



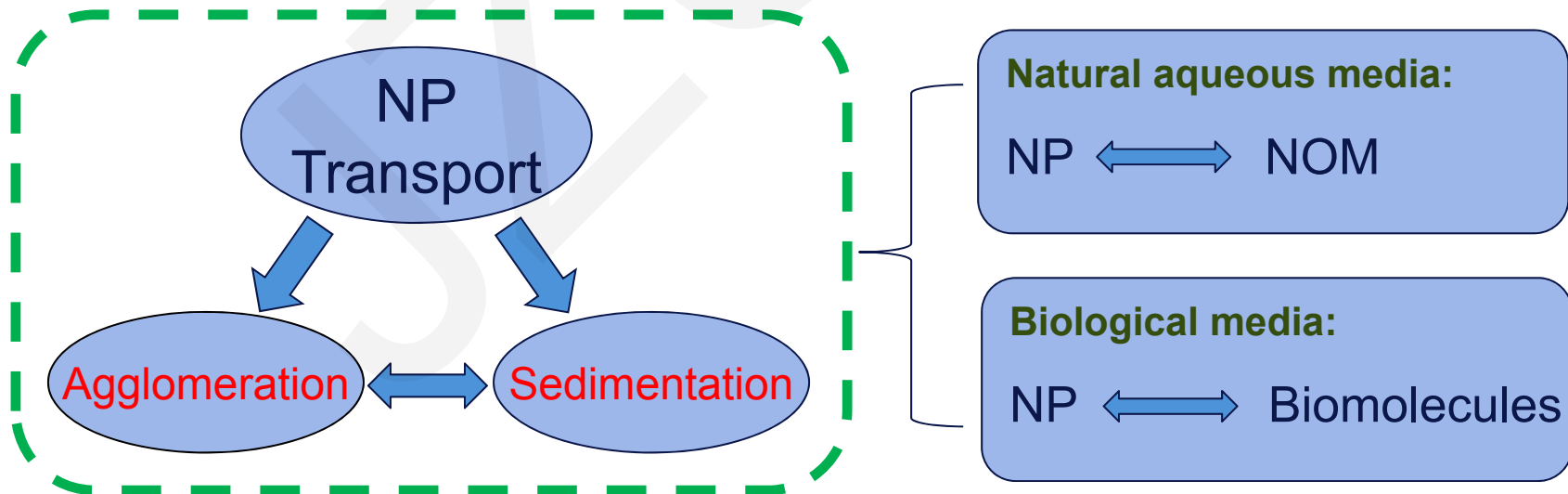
Effects of humic acid and bovine serum albumin on agglomeration and sedimentation of oxide nanoparticles

Cited this as: Fan-bao HU, Yong-feng LIN, Ru CHEN, Lei DING, Wei JIANG, 2014. Effects of humic acid and bovine serum albumin on agglomeration and sedimentation of oxide nanoparticles. *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, 15(8):643-652. [doi:10.1631/jzus.A1400138]



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	$\geq 99.9\%$	60 ± 5	208	35	37
SiO_2	Porous form	$\geq 98\%$	20-50	675	-7	-5
TiO_2	Anatase form	$\geq 99\%$	5-10	324	5	11

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

◆ Experiments

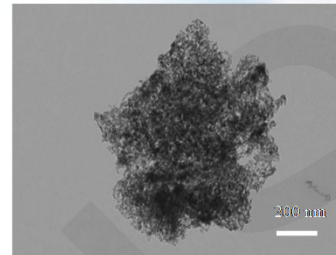
- TEM imaging—Morphology of NP agglomerates
- Zeta Potential measurement—Charges of NP agglomerates
- Dynamic light scattering (DLS) — Size of NP Agglomerates
- Optical absorbance at 800 nm—NP sedimentation rates



