

Electronic Supporting Information for:

Water-Dispersible, Sulfonated Hyperbranched Poly(ether-ketone) Grafted Multi-Walled Carbon Nanotubes as Oxygen Reduction Catalysts

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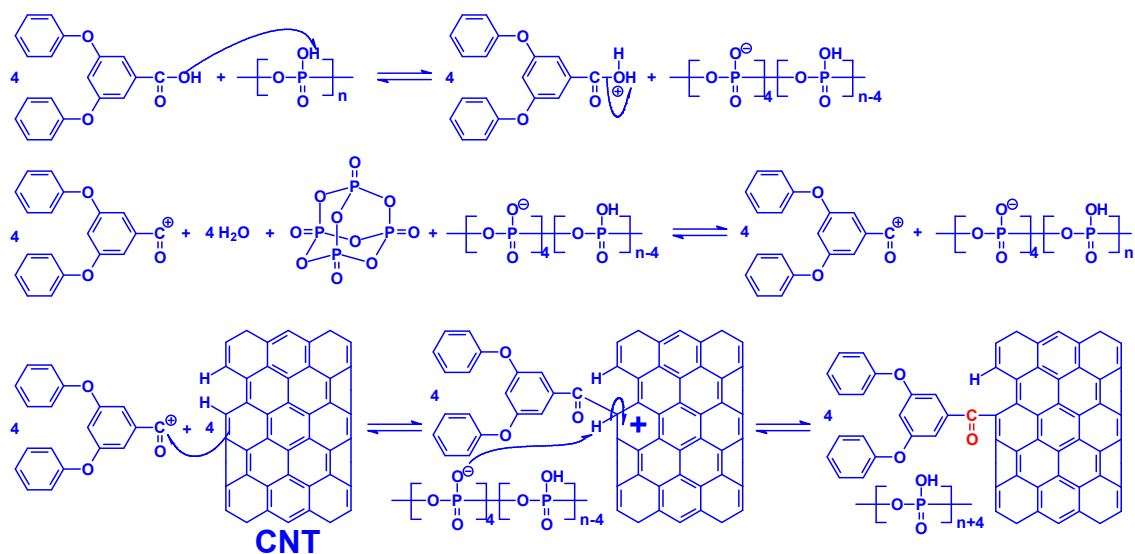


Figure S1. Proposed mechanism of Friedel-Crafts acylation reaction in PPA/P₂O₅ medium, showing defect-selectively grafting of AB₂ monomer to the site of sp² hybrid C-H on CNT defects (The structure of CNT was simplified for easy understanding).

