

Supplementary Information

Influence of Dispersible and Immobilized Humic Acid on the Transport of Two Types of Synthesized Zinc Oxide Nanoparticles in Quartz Sand

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Additional Details on Materials and Methods

Synthesis and Characterization of two ZnO-NPs used in this study

ZnO-NPs were prepared in different synthesis condition using modified published procedures (Becheri et al., 2008; Han et al., 2014; Wang and Muhammed, 1999). In a typical fabrication for synthesis 1, 1.0 g of ZnCl₂ was dissolved in 40 mL of Milli-Q water and 10 mL of isopropyl alcohol and stirred at 25 °C. Then, 5 mL of 5 M NaOH aqueous solution was added into the zinc chloride solution and then stirred for 2 h at 90 °C. The precipitated product was filtered, washed thoroughly with Milli-Q water, and dried at 80 °C for 24 h. In synthesis 2, 5.0 g of ZnCl₂ was dissolved in 100 mL of ethanol and stirred at 25 °C for 1 h. To this solution, 100 g of 4-methyl-morpholine and 20 mL of 5 M NaOH aqueous solution were added and heated to 70 °C for 24 h. Then, 20 mL of Milli-Q water was added to the solution and then stirred for 2 h at 70 °C. The final solution was aged at 70 °C for 50 h. The precipitated product was filtered, washed thoroughly with Milli-Q water, and dried at 70 °C for 24 h. The synthesized ZnO-NP samples from synthesis 1 and synthesis 2 were designated as *n*ZnO-1 and *n*ZnO-2, respectively.

Fourier transform infrared (FTIR) spectra were recorded using a JASCO FT/IR-4100 spectrometer by measuring the absorbance of the ATR PRO450-S. The spectra were collected in the range of 1900-1100 cm⁻¹ at a resolution of 1.0 cm⁻¹. Thermogravimetric analysis (TGA) was carried out on TGA S-1000 of SCINCO under N₂ flow at a heating rate 10 °C min⁻¹.

Additional Results and Discussion

Characterization of *n*ZnO

Physicochemical properties of two NPs (*n*ZnO-1 and *n*ZnO-2) that were prepared by different synthesis methods were investigated. First, the crystal structure of two NPs was examined via X-ray diffraction (XRD) analysis, and the results are presented in Figure 1a. Hexagonal wurzite ZnO JCPDS 36-1451 is also presented along with the diffraction patterns of the NPs. Overall, the peaks for two NPs were observed at identical 2θ positions, indicating that both NPs had same hexagonal wurzite structure. Figure 1b and 1c show the TEM images for *n*ZnO-1 and *n*ZnO-2, respectively. The TEM results showed that *n*ZnO-2 was relatively more regular and spherical with greater uniform size distribution compared to *n*ZnO-1. The average primary size of two NPs was also determined from the TEM images ($n \geq 400$), and the average size of *n*ZnO-1 and *n*ZnO-2 was determined to be about 52.4 nm and 21.5 nm, respectively.

Figure S1 shows TGA profiles for two NPs. Although the extent of weight loss is different each other, overall trend of both TGA curves is nearly same. Specifically, the weight loss occurring up to 200 °C for both NPs is due to the desorption of physically adsorbed water from the surface of the NPs, and the weight loss that occurred between 200 °C and 600 °C is attributed to the removal of organic compounds from the NPs' surfaces (Han et al., 2012). Based on the results from the TGA analyses, the moisture content and the organic content of *n*ZnO-1 and *n*ZnO-2 were about 0.29% and 2.93%, and 1.57% and 2.34%, respectively. The results indicate that *n*ZnO-2 contains greater amount of moisture and organic compounds than *n*ZnO-1.

In order to obtain the information on the distribution of surface functional groups of two *n*ZnO NPs used in this study, FT-IR analysis was conducted. The results are presented in Figure S2. Both NPs showed the absorption band at 1630 cm^{-1} , which was attributed to zinc carboxylate functional groups (Bian et al., 2011; Gu et al., 1995). Additionally, the broad

absorption band between 1725 and 1605 cm^{-1} that corresponds to $-\text{COOH}$ or $-\text{COO}^-$ functional groups was also observed for both NPs; however, the band intensity was much greater for *n*ZnO-2 than *n*ZnO-1. Similar to this observation, the absorption peak at 1384 cm^{-1} for both NPs, which was originated from symmetric stretching zinc carboxylate (Bian et al., 2011; Xiong et al., 2006), was also relatively higher for *n*ZnO-2 than *n*ZnO-1. It is obvious from the FT-IR results that the surface of *n*ZnO-2 possesses greater amount of carboxylate functional groups than *n*ZnO-1, and this result is well supported by the TGA result that showed higher organic content for *n*ZnO-2.

