Electronic Supplementary Information for

Insights into N-doping in single-walled carbon nanotubes for enhanced activation of superoxides: a mechanistic study

Xiaoguang Duan[1], Zhimin Ao[2], Hongqi Sun[1,*], Li Zhou[1], Guoxiu Wang[2], Shaobin Wang[1,*]

[1]Department of Chemical Engineering, Curtin University, GPO Box U1987, WA 6845, Australia

[2]Centre for Clean Energy Technology, School of Chemistry and Forensic Science, University of Technology, Sydney, PO Box 123, Broadway, Sydney, NSW 2007, Australia

*Corresponding Authors.

Email: shaobin.wang@curtin.edu.au (S. Wang), h.sun@curtin.edu.au (H. Sun)

Experimental Section

Single-walled carbon nanotubes (OD: 1 ~ 2 nm, length: 5 ~ 30 um, CNTs purity> 95 wt.%, SWCNTs purity > 90 wt.%) were obtained from Chengdu Organic Chemical, China. Melamine ($C_3H_6N_6$, 99 wt.%) was purchased from Sigma-Aldrich, Australia.

Catalytic Oxidation Procedure. Phenol oxidation was carried out in a 500 mL conical flask with 20 mg/L phenol solution and dipped in a constant-temperature water bath (25 °C). The catalyst (0.2 g/L) was first added to the solution and stirred for 5 min and then PMS or PS (6.5 mM) or H_2O_2 (30 mM) was added to the solution to start the reaction. At each time interval, 1 mL of solution was withdrawn by a syringe, filtered by a 0.45 μm Millipore film, and injected into a HPLC (high performance liquid chromatography) vial. The sample was mixed immediately with 0.5 mL of methanol to quench the reactive radicals, and then analyzed on a Varian HPLC using a UV detector (λ = 270 nm) and a C18 column. The statistical analysis was obtained via performing three parallel experiments on the different carbocatalysts. Phenol degradation efficiency was estimated by the phenol removal ratio (C/C_0) of the phenol concentration to the initial concentration.

Table S1 Physicochemical properties and reaction rate of superoxides activation for the

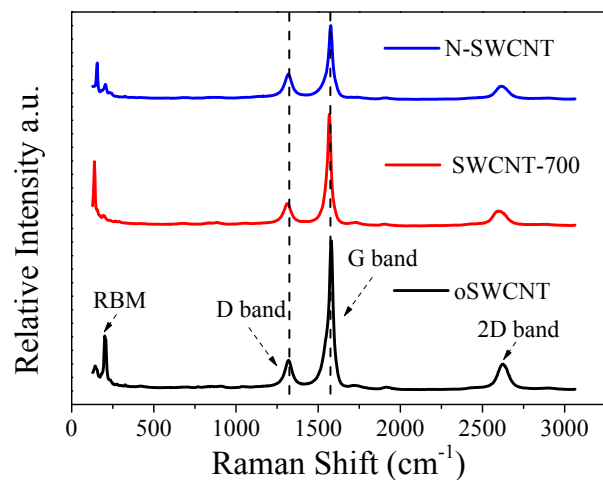|	S_{BET} m^2/g	V_{Pore} cm^3/g	I_D/I_G	C at.%	O at.%	N at.%	Reaction rate ppm·min^{-1} PMS	PS	H_2O_2
oSWCNT	407.4	0.58	0.20	97.66	2.34	-	0.09	0.32	0.01
SWCNT-700	445.9	0.95	0.21	98.60	1.40	-	0.46	0.42	0.03
N-SWCNT	379.7	0.54	0.35	98.05	1.15	0.80	4.93	0.60	0.02

carbocatalysts.

