Electronic Supplementary Information

Design and synthesis of nitrogen-containing calcined polymer/carbon nanotube hybrids that act as a platinum-free oxygen reduction fuel cell catalyst

Tsuyohiko Fujigaya, [a,c] **Takeshi Uchinoumi,** [a] **Kenji Kaneko,**[b] **and Naotoshi Nakashima*** [a,c,d]

[a]*Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. Fax and Tel: +81-92-802-2840*
E-mail: nakashima-tcm@mail.cstm.kyushu-u.ac.jp
[b]*Department of Materials Science and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.*
[c]*World Premier International (WPI) Research Center International Institute for Carbon-Neutral Energy Research (I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395*
[d]*JST-CREST, 5 Sanbancho, Chiyoda-ku, Tokyo, 102-0075, Japan*

Experimental Section

Materials

3,3'-Diaminobenzidine tetrahydrochloride hydrate, cobalt(II) (Co) chloride hexahydrate, and Nafion® (5 wt%) were purchased from Aldrich and used as received. Polyphosphoric acid, sulfuric acid, *N, N*-dimethylacetamide (DMAc), L(+)-ascoric acid, and hydrochloric acid were purchased from Wako Pure Chemical Industries, Ltd., and used as received. Isophthalic acid and 2,6-pyridinedicarboxylic acid for PBI synthesis were purchased from TCI and used after recrystallization from hydrochloric acid. 2-Propanol was purchased from Kishida Reagents Chemicals. DMSO-d_6 was purchased from ACROS ORGANICS. The MWNT (diameter = ~30 nm) were kindly provided from the Nikkiso Co. Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PhPBI) and poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) were synthesized as previously reported.[1] MWNT/PhPBI and MWNT/PyPBI were prepared according to the previously described method.[2]

Measurements:

The TGA curves were measured using an SSC 5200 (SII) operated in conditioned air at the heating rate of 10 ˚C/min. XPS spectra were measured using an ESCA 5800 (ULVAC-PHI). The binding energy was calibrated using the C 1s peak that appeared at 284.5 eV. Indium sheet (Nilaco) was used as a substrate. The TEM measurement was conducted using a Tecnai-20 (Philips) at 200 kV. SEM was taken using a SU8000 (Hitachi). The Raman spectra were measured by a Raman RXN System (Kaiser Optical Systems) at an excitation with 785 nm by a 3 ms exposure (10 times accumulation).

Co-ion coordination treatment

The prepared MWNT/PhPBI (or MWNT/PyPBI) in 0.1 M methanol solution of Co(II) chloride hexahydrate was mixed by sonication for 10 min and a successive shaking for 19 h in the presence of L(+)-ascorbic acid. The solid material was collected by filtration and then washed with methanol. After further shaking in methanol for 1 h, the solid material was filtered and dried under vacuum.

Calcination of the composites

The MWNT/PyPBI(Co) (or MWNT/PhPBI(Co)) were calcined at 600 ºC for 1 h under flowing N_2 in TGA oven, followed by washing with a conc. hydrochloric acid aqueous solution to remove the residual Co ions. The solid material were filtered and dried under vacuum to produce c-MWNT/PyPBI(Co) (c-MWNT/PhPBI(Co)). C-PyPBI(Co) was prepared by the similar manner in the absence of MWNTs.

Electrochemical measurements

An electrolyte solution (0.5 M H_2SO_4) was deaerated with N_2 gas. An Ag/AgCl (3.0 M NaCl) and a Pt wire were used as the reference and counter electrodes, respectively. A 20 μL aliquot of the mixture of composites (0.21 mg) with Nafion® solution (7.07 μL, 5.0 wt%) in 2-propanol/water = 80/20 (v/v) solution (105 mL) was placed on a polished glassy carbon electrode (4.0 mm in diameter) and then air-dried. The dispersibility of the MWNTs was improved by the PyPBI wrapping even after the calcination. Although the stability of the dispersion was not enough, the addition of Nafion to the solution improved the stability, which enabled us to prepare a homogeneous cast film of the composite on the electrode. Linear sweep voltammograms (LSV) were measured at a scan rate of 10 mV/s using an electrochemical analyzer (BAS Inc., model DY2323) under N_2 or O_2 saturation. Temperature was maintained at 25 ± 1 ºC.

