

Colloidal Crystals -Self-Assembly of Monodispersed Colloidal Particles-

Hiroshi Nakamura

コロイド結晶ー単分散コロイド粒子の自己秩序化ー

中村浩

Abstract

Colloidal crystals are three-dimensionally periodic lattices assembled from monodispersed spherical colloids. The ability to crystallize spherical colloids into spatially periodic structures has enabled interesting and often useful functionality not only from the constituent colloidal particles, but also from the long-range order exhibited by these periodic structures.

A variety of methods by which to assemble spherical colloids into crystalline lattices have been successfully demonstrated, with notable examples including sedimentation in a gravitational field, crystallization through attractive capillary forces caused by solvent

evaporation, and self-organization via entropic forces or repulsive electrostatic interactions.

Similar to the diffraction of X-rays from atomic and molecular crystals, crystalline lattices of spherical colloids diffract light according to the Bragg equation.

These periodic structures have also been actively explored as functional components in fabricating new types of diffractive devices such as filters and switches, smart optical sensors, and photonic bandgap structures. Recent studies on the unique optical properties of these materials, often referred to as photonic bandgap crystals, have lead to a new and exciting field of research.

Keywords

Colloidal particles, Monodispersed particles, Colloidal crystals, Crystalline lattice, Opals, Self-assembly, Bragg diffraction, Photonic crystals

要 旨

コロイド結晶とは単分散なコロイド粒子が結晶格子状に3次的に規則配列したものである。このコロイド結晶は粒子が自己組織的に配列することで非常に興味深い、その粒子特性だけでなく、長距離的な秩序構造に由来して、種々の機能性材料として期待されている。

単分散粒子を配列させてコロイド結晶を作製するためには、重力による粒子の沈降堆積を利用する方法や粒子分散液の溶媒の蒸発に伴う毛管力を利用する方法、あるいは粒子分散液中での粒子間

の静電反発を利用する方法など種々の方法が知られている。

このコロイド結晶は原子や分子の結晶がX線を回折するように、ブラッグの条件に従って光を回折する。その特性を利用して新たな光学デバイス(フィルター、スイッチ、センサー)として検討が進められている。特に最近、フォトニック結晶への可能性が期待され、精力的に研究が進められている。

キーワード

コロイド粒子, 単分散粒子, コロイド結晶, 結晶構造, オパール, 自己秩序化, ブラッグ回折, フォトニック結晶

1. Introduction

'Colloids' are small solid particles dispersed in a medium, which is typically a fluid. The typical size of colloidal particles ranges from nanometers to micrometers. Colloidal particles are important in a broad range of technologies and in the processing of various materials including foods, inks, paints, coatings, cosmetics, and photographic films.

Colloidal crystals are three-dimensionally periodic lattices assembled from monodispersed spherical colloids (**Fig. 1**). For example, the beautiful and attractive iridescence (opalescence) of natural opals, which diffract visible or near-infrared light, is attributed to the periodic modulation of the refractive index contrast between silica colloids and the surrounding medium, both of which are colorless by themselves (**Fig. 2**).¹⁻²⁾ Over the past several decades, colloidal crystals have been used extensively as model systems to experimentally probe fundamental physical phenomena such as crystallization, melting, and many other types of phase transitions.

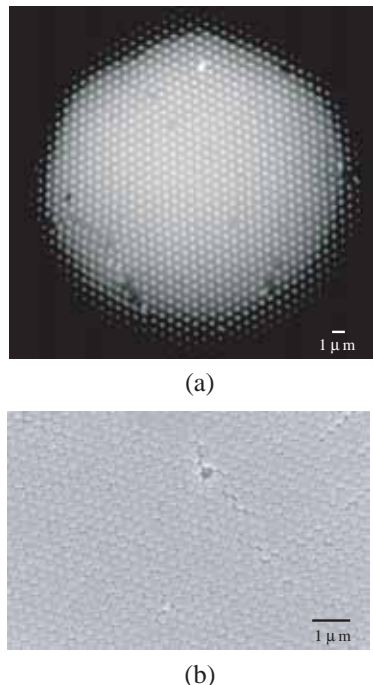


Fig. 1 Microscopic images of colloidal crystals fabricated with monodispersed polystyrene particles.
(a) Crystallization by electrostatic interaction in aqueous suspension.
(b) Crystallization by solvent evaporation of aqueous suspension.

