Supplementary Information

Stability of carboxyl-functionalized carbon black nanoparticles: the role of solution chemistry and humic acid

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Additional Details on Materials and Methods

SRHA Adsorption Tests

SRHA adsorption isotherms were obtained using a batch equilibrium technique at room temperature. The initial concentrations of SRHA in the glass reactor were 1 mg/L and 5 mg/L. The mass dosage of CB-NPs added in glass reactors was 10 mg. The glass reactors were placed on a magnetic stirrer (MS2024, Misung Scientific Co., LTD, South Korea) and stirred again for 1 h. The supernatant was filtered using a syringe filter (pore size=20 nm) and the filtered supernatant was analyzed by UV/Vis spectrophotometer analysis. To investigate the reliability of the method for separating the nanoparticles from the suspended SRHA, the presence of the particles in the filtered supernatant was confirmed using TEM and a UV/Vis spectrophotometer (in the range of 200-650 nm) [1]. No particles were observed in TEM, and no peak intensity was observed in UV/Vis spectrophotometer measurements. The adsorbed SRHA content by CB-NPs was calculated directly by the difference in mass determined by the calibration curve (Fig. S1) that was obtained at the optical absorbance of 254 nm using SRHA prepared according to the protocols in references [2, 3].

Additional Details on Results and Discussion

Adsorption of SRHA on CB-NPs in NaCl and CaCl$_2$ Solutions

The amount of SRHA adsorbed into the CB-NPs in the representative ionic strength conditions of NaCl and CaCl$_2$ solutions was measured, and the results are shown in Table S1. The SRHA adsorption was greater in the CaCl$_2$ solution than in the NaCl solution. In the latter, the adsorption amount was constant at approximately 4.11 to 5.97 mg-SRHA/g-CB-

NPs, regardless of the concentration of SRHA added and the ionic strength. In the $CaCl_2$ solution, however, the SRHA adsorption amount increased with the increase in the ionic strength. More precisely, the amount of SRHA adsorbed into CB-NPs was approximately 18.06 mg-SRHA/g-CB-NPs when 1 mg/L SRHA was added to 1 mM $CaCl_2$ solution, and the adsorption amount increased up to 35.10 mg-SRHA/g-CB-NPs when the SRHA concentration (5 mg/L SRHA) was high. According to recent studies, the humic acid adsorption onto the nanomaterial surface is attributable to three mechanisms. The first mechanism relies on the uniquely high specific surface area of the NPs, which provides humic acid with a large adsorption space [4, 5]. The second mechanism is the access of the humic acid molecules to the sites that have low levels of hydrophilicity and low negative charge on the particle surface [6]. Finally, the humic acid adsorption occurs because of the electrostatic attraction and ligand-exchange reactions between humic acid and nanomaterials [5, 7]. According to the zeta potential results, a positive charge was confirmed in the $CaCl_2$ solution at high ionic strength, unlike the negative charge of the CB-NP surface in the NaCl solution. Additionally, the charge positively increased with the increasing ionic strength of the $CaCl_2$ solution. In the $CaCl_2$ solution, an electrostatic attractive force is present between CB-NPs and SRHA at high ionic strength. Consequently, more SRHA adsorption was induced than in NaCl at same ionic strength. This assumption was indirectly supported by the experiments that confirmed the negative reversal of CB-NP zeta potential at high ionic strength in the presence of SRHA in the $CaCl_2$ solution (Table 2, Table S1, and Fig. 7(b)).

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		Ionic strength (mM)	Q (mg-SRHA/g-CB-NPs)
NaCl	w/ SRHA (1 mg/L)	0.1	4.11±0.30
		1	4.43±0.64
		10	4.84±0.65
	w/ SRHA (5 mg/L)	0.1	5.97±0.85
		1	5.11±0.25
		10	5.41±0.60
$CaCl_2$	w/ SRHA (1 mg/L)	0.1	16.54±1.25
		1	18.06±1.53
	w/ SRHA (5 mg/L)	0.1	28.52±0.80
		1	35.10±1.55

