Electrophilic oxygen on defect-rich carbon nanotubes for selective oxidation of cyclohexane

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Supporting Information

S1. Materials and Methods.

S2. Characterization of CNT catalyst.

S3. Computational Calculation.

S1. Materials and Methods.

CNTs (length: 3 - 12 μm, diameter $\approx$ 12 - 15 nm, purity: 96%) were obtained from Shandong Dazhan Nano Materials Co. Ltd.. All other starting materials were purchased from Alfa Aesar and Innochem. All reagents were used as received without further purification. Pristine CNTs were oxidized to introduce surface functional groups. Briefly, 10 g of CNTs was added in the mixture of 125 mL concentrated HNO_3 (65-68%) and 375 mL concentrated H_2SO_4 (95-98%) under sonication at 50 °C for 6 h. The precipitates were filtered and rinsed with deionised water for several times until the pH of the filtrates reached 7. Finally, the functionalized CNTs (o-CNTs) were dried in the oven at 120 °C for 12 h. The formed o-CNTs were then calcined under N_2 protection for 5 h at the temperature of 500 °C, 700 °C, 900 °C and 1100 °C, with a heating rate of 5°C min^{-1}, yielding o-CNT-500, o-CNT-700,o-CNT-900 and o-CNT-1100, respectively.

Transmission electron microscopy (TEM) measurements were taken on a FEI Tecnai F20 microscope with an accelerating voltage of 200 kV. Raman spectra were recorded under ambient conditions on a JY LabRAM HR Raman spectrometer with a 325 nm laser beam. The weight concentrations of element C, H, and O were determined on an Elementar Micro Cube elemental analyzer. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was around 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.6 eV from defect free graphite. Deconvolution of O 1s spectra were performed using mixed Gaussian-Lorentzian component profiles after subtraction of a Shirley background using XPSPEAK41 software.

S2. Characterization of CNT catalyst

Iodometric Titration Method

The electrophilic oxygen on the surface of CNT samples was quantified using iodometric titration, which was able to determine the liquid phase peroxide concentration. Electrophilic peroxide and superoxide species can oxidize aqueous I$^-$ into I$_2$ for subsequent titration with $Na_2S_2O_3$. For convenient calculation, the electrophilic oxygen species were supposed to be composed of peroxides in this study. The titration procedure is as follows. 0.3 g CNT sample was added in a KI solution that consisted of 10 mL of KI (100 g/L), 5 mL of H_2SO_4 (0.1 mol/L), 30 mL of deionized water, and 3 drops of $(NH_4)_6Mo_7O_{24}$ (30 g/L). The reaction between peroxides on the surface of CNTs and KI is shown in eq1.

$$O_2^{2-} + 2KI + 2H_2SO_4 \rightarrow O^{2-} + 2KHSO_4 + I_2 + H_2O \tag{1}$$

After sonication at 25°C in the dark for 30 minutes, I$^-$ was oxidized into I$_2$. The precipitate was then filtered and washed several times. I$_2$ in the filtrate was titrated with $Na_2S_2O_3$ (0.002 mol/L) as presented in eq2.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \tag{2}$$
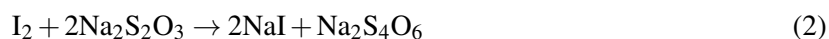
and the concentration of electrophilic oxygen (moles per gram) on CNTs was calculated with eq3.

$$c \text{ (electrophilic oxygen)} = 2 \times 10^{-6} \text{ V/m} \tag{3}$$

where c (moles per gram), V (milliliters), and m (grams) represent the concentration of electrophilic oxygen, the volume consumption of the $Na_2S_2O_3$ solution, and the mass of CNT samples for titration, respectively. The obtained iodometric titration data were averaged results from repeated experiments.

