Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Heteroaggregation of Bare Silver Nanoparticles with Clay Minerals

Supporting Information

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Table S1. Summary of the literature on clay mineral aggregation

References	Type of Clay Minerals	Saturating Cations	Electrolyte	pH	Aggregation Experiments
1	Kaolinite from Zettlitz kaolin (Germany)	Na^+	NaCl	4–8	Huge aggregates were formed only below pH~7 in kaolinite suspensions, with CCC around 1 mM NaCl. The CCC measured in the alkaline region was ~ 100 mM NaCl.
2	Montmorillonite from Wyoming bentonite (Swy-1 and Swy-2 samples)	Na^+	NaCl	4–8.5	The CCC of montmorillonite suspensions was reported as ~ 25 mM and ~ 100 mM NaCl at pH ~ 4 and ~ 8, respectively. The CCC at the pH of PZC of edges (~ 6.5) approximated as ~ 50mM NaCl.
3	Montmorillonite from Cheto, Arizona (SAz-1) and kaolinite from Georgia (KGa-1). Both were obtained from The Clay Minerals Society's Source Clays Repository.	Na^+, Ca^{2+}, and Mg^{2+}	NaCl, $CaCl_2$, or $MgCl_2$ to match the saturating cations of the clays.	5–10	The CCC of all types of clays were found to be pH-dependent. The effect of pH was greater for the kaolinite than the montmorillonite.
4	Silver Hill illite (IMt-1) from the Source Clays Repository of the Clay Mineral Society	Na^+ and K^+	$NaClO_4$ and $KClO_4$ for Na- and K-illite, respectively.	6–11	K^+ was three times more effective than Na^+ for flocculating illite due to greater surface complexation of K-illite.

1. E. Tombácz and M.S. Szekeres, *Applied Clay Science* 2006, **34**, 105-124
2. E. Tombácz and M. Szekeres, *Applied Clay Science*, 2004, **27**, 75-94
3. S. Goldberg and R.A. Glaubig, *Clays Clay Min.*, 1987, **35**, 220-227
4. D. Hesterberg and A. Page, *Soil Sci.Soc.Am. J.*, 1990, **54**, 735-739.

Table S2. Volume of stock suspension used to prepare working particle suspensions. In each case the working suspension volume was 50 mL.

	Homoaggregation	Heteroaggregation
AgNP	2mL	4mL
Na-MONT	0.2mL	0.4mL
Ca-MONT	0.1mL	0.2mL
Na-illite	2mL	4mL
Ca-illite	1mL	2mL

Table S3. Values of the d*r*/d*t* for single component systems used to determine k_{rapid}.

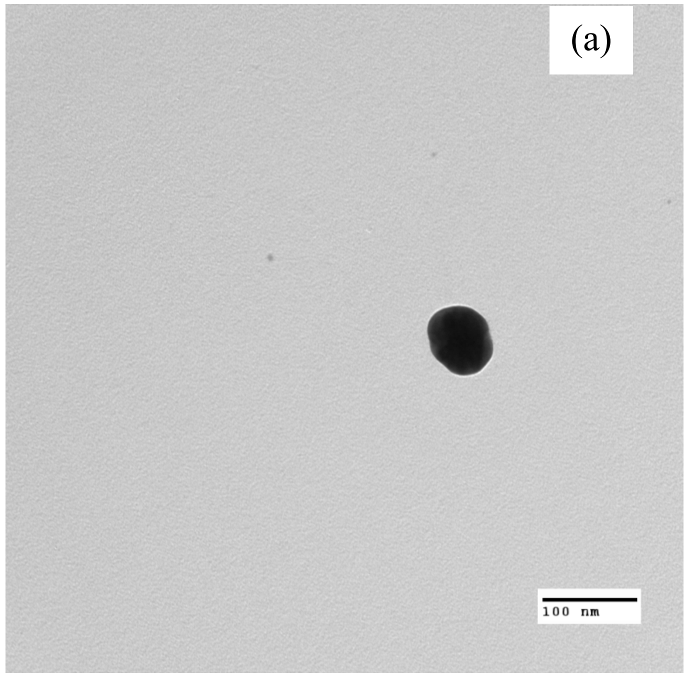
Electrolyte	**d*r*/d*t* (nm/s)**				
	Bare-AgNP	**Na-MONT**	**Ca-MONT**	**Na-illite**	**Ca-illite**
NaCl	0.10	5.53	4.41	0.53	1.24
$NaNO_3$	0.12	7.52	5.47	1.04	1.06
$CaCl_2$	0.14	6.83	2.66	1.33	1.35

