

Electronic Supplementary Information

Polymeric Acid-doped Transparent Carbon Nanotube Electrodes in Organic Solar Cells with the Longest Doping Durability

*Il Jeon,¹ Clement Delacou,¹ Hiroshi Okada,¹ Graham E. Morse,² Tae-Hee Han,³ Yuta Sato,⁴ Anton Anisimov,⁵ Kazu Suenaga,^{1,4} Esko I. Kauppinen,⁶ Shigeo Maruyama,^{*1,7} and Yutaka Matsuo^{*1,8}*

1 Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

2 Chilworth Technical Centre, Merck Chemicals Ltd., University Parkway, SO16 7QD Southampton, UK

3 Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA 90095, USA

4 Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8565, Japan

5 Canatu Ltd., Konalankuja 5, FI-00390 Helsinki, Finland

6 Department of Applied Physics, Aalto University School of Science, FI-00076 Aalto, Finland

7 Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8565, Japan

8 Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, China

Contents:

1. Doping Effect Comparison between CNT and Graphene

2. EDX Analysis

3. TEM Images

4. AFM Morphology Analysis

5. Cross-sectional SEM

6. Water Contact Angle Test

7. Surfactant-added PEDOT:PSS-used Device

8. Current Density–Voltage (J – V) Curves

9. Statistical Analysis

1. Doping Effect Comparison between CNT and Graphene

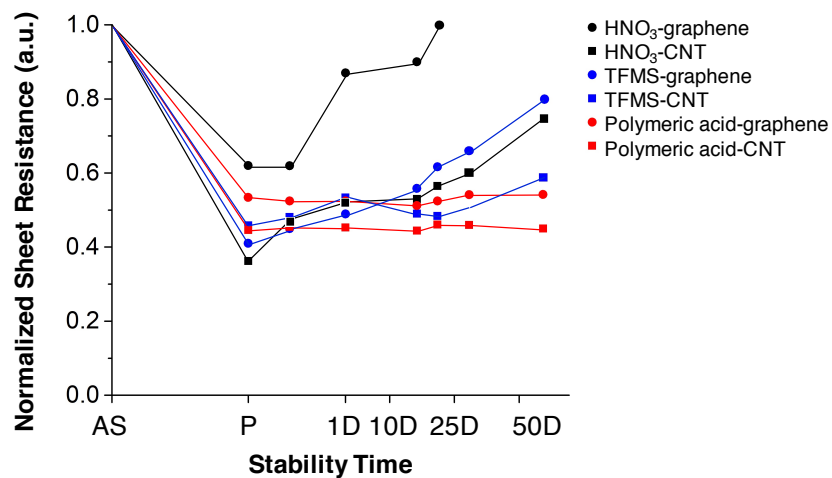


Figure S1. Normalized four-probe sheet resistance stability data for the three types of dopants applied to graphene and CNT electrodes.

2. EDX Analysis

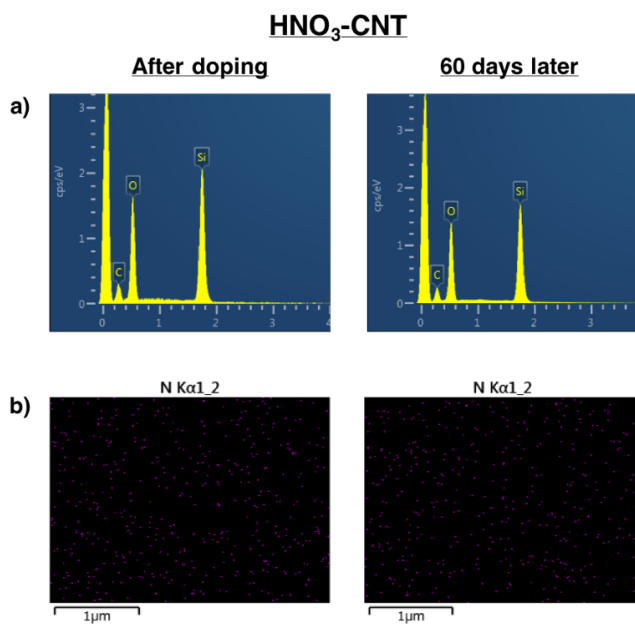


Figure S2-1. EDX analysis of a HNO₃-CNT film after doping and 60 days later. (a) cps count vs keV spectra and (b) EDX chemical mapping of nitrogen.

