Small angle X-ray scattering of the colloidal crystal*

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Abstract The monodisperse polystyrene spheres are assembled into the colloidal crystal on the glass substrate by vertical deposition method, which is aimed at the so-called photonic crystal applications. The structural information of the bulk colloidal crystal is crucial for understanding the crystal growth mechanism and developing the various applications of colloidal crystal. Small-angle X-ray scattering (SAXS) technique was used to obtain the bulk structure of the colloidal crystal at Beamline 1W2A of BSRF. It is found that the SAXS pattern is sensitive to the relative orientation between the colloidal sample and the incident X-ray direction. The crystal lattice was well distinguished and determined by the SAXS data.

Key words colloidal crystal, small angle X-ray scattering, photonic crystal

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1 Introduction

Photonic crystals possess periodically three-dimensional dielectric structures with lattice parameters comparable to the wavelength of light and can control the emission and propagation of light. Photonic crystal, which is expected to lead to innovations in optics and quantum optics, has a range of forbidden frequencies, called photonic band gap[1, 2]. Colloidal crystal can be used as a template to fabricate photonic crystal. Since the optical properties are intimately connected to the crystal structure, it is important to obtain the structural information of the colloidal crystal.

In order to probe the structure of the colloidal crystals, confocal microscope and electron microscopy have been widely used[3—6]. However, these real-space structure detecting techniques have many disadvantages. Firstly, only a small part of the sample can be imaged, which results in difficulty to obtain large-scale morphology information. Secondly, electron microscopy can only provide topological data of sample surface. In order to get the 3-D structure information of the bulk colloidal crystal, the sample has to be cut into small pieces, which inevitably damages the whole structure of the colloidal crystal. In addition, confocal microscopy technique also requires the refractive-index matching between the particles and the surrounding medium, which is almost impossible for some cases.

Due to the multiple-scattering effect, light scattering can only be used to detect low-order diffractions. Consequently, visible light scattering technique was extremely limited in resolving the problem of the colloidal crystal structure. In contrast, X-ray has an extremely small refractive-index contrast (typically in the order of 10^{-6}). Therefore, small angle X-ray scattering (SAXS)[7—10] can be well applied to study the structure of these colloidal crystals which strongly scatter or absorb the visible light.

In this paper, the diffraction patterns of the colloidal crystals were taken at different elevation angles with SAXS technique. The reciprocal lattice reflections are found to be very sensitive to the elevation angle.

2 Experiment

Polystyrene latex spheres with a diameter of

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220 nm were synthesized in the laboratory according to the normal procedure[11]. The particle size deviation was within 2%. Polystyrene spheres were homogeneously dispersed in Milli-Q water with a volume fraction of 0.08%. This solution was transferred into a cylindrical glass growth cell. A glass slide (thickness is 0.2 mm) was fixed vertically into the glass growth cell. To guarantee the good wetting ability between water and the substrate, the glass slide and the growth cell were cleaned with detergent, and then were immersed into chromic acid for about 24 hours. The cleaned glass plates were kept in Milli-Q water for about 8 hours and dried naturally in the clean room before experiment. The growth cell was then put into an incubator chamber. The temperature and the humidity were kept at 55℃ and 35%, respectively. The total growth procedure lasted 4 days. Fig. 1 shows the SEM image of the synthesized colloidal crystal.

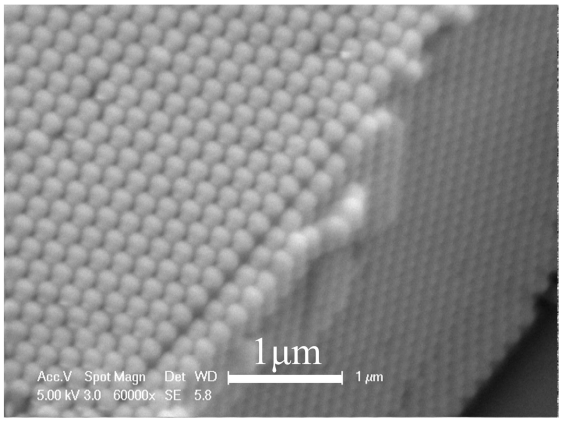

Fig. 1. SEM image of the colloidal crystal sample.

