



THE INFLUENCE OF LIGHT IRRADIATION CONDITIONS ON THE STRUCTURE OF THE POLYMERIZATION CRYSTALLINE COLLOIDAL ARRAYS

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Abstract

Dyes doped polymerization crystalline colloidal arrays (PCCA) consisted of monodisperse polystyrene particles with diameters of 150 nm are

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fabricated by light polymerization method. The influence of light irradiation conditions on the structure of the PCCA is investigated. The results show that the PCCA with homogeneous structure are obtained when two surfaces of the quartz cell are irradiated in turn for 10s with total illumination time of 5 minutes. The influence of photonic band gap on photoluminescence of dyes is also investigated. Suppression of the emission is observed if the photonic bandgap overlapped with emission band of the dyes.

1. Introduction

Recently, much attention has been focused on the three-dimensional (3D) photonic crystals since the concept was proposed by Yablonovitch [1] and John [2] for application potential in an area of photonics, including near-zero threshold lasers, sensors, waveguides, photonic crystal fibers, etc [3-5]. Photonic crystals with various 3D periodical structures, such as opal, inverse opal, woodpile, diamond structure, crystallization colloidal arrays, etc, have been fabricated [6-9]. The crystallization colloidal arrays (CCA) consist of order colloidal suspension particles [10-13], which can diffract the light and form the photonic band gap at the angles that meet the Bragg condition. Unfortunately, CCA with liquid-phase-based structures do not exhibit a high degree of mechanical and chemical stability. For example, a liquid-phase CCA will undergo transitory disordering when it is subjected to a mechanical shock, whereas permanent disordering can be induced to incur by the addition of ionic impurities [9, 13]. Recently, polymerization hydrogels around the CCA were developed to stabilize the array, which resulted in a relatively robust polymerized crystalline colloidal array (PCCA) [14-16]. At present, the PCCA is investigated extensively due to potential applications in many fields, such as chemical and thermal sensors [14-16]. As far as we know, there have been few reports about the influence of preparation parameters on the structure of the PCCA. In this work, the dyes doped PCCA were prepared by light polymerization method, and the influence of light irradiation condition on the microstructure of the PCCA was investigated. In addition, the influence of photonic band gap on photoluminescence of dyes was also investigated in the PCCA. Suppression of the emission was observed if the photonic bandgap overlapped with the emission band of dyes.

2. Experimental

Acrylamide, NN'-Methylenebisacrylamide and 2, 2-Diethoxyacetophenone were purchased from the Alfa Aesar corporation. The commercial monodisperse polystyrene (PS) spheres with 150nm in diameter were used. CCA were prepared by the ionic resins exchange methods reported in the literature [9].

The PCCA were prepared by light polymerization method. Initially, acrylamide and NN'-Methylenebisacrylamide were dissolved in the water solvent. Then, NN'-Methylenebisacrylamide and acrylamide water solution, Fluorescein dye ethanol solution and 2, 2-Diethoxyacetophenone were added into CCA. The Fluorescein concentration is 4×10^{-4} M in CCA. The CCA mixtures were injected into a cell made of two quartz plates separated by a 70 μ m thick spacer. UV-light irradiation of CCA in the quartz plates was performed at different condition with a 50W mercury lamp (CURE SPOT™ 50), with a shutter timer to control the irradiated period. In order to investigate the effect of the photonic band gap structure on the photoluminescence of the Fluorescein dyes in the PCCA, the suspension of the disorder polystyrene microspheres was polymerized as the reference sample by a similar procedure.

The photoluminescence (PL) measurements of the PCCA were carried out on fluorescence microscope (Imager Z1m, Zeiss) using the mercury lamp as light source. The reflective spectra of the CCA and PCCA were measured by optical microscope (Imager Z1m, Zeiss). The fluorescence and reflective spectra was collected by micro-region ultraviolet-visible fiber spectroscopy (USB2000, Ocean Optics, Dunedin, FL). The structures of the PCCA were observed by optical microscope (Imager Z1m, Zeiss), AFM (Veeco diDimension V) and SEM (SEM; FEI QUANTA 200F).

3. Results and Discussion

In order to investigate the influence of light irradiation condition on structure of the PCCA, three kinds of irradiation condition were used to prepare PCCA. (1) Two surface of the quartz cell were irradiated in turn for 10s with total illumination time of 5 minutes. (2) Two surface of the quartz cell were irradiated in turn for 1min with total illumination time of 5 minutes. (3) one of two surfaces of the quartz cell were irradiated for 5 min. PCCA prepared under irradiation conditions 1, 2 and 3 were designated as PCCA I, PCCA II and PCCA III, respectively

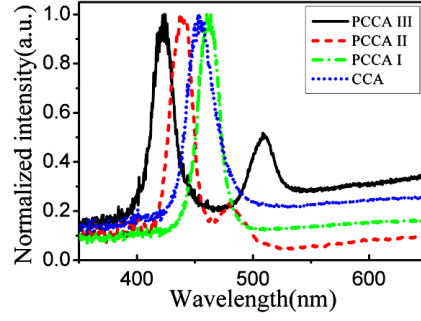


Figure 1. The reflective spectra of the PCCA I, PCCA II, PCCA III and CCA.

