Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information

Direct *in Situ* Measurement of Dissolved Zinc in the Presence of Zinc Oxide Nanoparticles Using Anodic Stripping Voltammetry

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Content

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This Supporting Information provides:

1. Details of ZnO NP synthesis.
2. Method for measuring dissolved zinc concentration in the ZnO NP stock suspensions.
3. Method for calculating the solubility product of the ZnO NPs.
4. Four tables and 10 figures.

Details of ZnO NP synthesis

In a typical procedure of synthesizing the Ac-5 ZnO NP, 0.88 g (4 mmol) of zinc acetate dihydrate was dissolved in 40 mL of boiling ethanol in a reflux and then cooled to ~0 °C in ice bath. To this solution, 0.288 g (7.2 mmol) of NaOH dissolved in 40 mL of ethanol was added dropwise under vigorous stirring in an ice bath. The resultant colloidal suspension was stirred in the ice bath for an additional 30 min, equally distributed to four 60-mL glass centrifuge tubes, and stored at 4 °C for 7 d. In order to remove Na^+ and excess acetate, the ZnO colloids were washed with hexane. After 40 mL of hexane was added to each centrifuge tube, the colorless clear colloidal suspension turned white and turbid, indicative of ZnO NP aggregation. The sample was centrifuged at 600 rpm (46 g) for 2 min (5804 R, Eppendorf), and the supernatant was decanted. Then, the precipitate was rinsed with approximately 20 mL of ethanol and redispersed with 20 or 12 mL of ethanol by sonication. The general procedure for synthesizing the PVP-4 ZnO NP was similar, except that PVP was present in the zinc precursor solution. In this case, the PVP monomer: Zn molar ratio was 3:5.

For synthesizing the larger ZnO NPs (i.e. PVP-21), the zinc to NaOH molar ratio in the recipe was not changed (i.e., 1:1.8), but a higher PVP monomer: Zn molar ratio of 3:2 was used. NaOH (7.2 mmol) was dissolved in 40 mL of ethanol-water mixture (volume ratio of ethanol:water = 4:1). In this case, the zinc precursor solution was not cooled to 0 °C before adding NaOH. Instead, the NaOH solution was added dropwise to the boiling zinc precursor solution and then stirred at boiling point for 30 min. Then, the heat source was removed and the sample was stirred for another 60 min, during which the mixture cooled to room temperature. After 7-d storage at 4 °C, the PVP-21 ZnO NPs precipitated to the bottom of the centrifuge tubes, probably because of the high water content and ion concentration in the reaction mixture.

Therefore, a hexane washing step was not needed, and the samples were centrifuged directly at 1800 rpm (415 g) for 3 min. The supernatant was decanted, and the precipitate was redispersed with 40 mL of ultrapure water containing 10 mg of PVP by sonication.

Method for measuring dissolved zinc concentration in the ZnO NP stock suspensions

For ZnO NPs dispersed in ethanol (i.e. PVP-4 and Ac-5), 2 mL of stock suspension was dispensed in 3-mL thickwall polyallomer centrifuge tubes (Beckman Coulter) and centrifuged at 60000 rpm (370000 g) and 25 ºC for 4 or 2 h (for PVP-4 and Ac-5 respectively). Then, 100 uL of supernatant was added to 50 mL of mixed acid (2% HNO_3 and 0.5% HCl) and left overnight prior to ICP-MS analysis. For ZnO NPs dispersed in water (i.e. PVP-21 and TES-21), 4 mL of the stock suspension was dispensed in Ultra-Clear centrifuge tubes (Beckman Coulter) and centrifuged at 30000 rpm (92500 g) and 25 ºC for 1 h. Then, the supernatant was diluted in the mixed acid, and zinc concentration was analyzed by ICP-MS.

