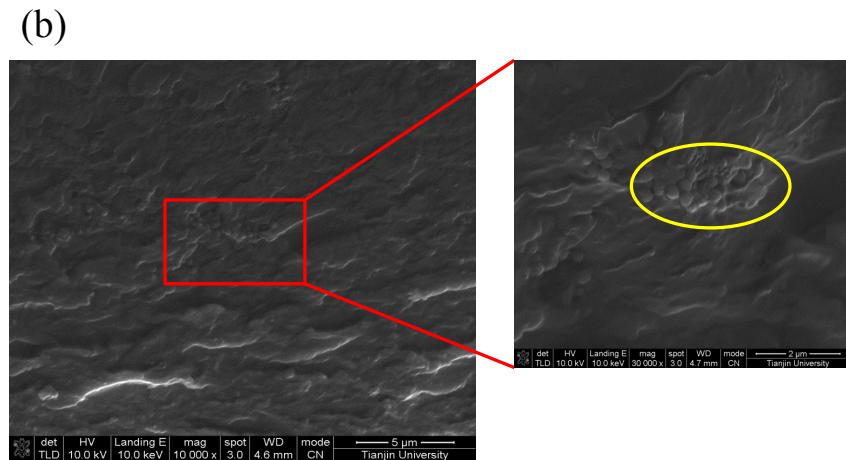
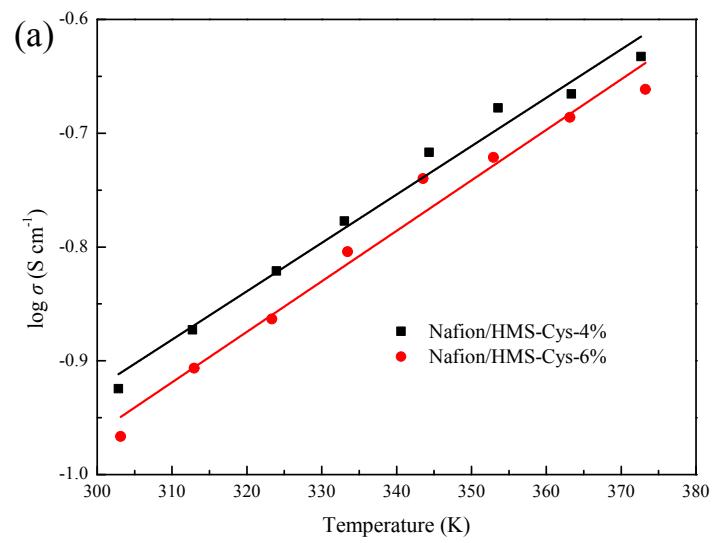


Fig. S3 (a) Proton conductivity of Nafion/HMS-Cys-4% and Nafion/HMS-Cys-6% hybrid membranes; (b) Cross-sectional SEM images of Nafion/HMS-Cys-6% hybrid membrane.

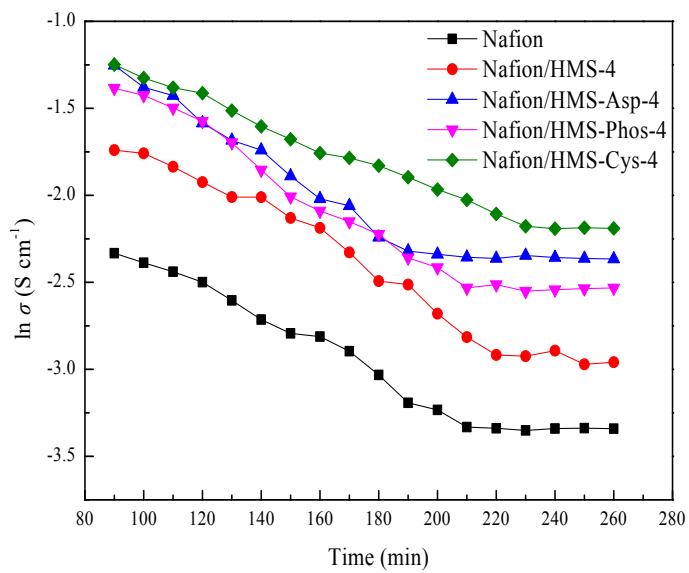


Fig. S4 Proton conductivity of hybrid membranes embedded with 4 wt% of HMS microspheres at 40°C and 20% RH after 90min.

Table S1 Typical proton conductivity of organic-inorganic hybrid membranes in literatures.