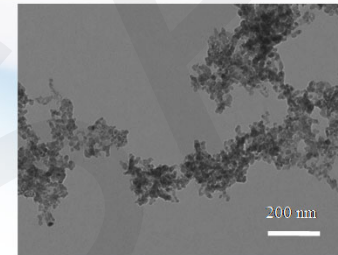
Results and Discussion

1. TEM Imaging

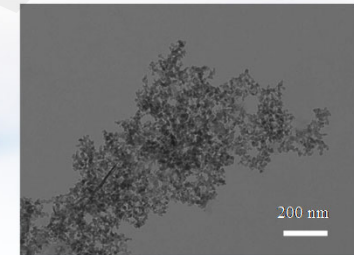
- Al_2O_3 NPs show better dispersion after BSA/HA treatment.
- BSA/HA-treated SiO_2 NPs look very similar to the untreated NPs
- TiO_2 NPs disperse better after BSA treatment, but HA induces more serious agglomeration.



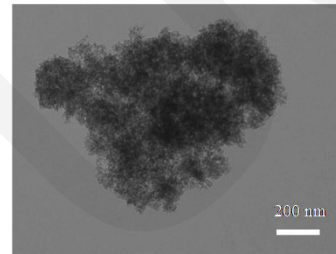
Al_2O_3 NPs



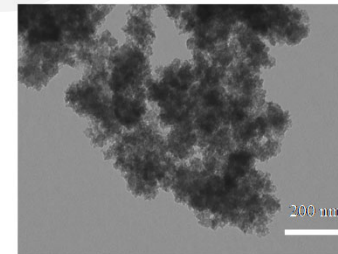
BSA-treated Al_2O_3 NPs



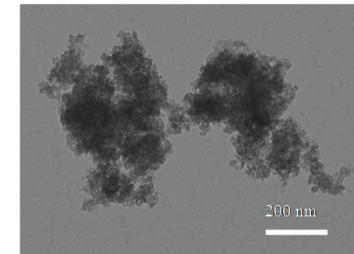
HA-treated Al_2O_3 NPs



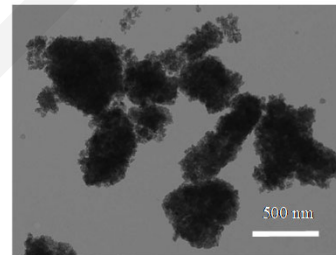
SiO_2 NPs



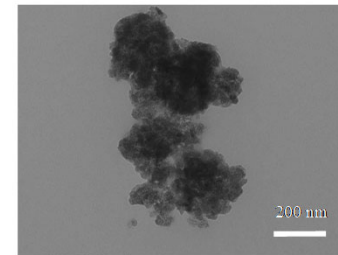
BSA-treated SiO_2 NPs



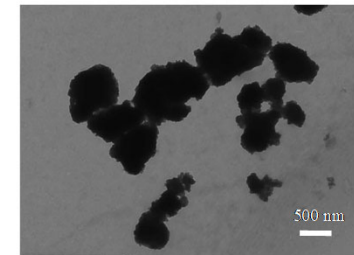