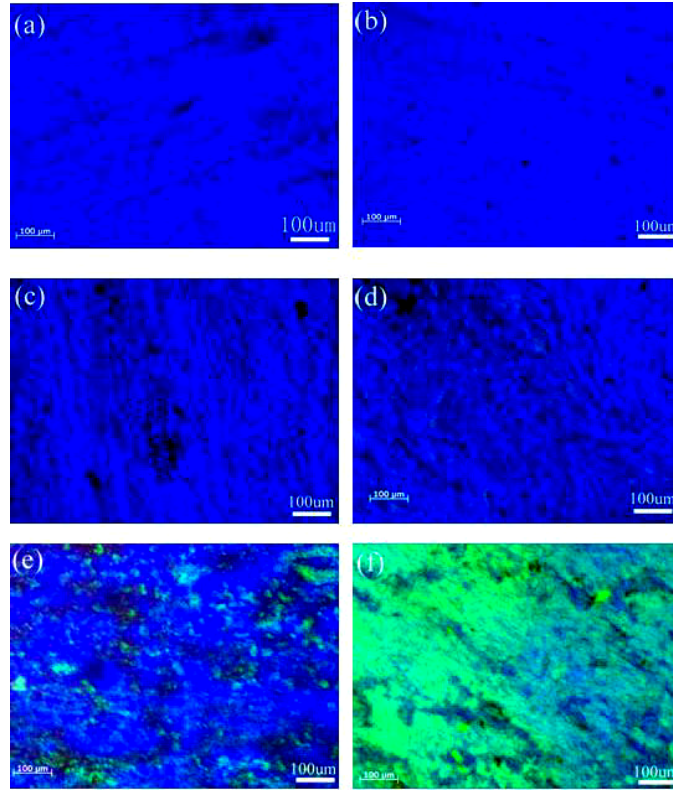


Figure 2. Optical micrograph of up and down surfaces of the PCCA (a) down surface of the PCCA I, (b) up surface of the PCCA I, (c) down surface of the PCCA II, (d) up surface of the PCCA II, (e) down surface of the PCCA III, (f) up surface of the PCCA III.

Figure 1 shows the reflective spectra of CCA before polymerization. The photonic band gap of CCA was located at 451nm. The center to center distance between polystyrene microspheres and volume fraction of microspheres in CCA can be calculated using Eqs. (1) and (2) [13],

$$d = 0.6124\lambda n^{-1}, \quad (1)$$

$$d = 0.904d_0\rho^{-\frac{1}{3}}, \quad (2)$$

where λ , d , ρ and d_0 denote the photonic band gap position of CCA and center to center distance between polystyrene microspheres, the volume fraction of the polystyrene microspheres and the diameter of microspheres (150nm), respectively. n denotes refractive index of the CCA, which is approximated to that of water (1.333). The calculated result shows that the center to center distance between microspheres and volume fraction of polystyrene microspheres is 207nm and 28% in CCA, respectively.

The reflective spectra of the PCCA I, PCCA II, PCCA III were also shown in the Figure 1. It can be found that irradiation conditions have significant influence on the photonic bandgap properties of the PCCA. The PCCA I exhibited only one photonic band gap located at the 462nm, while the PCCA II and PCCA III exhibited two photonic bandgaps, respectively. In comparison with the band gap of CCA before polymerization, the band gap of the PCCA I shift to the longer wavelength, which is due to the change of refractive index and volume during the polymerization reaction [17]. PCCA II has two photonic bandgaps located at 440 nm and 478 nm. Also, PCCA III has two photonic bandgaps of PCCA III at 423 nm and 510 nm. Existence of two bandgaps in the PCCA II and PCCA III was attributed to their unhomogeneous structures. The PCCA surface illuminated firstly was designated as up surface, and another surface was designated as down surface. Figure 2 shows the optical micrograph of up and down surfaces of the PCCA I, PCCA II and PCCA III. It can be found that both up and down surfaces of the PCCA I exhibited the blue color, which suggested that the PCCA with homogeneous structures were obtained when the two surfaces of the quartz cell were alternately illuminated for 10s. Up surface of the PCCA III exhibited the green color, while down surface is blue color, which suggested unhomogeneous reaction existed in the cell. The difference of the photonic band gap properties in the PCCA I, PCCA II and PCCA III was attributed to the ununiformity of the polymerization reaction in the cell, as shown in Figure 2.