Catalytic Activity Measurement

The catalytic activity of CNT samples in the oxidation of cyclohexane was measured at 403 K in batch mode using a mechanically stirred (1500 rpm) 300 mL Parr autoclave. Prior to the experiments, the reactor wall was passivated with a saturated sodium pyrophosphate solution. In each batch, the reactants (cyclohexane 90 mL) along with butanone (15 mL) as an internal standard, acetone (60 mL) as solvent, and the catalyst (150 mg) were loaded into the autoclave and the reactor was flushed with N_2 under mechanical stirring at 500 r/min. It was heated to a stable operational temperature, whereupon pure O_2 was introduced, defining t=0. The concentrations of cyclohexane, cyclohexanol, and cyclohexanone with reference to the butanone internal standard were measured by online gas chromatography (Agilent model 7890B) equipped with a HayeSep Q column, a HayeSep N column, and a molecular sieve column connected to a thermal conductivity detector, and a HP-PLOT Al_2O_3 column (50 m $\times$ 0.53 mm $\times$ 15 μm) connected to a flame ionization detector. The selectivity and conversion of products are calculated as follows:

$$sel_{CYHAOL} = \frac{[m_{CYHAOL}]}{[m_{CYHA}]_{in} - [m_{CYHA}]_{out}} \times 100\% \tag{4}$$

$$sel_{CYHAONE} = \frac{[m_{CYHAONE}]}{[m_{CYHA}]_{in} - [m_{CYHA}]_{out}} \times 100\% \tag{5}$$

$$sel_{KA} = \frac{[m_{KA}]}{[m_{CYHA}]_{in} - [m_{CYHA}]_{out}} \times 100\% \tag{6}$$

$$Conversion_{CYHA} = \frac{[m_{CYHA}]_{in} - [m_{CYHA}]_{out}}{[m_{CYHA}]_{in}} \times 100\% \tag{7}$$

where sel_i (percent) and m_i are the selectivity and number of moles of each product respectively, $[m_{CYHA}]_{in}$ and $[m_{CYHA}]_{out}$ are the number moles of cyclohexane before and after the reactions, respectively. CYHA, CYHAOL and CYHAONE stand for cyclohexane, cyclohexanol and cyclohexanone.

Table S1: O/C weight content ratio of o-CNT under different annealing temperatures.

Entry	C (*wt%*)	O (*wt%*)	H (*wt%*)
o-CNT	82.9	10.6	1.2
o-CNT-500	92.2	2.78	0.61
o-CNT-700	95.7	0.45	0.58
o-CNT-900	96.0	0.34	<0.5
o-CNT-1100	96.7	0.32	<0.5

Table S2: Reaction selectivity of o-CNT and annealed o-CNTs

Entry	K (%)	A (%)	AA (%)
CNT	30.6	31.7	19.6
o-CNT	20.6	35.4	21.1
o-CNT-500	38.9	31.9	17.7
o-CNT-700	37.4	48.4	2.09
o-CNT-900	37.0	39.2	2.94
o-CNT-1100	26.9	25.7	39.8