TFMS-CNT

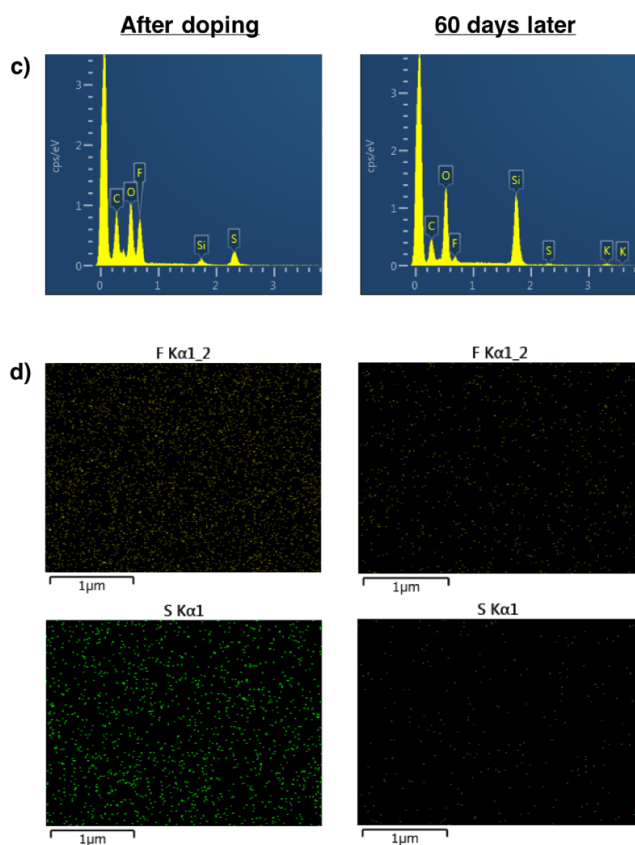


Figure S2-2. EDX analysis of a TFMS-CNT film after doping and 60 days later. (b) cps count vs keV spectra and (c) EDX chemical mapping of fluorine and sulphur.

