Supplementary Information

Polybenzimidazole Membranes Modified with Polyelectrolyte-Functionalized Multiwalled Carbon Nanotubes for Proton Exchange Membrane Fuel Cells

Suryani[a], Chia-Ming Chang[a], Ying-Ling Liu[a]*, and Young Moo Lee[b]

[a] Department of Chemical Engineering and R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan 32023, Taiwan. Fax: +886-3-2654199; Tel: +886-3-2654130; E-mail: ylliu@cycu.edu.tw
[b]WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea, College of Engineering, Hanyang University, Seoul 133-791, Korea

Synthesis of MWCNT-PBI

MWCNT (0.05 g) was fully dispersed in PBI solution (0.1 g PBI/30 mL DMAc). The solution was purged with O_3/O_2 mixture (flow rate 6 L/min, O_3 concentration 28 g/m^3) generated by ozone generator (Ozone Group, Taiwan) for 15 min, then with argon for 15 min at room temperature. The nanotubes were then collected with filtration, washed with DMAc, and dried under vacuum to give the product MWCNT-PBI (0.038 g).

Characterization

Fourier transform infrared (FTIR) spectra were obtained through attenuated total reflectance method using Perkin-Elmer Spectrum One FTIR equipped with multiple internal reflectance apparatus and ZnSe prism as internal reflection element. Raman spectra were obtained by Renishaw InVia Raman spectrometer employing He-Ne laser of 1 mW radiating on the sample operating at 632.8 nm. X-ray photo-electron spectroscopy (XPS) analysis was conducted with VG MICROTECH MT-500 ESCA (British) using MgKa line as radiation source.

Figure S1 shows the FTIR spectra of MWCNT-PBI. Pristine MWCNT does not show obvious absorption peaks in FTIR analysis. After PBI functionalization, MWCNT-PBI shows absorption peak at 3415 cm^{-1} corresponding to N-H stretching, 1616 cm^{-1} attributed to C-N stretching, 1532 cm^{-1} arising from in-plane deformation of benzimidazole, 1282 cm^{-1} from breathing mode of benzimidazole, and 1730 cm^{-1}

from C=O generated from ozone treatment, suggesting successful incorporation of PBI onto MWCNT.

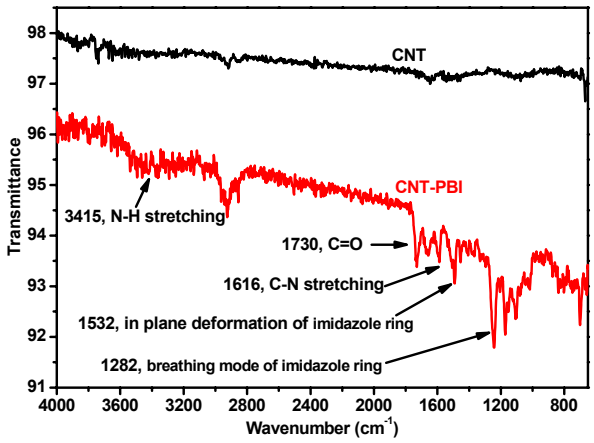

Fig. S1 FTIR of MWCNT and MWCNT-PBI.

Figure S2 shows the Raman spectra of MWCNT-PBI. Pristine MWCNTs show tangential band (G-band) at about 1588 cm^{-1} and disorder band (D-band) at around 1333 cm^{-1}. Functionalization of MWCNTs results in more sp^3 carbons on MWCNT surfaces, characterized by the increases in the D- to G- band intensity ratios (I_D/I_G) and in the intensity of D′-band at about 1614 cm^{-1}. Compared to pristine MWCNT, MWCNT-PBI shows an increase in the I_D/I_G from 1.13 to 1.51 and in the intensity of the D′-band.