Table S3: Selectivity of annealed o-CNTs at similar conversion

Entry	K (%)	A (%)	Conversion (%)
o-CNT-500	33.9	30.4	10.1
o-CNT-700	36.0	40.2	8.57
o-CNT-1100	26.9	25.7	8.92
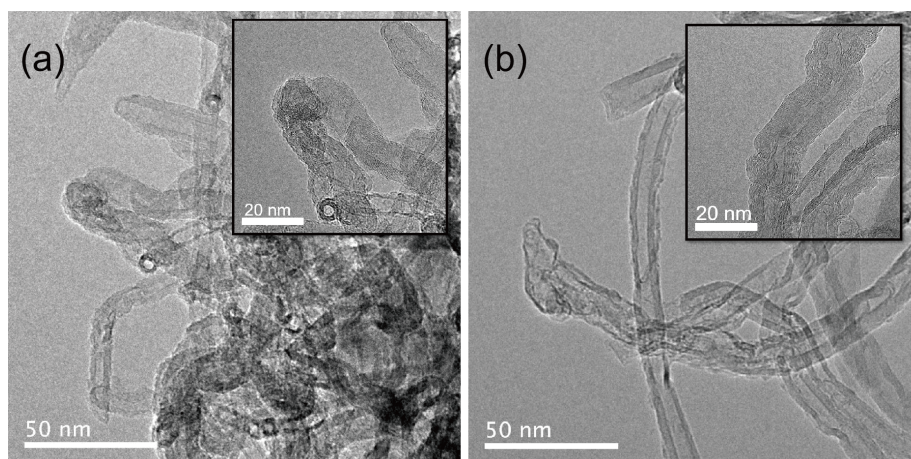
Figure S1: TEM images of (a) o-CNT and (b) o-CNT-1100.
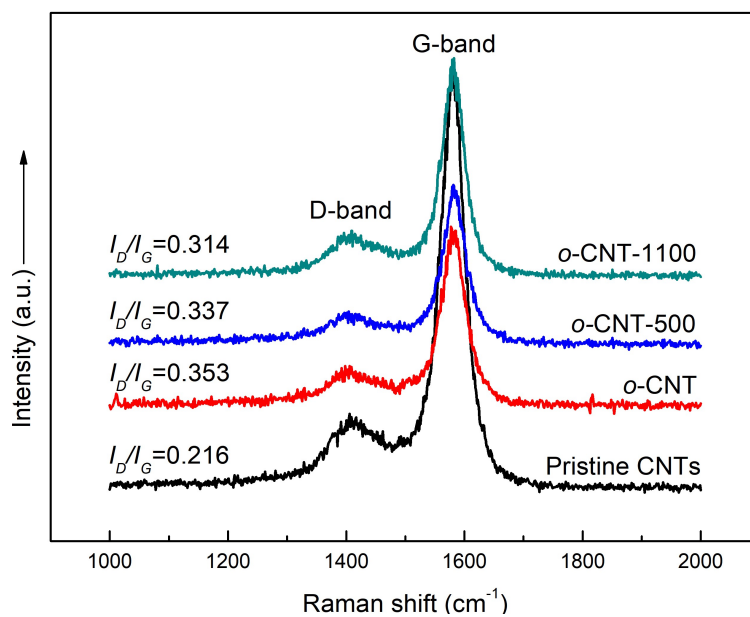
Figure S2: Raman spectra of pristine CNTs, o-CNT and annealed o-CNT. Note: spectra are stacked for comparison.
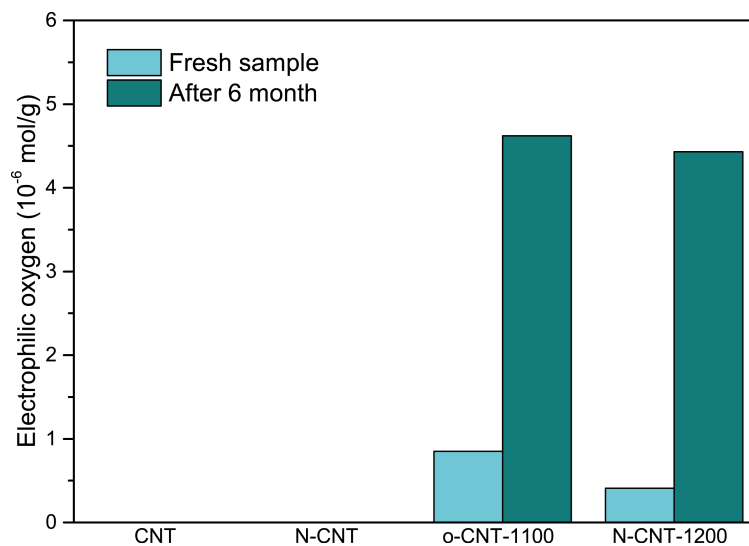

