Supporting Information for

Mechanically reinforced phosphoric acid doped quaternized poly (ether ether ketone) membranes via cross-linking with functionalized graphene oxide

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1. Experimental

Materials

3,3,5,5-Tetramethyl-4,4-bisphenol and 4,4-difluorobenzophenone were obtained from Shanghai Jiachen Chemical Company. Potassium carbonate, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and toluene were purchased from Tianjin Tiantai Fine Chemicals Co., Ltd. *N*-Bromosuccinimide (NBS) and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich. Graphite power, hydrochloric acid, sodium nitrite and potassium permanganate were obtained from Sinopharm Chemical Reagent Co., Ltd. Chloroform, phosphoric acid solution (85 wt.%), *p*-aminobenzene sulfonic acid, concentrated sulfuric acid (98 %) and 1-methylimidazole were purchased from Tianjin Guangfu Fine Chemicals Co., Ltd. Hydrogen peroxide aqueous solution (30 %) was purchased from Xilong Chemical Co., Ltd. All chemicals were used as they received without further purification.

Preparation of polymers

The poly(ether ether ketone) (PEEK) and bromomethylated PEEK (BrPEEK) were synthesized according to our previous work [1]. The synthesis procedure of quaternized PEEK (QPEEK) was stated as follow. BrPEEK was dissolved in NMP solution. The 1-methylimidazole (1.1 equivalents) was dropped in BrPEEK solution and temperature was hold at 60 °C for 4 h. Then the mixture of reaction was poured into acetone to precipitate QPEEK out. QPEEK was washed with acetone for three times and then dried in oven at 60 °C.

Preparation of functionalized GO

GO was prepared via a modified-Hummers method from graphite powder [2]. Graphite powder and $NaNO_3$ were added to concentrated sulfuric acid and were mixed uniformly. Then, $KMnO_4$ was added into the mixture. The rate of addition was controlled to prevent the temperature from exceeding 20 °C. The mixture of reaction was stirred for 1 h before the temperature was raised to 35 °C. After 30 min, water was added to the mixture and the temperature was raised to 98 °C. After 15 min, more water was added in the mixture. The mixture was cooled to 30 °C and treated with hydrogen peroxide aqueous solution (30 %). The mixture was separated by centrifuge and washed with water until PH was 7, then dried in oven at 60 °C.

1 g graphite oxide was dispersed in 10 ml water by an ultrasonic generator to obtain GO solution. The *p*-aminobenzene sulfonic acid was added in GO solution and the reaction was carried out at reflux temperature of water. The obtained FGO solution was washed by water using a centrifuge until the PH was 7, then dried in oven at 60 °C.

Preparation of PA-QPEEK-*x*%GO and PA-QPEEK-*x*%FGO

GO and FGO with different weight were dispersed in DMSO using an ultrasonic generator, respectively. 1 g QPEEK was dissolved in 10 ml DMSO. QPEEK solution and GO or FGO solution were mixed together, then poured on the glass and dried in oven at 60 °C to obtain QPEEK-*x*%GO or QPEEK-*x*%FGO membrane. The QPEEK-*x*%GO or QPEEK-*x*%FGO membranes were immersed in phosphoric acid solution at 60 °C for 4 h. Then, membranes were taken out and dried in vacuum oven to remove water. And the PA-QPEEK-*x*%GO and PA-QPEEK-*x*%FGO membranes were obtained.

Characterization and measurements

Nuclear magnetic resonance (NMR) spectrum was performed by a Bruker 510 spectrometer (500 MHz). X-ray diffraction (XRD) data were collected using a Rigaku D/Max 2550 X-ray diffractometer with Cu*K*α radiation (λ=1.54 Å) at 50 kV and 200 mA over the angular range 3-30°. X-ray photoelectron spectroscopy (XPS) data were obtained on an ESCALAB 250 X-ray photoelectron spectroscopy. The cross-section morphology of membrane was observed by SHIMADZU SSX-500 scanning electron microscope (SEM) after having been gold-sprayed. The cross-section of membrane was obtained by a quenching operation in liquid nitrogen. The mechanical properties were measured on SHIMADZU AG-I 1KN equipment with an extension rate of 2 mm min^{-1}. Before test, each membrane was treated as 4 mm × 15 mm and the thickness was recorded. And 6 samples were tested to obtain an average value. The thermal gravimetric analysis (TGA) was carried on a Perkin-Elmer TGA-1 thermo-gravimetric

analyzer at a heating rate of 10 °C min^{-1} from 100 °C to 700 °C.

PA doping level (W_{doping}) and in-plane proton conductivity (σ)

The W_{doping} was recorded as the weight increment of QPEEK membranes before and after doping with PA. Each QPEEK membrane was cut into 5 cm × 5 cm, and its weight was recorded ($W_{undoped}$). After being immersed in PA (85 wt.%) solution at 60 °C for 4 h, membrane was taken out, wiped the PA solution on surface and dried in vacuum oven at 80 °C to remove water. The weight of anhydrous PA doped membrane was recorded as W_{doped}. The PA doping level was calculated by following equation.

$$W_{doping} = \frac{W_{doped} - W_{undoped}}{W_{undoped}} \times 100\% \quad (1)$$

The in-plane proton conductivities of anhydrous PA doped membranes were measured on a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA with a four-probe AC impedance method from 0.1 Hz to 100 kHz. All membranes were treated as 1 cm × 4 cm and the thicknesses were measured before test. The proton conductivity was calculated by the following equation.

$$\sigma = \frac{L}{RS} \quad (2)$$

where the L was the distance of two electrodes (cm), R was the membrane resistance and S was the cross-sectional area of membrane (cm^2).

