

Dye/Gelled Colloidal Photonic Crystal Composites and Their Reversible pH-Responsive Optical Behaviors

Jian Dong and Weiping Qian*

State Key Laboratory of Bioelectronics, Department of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, People's Republic of China

Received: June 29, 2006; In Final Form: July 31, 2006

We introduced dyes, the colors of which are variable by changing the pH of their medium solutions, into gelled colloidal photonic crystals (GCPCs) and investigated their reversible pH-responsive optical behaviors. When the extinction position of the dye overlaps with the Bragg peak of the GCPC, the Bragg-diffracted light can be trapped in the GCPC; when the extinction position of the dye is shifted out of the Bragg peak of the GCPC, the Bragg diffracted light is free and can escape out of the GCPC. The optical behaviors of dye/gelled colloidal photonic crystal composites are reversible to the pH changes of their surrounding medium.

Introduction

Photonic crystals (PCs) are materials of periodic dielectric structures that forbid propagation of electromagnetic waves in a certain frequency range^{1,2} and have been intensively investigated for their wide potential applications since the presence of the concept.^{3–8} Like the doping of a semiconductor, introducing defects into PCs is one of the approaches to extend their potentials in manipulating photons. Both top-down and bottom-up techniques have been widely developed to fabricate PCs with controlled defects.^{9–13} Embedding defects in PCs, such as linear and planar defects, provides a narrow transmission window within the PC's stop band,^{14–20} which can be used as optical devices such as waveguide, optical filter, etc.^{3,21,22}

Hybrid materials have been fabricated by introducing optically active elements into PCs to enhance their optical properties, particularly when the emission wavelength of the active element overlaps with the stop band. The intensity and position of the dye emission in PCs can be changed due to the ordered structure and defects in the PCs.^{23–26} Composite materials made by embedding quantum dots in PCs have also been fabricated and their optical properties have been investigated.^{27,28}

Dyes contain active organic chromophores, and some of them are often used as acid-based indicators. Here we introduce the pH sensitive dyes into GCPCs to form dye-doped GCPCs. The Bragg diffracted light of GCPCs can be tuned with respect to the extinction bands of dyes. When the extinction band of a dye is within the Bragg diffracted range of a GCPC, the dye can capture the diffracted light of the GCPC; when the extinction band of a dye is shifted out of the diffracted range of a GCPC, the diffracted light freely escapes out of the GCPC.

Experimental Details

The suspensions of silica colloidal particles of ~110 nm in diameter were obtained from Nissan Chemical Corporation

(Japan). Acrylamide and *N,N*-methylene bisacrylamide (Ultra-pure) were from Shanghai Sangon Inc. (China). 2,2'-Azo-bis-iso-butyronitrile (AIBN) was a product of Shanghai Sanwei Inc. (China). Bromophenol blue (BB) and Congo red were the products of Shanghai Jinxi Inc. (China).

Impurities in the suspension of silica colloidal particles were driven off by the strong electric field dialysis as described in detail elsewhere.²⁹ The fabrication process of GCPCs was as follows. The purified colloidal suspension was mixed with the aqueous solutions of acrylamide, *N,N*-methylene bisacrylamide, and AIBN, which is an initiator for UV or thermal polymerization. 80 mg acrylamide, 2.7 mg *N,N*-methylene bisacrylamide, and 1 μ g AIBN were added in 1 mL of the purified colloidal suspension. The mixed solution was injected into an experimental cell which was composed of two parallel quartz slides and one spacer with a thickness of 160 μ m. Then, the experimental cell was kept stationary in the dark to form a colloidal photonic crystal. Finally, the mixed solution in the cell on a stainless steel plate was exposed to UV light (Hg-lamp, 300 W) for 40 min to form the GCPC with double Bragg peaks at room temperature. The dye-doped GCPCs were obtained by immersing the GCPCs into the aqueous solutions of the pH sensitive dyes, BB, and Congo red, at different concentrations.

All optical measurements were performed at normal incidence and at room temperature. A CCD spectrometer (PC-1000, Ocean Optics Inc.) was employed to detect the reflection spectra of the GCPCs. A UV-vis spectrometer (UV3150, Shimadzu) was used to obtain the absorption spectra of the GCPCs.

