Electronic Supplementary Information of

Optical Sensitivity of Mussel Protein-Coated Double-Walled Carbon Nanotube on Iron-DOPA Conjugation Bond

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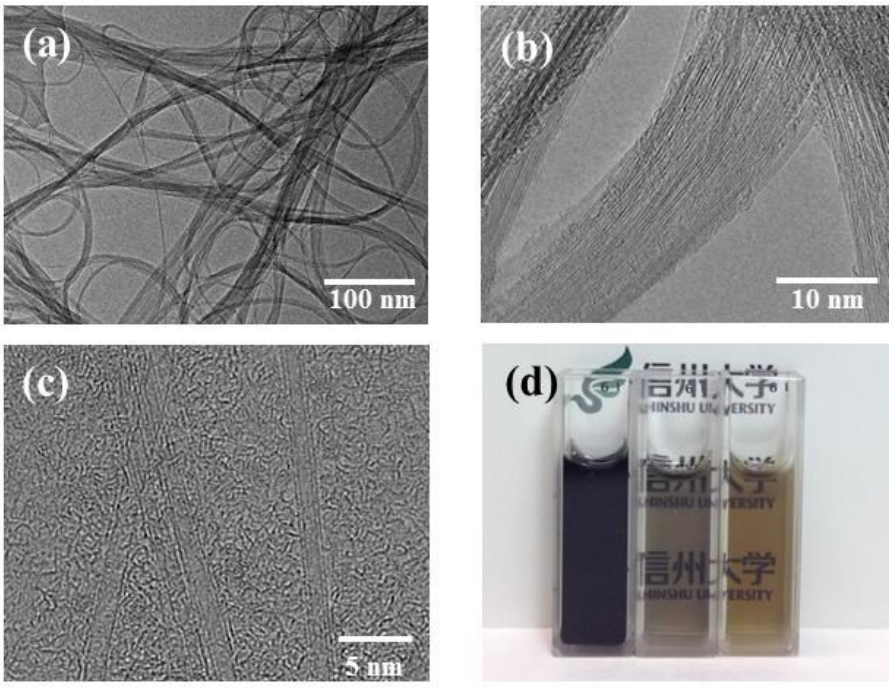

Figure S1. TEM images of (a, b) pristine bundled DWNTs at different magnifications and (c) $FeCl_3$ solution added-MAP-dispersed DWNT supernatant. (d) The sonicated opaque DWNT suspension (left), the following ultra-centrifuged semi-transparent MAP-dispersed DWNT supernatant (middle), and after adding 100 μl of $FeCl_3$ solution (100 mM) to the MAP-dispersed DWNT supernatant.

