Electronic Supplementary Information (ESI) for *Environmental Science: Nano*

Enhanced adsorption of aromatic chemicals to boron and nitrogen co-doped single-walled carbon nanotubes

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Number of pages: 9

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Dubinin−Astakhov (DA) model and multiple liner regression analysis between the characteristic energy of adsorption (E) and solvatochromic parameters of organic compounds

To further understand the effects of B and N co-doping on the electron donor−acceptor interactions, in particular, how the enhanced surface polarization can affect adsorption energy, the adsorption data were analyzed using the approach developed by Yang et al.[S1, S2] Specifically, multiple linear relationship of the Dubinin−Astakhov (DA) model characteristic energy of adsorption and the solvatochromic parameters of the aromatics (i.e., the hydrogen bonding donor parameter α_m and the π-electron polarizability parameter π^*) were obtained, to understand the relative significance of specific/polar interactions of BN-SWCNT, as compared with the undoped SWCNT.

The DA model is expressed as:

$$\log q_e = \log Q^0 - (\varepsilon / E)^b$$

where q_e (mg/g) is the adsorbed amount of organic compound in equilibrium; Q^0 (mg/g) is the adsorption capacity of organic compound; ε (kJ/mol), $\varepsilon = RTln(C_s/C_e)$, is the effective adsorption potential; C_e (mg/L) is the equilibrium concentration of organic compound in aqueous phase; C_s (mg/L) is the water solubility of organic compound; R (8.314×10^{-3} kJ/(mol·K)) is the universal gas constant; T (K) is the absolute temperature; E (kJ/mol) is the "correlating divisor" of the effective adsorption potential ε, and can be understood as the characteristic energy of adsorption; and b is a fitting parameter. The fitting results were list in **Table S2**.

Multiple linear regressions were conducted by SigmaPlot 10.0 to establish the linear solvation energy relationships (LSERs) combining the DA model fitted adsorption affinity parameter, E, with the solvatochromic parameters, π* (the π-

electron polarizability parameter) and $\boldsymbol{\alpha_m}$ (the hydrogen bonding donor parameter), of the investigated organic compounds for SWCNT and BN-SWCNT, respectively.

Reasonable good linear relationship between E and the solvatochromic parameters α_m and π^* of the organic compounds (except 1-naphthylamine) was observed for both SWCNT and BN-SWCNT:

SWCNT:

$$E = 24.93\ (\pm 3.25) \times \alpha_m + 9.96\ (\pm 3.41) \times \pi^* + 4.91\ (\pm 3.35)$$

$$R^2 = 0.968$$

BN-SWCNT:

$$E = 44.20\ (\pm 4.46) \times \alpha_m + 16.67\ (\pm 4.67) \times \pi^* + 9.80\ (\pm 4.59)$$

$$R^2 = 0.978$$

The fitted π^* coefficient for BN-SWCNT (16.67) is significant greater than that for SWCNT (9.96), indicating that doping with B and N can significantly enhance the π–π EDA interactions.

Table S1 Summary of Log K_d values of the adsorbates on carbon nanotubes and on activated carbons. [a]

	CNT [b]		Activated carbons	
	SWCNT	**BN-SWCNT**	**Modeled [c]**	**Experimental**
benzene	3.60	4.14	4.32	4.46 (2.30E-02) [S4] 4.13 (7.30E-02) [S5]
benzonitrile	3.90	4.34	3.72	data not found
nitrobenzene	4.08	4.70	4.20	2.78 (8.13E-01) [S6] 3.95 (2.44E-01) [S7] 3.81 (2.00E-01) [S8]
1,3-dinitrobenzene	4.44	4.71	4.05	data not found
2-naphthol	4.94	5.10	5.75	4.99 (1.00E-02) [S9]
1-naphthylamine	5.43	5.40	4.33	data not found

[a] K_d (L/kg) represents solid–water distribution coefficient of an adsorbate. Data in parentheses are the corresponding equilibrium aqueous concentrations (C_w, mmol/L).

