Electronic Supporting Information (ESI)

Metal organic framework-Graphene Oxide Composites: a facile method to highly improve the proton conductivity of PEM operated under low humidity

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Experimental Section

Materials:

Expandable graphite powders were provided by Yingtai Co. (China). Nafion solution (perfluorinated resin solution, 5% (w/w) in lower aliphatic alcohol and water mixture, Mw 100,000 g/mol) was obtained from DuPont. $Zn(NO_3)_2.6H_2O$, 2-methylimidazole were obtained from Aladin. All the reagents and solvents were commercially available and used as supplied without further purification.

Preparation of ZIF:

ZIF-8 was prepared according to Cravillon et al [1]. The molar ratios of $Zn(NO_3)_2.6H_2O$, 2-methylimidazole and methanol was 1:2:1000. After mixing the ligand and metal salt together and keeping it sonication for about 10 min, the mixture became milky. Then, kept the mixture sit for 2 hours. Gel-like solid was recovered by centrifugation and washed with methanol at least three times, then dried under vacuum.

Preparation of ZIF@GO:

GO was synthesized by modified Hummers method as reported in our previous works. [2, 3] First, 8mg GO (1wt% of metal salt) was dispersed in 50 ml methanol and kept sonication for at least 2h. Then GO solution was added during the preparation of ZIF-8 in the sonication condition. The subsequent steps were the same as purify ZIF-8. The obtained product was named as ZIF-8@GO.

Membrane preparation:

ZIF-8@GO, GO and ZIF-8 were dispersed in DMF solution respectively. For the synthesis of membrane preparation, different amounts of ZIF-8@GO were added into Nafion/DMF solution where DMF substituted the solution of Nafion resin by rotary evaporator according to our previous reports. For simplicity, the notations of composite membranes with theoretical ZIF-8@GO content varied in 0.5, 1, 1.5% (w/w) based on Nafion were denoted as ZIF-8@GO/Nafion-x, where x is the weight percentage of ZIF-8@GO in the Nafion matrix. For comparison, composite membranes containing 1% (w/w) ZIF-8, 1% (w/w) GO, 1% (w/w) ZIF-8&GO (the weight ratio of ZIF-8:GO=1:3.3, according to the element analysis result of ZIF-8@GO) were obtained through the same method. The resulted membranes were denoted as ZIF-8/Nafion-1, GO/Nafion-1, ZIF-8&GO/Nafion-1. Unless otherwise stated, ZIF-8@GO/Nafion hybrid membrane meant the incorporation of ZIF-8@GO was 1.0% (w/w) with respect to Nafion.

Characterization

Characterizations of ZIF-8@GO:

Fourier transform infrared (FT-IR) spectra were recorded on Nicolet Nexus 470 with a resolution of 4 cm^{-1} and 32 scans. The TGA analyses were performed under N_2 atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 20 $^oC \cdot min^{-1}$ from 100 ^oC to 700 ^oC. X-ray diffraction patterns (PANalytical X'pert diffractometer with Cu Kα radiation) and the Transmission Electron Microscope images (Tecnai G2 20 TWIN, FEI, USA) were used to confirm the synthesis of ZIF-8@GO. Element analysis was measured by EDS (Oxford Instrument X-MAX 50).

Characterizations of membranes:

The FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer. FE-SEM (Ultra 55, Zeiss, German) and AFM (Multimode 8) images were employed to observe membranes' cross-sectional morphologies and phase separation. Field emission electron microscope TEM (JEM-2100) was used to have a deeper insight into the particle dispersion. The water uptake (WU) measurements of PEMs were conducted after having the membranes been equilibrated for 24 h under both 60 and 120 ^oC at 40% RH. The proton conductivities of membranes were obtained

using the four-point probe technique by Autolab CHI660d (Shanghai, China). Proton activation energy of membranes is determined according to the Arrhenius equation: $\sigma = \sigma_0 \cdot e^{-Ea/RT}$. The methanol permeability of the PEM was measured under 40 °C with initial methanol concentration of 80% (v/v). The detailed description of experiment of WU, proton conductivity, and methanol permeability of PEM can be achieved in our previous papers [2].

