

Preparation and Characterization of Au Nanoparticles/Polymer Composite Photonic Crystals

Takaaki Tsuruoka¹, Shoji Samitsu¹, Tomoya Aokata¹, Jun Matsui¹, Takashi Murashima¹, Kensuke Akamatsu^{1,2}, and Hidemi Nawafune¹

¹Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan,

²PRESTO Japan Science and Technology Agency (JST), 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

Fax: +81-78-435-2539, e-mail: akamatsu@center.konan-u.ac.jp

We report a simple approach to prepare Au/polystyrene (PS) composite photonic crystals. In this approach, Au nanoparticles protected by thiol molecules were synthesized by two-phase system using dimethylamine-boran as reducing agent at low temperature. PS microstructures containing the obtained Au nanoparticles were prepared by polymerization of styrene monomer in the presence of Au nanoparticles using a silica inverse opal as template. The composites with different Au content were prepared, and their structural and optical characteristics were characterized by transmission electron microscopy (TEM) and optical absorption spectroscopy, respectively. The relationship between microstructures including particle size and volume fraction of metal phase, and optical properties has been systematically evaluated. These characterization indicate that reflection peak of the obtained composite can be controlled by the volume fraction of Au nanoparticles.

Key words: Au nanoparticles, Nanocomposite, Photonic Crystal

1. INTRODUCTION

In recent years, much attention has been paid to studies of composite nanostructures consisting of inorganic nanoparticles and organic matrices.[1-3] Such nanocomposite can be useful in the field of optics and electronics.[4-6] On the other hand, they have been of great interest because they provide a good model system for studying experimentally interaction with inorganic and organic materials.[7-9] Thus, preparation of nanocomposite containing nanoparticles has become a significant research field.

Photonic crystals, which are ordered dielectric structures with lattice parameters comparable to the wavelength of light, have shown attracted much attention because they exhibit characteristic photonic band gap.[10,11] In particular, much effort has focused on fabricating three-dimensional photonic crystals. Monodisperse polymer latex and SiO₂ spheres are the most widely utilized materials for the fabrication of 3D colloidal photonic crystals.[12-14] Various methods based on self-assembly have been developed to prepare colloidal photonic crystals, including vertical deposition,[12] gravitational sedimentation,[13] and Langmuir-Blodgett approach.[14] The optical properties of photonic crystals prepared by these techniques mainly depend on the latex diameter (lattice constant) and the refractive indexes of the dielectrics. A variety of methods are now accessible for controlling the optical properties of photonic crystals. Control of the photonic

band gap has mostly been achieved via preparation of elastic photonic crystals.[15,16] The lattice constant of such crystals can be controlled by applying compression, resulting in tune of photonic band gap. Other approaches have tuned the photonic band gap by infiltrating mediums (organic solvents and liquid crystals) into voids of crystal.[17,18] However, the both processes usually require an external stimulus, and the filtration of organic solvents does not provide control of photonic band gap over a wide spectral range.

The development of facile methods for controlling the photonic band gap is an important challenge. Herein, we report a simple method that allows control of the photonic band gap. Control is achieved through incorporation of Au nanoparticles in polystyrene photonic crystal during styrene polymerization using SiO₂ inverse opal as a template. The reflection peak is controlled simply by altering volume fraction of Au nanoparticles in PS photonic crystal, thus providing an alternative process to conventional approaches.

2. EXPERIMENTAL

Synthesis of DDT-stabilized Au Nanoparticles

Au nanoparticles were prepared by Brust method.[19] Briefly, a solution of tetraoctylammonium bromide (328 mg, 0.60 mmol) in toluene (40 mL) was added to an aqueous solution of HAuCl₄ · 4H₂O (15 mM, 20 mL, 0.30 mmol). A solution of 1-dodecanethiol (DDT) (65.5 mg, 0.3 mmol) in toluene (10 mL) was then gradually