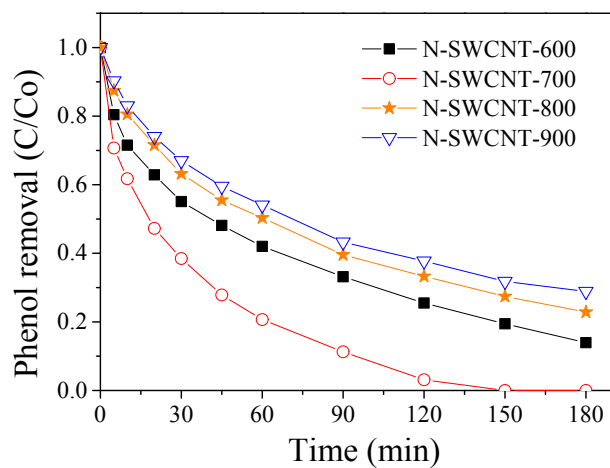**Fig. S1** Raman spectra of various single-walled carbon nanotubes.

Fig. S2 Effect of annealing temperature of N-SWCNTs on PS activation. [Phenol] = 20 ppm, [Catalyst] = 0.1 g/L, [Temperature] = 25 °C, [PS] = 6.5 mM.
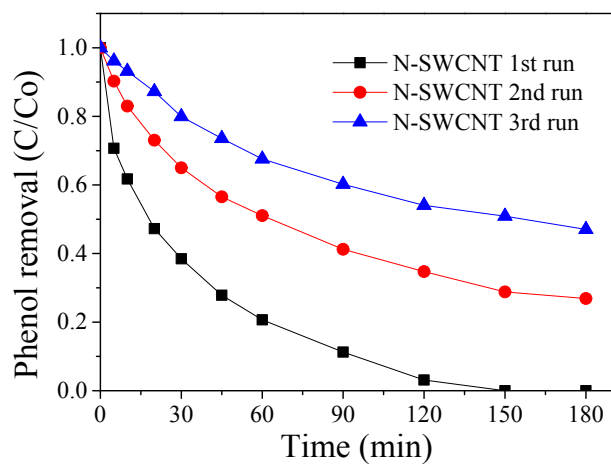
Fig. S3 Stability test of N-SWCNT for PS activation. [Phenol] = 20 ppm, [Catalyst] = 0.1 g/L, [Temperature] = 25 °C, [PS] = 6.5 mM.
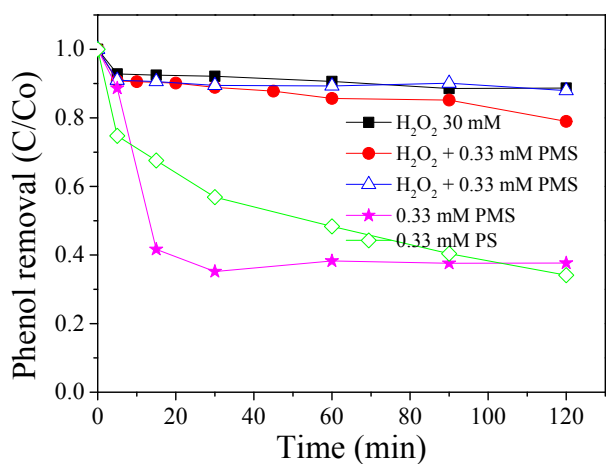