Polymeric acid-CNT

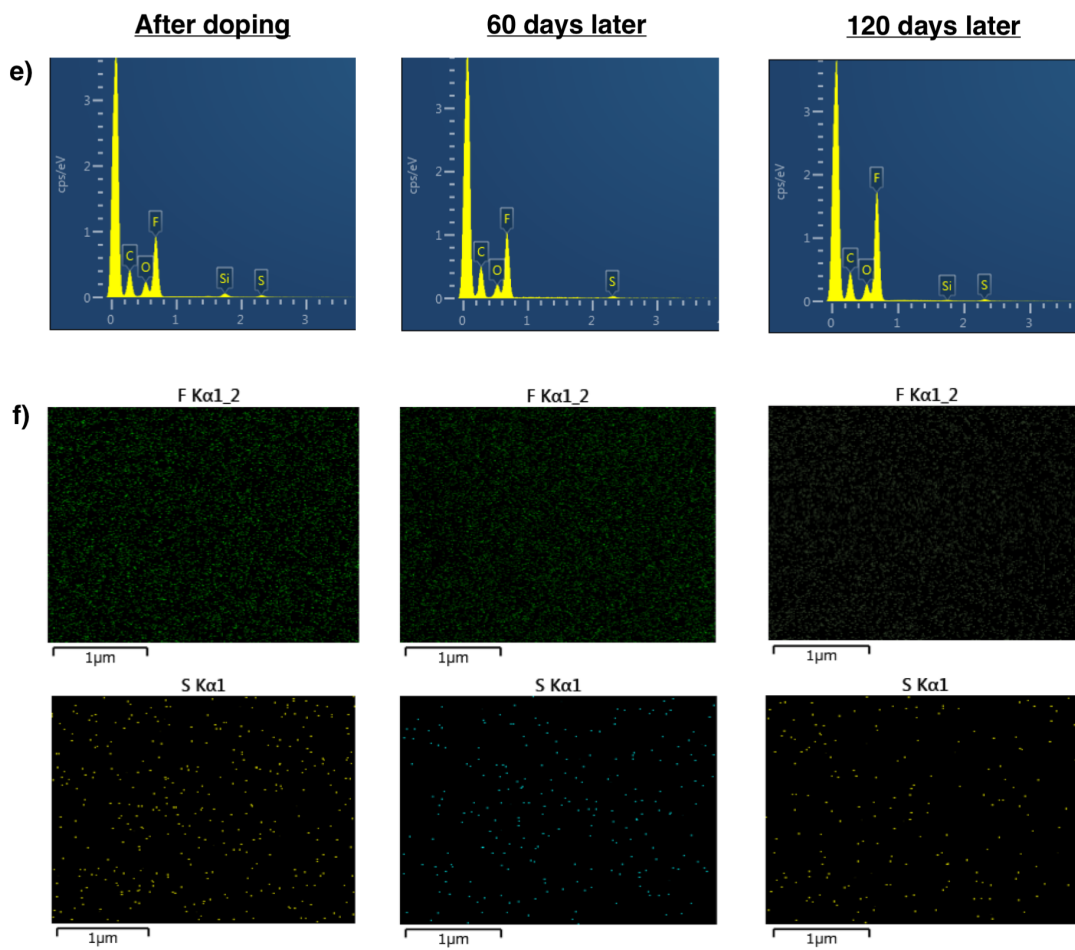


Figure S2-3. EDX analysis of a polymeric acid-CNT film after doping, 60 days later, and 120 days later. (b) cps count vs keV spectra and (c) EDX chemical mapping of fluorine and sulphur.

Table S1. EDX atomic weight% analysis results of HNO₃-CNT, TFMS-CNT, and polymeric acid-CNT after doping and 60 days later.

Sample Type	Condition	Atom	Average weight (%)	Error range (%)
HNO ₃ -CNT	After doping	C	9.50	±0.87
		O	32.03	±0.78
		Si	58.47	±0.66
	60 days later	C	9.70	±0.70
		O	31.50	±0.26
		Si	58.8	±0.94
TFMS-CNT	After doping	C	20.71	±6.70
		O	29.27	±1.76
		F	23.61	±7.58
		Si	12.06	±16.72
		S	14.36	±4.68
	60 days later	C	11.55	±4.69
		O	32.99	±0.95
		F	1.96	±0.64
		Si	52.26	±6.64
		S	1.22	±0.47
Polymeric acid-CNT	After doping	C	23.12	±3.90
		O	9.01	±0.88
		F	63.74	±2.55
		Si	1.11	±0.15
		S	3.03	±0.33
	60 days later	C	23.02	±5.86
		O	12.60	±4.15
		F	52.32	±15.13
		Si	2.43	±2.63
		S	4.11	±1.00

3. TEM Images

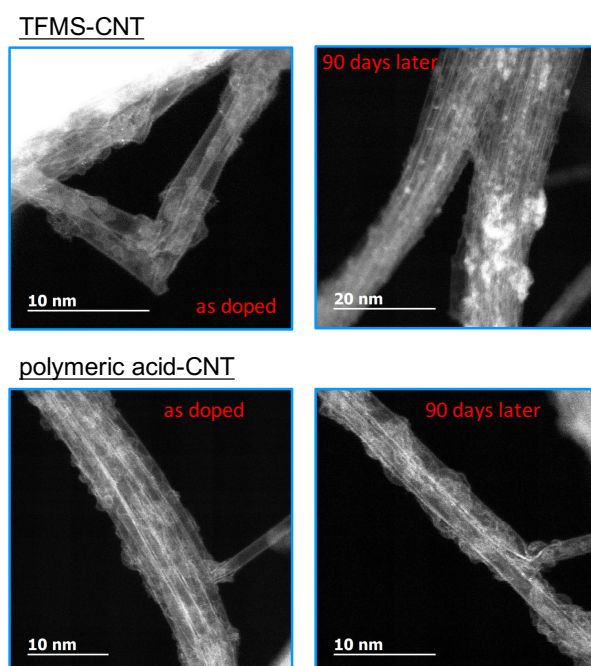


Figure S3. STEM images of TFMS-CNT and polymeric acid-CNT after doping and 90 days later.