Method for calculating the solubility product of the ZnO NPs

The solubility product (K_{sp}) of the ZnO NPs was calculated from pH and equilibrium dissolved zinc concentration measured by ASV ($[\mathrm{Zn}]_{\mathrm{ASV,\ eq}}$) in **Figure 3** and **Figure 4** (only data from experiments performed without natural organic matter), using the following equation:

$$K_{\mathrm{sp}} = \frac{[\mathrm{Zn}^{2+}]}{1\ \mathrm{M}} \gamma_{\mathrm{Zn}^{2+}} \left(10^{\mathrm{pH}} K_{\mathrm{W}}\right)^2$$

where $[\mathrm{Zn}^{2+}]$ is the molar concentration of the free zinc ion, which was calculated from $[\mathrm{Zn}]_{\mathrm{ASV,\ eq}}$, pH, chloride concentration and stability constants of relevant zinc-ligand complexes, using MINEQL+ (Version 4.5); $\gamma_{\mathrm{Zn}^{2+}}$ is the activity coefficient of the Zn^{2+} ion, and a value of 0.36 was used at 0.1 M ionic strength and 25 ºC, according to the Davies equation; K_W is the ionic product of water, which is $10^{-14.0}$ at 25 ºC.

Table S1. Dissolve and total zinc concentration in ZnO NP stock suspensions, as quantified by ultracentrifugation/ICP-MS. The values represent mean and standard deviations (SD) of 2 to 3 measurements.

Sample	$[Zn]_{dissolved}$ (μM)		$[Zn]_{total}$ (mM)		percent dissolved (%)
	mean	SD	mean	SD	
PVP-4, batch #1	73.5	0.8	25.5	-	0.29
PVP-4, batch #2	208.9	9.6	53.0	-	0.39
Ac-5, batch #1	245.6	17.6	36.9	-	0.67
Ac-5, batch #2	184.6	-	34.2	-	0.54
Ac-5, batch #3	281.5	9.0	55.4	-	0.51
Ac-5, batch #4	333.0	-	69.4	-	0.48
PVP-21	236.9	2.9	22.4	0.4	1.06
TES-21, batch #1	111.6	0.9	19.2	0.2	0.58
TES-21, batch #2	121.9	2.0	19.8	0.1	0.62
TES-21, batch #3	110.4	1.1	20.6	0.4	0.54

Table S2. Method detection limit (DL, in μg L^{-1}) and concentrations (in μg $L^{-1}$and μM) of major metal elements (> 0.1 μM) in filtered wetland surface water. Values are mean and SD of triplicate measurements.

Element	DL[a] (μg L^{-1})	concentration (μg L^{-1})	concentration (μM)
Na	129	5784±83	252±4
Mg	1.7	1537±24	63±1
Al	7.5	11±2	0.42±0.05
K	536	932±4	24±0
Ca	100	3202±40	80±1
Mn	1.3	31±1	0.56±0.01
Fe	3.5	21±0	0.38±0.00
Sr	0.03	28±4	0.32±0.04
Ba	0.20	19±3	0.14±0.02

Notes: [a] The method DL was calculated as 3 times the instrument DL, because the water sample was diluted in a mixed acid (2% HNO_3 and 0.5% HCl) by a factor of 3 before ICP-MS analysis.

Table S3. Method detection limit (DL, in μg L^{-1}) and concentrations (in μg L^{-1}and nM) of trace metal/metalloid elements (< 0.1 μM) in filtered wetland surface water. Values are mean and SD of triplicate measurements.

Element	DL (μg L^{-1})	concentration (μg L^{-1})	concentration (nM)
Be	0.09	< DL	< DL
V	1.2	< DL	< DL
Cr	1.4	< DL	< DL
Co	0.02	0.24±0.01	4.0±0.2
Ni	0.03	0.96±0.06	16±1
Cu	1.6	1.9±0.1	29±1
Zn	1.1	4.4±0.7	68±10
As	0.08	1.0±0.0	14±0
Cd	0.12	< DL	< DL
Ce	0.003	0.19±0.03	1.3±0.2
Pb	0.04	0.08±0.01	0.4±0.0
U	0.002	0.024±0.003	0.1±0.0

Table S4. Solubility product (K_{sp}) of ZnO NPs calculated from pH and equilibrium dissolved zinc concentration measured by ASV ($[Zn]_{ASV,\ eq}$)**.** K_{sp} values correspond to this reaction stoichiometry: $ZnO_{(s)} + H_2O = Zn^{2+} + 2OH^-$.

