Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The Electrocatalytic Characterization and Mechanism of Carbon Nanotubes with Different Number of Walls for the VO_2^+/VO^{2+} Redox Couple

Zhaoqian Lv[¶,a], Jin Zhang[¶,a], Yang Lv[a], Yi Cheng[b], San Ping Jiang[b], Yan Xiang[a], Shanfu Lu[a,*]

¶ This two authors contribute equally.

[a] Beijing Key Laboratory of Bio-inspired Materials and Devices & School of Space and Environment, Beihang University, Beijing, 100191, China

[b] Fuels and Energy Technology Institute & Department of Chemical Engineering, Curtin University, Perth, WA6102, Australia

Table S1 Metal impurities in as-received carbon nanotubes (CNTs) and purified CNTs by ICP-OES analysis.

CNTs		CNTs-1	CNTs-2	CNTs-3	CNTs-4	CNTs-5
As received W/W%	Ash	1.56	5.2	5.16	2.16	2.31
	Co	0.08	2.02	0.5	-	-
	Fe	0.43	2.06	0.35	0.28	0.54
	Mo	0.04	0.73	0.11	-	0.84
	Ni	0.08	0.04	0.019	0.25	0.21
Purified W/W%	Ash	1.21	2.15	2.28	2.08	1.83
	Co	0.07	0.57	0.38	-	-
	Fe	0.29	0.23	0.17	0.21	0.29
	Mo	0.03	0.27	0.09	0.01	0.49
	Ni	0.05	0.03	0.015	0.2	0.17

100 CNTs were randomly selected from TEM images for each CNTs category and the measured number of walls and diameter were listed in Table S1. The average value ($\bar{n}$) and the standard deviation (S_1) of wall number and average outer diameter ($\bar{OD}$) and the standard deviation (S_2) of each CNTs category were calculated from the measured data. More specifically, the results of mathematical statistics indicate that the proportion of single walled CNT in CNTs-1 is up to 79%, whilst the proportion of double walled CNT and triple walled CNT is 16% and 5%, respectively. For CNTs-1, the average wall number ($\bar{n}$) is 1.26 and the standard deviation(S_1) of the data is 0.54.

$$C.I. = \bar{n} \pm t \cdot s \qquad \text{Equation 1}$$

To describe the distribution of wall number thoroughly, the confidence interval (C.I.) should be taken into consideration. The value of t in Equation 1 is applied to specify the degree of certainty of the result. Confidence level of 95% is typically used in chemical analysis and the value of t is 1.96 when the number of data is 100. It is calculated that the interval is 1.26±1.06 for CNTs-1 and can precisely describe the

distribution of wall number in this sample. The distributions of wall number and outer diameter for each CNTs category are shown in Table S2.

Table S2 The detailed information on wall numbers(n), average wall numbers($\bar{n}$)and the standard deviation(s_1), average outer diameter ($\bar{OD}$) and standard deviation(s_2) of the five CNTs samples.

Catalysts	CNTs-1	CNTs-2	CNTs-3	CNTs-4	CNTs-5
Wall Number (n) and Proportion	1 (79%) 2 (15%) 3 (6%)	2 (25%) 3 (52%) 4 (14%) 5 (9%)	3 (5%) 4 (8%) 5 (11%) 6 (11%) 7 (28%) 8 (21%) 9 (16%)	8 (3%) 9 (6%) 10 (9%) 11 (14%) 12 (26%) 13 (24%) 14 (11%) 15 (8%) 16 (7%) 17 (2%)	26 (5%) 27 (4%) 28 (8%) 29 (12%) 30 (15%) 31 (11%) 32 (8%) 33 (6%) 34 (7%) 35 (9%) 36 (7%) 37 (4%) 38 (3%) 39 (1%)
$\bar{n}$	1.26	3.08	6.76	12.36	31.61
s_1	0.54	0.86	1.70	2.09	3.26
$\bar{n} \pm t \cdot s_1$	1.26 ± 1.06	3.08 ± 1.69	6.76 ± 3.33	12.36 ± 3.05	31.61 ± 6.39
$\bar{OD}$	1.97	3.80	6.90	13.8	35.2
s_2	0.40	0.63	0.98	5.2	8.5
$\bar{OD} \pm t \cdot s_2$	1.97±0.78	3.80 ± 1.23	6.90 ± 1.92	13.8 ± 10.2	35.2 ± 16.7