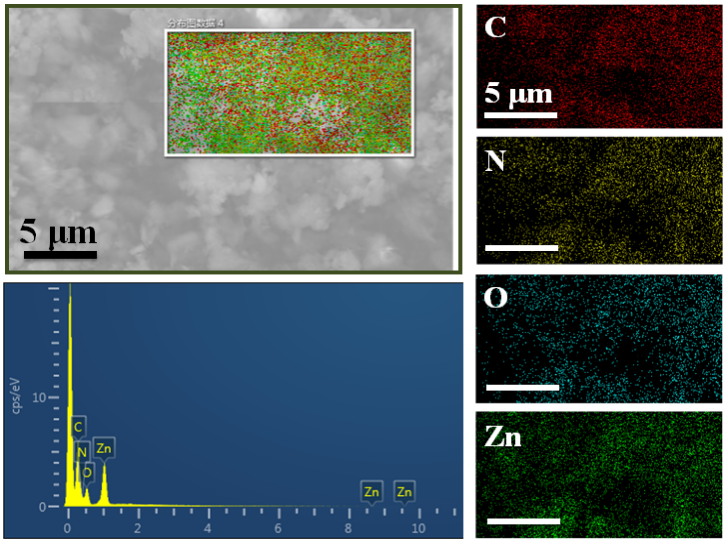

Fig. S1. Element mapping and EDS of ZIF-8@GO showing the presence of Zn, O, N and C elements. By calculation, the weight ratio of ZIF:GO is 1:3.3.

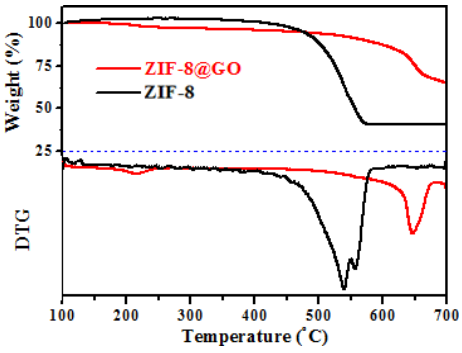

Fig. S2 TGA and DTG measurements of ZIF-8 and ZIF-8@GO.

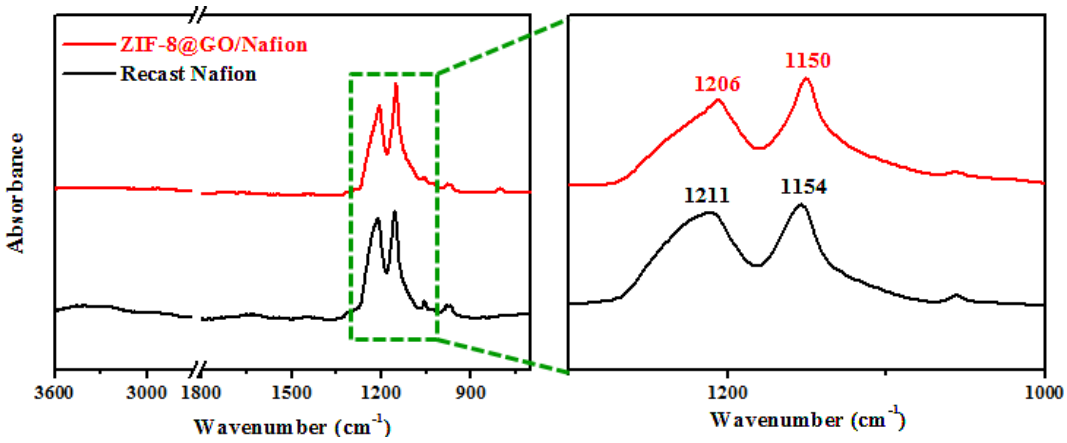

Fig. S3 FT-IR spectra of recast Nafion and ZIF-8@GO/Nafion.

