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正および負に荷電したチタニア粒子の会合体形成と宇宙実験検討

Cluster Formation of Oppositely Charged Titania Particles and Space Experiments

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1. Introduction

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

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 concentration on the cluster structure was studied also by numerical simulations.

Materials having high refractive index values usually possess large densities as well. The titania particles have a density of approximately 3.0, and they exhibit remarkable sedimentation by gravity. In order to study the effect of gravity on the cluster formation, the space experiments have been carried out in the microgravity environment of International Space Station, in collaboration with the Japan Aerospace Exploration Agency (JAXA). The preparation of the space experiments will be reported.

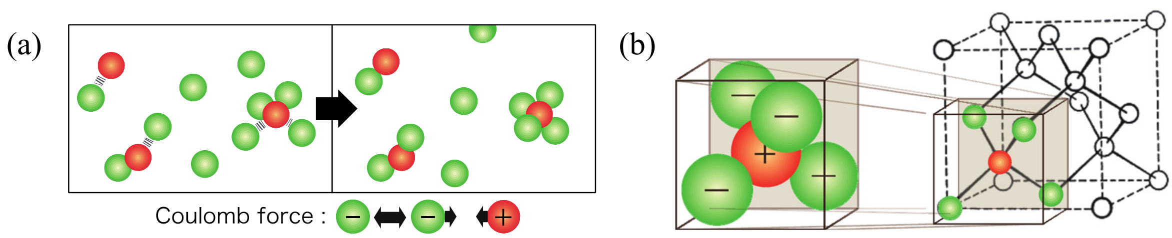

Fig. 1 Illustrations of (a) clustering of oppositely charged particles due to electrostatic attraction, and (b) diamond structure and tetrahedral cluster.

2. Materials and Method

2-1. Synthesis of Titania Particles

Amorphous titania particles were synthesized by sol-gel method[1] from titan alkoxides, and then heated at 400°C for 4 hours in an electric furnace. Wide-angle X-ray scattering measurements showed that the resulted titania particles were anatase-type crystals. The particle size determined by SEM were approximately 1000 nm.

The surface of the titania particles were coated by silica layer + fluorescent dye molecules[2] (fluorescein (green) or rhodamine (red)). Then, we modified the particle surfaces by charged polymers. We introduced poly(ethyleneimine) and poly(styrenesulfonic acid) sodium salt for the positively and negatively charged polymers. A SEM image of the titania particles before introduction of silica shell, and optical micrographs of the positively and negatively charged particles are shown in **Fig. 2(a)**, **(b1)**, and **(b2)** respectively.

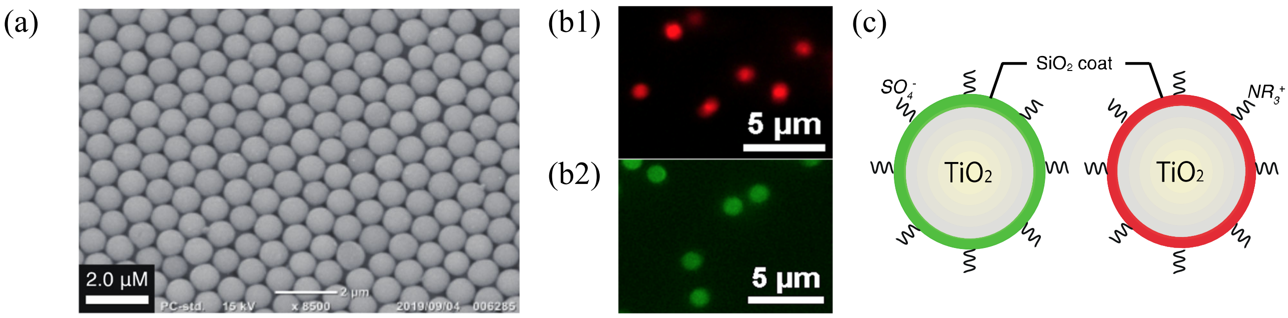

Fig. 2 (a) A SEM image of titania particle before surface modification. Positively and negatively charged titania particles. (b) Optical micrographs and (c) illustrations.

