# Optical and Electrical Properties of Conducting Polymer Replicas

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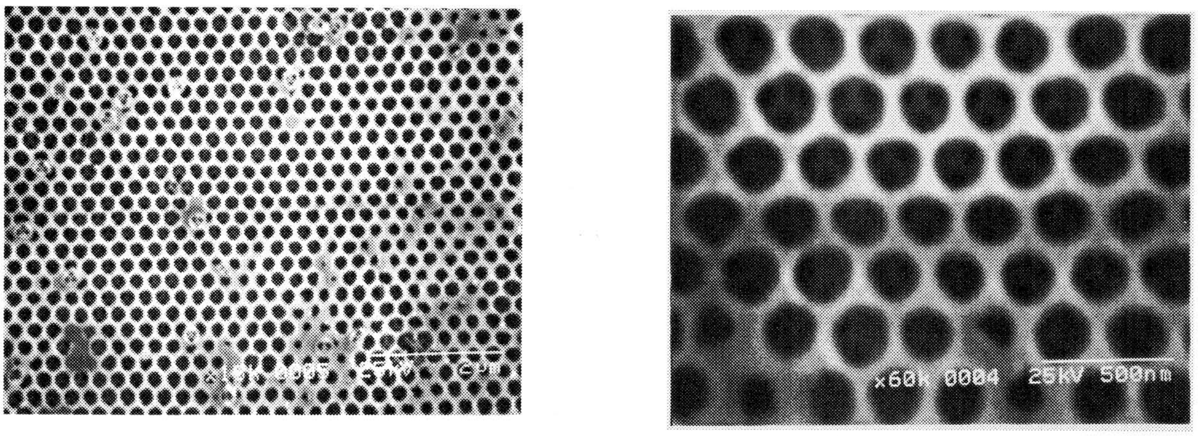
Recently, photonic crystals with a three-dimensional periodic structure, whose periodicity is the order of optical wavelength, have attracted much attention from both fundamental and practical viewpoints. The various novel properties of photonic crystals, which are desirable for future electronics and optoelectronics, are expected as a new class of materials [1-5]. Among various materials, conducting polymers with extended $\pi$-conjugation in their main chains exhibit numerous attractive characteristics, that could be one of the candidates of the stuff for the photonic crystals.

Previously, we have succeeded to prepare synthetic opals as one example of photonic crystals by the sedimentation of $SiO_2$ spheres of 300nm in diameter. Inverse opals (Replicas of opals) which are prepared by infiltrating various secondary materials into percolated periodic array of voids in the synthetic opals and then removing $SiO_2$ spheres by HF, also exhibit unique characteristics as photonic crystals [6].

In this study, we demonstrate the optical and electrical properties in inverse opals of poly(3-dodecylthiophene) (PAT-12) or poly(3-octadecylthiophene) (PAT-18).




(a)　　　　　　　　(b)

Fig. 1　SEM images of PAT-18 replica.
The scale of these periodic hollow cages is 300nm.

As is evident from a scanning electron microscope (SEM) image of the replica film with 25 μm thick shown in Fig. 1 (a), a regular array of roles at 300nm interval was observed over a wide area. It could be also observed that 3D periodic void structure was formed as shown in Fig. 1 (b).

The optical properties of the inverse opals depend on the periodicity and refractive indices of constituents. Figure2 shows the reflection spectra of the 9μm-thick synthetic opal film with 300nm $SiO_2$ spheres, the opal film infiltrated with PAT-18 and the replica of the opal infiltrated with PAT-18. It is considered that the difference in these reflection spectra is originated from the gap of refractive indices between the materials of the sphere part and the void part. By changing the

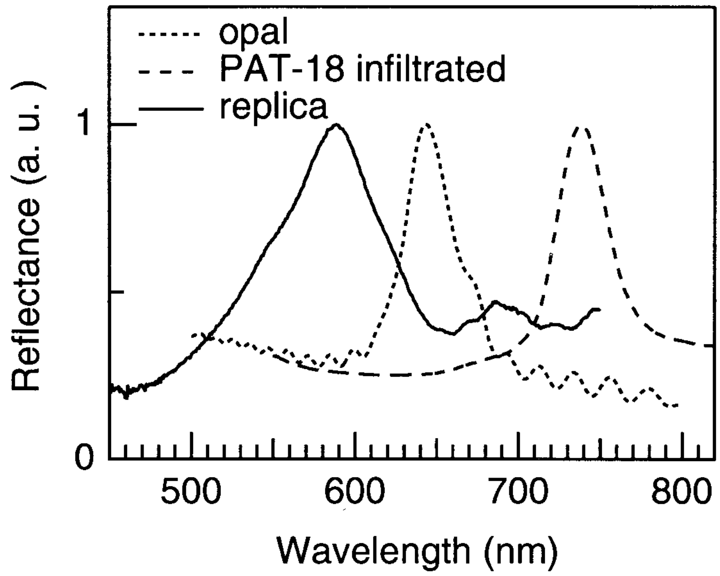



Fig. 2　The reflection spectra of synthetic opal, synthetic opal infiltrated with PAT-18 and replica of opal infiltrated with PAT-18.