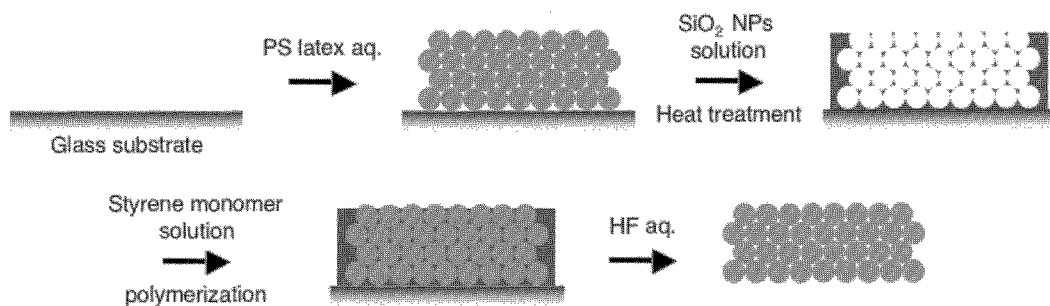


Figure 1. Schematic illustration for preparation of PS sphere-linked photonic crystals.

added to the resulting mixture while stirring vigorously, followed by dropwise addition of a freshly prepared aqueous solution of NaBH_4 (0.30 M, 10 mL, 3.0 mmol). After stirring the mixture for 3 h, the organic layer was separated, and concentrated to dryness under reduced pressure. The black solid thus obtained was heated at 170 °C for 20 min to grow Au nanoparticles.[20]

Preparation of SiO_2 Inverse Opals.

Aqueous suspension of polystyrene (PS) latex spheres (diameter: 230 nm) were purchased from Seradyn. Photonic crystals based on PS spheres were prepared by evaporation-induced self-assembly on a glass substrate. The PS PCs were then heated at 80 °C for 30 min to induce the interconnection between PS spheres. 1-Propanol solution containing SiO_2 nanoparticles with a diameter of 5 nm and 11 nm was infiltrated in the PS substrate. Finally, the substrate was heated at 450 °C for 10 h to remove PS spheres.

Preparation of Au Nanoparticles/PS Composite.

The mixture of toluene containing DDT-stabilized Au nanoparticles and monomer solution (styrene, divinylbenzene, and 2, 2'-azoisobutyronitrile) was infiltrated in the SiO_2 inverse opal template. The sample was heated at 60 °C for 12 h under Ar atmosphere. The obtained polymer-silica composite was then immersed into aqueous HF.

3. RESULTS AND DISCUSSION

Preparation of PS Photonic Crystals using SiO_2 Inverse Opal as a Template.

Figure 1 schematically describes the procedure for the preparation of PS photonic crystals, SiO_2 inverse opals, and PS spheres-linked photonic crystals. SEM image of the obtained PS photonic crystals are shown in Figure 2A. It can be seen that the colloidal crystals shown a highly ordered face-centered cubic packing. The average latex diameter is around 230 nm, almost the same size as the initial latex dispersed in aqueous solution. After the infiltration of SiO_2 nanoparticles into voids of PS photonic crystals and the heat treatment, the spherical

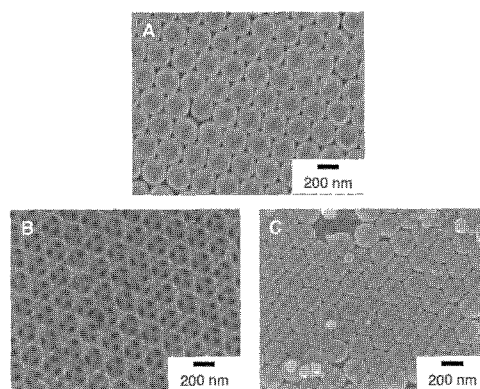


Figure 2. FE-SEM images of PS photonic crystals (A), SiO_2 inverse opals prepared from nanoparticles (B), and PS sphere-linked photonic crystals prepared by polymerization of styrene monomers (C).

voids in the SiO_2 films are arranged in well-ordered, closed-packed structures over areas of more than 40000 μm^2 . However, the appearance of cracks was observed because of shrinkage of SiO_2 during the process. For PS photonic crystal and SiO_2 inverse opal, reflection peak is clearly observed at 560 and 398 nm, respectively (Figure 3). The wavelengths of these peaks are comparable to those of calculated peaks (PS: 580 nm and SiO_2 : 396 nm) from the following Bragg's equation with Snell's law[21]

$$\lambda = 2d\sqrt{(n_e^2 - \sin^2\theta)} \quad (1)$$

where λ , d , n_e , and θ are peak position, interplanar spacing of the plane, effective refractive index, and angle of incident light, respectively.