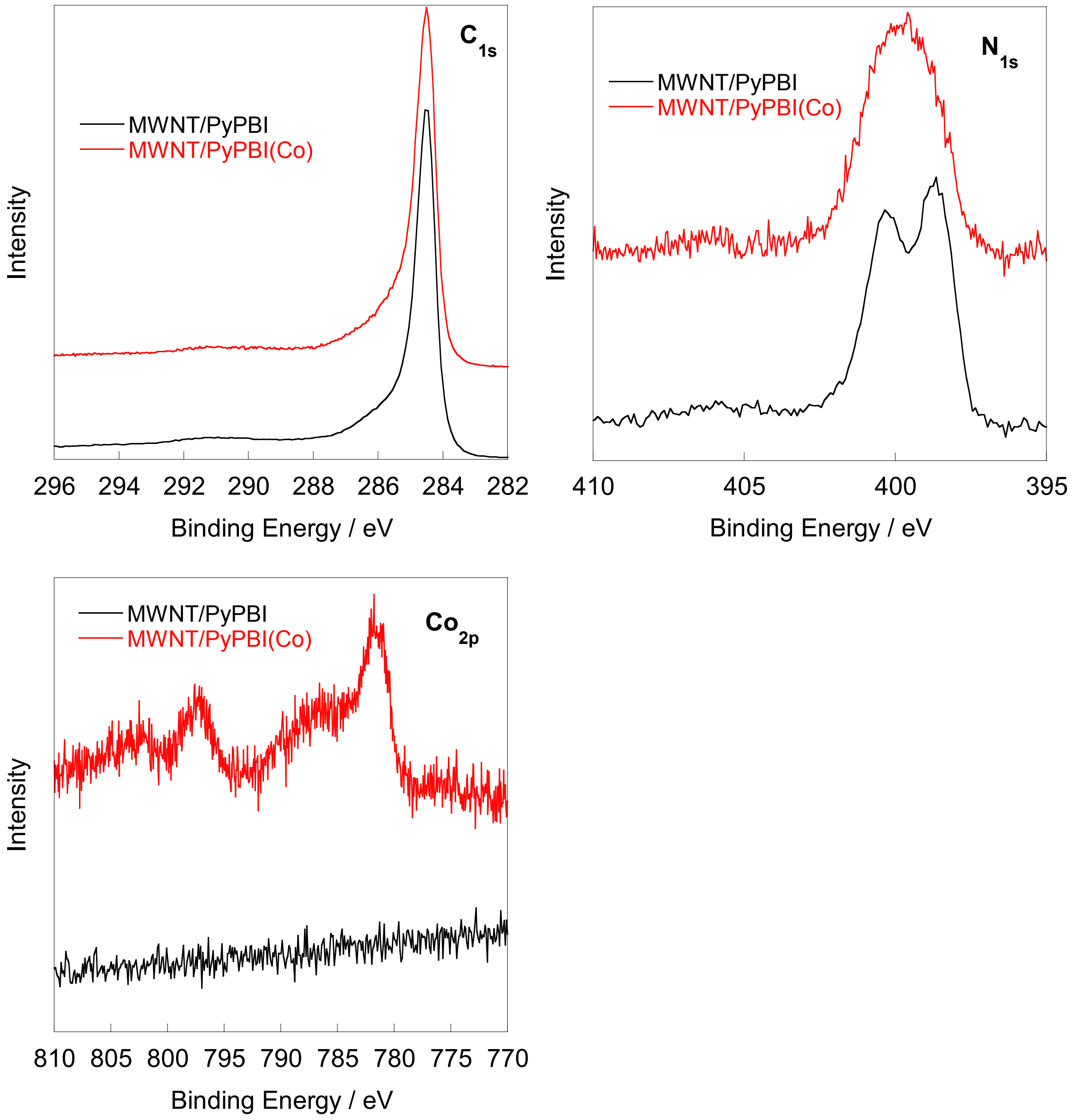

Fig. S1. Narrow scans of the XPS spectra of MWNT/PyPBI (black lines) and MWNT/PyPBI(Co) (red lines) in different regions. A broad Co $2p_{3/2}$ peak and a shakeup satellite peak is observed at about 779.3 and 786.0 eV, respectively, indicating the oxidation state of the Co is Co(II).[3]