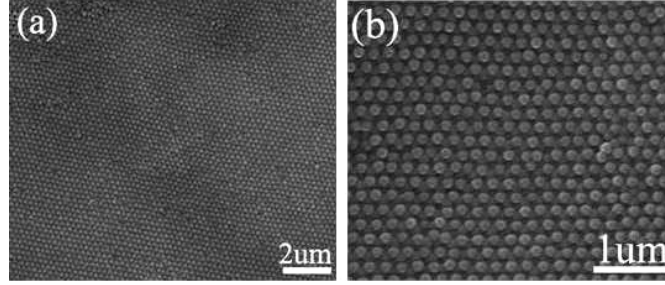


Figure 3. The low (a) and high-magnified (b) SEM micrographs of the PCCA I.

In order to observe the microstructures of the PCCA, the quartz cell containing PCCA was opened. The PCCA kept at one of two quartz plates were dried for 24h. Microstructures of the PCCA I was observed by SEM and AFM. Figures 3(a) and (b) show the low- and high-magnified SEM micrographs of the PCCA I, respectively, which demonstrate a highly-order degree. The microspheres form into a face-centered cubic (fcc) structure with (111) plane parallel to the surface of the quartz cell. The center-to-center distance between microspheres is about 205nm in the PCCA I.

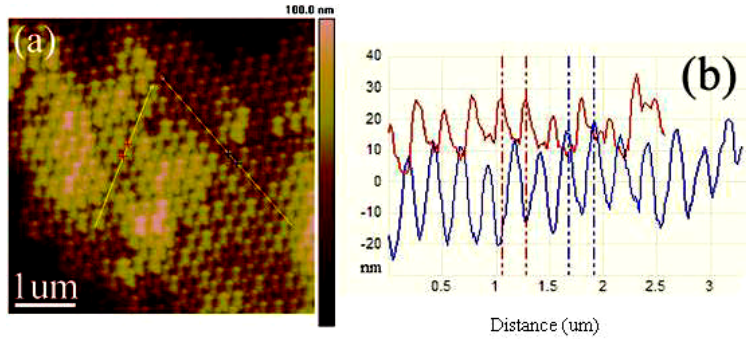


Figure 4. AFM micrograph (a) and the microsphere distance (b) of the PCCA I.

Figure 4(a) shows AFM micrograph of the PCCA I, which demonstrate a highly-order degree, as shown in SEM micrographs. It can be found that there are lots of craterlets and grooves on the PCCA I surface, which may be attributed to the inhomogeneous polymerization reaction and the uneven surface of quartz. Figure 4(b) shows center-to-center distance between microspheres on the level surface. The center-to-center distance between microspheres is about 220nm, which is consistent with that obtained by SEM.

The center-to-center distance between microspheres on the (111) planes of PCCA I was calculated by the modified form of Bragg's law [18]:

$$\lambda = 1.633D(n_{eff}^2 - \sin^2 \theta)^{1/2},$$

where λ , D and θ denote the position of the photonic band-gap, the center to center distance between microspheres on the (111) planes of PCCA I and the angle between the incidence light and the normal line of the (111) planes, respectively. n_{eff} represent average refractive indexes of PCCA I. Assumed that $n_{eff} = 1.368$ [19], the center to center distance between microspheres of PCCA I were 207 nm, which is in agreement with those estimated from the AFM and SEM micrographs.

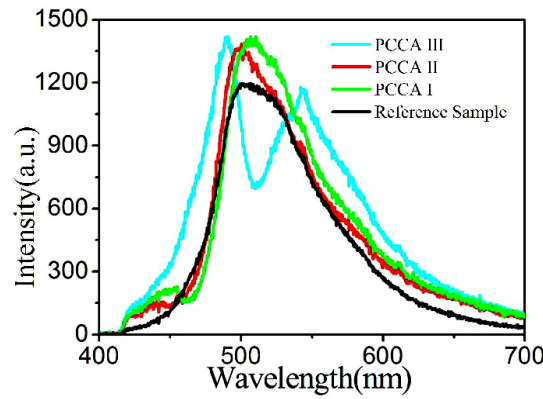


Figure 5. The photoluminescence spectra of the PCCA I, PCCA II, PCCA III and the reference sample.