Results and Discussions

The GCPC and the BB-doped GCPC have different colors (shown in the Figure S1), and they also have different reflection and absorption spectra (shown in Figure 1). At the shorter Bragg peak wavelength, i.e., at $\lambda = 592$ nm, the reflectance of the BB-doped GCPC is weaker than that of the GCPC while the absorbance of the former is much stronger than the latter. At

* Corresponding author: Fax: (+86)25-83795719, E-mail: wqian@seu.edu.cn.

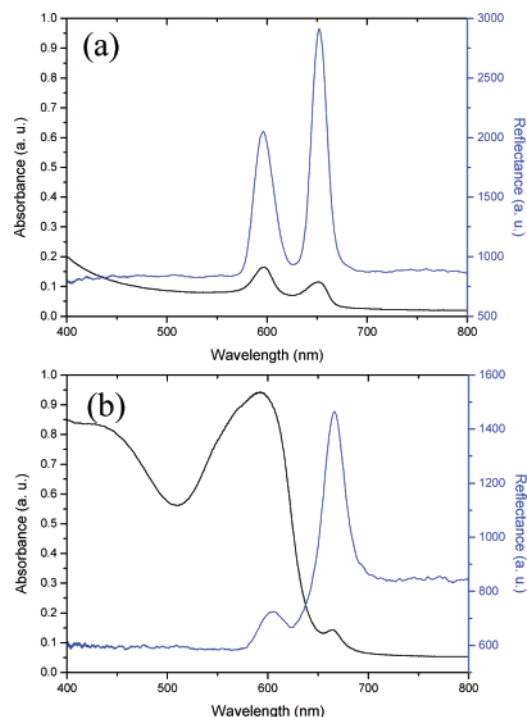


Figure 1. (a) Reflection and absorption spectra of a GCPC with double Bragg peaks when the layer with the shorter Bragg peak is a top layer. (b) The reflection and absorption spectra of the GCPC containing 20 g/L BB when the layer of the shorter Bragg peak is a top layer.

the longer Bragg peak wavelength, both reflectance and absorbance of the two samples have little difference. The results are mainly due to the presence or absence of BB whose extinction band is centered at 592 nm in an alkaline condition (Figure S2b). In the reflection spectra, the reflectance at 592 nm is a result of the reflectance of the GCPC subtracted by the absorbance of the BB in optical paths. While in the absorption spectra, the absorbance at 592 nm is a result of the reflectance of the GCPC added by the absorbance of the BB. Thus, the reflectance at 592 nm decreased while the absorbance at 592 nm increased after doping BB in the GCPC; at the longer Bragg diffraction range the intensities of absorbance and reflectance have little difference with or without doping BB into the GCPC.

Figure 2 shows the evolution of the reflection spectra of a BB-doped GCPC and the reversed BB-doped GCPC after they were immersed and equilibrated in BB solutions with a series of concentrations. When the layer with the shorter Bragg peak at 592 nm is made as the top layer, the reflection spectra dependence on the BB concentration is shown in Figure 2a; when reversed, the reflection spectra dependence on the BB concentration is shown in Figure 2b. The increase of the BB concentration significantly decreased the reflectance of the two GCPCs at 592 nm. From Figure 2a and 2b, the light extinctions of the dyes in the two cases were different when the dye concentrations in the two GCPCs were equal. The results are due to the difference of optical paths in the two cases (shown in Figure S3). Because the light which meets Bragg diffraction regime can almost be diffracted by a crystal of colloids with 50 layers,³⁰ in the former, the optical path of the light at 592 nm is almost twice the thickness of the GCPC, while in the latter, the optical path of the light at 592 nm is less than twice the thickness of the layer with the Bragg peak at 592 nm.

Figure 3 shows pH-responsive optical behaviors of a BB/GCPC composite. After immersed and equilibrated in 25 g/L BB aqueous solution, the GCPC was laid onto a glass slide with the layer of the shorter Bragg peak at 592 nm as the top layer,

