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Novel Electrical, Optical and Rheological Properties of Conducting Polymer in Liquids and Solutions Infiltrated in Opals and Inverse Opals

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Abstract

Conducting polymers with highly extended π-electron system in their main chains can be infiltrated into nano-scale interconnected regular array of voids in synthetic opals either in solution or liquid states upon heating. Optical properties of opals and inverse opals such as transmission spectra and reflection spectra were found to change drastically upon infiltration of conducting polymer liquids or solutions.

Amplified spontaneous emission, amplified resonant Raman line and multi-mode lasing were observed in opals infiltrated with conducting polymer solutions upon optical excitation.

Introduction

Conducting polymers whose main chains consist of conjugated π-electron system have attracted much attention from both scientific and practical viewpoints. Among various conducting polymers, those with long side chains such as poly(3-alkylthiophene) and poly(2,5-dialkoxy-p-phenylenevinylene) have been confirmed to be fusible upon heating and also soluble in common solvents. Various interesting properties such as thermochromism, solvatochromism, anomalous luminescence and electrorheology have been found in such liquid conducting polymers.

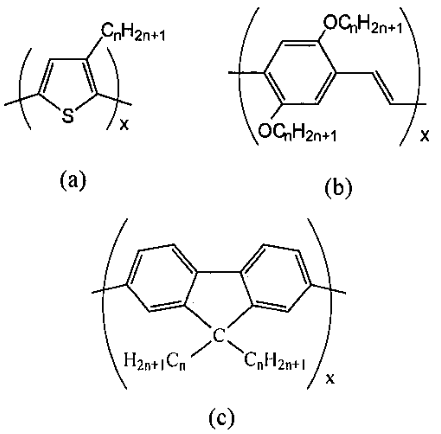
On the other hand, recently, photonic crystals with a three-dimensional periodicity of optical wavelength have attracted much interests from both fundamental and practical viewpoints, because a new concept of a photonic band gap has been theoretically predicted and various novel functional applications have been proposed in this new class of materials.[1-3]

We have demonstrated the preparation of a three-dimensional periodic structure by a self-assembly method, that is, by sedimentation of monodispersed SiO_2 spheres of several hundreds nanometer in diameter[4]. This three-dimensional periodic array of SiO_2 spheres can also be called a synthetic opal, because of its opalescent color. We have also proposed to realize new functionality by infiltration of various materials in the percolated nano-scale voids in synthetic opals and found interesting phenomena.[4-6]

In this paper, we report properties of opals and inverse opals (replica) infiltrated with conducting polymer liquids and solutions. In the case of solutions, the properties are studied as functions of solvents and the concentration of conducting polymers in solution.

Experimental

Soluble and fusible conducting polymers such as poly(3-alkylthiophene) (PAT), poly(2,5-dialkoxy-p-phenylenevinylene) (ROPPV) and poly(9,9-dialkoxyfluorene) (PDAF) whose molecular structures are shown in Fig.1 were prepared by the method already reported in our previous papers.[7-9]



(a) (b) (c)

Fig. 1. Molecular structures of (a) poly(3-alkylthiophene)(PAT),(b) poly(2,5-dialkoxy-p-phenylenevinylene)(ROPPV) and (c) poly(9,9-dialkoxyfluorene)(PDAF)

Synthetic opals with a three-dimensional periodic structure were fabricated by sedimentation of mono-dispersed SiO_2 spheres of 150 - 550nm diameters. The obtained three dimensional periodic structure of SiO_2 spheres (synthetic opals) was confirmed to have a face-centered-cubic (f.c.c.) structure and contain interconnected nano-scale voids by the measurements of optical transmission and reflection spectra using a Hitachi 330 spectrometer and CCD multi-channel photodetector PMA-11 (Hamamatsu Photonics) and also electron microscope observation by a S-2100C Hitachi scanning electron microscope.

A polymer replica of an opal was prepared by infiltration of polymer or polymer precursor into nano-scale voids of the opal and then by the removal of SiO_2 spheres by hydrofluoric acid. Transmission and reflection spectra were measured utilizing a Hitachi 330 spectrophotometer and CCD multi-channel photodetector PMA-11.

Various conducting polymers shown in Fig.1 were used for infiltration in thin opal films either in solution or liquid states.

For the observation of spectral narrowing of photoluminescence (PL), a second harmonic generation (SHG) light (532nm) of Nd-YAG laser (1064 nm) of 10 ns pulse width was used as an exciting light source. The PL from conducting polymer infiltrated into opals was measured utilizing a PMA-11 or InstaSpec IV CCD detector (Oriel) with a MultiSpec 257 spectrograph (Oriel).