The SAXS experiments were performed at the SAXS Station (Beamline 1W2A) of the Beijing Synchrotron Radiation Facility (BSRF). The experimental setup is shown in Fig. 2. The working distance between the sample and the detector was chosen as 5200 mm and the X-ray wavelength was 1.536 Å.

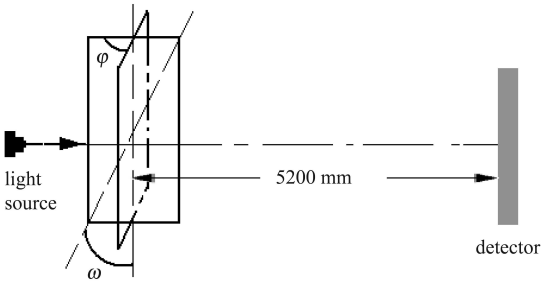

Fig. 2. A schematic map of the SAXS experiment setup.

3 Results and discussion

It is well-known that the colloidal crystal consists of a series of hexagonally packed layers[10]. The three-dimensional real-space lattice depends on the stacking sequence of the layers. Generally, the colloidal crystal is of Face-Centered Cubic (FCC) structure. Due to the small thickness compared with its area, the sample can be approximately regarded as a quasi-two-dimensional structure. Therefore, the diffraction data can be analyzed on the basis of a hexagonal lattice. Assuming that the hexagonal lattice has a lattice constant a, its reciprocal lattice is also a hexagonal lattice packed with Bragg rods[12]. The axial direction of the Bragg rods is perpendicular to the surface of the sample. The lattice constant in reciprocal space is $b = 4\pi/\sqrt{3}a$.

In general, there are two types of Bragg rods[12] for the hexagonal close-packed layers as shown in Fig. 3. For these Bragg rods with $h - k = 3n$, where n and the Miller index h and k are integers, reciprocal lattice points occur on the rods at integral values l. In Fig. 3, the central (0, 0) rod and the rods drawn as filled circles belong to this type of diffraction. For the rods with $h - k = 3n \pm 1$ as shown by the open circles, the distribution of diffraction spots depends on the stacking order of the hexagonal close-packed layers. For a FCC structure, the maximum intensity spots occur at l+1/3 or l-1/3 alternatively as shown in Fig. 4.

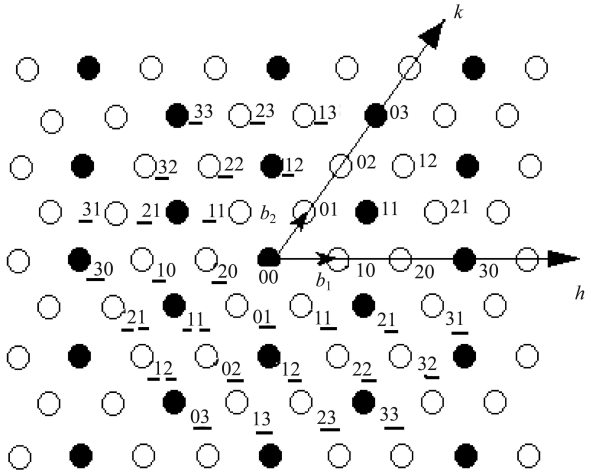

Fig. 3. A hexagonal layer in reciprocal space with Miller indices h, k.

In reciprocal space, only these lattice points intersected with the Ewald sphere can be probed. As the radius of the Ewald sphere $2\pi/\lambda$ is about 1000 larger than the distance Q_{hkl} of the reciprocal lattice

point (hkl), the Ewald sphere is nearly flat and perpendicular to the X-ray beam (shown in Fig. 4). In this case, the scattering pattern is just these crossing points between the Ewald plane and the Bragg rods.

