Electronic Supporting Information for

A "H_2O donating/methanol accepting" platform for preparation of highly selective Nafion-based proton exchange membranes

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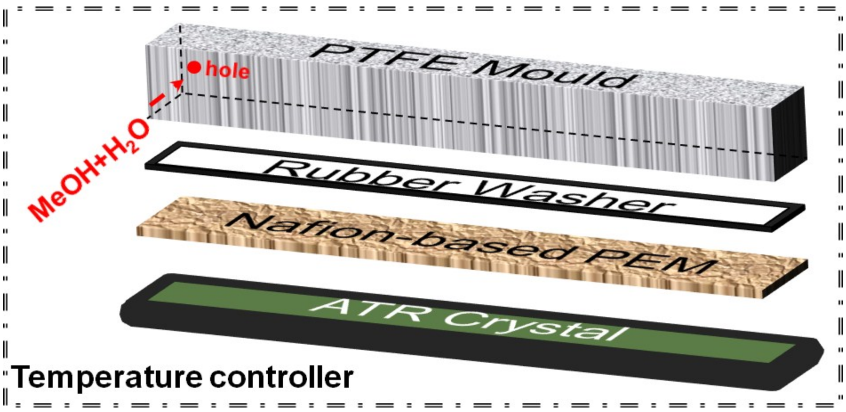

Fig. S1 Schematic illustration of the home-made equipment used to characterize the methanol permeability of PEMs.