The specific surface area of two ZnO NPs was determined using the BET model from nitrogen adsorption data, and the results are presented in Figure S3. The specific surface area of *n*ZnO-1 and *n*ZnO-2 was determined to be ca. 10.4 m^2/g and 58.9 m^2/g , respectively. The sixfold higher specific surface area for *n*ZnO-2 can be explained by the results from XRD and TEM analyses that showed smaller crystalline size and primary particle size for *n*ZnO-2. Overall characterization results suggest that the difference in the *n*ZnO synthesis method led to the differences in the physicochemical properties of two *n*ZnO NPs used on this study.

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Table S1. Parameters used to calculate DLVO interactions energy profiles. The measured average values are presented for the zeta potential and the particle size of ZnO-NPs.

NPs	Ionic strength (mM)	SRHA (mg L ⁻¹)	Zeta potential (mV)		Particle size (nm)
			Silica	ZnO	
<i>n</i> ZnO-1	0.1	0		-11.8	191.9
		1	-76.9	-32.6	170.8
		5		-37.3	149.1
	1	0		-5.9	194.4
		1	-72.3	-34.8	168.2
		5		-38.2	147.3
	10	0		-5.2	219.0
		1	-61.4	-37.0	176.9
		5		-38.1	160.3
<i>n</i> ZnO-2	0.1	0		-6.7	309.6
		1	-76.9	-37.6	248.8
		5		-40.0	246.2
	1	0		9.27	310.6
		1	-72.3	-38.4	250.6
		5		-39.2	258.3
	10	0		-3.1	326.3
		1	-61.4	-38.2	252.0
		5		-36.3	237.0

Table S2. Mass balance for two types of *n*ZnO in column experiments.

NPs	Ionic strength (mM)	Sand Type	SRHA (mg L ⁻¹)	BTC (%)	RP (%)	Total (%)	
<i>n</i> ZnO-1	0.1	bare sand	0	2.1	91.1	93.2	
			1	53.2	49.4	102.6	
			5	53.0	55.8	108.8	
	1		0	1.4	95.9	97.3	
			1	47.0	54.4	101.4	
			5	49.8	31.3	81.1	
	10		0	0.8	104.5	105.3	
			1	51.5	54.7	106.2	
			5	48.0	55.7	103.7	
	0.1	SRHA coated sand	0	23.8	68.7	92.5	
			5	49.3	42.1	91.4	
	10		0	17.2	75.6	92.8	
			5	52.6	43.8	96.4	
<i>n</i> ZnO-2	0.1		bare sand	0	0.8	91.7	92.5
				1	40.0	68.3	108.3
		5		47.5	60.6	108.1	
	1	0		0.4	91.7	92.1	
		1		33.4	69.5	102.9	
		5		41.4	59.2	100.6	
	10	0		1.0	90.0	91.0	
		1		37.7	70.2	107.9	
		5		43.9	63.0	106.9	
	0.1	SRHA coated sand	0	2.7	84.5	87.2	
			5	51.0	50.1	101.1	
	10		0	5.0	91.0	96.0	
			5	44.9	60.7	105.6	

