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Polycrystalline SiO_2 Colloidal Crystal Film with Ultra-Narrow Reflections

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This work reported a high quality photonic crystal film with ultra-narrow photonic bandgap via chemical synthetic route. The bandgap is much narrower than that of traditional colloidal crystals, which makes the film qualified for optical devices. The narrow PBG originates from not only the high crystallinity and uniform orientations of microcrystals within the film but also the very close refractive indices between silica and polymer matrix. Due to the matching of refractive index, the amorphous contents of the film are optically transparent and do not interfere with the reflection, so that the photonic crystal film is tolerant to the existence of disordered contents.

Recently, photonic crystal materials have attracted great attention due to their wide applications in sensing [1], biological detection [2], display unit [3], photonic printing [4], security devices [5], optical enhancement [6] and solar cells [7]. Compared to the “top-down” techniques based on lithographic process, the self-assembly of monodisperse particles into colloidal crystals provide “bottom up” methods to obtain photonic materials, which potentially has advantages in large scale and low cost production. In the past decade, various methods including sedimentation, thermal evaporation, spin coating, sonication and electromagnetic field assisted assembly etc. have been developed to prepare colloidal crystals. However, up till now, it is still a great challenge to prepare large scale and high-crystallinity colloidal crystals qualified for optical devices.

Cracks and defects within the colloidal crystals are the major obstacles for the acquirement of perfectly ordered structures. Although the synthetic parameters such as evaporation rate, pressure and temperature have been carefully tuned to improve the assembly quality, the cracks are inevitable in an evaporation based assembly process. Because the shrinkage of particle due to evaporation of solvation layer and the adhesive interaction between particle and substrate will cause a localized tensile stress during the final stage of evaporation, which lead to cracks even if the particles have been perfectly assembled in solution by electrostatic repulsion. Therefore, various assembly methods and material systems have been developed to avoid cracking and improve the assembly quality.[8] First of all, the cracks can be avoided by using a low-adhesive substrate, which allow the particle to shrink freely into a close pack structure. For example, Wang and Song et al. have reported a crack free colloidal crystal with FWHM of 12-15 nm assembled on a super-hydrophobic substrate. [8f] Second, the cracks can be removed by filling the interparticle gaps through co-assembly with smaller colloidal particles or addition of reactive precursor during assembly. For instance, Aizenberg et al. prepared the crack free colloidal crystals in centimeter scale through evaporative deposition of polymeric particles suspended in a hydrolyzed silicate sol-gel precursor solution. [8e] Furthermore, the crack free colloidal crystals can also be assembled from sintered particles, whose shrinkage are intrinsically inhibited and the cracks are thereby avoided. [8a]

Since the aforementioned synthesis usually requires sophisticated control, time consuming process or specially treated substrates, people can’t help wondering whether the “**crack free**” colloidal crystal is the only solution to high quality photonic materials. Is it possible to prepare a “**crack-tolerant**” colloidal crystal, which also has narrow and strong reflection peak? In this work, we report a high quality SiO_2/PEGDA photonic crystal film which is composed of colloidal microcrystals and amorphous stacks of silica particles. Because the amorphous stacks are optically transparent due to the matching of refractive index, the film is actually tolerant to the existence of cracks and even amorphous contents. Therefore, it presents brilliant structural colors and ultra-narrow reflection peak due to the Bragg scattering of colloidal microcrystals. Through the optimization of assembly temperature and film thickness, the FWHM of reflection peak reaches about 6 nm, which makes it qualified for monochromatic optical filter.

Photonic crystal film with ultra-narrow photonic band gap (PBG) is prepared by fixing the metastable SiO_2 colloidal microcrystals in polymer matrix through photo polymerization. The synthesis is developed from the recently reported technique of metastable colloidal crystal arrays (CCAs), which provides a convenient way to obtain three dimensional colloidal crystals suspended in many organic solvents including liquid monomers.[9] Typically, silica particles dispersed in ethanol are mixed with poly(ethylene glycol) diacrylate (PEGDA) to form a homogeneous solution, which turns to a highly concentrated solution of particles after evaporating the ethanol at 90 °C. As the solution is cooled down to room temperature and kept steady for several minutes, only part of the particles will precipitate from the supersaturated solution to form metastable CCAs in liquid monomer. Here, the spontaneous crystallization of particles is driven by the maximization of structural entropy, because the ordered close packing (φ = 0.74) leaves a larger free volume than the random close packing (φ = 0.64).[10] Phase separation then occurs, because the homogeneous dispersion separated into a "crystal phase" with orderly packed particles and a "liquid phase" with randomly dispersed particles. Since PEGDA is photo curable, the colloidal microcrystals can be fixed in polymer under UV irradiation, which produces a photonic crystal (PC) film composed of microcrystals and randomly packed particles eventually. (Figure 1a, 1b) Measured by probe-type reflection spectrometer, a circular film with diameter of 1.5 cm shows intense reflection signals and narrow reflection peak with full width at half maximum (FWHM) of about 6 nm, which is much narrower than most previous results. (Figure 1d) It is also worth mentioning that the synthesis can be amplified without too much sacrificing in the assembling quality. On a 7×7 array of square PC films, the reflection spectra are measured in each block and the corresponding FWHMs show a normal distribution from 8.4 to 13.5 nm with an average value of 10.9 nm, which suggest large-scale production, fast preparation and good optical performance can be achieved simultaneously with this synthetic method. (Figure 1c, 1f)