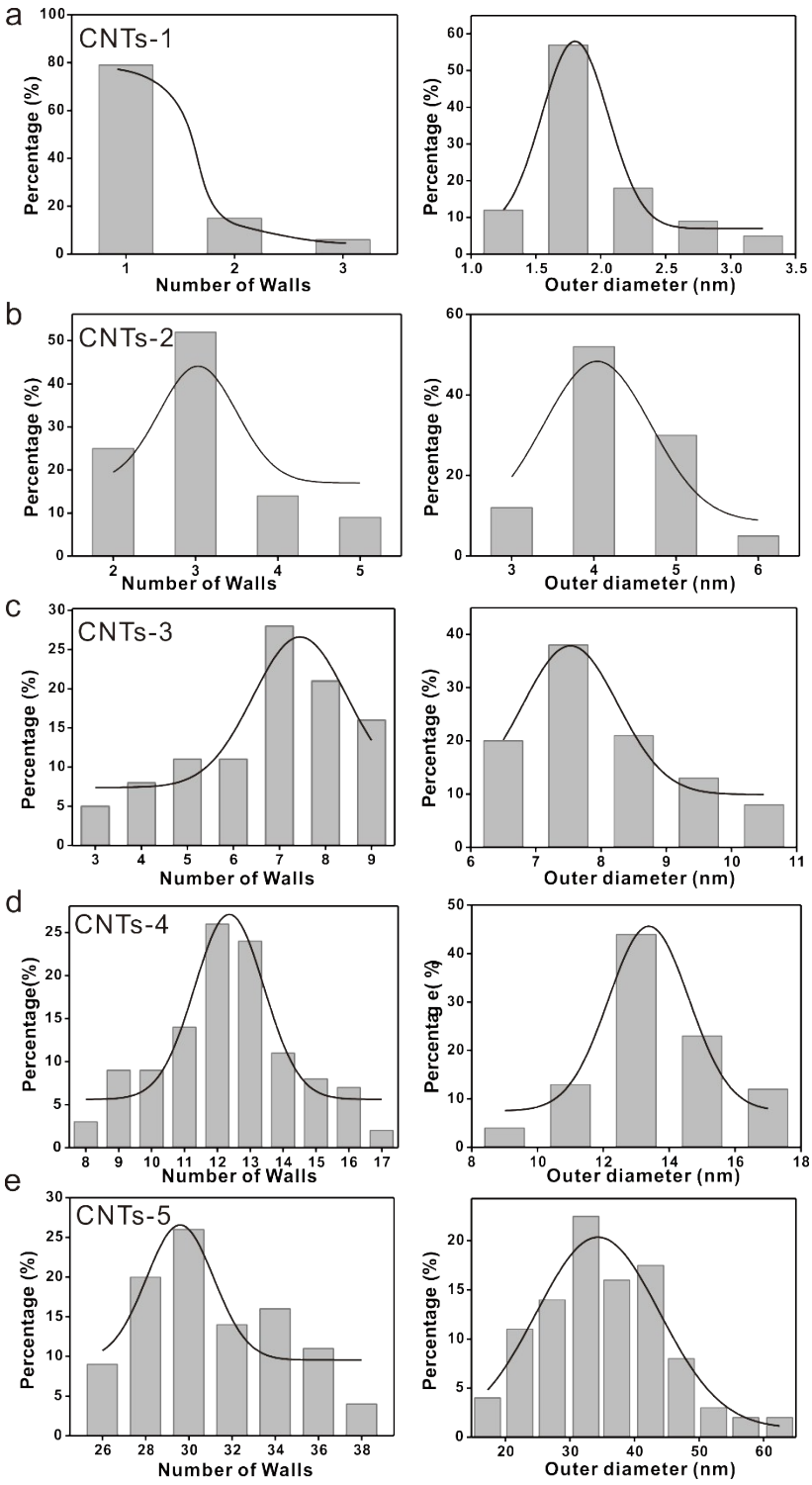

Figure S1 The distributions of the number of walls ($\bar{n}$) and outer diameter ($\bar{OD}$) of each CNTs category, (a) CNTs-1, (b) CNTs-2, (c) CNTs-3, (d) CNTs-4, (e) CNTs-5.