These periodic structures have also been actively explored as functional components in fabricating new types of diffractive devices such as filters and switches,³⁾ smart optical sensors,⁴⁾ and photonic bandgap structures.⁵⁾ Recent studies on the unique optical properties of these materials, often referred to as photonic bandgap crystals, have evolved into a new, exciting field of research.⁶⁾

In this review, various methods of self-assembly of spherical colloids into crystalline lattices and a number of typical applications of colloidal crystals are explained.

2. Self-assembly of monodispersed colloidal particles

2.1 Sedimentation in a gravitational field

Colloidal crystallization by sedimentation is one of the most commonly used techniques for making colloidal crystals for application.⁷⁻⁸⁾ Sedimentation provides a simple and efficient method by which to achieve multilayer assemblies of mesoscale particles (**Fig. 3**). However, one major disadvantage of this method is the limited range of sizes that can be used to make photonic bandgap materials. Small particles

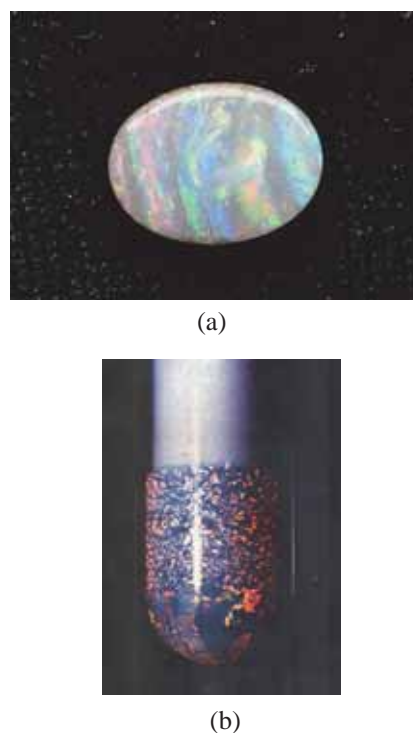


Fig. 2 Pictures of the natural opal (a) and an artificial opal (b), which are composed of colloidal crystals fabricated with monodispersed silica particles and medium.

(smaller than 300 nm) take a very long time to deposit or do not deposit at all, and large particles (larger than 550 nm) deposit too quickly, resulting in poor periodicity.⁹⁾ Another major disadvantage is the structure of the crystalline lattice, which usually consists of many randomly oriented domains, so that it is not easy to obtain a uniform surface topology, which makes optical characterization difficult.^{5, 10-12)}

Blaaderen et al. reported that slow sedimentation of colloidal particles onto a patterned substrate (or template) can direct the crystallization of bulk colloidal crystals, and so permit tailoring of the lattice structure, orientation and size of the resulting crystals. This process is referred to as 'colloidal epitaxy'.¹³⁻¹⁴⁾

2.2 Attractive capillary forces caused by solvent evaporation

Compared to earlier methods of colloidal crystal formation via sedimentation, vertical deposition via evaporation-induced self-assembly driven by capillary forces has been found to produce superior quality colloidal crystals (Fig. 1 (b)), which have fewer defects and are not polycrystalline, due to directional crystallization in the meniscus. The theory of evaporation-induced self-assembly of particles on a substrate, which was developed primarily by Nagayama et al.,¹⁵⁻¹⁸⁾ considers evaporation in the motion of the colloidal particles toward the meniscus (**Fig. 4 (a)**). In a procedure developed by Jiang and Colvin,¹⁹⁾ silica sphere dispersions are left to evaporate naturally, depositing high-quality thin colloidal crystal films on a vertical substrate via the meniscus of an evaporating solvent (Fig. 4 (b)). This approach has two limitations: the

