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Experiment Report for Prefectural Beamline

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Characterizing structures of binary and ternary polymer opals using small angle x-ray scattering

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1. Summary

Both single and multi-component polymer opal films processed with different degrees of biaxial bending induced oscillatory shearing (B-BIOS) and uniaxial bending induced oscillatory shearing (U-BIOS) methods have been characterized. In agreement with our previous results, clear hexagonal patterns were observed in all the sheared samples with different degrees of structure order. Asymmetric intensity distribution between (10) and (1-1) spots was also observed, and it varies depending on different shearing methods and degrees of shearing.

2. Purpose of experiment and background

Polymer opals are novel stretchable 3D photonic crystals comprised of densely packed core-shell spheres [1-3]. The spheres, with a hard polystyrene core and a low glass transition soft PEA shell, are pressed into thin films and sheared in solid phase without using any liquid solvent. By using small angle x-ray diffraction technique, the goal of the experiment is expected to be in two aspects: the first is to investigate the arrangement of the nanospheres in binary and ternary polymer opal films after shear ordering, and the second is to clarify the puzzles from our previous SAXS experiment on single component polymer opals, including peculiar intensity distribution along the tubes and large intensity contrast between spots at the same Q range. The experiment is supposed to be able to provide valuable information on ordered as well as disordered structures within the films, which therefore promises a deeper look on how spheres of either the same size or different sizes rearrange under shearing force in highly viscoelastic medium.

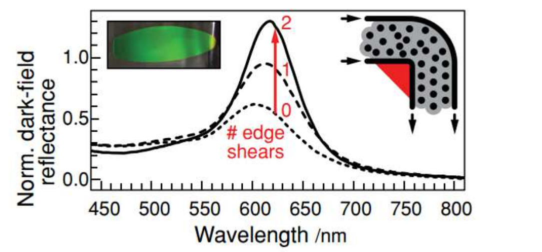

Figure 1. Dark-field spectra of polymer-opal films show improving order with BIOS process.

Compared to most of the top-down methods which are time costing and expensive, bottom-up assembly seems to be more promising and commonly used for fabricating low cost industrial applicable 3D photonic crystals. However, due to the intrinsic properties of the method, the existence of disordered structures is always a serious problem, which is detrimental for the optical performance and the potential applications. Shearing technique has been used for improving the order of self-assemblied colloidal structures, however, for those systems, viscosity of the medium is usually low, and shearing is done in liquid phase. Different from most of the colloidal systems, our efforts in recent years on making well-ordered polymeric opaline photonic crystals [4-11] show how shearing works in highly viscoelastic medium in solid phase. By using shearing force, we have fabricated industrial scale (>100m) flexible photonic crystal films which exhibit strong structural colours uniformly over large areas. Since optical properties of the film comes from the interplay of order and disorders of the structure, understanding how the spheres are arranged in bulk is of great importance for both science and applications [3,4,8,11]. However, due to the small size of the spheres (~200nm) as well as the low electron density contrast between the spheres and the medium, it has been a great challenge to characterize the structure. The setup of small angle x-ray diffraction in Saga provides very high resolution and intensity which facilitates the characterization of structures in submicron scale, which is a perfect technique for our polymer opal system.

3．Experimental（Note: Description of sample, method of experiment and analysis, etc.）

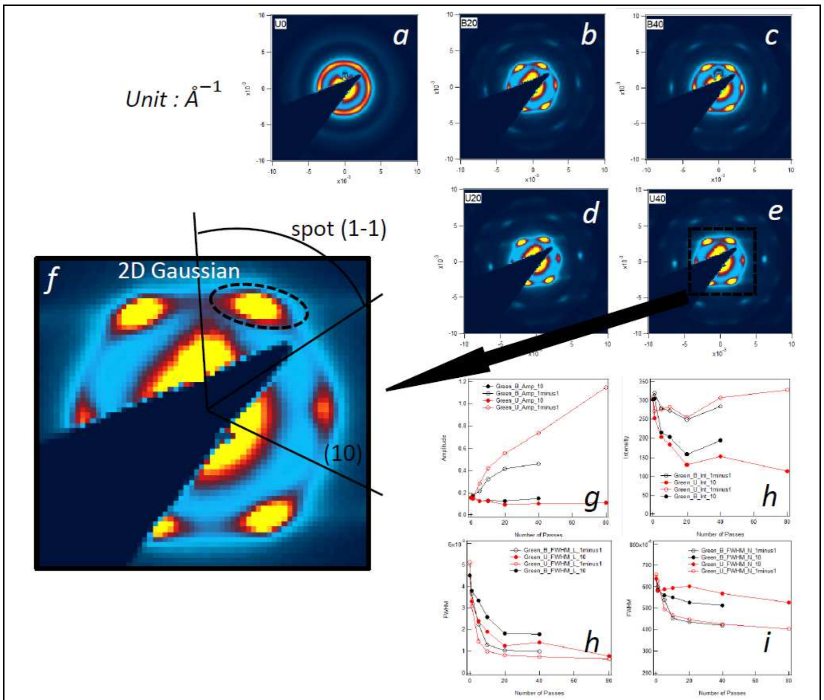

Figure 1. 2D SAXS patterns of polymer opals with different shear ordering methods. (a), before shearing, (b), biaxial-BIOS 20 passes, (c), biaxial-BIOS 40 passes, (d), uniaxial-BIOS 20 passes, (e), uniaxial-BIOS 40 passes, (f), zoom in of the first ring in (e), spots are analyzed with 2D Gaussian fit, (g)-(i) amplitude and integrated intensity of (10) spot and (01) spot for different samples with different shearing methods and number of shearing.

