

# Cluster Formation of Oppositely Charged Titania Particles and a Space Study

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## Introduction

In aqueous dispersions, positively and negatively charged colloidal particles self-assemble by Coulomb force to form aggregate structures (clusters) under appropriate conditions (Fig.1(a)). Tetrahedral cluster is the basic unit of diamond structure, which has been expected as a novel photonic material (Fig.1(b)). The diamond structure has a complete photonic band gap, when a difference in the refractive indexes between the particles and the gap is more than approximately 2.

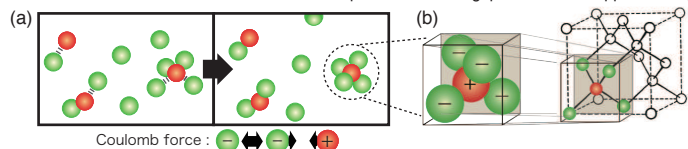


Fig.1 Illustrations of (a) clustering of oppositely charged particles due to electrostatic attraction, (b) diamond structure and tetrahedral cluster.

Here, we examined the clustering of titania (titanium dioxide) particle having high refractive index (about 2.5). Magnitude of the Coulomb force acting between the particles was adjusted by tuning the concentration of added salt. The influence of the salt concentrations, Cs on the cluster structure was studied also by numerical simulations.

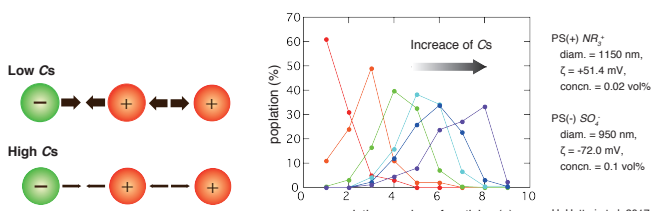


Fig. 2 Magnitude of the Coulomb force. The cluster structure was adjusted by tuning Cs.

## Experiments

### Materials and Methods

Titania particles were synthesized by sol-gel method. They were introduced fluorescent dye molecules and modified poly(ethyleneimine) and poly(styrenesulfonic acid) sodium salt for the positively and negatively charged polymers, respectively.

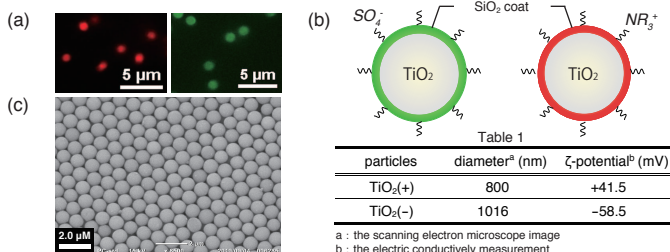


Fig. 3 Positively and negatively charged titania particles. (a) Optical micrographs and (b) illustrations. (c) A SEM image of titania particles before surface modification.

The clusters were formed in aqueous dispersions at various sodium chloride concentrations, Cs. The concentrations of the positively and negatively charged particles were prepared 0.002 vol% and 0.048 vol%, respectively. The samples were set to an automatic rotator (3 rpm). UV curable gelation reagents were dissolved in the sample beforehand, and the samples were gelled by UV irradiation after 48 hours. Association number of the clusters were determined by means of a fluorescence microscope.

### Results

On increasing Cs, the averaged value of  $\langle n \rangle$ , increased initially, and then decreased at Cs larger than 150  $\mu\text{M}$ .

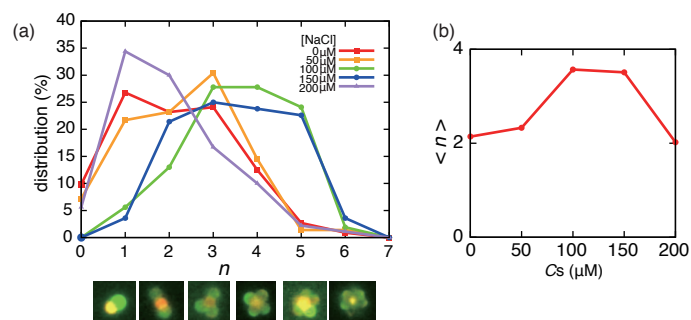


Fig. 4 (a) An influence of Cs on clustering of the titania particles.