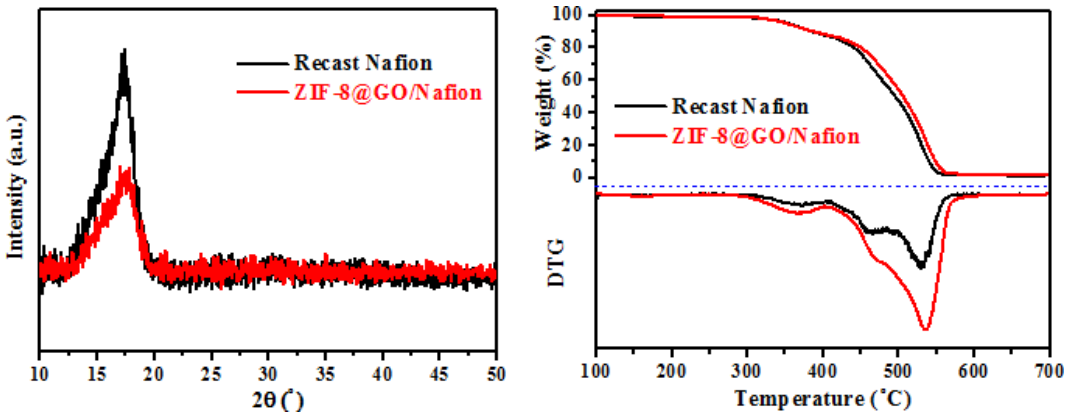

Fig. S4 (A) XRD patterns and (B) TGA/DTG measurements of recast Nafion and ZIF-8@GO/Nafion.

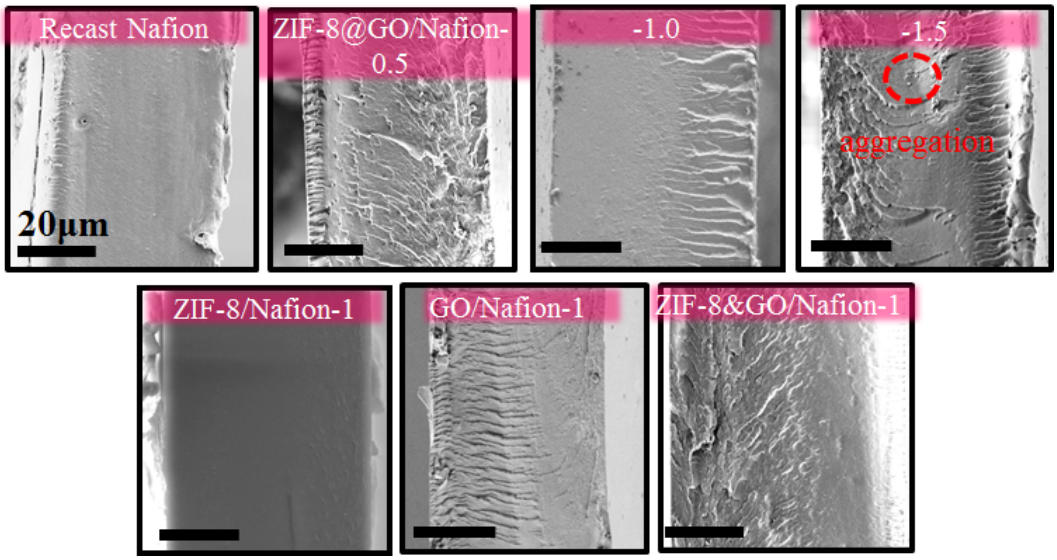

Fig. S5 Cross-sectional figures of different PEMs, circles indicate the aggregation of ZIF-8@GO in the membrane of ZIF-8@GO/Nafion-1.5.