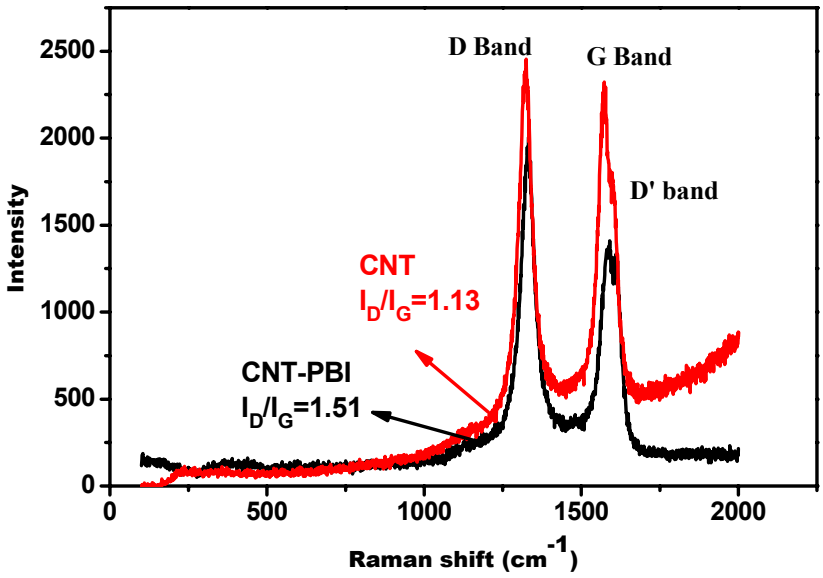

Fig. S2 Raman spectra of MWCNT and MWCNT-PBI

Figure S3 shows the TGA thermograms of the samples. The organic portion PBI of MWCNT-PBI exhibits the weight loss in the thermogram of MWCXNT-PBI, as pure MWCNT does not show weight loss in the test. MWCNT-PBI has been further characterized with XPS (Figure S4). The presence of nitrogen signal appears at about 400 eV in the wide scan spectrum (Fig. S3) arising from imidazole group of PBI indicates the success of incorporating PBI chains to MWCNTs. The C 1s core-level spectrum shows three major sources of carbon peaks: the peaks at 284.8 eV and 286.0 eV are attributed to C-C/C-H and C-N/C=N of PBI and at 291.8 eV is assigned to π-π bond of MWCNT. The N 1s core spectrum shows doublet peak at 397.9 and 399.8 eV, corresponding to double- and single-bonded nitrogen in the imidazole rings, suggesting the presence of PBI chain in MWCNTs.

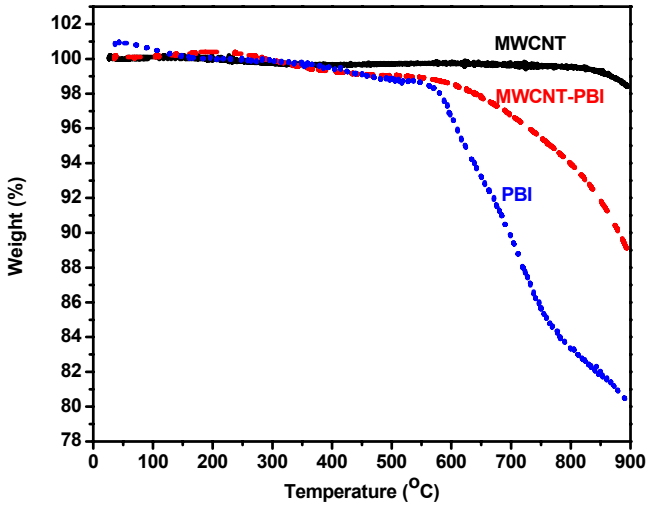

Fig. S3 TGA thermograms of MWCNT, MWCNT-PBI, and PBI.