Fig. S4 Effect of H_2O_2 activation on N-SWCNT with PS and PMS. [Phenol] = 20 ppm, [Catalyst] = 0.1 g/L, [Temperature] = 25 °C, [H_2O_2]=30 mM.
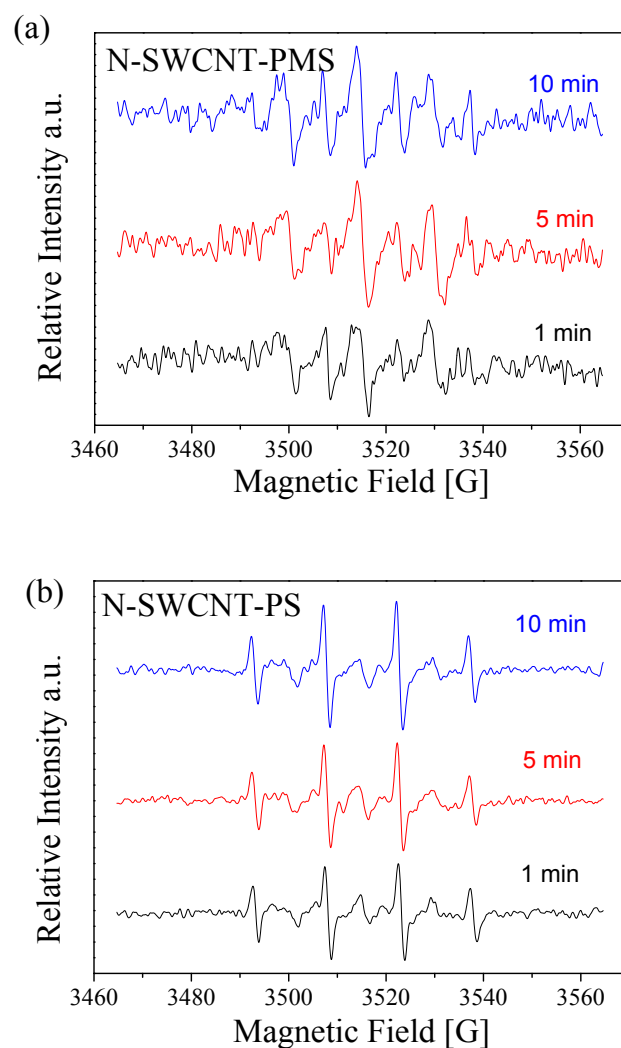
Fig. S5 EPR spectra of radical generation process of (a) PMS/N-SWCNT and (b) PS/N-SWCNT. [Phenol] = 20 ppm, [Catalyst] = 0.1 g/L, [Temperature] = 25 °C, [PMS]=6.5 mM, [DMPO]=0.08 M. Electron paramagnetic resonance (EPR) was employed on a Bruker EMS-plus instrument to probe the free radicals. The radicals were trapped with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) and the quantitative information was analyzed by Xeon software (Bruker) with hyperfine splitting constants DMPO-OH: αN=14.9G, αH=14.9 G; DMPO-SO4: αN=13.2 G, αH=9.6 G, αH=1.48G, αH=0.78 G.

