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Supporting Information File

An Insight into Outer- and Inner- Sphere Electrochemistry on Oxygenated Single-Walled Carbon Nanohorns (*o*-SWCNHs)

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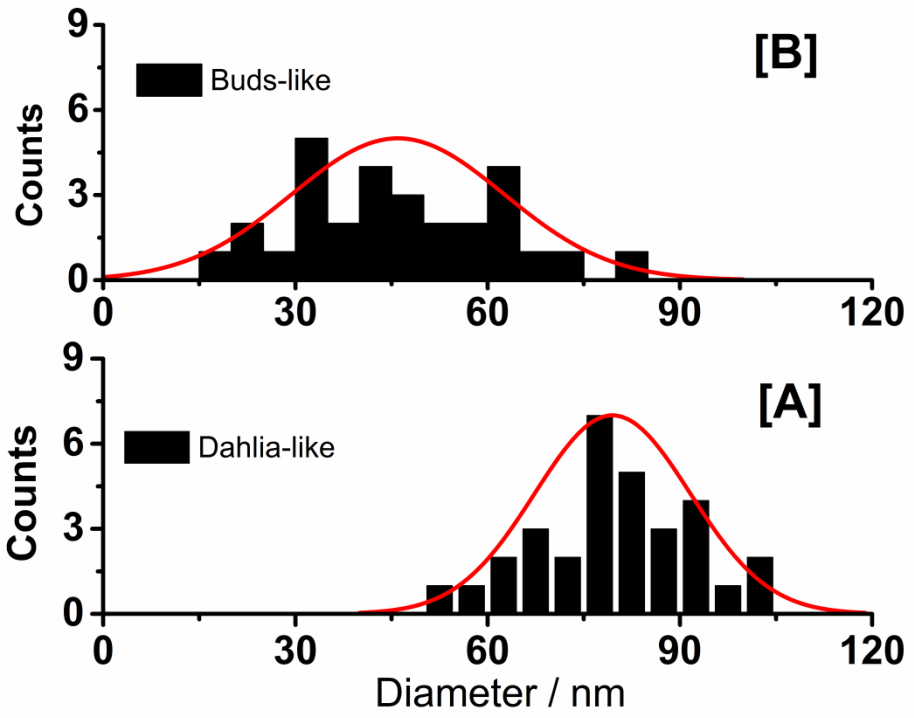

Fig. S1 *The histograms of the diameters of the* ***[A]*** *dahlia-like and* ***[B]*** *bud-like aggregates calculated from Fig. 1[A].*