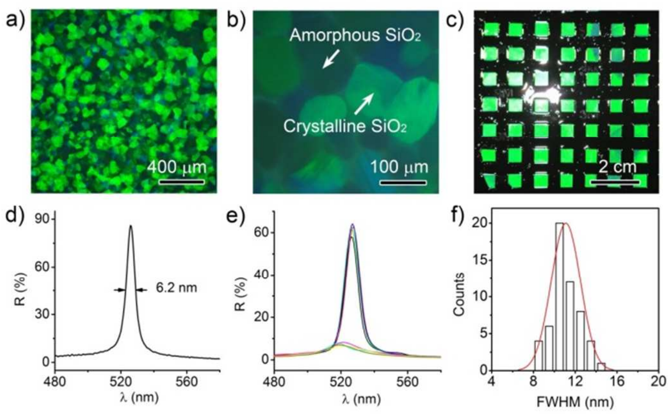

Figure 1. (a, b) Optical Microscope images of polycrystalline SiO_2 colloidal crystal film. d) Reflection spectra of the film measured by probe-type spectrometer and e) microscopic spectra measured at 4 crystalline and 4 amorphous regions. c) Digital photo of a PC array and f) the distribution of FWHM measured in each block.

The colloidal crystal film contains "crystalline region" with highly ordered particle assemblies and "amorphous region" with randomly stacked particles. This unique structure is originated from the phase separation in metastable CCAs precursor before UV curing. In microscope images (Figure 1b), one can find that the film has a typical polycrystalline characteristic with many colloidal microcrystals dispersed in it. These microcrystals have an average size of 80 - 120 μm. As three dimensional photonic crystals, they reflect green light due to Bragg scattering, and the brilliant structural color proves their high crystallinity. The calculation of PBG of typical colloidal microcrystal shows they have a non-close packed fcc structure with interparticle spacing larger than the diameter of particles, and the calculated reflection wavelength is consistent with the measured results.(See SI) Meanwhile, the transparent gaps between the crystals show no structural color at all, which suggests this region could be random stacks of particles. The polycrystalline structure can also be verified by micro-scale reflection spectra which collects reflection signals within a circular region of 5 μm. Through repeated measurements at 4 different crystalline and amorphous positions, the microcrystals consistently show strong and narrow reflection peaks, while the transparent gaps show weak reflection possibly caused by microcrystals below the focusing plane of current image. (Figure 1e) It should be noted that the FWHM (10 nm) of microscopic reflection is slightly larger than that measured by probe spectrometer, because the numerical aperture of the microscopic reflection system is larger than that of the fiber probe coupled spectrometer, so that the former spectra present more reflection signals from the tilted incident light. The micro-scale reflection signals suggest that the ultra-narrow reflection come from the crystalline region only. Through a splicing picture of 18 individual SEM images from the film's cross section (SI Figure 3), one can directly observe the orderly arranged SiO_2 particles and the randomly packed particles dispersed in PEGDA. (Figure 2) The crystalline regions are highlighted in green according to the amplified SEM images, and it confirms the polycrystalline characteristic once again.

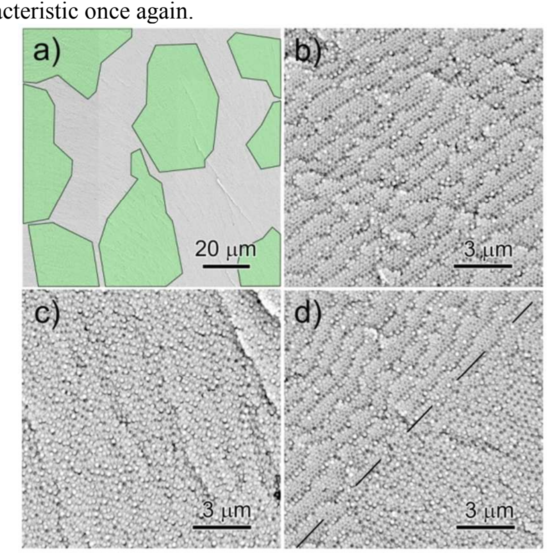

Figure 2. a) Cross-section SEM images of a SiO_2/PEGDA PC film with crystalline region highlighted in green and amplified images of b) crystalline region, c) amorphous region and d) the boundary.