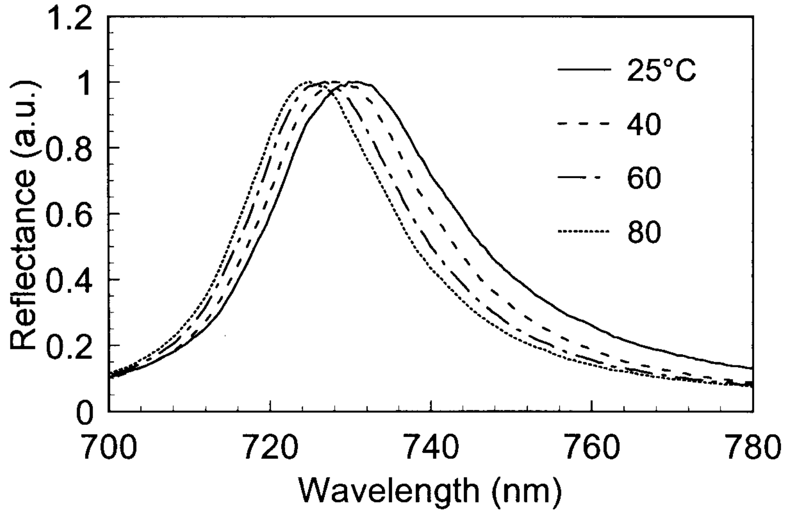



Fig. 3　The reflection spectra of PAT-12 replica with 300nm periodicity at different temperatures from 25°C to 80°C in ethanol.

refractive indices of the infiltrated materials, it is possible to tune the photonic band gap. Therefore, we measured optical properties of PAT-18 and PAT-12 replicas under various conditions.

Figure3 shows the temperature dependence of reflection spectra of PAT-12 replica with 300nm period. The measurement was carried out in ethanol using PAT-12 replica film on glass substrate by heating at the rate of 1°C/min. With increasing temperature, the reflection peak shifted towards higher energy. It should also be noted that these peak shifts of reflection spectra depending upon the temperature were confirmed to be reversible. The blue-shift of the peak wavelength can be interpreted to be attributed to the decrease of the refractive index of PAT-12 with increasing temperature.

We have also demonstrated that the optical properties of the conducting polymer replicas were controlled by electrochemical doping. The reflectance measurements of PAT-18 replica film with 25μm-thickness during electrochemical doping were carried out with a three-electrode system consisting of a working electrode with the PAT-18 replica film stuck on ITO-coated glass plate, a platinum counter electrode and silver reference electrode in an electrolytic solution of tetrabutylammonium tetrafluoroborate/acetonitrile. Figure4 shows the change of reflection spectra of PAT-18 replica with 300nm period in electrochemical doping. The electrochemical doping into PAT-18 replica film was carried out with applied positive potential up to 2V. These shifts of reflection spectra with electrochemical doping are attributed to the decrease in the refractive index of PAT-18 by electrochemical doping and these spectral shifts are reversible.

In conclusion we have demonstrated that refractive index of PAT could be controlled and tuning of optical properties in conducting polymer inverse opals could be realized by changing temperature and electrochemical doping.

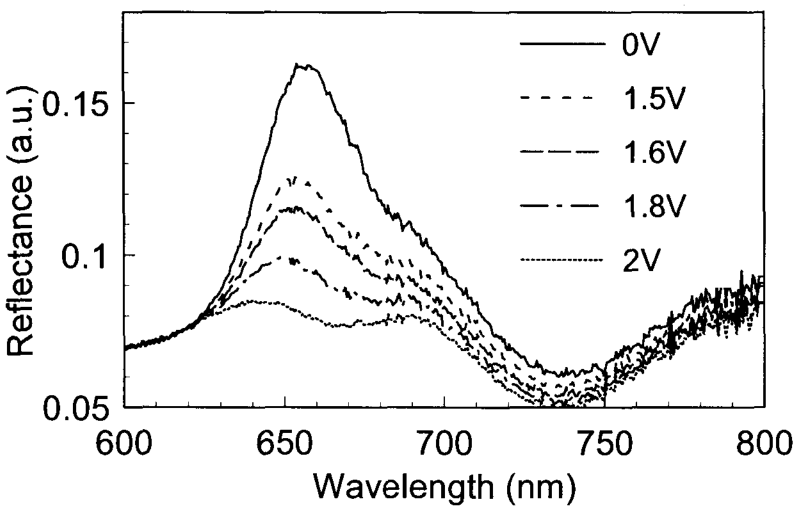



Fig. 4 The reflection spectra of PAT-18 replica with 300nm periodicity in electrochemical doping.

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