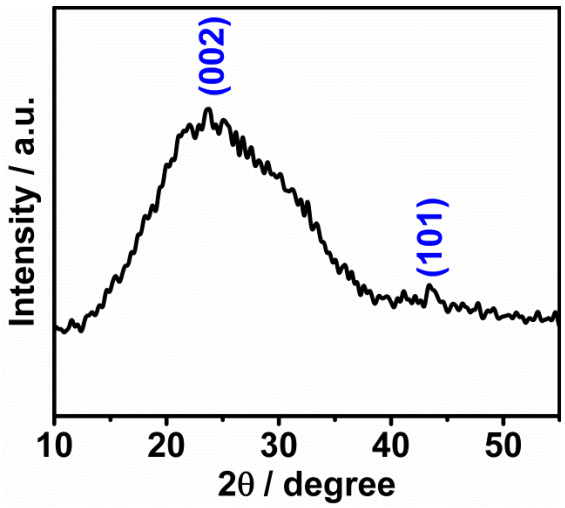

Fig. S2 *The XRD pattern of o-SWCNH.*

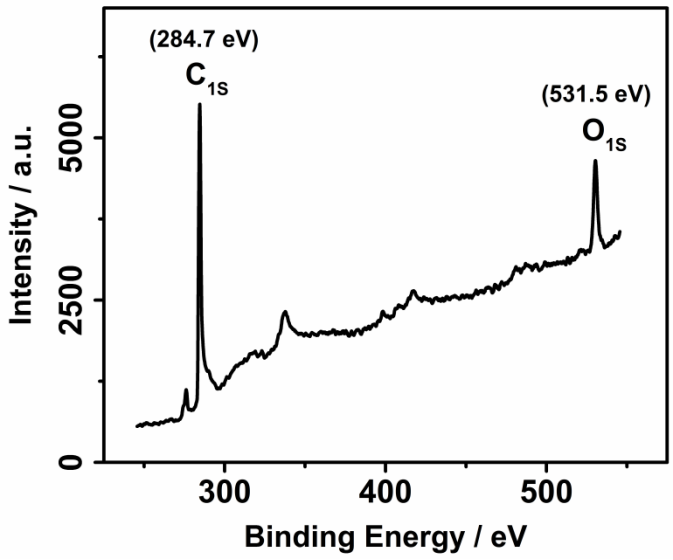

Fig. S3 The XPS survey spectrum of *o*-SWCNH.

Table S1 *The peak parameters of the CVs of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl on GC and o-SWCNH/GC.*

Scan Rate / mV s^{-1}	GC					*o*-SWCNH/GC				
	E_p^a / V	E_p^c / V	ΔE_p / V	I_p^a / µA	I_p^c / µA	E_p^a / V	E_p^c / V	ΔE_p / V	I_p^a / µA	I_p^c / µA
25	0.2978	0.2276	0.0702	46.8	-46.0	0.2950	0.2330	0.0620	53.8	-51.5
50	0.2982	0.2260	0.0722	65.5	-64.8	0.2960	0.2330	0.0630	75.1	-73.3
75	0.2997	0.2260	0.0737	79.8	-78.8	0.2970	0.2320	0.0650	90.6	-89.7
100	0.3004	0.2250	0.0754	91.4	-90.9	0.2980	0.2310	0.0670	105.3	-103.2
150	0.3018	0.2240	0.0778	110.8	-109.9	0.2990	0.2300	0.0690	128.8	-115.1
200	0.3022	0.2230	0.0792	127.5	-126.2	0.3000	0.2290	0.0710	148.6	-146.2
250	0.3030	0.2220	0.0810	142.0	-140.4	0.3010	0.2280	0.0730	166.0	-163.5
300	0.3035	0.2217	0.0818	154.1	-153.3	0.3020	0.2270	0.0750	182.6	-180.0