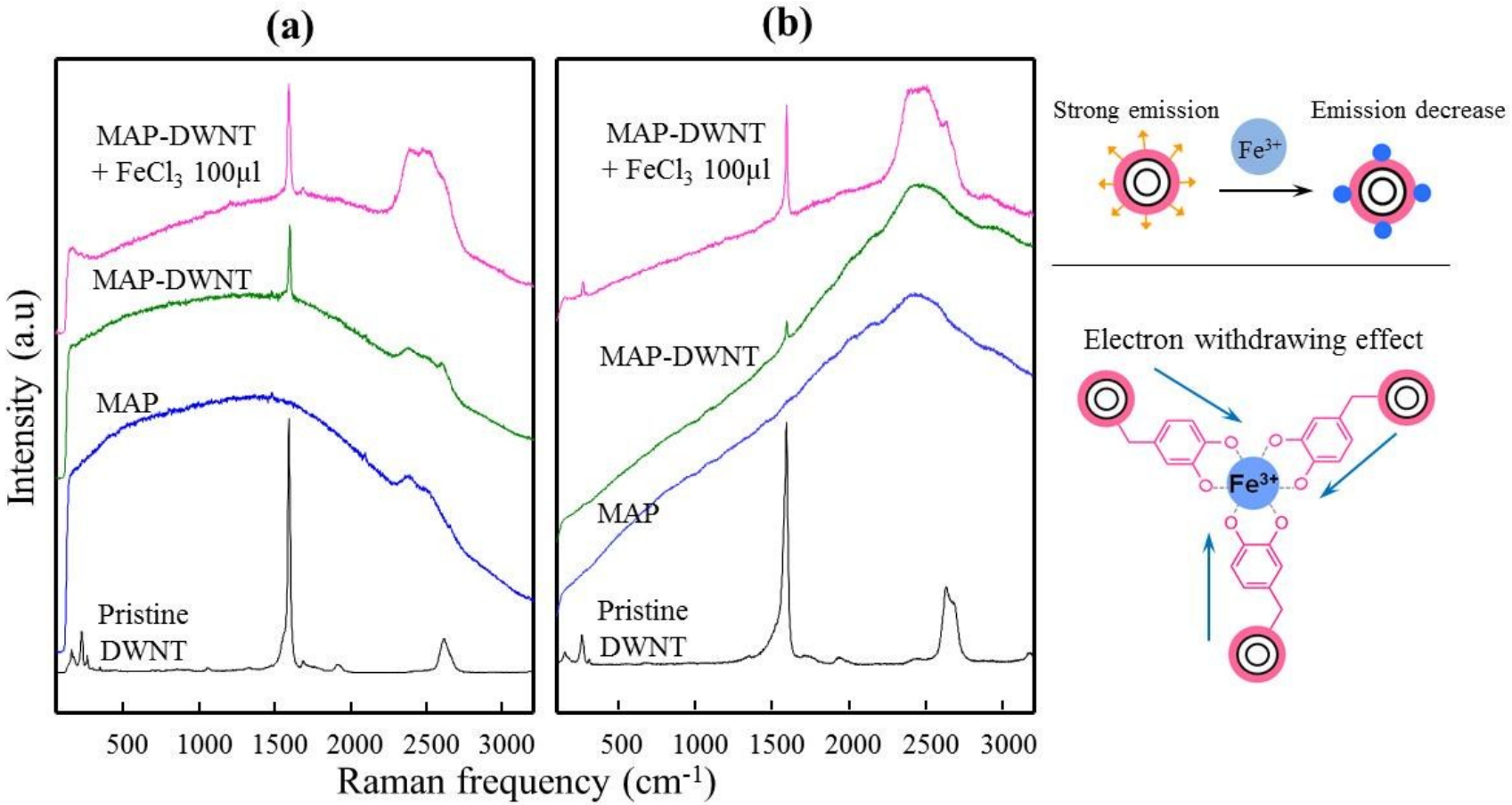

Figure S2. Raman/fluorescence spectra taken with laser excitation wavelengths of (a) 633 nm and (b) 532 nm for pristine DWNTs and MAP-dispersed DWNT solutions at different dispersion states (remnant (blue), supernatant (green), and after adding $FeCl_3$ solution (pink)).

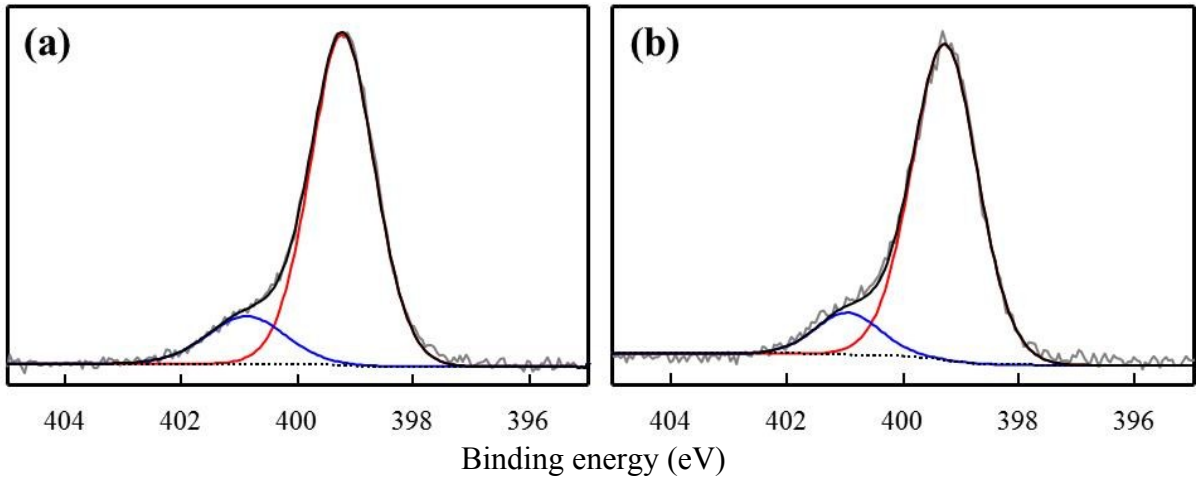

Figure S3. The XPS spectra of N1s of (a) MAP-DWNT and (b) Fe-MAP-DWNT sample (note that the concentration and amount of $FeCl_3$ solution were 100 mM and 30 μl).