Table S4. Values of the d*r*/d*t* for binary component systems used to determine k_{rapid}.

Electrolyte	d*r*/d*t* (nm/s) AgNP + Na-MONT	AgNP + Ca-MONT	AgNP + Na-illite	AgNP + Ca-illite
NaCl	5.73	5.60	0.63	1.41
$NaNO_3$	4.92	4.57	1.04	1.16
$CaCl_2$	7.44	2.99	1.24	1.21

Table S5. Values of the mean count rates for systems with d*r*/d*t* for binary component systems used to determine k_{rapid}.

Electrolyte	d*r*/d*t* (nm/s) AgNP + Na-MONT	AgNP + Ca-MONT	AgNP + Na-illite	AgNP + Ca-illite
NaCl	5.73	5.60	0.63	1.41
$NaNO_3$	4.92	4.57	1.04	1.16
$CaCl_2$	7.44	2.99	1.24	1.21



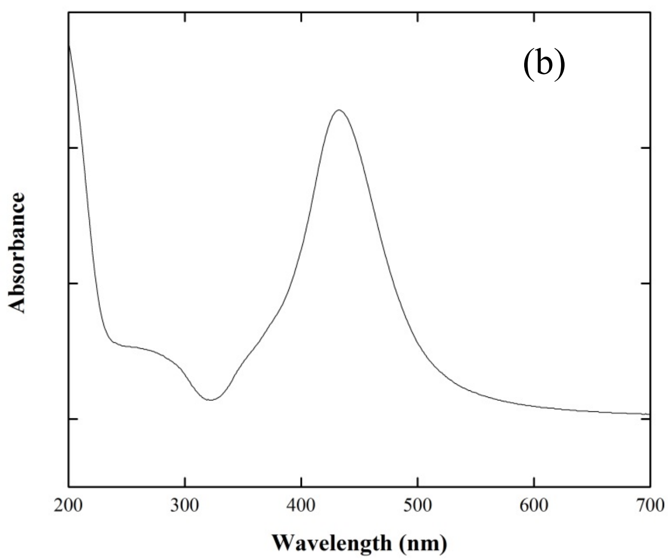


Figure S1. Characterization of the silver nanoparticles suspended in background $NaCl/NaHCO_3$ electrolyte: (a) TEM image and (b) UV-vis absorption spectrum.