Figure S3: Amount of electrophilic oxygen on CNT, N-CNT, annealed o-CNT and N-CNT in both fresh state and aged stage determined by iodometric titration.
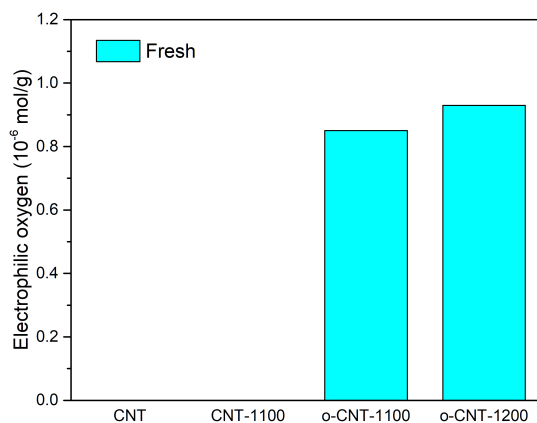
Figure S4: Amount of electrophilic oxygen on CNT, CNT-1100, annealed o-CNT-1100 and o-CNT-1200 in the fresh state by iodometric titration.
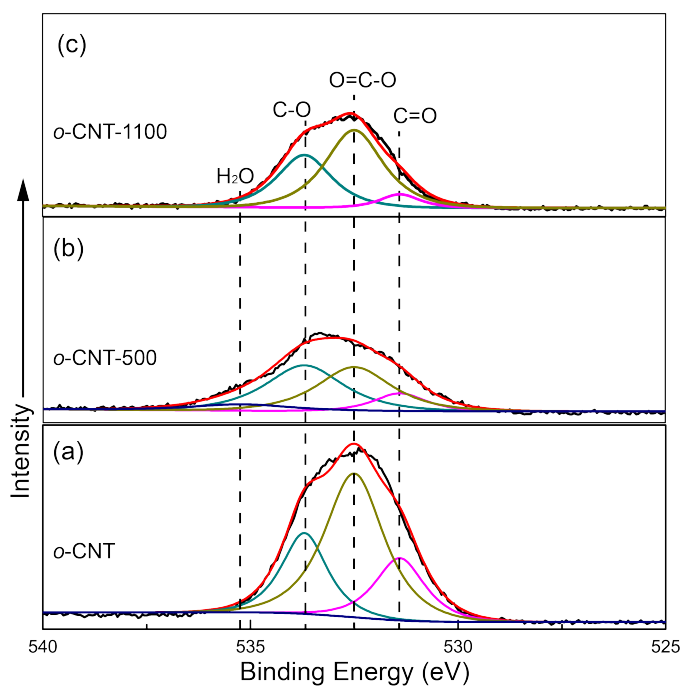

Figure S5: Deconvolution of O 1s XPS spectra of o-CNT, o-CNT-500 and o-CNT-1100.

S3. Computational Calculation

All the density functional theory calculations were carried out by using MedeA VASP software. The Generalized Gradient Approximation (GGA) form of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is employed for calculating the interactions[1,2]. The Projector Augmented Wave (PAW) potential and a plan-wave cutoff energy of 400 eV is adopted. The K-mesh in Brillouin zone was $1 \times 1 \times 6$ using the Monkhorst and Pack scheme[3]. An armchair (8×8) single walled carbon nanotube (CNT) was built as the model to investigate the adsorption of oxygen on CNT[4].

The adsorption energy of oxygen on the CNT was calculated according to the following equation:

$$E = E_{CNT-O_2} - E_{CNT} - E_{O2}$$

Where E_{CNT-O_2}, E_{CNT}, E_{O_2} is the energy of the CNT-oxygen complex, CNT, and oxygen, respectively.
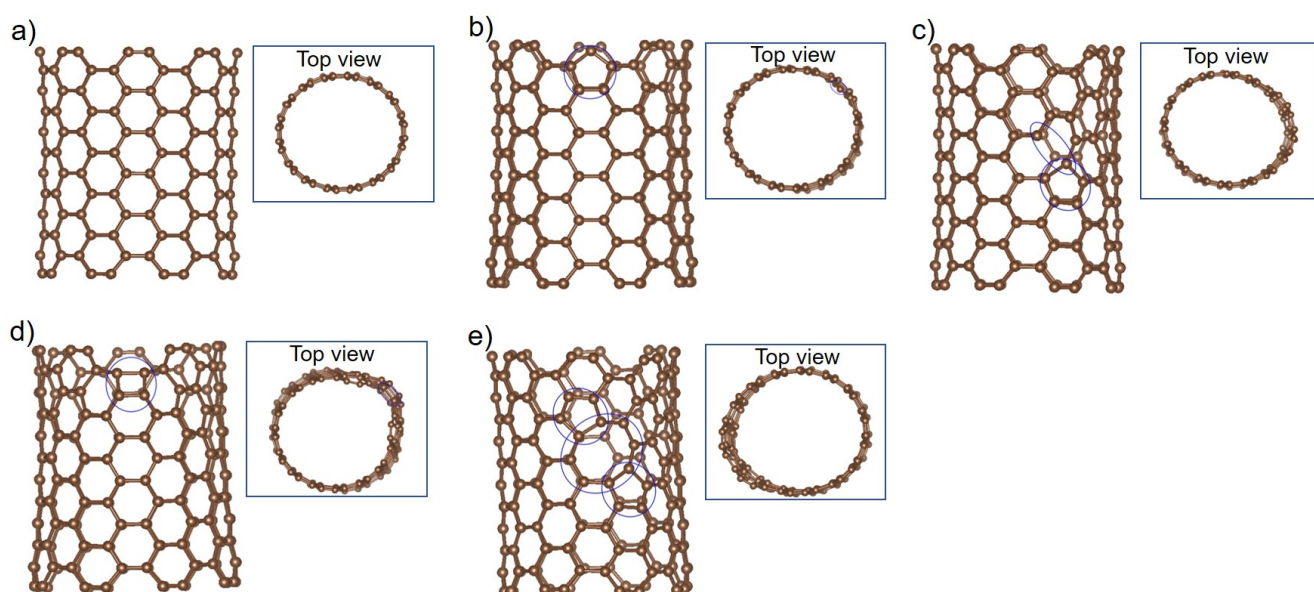

Figure S6: Optimized geometries of different types of CNTs, a) pristine CNT; b) CNT with single vacancy located on the edge (CNT-SVE); c) CNT with single vacancy located on the wall (CNT-SVW); d) CNT with double vacancy located on the edge (CNT-DVE) and e) CNT with double vacancy located on the wall (CNT-DVW).
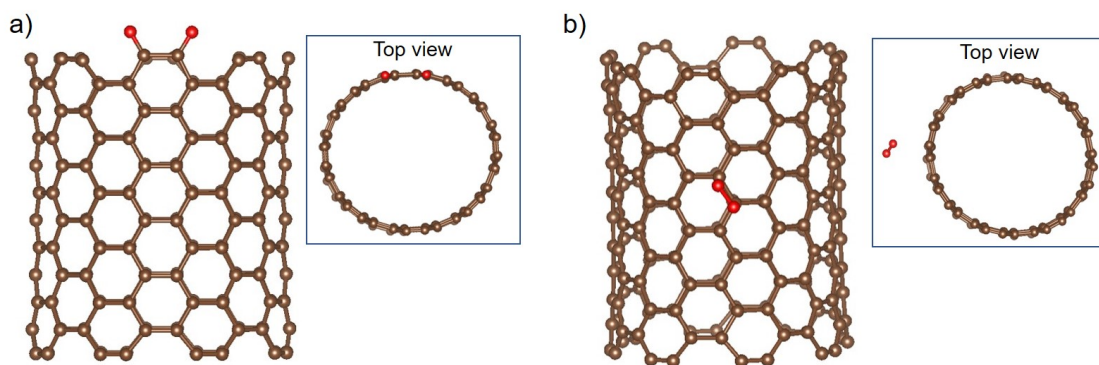
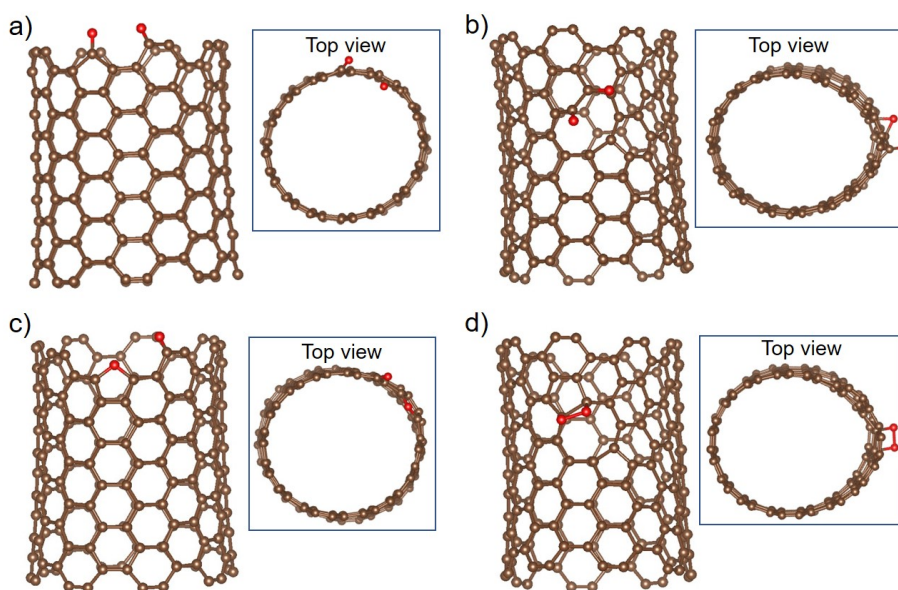**Figure S7:** O_2 interaction on the pristine CNT's a) edge and b) wall.