Theoretical Calculation Section

Theoretical methodology. The spin−unrestricted density functional theory (DFT) calculations were carried out by using Dmol^3 package. Generalized gradient approximation (GGA) with Perdew−Burke− Ernzerhof (PBE) is taken as the exchange−correlation function. All electron core treatment is implemented for relativistic effects. Double numerical plus polarization (DNP) is employed as the basis set. The convergence tolerance of energy of 10^{-5} Hartree is taken (1 Hartree = 27.21 eV), and the maximal allowed force and displacement are 0.002 Hartree/Å and 0.005 Å, respectively. The DFT-D method within the Grimme scheme[i] is used in all calculations to consider the van der Waals forces. In the simulation, three−dimensional periodic boundary conditions are taken. In this work, (6,6) single wall carbon nanotubes (SWCNTs) is taken as an example to consider the catalytic effect for pollution molecules activation as shown in Fig. S3. The size of the simulation cell is $a \times b \times c = 30 \times 30 \times 9.838$ Å. The much bigger a, b is taken to minimize the interaction among different SWCNTs. The k−point is set to $6 \times 6 \times 1$, and all atoms are allowed to relax. To understand the catalytic effect on activation of some pollution molecules, such as PMS, H_2O_2, PS molecules, their adsorption on SWCNTs is studied by DFT calculations.
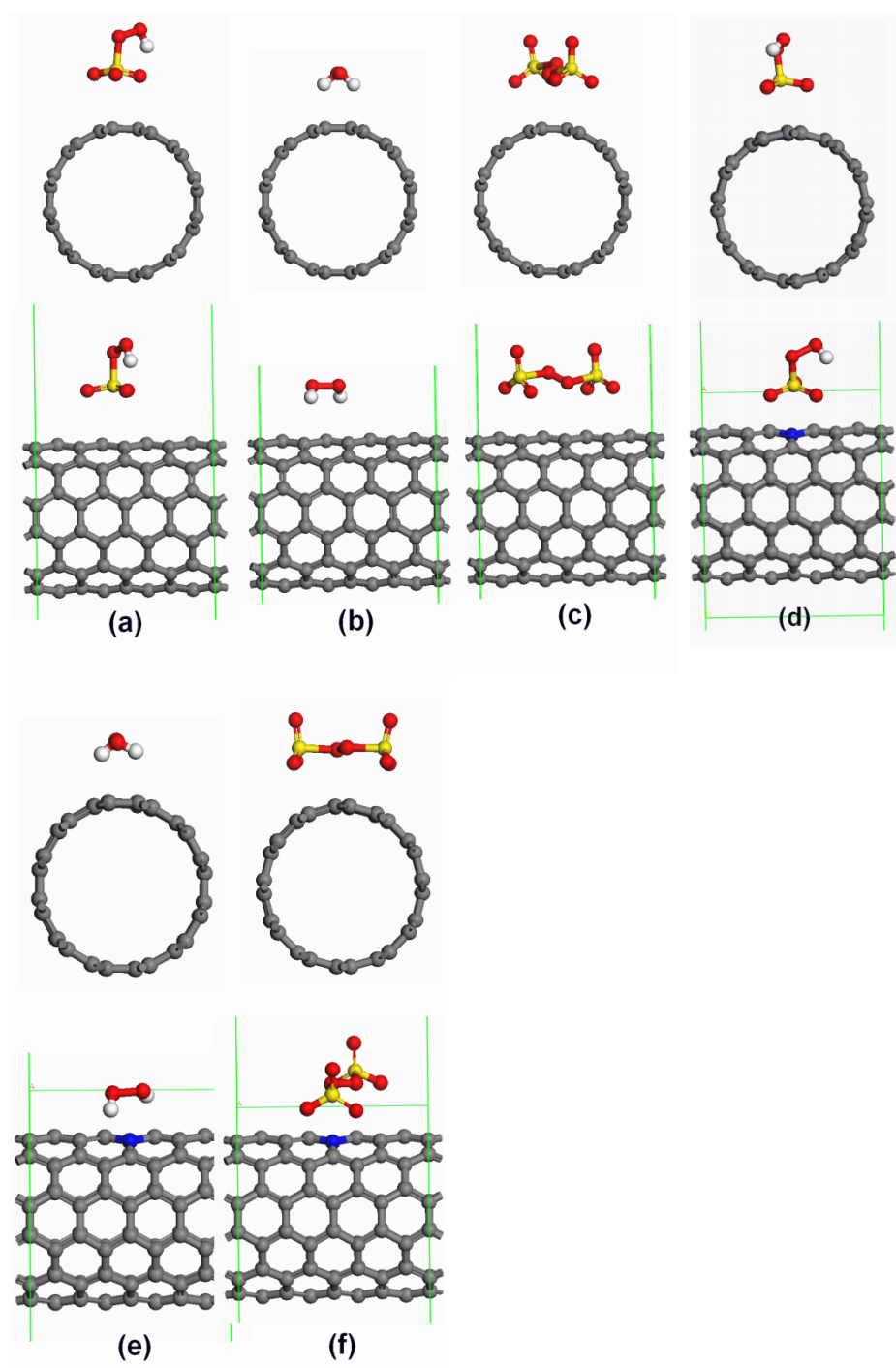
Fig. S6 The favourite adsorption configuration of PMS, H_2O_2, and PS on SWCNT and N-doped SWCNT, respectively. Both the front view and side view are shown here. (a) PMS on SWCNT, (b) H_2O_2 on SWCNT, (c) PS on SWCNT, (d) PMS on N-doped SWCNT, (e) H_2O_2 on N-doped SWCNT, (f) PS on N-doped SWCNT. The grey, blue, red, yellow, and white atoms are C, N, O, S, and H atoms, respectively.

Table S2 The adsorption energy E_{ads}, electrons transfer between SWCNT and the adsorbed molecule Q, and the O-O bond length of free molecule, PS or H_2O_2 adsorbed on N-SWCNT and PS adsorbed on N-SWCNT together with H_2O_2.

Type of CNT	Molecules	E_{ads} (eV)	Q (e)	l_{O-O} (Å)
Free molecule	PS	-	-	1.222
	H_2O	-	-	0.970
N-doped SWCNT	PS	-2.99	-0.945	1.344
	H_2O	-0.23	0.008	0.971
N-SWCNT with H_2O and PS	PS	-3.43	-1.021	1.356
	H_2O	-0.66	0.059	0.980