

## Supplementary Material

# Opening the Structure for Transport of Ions: Improvement of the Structural and Chemical Properties of Single-walled Carbon Nanohorns for Supercapacitor Electrodes

*Wojciech Zieba,<sup>1</sup> Piotr Olejnik,<sup>2</sup> Stanisław Koter,<sup>3</sup> Piotr Kowalczyk,<sup>4</sup>*

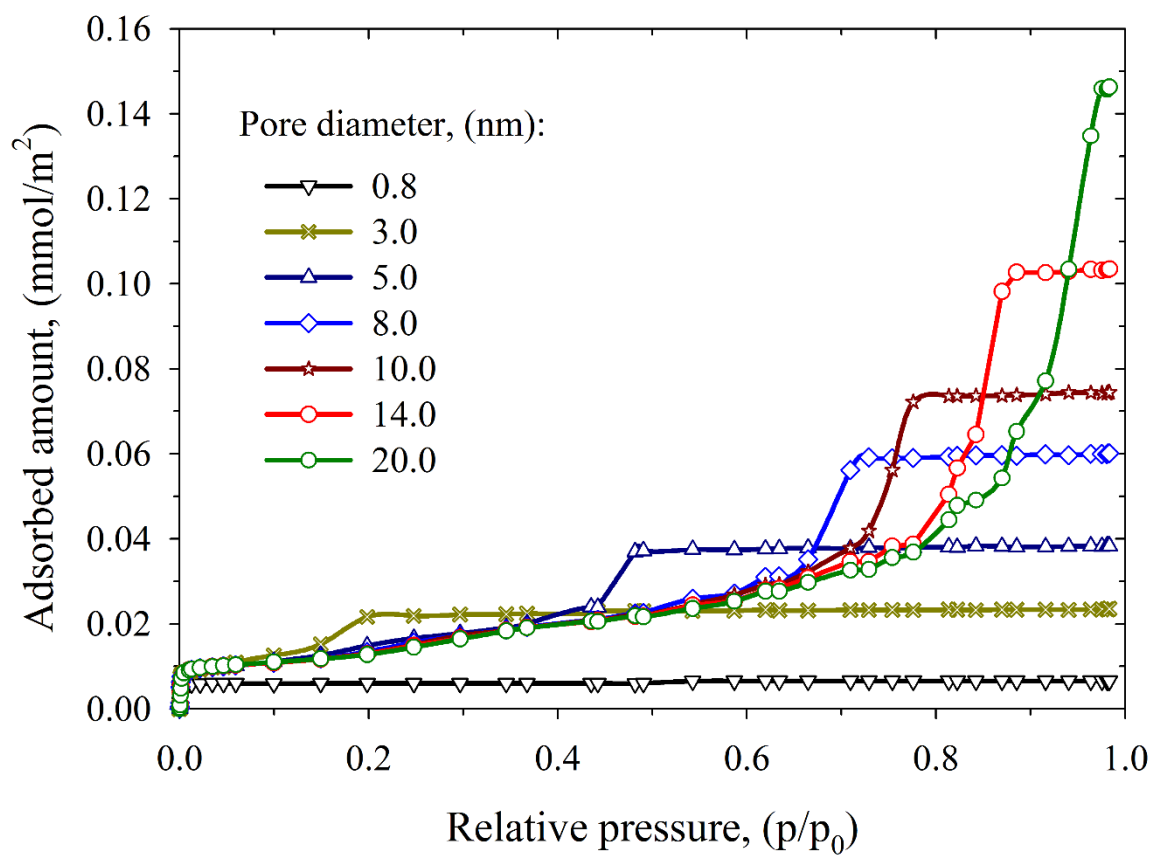
*Marta E. Plonska-Brzezinska<sup>2\*</sup> and Artur P. Terzyk<sup>1\*</sup>*

<sup>1</sup> Faculty of Chemistry, Physicochemistry of Carbon Materials Research Group, Nicolaus Copernicus University in Toruń, Gagarin Street 7, 87-100 Toruń, Poland