Figure 5 shows the photoluminescence spectra of the PCCA I, PCCA II, PCCA III and reference samples, exhibiting that there was only one broad emission with a peak located at 510nm in the reference sample, while for the PCCA I, PCCA II, PCCA III, a dip of the emission band of the Fluorescein corresponding to the photonic band gap position can be observed. The emission intensity is significantly reduced in the spectral region of the photonic stopband [20, 21]. This dip was attributed to the photon trapping of the Bragg reflection when the emission band overlapped with the photonic band gap [13, 19, 22]. The spontaneous emission of the Fluorescein was enhanced near the band gap edge. Galstyan et al proposed mechanism for enhanced emission was the formation of standing wave at the edges of photonic band gap. At the long wavelength and short wavelength edges of

photonic band gap, the enhancement of emission occurs in the high refractive index materials and in low refractive index materials, respectively [23]. In our present work, we observe the enhancement of the photoluminescence of dye at the both edges of photonic band gap. It is suggested that the dyes in water solution with low refractive index were partially absorbed polystyrene spheres with the high refractive index.

4. Conclusion

The influence of light irradiation condition on the microstructure of polymerization crystalline colloidal arrays was investigated in this paper. When two surfaces of the quartz cell were irradiated in turn for 10s, the polymerized crystalline colloidal arrays with homogeneous structure were obtained due to the homogeneous polymerization reaction in the cell. Suppression of the fluorescence emission of dyes was observed because of the photon trapping of the Bragg reflection. The polymerization crystalline colloidal arrays with homogeneous structure can find potential applications in many fields, such as sensors and near-zero threshold lasers and so on.

References

- [1] E. Yablonovitch, Phys. Rev. Lett. 58 (1987), 2059.
- [2] S. John, Phys. Rev. Lett. 58 (1987), 2486.
- [3] W. M. Lee, S. A. Pruzinsky and P. V. Braun, Adv. Mater. 14 (2002), 271.
- [4] P. Russell, Science 299 (2003), 358.
- [5] Y. N. Xia, B. Gates and Z. Y. Li, Adv. Mater. 13 (2001), 409.
- [6] J. Wang, Q. Li, W. Knoll and U. Jonas, J. Amer. Chem. Soc. 128 (2006), 15606.
- [7] Z. W. Yang, X. G. Huang, G. Yang, Q. Xie, B. Li and J. Zhou, J. Alloy Comp. 468 (2009), 295.
- [8] G. S. Pan, A. S. Tse, R. Kesavamoorthy and A. S. Asher, J. Amer. Chem. Soc. 120 (1998), 6518.
- [9] X. G. Huang, Z. W. Yang, L. Sun, B. Li, J. Zhou and L. T. Li, Chin. Sci. Bull. 21 (2008), 2587.
- [10] P. A. Rundquist, P. Photins and S. Jagannathan, J. Chem. Phys. 91 (1989), 932.
- [11] S. A. Asher, J. M. Weissman, A. Tikhonov, R. D. Coalson and R. Kesavamoorthy, Phys. Rev. E 69 (2004), 066619.

- [12] S. H. Kim, S. J. Jeon and S. M. Yang, *J. Amer. Chem. Soc.* 130 (2008), 6040.
- [13] S. Kiyoshi, K. Hiroshi, T. Akira and T. Okubo, *Colloid Polym. Sci.* 285 (2006), 127.
- [14] A. S. Asher, J. Holtz and L. Liu, *J. Amer. Chem. Soc.* 116 (1994), 4997.
- [15] K. Lee and A. S. Asher, *J. Amer. Chem. Soc.* 122 (2000), 9534.
- [16] A. S. Asher, W. K. Kimble and P. J. Walker, *Chem. Mater.* 20 (2008), 501.
- [17] H. S. Foulger, S. Kotha, B. Sweryda-Krawiec, T. W. Baughman, J. M. Ballato and P. Jiang, *Opt. Lett.* 25 (2000), 300.
- [18] Z. W. Yang, J. Zhou, X. G. Huang, G. Yang, Q. Xie, L. Sun and B. Li, *Chem. Phys. Lett.* 445 (2008), 55.
- [19] S. H. Foulger, P. Jiang, A. C. Lattam, D. W. Smith, Jr. and J. Ballato, *Langmuir*, 17 (2001), 6023.
- [20] D. D. Evanoff, S. E. Hayes, Y. Ying, G. H. Shim, J. R. Lawrence, J. B. Carroll, R. D. Roeder, J. M. Houchins, C. F. Huebner and S. H. Foulger, *Adv. Mater.* 19 (2007), 3507.
- [21] J. Lawrence, G. Shim, P. Jiang, M. Han, Y. Ying and S. H. Foulger, *Adv. Mater.* 17 (2005), 2344.
- [22] Z. W. Yang, X. G. Huang, L. Sun, J. Zhou, B. Li and C. L. Yu, *J. Amer. Ceram. Soc.* 92 (2009), 1596.
- [23] A. G. Galstyan, E. M. Raikh and V. Z. Vardeny, *Phys. Rev. B* 62 (2000), 1780.