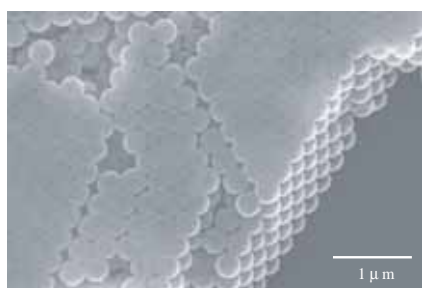


Fig. 3 Scanning Electron Microscopic images of three-dimensionally multilayer structure of colloidal crystals fabricated with monodispersed polystyrene particles.

long evaporation time and, more importantly, the deposition is limited to smaller colloidal particles that sediment at a rate that is slower than the evaporation of the solvent. If the sedimentation rate is faster than the evaporation rate sedimentation colloidal particles depart from the meniscus, and the deposition process is terminated. Two principal approaches have been proposed for keeping large particles suspended in the dispersion during the deposition process, mechanical agitation²⁰⁻²²⁾ and convection induced by a temperature gradient.²³⁾

2.3 Self-organization via entropic forces or electrostatic interactions

Colloidal crystals can be made from non-closely-packed monodispersed colloidal particles in a liquid, such as polystyrene particles in water (Fig. 1 (a)), in which the electrostatic repulsions order the particles into face-centered cubic (fcc) or body-centered cubic (bcc) lattices.

The method based on electrostatic interactions seems to be the most powerful and successful method for generating multilayer assemblies of mesoscale particles: three-dimensionally crystalline

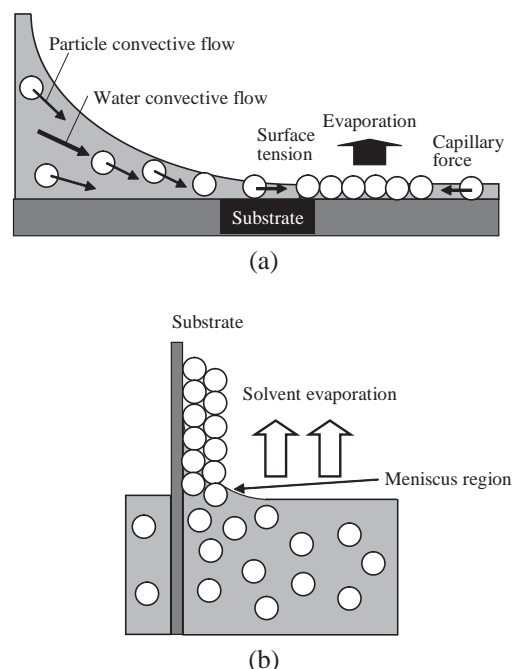


Fig. 4 Pictures of self-assembly of colloidal particles by solvent evaporation.
(a) Driven by surface tension and capillary force in horizontal plane.
(b) Driven by interaction between particles and substrate in vertical plane.

assemblies as large as $\sim 1 \text{ cm}^3$ have been generated. This method, however, has a very strict requirement with respect to the experimental conditions, such as the density of charges on the surface of the particle, the concentration of particles, and the concentration of free electrolyte molecules in the dispersion medium.

Charged monodispersed colloidal particles form colloidal crystals in dispersions by electrostatic interparticle interaction.²⁴⁻²⁵⁾ The colloidal crystals are also observed at lower particle concentrations when the ionic strength of the system is suitably low. In order to clarify the mechanism of crystal formation under such a condition, extensive experimental and theoretical research has been performed. A common approach to interpreting the colloidal crystal formation is based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory,²⁶⁻²⁷⁾ or the Kirkwood-Alder transition.²⁸⁻³¹⁾ The DLVO theory assumes a long-ranged electrostatic repulsion between particles in addition to the short-range van der Waals attraction. At low ionic strength, the electrostatic repulsion is so strong that the short-range attractive term can be ignored. However, microscopic observations reveal that colloidal crystals coexist as clusters or domains of finite size along with disordered regions of lower particle density. Thus, the colloidal crystal formation is hard to explain by the DLVO theory alone, and the existence of some kind of electrostatic attractive force has been suggested. This concept is supported theoretically by Sogami and Ise.³²⁻³³⁾