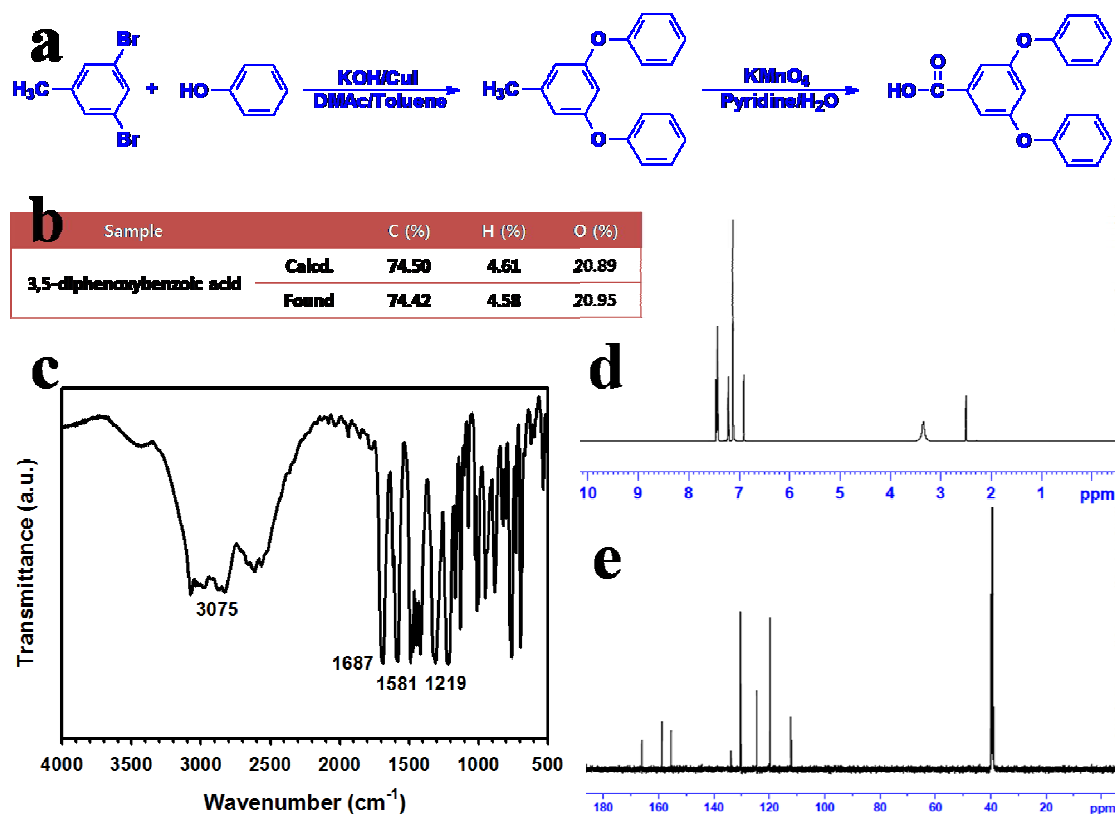


Figure S2. (a) Synthesis of AB₂ monomer , 3,5-diphenoxybenzoic acid, starting from 3,5-dibromotoluene and phenol; (b) elemental analysis of pure 3,5-diphenoxybenzoic acid; (c) FT-IR spectrum (KBr pellet) of 3,5-diphenoxybenzoic acid; (d) ¹H NMR (DMSO-d₆) spectrum of 3,5-diphenoxybenzoic acid; (e) ¹³C NMR (DMSO-d₆) spectrum of 3,5-diphenoxybenzoic acid.