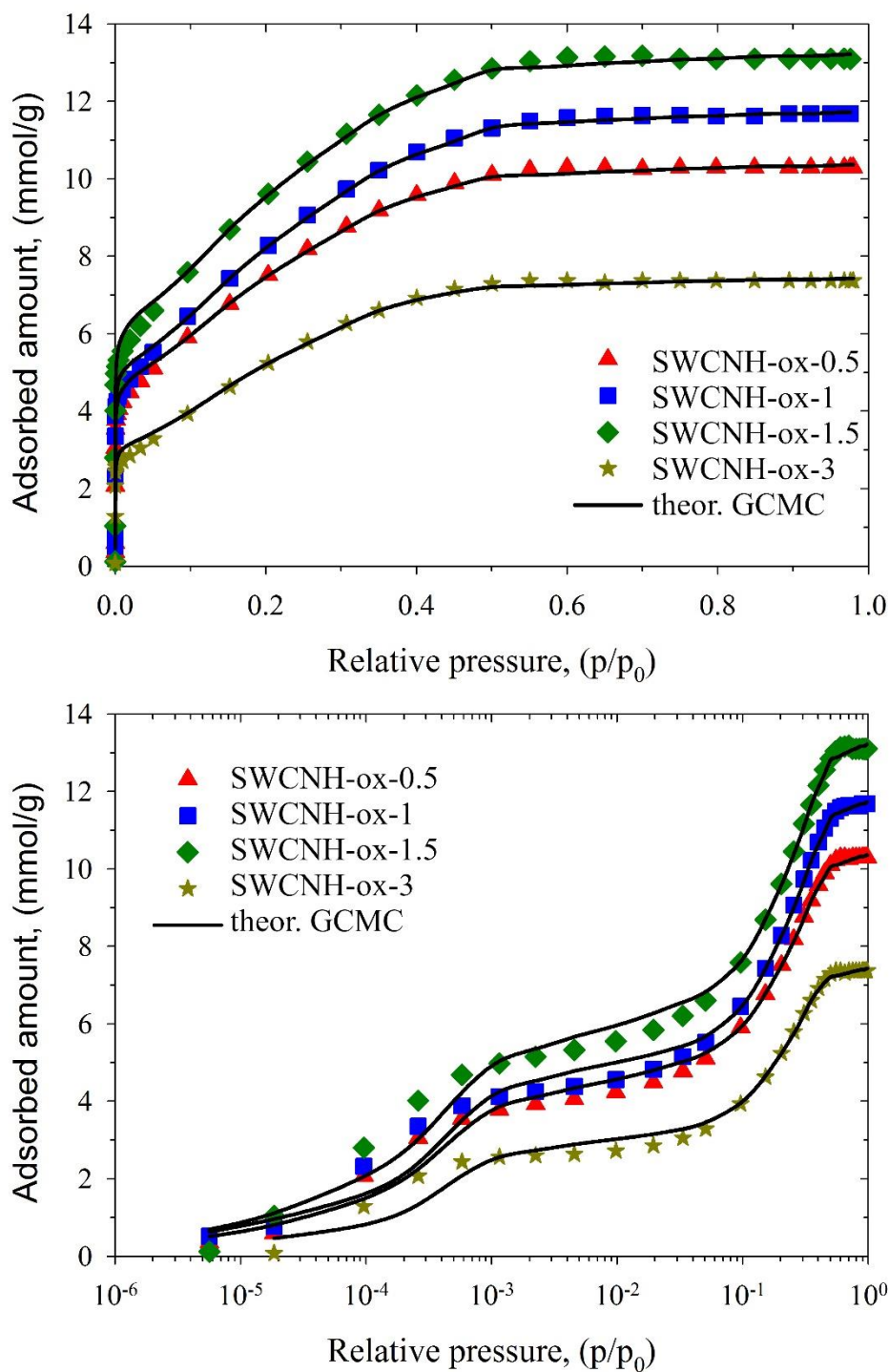
<sup>2</sup> Department of Organic Chemistry, Faculty of Pharmacy with the Division of Laboratory Medicine, Medical University of Białystok, Mickiewicza 2A, 15-222 Białystok, Poland

<sup>3</sup> Faculty of Chemistry, Department of Physical Chemistry, Nicolaus Copernicus University in Toruń, Gagarin Street 7, 87-100 Toruń, Poland