[b] Experimental data of this study (corresponding to a C_w of 0.01 mmol/L).

[c] Calculated using the linear solvation energy relationships developed by Blum et al.[S3]

Table S2 Results of DA model fits to adsorption data of six model adsorbates on SWCNT and BN-SWCNT.

Adsorbate	CNT	Q^0 (mg/g)	E (kJ/mol)	b	R^2
benzene	SWCNT	186.2	11.98	1.243	0.984
	BN-SWCNT	107.9	22.34	1.771	0.997
benzonitrile	SWCNT	302.0	12.04	0.992	0.986
	BN-SWCNT	152.1	25.21	1.672	0.999
nitrobenzene	SWCNT	283.8	14.60	1.142	0.994
	BN-SWCNT	213.3	27.12	1.060	0.960
1,3-dinitrobenzene	SWCNT	224.9	18.89	1.458	0.991
	BN-SWCNT	305.5	29.59	0.977	0.999
2-naphthol	SWCNT	415.0	28.29	1.066	0.996
	BN-SWCNT	384.6	50.43	1.057	0.992
1-naphthylamine	SWCNT	653.1	64.60	1.119	0.995
	BN-SWCNT	781.6	56.66	1.006	0.991

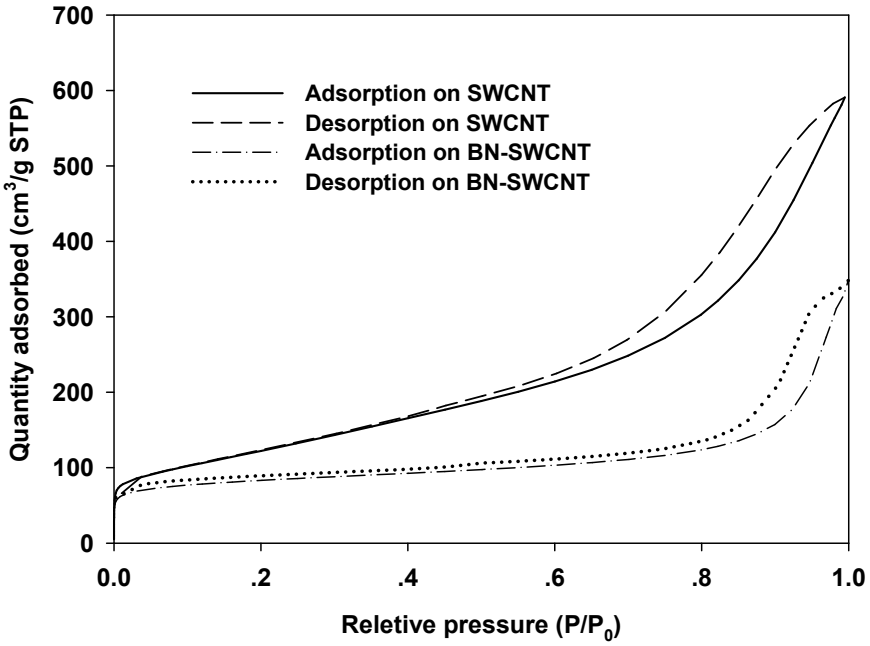

Fig. S1 N_2 adsorption and desorption isotherms to SWCNT and BN-SWCNT.