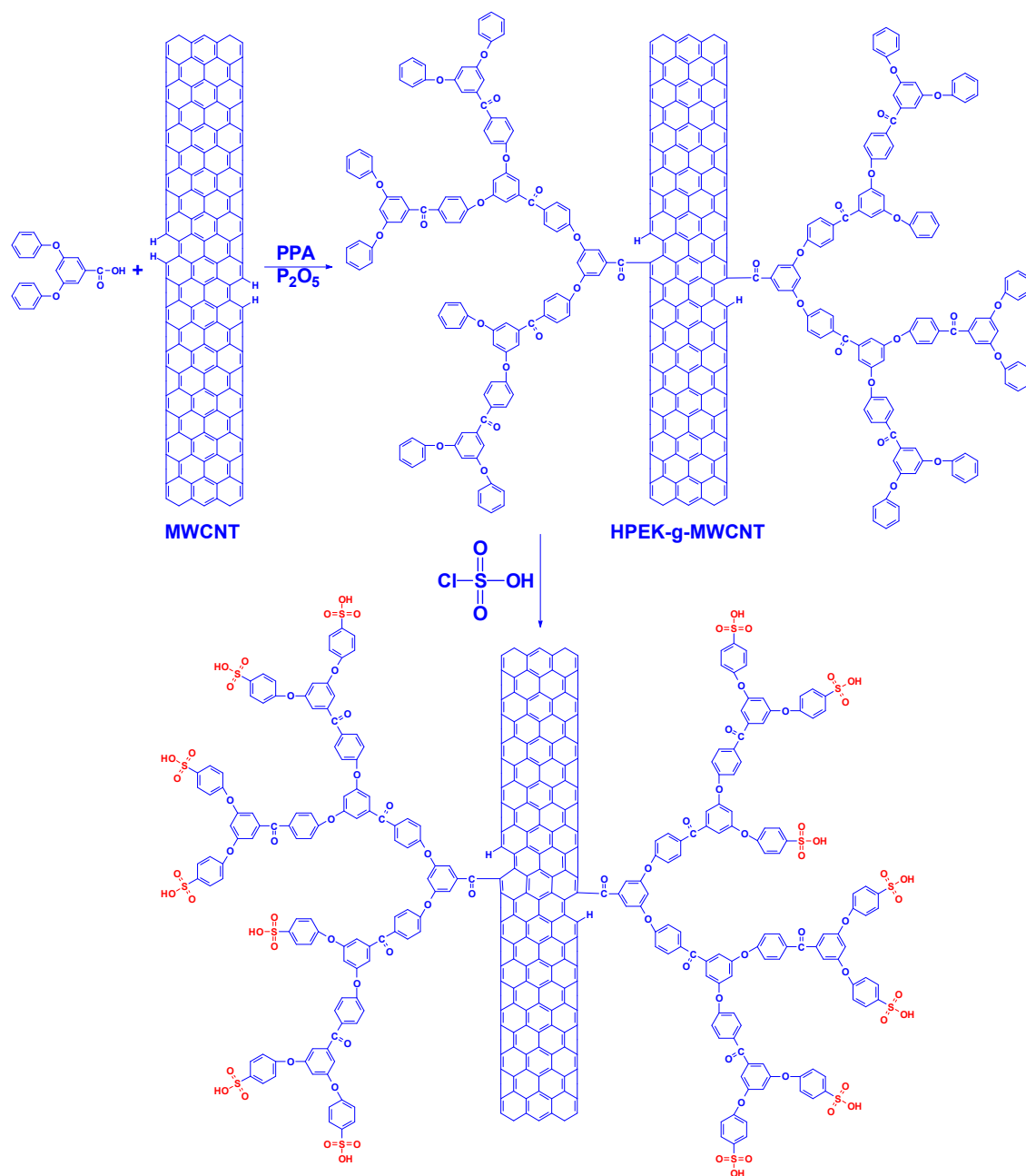


Figure S3. Schematic presentation of HPEK grafted MWCNT (HPEK-g-MWCNT) in PPA/ P_2O_5 medium and subsequent sulfonation of HPEK-g-MWCNT in chlorosulfonic acid to produce sulfonated HPEK-g-MWCNT (SHPEK-g-MWCNT).