ZnO NP	pH[a]	$[Zn]_{ASV,\ eq}$ (μM)[b]	$[Zn^{2+}]/[Zn]_{ASV,\ eq}$ [c]	$[Zn^{2+}]$ (μM)	K_{sp}
PVP-4	8.28±0.02	44.9±2.5	0.753	33.8±1.9	$(4.4\pm0.5)\times10^{-17}$
PVP-4	8.59±0.02	13.7±0.6	0.609	8.3±0.4	$(4.5\pm0.5)\times10^{-17}$
Ac-5	8.29±0.02	44.8±1.2	0.744	33.3±0.9	$(4.6\pm0.4)\times10^{-17}$
Ac-5	8.60±0.02	12.9±0.4	0.603	7.8±0.3	$(4.4\pm0.4)\times10^{-17}$
PVP-21	8.56±0.02	4.6±0.2	0.623	2.9±0.1	$(1.4\pm0.1)\times10^{-17}$
TES-21	8.30±0.02	14.1±0.4	0.743	10.5±0.3	$(1.5\pm0.1)\times10^{-17}$
TES-21	8.58±0.02	3.7±0.1	0.615	2.3±0.1	$(1.2\pm0.1)\times10^{-17}$
TES-21	8.57±0.02	3.4±0.1	0.602	2.1±0.1	$(1.0\pm0.1)\times10^{-17}$

Notes:

[a] The pH is reported as measured value (stable reading) ± precision of the pH meter.

[b] $[Zn]_{ASV,\ eq}$ is reported as arithmetic mean ± standard deviation of measured $[Zn]_{ASV}$ in the equilibrium sections of the dissolution curves, i.e. after 20 to 60 min.

[c] The ratio of free zinc ion concentration ($[Zn^{2+}]$) to $[Zn]_{ASV,\ eq}$ was calculated using MINEQL+.