The SiO_2 inverse opals can be used as template for preparation of PS spheres-linked photonic crystals. As shown in Figure 2C, SEM image of the product after polymerization of styrene exhibits that the ordered arrangement of PS spheres is consistent with the initial

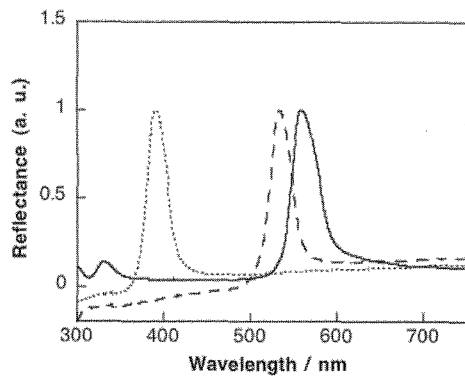


Figure 3. Reflection spectra of PS photonic crystals (solid line), SiO₂ inverse opals prepared from nanoparticles (dotted line), and PS sphere-linked photonic crystals prepared by polymerization of styrene monomers (dashed line).

PS photonic crystals. However, PS sphere size decreases to 220 nm, providing blue-shift of reflection peak of photonic crystals from 560 to 535 nm (Figure 3). Changes in diameter of sphere can be caused by the shrinkage of SiO₂ nanoparticles during the preparation of inverse opals.

Preparation of Au Nanoparticles/PS Composite.

PS sphere-linked photonic crystals containing Au nanoparticles were prepared by the polymerization of styrene monomer with Au nanoparticles using SiO₂ inverse opal as the template. The SEM in Figure 4 confirms that no change in the arrangement of PS spheres without and with Au nanoparticles was observed. To evaluate the dispersibility of Au nanoparticles in PS photonic crystals, TEM observation was performed for the PS photonic crystals containing 10 mass% Au nanoparticles. The nanoparticles were dispersed in PS photonic crystals without the formation of aggregates (Figure 5). Figure 6 shows the effect of Au volume fraction in photonic crystals on the wavelength of reflection peak. The reflectance spectra indicate that the peak position depends on the volume fraction of Au nanoparticles. The reflection peak shifted from 535 nm to 480 nm as the contents of Au nanoparticles increased from 0 to 10 mass%. One possible explanation is that the lattice constant decreases with increasing volume fraction of Au nanoparticles. However, SEM observation reveals the formation of PS spheres with 220 nm, almost the same size for every sample. Therefore, the blue-shift may be induced by changing the effective dielectric constant of Au/PS composite with different Au volume fraction.

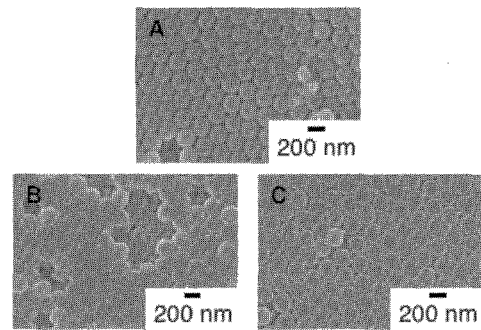


Figure 4. FE-SEM images of PS sphere-linked photonic crystals prepared by polymerization of monomer solution containing 0 mass% (A), 5 mass% (B), and 10 mass% Au nanoparticles (C).

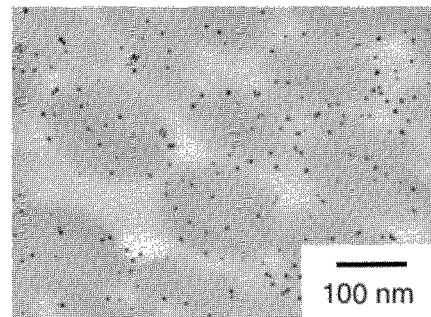


Figure 5. TEM images of PS sphere-linked photonic crystals prepared by polymerization of monomer solution containing 10 mass% Au nanoparticles.

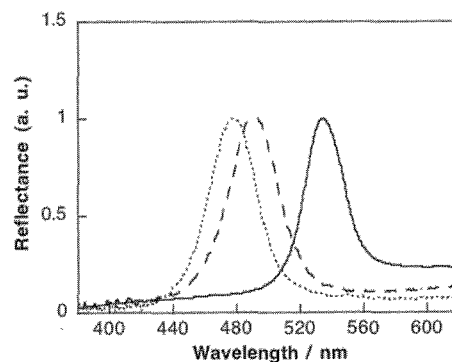


Figure 6. Reflection spectra of PS sphere-linked photonic crystals prepared by polymerization of monomer solution containing 0 mass% (solid line), 5 mass% (dashed line), and 10 mass% Au nanoparticles (dotted line).