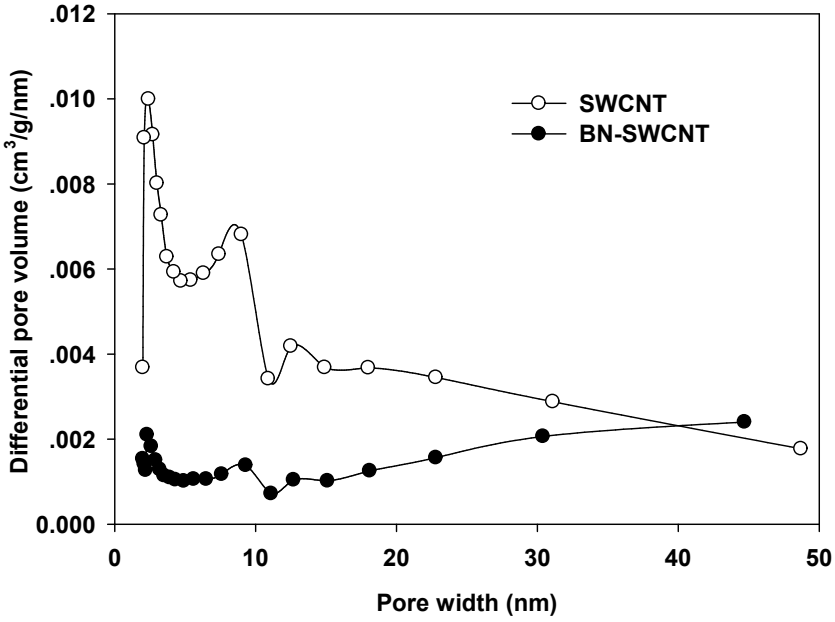

Fig. S2 Pore size distributions of SWCNT and BN-SWCNT, plotted as differential pore volume versus pore width.

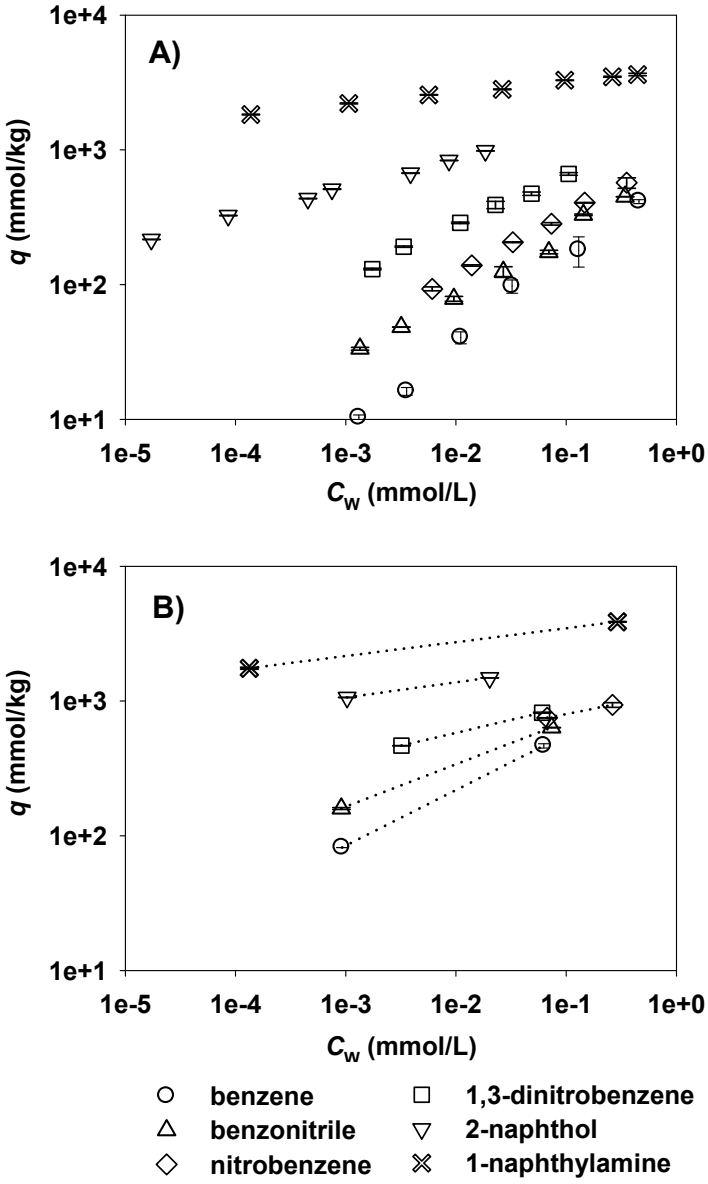

Fig. S3 Adsorption data of six model aromatics to: A) SWCNT; and B) BN-SWCNT.

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