2. Figures and table

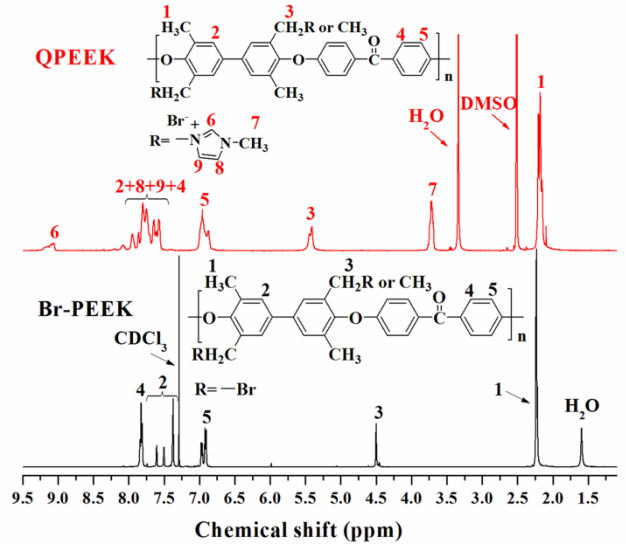

Figure S1. The ^{1}H-NMR spectra of Br-PEEK and QPEEK.

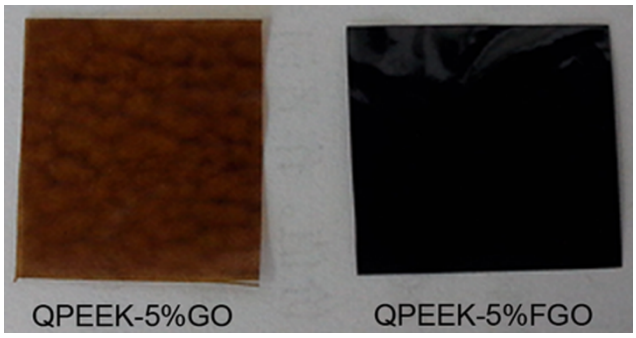

Figure S2.The pictures of QPEEK-5%GO and QPEEK-5%FGO membranes

Table S1. The mechanical properties of PA undoped and PA doped membranes.

Samples	Undoped			PA-doped		
	Young Modulus (MPa)	Elongation at the break (%)	Maximum Tension strength (MPa)	Young Modulus (MPa)	Elongation at the break (%)	Maximum Tension strength (MPa)
QPEEK-3%GO	1019±32	22±3	39±1	185±18	104±4	8±1
QPEEK-5%GO	1060±16	21±1	40±1	201±12	97±5	9±1
QPEEK-7%GO	1069±8	20±1	44±1	220±11	80±6	10±1
QPEEK-10%GO	1210±44	11±1	46±1	302±18	42±10	12±1
QPEEK-3%FGO	1056±11	48±9	44±1	213±7	127±9	30±1
QPEEK-5%FGO	1122±30	43±10	48±2	221±2	113±7	32±1
QPEEK-7%FGO	1194±26	40±1	48±2	262±31	90±5	36±1
QPEEK-10%FGO	1264±23	11±5	53±2	413±12	12±1	40±1

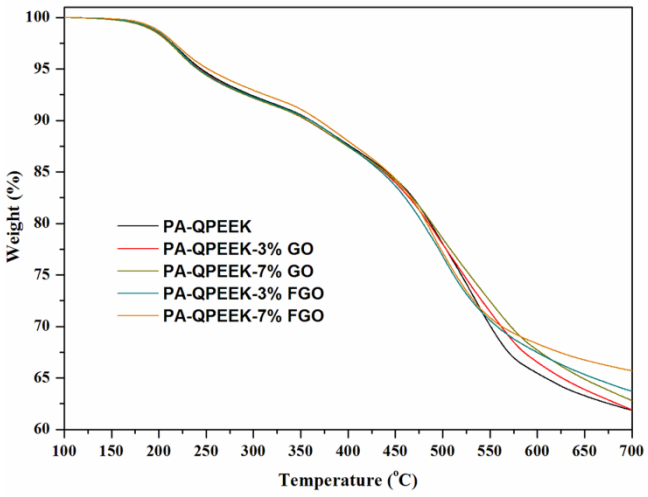

Figure S3. The TGA curves of PA doped membrane

The TGA curves of PA doped membranes are shown in Figure S3. All the curves have similar shape. They begin to lose weight at about 160 °C where the condensation polymerization of PA takes place and lose water. The 5 % weight loss temperature ($T_{5\%}$) is used to evaluate the thermal stability of membranes. The $T_{5\%}$ of PA-QPEEK, PA-QPEEK-3%GO, PA-QPEEK-7%GO, PA-QPEEK-3%FGO PA-QPEEK-7%FGO is higher than 240 °C, which indicates these membranes have excellent thermal stability.

References

[1]. N. Zhang *et al.*, *J. Mater. Chem. A*, 2014, **2**, 13996-14003
[2]. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339