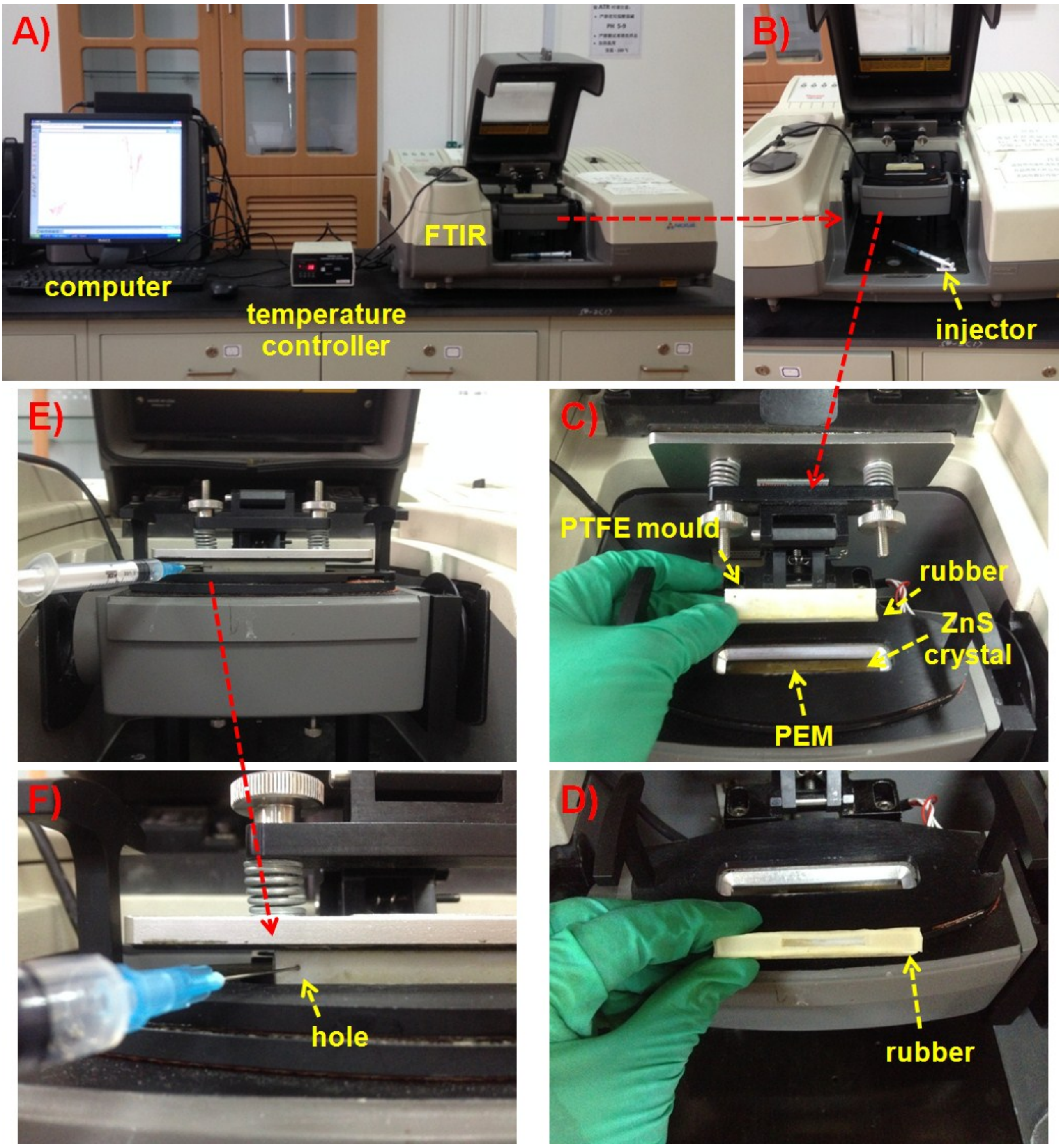

Fig. S2 (A) A digital photo of the whole set used to characterize the methanol permeability of PEMs; (B-D) Magnified observation of some important components, such as the PTFE mould, ZnS crystal and rubber washer, *etc.*; (E-F) Digital photos of the assembly of different components as illustrated in Fig. S1.

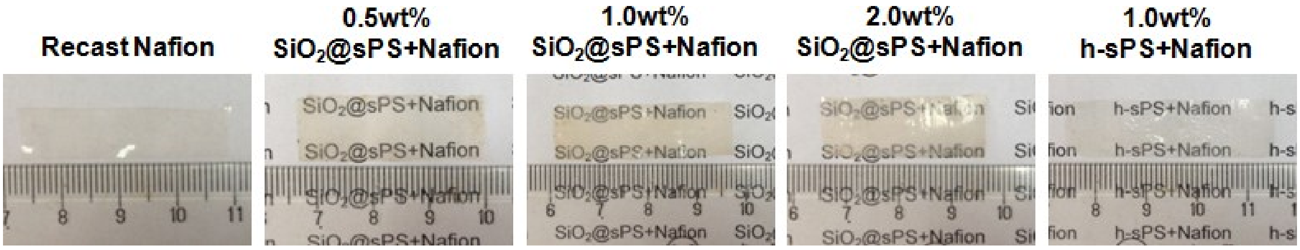

Fig. S3 Digital photos of the recast Nafion, 0.5~2.0 wt% SiO_2@sPS+Nafion and 1.0 wt% h-sPS+Nafion membranes.

Table S1 Detailed information about the optimized proton conductivity of Nafion-based PEMs modified by various other sulfonated materials.

Composite PEMs	Proton conductivity (S/cm)	Conditions	Publications
MMT-SO_3H (1, 4-BS) + Nafion	0.081	30°C-98%RH	1
	0.11	50°C-98%RH	
MMT-SO_3H (1, 3-PS) + Nafion	0.075	30°C-98%RH	
	0.112	50°C-98%RH	
MMT-SO_3H (FMES) + Nafion	0.088	30°C-98%RH	
	0.128	50°C-98%RH	
Laponite-SO_3H + Nafion	0.0025	25°C-50%RH	2
	0.0035	25°C-60%RH	
	0.0045	25°C-70%RH	
	0.016	25°C-80%RH	
	0.022	25°C-90%RH	
	0.028	25°C-95%RH	
	0.03	25°C-98%RH	
	0.039	50°C-98%RH	
	0.052	65°C-98%RH	
	0.07	80°C-98%RH	
	0.082	95°C-98%RH	
PSSA-Nafion	0.032	r.t.-100%RH	3
mesoporous SiO_2-SO_3H + Nafion	0.088	40°C-95%RH	4
	0.101	50°C-95%RH	
	0.115	60°C-95%RH	
	0.125	70°C-95%RH	
	0.127	80°C-95%RH	
	0.113	90°C-95%RH	
	0.108	100°C-95%RH	
Nafion + Sulfonated poly(propylene oxide) oligomers	0.104	r.t.-100%RH	5
Sulfonated β-cyclodextrin + Nafion	0.0125	10°C-100%RH	6
	0.014	20°C-100%RH	
	0.016	30°C-100%RH	
	0.019	40°C-100%RH	
	0.021	50°C-100%RH	
	0.023	60°C-100%RH	
	0.026	70°C-100%RH	
	0.029	80°C-100%RH	
zeolite beta-SO_3H + Nafion	0.047	21°C-100%RH	7
	0.067	80°C-100%RH	
Polysilsesquioxane-SO_3H + Nafion	0.048	30°C-90%RH	8
	0.103	30°C-100%RH	
	0.123	50°C-100%RH	
	0.145	70°C-100%RH	
	0.152	80°C-100%RH	
	0.09	80°C-90%RH	
	0.014	80°C-40%RH	
	0.02	120°C-40%RH	
	0.16	120°C-90%RH	

Table S1 (continued)