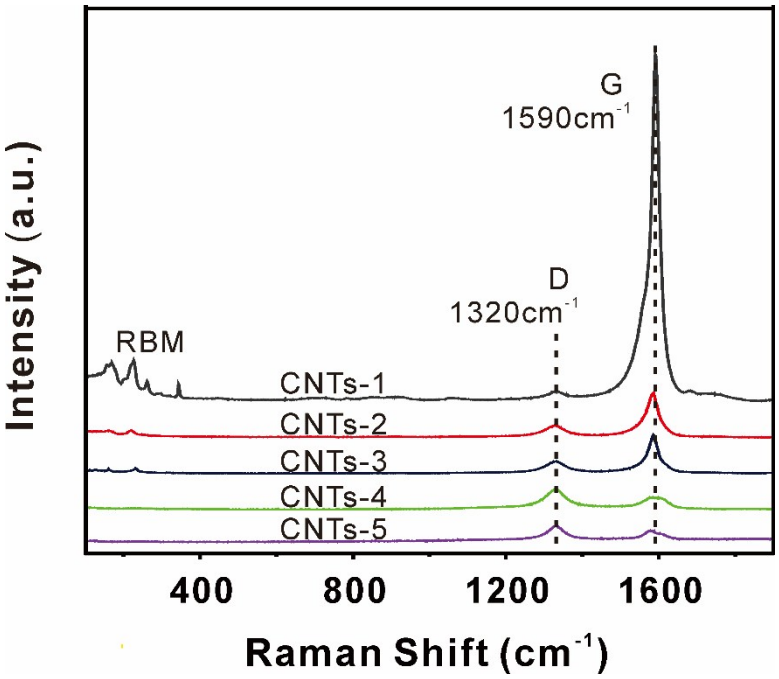

Figure S2 The Raman spectra of the CNTs samples.

To avoid the contamination of the samples, we carefully deposited the CNT samples on clean Au-coated silicon wafers.