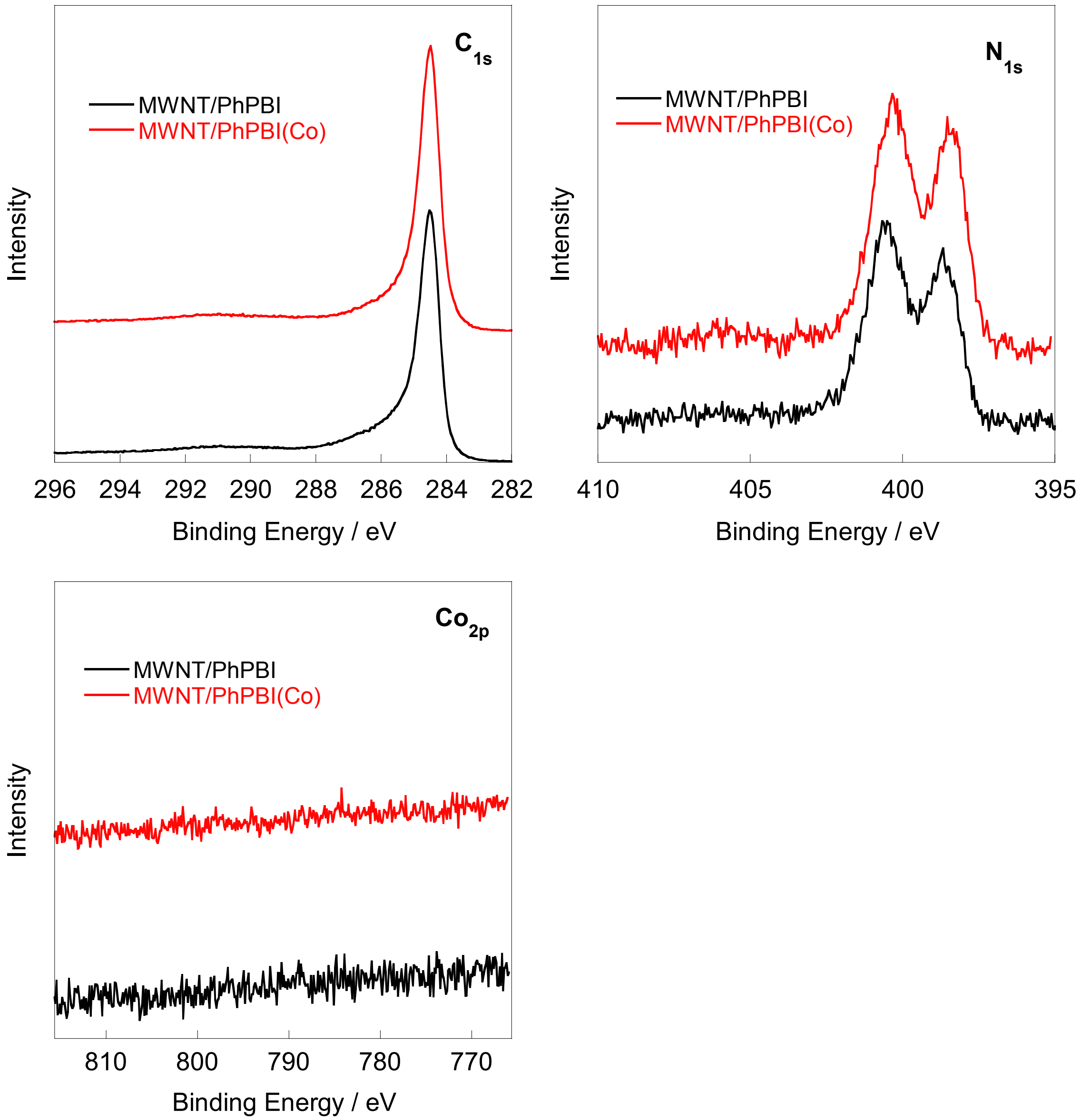

Fig. S2 Narrow scans of the XPS spectra of MWNT/PhPBI (black lines) and MWNT/PhPBI(Co) (red lines) in different regions.