4. CONCLUSION

We have successfully prepared PS spheres-linked photonic crystals. The SiO₂ inverse opals can be used to prepare the linked PS photonic crystals. Since the resultant photonic crystals are becoming free-standing and have good stability. In addition, PS photonic crystals containing Au nanoparticles can be prepared using the mixed solution of styrene monomer and Au nanoparticles during the process for preparation of photonic crystals. We have demonstrated that the photonic band gap of the composite crystals can be controlled by changing the volume fraction of Au nanoparticles, which can be caused by changes of the dielectric constant of composite films. This method allows control of photonic band gap without changes in the arrangement and lattice constant of PS photonic crystals, the ability of which is expected to be useful for fabrication of optical devices.

ACKNOWLEDGEMENT

T. T. is grateful for research fellowship support from Japan Society for the Promotion of Science.

REFERENCES

- [1] M. MacLachlan, M. Ginzburg, N. Coombs, T. W. Coyle, N. P. Raju, J. E. Greedan, G. A. Ozin, and I. Manners, *Science*, 287, 1460 (2000)
- [2] A. S. Korchev, M. J. Bozack, B. L. Slaten, and G. Mills, *J. Am. Chem. Soc.*, 126, 10 (2004)
- [3] K. Akamatsu, H. Shinkai, S. Ikeda, S. Adachi, H. Nawafune, and S. Tomita, *J. Am. Chem. Soc.*, 127, 7980 (2005)
- [4] S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, and A. A. G. Requicha, *Nat. Mater.*, 2, 229 (2003)
- [5] W. Kleemann, O. Petracic, C. Binek, G. N. Kakazei, Y. G. Pogorelov, J. B. Sousa, S. Cardoso, and P. P. Freitas, *Phys. Rev. B*, 63, 134423 (2001)
- [6] U. Ebels, J. L. Duvail, P. E. Wigen, L. Piroux, L. D. Buda, and K. Ounadjela, *Phys. Rev. B*, 64, 144421 (2001)
- [7] C. Laurent, D. Mauri, E. Kay, and S. S. P. Parkin, *J. Appl. Phys.* 65, 2017 (1989)
- [8] A. Heilmann, J. Werner, D. Schwarzenberg, S. Henkel, P. Grosse, and W. Theiss, *Thin Solid Films*, 270, 103 (1995)
- [9] D. Salz, R. Lamber, M. Wark, A. Baalman, and N. Jaeger, *Phys. Chem. Chem. Phys.*, 1, 4447 (1999)
- [10] E. Yablonovitch, *Phys. Rev. Lett.*, 58, 2059 (1987)
- [11] S. John, *Phys. Rev. Lett.*, 58, 2486 (1987)
- [12] P. Jiang, J. F. Bertone, K. S. Hwang, and V. L. Colvin, *Chem. Mater.*, 11, 3158 (1999)
- [13] J. X. Zhu, M. Li, R. Rogers, W. Meyer, R. Ottewill, W. B. Russell, and P. M. Chaikin, *Nature*, 387, 883 (1997)
- [14] S. Reculosa, and S. Ravaine, *Chem. Mater.*, 15, 598 (2003)
- [15] H. Fudouzi, and Y. Xia, *Adv. Mater.*, 15, 892 (2003)
- [16] A. C. Arsenault, T. J. Clark, G. V. Freymann, L. Cademartiri, R. Sapienza, J. Bertolotti, E. Vekris, S. Wong, V. Kitaev, I. Manners, R. Z. Wang, S. John, D. Wiersma, and G. A. Ozin, *Nat. Mater.*, 5, 179 (2006)
- [17] F. García-Santamaría, V. Salgueirino-Maceira, C. López, and L. M. Liz-Marzán, *Langmuir*, 18, 4519 (2002)
- [18] S. Kuno, Z.-Z. Gu, K. Takahashi, A. Fujishima, H. Segawa, and O. Sato, *J. Am. Chem. Soc.*, 126, 8314 (2004)
- [19] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 801 (1994)
- [20] T. Teranishi, S. Hasegawa, T. Shimizu, and M. Miyake, *Adv. Mater.*, 13, 1699 (2001)
- [21] H. Fudouzi, and T. Sawada, *Langmuir*, 22, 1365 (2006)

(Received December 7, 2007 ; Accepted March 4, 2008)