



Review

In-situ observation of colloidal crystallizationJunpei Yamanaka ^{a,*}, Yoshihisa Suzuki ^b, Jun Nozawa ^c, Tsutomu Sawada ^d^a Nagoya City University, 3-1 Tanabe, Mizuho, Nagoya City, Aichi 467-8603, Japan^b Tokushima University, 2-1 Minamijosanjima, Tokushima City, Tokushima 770-8506, Japan^c Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai City, Miyagi 980-8577, Japan^d National Institute of Materials Sciences, 1-1, Namiki, Tsukuba City, Ibaraki 305-0044, Japan

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Abstract

We report contents of colloidal crystallization experiments in ISSCG-16. The participants produce two kinds of colloidal crystals, i.e., close-packed opal type crystals, and non-close-packed charged colloidal crystals. They can observe the crystallization processes by using optical microscopy and reflection spectroscopy.

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1. Introduction

Submicron-sized colloidal particles dispersed in liquid media self-assemble into ordered “crystal” structures under appropriate conditions [1,2]. Colloids have been important models to study phase transitions, because (i) the large sizes of colloidal particles relative to atoms enable direct visualizations of individual particles and their spatial arrangements by optical microscopy, and (ii) the magnitude of the interaction between the particles is easily tunable, whereby experimental conditions for extremely high pressures and temperatures in atomic and molecular systems are readily accessible. In addition, (iii) long characteristic times of colloids facilitate *in situ* observations of non-equilibrium, dynamic processes, including crystal growth process. Furthermore, because the Bragg wavelengths of the colloidal crystals can be set in visible to near infrared regime, material applications

of colloidal crystals have been attracted considerable attention as photonic crystals [3].

The colloids in which the particles interact via hard sphere repulsion are referred to as “hard sphere (HS)” colloids. The crystallization of HS colloids is analogous to ordering phenomena of macroscopic, uniformly sized spheres, when they are packed in a finite volume. (Note that, however, unlike the macroscopic balls, the colloidal particles in dispersions exhibit rigorous Brownian motion due to thermal motion of the surrounding liquid molecules.) Because enthalpy of the HS colloids is zero, change in free energy associating with phase transition ΔG is given by $\Delta G = -T\Delta S$, where T and ΔS are temperature and entropy change. Thus, the phase behavior of HS colloid is purely entropic, and governed solely by the particle volume fraction ϕ . In Fig. 1, crystallization phase diagram of HS colloid is illustrated. Upon increasing ϕ from dilute condition, the HS colloid crystallizes at ϕ of approximately 0.49, not at the close-packed condition ($\phi = 0.74$) [4]. This behavior was first predicted by a numerical simulation study by Alder and Wainwright [5]. They demonstrated that at sufficiently high ϕ s, number of microstates of the particle

* Corresponding author. Nagoya City University, 3-1 Tanabe, Mizuho, Nagoya City, Aichi 467-8603, Japan. Tel.: +81-52-836-3444; fax: +81-52-836-3444.

E-mail address: yamanaka@phar.nagoya-cu.ac.jp (J. Yamanaka).

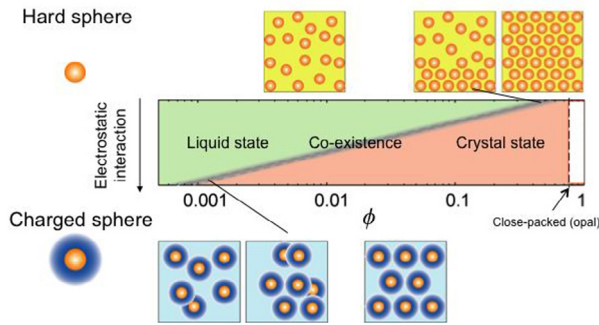


Fig. 1. An illustration of crystallization phase diagram of HS colloids (top) and charged colloids. The colloids crystallize at lower ϕ s on increasing magnitude of the electrostatic interaction. The shaded circle around the charged sphere represents the “effective” particle size due to the inter-particle Coulombic force.

arrangements for the crystal state was larger than that for random, disordered state. This implies that S for the crystal is larger than for the disordered state, resulting in the crystallization. The HS colloids take crystal–liquid (disordered) state coexistence state in approximately $0.49 \leq \phi < 0.55$ and uniform crystal structure in $0.55 \leq \phi \leq 0.74$ (Sometimes glass structures are found in this ϕ region).

At $\phi = 0.74$, the particles are arranged in the close-packed crystal structure. Since precious opals are composed of the close-packed array of the silica-based particles, the close-packed colloidal crystals are often referred to as (synthetic) opals.

When the colloidal particles bare electronic charges on their surfaces, the crystallization occurs at much smaller ϕ s due to long-ranged electrostatic interaction acting between the particles. As illustrated in Fig. 1, charged colloids crystallize in the lower ϕ s for the stronger interaction.

In this experimental course, we are concerned with the closest-packed, opal crystals and non-closest-packed, charged colloidal crystals. The aim of this experiment is to experience preparation of these two kinds of colloidal crystals, and to observe their crystallization processes, by using optical microscopy and reflection spectroscopy.

2. Materials

We use aqueous dispersions of polystyrene (PS) and colloidal silica particles (diameter $d = 100$ nm to $3 \mu\text{m}$), which have frequently been used to study the colloidal crystallization. The PS particles have strongly acidic sulfuric acid ($-\text{SO}_3\text{H}$) and sulfonic acid ($-\text{SO}_3\text{H}$) groups on their surfaces, which were resulted from ionic

polymerization initiator and co-monomer on the particle synthesis. Silica particles have weak acidic silanol (Si-OH) groups. These ionizable groups dissociate to provide negative surface charges when dispersed in aqueous media.

3. Method

3.1. Optical microscopy

We observed micron ~ submicron sized particles by using an inverted type optical microscope (Olympus Co. Ltd., IMT-2) equipped with $40\times$ or $100\times$ objectives. By performing *in situ* observation of the ordering processes of the particles, we can discuss fundamentals of the crystallization processes in a single particle level.

3.2. Reflection fiber optics spectroscopy

Atomic and molecular crystals have Bragg wavelength in x-ray regime. In the case of present colloidal crystals, the Bragg wavelengths lay in visible to near infrared regime. We observe the crystal growth processes by using a multichannel visible-light spectrophotometer, type USB2000 (covering wavelengths of 400–900 nm), Ocean Optics Inc., USA. It was equipped with optical fiber probes that enabled measurements of the area-averaged right-angle reflection spectra of circular spots with diameters of approximately 1 mm.

4. Opal colloidal crystals

Opal crystals are regular arrays of particles in which particles are close-packed each other as described in Section 1. Following two processes have mainly been used for fabrication of the opal crystals.

- (1) Concentration of particle by gravitational sedimentation of dispersions, and resulted phase transition of the sediments into opal crystals on increasing ϕ in the settled particles.
- (2) Regular arrangements of the particles under the evaporation-driven convective flux of dispersion media [6].

Naturally occurring opals are presumably produced by the above processes (1) and/or (2). In this exercise, to achieve growth of opal crystals over a short period of time, we conduct regular array formation under an action of immersion capillary force and an evaporation-driven convective flux of water [7] as shown in Figs. 2,

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