doi:10.1246/cl.2011.1233

In Situ Generation of Silver Nanoparticles in Ion-exchangeable Polymer Photonic Crystals

Takaaki Tsuruoka, Shota Kumazaki, Hidemi Nawafune, and Kensuke Akamatsu*
Department of Nanobiochemistry, Frontiers of Innovative Research in Science and Technology (FIRST),
Konan University, 7-1-20 Minatojimaminami, Chuo-ku, Kobe, Hyogo 650-0047

(Received July 7, 2011; CL-110576; E-mail: akamatsu@center.konan-u.ac.jp)

Silver/polymer composite photonic crystals have been synthesized via the controlled in situ growth of silver nanoparticles in an ion-exchangeable polymer as host photonic crystals. This in situ approach using ion-doped precursors allows for size of silver nanoparticles and the optical reflection wavelength of the obtained crystals to be systematically controlled. This synthesis represents a simple methodology for the synthesis of functional composite photonic crystals with tunable microstructures and thus optical properties.

Photonic crystals (PCs) are of significant interest for both fundamental studies and technological applications in photonics.[1] The reflection wavelength of PCs is simply tunable via the structural periodicity, so that close-packed microspheres have become the most extensively investigated type of PCs.[2] In particular, polymer-based PCs are widely studied with respect to inducing structural deformation. Much experimental work is devoted to three-dimensional structural changes to control periodic geometries of polymer PCs for tuning of the reflection wavelength. For example, control of reflection wavelength has been achieved by changing the distance between individual spheres through mechanical deformation using a rubber matrix[3] or polymers that can be deformed by swelling with a solvent[4] and/or electrochemical stimuli.[5]

The incorporation of inorganic nanoparticles into base PCs also affects the dielectric constant of the crystals and thus their optical response, which has been demonstrated for magnetic,[6] and metallic[7] nanoparticles in silica and polymer PCs. These studies utilize mainly incorporation of the nanoparticles into the voids of base PCs or deposition of the nanoparticles on the surface of primary spheres, and there are no reports of attempting incorporation and growth of the nanoparticles in the polymer PCs for control of their optical properties. Herein, we report on the formation of metal/polymer nanocomposite PCs using ion-doped polymer precursors, in which metallic ions are reduced in situ to form metal nanoparticles in the host polymer PCs. We describe the formation of 2–10 nm silver nanoparticles in crosslinked poly(methacrylic acid) (PMAA) and the tuning of their optical properties by means of the size of silver nanoparticles formed.

Our process relies on the synthesis of polymer PCs with ion-exchangeable groups and adsorption of metallic ions followed by reduction of the ions to form metal nanoparticles in a hydrogen atmosphere. Briefly, the PCs were prepared by polymerization of a monomer solution consisting of styrene, methacrylic acid, and divinylbenzene using silica inverse opals made by using sub-micrometer polystyrene (PS) spheres. The obtained PCs are made of highly crosslinked polymer bearing carboxylic acid groups that can act as ion-exchange sites (PS–PMAA). The silver ions were introduced into the PS–PMAA PCs through ion-exchange using silver nitrate solution. The silver ion-doped PCs were then sealed in a quartz tube under hydrogen gas flow, followed by annealing in a tube furnace, which was heated up to an appropriate temperature in order to reduce the silver ions to metallic silver (see Supporting Information; SI for detailed description of experimental procedures and Figure S1[9]).

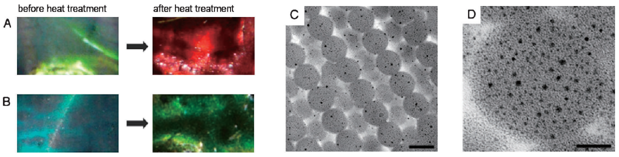

Figure 1. (A and B) Photograph of PS–PMAA photonic crystals before and after heat treatment. The photonic crystals were initially prepared using (A) 260- and (B) 180-nm PS spheres. (C and D) Cross-sectional TEM images of composite photonic crystals obtained after heat treatment at 100 °C for 30 min in hydrogen atmosphere. Scale bars: 200 (C) and 50 nm (D).