HA-treated SiO_2 NPs



TiO_2 NPs



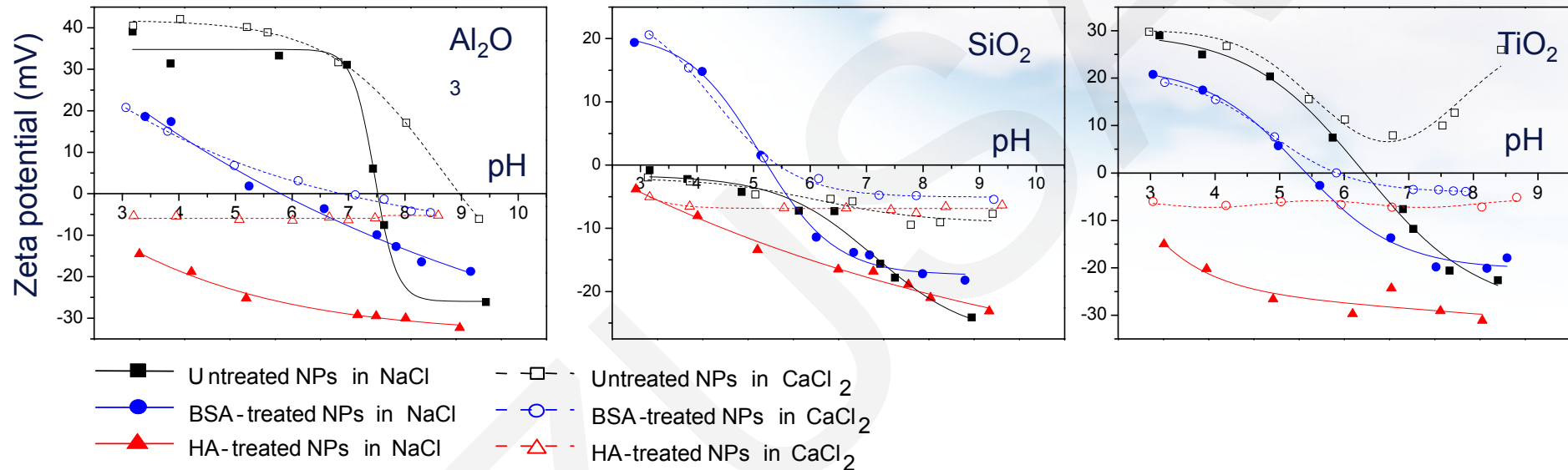
BSA-treated TiO_2 NPs



HA-treated TiO_2 NPs



2. Zeta potential measurement

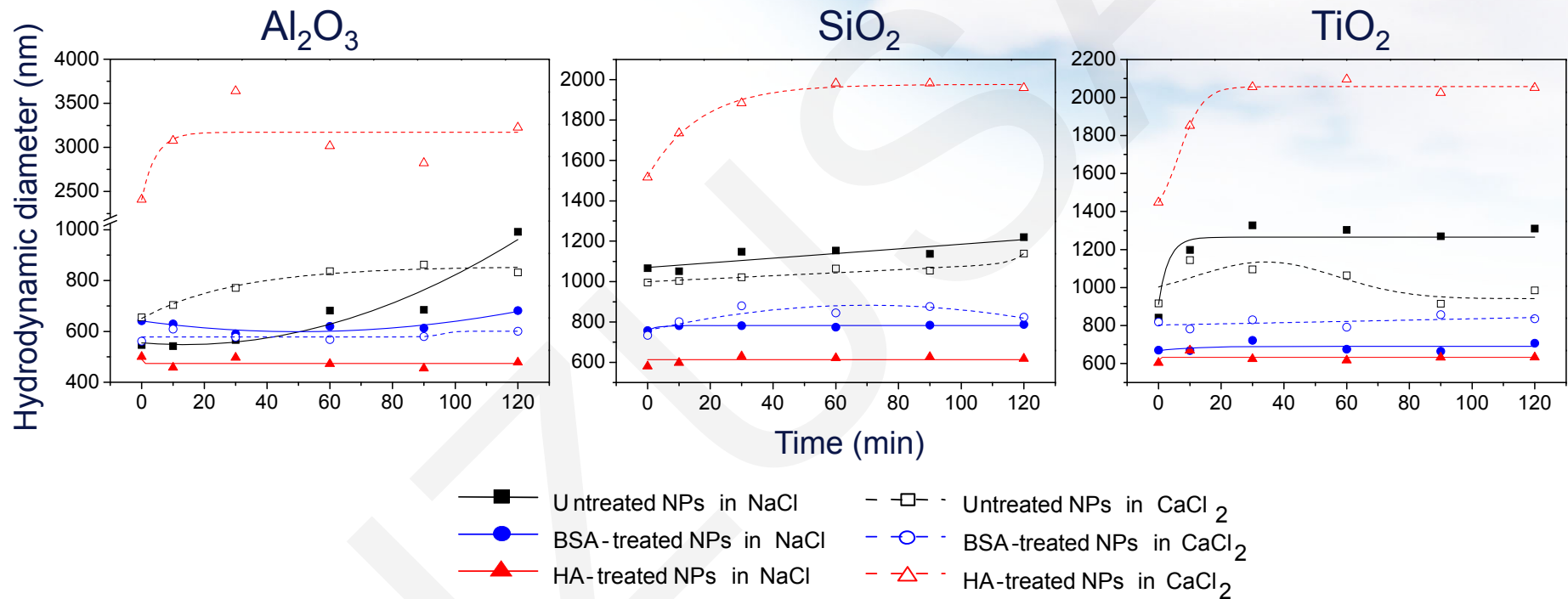


➤ BSA-treated NPs show similar zeta potential curves in NaCl, which reflects the effects of the BSA coatings. The zeta potentials are higher in CaCl_2 than in NaCl for the alkaline pH region.

➤ 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 CaCl₂, which indicates that BSA prevents NP agglomeration and sedimentation due to the steric repulsive forces.
- HA-treated NPs show the fastest sedimentation rates in CaCl₂, 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.