2.4 Other methods

Park et al. have also developed a convenient method that utilizes the hydrodynamic flow and physical confinement of a specially designed cell to crystallize spherical particles (polystyrene or silica spheres) into three-dimensionally periodic lattices with relatively large domain sizes.³⁴⁻³⁵⁾ When flat substrates were used as solid supports, this method provided only face-centered cubic (fcc) lattices with their (111) planes oriented parallel to the substrates. In order to obtain colloidal crystals with planes other than (111) planes oriented parallel to the supporting substrates, the surfaces of these substrates must be patterned with appropriate arrays of relief structures. These relief patterns can serve as templates to direct

and control the nucleation and growth of colloidal crystals with adjustable orientations.³⁶⁻³⁹⁾

Electric fields have also been applied, including direct current (dc) electrophoresis to accelerate gravitational settling,⁴⁰⁾ low-frequency electrohydrodynamics to create close-packed structures in charged colloidal particles,⁴¹⁻⁴²⁾ and dielectrophoresis to create two-dimensional crystals.⁴³⁾

3. Optical properties and microstructures of colloidal crystals

Monodispersed highly charged colloidal particles spontaneously assemble into face-centered cubic (fcc) or body-centered cubic (bcc) crystalline arrays in low-optical-strength aqueous solutions. In general, the optical dielectric constant of these colloidal particles differs from that of the surrounding medium, which results in a periodic variation in the refractive index of the material. Similar to the diffraction of X-rays from atomic and molecular crystals, the resulting colloidal crystals diffract UV, visible, or near-IR light, depending on their lattice constant (**Fig. 5**). These colloidal crystals are the simplest photonic crystals to show bandgaps for propagation of electromagnetic radiation in a particular direction.

A colloidal crystal diffracts light according to the Bragg equation:

$$m\lambda_{\text{peak}} = 2d_{111}(n_{\text{eff}}^2 - \sin^2\theta)^{1/2}$$

where m is the order of diffraction, λ_{peak} is the wavelength of the diffraction peak, d_{111} is the spacing between (111) planes, θ is the angle between

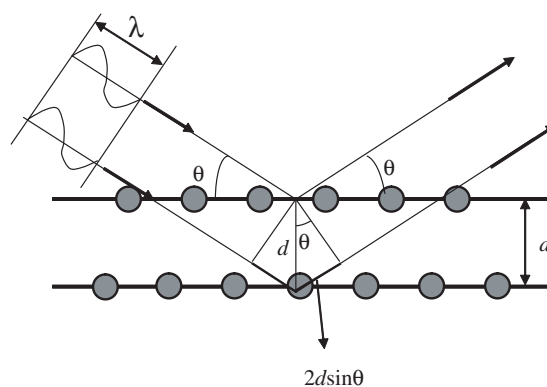


Fig. 5 Scheme of Bragg diffraction with crystalline lattice of colloidal particles.

the incident light and the normal to the diffraction planes (at normal incidence, $\theta = 0$), and n_{eff} is the mean refractive index of the crystalline lattice.

Angle-resolved reflection spectroscopy (**Fig. 6**) is applied for determination of both d_{111} and n_{eff} . The wavelength of the reflection peak λ_{peak} was measured from the spectra and plotted against θ . By fitting the Bragg condition to the plotted data, d_{111} and n_{eff} were obtained.