Results and discussion

Figure 2 indicates the transmission spectra of a pristine red opal made of SiO_2 spheres of 300 nm diameter and the opal infiltrated with various liquids. As evident in this figure, a clear stop band was observed. It should be noted in this figure that the stop band shifts with changing liquid infiltrated in the opal. As clearly shown in Fig.2, the stop band shifts to longer wavelength with increasing a refractive index of the liquid.

In the reflection spectra of the pristine and infiltrated opals, reflection peaks were observed depending on the solvent. In this case, also, the reflection peak is located at longer wavelength in the case of opals infiltrated with solvents of larger refractive index.

These results can be interpreted in terms of the periodicity of the opal and the change of an effective optical path length depending on the refractive index of the liquid.

Figure 3 shows the reflection spectra of a phenolic resin replica of the opal in air and also the replica infiltrated with various solvents. In this case, reflection peaks appeared at longer wavelength in the case of infiltration of solvents with larger dielectric constant. As more clearly indicated in Fig.4, the reflection peak wavelength increases with increasing the refractive index of the liquid.

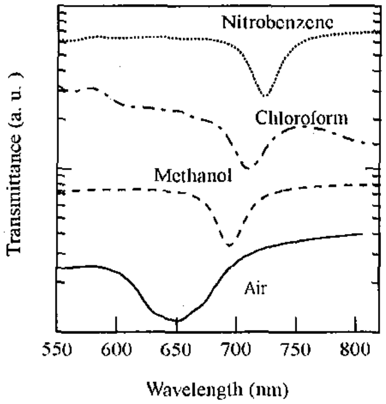


Fig. 2. Transmission spectra of a red opal in air and the opal infiltrated with various solvents for normal incident.

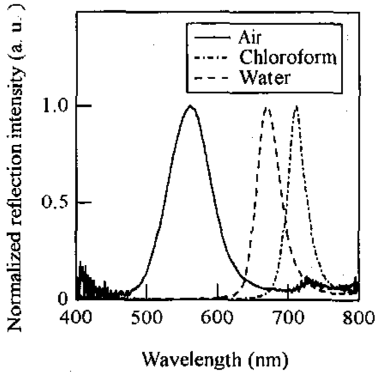


Fig. 3. Reflection spectra of a phenolic resin replica in air and the replica infiltrated with various solvents. In those case, the incident angle is 20°.

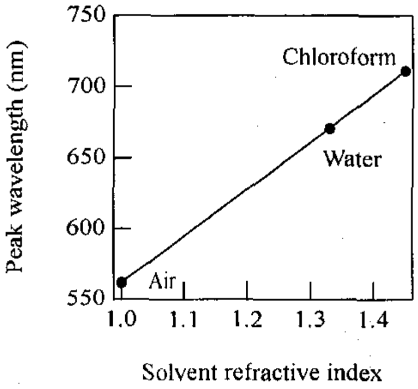


Fig. 4. The dependence of the wavelength of reflection peak on the refractive index of a phenolic replica infiltrated with liquids.

It should also be noted that even with the same liquid for infiltration the reflection peak wavelength of the phenolic resin replica is much different from that of an original silica opal. As shown in Fig.5, with changing incident angle of the light impinging on the phenolic resin replica, the reflection peak also shifts.

Figure 6 shows the reflection spectra of a carbon replica of the opal in air and the replica infiltrated with various solvents. Also in this case, the peak shifts in wavelength with changing solvent. As shown in Fig. 7, the wavelength of the reflection peak increases with increasing the refractive index of the solvent. This result can also be explained in terms of the change of an effective optical path length with increasing the refractive index of the solvent.

These experimental results indicate that utilizing these effects of dependence of the reflection peak and the stop band on the refractive index of the liquid, a simple new method for the precise measurements of the refractive

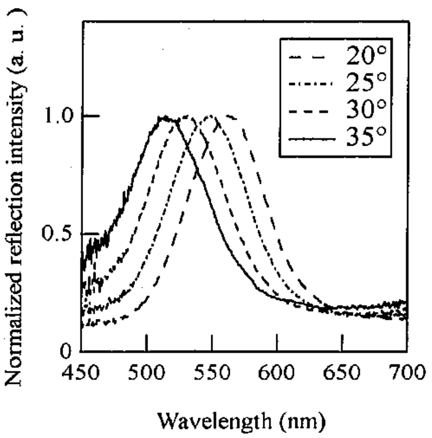


Fig. 5. Reflection spectra of a phenolic resin replica as function of incident angle.