Heat treatment caused a significant change in the reflection color of the obtained PCs. In the case of the PS–PMMA PCs prepared using 260-nm PS spheres, the reflection color of the sample changed from light green to red after heat treatment in a hydrogen atmosphere (Figure 1A). SEM observations demonstrated that the geometric structures in the PCs remained unchanged after heat treatment; average center-to-center distances for samples before and after heat treatment were 235 ± 10 and 230 ± 10 nm, respectively, due to the highly crosslinked (rigid) nature of the polymer matrices (see SI, Figure S2[9]). Figures 1C and 1D show cross-sectional TEM images that reveal the presence of small silver nanoparticles in the interior of the polymer matrix. The formation of the nanoparticles, even at the center of the spheres, indicates the uniform distribution of silver ions initially doped in the PCs. The size of the silver nanoparticles was 2 to 10 nm, depending on the heat treatment temperature.

The TEM images in Figure 2B show that small silver nanoparticles of ca. 2 nm in size form in the polymers by exposure of the ion-doped samples to hydrogen gas, even at 50 °C for 30 min. Heat treatment at higher temperature caused the growth of silver nanoparticles (Figures 2C and 2D): 5.2 and 8.3 nm silver nanoparticles were observed for samples heat-treated at 100 and 180 °C, respectively. After heat treatment at 100 °C, silver ions were no longer detectable, which indicates their complete reduction (Figure S3[9]). From these results, we suggest that the silver ions are reduced by hydrogen molecules to form silver atoms, accompanying protonation of carboxylate anions to form carboxylic acid groups. The silver atoms form Ag nanoparticles, thus providing nanocomposite photonic crystals consisting of silver nanoparticles dispersed in a PS–PMAA matrix.

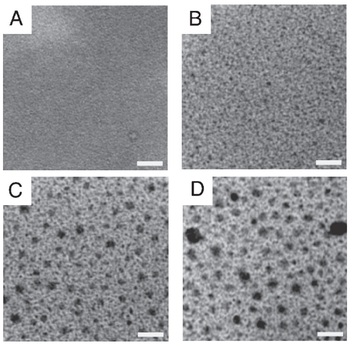

Figure 2. Cross-sectional TEM images of composite photonic crystals obtained (A) before and after annealing at (B) 50, (C) 100, and (D) 180 °C for 30 min. Scale bar: 20 nm.

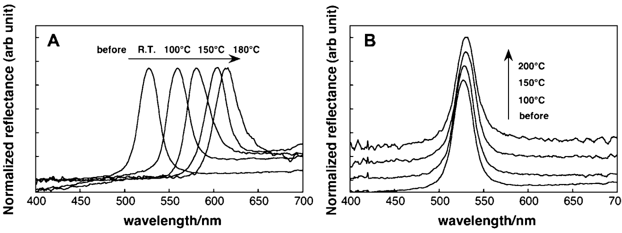

Figure 3. Reflectance spectra of photonic crystals (A) with and (B) without silver nanoparticles, as a function of heat treatment temperature.

The growth of silver nanoparticles upon heat treatment is clearly related to the change in the reflection color of the composite PCs. As the heat treatment temperature increases, the reflection wavelength shifts from ca. 525 nm for the ion-doped sample to ca. 615 nm for the sample heat-treated at 180 °C for 30 min (Figure 3A). In general, the formation of electron-rich metal nanoparticles in polymers results in an increase of the dielectric constant of the composite material. The polymer PCs with no metallic ions did not exhibit distinct changes in reflection wavelength upon heat treatment (Figure 3B), which demonstrates that the red shift is caused by a change in the effective dielectric constants of the composite PCs. This effect might also cause the increase in reflectance at longer wavelength. Classical effective medium theory suggests that the effective dielectric constant of composite materials consisting of metal nanoparticles and dielectrics is dependent on the nanoparticle size (due to the quantum size effect) and volume fraction of the metal phase (due to interparticle interaction).[8] For the samples obtained after heat treatment above 100 °C, no metallic ions remained in the polymer matrix (Figure S3[9]), although the reflection wavelength gradually became longer and the silver nanoparticle size gradually increased in this temperature range (Figure 2). Therefore, the shift of the reflection wavelength for these samples could be caused by the increase in the silver nanoparticle size (the volume fraction of silver remained constant due to no change in periodic structures of the photonic crystals).

The typical wavelength range that can be tuned by the formation of silver nanoparticles is ca. 100 nm, which does not cover the entire visible range. However, the polymer PCs with different periodic structures could be used to display different colors, such as in the blue-green range, in the case of composite PCs made from smaller-sized (180 nm) PS spheres (Figure 1B). Since the synthesis of monodispersed, crosslinked poly(PS–PMAA) spheres that can be used for formation of photonic crystals is generally difficult by emulsion and/or suspension polymerization, the use of inverse opals as the template is crucial for the present in situ synthesis of nanocomposite photonic crystals.