4. Applications of colloidal crystals

4.1 Photonic crystals

Photonic bandgap (PBG) crystals have received considerable attention since the concept was first proposed by Yablonovitch⁴⁴⁾ and John⁴⁵⁾ in 1987. A PBG crystal is a long-range ordered structure for which the dielectric constant varies as a spatially periodic function.⁴⁶⁾ Under appropriate conditions (for example, with a suitable lattice structure and a sufficiently high contrast between different dielectric regions), a PBG crystal may exhibit a forbidden bandgap in the photonic band structure, within which no photons will be allowed to propagate in three-dimensional space.⁴⁷⁾ All of these properties are technologically important because they have potential application, for example, for greatly improving the performance of semiconductor lasers and several other kinds of quantum electronic

devices.

Computational studies have revealed the conditions under which a PBG crystal will exhibit a complete bandgap in the optical regime. The fundamental challenge at present is one of materials science: i.e., the fabrication of such three-dimensionally periodic lattices in a controllable way, in copious quantities, and at a reasonable cost. Several strategies have been used to create three-dimensionally PBG structures, including chemical methods such as colloidal self-assembly^{10, 48-50)} and colloidal crystal templating,⁵¹⁻⁵⁹⁾ microfabrication techniques such as mechanically drilling holes within a dielectric slab or stacking logs of dielectric or metallic materials,⁶⁰⁻⁶²⁾ and holographic patterning using multiple laser beams.⁶³⁻⁶⁵⁾ Among these approaches, the fabrication of three-dimensionally PBG crystals via colloidal self-assembly is particularly attractive. In addition to being inexpensive, colloidal self-assembly offers relative ease of processing and short processing time, compared to stepwise microfabrication techniques.

4.2 Chemical sensors

Asher et al. fabricated temperature, pH-, and ion-responsive sensors by embedding colloidal crystals in appropriate polymer hydrogels^{3, 4)} (**Fig. 7**). The hydrogel colloidal crystals developed by Hu et al.⁶⁶⁾ and Bebord et al.⁶⁷⁾ have enabled the tuning of the color of diffracted light by either changing the temperature or applying an electric field. Blanford et al. have demonstrated the use of a ceramic inverse opal in detecting organic solvents through the change in refractive index.⁶⁸⁾ Cassagneau et al. and Gu et al. have recently shown that the reversible color tuning of a colloidal crystal could be potentially adopted for biosensing.⁶⁹⁻⁷⁰⁾ Jethmalani and Ford, Foulger et al., and Sumioka et al. have further demonstrated that colloidal crystals embedded in appropriate polymer films could serve as mechanical sensors for measuring strain caused by uniaxial tension or compression.⁷¹⁻⁷⁴⁾ In these demonstrations, the lattice constant

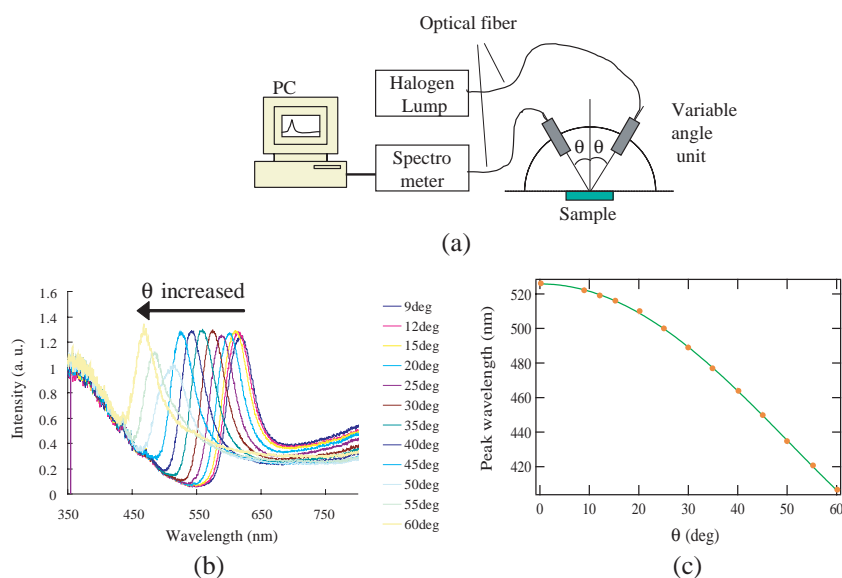


Fig. 6 Angle resolved reflection spectroscopy.
(a) Instruments (b) Reflection curves with different angles
(c) Fitting curve of angle θ vs peak wavelength.

and/or mean refractive index (and thus the color of light diffracted by the colloidal crystal) varied in response to the environmental changes.