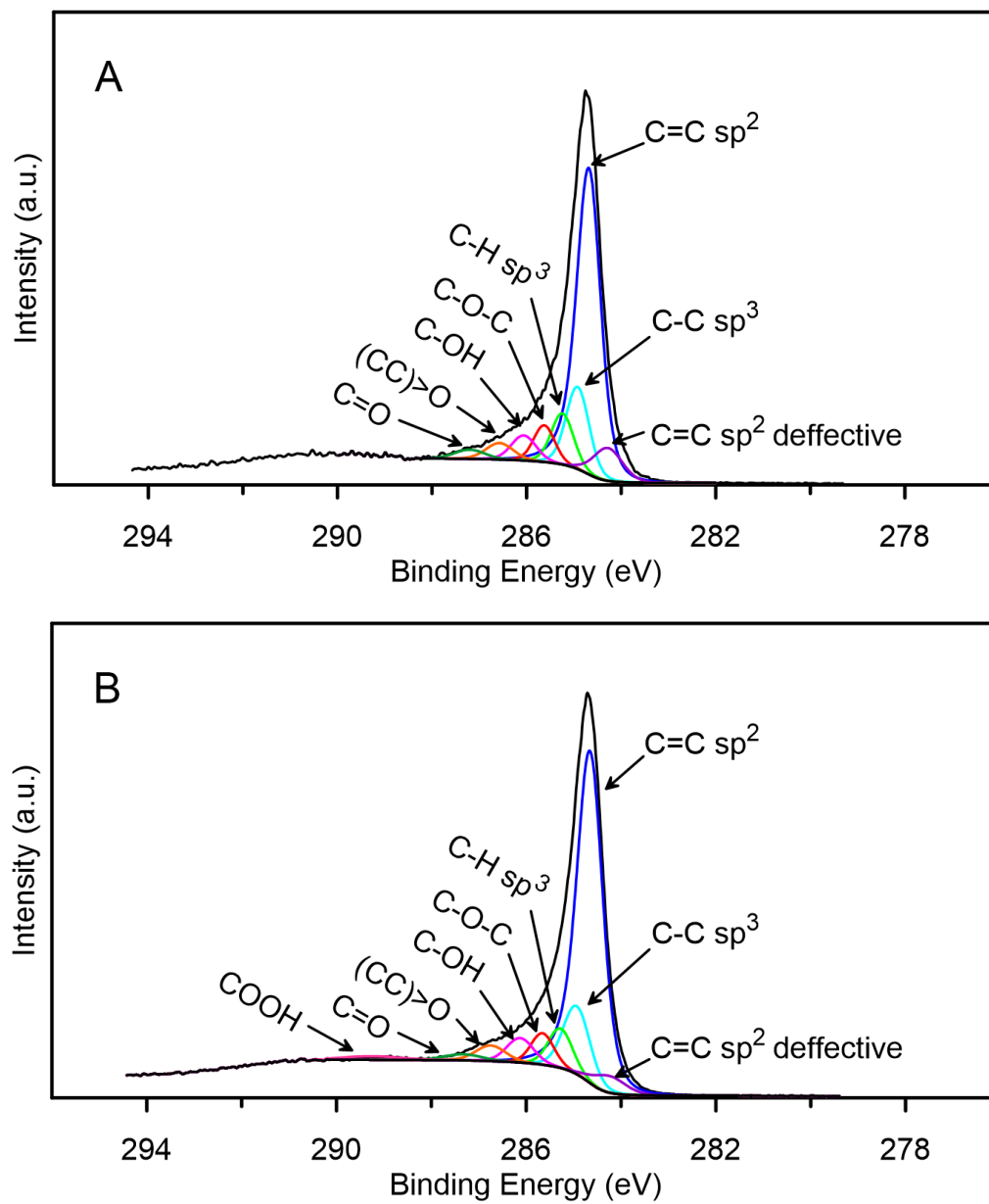
<sup>4</sup> College of Science, Health, Engineering and Education, Murdoch University, WA, 6150, Australia