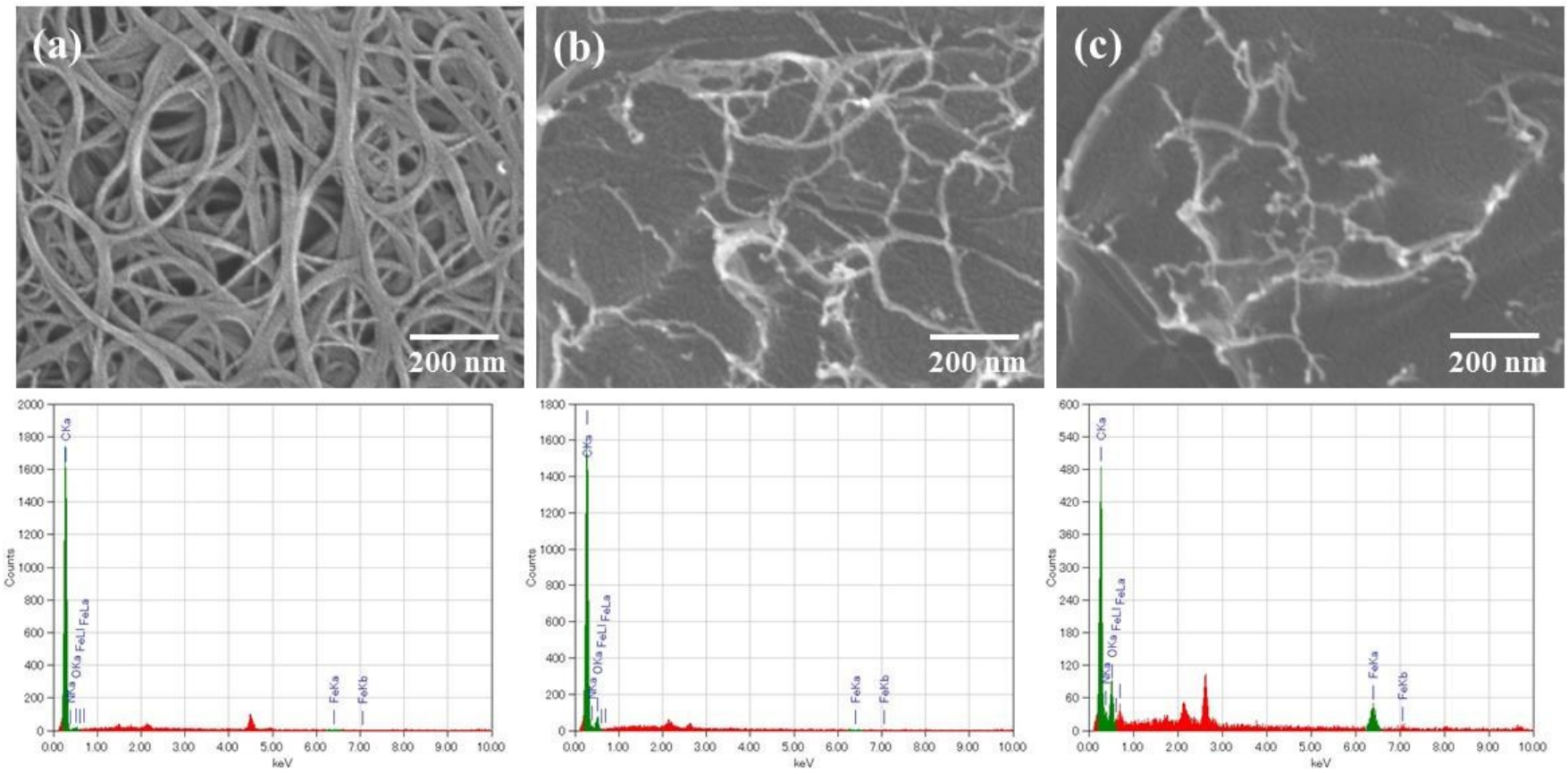

Figure S4. SEM images and EDS measurements of (a) pristine DWNT, (b) MAP-DWNT and (c) MAP-DWNT with $FeCl_3$ (50µl) solution. All samples were prepared by buckypaper through filtration with an Omnipore membrane filter (JVWP 0.1 µm).

Table S1. Structures and first van Hove optical transitions for semiconducting SDBS- and MAP-dispersed DWNTs from the obtained Raman/fluorescence spectra.