Figure S8: O_2 interaction on different CNTs, a) CNT-SVE-O_2; b) CNT-SVW-O_2; c) CNT-DVE-O_2 and d) CNT-DVW-O_2 .
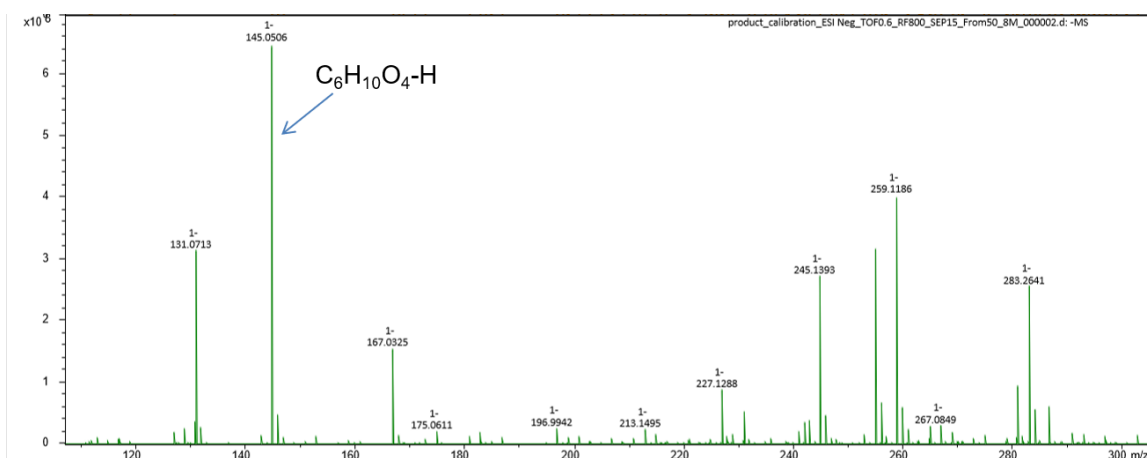

Figure S9: Mass spec results showing the existence of adipic acid in the product

References

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[2] Perdew, J. P., et al. (1976) Generalized gradient approximation made simple. *Phy. rev. lett.* 77:3865.

[3] Brack, N., et al. (1976) Special points for Brillouin-zone integrations. *Phy. rev. B.* 13:5188.

[4] Mielke, S. L. et al. (2004) The role of vacancy defects and holes in the fracture of carbon nanotubes. *chem. phy. lett.* 390:413.