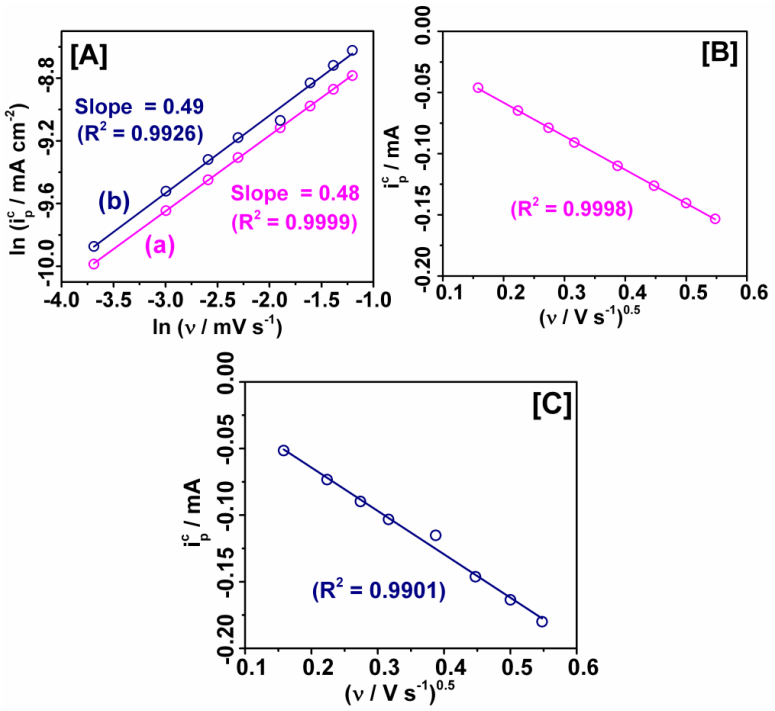

Fig. S4 [A] *Plot of ln(I_p^c) versus ln(ν) for the redox reaction of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in 0.1 M KCl (pH 6.8) on* ***(a)*** *GC and* ***(b)*** *o-SWCNH/GC. Plots of i_p^c versus $\upsilon^{\frac{1}{2}}$ for the same reaction on* ***[B]*** *GC and* ***[C]*** *o-SWCNH/GC electrodes.*

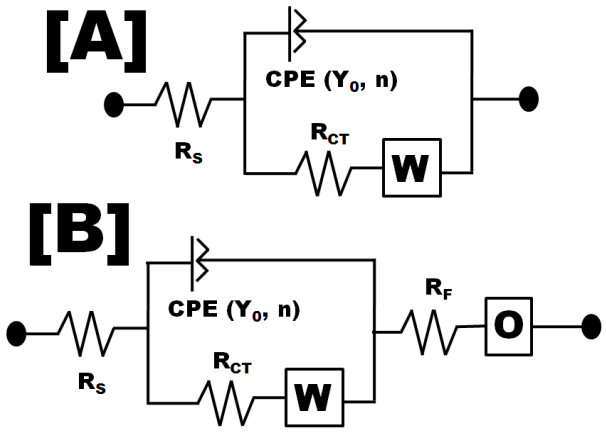

Fig. S5 *The electrical equivalent circuits fitted with the impedance data of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl on* ***[A]*** *GC and* ***[B]*** *o-SWCNH/GC.*

Table S2 *The values of the elements of electrical equivalent circuits fitted with the impedance data of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl on* ***[A]*** *GC and* ***[B]*** *o-SWCNH/GC. The potential was kept constant at 0.263 V with sine potential perturbation with amplitude of 5 mV in the frequency range 1×10^5 to 1×10^{-1} Hz.*

Electrode	R_s / Ω	R_{CT} / Ω	CPE		W	R_F / Ω	O		χ^2
			Q_0 / mMho	n'	Y_0 / mMho		Y_0 / mMho	B	
GC	23.1	55.6	0.0011	0.88	1.07	-	-	-	0.0109
o-SWCNH/ GC	12.1	0.027	0.0001	0.73	1.19	12.07	6.09	0.033	0.0192

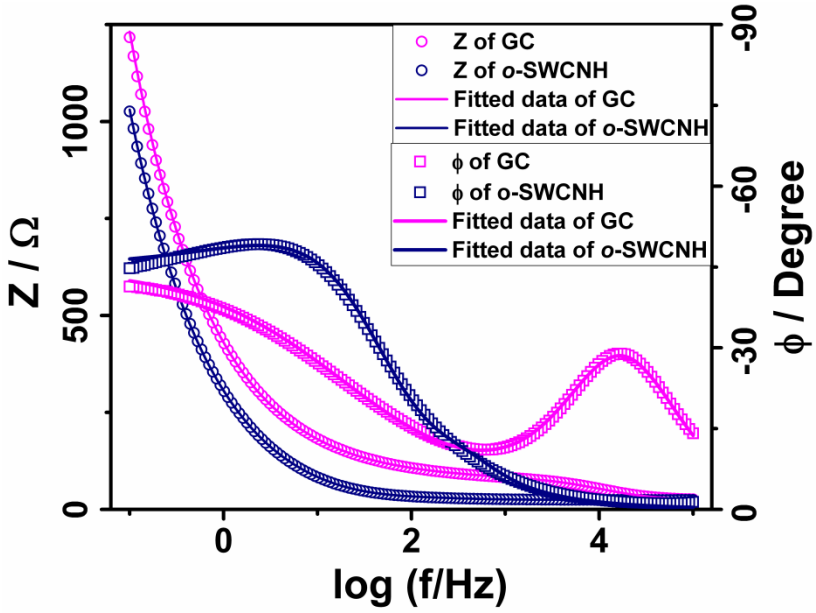

Fig. S6 *The Bode plots of modulus impedance (Z) and phase difference (φ) between the applied potential and recorded current of the electrochemical impedance spectra of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl on GC and o-SWCNH/GC.*