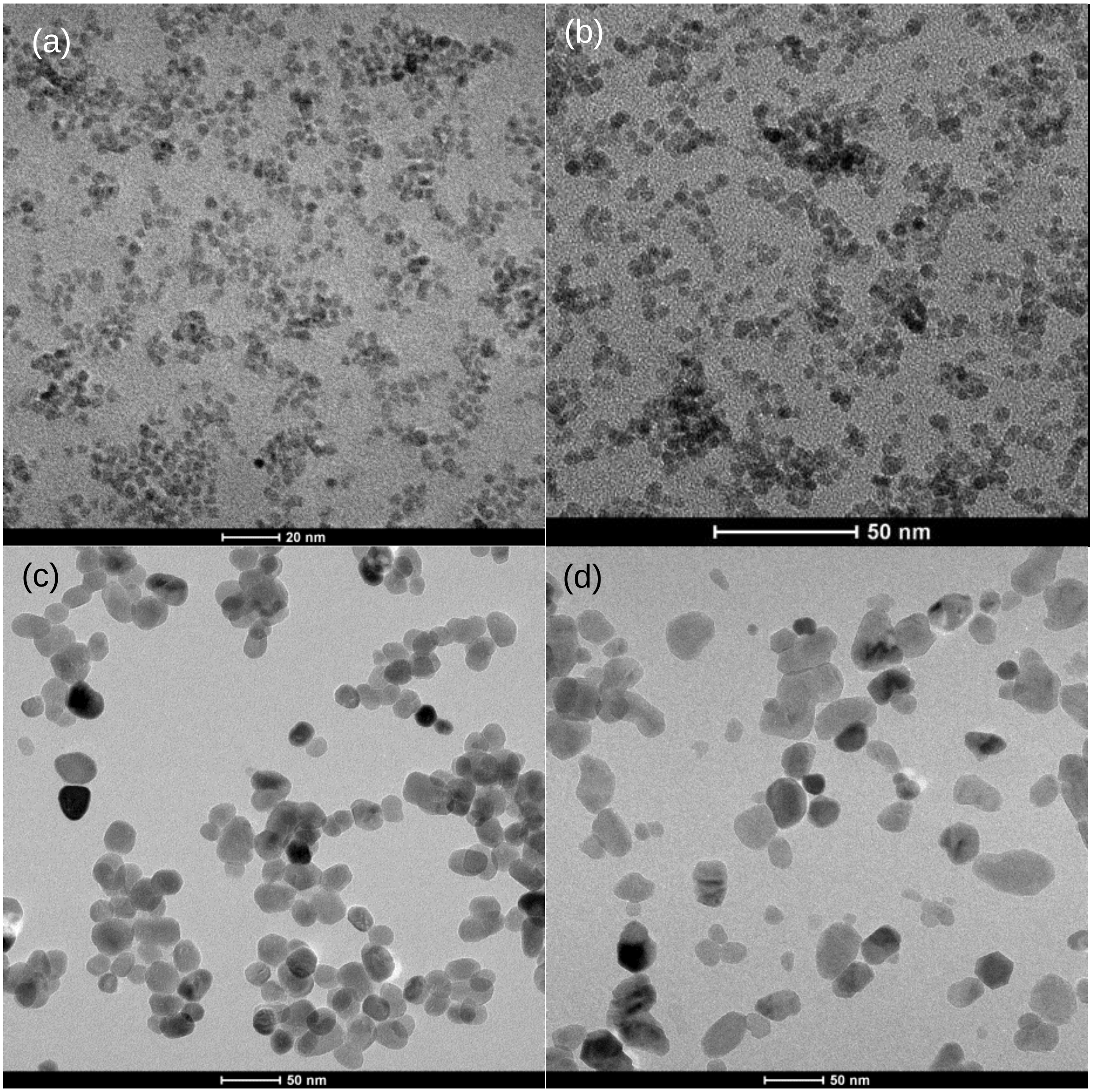

Figure S1. TEM images of ZnO NPs: (a) PVP-4, (b) Ac-5, (c) PVP-21 and (d) TES-21. Scale bar: (a) 20 nm; (b)-(d) 50 nm.

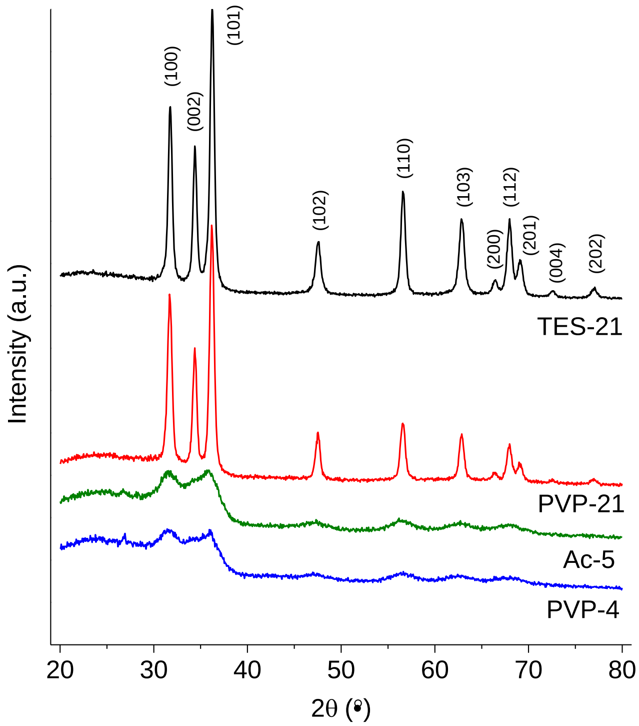

Figure S2. X-ray diffraction spectra of ZnO NPs. The Miller indices in parentheses correspond to those for ZnO zincite.