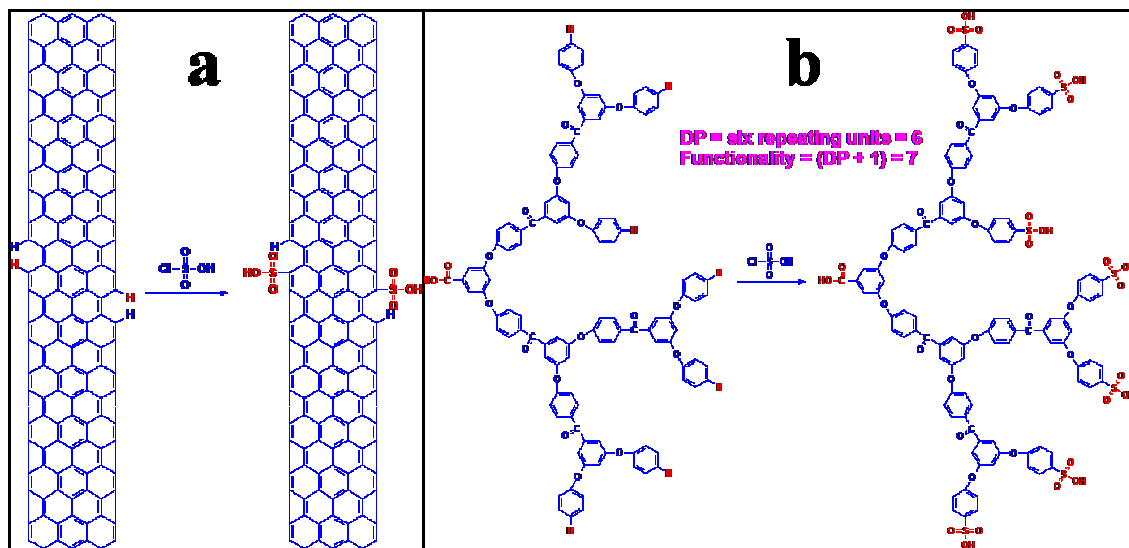


Figure S4. (a) Direct sulfonation of MWCNT in chlorosulfonic acid to yield sulfonated MWCNT (S-MWCNT). The sulfonation should be to the site of sp^2 hybrid C-H on MWCNT defects; (b) the structure of HPEK with six repeating units (the degree of polymerization (DP) = 6) and sulfonation of HPEK in chlorosulfonic acid. The available reactive sites for the sulfonation are $DP + 1 = 7$. Thus, grafting HPEK to the surface of MWCNT could increase as much as average number of HPEK molecules (n) per MWCNT multiplied by average degree of polymerization (DP) + 1, i.e., $n(DP + 1)$. For example, if n is 10 and DP is 99, $n(DP + 1)$ becomes 1000. As a result, 1000 of sulfonic acids could be introduced to the HPEK-g-MWCNT to produce SHPEK-g-MWCNT, which could provide enough hydrophilicity for water dispersion.

