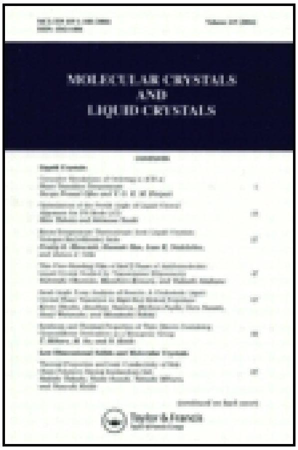

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Electrical and Optical Properties of Conducting Polymer and Carbons in Nano-Scale Periodic Structure and their Intercalation Effects

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Electrical and Optical Properties of Conducting Polymer and Carbons in Nano-Scale Periodic Structure and their Intercalation Effects

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Nano-scale periodic structures of conducting polymer and carbons, which were prepared by infiltration of polymers and carbons in nano-scale interconnected periodic pores in synthetic opals made of regular array of SiO_2 spheres and then removing SiO_2 by etching, have been found to exhibit novel electrical and optical properties. Their electrical and optical properties in thus fabricated conducting polymer and carbon replicas change drastically upon pyrolysis due to progress of carbonization and graphitization. That is, due to the changes in periodicity, pore size, carbonization degree and crystal structure, electrical conductivity, magnetoconductance and their temperature dependences and optical reflection spectra have changed drastically. These replicas with porous nature can be infiltrated and also intercalated with various materials, resulting in also remarkable changes of properties. The synthetic opal infiltrated with conducting polymer can be electrochemically doped, with which remarkable change of optical properties have been observed due to the shift of the diffraction peak accompanying with the change in refractive index. Alkali metal intercalated carbon and graphite with nano-scale periodic structures have been also studied. The applications of these nano-scale periodic structures of conducting polymer and carbon are also discussed.

Keywords: opal; carbon; conducting polymer; replica; intercalation

1. INTRODUCTION

Recently photonic crystals with three dimensional regular structure of the optical wavelength order have attracted much attention from both fundamental and practical view points, because novel concepts such as photonic band gap have been introduced and also various applications of the photonic crystals have been proposed[1,2]. We have studied the synthetic opal made of regular array of silica spheres as prototype of photonic crystal and also demonstrated that various materials can be infiltrated in the interconnected nano-scale voids of the synthetic opal[3,4]. It was also demonstrated that upon removing silica spheres of the infiltrated opals with HF, various opal replicas can be prepared[5,6].

In this paper, we report properties of opals infiltrated with conducting polymer and carbons and also their replicas. Especially effects of doping and intercalation in these infiltrated opals and replicas are discussed.

2. EXPERIMENTAL

Three-dimensionally ordered colloidal crystals were formed by sedimentation of the suspension of mono-dispersed silica spheres of several hundreds nano meter (120 - 550 nm) in diameter. By changing preparation condition various thickness of mechanically robust samples (several μm-several mm) were prepared[7].
Synthetic opal prepared by this procedure has a face-centered cubic (f.c.c.) crystal lattice structure and contains interconnecting structure of tetrahedral and octahedral voids. For example tetrahedral and octahedral voids of 56 nm and 104 nm in diameter, respectively, were formed in the case of the photonic crystal made of SiO_2 spheres of 250 nm in diameter.
The percolated porous structure permits the infiltration of various materials as already reported in our previous papers either in gas phase or liquid phase. For example conducting polymer was mostly infiltrated in the liquid (solution) phase and carbons were infiltrated by either gas or liquid phases followed by pyrolysis.
By removing SiO_2 spheres of infiltrated opals with HF, opal replicas of various materials were prepared. Carbon replica was pyrolized at various temperatures for 1 h in a high-purity Ar atmosphere.Intercalation and doping were carried out in either gas phase or solution phase by electrochemical method. Details of these methods were already reported in our previous papers[8,9].
The micrograph of scanning electron microscope (SEM) was taken with a S-2100C Hitachi microscope. The reflectance spectrum was evaluated by observing reflected light using a PMA-11 (HAMAMATSU) from sample surface which was irradiated with light of a wide spectral range in the visible region. The electrical conductivity and magnetoconductance (MC) were measured by a conventional four-probed technique employing a Quantum Design, PPMS[6].

3. RESULTS AMD DISCUSSION

3-1 Properties of opals infiltrated with various organic materials

Figure 1 indicates optical reflection spectra of opals made of SiO_2 spheres of 300nm in diameter observed at various incident angles of the light. As evident in this figure clear diffraction peaks were observed depending on the incident angle. The lattice

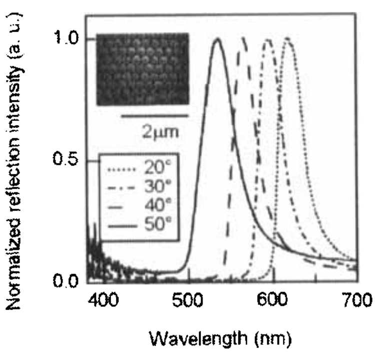

Fig. 1. Optical reflection spectra of opals made of SiO_2 spheres of 300 nm in diameter as a function of incident angle of the light. The inset indicates a SEM image of opal.

