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Photonic crystals with tunable optical stop band through monodispersed silica–polypyrrole core-shell spheres

Gyoujin Cho [a,*], Minhoon Jung [a], Hoetaeg Yang [a], Bokim Lee [a], Jae Hee Song [b]

[a] *Department of Chemical Engineering and Regional Research Center for Green Technology Fused Advanced Materials, Sunchon National University, Sunchon, Chonnam, 540-742, Republic of Korea*
[b] *Department of Chemistry, Sunchon National University, Sunchon, Chonnam, 540-742, Republic of Korea*

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Abstract

We prepared monodispersed silica–polypyrrole core-shell spheres (SiO_2–Ppy) using adsorbed surfactant bilayers on silica as templates and demonstrated the construction of photonic crystal with tunable stop band from SiO_2–Ppy core-shell spheres. Since the photonic stop band is very dependent on the refractive index, it can be tuned by simply changing the refractive index of Ppy shell *via* changing doping level. In fact, the stop band was shifted about 15 nm when the photonic crystal was exposed to fuming sulfuric acid due to the change of the doping level of Ppy shell.

Keywords: Conducting polymer; Polypyrrole; Photonic crystal

1. Introduction

Photonic crystals are crystals that afford unprecedented control over the propagation of light through an ordered periodic array of different dielectric media in three dimensions with sufficiently large contrasts in refractive indices resulting in an optical band gap [1,2]. The ordered periodic dielectric structures are often simply prepared from the sedimentation of monodispersed silica and polystyrene spheres, called artificial opals or from the infiltration of high refractive index materials in the interstitial sites of the opals and later removal of the opal templates, called inverse opals [3–5]. Although calculations indicate that those opals usually possess only a pseudo band gap [6], called stop band instead of a full band gap, those opals are very effective to apply in the field of inexpensive and simple optoelectronic devices which do not require complete photonic band gap.

The opals that can alter the refractive index or lattice constant by external stimuli could function as optical limiters for sensors and eye protection [7]. The challenge of opals as sensors is to develop not only optically sensitive photonic crystals but also electrically sensitive photonic crystals because the optical changes in the photonic crystals can be simultaneously related to the changes of electrical currents [8]. Therefore, the photonic crystals, completely formed by conducting materials, would be very plausible to apply in the field of optoelectronic sensors. By using the conducting materials, a few metallic opals have been reported using gold [9]. However, since the metallic opals are not sensitive enough to the external stimuli such as changes of temperatures, pH, pressure, gas concentrations, and so forth, they could not be effectively used as optoelectronic sensors.

Conducting polymers with metallic property has been often employed to construct sensors because their electrical properties are very sensitive to their doping levels which are sensitive to some of the external stimuli such as gases. Therefore, if the conducting polymers are successfully applied for the construction opals, the optoelectronic sensors could be successfully constructed. Based on our best known knowledge, there were no reported opals, constructed by metallic conducting polymers such as polypyrrole, polyaniline, or polythiophene but a few inverse opals, fabricated from polypyrrole and polyaniline, have been reported because those conducting polymers are not easy to produce as monodispersed latex particles nor infiltrated in the void of opals to construct inverse opals due to their intrinsic nature of solubility [10,11]. However, if the opals of conducting polymers can be constructed, the control of both refractive index and electrical conductivity of opals can be achieved

* Corresponding author. Tel.: +82 61 750 3585; fax: +82 61 750 3580.
E-mail address: gcho@sunchon.ac.kr (G. Cho).

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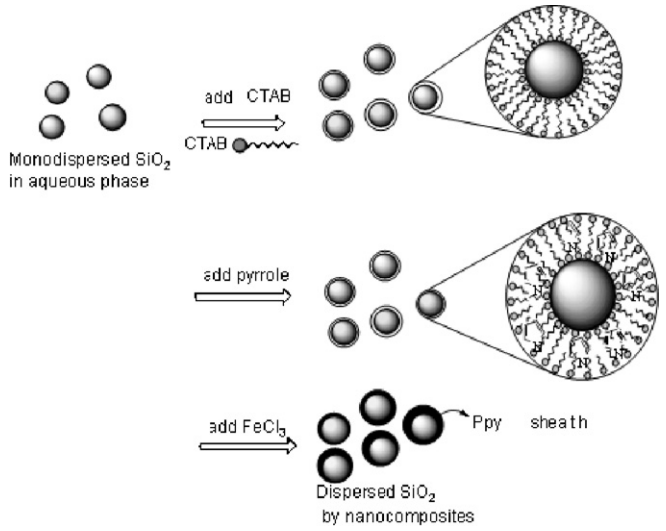