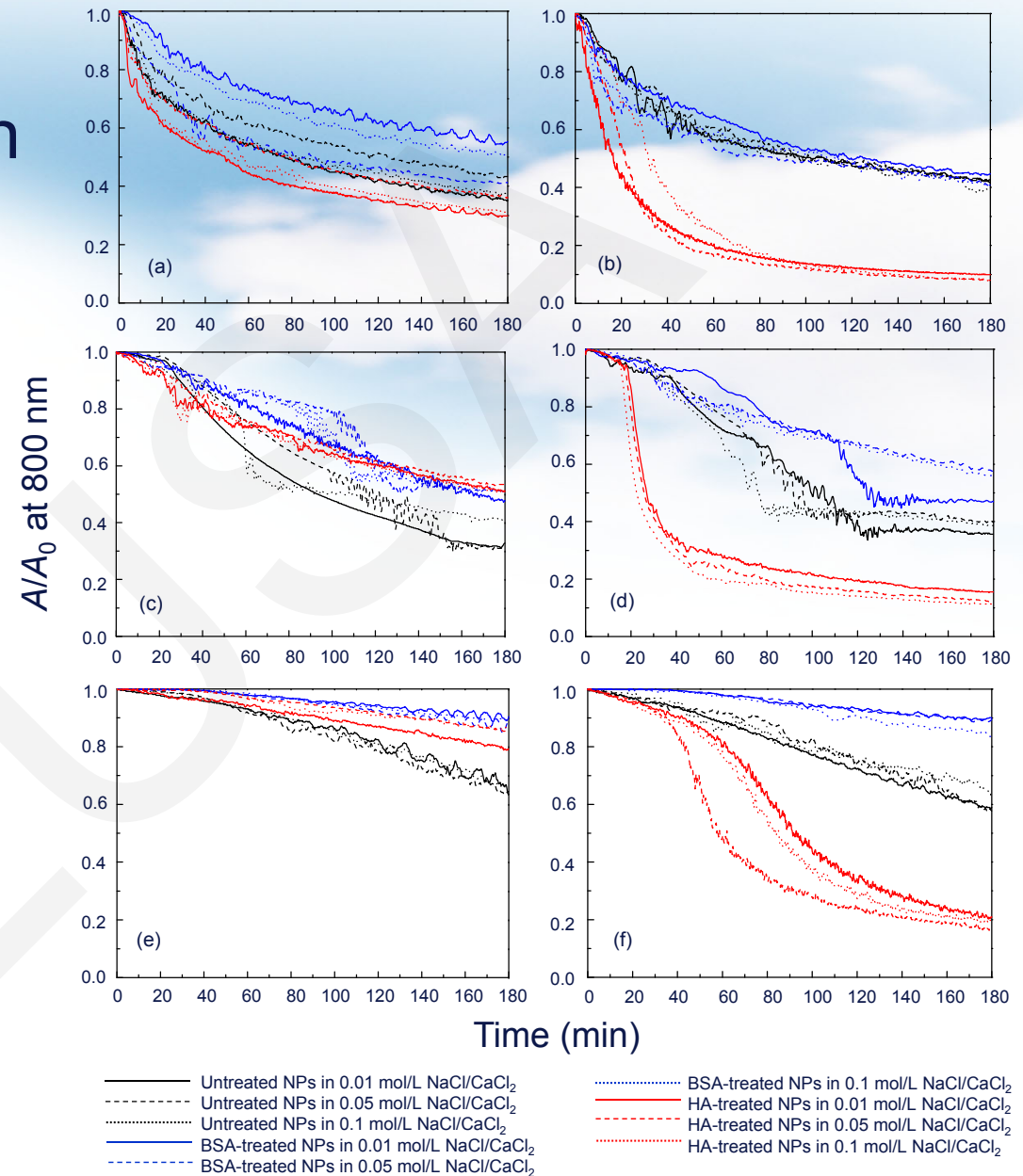


Fig. 5 Sedimentation curves of Al₂O₃, SiO₂, and TiO₂ NPs at pH 6

(a) Al₂O₃ in NaCl; (b) Al₂O₃ in CaCl₂; (c) SiO₂ in NaCl; (d) SiO₂ in CaCl₂; (e) TiO₂ in NaCl; (f) TiO₂ in CaCl₂; the absorbance intensity at 800 nm was divided by the intensity of initial time (A/A_0)

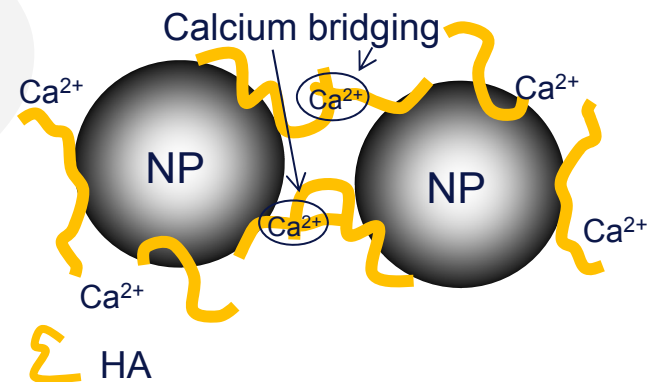
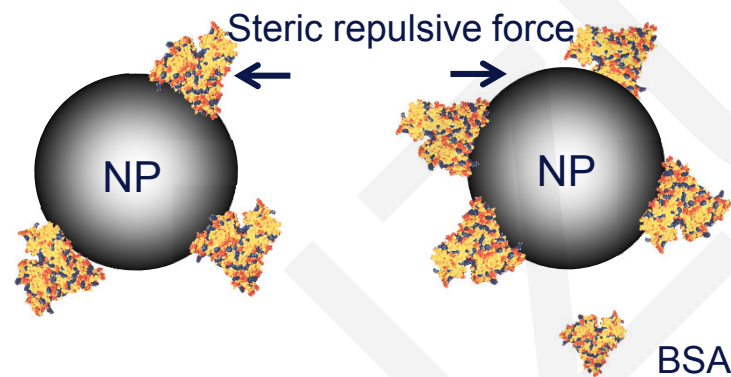


Conclusions

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

➤ BSA decreased the agglomerate size and retarded its sedimentation in both NaCl and CaCl₂ electrolytes because the BSA globular architecture induced steric repulsion.

➤ HA enlarged NP agglomerates and thereby accelerated its sedimentation in CaCl₂ due to calcium complexation.



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