The ultra-narrow reflection peak can be attributed to three factors including the high crystallinity of colloidal microcrystals, the uniform crystal orientations and the matching of refractive index between SiO_2 and PEGDA, based on the fact that the reflection comes from the microcrystals only. Frist of all, each microcrystals can be regarded as a single crystal because the particles are perfectly assembled and few defects exist inside. The high crystallinity narrows the distribution of crystal lattice constants and thereby the reflection peaks. Second, the uniform orientations of all microcrystals within the film also contribute to the ultra-narrow reflection. It is known that the reflection peak of a three-dimensional colloidal crystal will shift in spectrum when its orientation changes. Although the colloidal microcrystals have irregular shapes and their orientations are hard to be determined from the SEM images, the conclusion of close orientations among different microcrystals can be achieved according to the monochromic green color in optical microscope image and the same reflection peak in micro-scale reflection spectra. Considering the size of microcrystals (80-120 μm), their uniform orientation might be caused by the inductive effect and the spatial confinement of two glass slides during the assembly. Since the macroscopic reflection is composed of reflections from each colloidal microcrystal, the overall reflection signal will be strong and narrow accordingly. Finally, the matching of refractive index between SiO_2 (n = 1.46) and PEGDA (n = 1.47) is also important to the ultra-narrow reflections. The formation of

PBG is associated with the coherent scattering arising from the periodic interfaces between the different materials in photonic crystal. Generally, a strong coherent scattering process leads to a wide PBG. When the refractive index contrast approaches to zero, the coherent scattering and the periodic structure disappear, and the PBG will be closed accordingly. In our case, the refractive index contrast is quite small so that the PBG is opened in a very narrow window, which exhibit a narrow reflection in spectra. Theoretical calculation of the peak width also supports the explanation. (See SI)

The ultra-narrow reflection peak also benefits from the transparent appearance of amorphous SiO_2/PEGDA composite and its promotion to the crystallization of neighboring colloidal microcrystals. When SiO_2 particles are randomly packed in PEGDA, the composite will show neither structure color nor scattering induced white color but a transparent appearance due to the matching of refractive index between SiO_2 and PEGDA. Therefore, the amorphous region has no reflection and shows no interference with the ultra-narrow reflection produced by the colloidal microcrystals, which means the current PC film is tolerant to cracks and amorphous contents. In another aspect, the amorphous region will serve as a buffer zone to improve the crystallization of particles. During the synthesis, numerous metastable colloidal microcrystals precipitate out of the solution due to supersaturation of particles, and these microcrystals grow even larger when the liquid monomer turns to solid polymer matrix. Since whole process is accomplished in several minutes, it is impossible for these microcrystals to integrate into a large perfect crystal. Fortunately, the presence of amorphous region provides a buffer zone for the microcrystals to perfect the crystallization by themselves through adjusting the particles around the lattice point.

The ultra-narrow and strong reflection can be achieved by optimizing the assembly temperature and the film thickness. It has been proved that the reflections are originated from each colloidal microcrystal, so that their crystallinity and density inside the film intrinsically determines the reflection signal. Generally, a strong and narrow reflection will be expected when the film is full of microcrystals with relatively large crystal size. In order to achieve narrow reflection, the supersaturated solution of particles is transferred onto a substrate, which is placed in a thermostatic environment with different temperatures. As the temperature decrease from 90 to 0 °C, the FWHM of as-made PC film decreases from 13.9 to 8.7 nm and its intensity decreases from 111 % to 71 %. (Figure 3a, 3b) Corresponding microscope images show that the size of microcrystal increase from 5 to 50 μm and the crystal number decreases accordingly, which explains the evolution of reflection signals fairly well. (SI Figure S4) For the same SiO_2/PEGDA particle dispersions prepared at 90 °C, the particles will have a smaller solubility at lower temperature, so that more particles will be forced to precipitate from the dispersion to form larger microcrystals with narrower reflection peaks. Furthermore, the reflection peak can be narrowed by tuning the thickness of PC film. As the thickness increases from 50 to 360 μm, the FWHM first decreases to 6.8 nm then increases to 9.0 nm. Both the FWHM and the intensity of reflection show an optimal value for the thickness of 270 μm. (Figure 3c, 3d) Behind the experimental data, one can also find consistency between larger crystal size and narrow reflection signal from the microscope images. (SI Figure S6) Here, the thickness of the liquid precursor before UV curing may physically confine the growth of metastable colloidal microcrystals, so that larger microcrystals tend to form in a relatively thicker film.