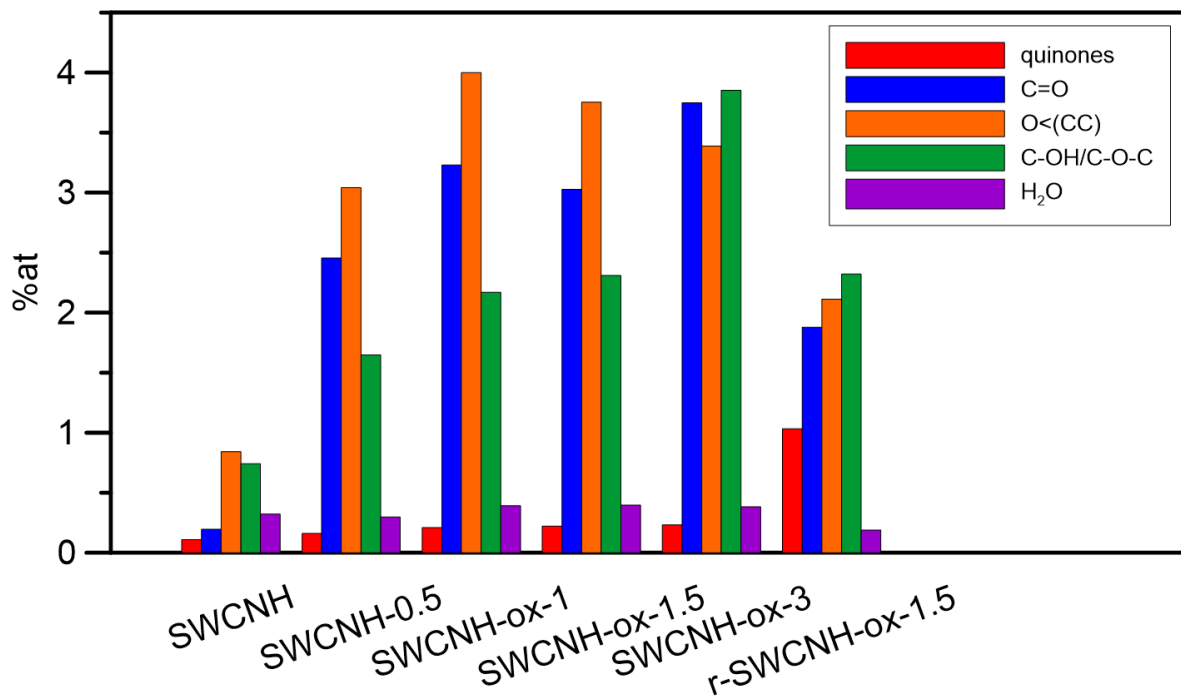
**Figure S1.** N<sub>2</sub> (77 K) adsorption isotherms in graphene cylinders simulated from GCMC method. Values of pore diameters are displayed on the plot.



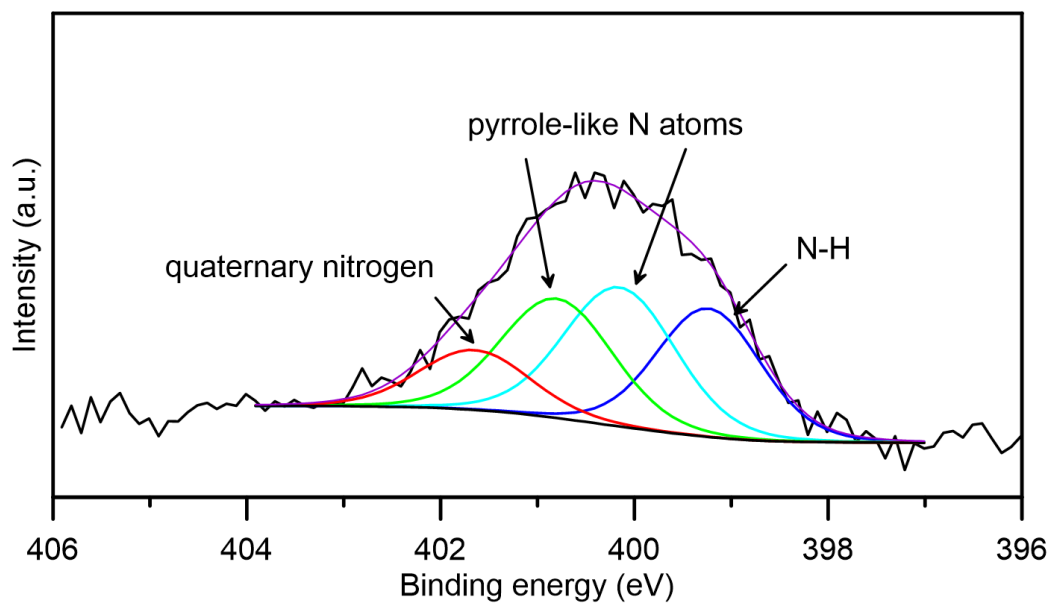
**Figure S2.** Experimental N<sub>2</sub> (77 K) adsorption isotherms inside SWNHs computed from Eq. (5) (in manuscript). The theoretical N<sub>2</sub> (77 K) adsorption isotherms inside SWNHs obtained from the fitting of the experimental ones by GCMC kernel are given by solid lines (Eq. (6) in manuscript).