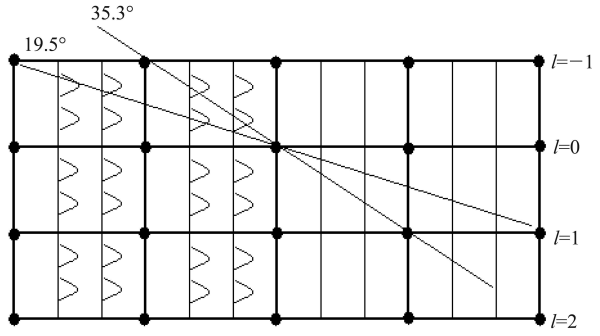

Fig. 4. Rod system of Fig. 3 rotated by 90° about the (1,0)-(0,0)-(−1,0) axis. $h-k=3n$ rods drawn as solid.

Figure 5 shows the diffraction patterns at different elevation angles. When the elevation angle was changed, the diffraction pattern changed accordingly. The intensity change of the diffraction spots indicates that the Ewald plane intersected with different reciprocal rods. Combining all these diffraction patterns, the 3D structure of the colloidal crystal can be figured out.

The lattice constant 'a' of the hexagonal layers can be determined from the diffraction pattern at normal incidence (Fig. 5a), which corresponds to the crossing points between the Ewald plane and the Bragg rods at l=0. The indices h and k meet the condition: $(h-k)=3n$. The Bragg condition is $Q_{hk}^2=(4\pi/\sqrt{3}a)^2(h^2+k^2+hk)$. The lattice constant was determined to be $a=214.4$ nm, which is smaller than the diameter of the spheres.

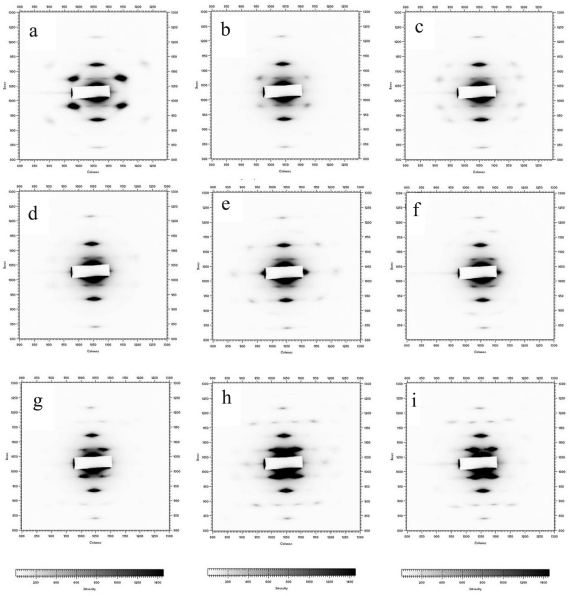

Fig. 5. Diffraction patterns at different elevation. From a to i, $\varphi=0°$ and $\omega=0°$, 5°, 10°, 15°, 20°, 25°, 30°, 35° and 40°, respectively.

In summary, the colloidal crystal was determined to be a hexagonal-layer-packed structure. The diffraction patterns can be attributed to the intersection between the Ewald plane and two kinds of Bragg rods. By tilting the sample, the change of diffraction pattern can be used to determine the 3D structure of a colloidal crystal.

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References

1 Yablonovitch E. Phys. Rev. Lett., 1987, **58**: 2059—2062
2 John S. Phys. Rev. Lett., 1987, **58**: 2486—2489
3 Blaaderen A V, Ruel R, Wiltzius P. Nature, 1997, **385**: 321—324
4 Blaaderen A V et al. Langmuir, 1992, **8**: 1514—1517
5 Blaaderen A V, Wiltzius P. Science, 1995, **270**: 1177—1179
6 Rengarajan R et al. Phys. Rev. E, 2005, **71**: 016615
7 Vos W L et al. Langmuir, 1997, **13**: 6004—6008
8 Versmold H, Musa S, Bierbaum A. J. Phys. Chem., 2002, **116**: 2658—2662
9 Petukhov A V et al. Phys. Rev. Lett., 2002, **88**: 208301
10 Petukhov A V et al. Phys. Rev. Lett., 2003, **90**: 028304
11 Okubo M, Nakagawa T. Colloid Polym. Sci., 1992, **270**: 853—858
12 Guinier A. X-Ray Diffraction. London: Freeman, 1963