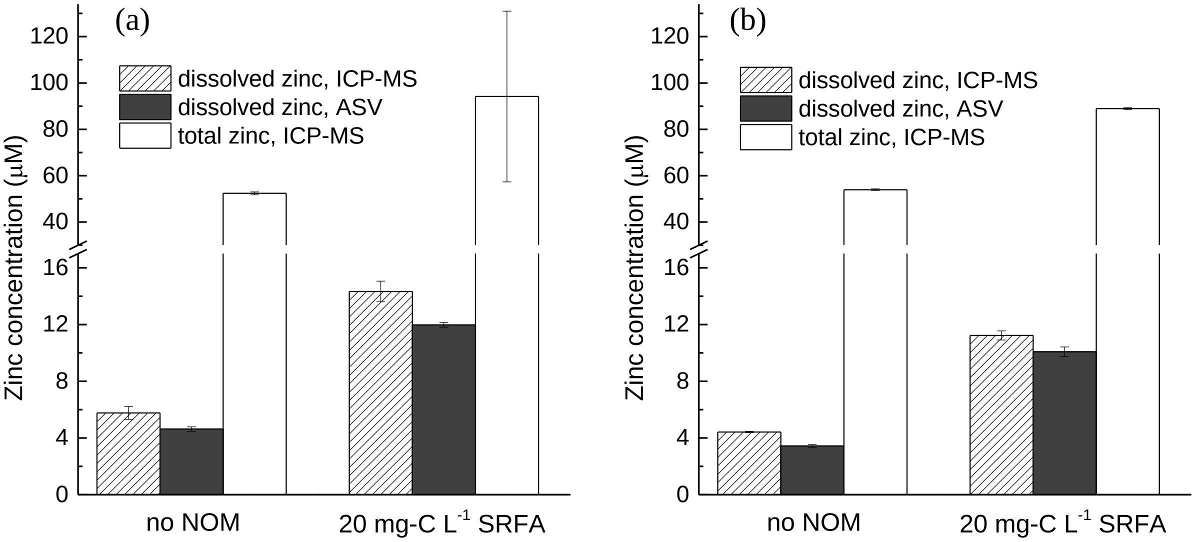

Figure S3. Equilibrium dissolved zinc concentration from (a) PVP-21 and (b) TES-21 ZnO NPs with or without 20 mg-C L^{-1} SRFA, measured by ICP-MS after ultracentrifugation or by ASV. Medium: 82 mM KCl solution buffered with 10 mM POPSO. *I* = 0.1 M, pH = 8.5-8.6. *T* = 25ºC. Nominal total zinc concentration: 75 μM. Total Zn concentration in the suspension at the end of the experiments was also measured by ICP-MS after digestion in 2% HNO_3 and 0.5% HCl overnight at room temperature.

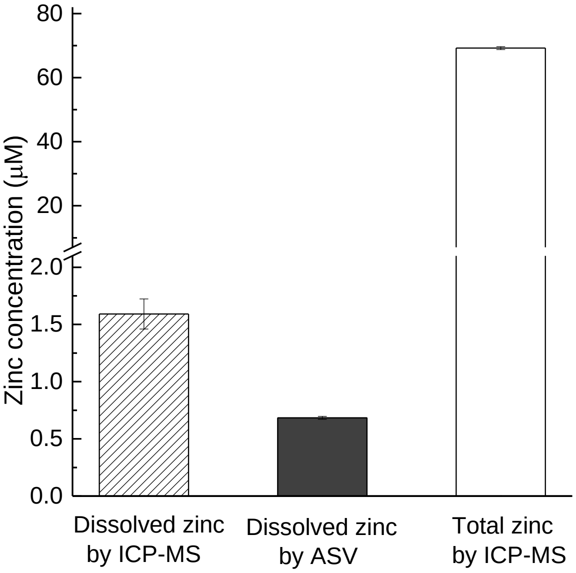

Figure S4. Equilibrium dissolved zinc concentration from TES-21 ZnO NPs in filtered wetland surface water, measured by ICP-MS after ultracentrifugation and by ASV. *I* ≈ 1 mM, pH = 8.9-9.2. *T* = 25ºC. Nominal total zinc concentration: 75 μM. Total Zn concentration in the suspension at the end of the experiments was also measured by ICP-MS after digestion in 2% HNO_3 and 0.5% HCl overnight at room temperature. Z-average hydrodynamic diameter measured at dissolution equilibrium (i.e. after 50 min) was 83 nm.