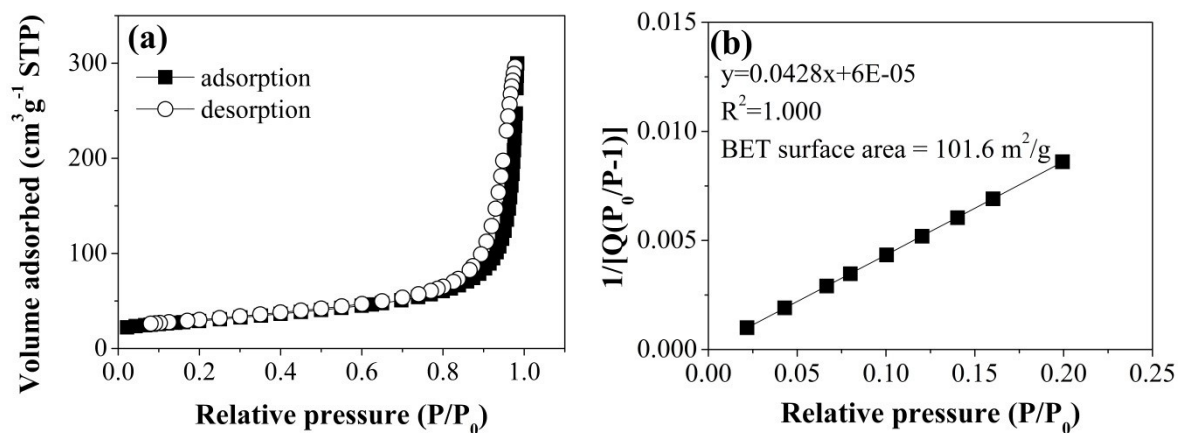**Figure S1.** UV/Vis calibration curve of SRHA solution at a wavelength of 254 nm