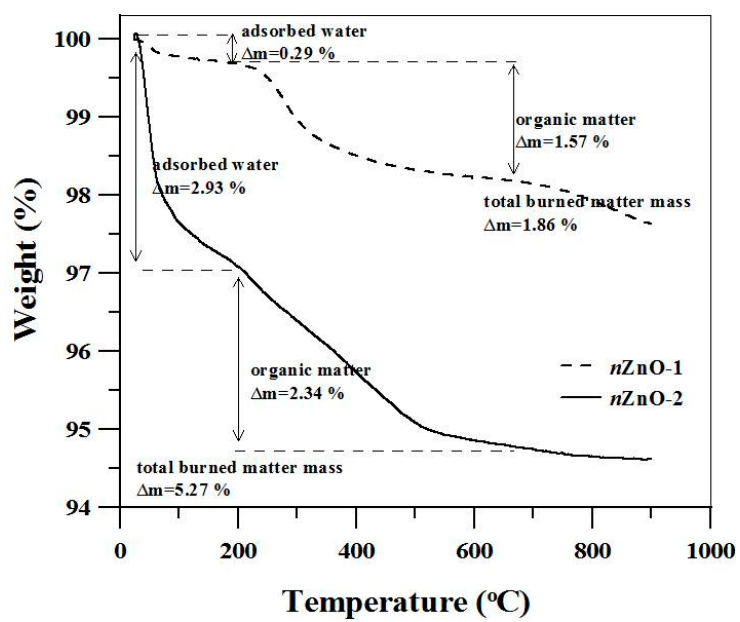


Figure S1. TGA profiles for the prepared two types of *n*ZnO by different synthesis conditions.

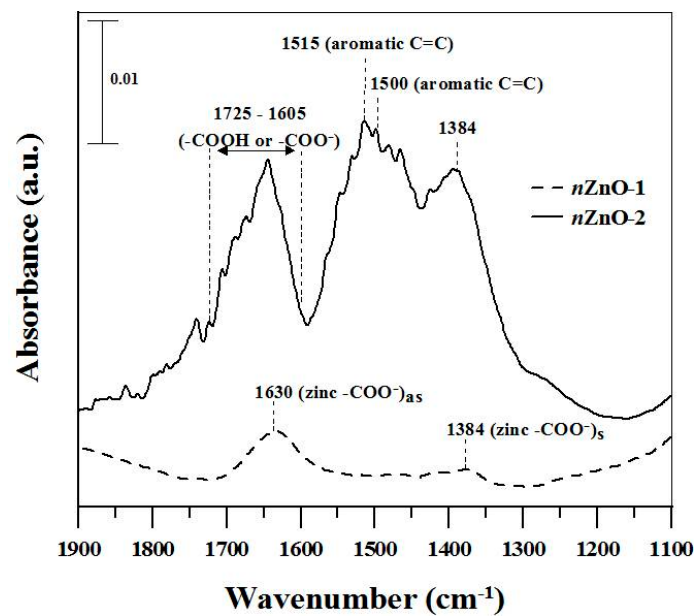


Figure S2. ATR-FTIR spectra of two types of *n*ZnO obtained from different synthesis conditions.

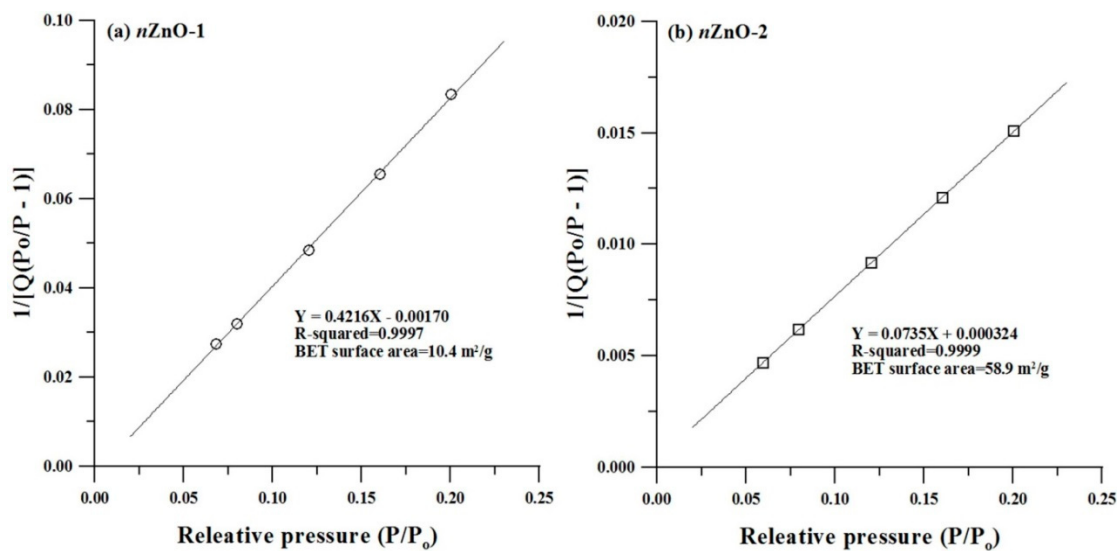


Figure S3. Specific surface areas of two types of *n*ZnO from Brunauer-Emmet-Teller (BET) method.