(b) The average of association number  $\langle n \rangle$  at various values of Cs.

## Numerical Simulation

### Monte Carlo simulation by metropolis algorithm

The principle of detailed balance

$$\frac{P_{jk}}{P_{ki}} = \frac{\exp(-\beta U_k)}{\exp(-\beta U_i)} = \exp(-\beta[U_k - U_i])$$

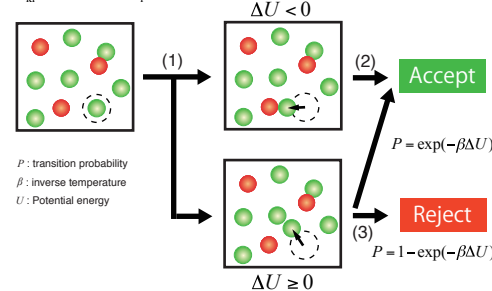


Fig. 5 An illustration of Monte Carlo simulation by metropolis algorithm.

### Yukawa-type pair potential (dimensionless)

$$U_{ij} = k_B T_B \tilde{Z}_i \tilde{Z}_j \frac{\exp(-\kappa |r_i - r_j|)}{|r_i - r_j|} \left( \tilde{Z}_i = Z_i \frac{\exp(\kappa a_i)}{1 + \kappa a_i} \right)$$

- (1) Randomly chose single particle and moved it within a certain distance, then calculated the difference of  $U$  before and after the movement.
- (2) If " $\Delta U < 0$ ", the transition is accepted, while in the case of " $\Delta U > 0$ " the transition was accepted with the probability  $\exp(-\beta \Delta U)$ . The state after the transition was set as the state of the new system.
- (3) Otherwise, the transition was rejected.

Repeated steps (1) to (3).

$k_B$ : Boltzmann constant  
 $l_D$ : Bjerrum length  
 $r$ : particle position  
 $T$ : temperature  
 $\kappa^{-1}$ : Debye length  
 $a$ : particle radius  
 $Z$ : charge number

### Results

Qualitative agree with the experimental results.

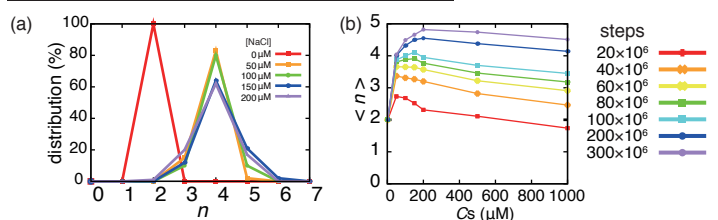


Fig. 6 (a) Influence of Cs on clustering of numerical simulation at  $300 \times 10^6$  steps, and (b) the average number of association  $\langle n \rangle$  at several steps.

## Discussion

As the salt concentration increases, the electrostatic repulsion is screened and the maximum number that can be associated increases (Fig.7(a)). The electrostatic attractive force also weakens, so the association number decreases when compared at the same steps or time (Fig.7(b)). The difference between the observed and simulation results may be attributable to the sedimentation of the titania particles which caused large aggregates in the experiment.

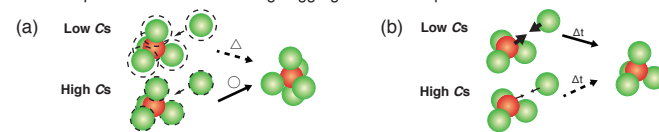


Fig.7 Cluster structure change with Cs because of varying the magnitude of Coulomb force.

## Space Experiments

We will determine the precise distribution of  $n$  by space experiments. The space experiments have been carried out in July 2020, and the gelled cluster samples will return to the earth in 2021.



Fig.8 Images of Space experiments. ©NASA/JAXA

## Conclusions

- We synthesized highly charged titania particles with high refractive index.
- On increasing salt concentration, the averaged association number increased initially and then decreased.
- The space experiments was carried out in international space station to obtain precise distribution of association number of titania particles.