Membrane	Temperature (°C)	Relative Humidity (%)	Proton conductivity (S cm ⁻¹)	Reference
PEO/GO	25	100	0.086	S1
Nafion/ TiO ₂ -RSO ₃ H-10	40	100	0.036	S2
SiO ₂ -SO ₃ H/terpolymer/ poly(VDF-co-HFP)	25	100	0.021	S3
Nafion/S-ZrO ₂	80	50	0.04	S4
PVDF/CSPTC/TEOS/ +PEG-c	120	50	0.0206	S5
Nafion/Sulfopropylated Polysilsesquioxane	80	45	0.018	S6
Nafion/Sulfopropylated Polysilsesquioxane	120	45	0.022	S6
PFSA/sPOSS/PAA	120	50	0.107	S7
PFSA-aluminosilica	80	50	0.012	S8
PFSA-aluminosilica	120	50	0.026	S8
Nafion/F-GO	80	40	0.04	S9
Nafion/F-GO	120	40	0.09	S9
Nafion/phytic@MIL	80	40	0.018	S10
Nafion/PNT-5%	80	40	0.016	S11
Nafion/CS-SPION	80	50	0.06	S12
Nafion/S-Ph-PMO	60	40	0.0063	S13
SPES/silica	120	50	0.0018	S14
Nafion/HMS-Cys-4%	30	100	0.119	This work
Nafion/HMS-Cys-4%	80	51	0.027	This work
Nafion/HMS-Cys-4%	120	51	0.082	This work

References in Electronic Supplementary Information:

- [S1] Y. C. Cao, C. Xu, X. Wu, X. Wang, L. Xing and K. Scott, *J. Power Sources*, 2011, **196**, 8377.
- [S2] D. Cozzi, C. de Bonis, A. D'Epifanio, B. Mecheri, A. C. Tavares and S. Licoccia, *J. Power Sources*, 2014, **248**, 1127.
- [S3] O. Sel, A. Soulès, B. Améduri, B. Boutevin, C. Laberty-Robert, G. Gebel and C. Sanchez, *Adv. Funct. Mater.*, 2010, **20**, 1090.
- [S4] Y. Yao, Z. Lin, Y. Li, M. Alcoutlabi, H. Hamouda and X. Zhang, *Adv. Energy Mater.*, 2011, **1**, 1133.
- [S5] V. Maneeratana, J. D. Bass, T. Azaïs, A. Patissier, K. Vallé, M. Maréchal, G. Gebel, C. Laberty-Robert and C. Sanchez, *Adv. Funct. Mater.*, 2013, **23**, 2872.
- [S6] K. Xu, C. Chanthat, M. R. Gadinski, M. A. Hickner and Q. Wang, *ACS Appl. Mater. Interfaces*, 2009, **1**, 2573.
- [S7] J. Choi, R. Wycisk, W. Zhang, P. N. Pintauro, K. M. Lee and P. T. Mather, *ChemSusChem*, 2010, **3**, 1245.
- [S8] G. L. Athens, D. Kim, J. D. Epping, S. Cadars, Y. Ein-Eli and B. F. Chmelka, *J. Am. Chem. Soc.*, 2011, **133**, 16023.
- [S9] H. Zarrin, D. Higgins, Y. Jun, Z. Chen and M. Fowler, *J. Phys. Chem. C*, 2011, **115**, 20774.
- [S10] Z. Li, G. He, B. Zhang, Y. Cao, H. Wu, Z. Jiang and Z. Tiantian, *ACS Appl. Mater. Interfaces*, 2014, **6**, 9799.
- [S11] G. He, J. Zhao, S. Hu, L. Li, Z. Li, Y. Li, Z. Li, H. Wu, X. Yang and Z. Jiang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 15291.
- [S12] E. Dashtimoghadam, J. J. VanDersarl, A. Bertsch, H. Moaddel, K. I. Jacob and P. Renaud, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7099.
- [S13] N. C. Rosero-Navarro, E. M. Domingues, N. Sousa, P. Ferreira and F. M. Figueiredo, *Int. J. Hydrogen Energy*, 2014, **39**, 5338.
- [S14] N. N. Krishnan, D. Henkensmeier, J. H. Jang, H. J. Kim, V. Rebbin, I. H. Oh, S. A. Hong, S. K. Nam and T. H. Lim, *Int. J. Hydrogen Energy*, 2011, **36**, 7152.