In conclusion, the synthesis of composite photonic crystals was demonstrated through a combination of ion-exchangeable polymer photonic crystals and in situ formation of silver nanoparticles inside the crystals. The silver nanoparticle size could be controlled simply by adjustment of the reduction temperature, which allowed systematic control of the reflection wavelength of the composite PCs. This approach allows fine tuning of the structural variables for precursor polymers, including concentration of ions, degree of crosslinking, and dimensions of the host PCs and is also applicable to various kinds of metallic species; therefore, we anticipate that this method could be used as an effective approach for the synthesis of multifunctional photonic crystals with tunable micro- and nanostructures.

References and Notes

1 E. Yablonovitch, *Phys. Rev. Lett.* **1987**, *58*, 2059; S. John, *Phys. Rev. Lett.* **1987**, *58*, 2486; J. M. Weissman, H. B. Sunkara, A. S. Tse, S. A. Asher, *Science* **1996**, *274*, 959; S.-Y. Lin, E. Chow, V. Hietala, P. R. Villeneuve, J. D. Joannopoulos, *Science* **1998**, *282*, 274.

2 S. A. Asher, J. Holtz, L. Liu, Z. Wu, *J. Am. Chem. Soc.* **1994**, *116*, 4997; S. H. Park, Y. Xia, *Adv. Mater.* **1998**, *10*, 1045; P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone, V. L. Colvin, *J. Am. Chem. Soc.* **1999**, *121*, 11630; T. Cassagneau, F. Caruso, *Adv. Mater.* **2002**, *14*, 34; P. Jiang, M. J. McFarland, *J. Am. Chem. Soc.* **2004**, *126*, 13778.

3 H. Fudouzi, Y. Xia, *Adv. Mater.* **2003**, *15*, 892; H. Fudouzi, T. Sawada, *Langmuir* **2006**, *22*, 1365; A. C. Arsenault, T. J. Clark, G. von Freymann, L. Cademartiri, R. Sapienza, J. Bertolotti, E. Vekris, S. Wong, V. Kitaev, I. Manners, R. Z. Wang, S. John, D. Wiersma, G. A. Ozin, *Nat. Mater.* **2006**, *5*, 179.

4 S. Katayama, Y. Hirokawa, T. Tanaka, *Macromolecules* **1984**, *17*, 2641; J. Y. Wang, Y. Cao, Y. Feng, F. Yin, J. P. Gao, *Adv. Mater.* **2007**, *19*, 3865; X. Xu, A. V. Goponenko, S. A. Ashher, *J. Am. Chem. Soc.* **2008**, *130*, 3113.

5 K. Busch, S. John, *Phys. Rev. Lett.* **1999**, *83*, 967; M. Ozaki, Y. Shimoda, M. Kasano, K. Yoshino, *Adv. Mater.* **2002**, *14*, 514; P. Mach, P. Wiltzius, M. Megens, D. A. Weitz, K.-h. Lin, T. C. Lubensky, A. G. Yodh, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2002**, *65*, 031720; A. C. Arsenault, D. P. Puzzo, I. Manners, G. A. Ozin, *Nat. Photonics* **2007**, *1*, 468.

6 J. Ge, Y. Hu, Y. Yin, *Angew. Chem., Int. Ed.* **2007**, *46*, 7428; J. Ge, H. Lee, L. He, J. Kim, Z. Lu, H. Kim, J. Goebl, S. Kwon, Y. Yin, *J. Am. Chem. Soc.* **2009**, *131*, 15687; S. A. Grudinkin, S. F. Kaplan, N. F. Kartenko, D. A. Kurdyukov, V. G. Golubev, *J. Phys. Chem. C* **2008**, *112*, 17855.

7 W. Wang, S. A. Asher, *J. Am. Chem. Soc.* **2001**, *123*, 12528; F. García-Santamaría, V. Salgueiriño-Maceira, C. López, L. M. Liz-Marzán, *Langmuir* **2002**, *18*, 4519; B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893; Y. Tan, W. Qian, S. Ding, Y. Wang, *Chem. Mater.* **2006**, *18*, 3385; V. Morandi, F. Marabelli, V. Amendola, M. Meneghetti, D. Comoretto, *J. Phys. Chem. C* **2008**, *112*, 6293.

8 U. Kreibig, L. Genzel, *Surf. Sci.* **1985**, *156*, 678.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.