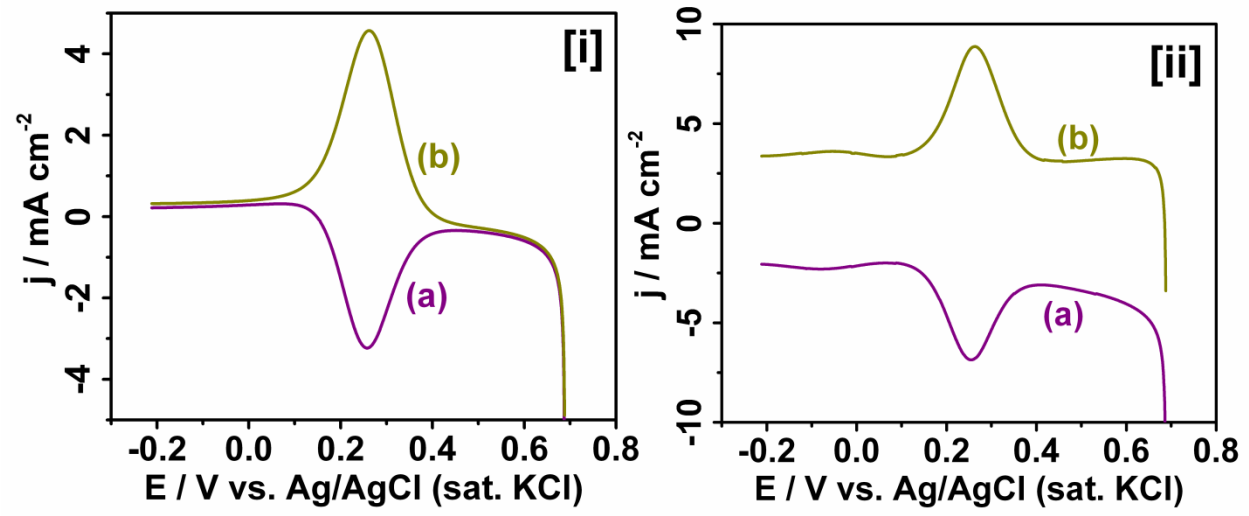

Fig. S7 *Current sampled during the application of* ***(a)*** *forward and* ***(b)*** *reverse pulses in the square wave voltammograms of* $[Fe(CN)_6]^{3-}$ *in 0.1 M KCl (pH 6.8) on* ***[i]*** *GC and* ***[ii]*** *o-SWCNH/GC.*

Table S3 *The peak parameters of the CVs of 5 mM* $[Ru(NH_3)_6]$ *in 0.1 M KCl on GC and o-SWCNH/GC.*

Scan Rate / mV s^{-1}	GC					*o*-SWCNH/GC				
	E_p^a / V	E_p^c / V	ΔE_p / V	I_p^a / µA	I_p^c / µA	E_p^a / V	E_p^c / V	ΔE_p / V	I_p^a / µA	I_p^c / µA
25	-0.095	-0.170	0.075	45.3	-45.1	-0.095	-0.176	0.081	42.6	-48.9
50	-0.093	-0.171	0.078	63.3	-62.8	-0.093	-0.180	0.087	54.1	-68.9
75	-0.091	-0.173	0.082	77.0	-76.1	-0.091	-0.183	0.092	64.4	-83.4
100	-0.089	-0.174	0.085	88.5	-87.9	-0.090	-0.186	0.096	71.1	-96.2
150	-0.087	-0.177	0.090	106.8	-106.0	-0.086	-0.192	0.106	83.1	-118.6
200	-0.084	-0.179	0.095	121.9	-123.1	-0.084	-0.196	0.112	89.9	-137.5
250	-0.083	-0.181	0.098	135.9	-136.2	-0.081	-0.201	0.120	99.8	-151.9
300	-0.082	-0.183	0.101	148.6	-148.4	-0.079	-0.204	0.125	109.8	-167.2