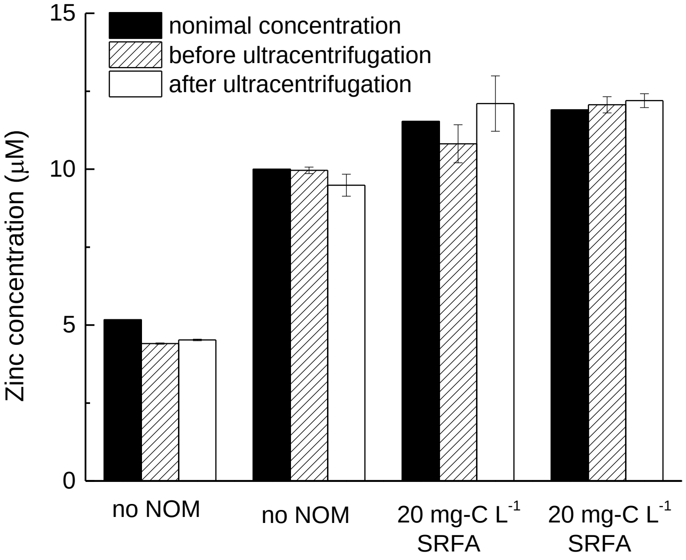

Figure S5. Zinc concentration in dissolved Zn calibration solutions with or without 20 mg-C L^{-1} SRFA, measured by ICP-MS before and after ultracentrifugation. Medium: 82 mM KCl solution buffered with 10 mM POPSO. *I* = 0.1 M, pH = 8.4-8.5, *T* = 25ºC.

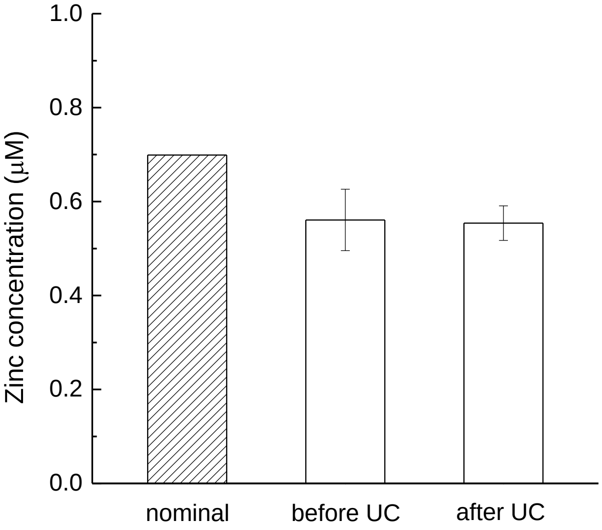

Figure S6. Zinc concentration in filtered wetland surface water amended with dissolved Zn. Zn concentration was measured by ICP-MS before and after ultracentrifugation (UC). $I \approx 1$ mM, pH = 8.9-9.0, *T* = 25ºC.