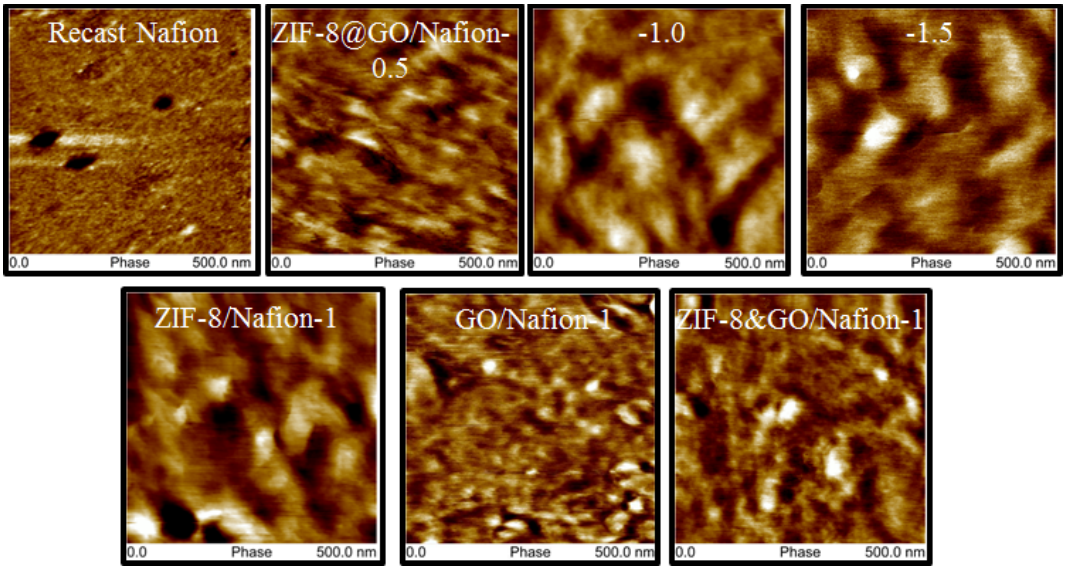

Fig. S6 AFM phase figures of recast Nafion and hybrid membranes in tapping mode.

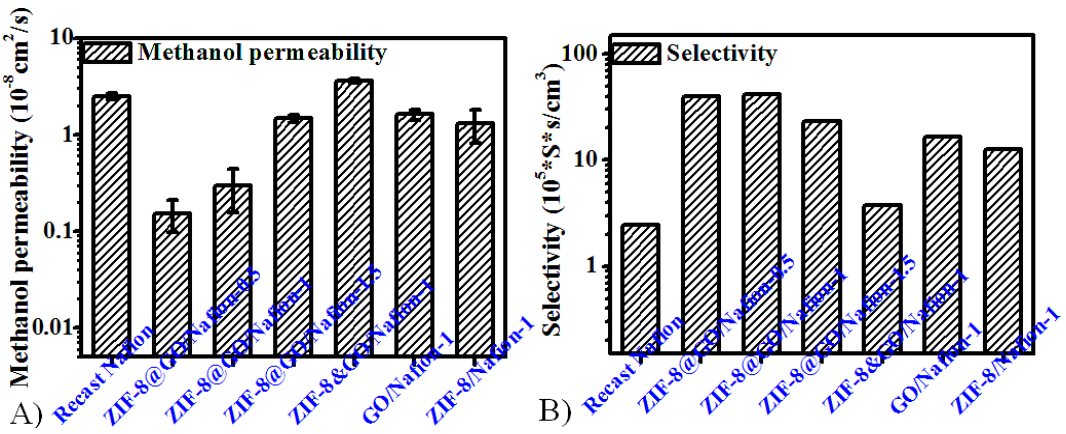

Fig. S7 (A) Methanol permeability and (B) selectivity of membranes (at 40°C).

Table. S1 Comparisons of proton conductivity at high temperature.

Membranes	Testing environment	Proton conductivity (S cm^{-1})	References
Sulfonated GO/Nafion	100 °C	0.12	B. G. Choi [4]
GO/Nafion	100 °C	0.06	B. G. Choi [4]
Nafion-GO-SPEEK	90 °C, 100% RH	0.32	J. H. Lee [5]
Sulfonic acid-GO/Nafion	120 °C, 40% RH	0.10	H. Zarrin [6]
PDA-GO/SPEEK	120 °C, anhydrous	0.0033	Y. He [7]
PW-mGO/Nafion	80 °C, 25% RH	0.014	S. Shanmugam[8]
ZIF-8@GO/Nafion	120 °C, 40% RH	0.28	Our work

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