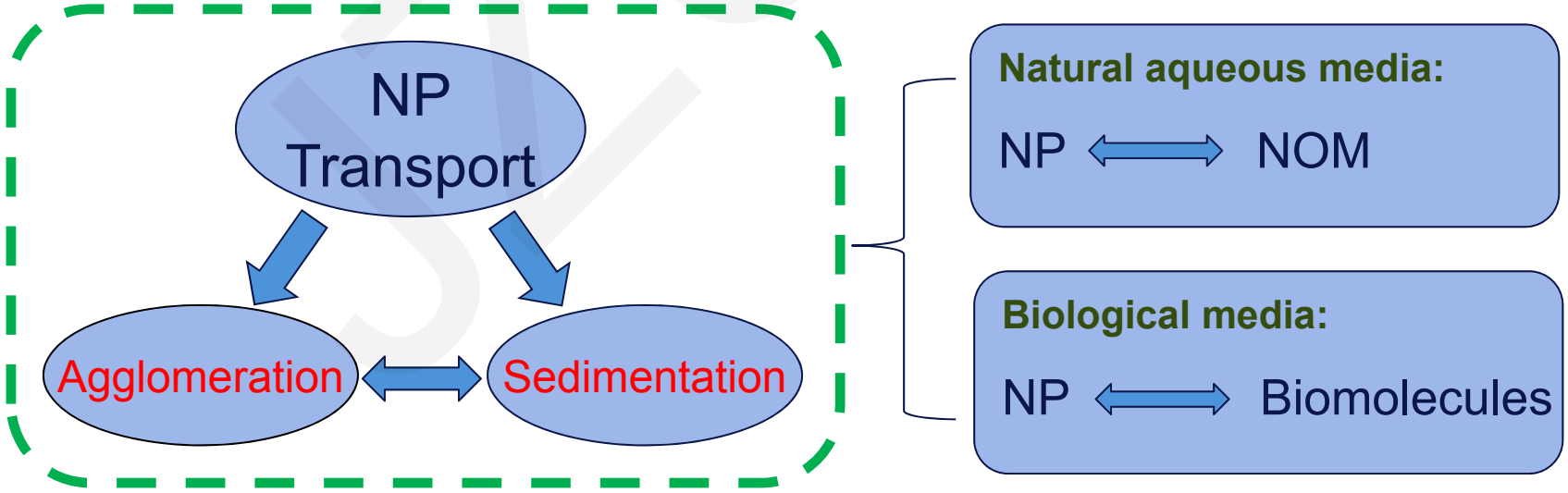
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Effects of humic acid and bovine serum albumin on agglomeration and sedimentation of oxide nanoparticles

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Background

- The wide applications of nanoparticles (NPs) cause potential threats to human health. The transport of NPs in nature has become an important environmental issue. *(Nel et al., 2006)*
- Agglomeration and sedimentation are two important and related processes when we study NP transport. *(Chen and Elimelech, 2007; Ghosh et al., 2008; Petosa et al., 2010)*
- In the natural aqueous media, NPs may interact with natural organic matter (NOM); while in the biological media, NPs interact with biomolecules. *(Chowdhury et al., 2012; Chae et al., 2012)*



Materials and Experiments

◆Oxide Nanoparticles:

Particles	Crystal	Purity	Primary size (nm)	S_{BET} (m^2/g)	ζ at pH 6 (mV)	
					ζ_{Na}	ζ_{Ca}
Al_2O_3	γ form	≥99.9%	60±5	208	35	37
SiO_2	Porous form	≥98%	20-50	675	-7	-5
TiO_2	Anatase form	≥99%	5-10	324	5	11

◆NOM: Humic acid (HA); Biomolecules: Bovine serum albumin (BSA)