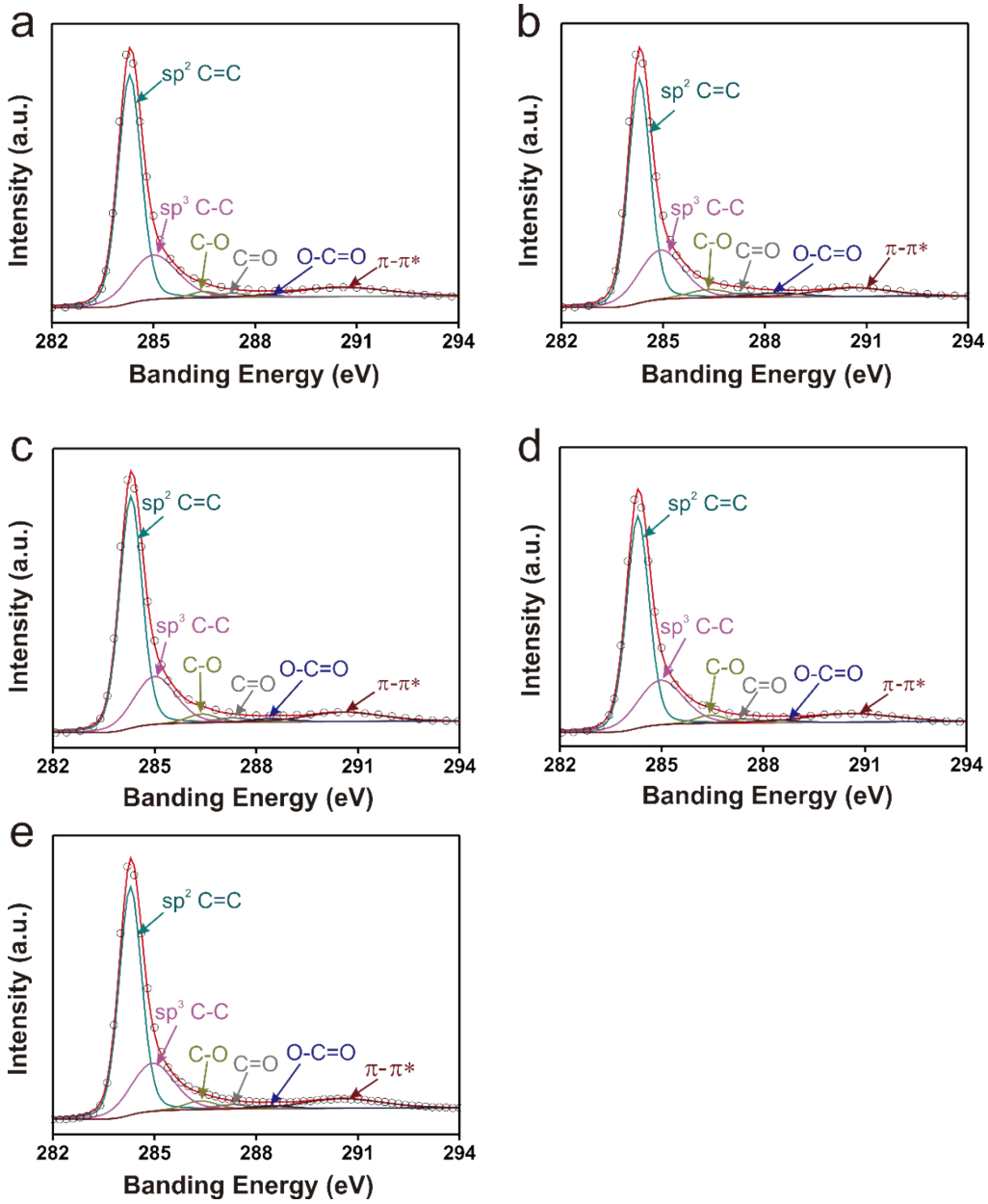

Figure S3 C1s core level XPS of (a) CNTs-1, (b) CNTs-2, (c) CNTs-3, (d)CNTs-4, (e) CNTs-5