4. AFM Morphology Analysis

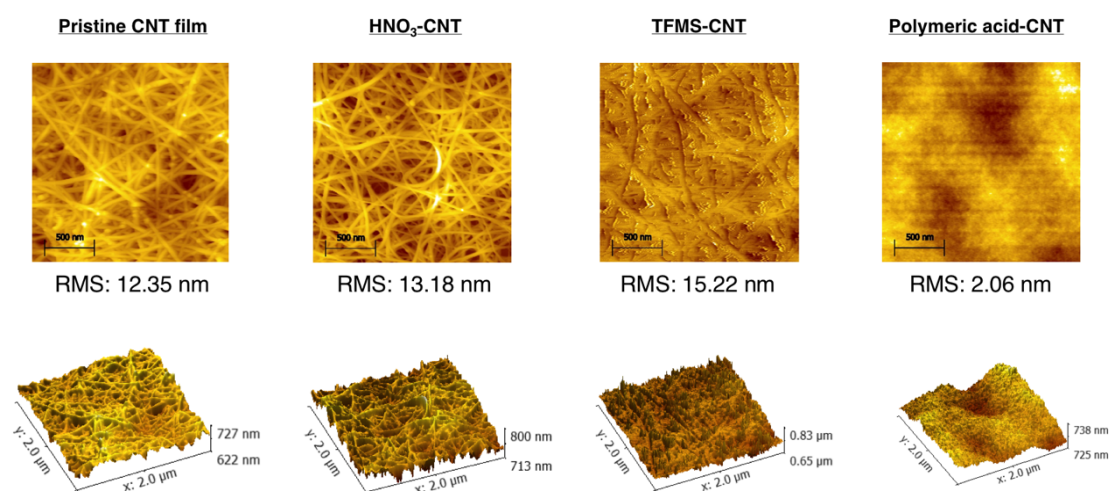


Figure S4. AFM 2D and 3D images, and the roughness mean squared of (a) a pristine CNT film, (b) a HNO₃-CNT film, (c) a TFMS-CNT film, and (d) a polymeric acid-CNT film.

5. Cross-sectional SEM

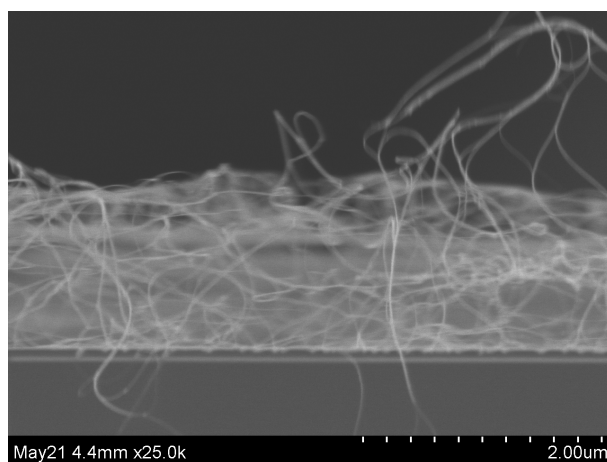


Figure S5. Cross-section SEM image of 2%-diluted Nafion-deposited CNT film.

6. Water Contact Angle Test

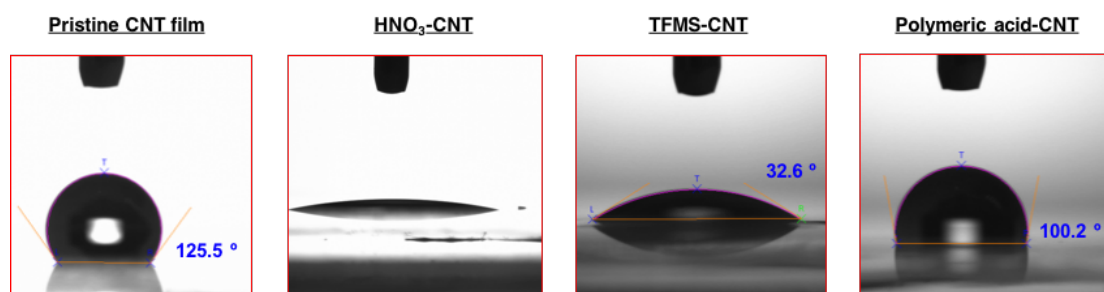


Figure S6. Water contact angle data showing the surface energy of (a) a pristine CNT film, (b) a HNO₃-CNT film, (c) a TFMS-CNT film, and (d) a polymeric acid-CNT film.