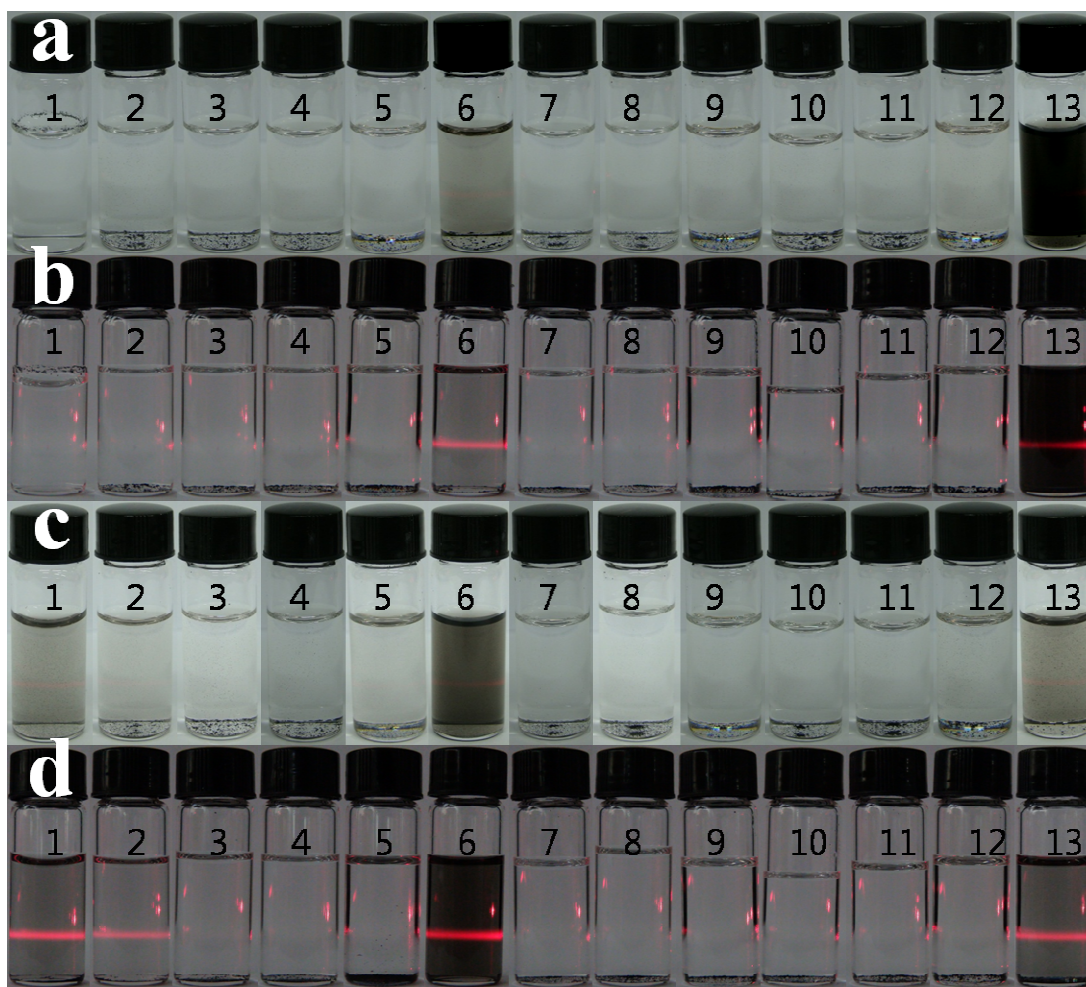


Figure S5. Photographs of samples dispersed in different solvents: (a) as-prepared HPEK-g-MWNT solutions without hand held laser shining; (b) HPEK-g-MWCNT solutions after one week at ambient condition with hand held laser shining; (c) as-prepared SHPEK-g-MWCNT solutions with hand held laser shining (d) SHPEK-g-MWCNT solutions after one week at ambient condition with hand held laser shining. (1) distilled water, (2) methanol, (3) ethanol, (4) acetic acid, (5) toluene, (6) DMAc, (7) heptane, (8) acetone, (9) benzene, (10) dichloromethane, (11) THF, (12) pyridine, and (13) NMP.

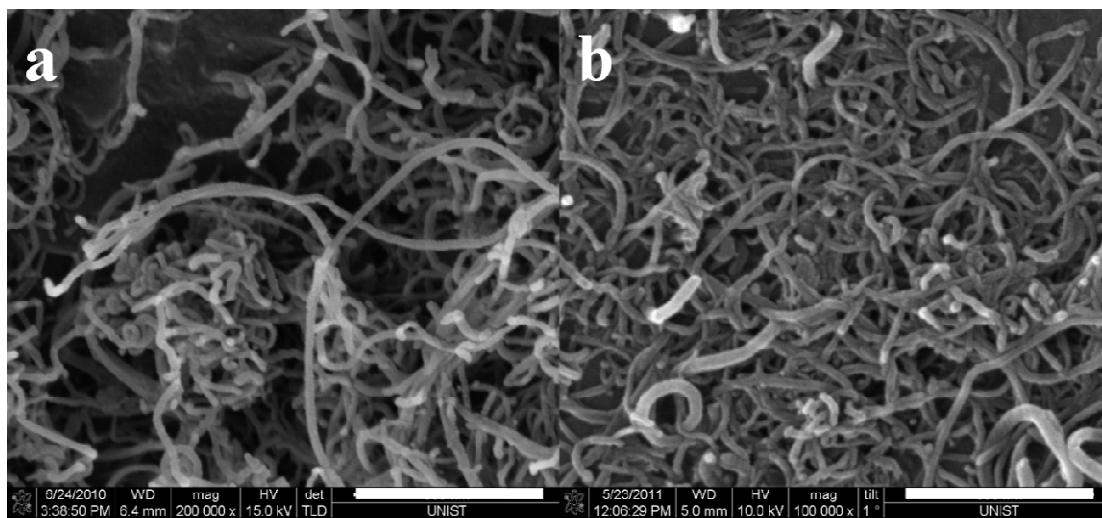


Figure S6. SEM images: (a) pristine MWCNT; (b) SHPEK-g-MWCNT. Scale bars are 0.5 μ m.