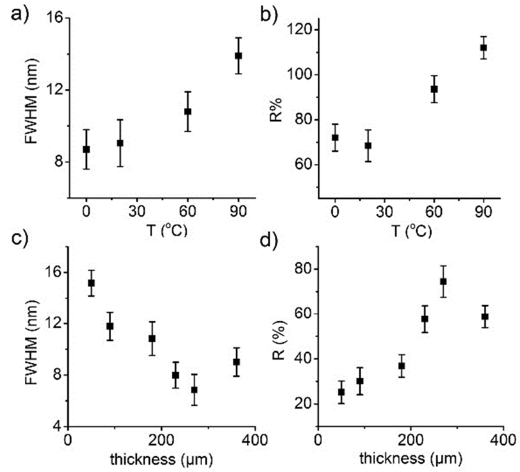

Figure 3. Evolution of reflection peak width at half maximum and reflection intensity of PC film with the change of a, b) assembly temperature and c, d) film thickness.

Due to the ultra-narrow PBG, the current PC film combined with a commercial optical filter can be used to obtain monochromatic transmitted light. (Figure 4) In order to demonstrate the function of narrow PBG in optical filter, two PC film with same central reflection wavelength (528 nm) but different FWHM (6.8 and 16.6 nm) are first fabricated using the same silica particles. Here, the PC film with broader PGB is achieved by replacing the short-chain monomer ($PEGDA_{250}$) with a long-chain monomer ($PEGDA_{700}$) in synthesis. A commercial optical filter can effectively filter most of the visible incident light and allowed the transmission of light from 527 to 538 nm. Since part of the transmissions coincides with the reflection of photonic crystal, the PC film can be used to further narrow the transmittance. When the commercial filter is coupled with narrow-PBG film, the transmittance at 527 nm can be completely eliminated, which output a monochromatic transmitted light at 538 nm with 40% decrease in intensity. However, for the case of broad-PBG film, 63 % and 33 % of the light at 527 and 538 nm are filtered simultaneously, which suggests the PBG is not narrow enough to selectively eliminate one of the two transmitted light with close wavelength. Compared to most reports of PC materials based on silica or polystyrene particles whose reflection FWHM are around 30-50 nm, the current work proves that a chemically prepared photonic material can also be qualified for sophisticated optical devices.

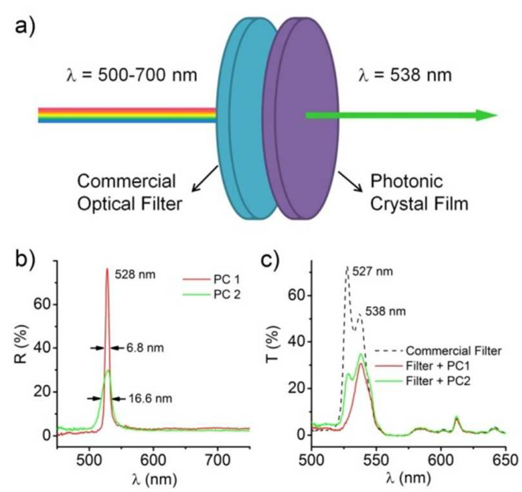

Figure 4. a) Schematic illustration to the achievement of monochromic light by filtering the visible light with commercial optical filter coupled with PC film. b) Reflection spectra of two PC film with different FWHM. c) Transmission spectra of incident light tuned by commercial filter (dash line) and filter coupled with PC film (green or red line).

Conclusions

In summary, polycrystalline colloidal crystal films with ultra-narrow PBG have been prepared in large scale by fixing the metastable SiO_2 colloidal microcrystals in PEGDA through photo polymerization. The photonic crystal film is composed of colloidal microcrystals and randomly packed particles embedded in PEGDA. The microcrystals are responsible for the ultra-narrow PBG due to their high crystallinity, uniform crystal orientations and very close refractive indices between silica and PEGDA. While the amorphous part are optically transparent and do not interfere with the reflection and structural color, so that the current PC film is tolerant to the existence of disordered particle stacks. Through optimization of the assembly temperature and the film thickness, the FWHM of the reflection peak reaches approximately 6 nm. Combined with a commercial optical filter, the current photonic crystal film with narrow PBG can produce a monochromatic transmitted light.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, calculation of photonic band gap and PBG width, high resolution and large scale SEM image of the cross section of photonic film, microscope images and reflection spectrum of photonic film prepared at different temperature and with different thickness. See DOI: 10.1039/c000000x/

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