7. Surfactant-added PEDOT:PSS-used Device

Table S2. Photovoltaic performance comparison of surfactant-added PEDOT:PSS-used devices and MoO₃/PEDOT:PSS-used devices in a structural configuration of polymeric acid-CNT/HTL/ PBTZT-stat-BDTT-8:PC₇₁BM/LiF/Al.

Hole-Transporting Layer (HTL)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
Surfactant-added PEDOT:PSS	14.9	0.78	0.65	7.6
MoO ₃ /PEDOT:PSS	14.3	0.80	0.70	8.0

8. Current Density–Voltage (J – V) Curves

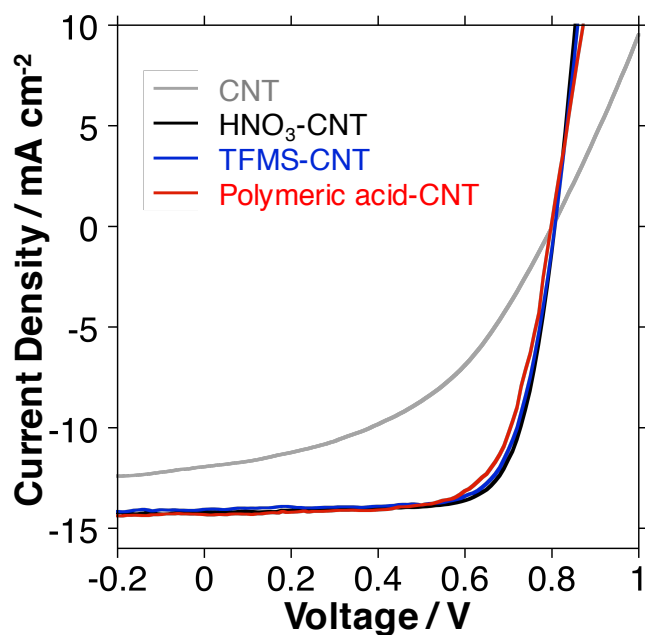


Figure S7. J – V curves of the OSCs using bare CNT, HNO₃-doped CNT films, TFMS-doped CNT films, and polymeric acid-doped CNT films.

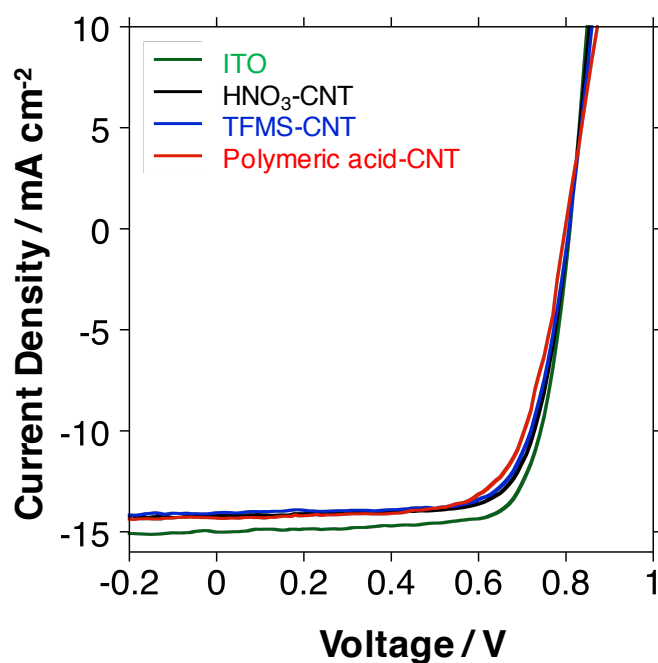


Figure S8. J – V curves of the OSCs using ITO, HNO₃-doped CNT films, TFMS-doped CNT films, and polymeric acid-doped CNT films.

9. Statistical Analysis

Table S3. Statistical Analysis of the average device PCEs and their error ranges.

Electrode	PCE (%) After doping	PCE (%) 60 days later
ITO	8.7 ±0.48	6.5 ±0.53
CNT	4.0 ±0.49	2.0 ±0.97
HNO ₃ -CNT	8.2 ±0.17	2.4 ±1.11
TFMS-CNT	8.1 ±0.38	4.2 ±1.12
polymeric acid-CNT	7.0 ±0.94	6.5 ±1.39