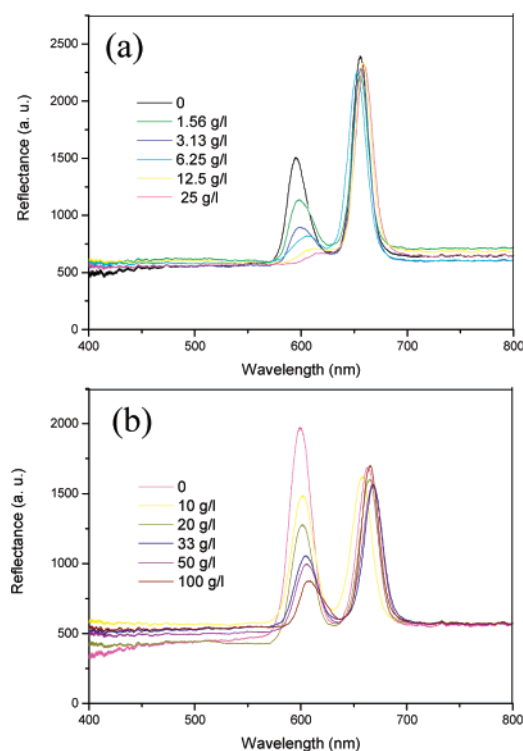


Figure 2. (a) Reflection spectra of a GCPC with a series of concentrations of BB when the layer with the shorter Bragg peaks is a top layer. (b) The reflection spectra of the reversed GCPC with a series of concentrations of BB.

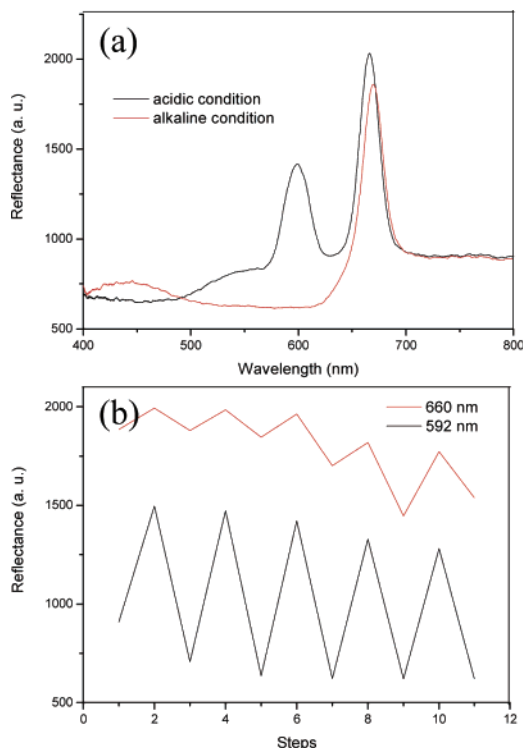


Figure 3. (a) Reflection spectra of the GCPC containing 25 g/L BB when the layer with the shorter Bragg peak is the top layer. (b) The changing of the two Bragg peaks of the GCPC in (a) when alternating the acidic and alkaline solution (odd number: in the alkaline solution; even number: in the acidic solution).

and then the pH was adjusted to change the BB's extinction position by adding acidic or alkaline solution. Figure S4 shows the GCPC's color is reversibly variable with the change of the pH of the medium. As shown in Figure 3a, once shifting the