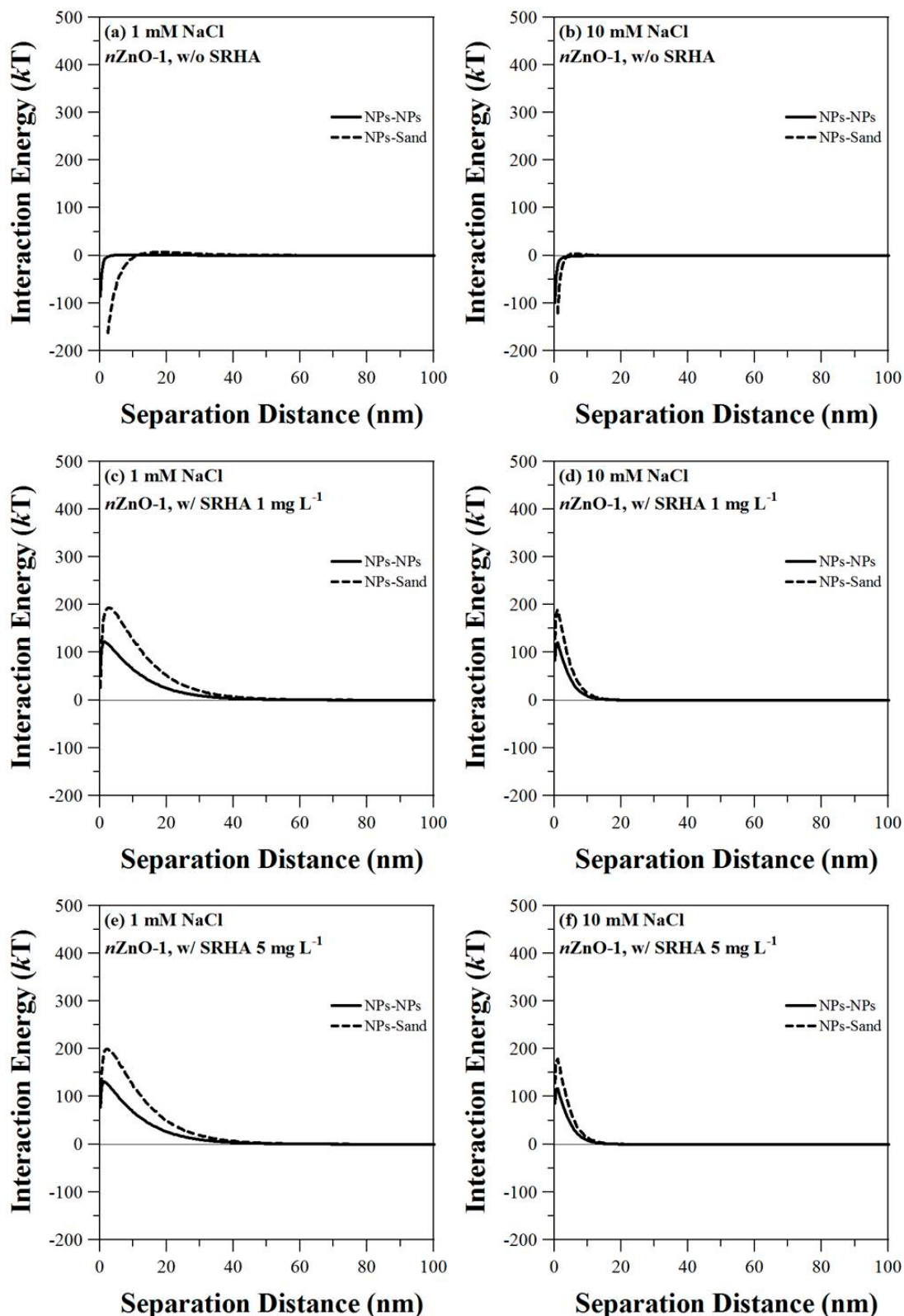


Figure S4. DLVO interaction energy profiles of *n*ZnO-1 for NPs-NPs (solid line) and NPs-sand (dashed line) surfaces in NaCl (1-10 mM) solutions in the absence/presence SRHA.