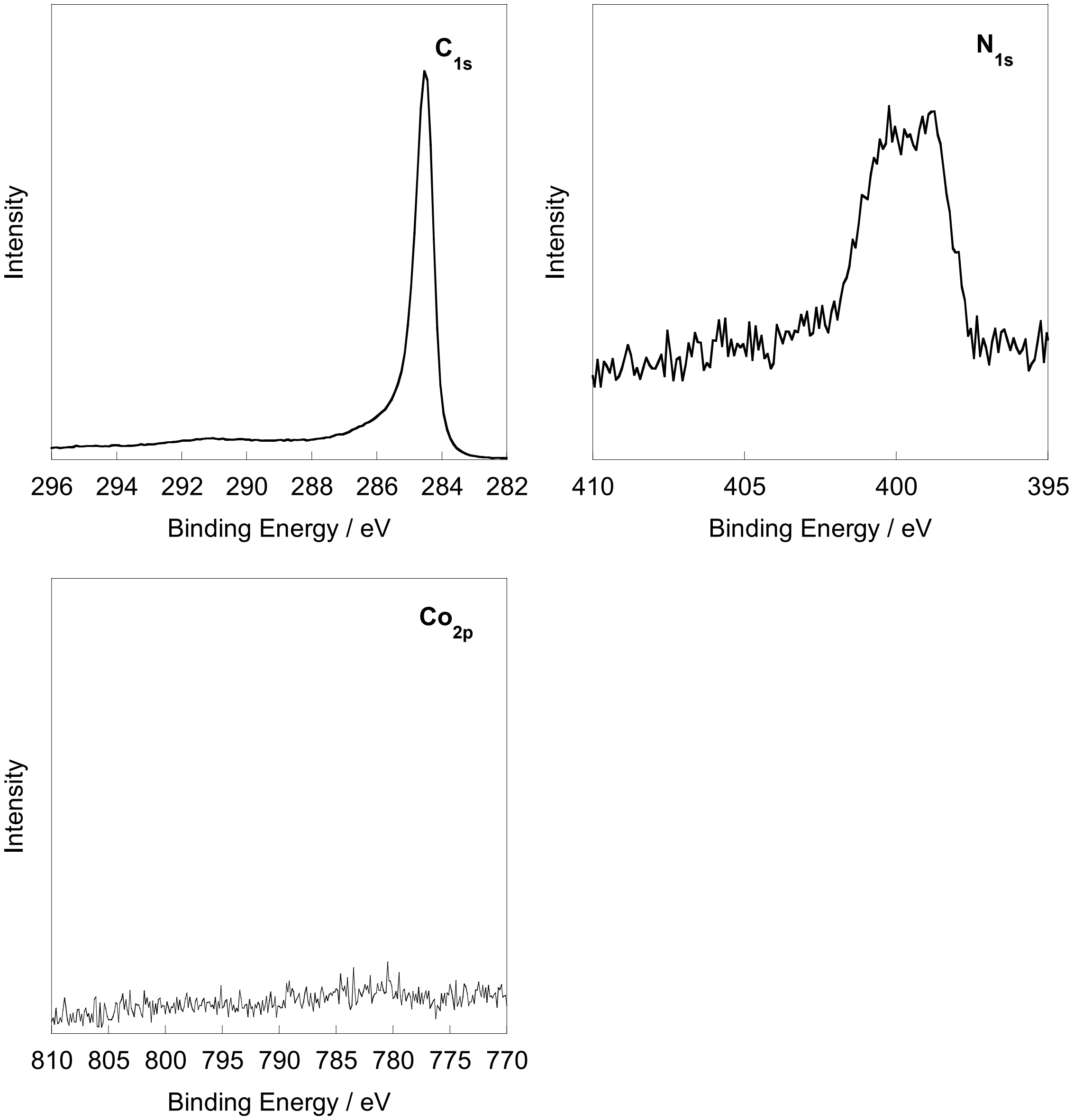

Fig. S3 Narrow scans of the XPS spectra the c-MWNT/PyPBI(Co) in different regions. (The N-ratio for the pyridinic-N : pyrrole-N : quaternary-N = 24.7 : 75.2 : 0)

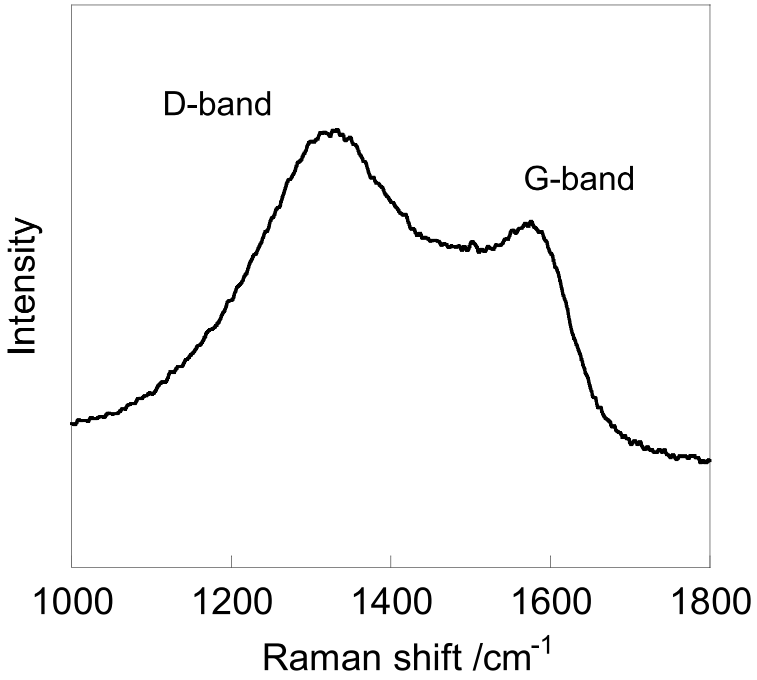

Fig. S4 Raman spectrum of the c-PyPBI(Co) (excitation wavelength: 785 nm). Raman spectrum of was used to consider the spectral feature of the shell since the selective detection of the shell in the c-MWNT/PyPBI(Co) was difficult due to the dominant signal from the MWNT in the core as shown in Fig. S5.