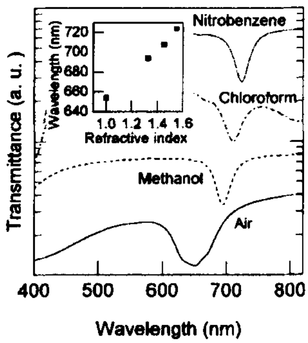

Fig. 2. The transmission spectra of opals made of SiO_2 spheres in various solvents. The inset shows depedence of stop band on refractive index of solvent.

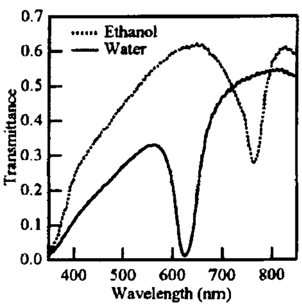

Fig. 3. The variation of stop band of insulating polymer replica infiltrated with various solvents.

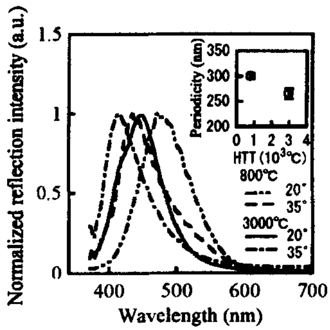

Fig. 4. The reflection spectra as a function of incident angle for pyrolized replicas. The inset shows the variation of periodicity as a function of heat treatment temperature.

constant evaluated from the spectra is consistent with that calculated from the SEM image shown in the inset of Fig.1 with the f.c.c. crystal structure. Similar clear diffraction peaks were also observed in opals made of various diameters of SiO_2 spheres. In the transmission spectra of thin opal film, a clear stop band, in which the range of optical transmission is suppressed, was observed as shown in Fig.2. It should be noted in this figure that the stop band depends on the diameter of SiO_2 spheres used for the fabrication of opals and shifts remarkably by infiltrating solvent. The difference in refractive index of the solvents can explain the observed shift of the stop band as shown in the inset of Fig.2. The diffraction peaks also shift depending on the refractive index of the solvent.

It should also be noted that the stop band and diffraction peak of opal replicas also shift drastically as shown in Fig.3 for the case of insulating polymer replica infiltrated with various solvents.

3-2 Optical and electrical properties of carbon replicas of opals

Carbon replicas of opal with various periodicity were prepared by either gas phase infiltration of carbon with CVD method directly or the pyrolysis of polymer (such as phenol resin) replica, followed by the removal of SiO_2 spheres. These carbon replicas exhibit also opalescent color depending on the viewing angle which is consistent with diffraction peak observed in the reflectance spectra as shown in Fig.4. It should also be noted that by increasing the heat treatment of the carbon replica, the diffraction peak shifts to shorter wavelength as shown in this figure. This can be explained by the decrease of the periodicity with the heat-treatment as also evident in the inset of this figure.

Temperature dependence of electrical conductivity of carbon replica pyrolized at 800 °C and 3000 °C was presented in Fig. 5. As evidence from this figure, the carbon replica pyrolized at 3000 °C seems to be well graphitized. However, it should also be mentioned that the absolute conductivity of the graphitized opal is relatively low compared with non-porous graphite. The pores seem to influence on both the electrical conduction process and also electronic energy states. The effect of periodic pores on the electronic energy states is now under study[10].

To explore the conduction process more in detail, we carried out the magnetoconductance (MC), $\Delta\sigma/\sigma = [\sigma(H)-\sigma(o)]/\sigma(o)$, measurements[11]. Figure 6 shows dependence of electrical conductivity on the applied magnetic field. It should be noted in this figure that both positive and negative MCs appear in these carbon replicas. In the carbon replica heat-treated at high temperatures, electron-phonon scattering seems to dominate the inelastic scattering. Existence of positive MC seems to be the evidence of the quantum interference effect. It should also be mentioned that these characteristics are also dependent on the periodicity of the carbon replica.

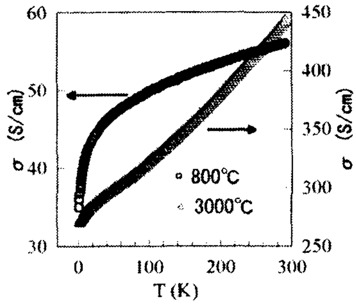

Fig. 5. The temperature dependence of electrical conductivity for pyrolized replicas.