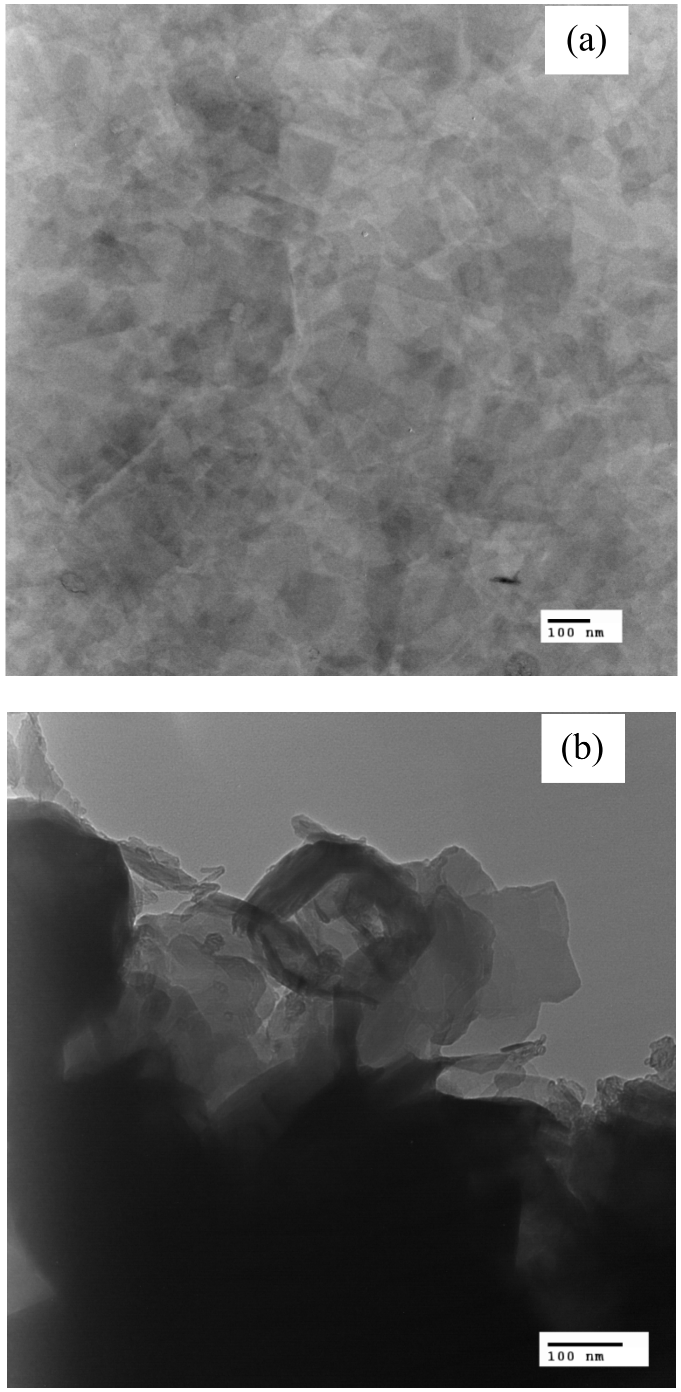


Figure S2. TEM image of clay mineral samples suspended in background NaCl/$NaHCO_3$ electrolyte: (a) montmorillonite and (b) illite.

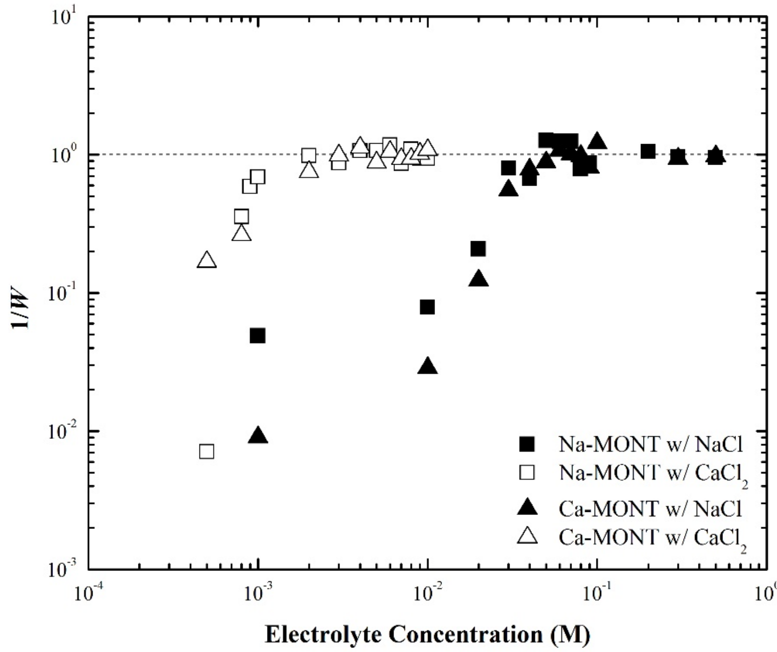


Figure S3. Inverse stability ratio (1/W) of Na- and Ca-montmorillonite as a function of NaCl and $CaCl_2$ concentrations.