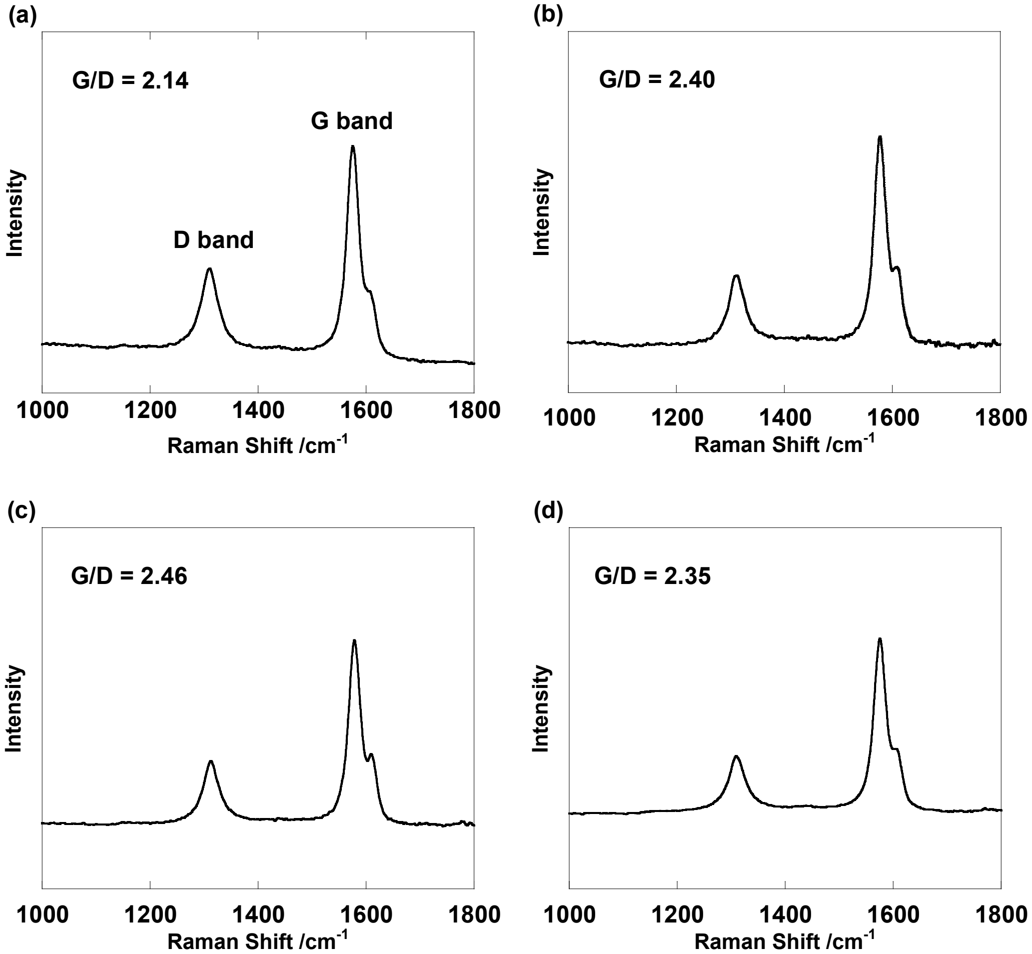

Fig. S5 Raman spectra of (a) MWNT, (b) MWNT/PyPBI, (c) c-MWNT/PyPBI(Co) and (d) c-MWNT/PyPBI-w/o-(Co). Raman spectra of (a) MWNT, (b) MWNT/PyPBI, (c) c-MWNT/PyPBI(Co) and (d) c-MWNT/PyPBI-w/o-(Co). The figure shows that the G/D ratios after the calcination in the presence and the absence of Co are almost identical, indicating that almost no defect formation occurs during the process. The ORR performance would be affected if a morphological transition such as defect formation occurs. However, in our case, because the MWNTs possess smooth and the porosity of MWNTs are much smaller than that of CB. Furthermore, the original surface morphology of the MWNTs remained even after the calcination as shown in Figs 5a and 5b, and the G/D ratio of the composite before calcination did not changed even after the calcinations, indicating that the surface structures of the materials are not much different. Based on these results, it is considered that in our case, the effect of the surface morphology on the ORR performance is limited.