2-2. Clustering Experiment

The clusters were formed in aqueous dispersions of positively and negatively charged particles at various sodium chloride concentrations, *C*s. The concentrations of the positively and negatively charged particles were 0.002 vol% and 0.048 vol%, respectively. The samples were introduced in 1.5 mL microtubes and 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 48 hours after prepare time. Association number of the clusters were determined by means of a fluorescence microscope.

2-3. Monte Carlo Simulation

A Monte Carlo simulation was performed using the metropolis algorithm. The electrostatic interaction between particles was assumed to be the Yukawa-type pair potential.

3. Result and Disccusion

3-1. Cluster Formation

In the clustering experiments, the titania particles were concentrated near the cell bottom because of the gravitational sedimentation, and formed large aggregates. We determined distribution of association number n of isolated clusters other than these large aggregates (**Fig. 3(a)**). Optical micrographs of the clusters having various values of n are also shown in **Fig. 3**. On increasing *C*s, the averaged value of n, $< n >$, increased initially, and then decreased at *C*s larger than 150 µM. This appears to be explainable in terms of changes in the electrostatic screening due to the added salt. At low values of *C*s, strong electrostatic repulsion between the negatively charged particles in the cluster and in the bulk prohibited further growth of the clusters. On the other hand, at sufficiently high *C*s, reduction of Coulomb attraction between the positively and negatively charged particles caused a decrease in $< n >$. Thus, the $< n >$ value had a maximum at the moderate value of *C*s.

Fig. 3(b) shows the numerical simulation results of the distribution of *n*, which showed a qualitative agreement with the experimental results. 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.

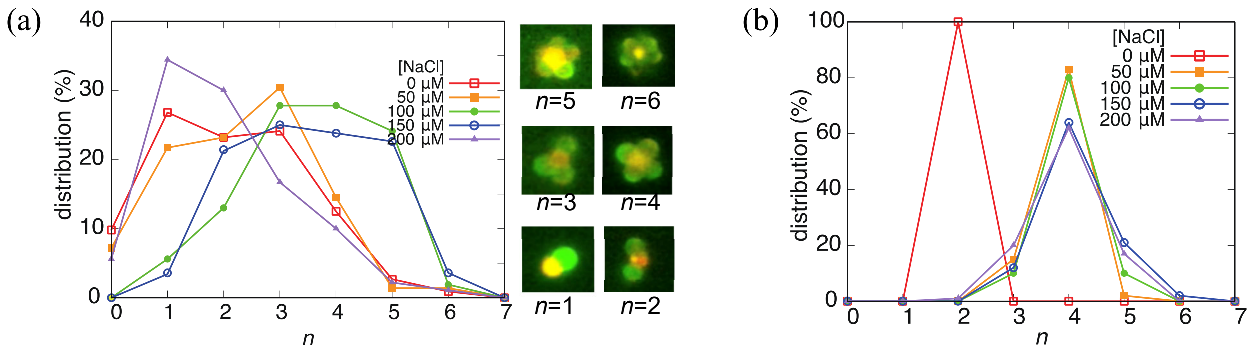

Fig.3 Influence of salt concentration on clustering of the titania particles. (a) Experiments and (b) numerical simulations at 3×10^8 steps.

3-3. Space Experiment

In the abovementioned experiments the aggregation of titania particles prevented precise determination of distribution of *n*. We conducted an experiment in a microgravity environment of the international space station. We prepared 28 samples containing titania, silica, and polystyrene particles. The value of salt concentration was chosen the clustering experiment using polystyrene particles. Polystyrene systems served as models for microgravity based on the results of experiments by matching the specific gravity with the medium. The space experiments have been carried out in July 2020, and the gelled cluster samples will return to the earth in 2021.

4. Conclusion

We synthesized highly charged titania particles with high refractive index. We studied clustering of oppositely charged titania particles. On increasing salt concentration, the averaged association number increased initially and then decreased. This appears to be explainable in terms of changes in the electrostatic screening due to the added salt. The numerical simulation result was quantitatively different from the experiments, which may be attributable to the sedimentation of the titania particles which caused large aggregates. We conducted space experiments in international space station to obtain precise distribution of association number of titania particles.

References

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