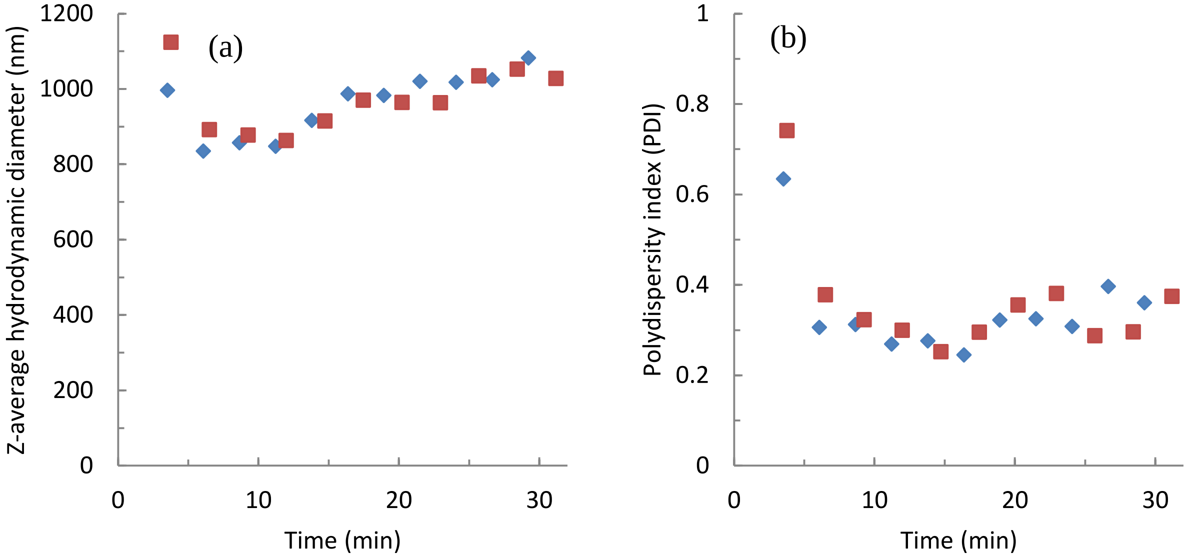

Figure S7. (a) Z-average hydrodynamic diameter and (b) polydispersity index (PDI) of PVP-4 ZnO NP aggregate in KCl solution, as measured by DLS. Medium: 80 mM KCl solution buffered with 10 mM POPSO. *I* = 0.1 M, pH = 8.56, *T* = 25ºC. Nominal total zinc concentration: 75 μM. Experiments were performed in duplicate. Notes: when PDI is high (e.g. > 0.5), NP aggregate size has broad distributions, and Z-average hydrodynamic diameter is not a reliable parameter for comparing NP aggregate size.

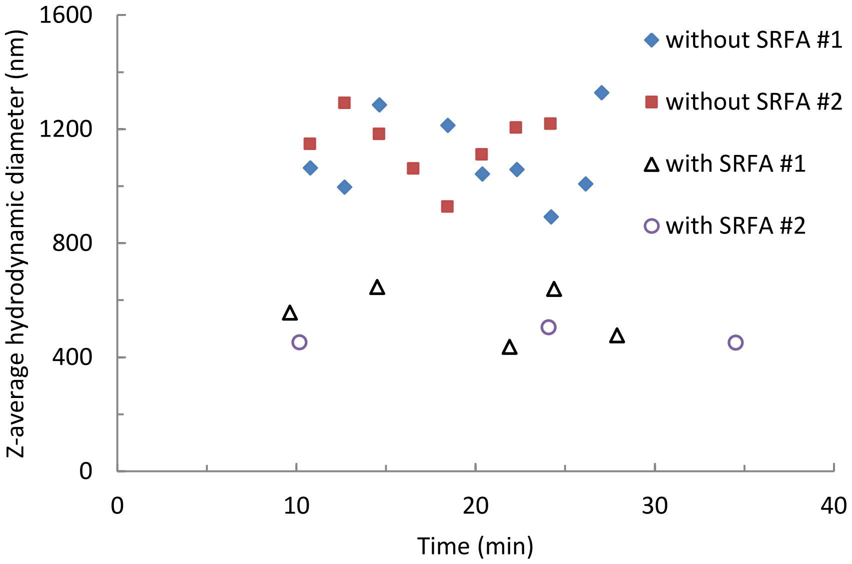

Figure S8. Aggregation kinetics of Ac-5 ZnO NPs with or without 4.6 mg-C L^{-1} SRFA. Medium: 81 mM KCl solution buffered with 20 mM MOPS. *I* = 0.1 M, pH = 8.5, *T* = 25ºC. Nominal total zinc concentration: 75 μM. Experiments were performed in duplicate. Data points with PDI > 0.65 were excluded.