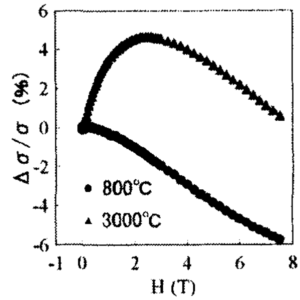

Fig. 6. The magnetic field dependence of conductivity for pyrolized replicas.

3-3 Effect of intercalation in carbon replicas

These carbon replicas can be intercalated with alkali metals such as K in both vapor phase and also solution phase using by electrochemical method. Both electrical and optical properties changed drastically upon intercalation. The intercalation effect was also dependent on both the pyrolysis temperature and the periodicity of the carbon

replicas.
Figure 7 shows the reflection spectra of the pristine and K-intercalated carbon replicas pyrolized at 2800 °C. In this case, K was intercalated in vapor phase. It should be noted in this figure that the diffraction peaks were clearly observed in the reflectance spectra for both samples. The K-intercalated carbon replica exhibits remarkable red shift in diffraction peak, which may originate in the change of effective refractive index. The change of the plasma frequency in this conductive porous graphite should be the origin of the refractive index change. The reflection spectrum in the wider spectral range in the K-intercalated porous replicas and also dynamic intercalation characteristics in the porous opals as function of the periodicity and the pyrolysis are now under study.

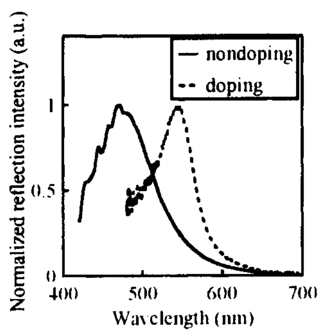

Fig. 7. The reflection spectra of the pristine and K-intercalated carbon replicas pyrolized at 2800°C.

3-4 Effect of doping in conducting polymer replica

Conducting polymer can also be infiltrated in the nano-scale voids of the opal film. However, in the case of poly(3-alkylthiophene) (PAT-6) we have confirmed that partial infiltration was realized. It was also confirmed that conducting polymer in the nano-scale voids of opal can be electrochemically doped by anion in electrolyte which was acetonitrile solution containing tetrabutylammonium tetrafluoroborate [9].
As shown in Fig. 8, the reflectance spectrum changed with increasing doping level by applying higher voltage in the electrochemical doping. The details of the shift in the reflection peak at various electrochemical doping potentials are more clearly shown in the expanded spectra near the peak as shown in the inset of Fig. 8. With increasing voltage the wavelength of the diffraction peak changed to shorter wavelength. That is, by this procedure we can perform fine tuning of the stop band by the electrochemical doping into the conducting polymer in the opal matrix.
By comparing the refractive index estimated from the diffraction peaks in electrolyte with the directly evaluated refractive index of PAT-6 by the measurement of Brewster angle, the filling factor of PAT-6 in the opal voids was evaluated to be 30.3%. Utilizing this filling factor and the peak wavelength at each voltage shown in Fig. 8, the dependence of the refractive index on voltage in the electrochemical doping was evaluated as shown in Fig. 9. That is, with increasing doping level, refractive index is confirmed to decrease.
Dynamic doping characteristics into conducting polymer infiltrated in the synthetic opal and also conducting polymer opal replica are now under study.

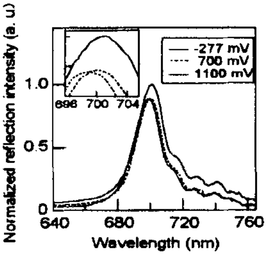

Fig.8. The reflection spectra as a function of electrochemically doping potential for PAT6 in the nano-scale voids of opal. The inset shows the expanded spectra near the peak.

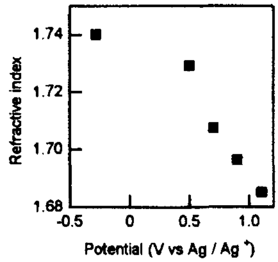

Fig.9. The dependence of refractive index on voltage in the electrochemical doping.

4. SUMMARY

Nano-scale periodic structures of conducting polymer and carbons have been prepared by the method utilizing synthetic opal as the template. Due to the changes in periodicity, pore size, carbonization degree and crystal structure, electrical conductivity, magnetoconductance and their temperature dependences and optical reflection spectra have changed drastically. Quantum interference effects in the transport properties of carbon replicas have been demonstrated through the measurements of electrical conductivity and magnetoconductance. The K-intercalated carbon replica pyrolized at 2800 °C exhibits remarkable red shift in diffraction peak. The synthetic opal infiltrated with conducting polymer can be electrochemically doped, with which remarkable change of optical properties have been observed due to the shift of the diffraction peak accompanying with the change in refractive index. By this procedure, we can perform fine tuning of the stop band by the electrochemical doping into the conducting polymer in the opal matrix.

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