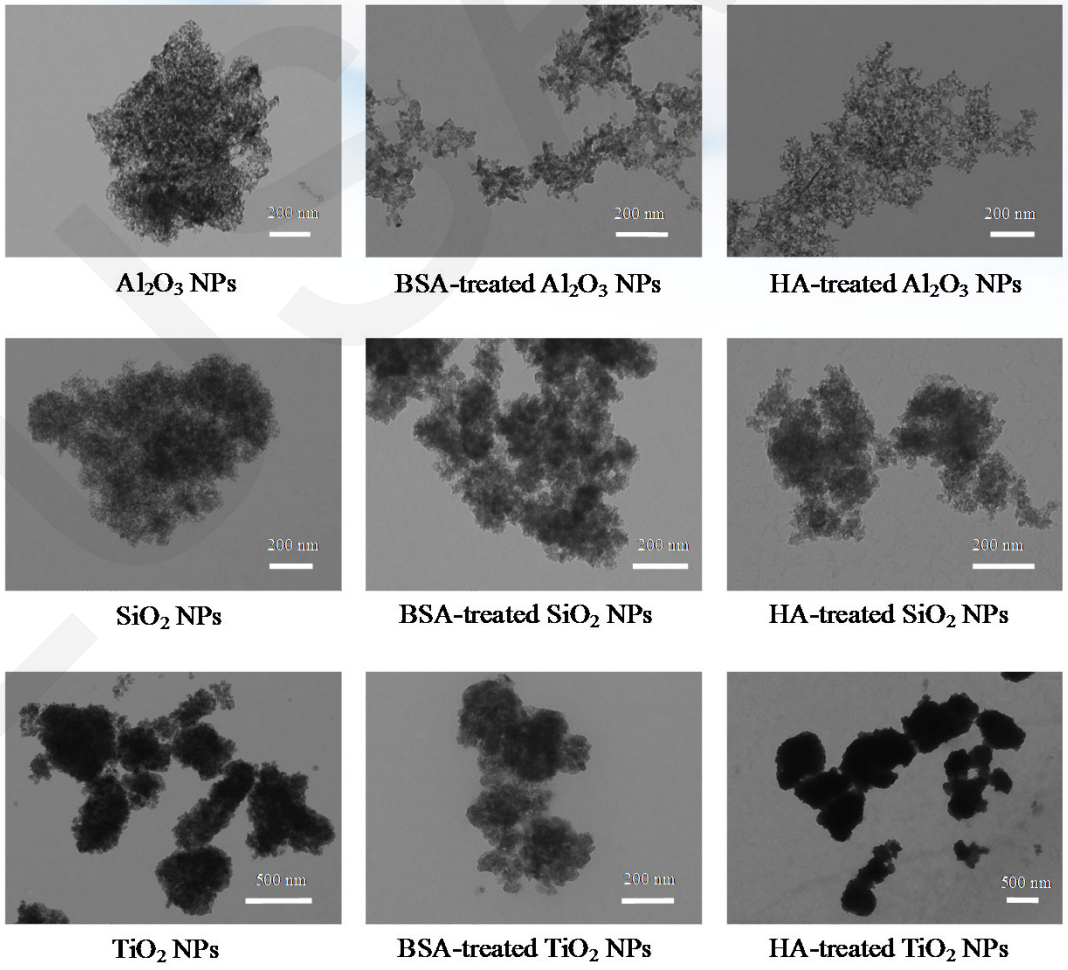
◆Experiments

- ➢TEM imaging—Morphology of NP agglomerates
- ➢Zeta Potential measurement—Charges of NP agglomerates
- ➢Dynamic light scattering (DLS) — Size of NP Agglomerates
- ➢Optical absorbance at 800 nm—NP sedimentation rates

Results and Discussion

1. TEM Imaging

- Al_2O_3 NPs show better dispersion after BSA/HA treatment.
- BSA/HA-treated SiO_2 NPs look very similar to the untreated NPs
- TiO_2 NPs disperse better after BSA treatment, but HA induces more serious agglomeration.