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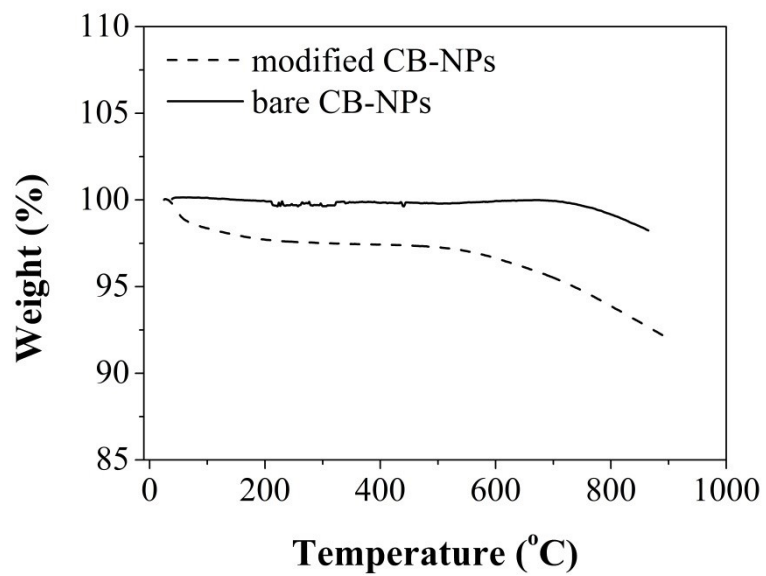
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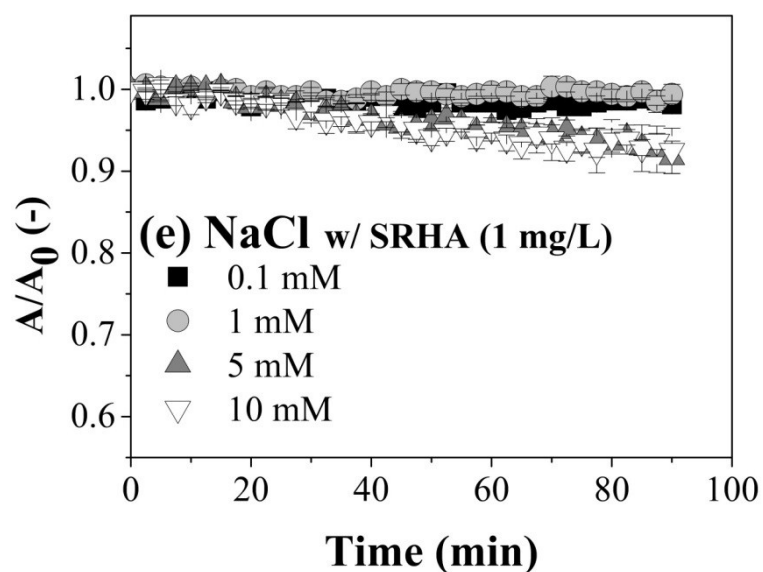
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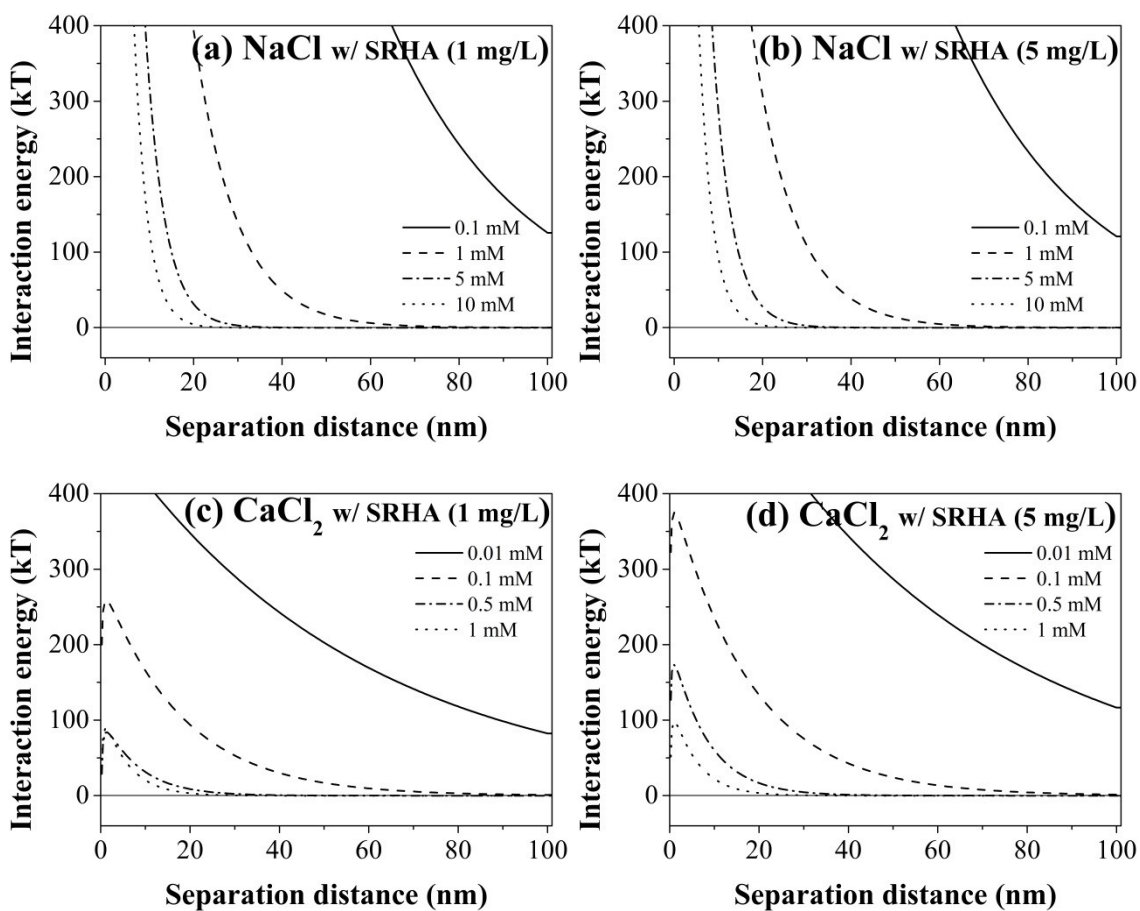
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