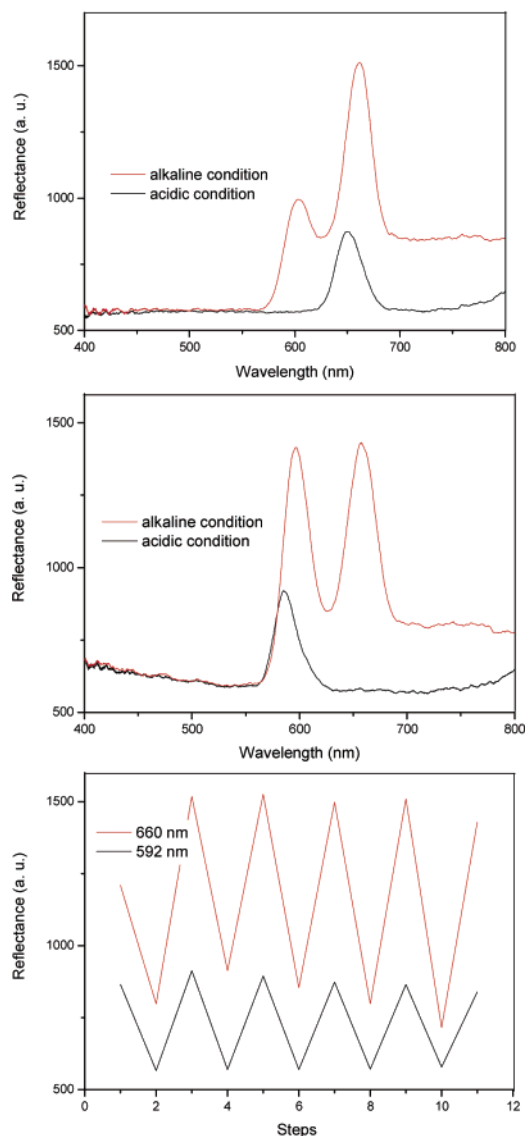


Figure 4. (a) Reflection spectra of the GCPC containing 25 g/L Congo red when the layer with the shorter Bragg peak is made as the top layer. (b) The reflection spectra of the reversed GCPC containing 25 g/L Congo red. (c) The changing of the two Bragg peaks of the GCPC in (a) when alternating acidic and alkaline solutions (odd number: in the alkaline solution; even number: in the acidic solution).

extinction position out of 592 nm, the Bragg diffracted light at 592 nm was free and escaped out of the GCPC. When the pH was adjusted back to an alkaline condition, the extinction band of the dye recovered and the Bragg-diffracted light at 592 nm was re-trapped in the GCPC. Figure 3b shows the reversible appearance/disappearance cycles of the GCPC's shorter Bragg peaks by adding acid and base in turn. In these cycles, longer Bragg peaks were just slightly fluctuated.

The above experiment was repeated using 25 g/L Congo red to replace the BB. Figure 4 shows optical behaviors of a Congo red/GCPC composite. Unlike the phenomena appearing in Figure 3, in this case, the shorter Bragg peak disappeared while the longer Bragg peak intensity significantly decreased after changing the pH (shown in Figure 4a). Doping Congo red into the GCPC, we can realize a yes/no optical behavior in the range of the shorter Bragg peak and a strong/weak optical behavior in the range of the longer Bragg peak. When we reversed the GCPC, the other results appeared, as shown in Figure 4b. Congo red has a wider extinction range from 500 to 700 nm in alkaline condition (Figure S2b), and it can absorb the two Bragg-

diffracted light simultaneously. Because of their difference in optical paths, the light diffracted by the top layer of the GCPC is almost absorbed entirely while that diffracted by the bottom layer is partly absorbed. Figure 4c shows both the reversible appearance/disappearance cycles of the shorter Bragg peaks and the reversible increase/decrease cycles of the longer Bragg peak of the Congo red-doped GCPC by adding acid and base in turn.

Conclusions

In conclusion, we have successfully modulated the optical properties of GCPCs by regulating the extinction bands of dyes. The influences of the pH sensitive dyes on the optical behavior of GCPCs have been investigated. The extinction position of dyes can be easily shifted by changing the pH of their medium solutions. Changing extinction position of BB doped into the GCPC can specifically modulate the GCPC's optical behavior at 592 nm. On the other hand, Congo red can modulate the GCPC's optical behavior both at 592 and 600 nm. The dye-doped GCPC's optical behavior was variable with dyes doped, and they can be used as pH-responsive optical devices.

Acknowledgment. The authors thank Dr. Fang Yu (Department of Chemistry, Stanford University) for many helpful discussions. This work was supported by the National Nature Science Foundation of China (Grant Nos. 20475009, 30370312), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (Grant No. 200252), and the Nature Science Foundation from Jiangsu province (Grant No. BK2005067).