The measurements are performed using the photon energy of 8.2 keV and a Rigaku high resolution detector. The radius of the beam stop is just at the edge of an acceptable level for imaging the reciprocal space lattices, which gives us as much information as we want but at the same time generated some distortions over the diffraction patterns.

Polymer opal films with different degrees of structural order as well as different ordering techniques have been characterized. Clear SAXS patterns were observed on both single component and multi-component polymer opals which are comprised of pure polymeric spheres embedded in medium of a different polymer with very low electronic density contrast between them.

4．Results and Discussions

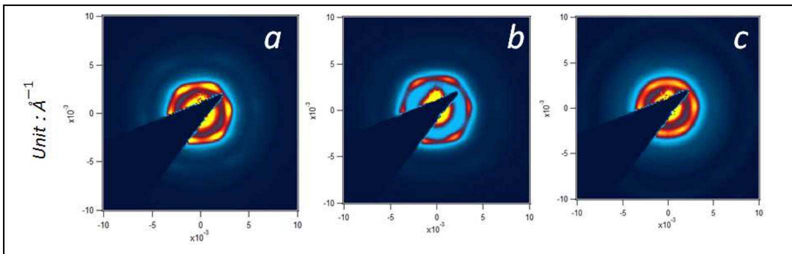

Figure2. 2D SAXS patterns of binary polymer opal films ordered with uniaxial 20 passes. (a), $R_L{:}R_s = 1.2$, (b), $R_M{:}R_s = 1.2$, (c), $R_L{:}R_s = 1.4$

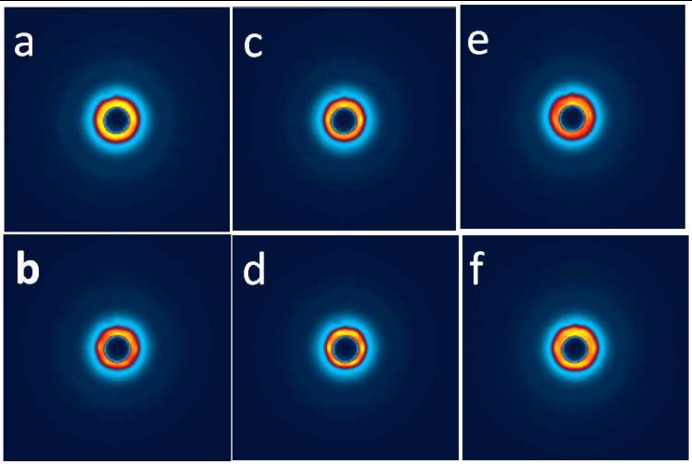

Figure 3. SAXS patterns of ternary polymer opals. a&b, R/G/B 1:1:1 ternary opal before and after ordering, c&d, R/G/B 3:2:1 ternary opal before and after ordering, e&f, R/G/B 1:2:3 ternary opal before and after ordering. Beam normal to the (001) plane.

By fitting the diffraction patterns with 2D Gaussian model, detailed analysis (Fig. 1) has been done, which provides insight into how spheres are rearranged with different shearing methods. Both B-BIOS and U-BIOS methods improved the structural order of polymer opals significantly. While integrated intensity of (1-1) spot remains approximately constant, amplitude increases drastically with increasing amount of shearing which is also accompanied with a rapid drop in FWHM. With same amount of shearing, structure order improves more effectively with U-BIOS. FWHM in radial direction (narrow axis of the spot) drops much slower than the hoop direction (long axis of the spot), which indicates orientational order improves much fast than positional order. Significant difference between (10) spot and (1-1) spot has been observed, which needs further investigation. Overall order of the films reaches a saturated level after approximately 40 passes of shearing with both methods, while structural order improves most effectively in the first ten passes. BIOS method can also be used in fabricating binary or ternary opal structures. Fig. 2 & 3 show clear *hcp* arrangement in binary polymer opals comprised of spheres with different sizes.

5. Future issues

1. Grazing angle SAXS in order to get structural order information by aligning the beam parallel to the planes
2. Tilting the samples in different orientations in order to get more information of the 3D reciprocal lattice strucuture
3. Explore the effect of staining on samples

6. References

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７．Publications, patents （Note: Typical deliverables related to this proposal.）

The experimental data obtained in this work will be submitted to an international scientific journal.

８．Keywords （Note: 2-3 words about samples and experimental methods.）

Polymer opals, SAXS, Shearing, Order and disorders

９．About the publication of research results

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