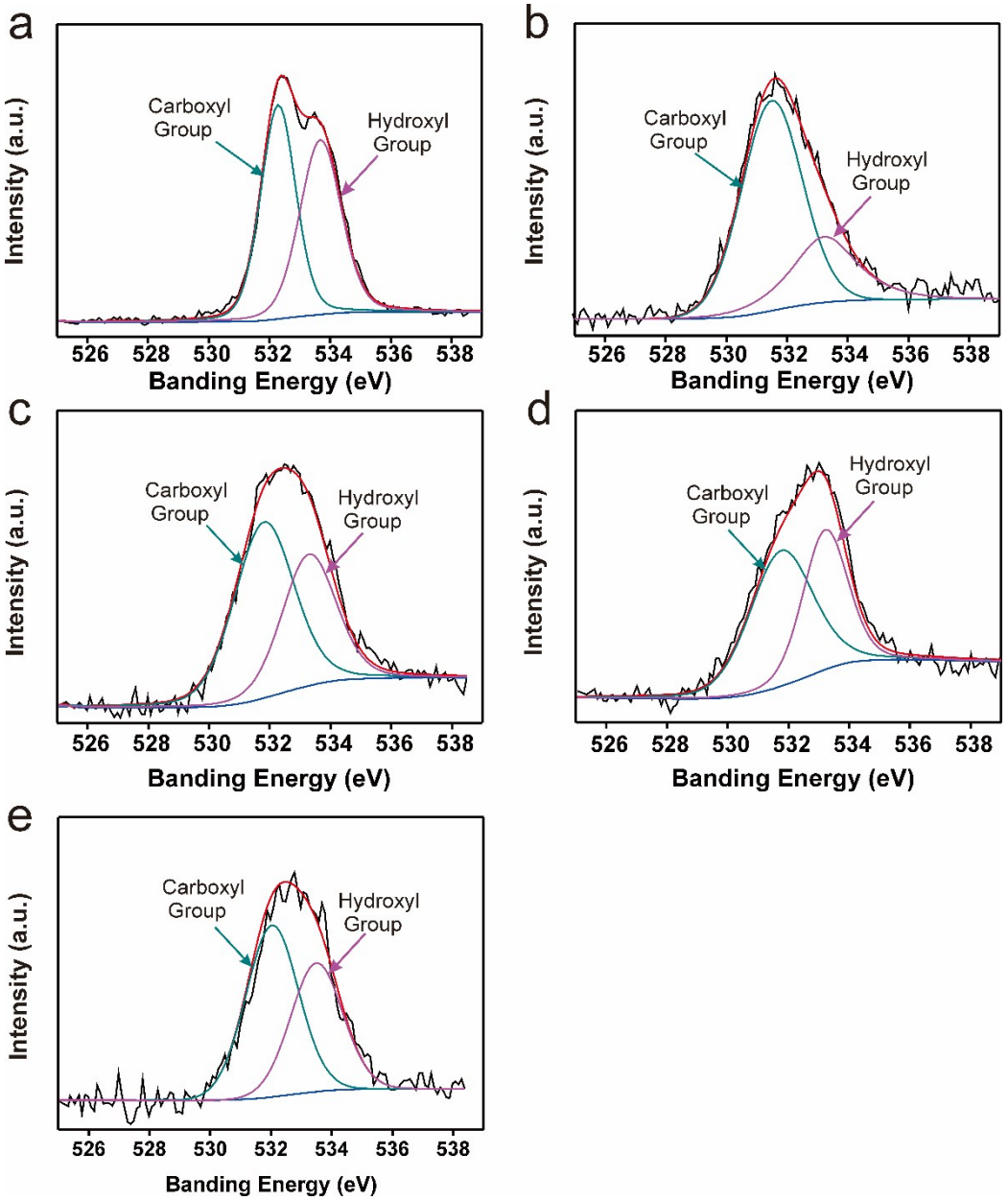

Figure S4 O1s core level XPS of (a) CNTs-1, (b) CNTs-2, (c) CNTs-3, (d) CNTs-4, (e) CNTs-5.

Table S3 The content (at. %) of carboxyl group obtained from the high resolution O1s spectrum.

Catalysts	CNTs-1	CNTs-2	CNTs-3	CNTs-4	CNTs-5
Carboxyl Group (at.%)	51.01	61.19	59.63	57.71	58.83

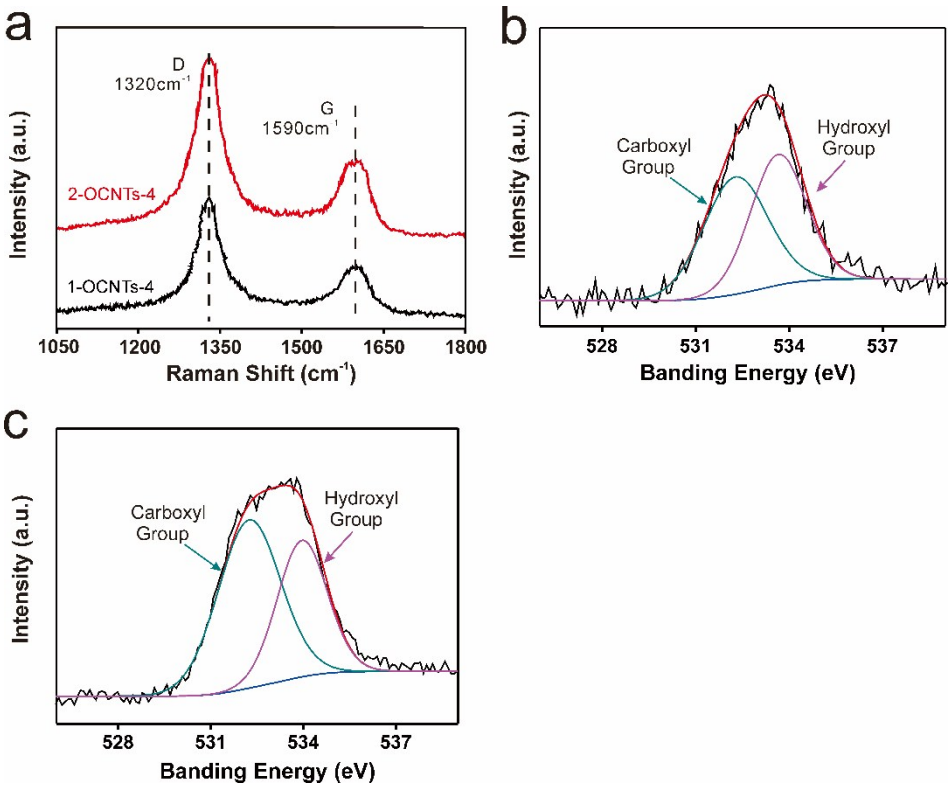

Fig. S5 (a) The Raman spectra of oxidized CNTs samples and the high resolution O1s XPS spectrum of (b) 1-OCNTs-4 and (c) 2-OCNTs-4, respectively.