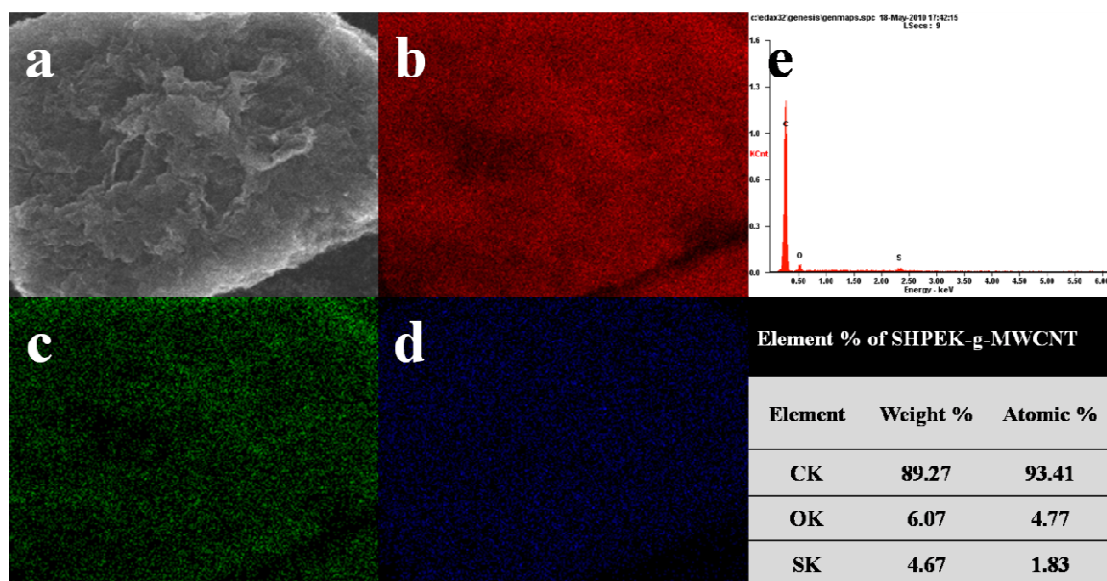


Figure S7. (a) SEM image of SHPEK-g-MWCNT; element mappings of SHPEK-g-MWCNT (b) C; (c) O; (d) S; (e) EDX spectrum and element percentages of SHPEK-g-MWCNT, indicating sulfur is uniformly distributed.