Supporting Information Available: Images of a GCPC and a dye-doped GCPC, the absorbance spectra of the two dyes in alkaline and acidic conditions, an illustration of the optical paths of light Bragg-diffracted by the two layers of the GCPC, respectively, and images of the cycles of GCPC's colors changed reversibly. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059.
- John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486.
- Knight, J. C.; Broeng, J.; Birks, T. A.; Russell, P. J. *Science* **1998**, *282*, 1476.
- Li, Z. Y.; Wang, J.; Gu, B. Y. *Phys. Rev. B* **1998**, *58*, 3721.
- Painter, O.; Lee, R. K.; Scherer, A.; Yariv, A.; O'Brien, J. D.; Dapkus, P. D.; Kim, I. *Science* **1999**, *284*, 1819.
- Noda, S.; Chutinan, A.; Imada, M. *Nature* **2000**, *407*, 608.
- Xia, Y.; Gates, B.; Li, Z. Y. *Adv. Mater.* **2001**, *13*, 409.
- Yang, S. M.; Miguez, H.; Ozin, G. A. *Adv. Funct. Mater.* **2002**, *12*, 425.
- Sun, H. B.; Nakamura, A.; Kaneko, K.; Shoji, S.; Kawata, S. *Opt. Lett.* **2005**, *30*, 881.
- Lee, W.; Pruzinsky, S. A.; Braun, P. V. *Adv. Mater.* **2002**, *14*, 271.
- Matthias, S.; Müller, F.; Jamois, C.; Wehrspohn, R. B.; Gösele, U. *Adv. Mater.* **2004**, *16*, 2166.
- García-Santamaría, F.; López, C.; Meseguer, F.; López-Tejeda, F.; Sánchez-Dehesa, J.; Miyazaki, H. T. *Appl. Phys. Lett.* **2001**, *79*, 2309.
- Aoki, K.; Miyazaki, H. T.; Hirayama, H.; Inoshita, K.; Baba, T.; Sakoda, K.; Shinya, N.; Aoyagi, Y. *Nat. Mater.* **2003**, *2*, 117.
- Palacios-Lidón, E.; Galisteo-López, J. F.; Juárez, B. H.; López, C. *Adv. Mater.* **2004**, *16*, 341.
- Vekris, E.; Kitaev, V.; von Freymann, G.; Perovic, D. D.; Aitchison, J. S.; Ozin, G. A. *Adv. Mater.* **2005**, *17*, 1269.
- Wang, L. K.; Yan, Q. F.; Zhao, X. S. *Langmuir* **2006**, *22*, 3481.
- Pozas, R.; Mihi, A.; Ocaña, M.; Míguez, H. *Adv. Mater.* **2006**, *18*, 1183.
- Tétrault, N.; Arsénault, A. C.; Mihi, A.; Wong, S.; Kitaev, V.; Mannes, I.; Miguez, H.; Ozin, G. A. *Adv. Mater.* **2005**, *17*, 1912.
- Fleischhaker, F.; Arsénault, A. C.; Kitaev, V.; Peiris, F. C.; von Freymann, G.; Mannes, I.; Zentel, R.; Ozin, G. A. *J. Am. Chem. Soc.* **2005**, *127*, 9318.

- (20) Friederike, F.; Arsenaault, A. C.; Wang, Z.; Kitaev, V.; Peiris, F. C.; von Freymann, G.; Manners, I.; Zentel, R.; Ozin, G. A. *Adv. Mater.* **2005**, *17*, 2455.
- (21) Painter, O. J.; Lee, R. K.; Scherer, A.; Yariv, A.; O'Brien, J. D.; Dapkus, P. D.; Kim, I. *Science* **1999**, *284*, 1819.
- (22) Stoffer, R.; Hoehstra, H. J. W. M.; de Ridder, R. M.; van Groesen, E.; van Beckum, F. P. H. *Opt. Quantum Electron.* **2000**, *32*, 947.
- (23) Lawrence, J. R.; Shim, G. H.; Jiang, P.; Han, M. G.; Ying, Y.; Foulger, S. H. *Adv. Mater.* **2005**, *17*, 2344.
- (24) Popov, O.; Lirtsman, V.; Kopnov, F.; Davidov, D.; Saraidarov, T.; Reisfeld, R. *Synth. Met.* **2003**, *139*, 643.
- (25) Koenderink, A. F.; Bechger, L.; Schriemer, H. P.; Lagendijk, A.; Vos, W. L. *Phys. Rev. Lett.* **2002**, *88*, 143903.
- (26) Megens, M.; Wijnhoven, J. E. G. J.; Lagendijk, A.; Vos, W. L. *Phys. Rev. A* **1999**, *59*, 4727.
- (27) Wang, W.; Asher, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 12528.
- (28) Arsenaault, A. C.; Clark, T. J.; Von Freymann, G.; Cademartiri, L.; Sapienza, R.; Bertolotti, J.; Vekris, E.; Wong, S.; Kitaev, V.; Manners, I.; Wang, R. Z.; John, S.; Wiersma, D.; Ozin, G. A. *Nat. Mater.* **2006**, *5*, 179.
- (29) Dong, J.; Qian, W. P.; Cao, Y. X.; Xiao, X. X.; Xiao, Z. D. *J. Nanosci. Nanotechnol.* **2006**, *6*, 1009.
- (30) Spry, R. J.; Kosan, D. J. *Appl. Spectrosc.* **1986**, *40*, 782.