Composite PEMs	Proton conductivity (S/cm)	Conditions	Publications
MWCNT-SO_3H + Nafion	0.082	25^{o}C-100%RH	9
	0.086	40^{o}C-100%RH	
	0.085	60^{o}C-100%RH	
	0.058	80^{o}C-100%RH	
	0.030	100^{o}C-100%RH	
	0.027	120^{o}C-100%RH	
SiO_2-SO_3H + Nafion	0.083	30^{o}C-100%RH	10
	0.103	40^{o}C-100%RH	
	0.125	50^{o}C-100%RH	
	0.155	60^{o}C-100%RH	
	0.175	70^{o}C-100%RH	
	0.200	80^{o}C-100%RH	
	0.079	80^{o}C-40%RH	
	0.207	90^{o}C-100%RH	
	0.218	100^{o}C-100%RH	
mesoporous SiO_2-SO_3H + Nafion	0.039	60^{o}C-60%RH	11
	0.08	60^{o}C-80%RH	
	0.13	60^{o}C-98%RH	
Montmorillonite-SO_3H + Nafion	0.08	30^{o}C-98%RH	12
	0.106	50^{o}C-98%RH	
	0.141	75^{o}C-98%RH	
	0.161	90^{o}C-98%RH	
mesoporous SiO_2-SO_3H + Nafion	0.013	r.t.-100%RH	13
Laponite-PSSA + Nafion	0.011	25^{o}C-100%RH	14
	0.03	55^{o}C-100%RH	
	0.05	85^{o}C-100%RH	

Table S1 (continued)

Composite PEMs	Proton conductivity (S/cm)	Conditions	Publications
ZrO_2-SO_3H + Nafion	0.0077	80°C-20%RH	15
	0.0336	80°C-50%RH	
	0.0684	80°C-70%RH	
	0.0063	120°C-20%RH	
	0.0448	120°C-50%RH	
	0.0965	120°C-70%RH	
SBA15 + Nafion	0.0066	80°C-20%RH	
	0.0259	80°C-50%RH	
	0.0482	80°C-70%RH	
	0.0065	120°C-20%RH	
	0.0429	120°C-50%RH	
	0.0883	120°C-70%RH	
MCM41 + Nafion	0.0058	80°C-20%RH	
	0.028	80°C-50%RH	
	0.0504	80°C-70%RH	
	0.0053	120°C-20%RH	
	0.0337	120°C-50%RH	
	0.0718	120°C-70%RH	
Si-SO_3H + Nafion	0.0026	80°C-20%RH	
	0.023	80°C-50%RH	
	0.0394	80°C-70%RH	
	0.0039	120°C-20%RH	
	0.0268	120°C-50%RH	
	0.0586	120°C-70%RH	
Phosphosilicate + Nafion (P:S=0.5)	0.010	80°C-20%RH	
	0.0391	80°C-50%RH	
	0.0622	80°C-70%RH	
	0.0087	120°C-20%RH	
	0.051	120°C-50%RH	
	0.1035	120°C-70%RH	
Phosphosilicate + Nafion (P:S=1)	0.0056	80°C-20%RH	
	0.026	80°C-50%RH	
	0.0492	80°C-70%RH	
	0.0044	120°C-20%RH	
	0.0363	120°C-50%RH	
	0.0798	120°C-70%RH	
Phosphosilicate + Nafion (P:S=1.5)	0.0069	80°C-20%RH	
	0.0298	80°C-50%RH	
	0.0627	80°C-70%RH	
	0.0067	120°C-20%RH	
	0.0402	120°C-50%RH	
	0.0898	120°C-70%RH	
TiO_2-SO_3H + Nafion	0.05	100°C-40%RH	16
	0.18	100°C-100%RH	
	0.1	120°C-40%RH	
Al-MSU-F + Nafion	0.099	30°C-100%RH	17
	0.134	80°C-100%RH	
Al-HMS + Nafion	0.125	30°C-100%RH	
	0.148	80°C-100%RH	
Al-MCM-41 + Nafion	0.185	30°C-100%RH	
	0.291	80°C-100%RH	

Table S1 (continued)

Composite PEMs	Proton conductivity (S/cm)	Conditions	Publications
PSSA-*g*-PVDF + Nafion	0.064	20^{o}C-95%RH	18
	0.072	40^{o}C-95%RH	
	0.082	60^{o}C-95%RH	
	0.093	80^{o}C-95%RH	
	0.106	95^{o}C-95%RH	
SiO_2@sPS + Nafion	0.196	25^{o}C-100%RH	This work
	0.216	30^{o}C-100%RH	
	0.249	50^{o}C-100%RH	
	0.253	70^{o}C-100%RH	
	0.260	90^{o}C-100%RH	
	0.0216	100^{o}C-40%RH	
h-sPS + Nafion	0.0285	100^{o}C-40%RH	

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