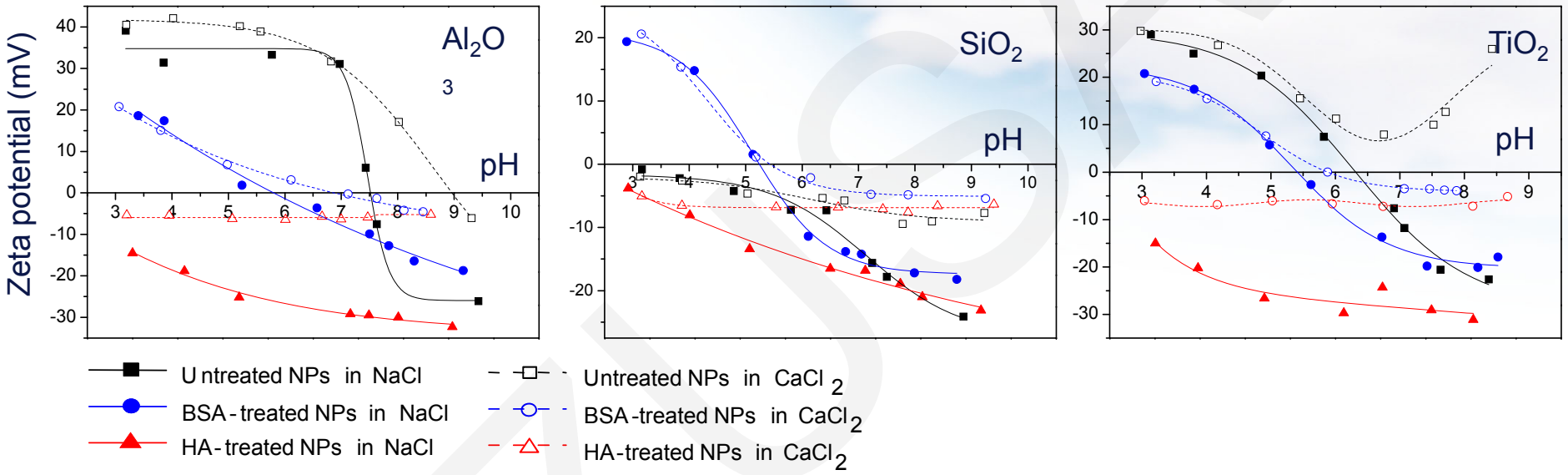


Al_2O_3 NPs | BSA-treated Al_2O_3 NPs | HA-treated Al_2O_3 NPs

SiO_2 NPs | BSA-treated SiO_2 NPs | HA-treated SiO_2 NPs

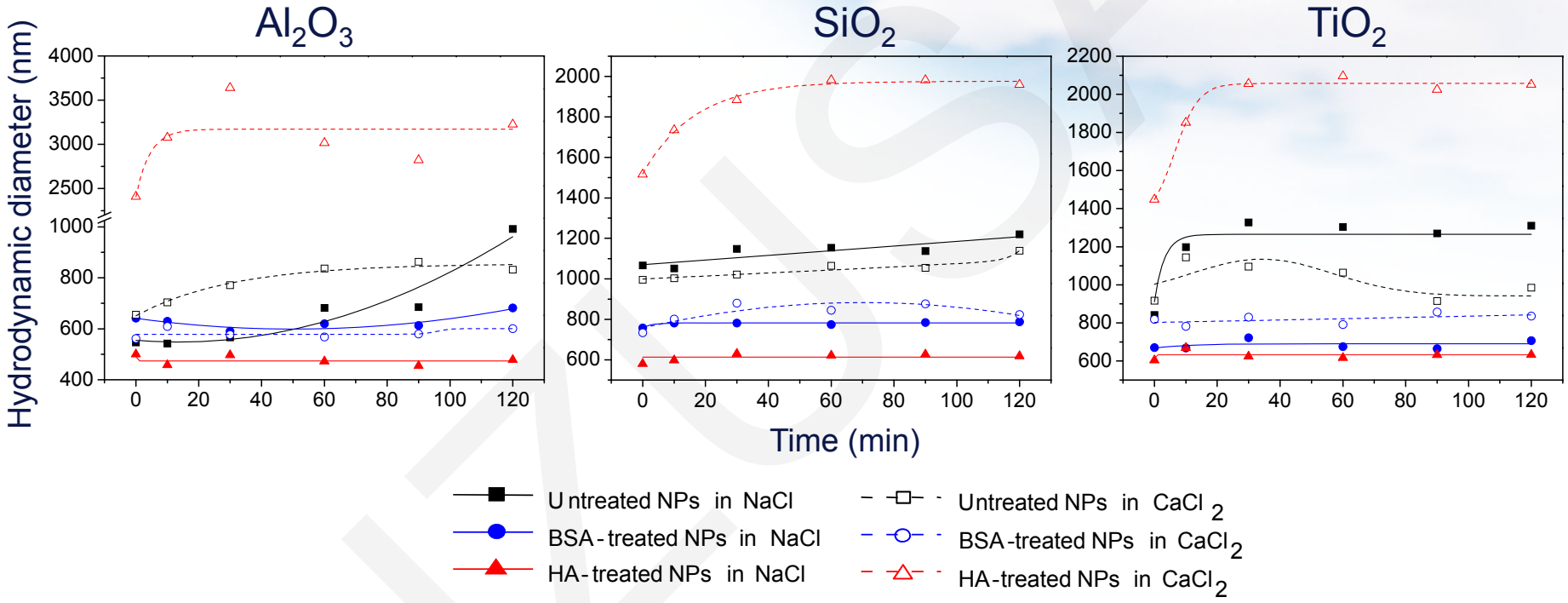
TiO_2 NPs | BSA-treated TiO_2 NPs | HA-treated TiO_2 NPs