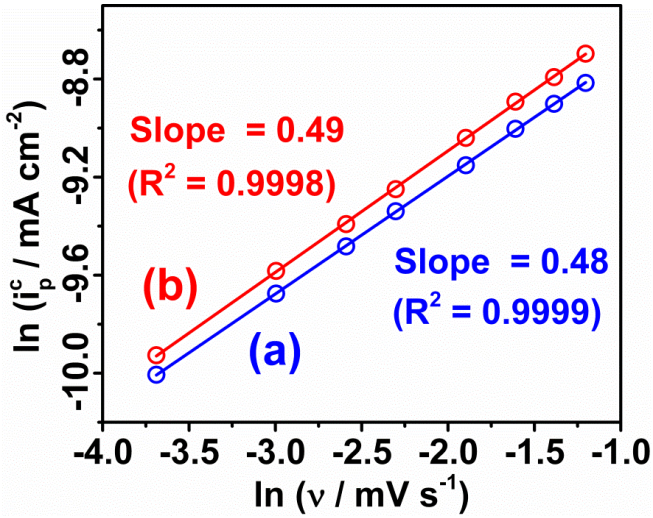

Fig. S8 *Plot of ln(I_p^c) versus ln(ν) for the redox reaction of $[Ru(NH_3)_6]^{3+}/[Ru(NH)_3]^{2+}$ in 0.1 M KCl on* ***(a)*** *GC and* ***(b)*** *o-SWCNH/GC.*

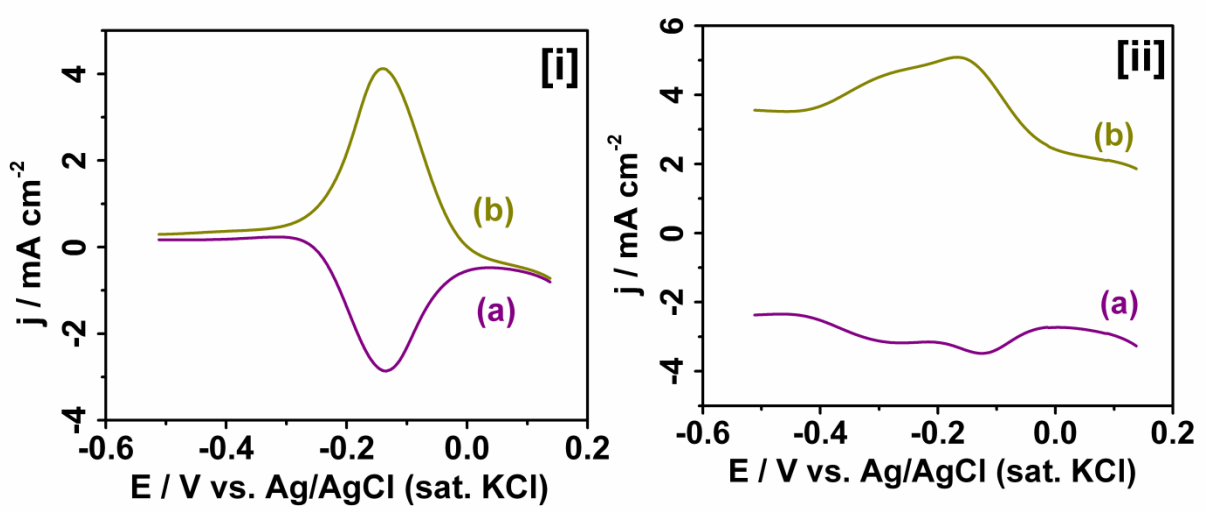

Fig. S9 *Current sampled during the application of* ***(a)*** *forward and* ***(b)*** *reverse pulses in the square wave voltammograms of $[Ru(NH_3)_6]^{3+}$ in 0.1 M KCl (pH 6.8) on* ***[i]*** *GC and* ***[ii]*** *o-SWCNH/GC.*