Scheme 1. Descriptive illustration of the preparation of silica–polypyrrole core-shell spheres.

through a reversible doping of the conducting polymers [12]. In other words, opals with both combining tunable photonic stop bands and electrical currents can be simply achieved by applying the external stimuli. In this paper, we would like to report a new route to construct opals with conducting polymer using the sedimentation process of monodispersed colloidal conducting polymer spheres. Among conducting polymers, we selected polypyrrole (Ppy) for producing the conducting polymer spheres because Ppy has been extensively studied due to its high conductivity and environmental stability. While many electrochemical applications of Ppy have been investigated [13–16], no study about a photonic crystal has been carried out because of its intractability. Furthermore, since it is impossible to produce monodispersed Ppy spheres with submicrometer sizes, we adopt core-shell type approach to produce monodispersed Ppy spheres. If the uniform thickness and morphology of Ppy can be deposited on monodispersed silica core, silica–Ppy core-shell spheres will be produced and ideal for the construction of opals with tunable stop band and electrical currents. To obtain the opals from the resulting core-shell spheres, ultrathin Ppy films (>50 nm) should be deposited on the surface of monodispersed silica spheres to avoid overgrowth of irregular Ppy film on the surface. Therefore, in this paper, we employ templates which can confine the growth of Ppy and adsorbed surfactant bilayers were used as templates for the fine controlled growing of Ppy as a sheath on the core of silica for the formation of stable colloidal core-shell type spheres (Scheme 1). The results from the preparation of monodispersed silica–Ppy core-shell spheres and their application for the formation of tunable photonic crystals combining changeable electrical current will be reported here.

2. Experimentals

Monodispersed silica spheres (265 nm) used in our work were prepared exactly following the previously reported method using tetraethyl orthosilicate (TEOS) with 98% purity from Aldrich and 28–30% of ammonium hydroxide solution from Aldrich [17]. Silica spheres were redispersed (0.02 wt.% of silica) in deionized water (1 L), and the pH of the dispersed solution was 6.8. We used the dispersed solution without further pH adjustment. When the silica spheres were redispersed in water, no precipitation was observed due to the electrostatic repulsive forces between the silica. To determine the formation of adsorbed surfactant bilayers on the silica, cetyltrimethyl ammonium bromide (CTAB) was attained from Aldrich and used as received for adsorption studies on the silica. It was found that 10 mM of CTAB was required to form the bilayers on the silica surface at the given system [16,18,19]. For the formation of Ppy sheath on the silica, 3 mM to 30 mM of pyrrole (received with purity of 98% from Aldrich and further purified by passing through basic alumina column) was added into the equilibrated silica and CTAB solution, and the mixture was further equilibrated for 6 h. Polymerization of pyrrole was slowly initiated by adding an equimolar amount of ferric trichloride (97%, Aldrich), which is dissolved in 0.5 mL of water, to the loaded pyrrole. Particle sizes and morphologies of the resulting silica–Ppy core-shell spheres were studied using transmission electron microscopy (TEM; Philips EM 400 T) before and after removing free Ppy. To remove free Ppy, the solution was centrifuged, the supernatant was removed, and the remaining light black pellet was redispersed in water. This centrifugation/redispersion step was repeated until the supernatant practically contained no small free Ppy anymore. The photonic crystals respectively from the bare silica spheres and the core-shell spheres were simply prepared by leaving the

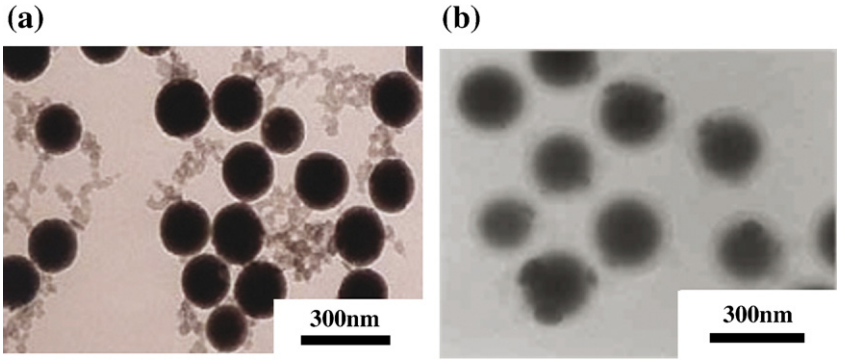

Fig. 1. TEM images of silica–polypyrrole core-shell spheres before (a) and after (b) removing free polypyrrole.