2. Zeta potential measurement



- BSA-treated NPs show similar zeta potential curves in NaCl, which reflects the effects of the BSA coatings. The zeta potentials are higher in $CaCl_2$ than in NaCl for the alkaline pH region.
- HA-treated NPs are highly negatively-charged in NaCl, which indicates that HA coatings dominate the charges. The zeta potentials of HA-treated NPs are around -6 mV in $CaCl_2$, and do not decrease when the pH increases.

3. Size of NP Agglomerates



- BSA decreases the size of NP agglomerates due to the steric repulsive forces.
- HA decreases the hydrodynamic diameters of NP agglomerates in NaCl, but greatly increase NP agglomeration in $CaCl_2$ via calcium complexation.

4. Sedimentation

- BSA-treated NPs have the slowest sedimentation rates in both NaCl and $CaCl_2$, which indicates that BSA prevents NP agglomeration and sedimentation due to the steric repulsive forces.
- HA-treated NPs show the fastest sedimentation rates in $CaCl_2$, indicating that the calcium complexation disrupts the stability of the NP suspension.
- Larger agglomerates do not always induce a faster sedimentation rate.
- Ionic strength does not cause obvious differences.

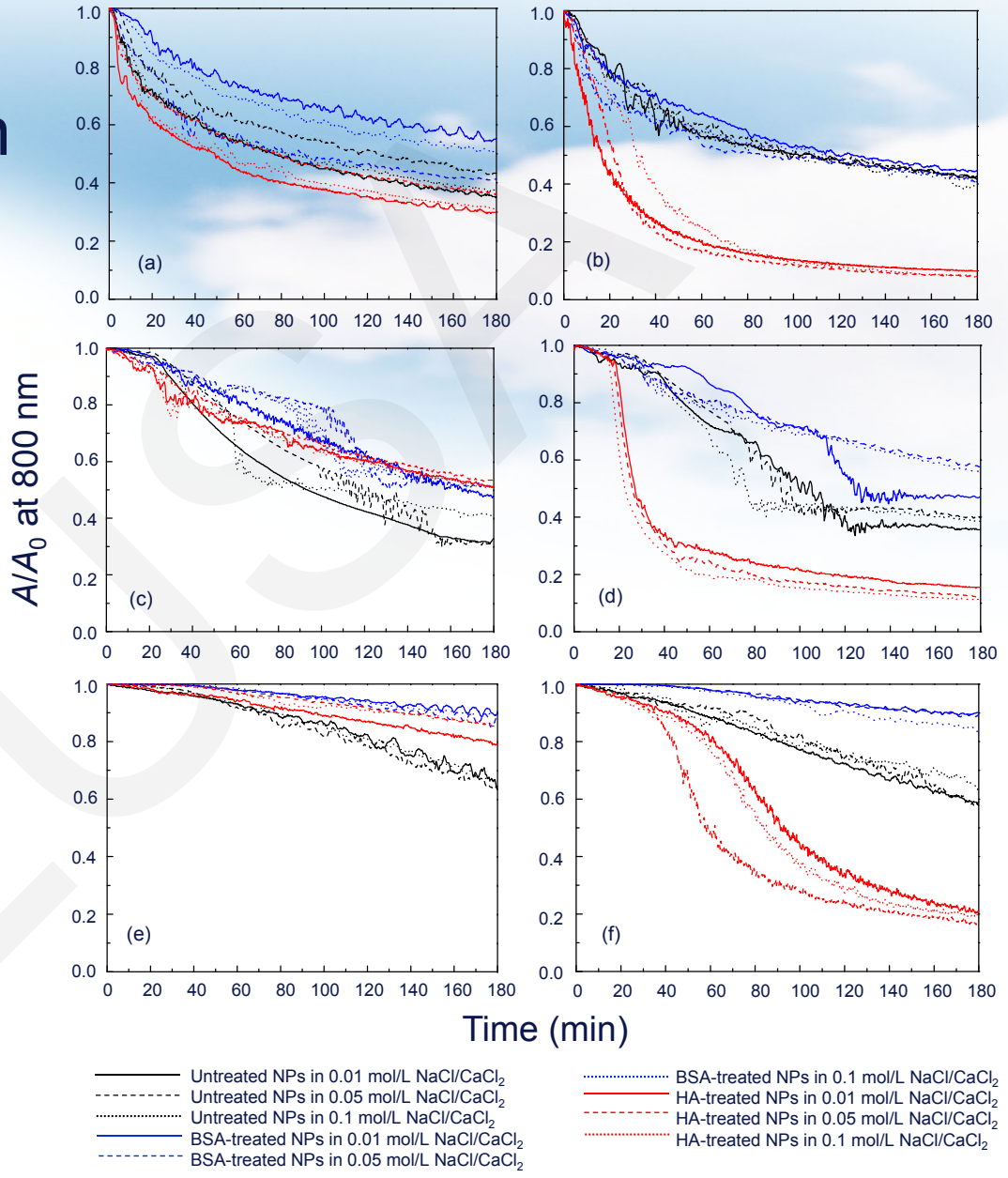
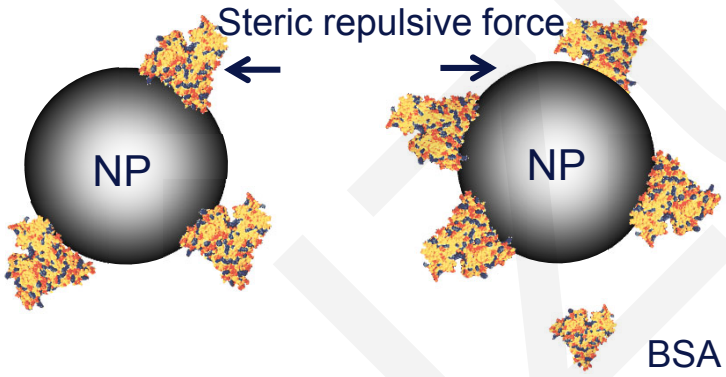


Fig. 5 Sedimentation curves of Al_2O_3, SiO_2, and TiO_2 NPs at pH 6
(a) Al_2O_3 in NaCl; (b) Al_2O_3 in $CaCl_2$; (c) SiO_2 in NaCl; (d) SiO_2 in $CaCl_2$; (e) TiO_2 in NaCl; (f) TiO_2 in $CaCl_2$; the absorbance intensity at 800 nm was divided by the intensity of initial time (A/A_0)

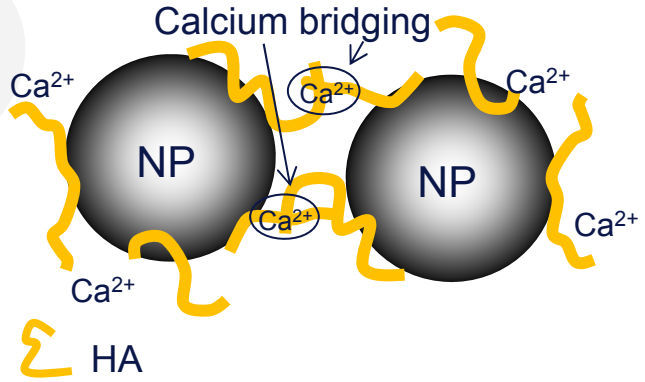
Conclusions

◆BSA and HA showed different influences on NP agglomeration and sedimentation.

➢BSA decreased the agglomerate size and retarded its sedimentation in both NaCl and $CaCl_2$ electrolytes because the BSA globular architecture induced steric repulsion.



➢HA enlarged NP agglomerates and thereby accelerated its sedimentation in $CaCl_2$ due to calcium complexation.



◆Agglomerate size was not the only determining factor in the NP sedimentation process.