A photonic paper/ink system has been developed by embedding three-dimensionally colloidal crystals of polymer beads in an elastomeric matrix and judiciously selecting liquids capable of swelling the elastomer.⁷⁵⁻⁷⁷⁾

4.3 Inverse opal

The use of colloidal crystals as templates has proven to be a promising approach for three-dimensional fabrication, highly ordered macroporous materials, and inverse opals.⁵⁾ Inverse opals are comprised of air spheres that are close-packed in a highly ordered three-dimensionally periodic lattice and are interconnected to each other by small channels (**Fig. 8**). These structures are routinely prepared by first allowing monodispersed particles to spontaneously self-assemble into face-centered cubic (fcc) or body-centered cubic (bcc) colloidal crystals. A range of inorganic or organic materials can then be used to infiltrate the voids between the particles in the colloidal crystal. After solidification, curing, or polymerization of the infiltrated material and removal of the templated colloids, inverse opals are obtained. By using this templating approach, a wide variety of inverse opals have been prepared, including metals, metal

oxides, semiconductors, carbon, silicon, and polymers.^{52, 57, 59, 78-89)}

The major advantage of this method is that it provides a simple and effective method for the fabrication of three-dimensionally ordered macroporous materials with controlled pore size (by variation of the colloid particle size) and composition (determined by infiltrating materials).

5. Conclusions

The use of colloidal crystals, which are crystalline arrays of monodispersed spherical colloids, has been demonstrated for a wide variety of applications. The success of these applications depends greatly on the ability to assemble monodispersed spherical colloids into crystalline lattices having well-defined structures, tightly controlled thicknesses, and sufficiently large domain sizes.

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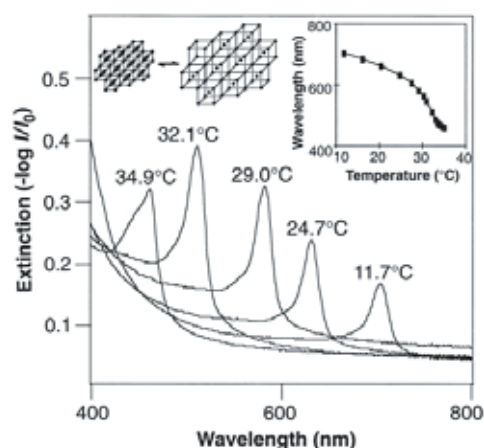


Fig. 7 Temperature tuning of Bragg diffraction from a colloidal crystal film of polystyrene particles embedded polymer gel. The shift of the diffraction wavelength results from temperature induced volume change of the gel, which alters the lattice spacing.

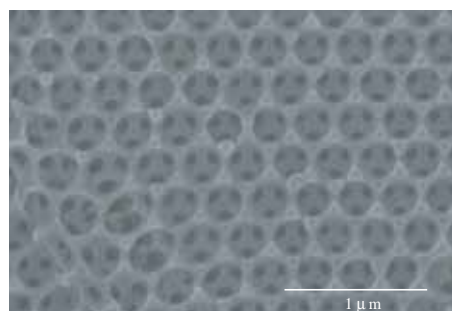


Fig. 8 Scanning Electron Microscopic images of the inverse opal of silica composite which is comprised of air spheres and interconnected by small channels. These structures are prepared by infiltration the voids in the colloidal crystal and removal of the templated colloids.

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Hiroshi Nakamura

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