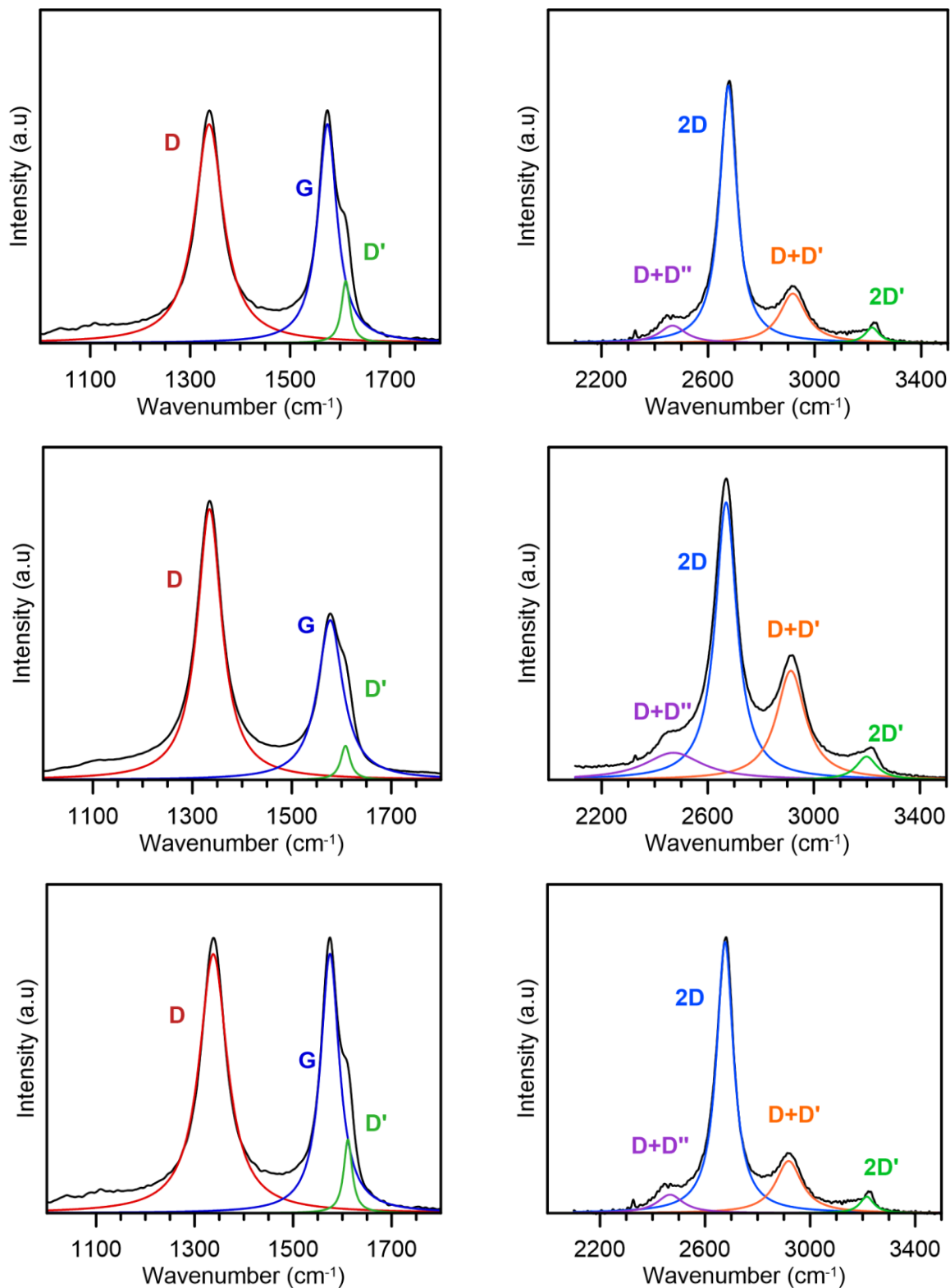
**Figure S3.** High-resolution C 1s XPS spectra for (A) SWCNH and (B) SWCNH-ox-1.5.