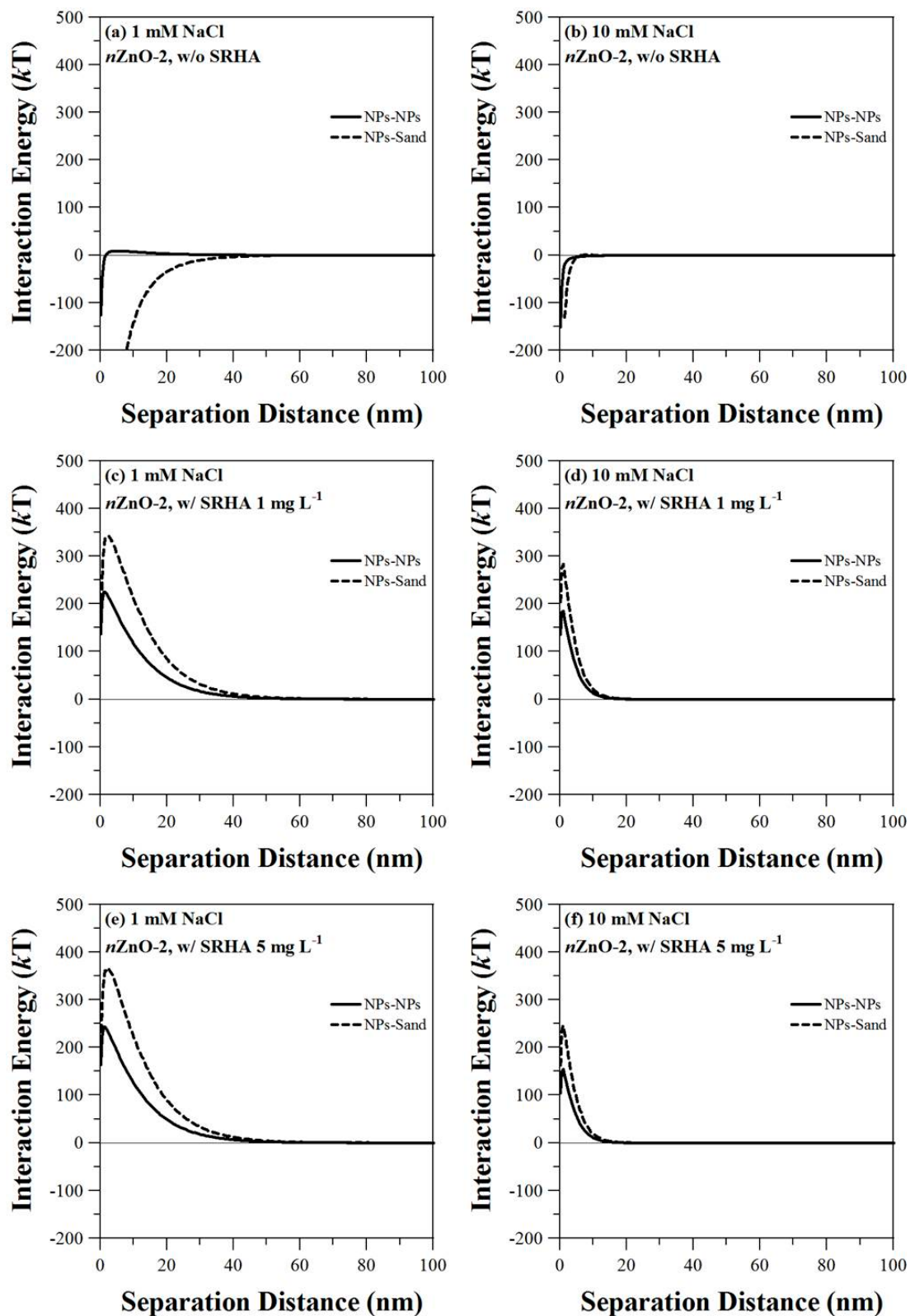


Figure S5. DLVO interaction energy profiles of *n*ZnO-2 for NPs-NPs (solid line) and NPs-sand (dashed line) surfaces in NaCl (1-10 mM) solutions in the absence/presence SRHA.