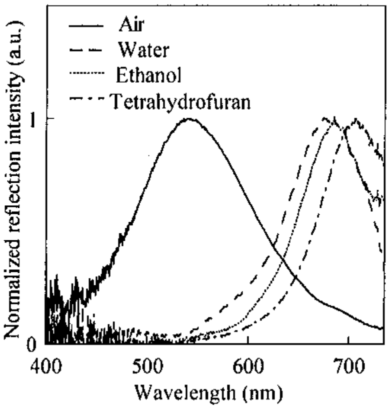


Fig. 6. Reflection spectra of a carbon replica with a heat treatment temperature of 700° C in various solvents.

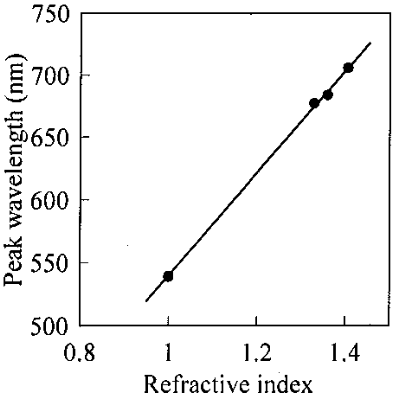


Fig. 7. The dependence of the wavelength of a reflection peak of a carbon replica on the refractive index of solvents.

index of various fluids, not only liquids but also liquid crystals and molten polymers, can be developed.

As evident in Fig.8, with increasing optical excitation intensity of a SHG light of Nd-YAG laser, PL (about 595 nm) intensity of the opal infiltrated with poly(2-methoxy-5-dodecyloxy-p-phenylenevinylene) (MDDOPPV) dissolved in toluene increases drastically accompanying with remarkable spectral narrowing, which can be explained in terms of the amplified spontaneous emission. Simultaneously new sharp emission lines evolve at around 608 nm and increases its intensity drastically with increasing excitation intensity, which can be interpreted in terms of multi-mode lasing on account of the optical feed back due to the periodic structure of the opal matrix.

It should also be noted in this figure that at intense excitation, a sharp emission line evolves at 581 nm and increases intensively with increasing excitation. This sharp line can be interpreted in terms of a resonant Raman line, because the separation between the SHG light of Nd-YAG laser and this line is 1584 cm^{-1} and coincides with a peak of the Raman spectrum of MDDOPPV. This line is negligible in MDDOPPV dissolved in pyridine in which PL peak located at a little longer wavelength and does not overlap with this line. The later fact is the origin of the resonance effect. It should also be mentioned that this resonant Raman is much intense in the opal matrix compared with the case of just in solution. This indicates that the signal is originated in an amplified resonant Raman line.

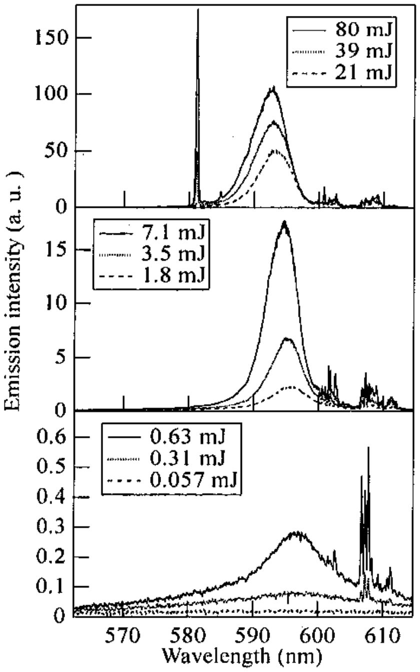


Fig. 8. Emission spectra of MDDOPPV solution (5×10^{-2} *mol/l* toluene solvent) infiltrated in an opal at various excitation intensities of a SHG light of Nd-YAG.

Similar results were also obtained in the replica of opals infiltrated with conducting polymers and fluorescent dyes in liquids.

From these results we can summarize that in the opal infiltrated with conducting polymer in liquids the multimode lasing occurs when the wavelength of the mode of feed back system in the opal matrix overlaps with the PL spectra and amplified resonance Raman can be observed when the Raman line overlaps with the PL spectra in the opal matrix.

Summary

The results of this experimental study can be summarized as follows.

Conducting polymers with highly extended π-electron system in their main chains can be infiltrated in nanoscale interconnected array of voids in synthetic opals either in solution or liquid states upon heating. Optical properties such as transmission and reflection spectra of an opal and a replica of the opal were found to change drastically upon infiltration of conducting polymers in liquids or solutions. This results indicates that we can develop a simple new method for the precise measurement of the refractive index of various fluids, such as not only isotropic liquids but also liquid crystals and molten polymers.

In the case of a synthetic opal infiltrated with conducting polymer in liquids, upon optical excitation above the threshold the multi-mode lasing occurs when the wavelength mode of feed back system in the opal matrix overlaps with the PL spectra, and amplified resonance Raman can be observed when the Raman line overlaps with the PL spectra in the opal matrix.

Acknowledgment

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