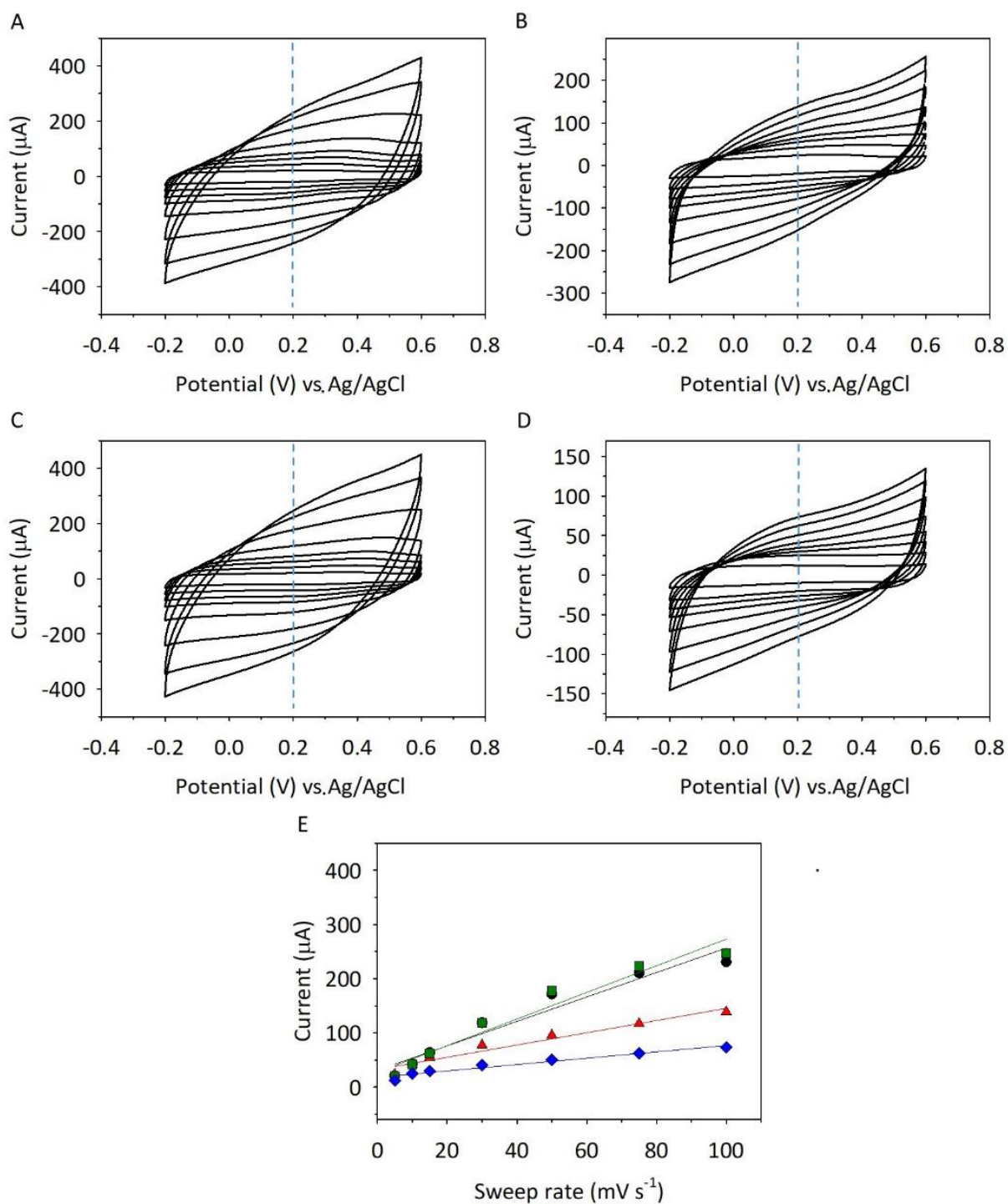
**Figure S4.** XPS atomic % of different forms of surface oxygen after wet HNO<sub>3</sub> modification based on O 1s XPS spectra.