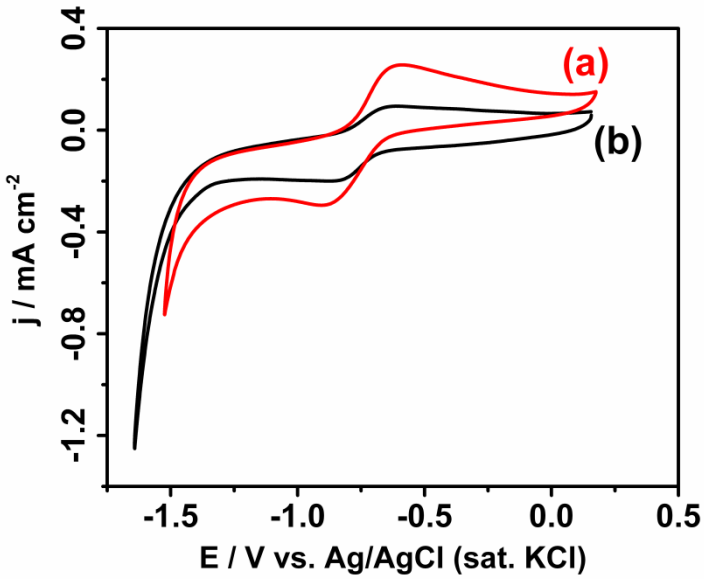

Fig. S10 *CVs of 0.8 mM* $[U^{(VI)}O_2(CO_3)_3]^{4-}$ *in sat.* Na_2CO_3 *(pH 10.9) on* ***(a)*** *o-SWCNH/GC and* ***(b)*** *electrochemically reduced o-SWCNH/GC at* $v = 25\ mV\ s^{-1}$.

Table S4 *The impedance parameters of 0.8 mM* $[U^{(VI)}O_2(CO_3)_3]^{4-}$ *in sat.* Na_2CO_3 *(pH 10.9) on GC and o-SWCNH/GC obtained by fitting the experimentally obtained impedance data with Randles EEC. The potential was kept constant at -0.742 V with sine potential perturbation with amplitude of 10 mV in the frequency range* 1×10^{5} *to* 1×10^{-2} *Hz.*

Parameters		**GC**	***o*-SWCNH/GC**
R_s / Ω		19.1	25.9
R_{ct} / kΩ		181	3.47
CPE	**Y_0 / µMho**	2.14	69.9
	n	0.86	0.87
W	**Y_0 / µMho**	9.9	509
χ^2		0.6451	0.1001

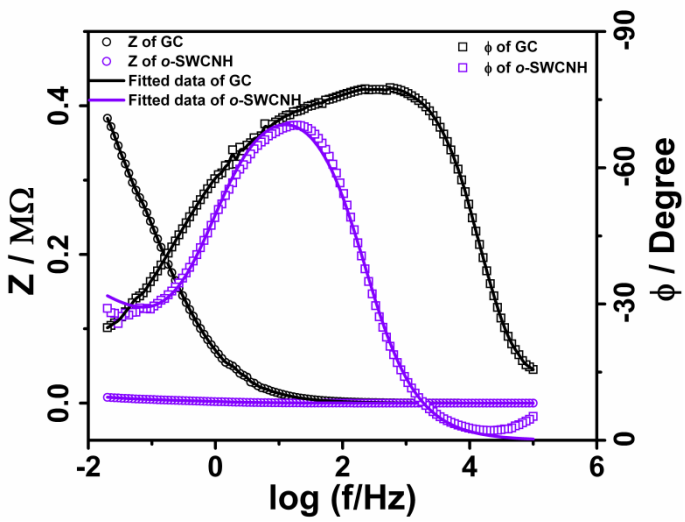

Fig. S11 *The Bode plots of modulus impedance (Z) and phase difference (φ) between the applied potential and recorded current of the electrochemical impedance spectra of 0.8 mM* $[U^{(VI)}O_2(CO_3)_3]^{4-}$ *in sat.* Na_2CO_3 *on GC and o-SWCNH/GC.*