Assignment (n,m)	SDBS-DWNT			MAP-DWNT			$\Delta\lambda$ [c] (nm)	ΔE [d] (eV)
	ω (cm^{-1})	λ (nm)	E (eV) [a]	ω (cm^{-1})	λ (nm)	E (eV) [b]		
(7,5)	2995.4	1026.3	1.209	3142.4	1042.1	1.191	15.7	-0.018
(6,5)	2529.7	979.5	1.267	2681.1	994.3	1.248	14.7	-0.019
(8,3)	2289.1	957.0	1.297	2460.0	972.9	1.275	15.9	-0.021
(9,1)	1810.2	915.0	1.356	1991.2	930.4	1.334	15.4	-0.022
(6,4)	1368.4	879.5	1.411	1513.8	890.9	1.393	11.4	-0.018
(5,4)	716.3	831.8	1.492	902.8	844.9	1.469	13.1	-0.023

[a,b] Band-gap values were calculated from the absorption wavelength by the following equations: $E=hc/\lambda$, (E: band gap, h : Planck's constant, c : speed of light in vacuum, and λ : wavelength); [c] The shifts of absorption wavelength ($\Delta\lambda_{ii}=\lambda_{ii}^{\text{MAP-DWNT}}-\lambda_{ii}^{\text{SDBS-DWNT}}$) are calculated; [d] The energy differences ($\Delta E_{ii}=E_{ii}^{b}-E_{ii}^{a}$) are calculated.

Table S2. Structures and first and second van Hove optical transitions for semiconducting SDBS- and MAP-dispersed DWNTs from the obtained UV-Vis-NIR spectra.

Van Hove transitions	SDBS-DWNT		MAP-DWNT		$\Delta\lambda$ [c] (nm)	ΔE_{ii} [d] (eV)	d_t (nm)	Assignment (n,m)
	λ_{ii} (nm)	E_{ii} (eV) [a]	λ_{ii} (nm)	E_{ii} (eV) [b]				
	1248	0.994	1281	0.969	33	-0.026	1.050	(10,5)
	1178	1.053	1198	1.036	20	-0.018	0.995	(12,1)
	1114	1.114	1137	1.091	23	-0.023	0.916	(9,4)
Semi	1058	1.173	1077	1.152	19	-0.021	0.884	(10,2)
-conducting	1026	1.209	1045	1.187	19	-0.022	0.829	(7,5)
(E_{11})	978	1.269	997	1.245	19	-0.024	0.757	(6,5)
	955	1.299	974	1.274	19	-0.025	0.782	(8,3)
	913	1.359	931	1.333	18	-0.026	0.757	(9,1)
	872	1.423	884	1.404	12	-0.019	0.692	(6,4)
	801	1.549	807	1.538	6	-0.012	0.995	(12,1)
	794	1.563	803	1.545	9	-0.018	1.05	(10,5)
							1.103	(9,7)
Semi-	734	1.690	739	1.679	5	-0.011	1.032	(8,7)
conducting							0.966	(8,6)
(E_{22})	675	1.838	677	1.833	2	-0.005	1.041	(12,2)
	646	1.921	652	1.903	6	-0.018	0.895	(7.5)
							0.829	(7,6)
	589	2.107	594	2.089	5	-0.018	0.840	(8,4)

[a,b]Band-gap was calculated from absorption wavelength by the following equations: $E=hc/\lambda$, (E: band gap, c : speed of light in vacuum, h : Planck's constant, and λ : wavelength); [c] The shifts of absorption wavelength ($\Delta\lambda_{ii}=\lambda_{ii}^{\text{MAP-DWNT}}-\lambda_{ii}^{\text{SDBS-DWNT}}$) are calculated; [d] The energy differences ($\Delta E_{ii}=E_{ii}^{b}-E_{ii}^{a}$) are calculated.

Table S3. The weight (wt %) and molar (mol %) ratio of Fe^{3+} with MAP for MAP-dispersed DWNT supernatant when adding different amounts of $FeCl_3$ solution (100 mM).

$FeCl_3$ Solution (μl)	Fe^{3+}		MAP [a]		Fe^{3+} / MAP	
	mg	μmol [b]	mg	μmol [b]	wt %	mol %
10	0.06	1.00	3	0.13	1.86	753.33
20	0.11	2.00	3	0.13	3.72	1506.67
30	0.17	3.00	3	0.13	5.58	2260.00
40	0.22	4.00	3	0.13	7.45	3013.33
50	0.28	5.00	3	0.13	9.31	3766.67
70	0.39	7.00	3	0.13	13.03	5273.33
100	0.56	10.00	3	0.13	18.61	7533.33

[a] 3 ml of MAP-dispersed DWNT supernatant was used in this experiment. The concentration of MAP was 1 mg/ml.

[b] The atomic weight of Fe^{3+} and MAP is 55.84 g/mol and 22,600 g/mol, respectively.