**Figure S5.** High-resolution N 1s XPS spectra for the r-SWCNH-ox-1.5.



**Figure S6.** Deconvolution of Raman spectra for SWCNH (first row), SWCNH-ox-1.5 (second row) and r-SWCNH-ox-1.5 (bottom row).



**Figure S7.** Cyclic voltammograms of SWCNH-ox-1.5 in 0.1 M different supporting electrolytes (A) NaCl, (B)  $\text{Na}_2\text{SO}_4$ , (C)  $\text{H}_2\text{SO}_4$ , and (D)  $(\text{Et})_4\text{NCl}$  at the different sweep rate: 5, 10, 15, 30, 50, 75, and 100  $\text{mV s}^{-1}$ . (E) Dependence of the current of SWCNH at 0.2 V (vs. Ag/AgCl) for (●) NaCl, (▼)  $\text{Na}_2\text{SO}_4$ , (▴)  $\text{H}_2\text{SO}_4$ , and (◆)  $(\text{Et})_4\text{NCl}$ .

**Table S1.** The specific element content based on the XPS results.

Element	SWCNH	SWCNH-ox-0.5	SWCNH-ox-1	SWCNH-ox-1.5	SWCNH-ox-3	r-SWCNH-ox-1.5
	%Atomic concentration					
C	97.79	92.4	90.0	90.3	88.4	89.6
O	2.21	7.6	10.0	9.7	11.6	7.5
N	0	0	0	0	0	2.9

**Table S2.** Studied ionic species: Stokes radius, hydrated radius and standard molar enthalpy of hydration.

Ions	$r_s$ (nm)	$r_h$ (nm)	$\Delta_{\text{hyd}}H^\circ$ (kJ mol <sup>-1</sup> )
Na <sup>+</sup>	0.184	0.358	-240.6
(Et) <sub>4</sub> N <sup>+</sup>	0.282	0.400	-154.9
SO <sub>4</sub> <sup>2-</sup>	0.230	0.379	-903.7
Cl <sup>-</sup>	0.121	0.332	-363.0

Stokes radius ( $r_s$ ), hydrated radius ( $r_h$ ) and standard molar enthalpy of hydration ( $\Delta_{\text{hyd}}H^\circ$ ). The reported Stokes and hydrated radii are from Ref. <sup>1</sup>. Standard molar enthalpy of hydration  $\Delta_{\text{hyd}}H^\circ$  values are from Ref. <sup>2</sup>.

**Table S3.** Specific capacitance of SWCNH, SWCNH-ox and r-SWCNH-ox in aqueous solution of different supporting electrolyte.

Materials	Specific capacitance (F g <sup>-1</sup> )			
	Integration $\Delta E_I$ (0.0 – 0.3 V vs. Ag/AgCl) <sup>[a]</sup>		$I - v$ (slope) $E_I$ (0.2 V vs. Ag/AgCl)	
	NaCl	H <sub>2</sub> SO <sub>4</sub>	NaCl	H <sub>2</sub> SO <sub>4</sub>
SWCNH	32	65	29	62
SWCNH-ox-0.5	127	175	118	165
SWCNH-ox-1.0	169	177	159	168
SWCNH-ox-1.5	230	233	212	228
SWCNH-ox-3.0	227	184	218	176
r-SWCNH-ox-1.5	95	134	88	130

[a] at  $v = 20 \text{ mV s}^{-1}$

1 A. K. Covington and T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Springer US, Boston, MA, 1973.

2 D. Dobos, *Electrochemical data: a handbook for electrochemists in industry and universities*, Elsevier Scientific Pub. Co, Amsterdam ; New York, 1975.