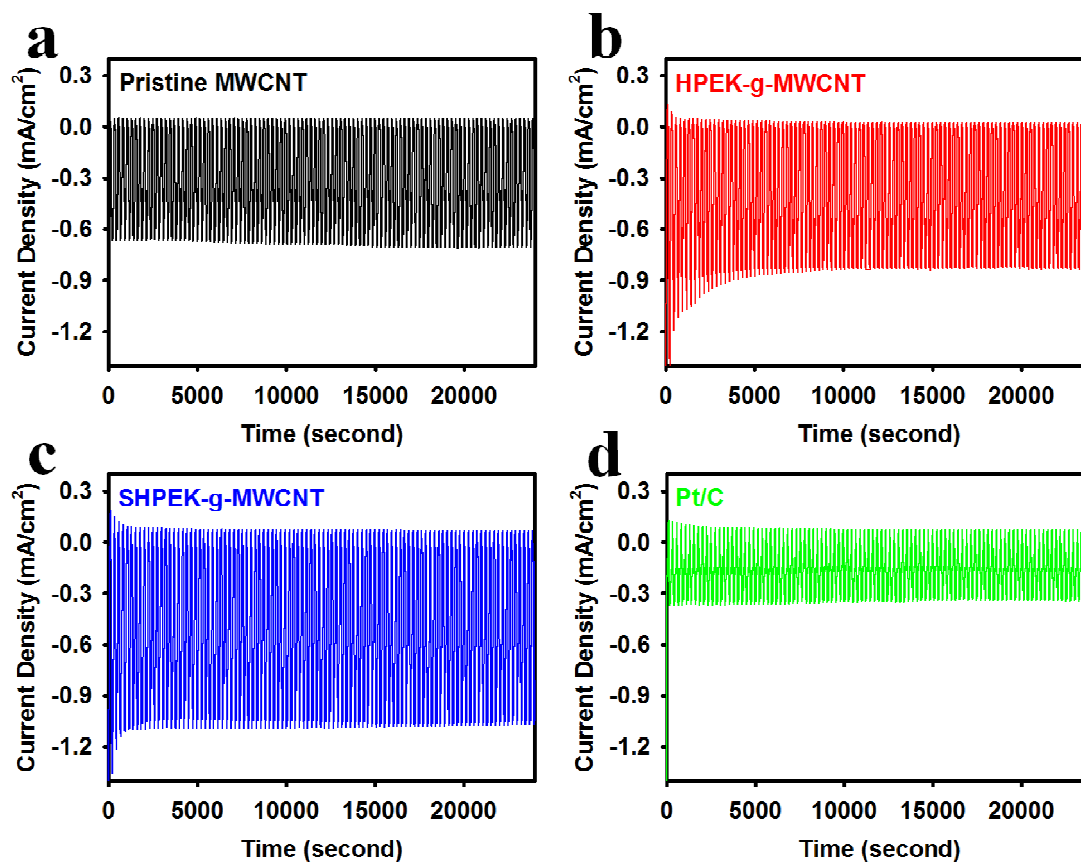


Figure S8. Current vs. time (*i-t*) curves obtained for 24,000 seconds showing cycling current stability: (a) pristine MWCNT; (b) HPEK-g-MWCNT; (c) SHPEK-g-MWCNT; (d) Pt/C.

Table S1. Elemental analysis of pristine MWCNT, HPEK-g-MWNCT and SHPEK-g-MWCNT

Sample		Elemental Analysis					
		C (%)	H (%)	O (%)	S (%)	C/H	C/S
Pristine MWCNT	Calc.	100.0	0.0	0.0	0.0		
	Found	98.2	0.3	BDL*	0.0	28	
S-MWCNT	Found	96.12	0.13	1.90	0.3		855
HPEK-g-MWCNT	Calc.	96.91	0.66	2.42	0.0		
	Found	94.95	0.65	4.39	0.0		
SHPEK-g-MWCNT	Calc.	91.41	0.85	5.80	1.94		
	Found	86.21	0.76	9.03	2.07		85

* BDL = below detection limit.

Table S2. The relationship between Zeta potential and colloidal stability¹

Zeta Potential [mV]	Stability behavior of the colloid
from 0 to ± 5	Rapid coagulation or flocculation
from ± 10 to ± 30	Incipient instability
from ± 30 to ± 40	Moderate stability
from ± 40 to ± 60	Good stability
more than ± 61	Excellent stability

¹ http://en.wikipedia.org/wiki/Zeta_potential

Table S3. Onset potential, current density, and capacitance (F/g) obtained from the 50th cycle of CV in nitrogen- and oxygen-saturated 0.1 M KOH solution

Sample	Onset Potential (V)	Current Density (mA/cm ²)	Capacitance (F/g)	
			N ₂	O ₂
Pristine MWCNT	-0.22	-0.66	22.5	60.0
HPEK-g-MWCNT	-0.22	-0.87	36.1	68.0
SHPEK-g-MWCNT	-0.18	-1.10	54.8	151.0
Pt/C (Vulcan XC-72R)	-0.06	-0.37	81.0	85.1

Table S4. Kinetic current (j_k) and average number of electrons transferred for oxygen reduction (n_i) at different potentials for heat-treated graphene in oxygen-saturated 0.1 M KOH solution

Sample	i	E_i (V) vs Ag/AgCl	n_i
Pristine MWCNT	1	-0.4	2.0
	2	-0.5	2.0
	3	-0.6	2.1
HPEK-g-MWCNT	1	-0.4	2.0
	2	-0.5	2.0
	3	-0.6	2.1
SHPEK-g-MWCNT	1	-0.4	3.7
	2	-0.5	3.7
	3	-0.6	3.8
Pt/C (Vulcan XC-72R)	1	-0.4	4.0
	2	-0.5	4.0
	3	-0.6	3.9