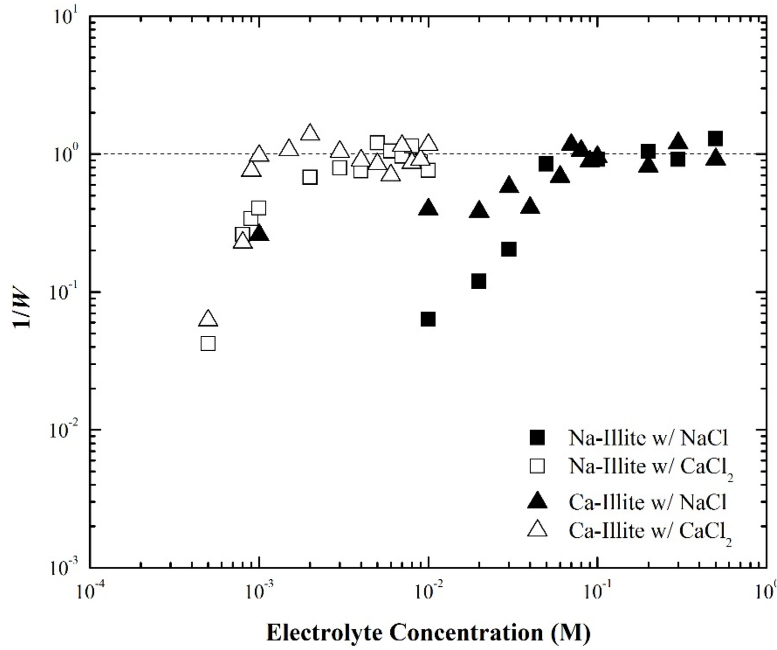


Figure S4. Inverse stability ratio (1/W) of Na- and Ca-illite as a function of NaCl and $CaCl_2$ concentrations.