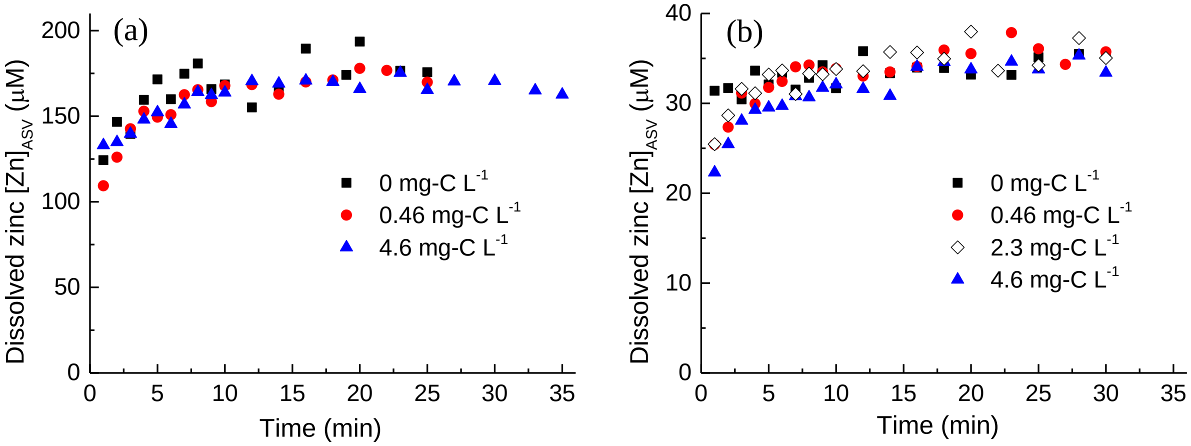

Figure S9. Dissolution of Ac-5 ZnO NPs at different pH values and with different concentrations of SRFA. Nominal total zinc concentration and pH: (a) 300 μM, 7.9-8.0; (b) 150 μM, 8.3-8.4. Medium: 81-83 mM KCl solution buffered with 20 mM MOPS. *I* = 0.1 M. *T* = 25ºC.

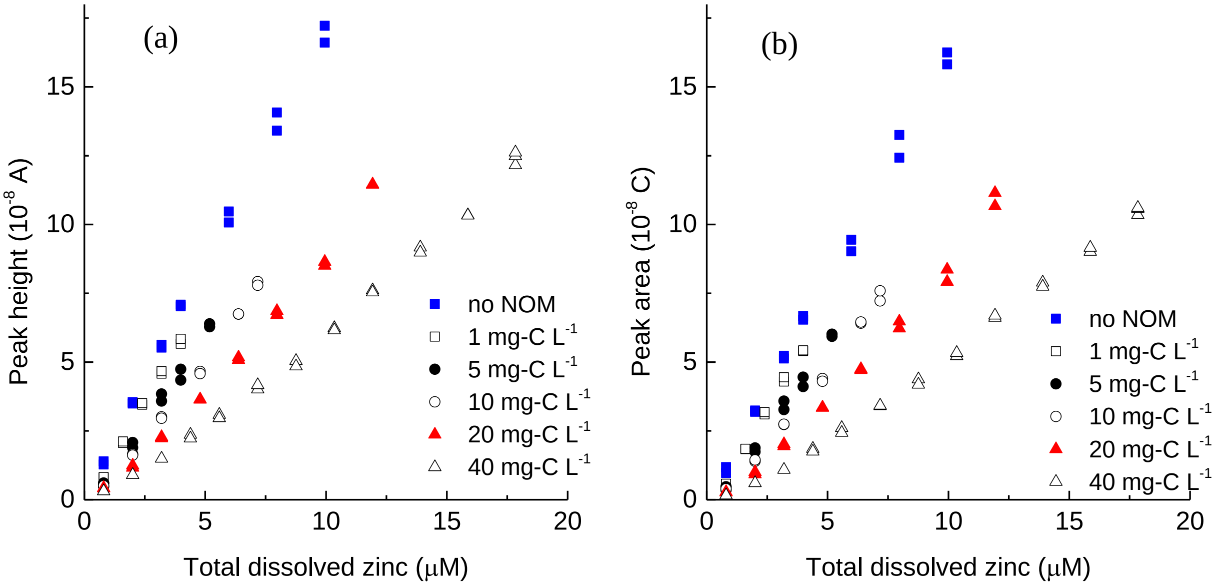

Figure S10. Dissolved zinc calibration curves in the presence of different concentrations of SRFA (0-40 mg-C L^{-1}). (a) peak current (height), (b) peak area.