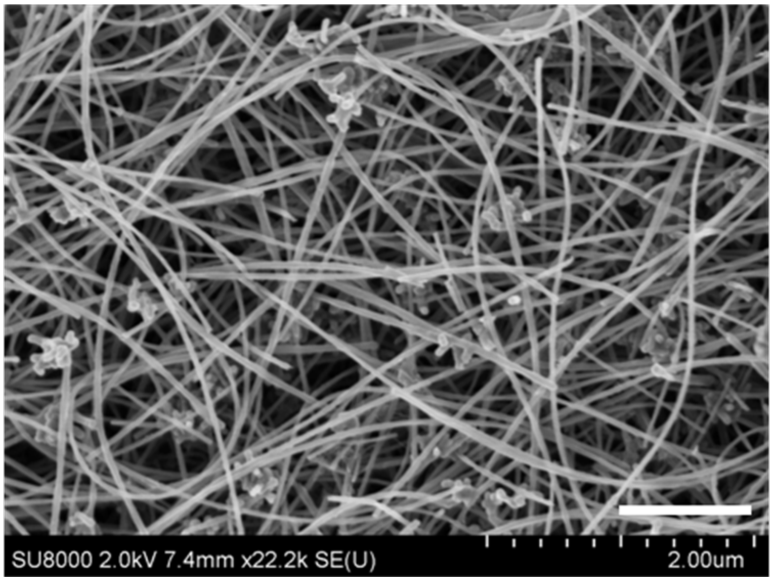

Fig. S6 SEM image of the c-MWNT/PyPBI(Co) after mixing with Nafion (scale bar, 1 μm). Mixing of the c-MWNT/PyPBI(Co) with Nafion was carried out in 2-propanol/water (8/2 v/v) which provided a stable dispersion.

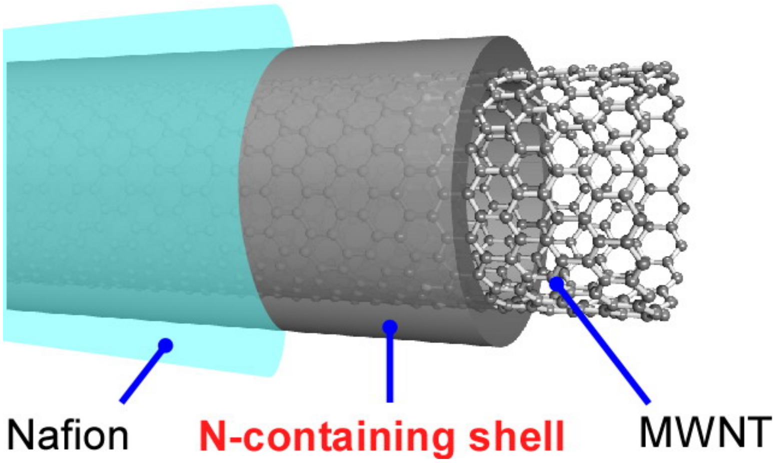

Fig. S7 Schematic illustration of N-containing core/shell CNT coated with Nafion.

Table S1. Lists of the chemical compositions in the composites determined from the XPS spectra shown in Figs. S1-S3.

	C (atomic%)	N (atomic%)	Co (atomic%)
MWNT/PyPBI	95.5	4.5	0
MWNT/PyPBI(Co)	95.4	3.5	1.0
MWNT/PhPBI	96.3	3.7	0
MWNT/PhPBI(Co)	96.7	3.1	0.2
c-MWNT/PyPBI(Co)	97.8	2.2	0

References for ESI

1 T. Brock, D. C. Sherrington and H. G. Tang, *Polymer*, 1991, **32**, 353.
2 T. Fujigaya, M. Okamoto and N. Nakashima, *Carbon*, 2009, **47**, 3227.
3 S. Kundu, T. C. Nagaiah, W. Xia, Y. Wang, S. V. Dommele, J. H. Bitter, M. Santa, G. Grundmeier, M. Bron, W. Schuhmann and M. Muhler, *J. Phys. Chem. C*, 2009, **113**, 14302.