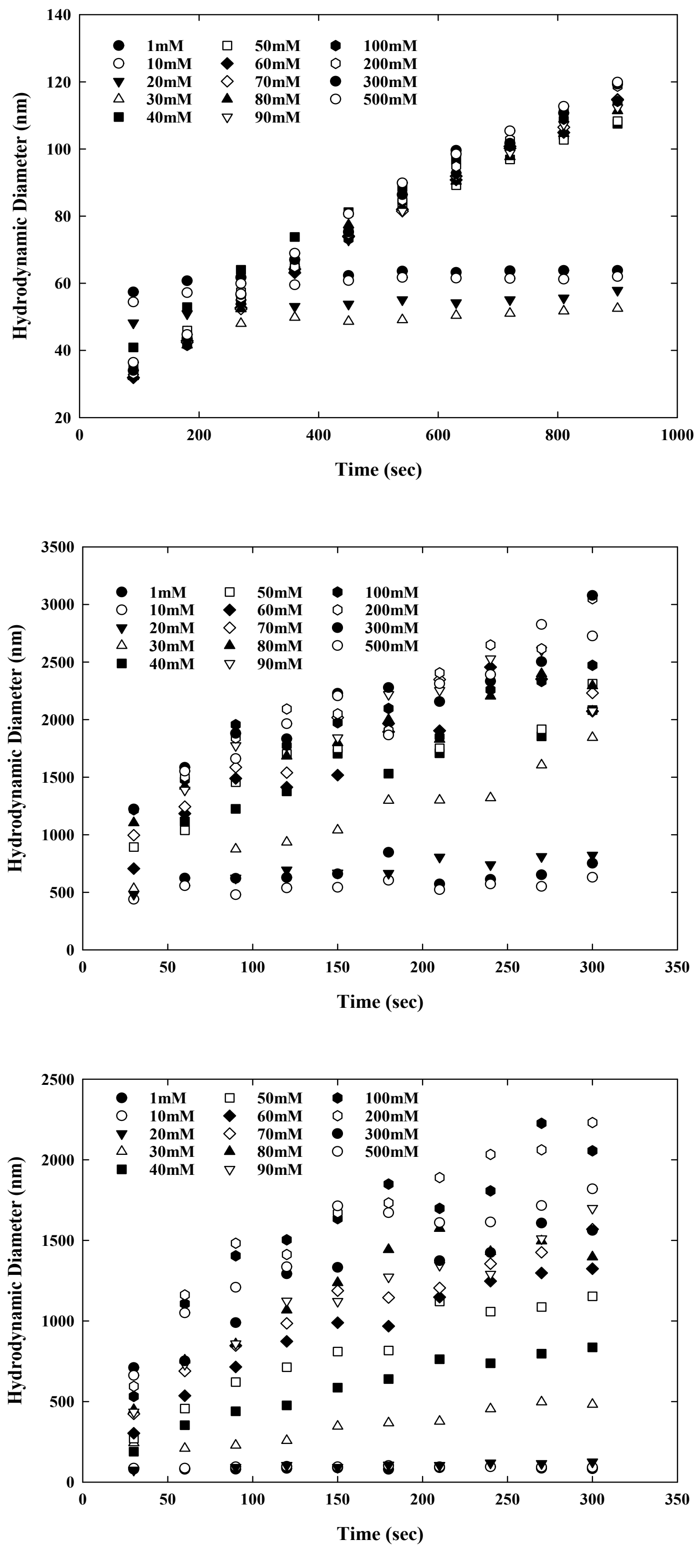


Figure S5. Example aggregation profiles for (a) AgNPs (b) Na-Mont and (c) AgNPs + NaMont used to determine stability plots shown in Figure 7a.

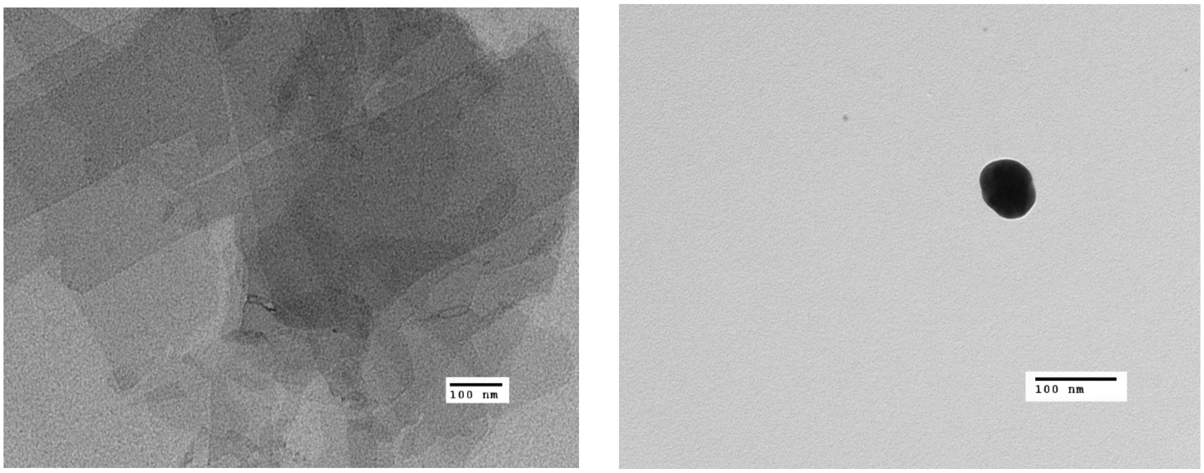


Figure S6. TEM images of heteroaggregated silver nanoparticles with Na-montmorillonite at 10mM NaCl showing (A) bare Na-montmorillonite and (B) isolated silver nanoparticles.