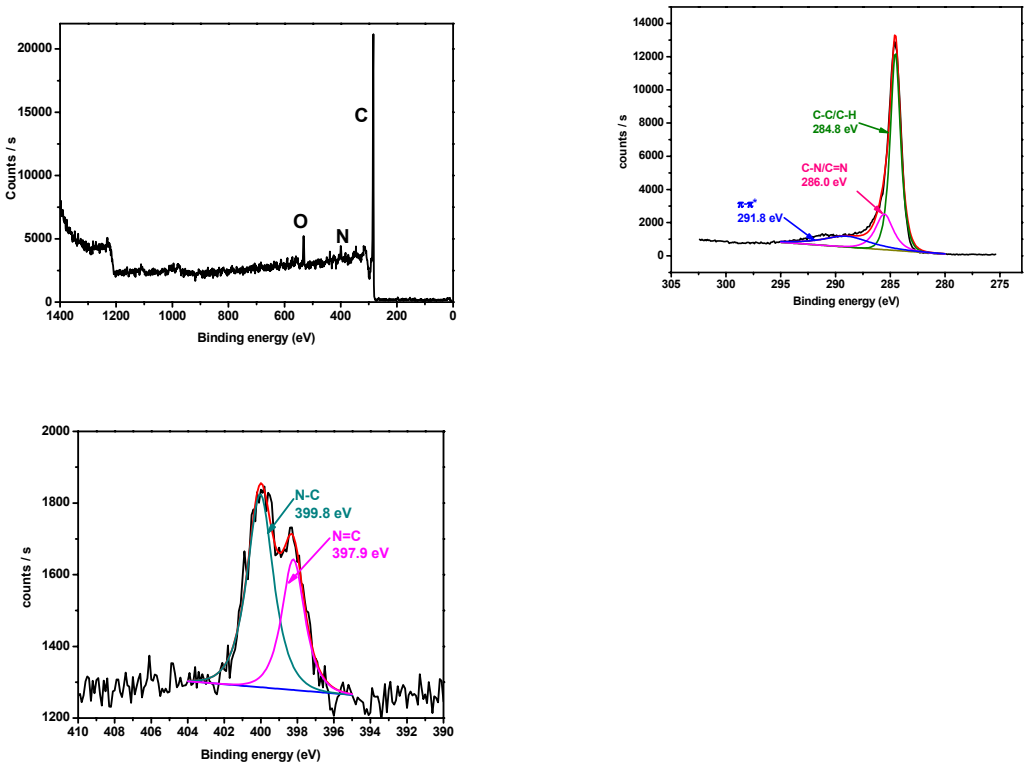

Fig. S4 (upper-left) wide-scan, (upper-right) C1s, and (lower) N1s core-level XPS spectra of MWCNT-PBI

Figure S5 shows the high-resolution TEM pictures of the samples. The incorporated amorphous PBI could be observed on the outter surfaces of MWCNT bundles.

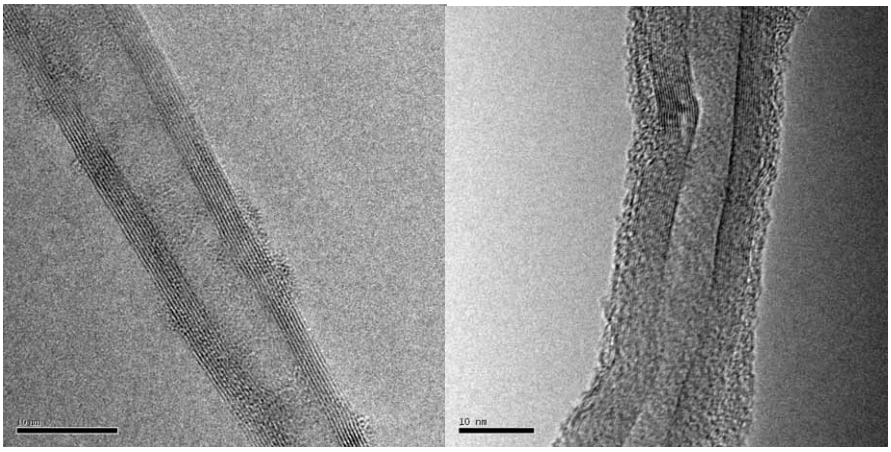

Fig. S5 HR-TEM micrographs of (left) MWCNT (x400k) and (right) MWCNT-PBI (x300k).

Figure S6 shows the dimensional stability of PBI/MWCNT nanocomposite membranes upon phosphoric acid doping. MWCNTs slightly depress the swelling behavior of the membranes. Nevertheless, the effect is not very significant as the contents of MWCNTs of the membranes are quite low.

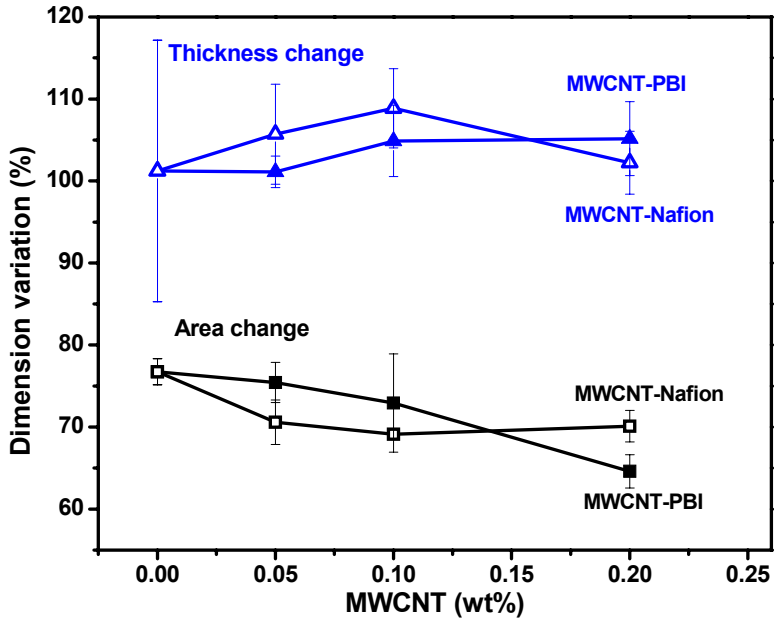

Fig. S6 the dimensional stability of PBI/MWCNT nanocomposite membranes upon phosphoric acid doping.