Table S4 The value of I_D/I_G, the content (at. %) of carboxyl group of 1-OCNTs and 2-OCNTs-4.

CNTs	I_D/I_G	Carboxyl Groups (at. %)
CNTs-4	2.50	57.71
1-OCNTs-4	2.62	58.97
2-OCNTs-4	2.83	64.56

Table S5 The peak potential and peak current density value, ΔE_p, $|I_{pa}/I_{pc}|$ and R_{ct} of CNTs-4, 1-OCNTs-4 and 2-OCNTs-4 for theVO_2^+/VO^{2+} redox reaction.

Sample	E_1(V)	I_{pa}(mA mg^{-1})	E_2(V)	I_{pc}(mA mg^{-1})	ΔE_p	$\lvert I_{pa}/I_{pc}\rvert$	R_{ct}(Ω)
CNTs-4	0.929	38.5	0.753	-27.4	0.176	1.40	74.9
1-OCNTs-4	0.938	41.8	0.740	-27.7	0.198	1.51	95.6
2-OCNTs-4	0.942	45.4	0.733	-28.1	0.209	1.62	137.1

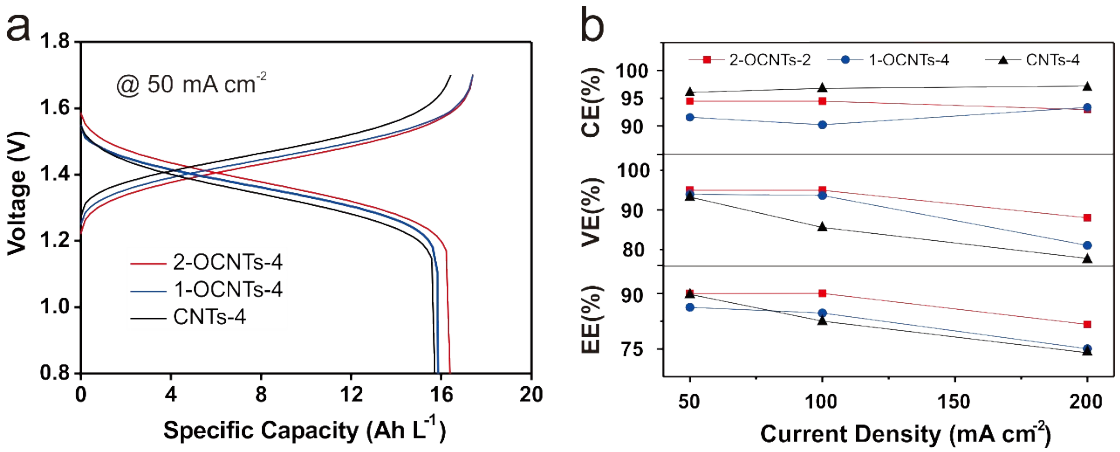

Fig. S6 (a) The charge/dscharge voltage profiles of VRFB cells based on CNTs at a current density of 50 mA cm^{-2}; (b) Coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) of VRFB cells based on oxidized CNTs-4 and CNTs at various current densities.

Three vanadium redox flow batteries were assembled and tested in a self-made device. The active area was 4 cm^{-2} of the single cell including a Nafion 212 membrane, a negative electrode and a positive electrode. The negative electrode was XC-72 modified carbon felt for all the three cells. The positive electrode was CNTs-4, 1-OCNTs-4 and 2-OCNTs-4 modified carbon felt for different cells. The loading of carbon materials on the carbon felt was 2 mg cm^{-2}. The positive and negative electrolytes were 1.5 mol L^{-1} VO^{2+} +3.0 mol L^{-1} H_2SO_4 and 1.5 mol L^{-1} V^{3+} + 3.0 mol L^{-1} H_2SO_4 solutions, respectively. The flow rate was 40 mL min^{-1} fed by peristaltic pumps. The cut-off voltage was between 1.7 V and 0.8 V for the charge and discharge tests.