Table S5 *The peak parameters of the CVs of 0.8 mM* $[U^{(VI)}O_2(CO_3)_3]^{4-}$ *in sat.* Na_2CO_3 *on GC and o-SWCNH/GC.*

Scan Rate / mV s^{-1}	GC					*o*-SWCNH/GC				
	E_p^a / V	E_p^c / V	ΔE_p / V	j_p^a / mA cm^{-2}	j_p^c / mA cm^{-2}	E_p^a / V	E_p^c / V	ΔE_p / V	j_p^a / mA cm^{-2}	j_p^c / mA cm^{-2}
25	-0.218	-1.265	1.047	0.10	-0.19	-0.588	-0.906	0.318	0.23	-0.26
50	-0.174	-1.321	1.147	0.15	-0.25	-0.547	-0.927	0.380	0.31	-0.33
75	-0.149	-1.346	1.197	0.19	-0.31	-0.523	-0.941	0.418	0.37	-0.37
100	-0.129	-1.370	1.241	0.21	-0.35	-0.504	-0.960	0.456	0.42	-0.42
150	-0.105	-1.390	1.285	0.26	-0.42	-0.476	-0.976	0.500	0.46	-0.49
200	-0.085	-1.407	1.322	0.29	-0.48	-0.455	-0.996	0.541	0.52	-0.53
250	-0.070	-1.417	1.347	0.33	-0.53	-0.431	-1.025	0.594	0.57	-0.58
300	-0.055	-1.428	1.373	0.35	-0.57	-0.410	-1.050	0.640	0.60	-0.61

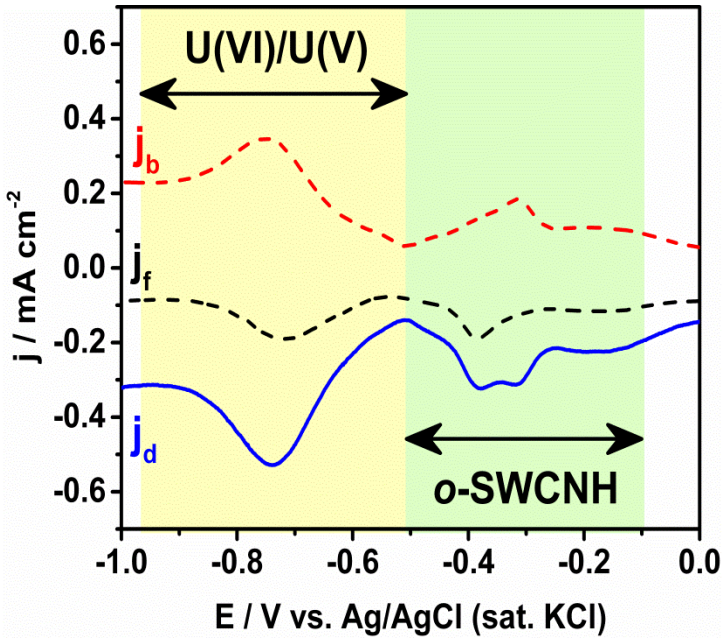

Fig. S12 *The forward (i.e., cathodic, j_f), backward (i.e., anodic, j_b) and difference (i.e., $j_d = j_f - j_c$) current densities in the cathodic square wave voltammogram of 0.8 mM $[U^{(VI)}O_2(CO_3)_3]^{4-}$ in sat. Na_2CO_3 (pH 10.9) on o-SWCNH at amplitude and frequency 0.05 V and 50 Hz, respectively.*