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Optical Properties of Opal Infiltrated with Dye-doped Polymer and Opal Replica

N.Takamoto, S.Satoh, M.Ozaki, K.Yoshino
Graduate School of Engineering, Osaka University,
2-1 Yamada-oka Suita, Osaka 565-0871, Japan
Tel: +81-6-6879-7759, Fax: +81-6-6879-7774
E-mail: ntakamot@ele.eng.osaka-u.ac.jp

1.Introduction

Recently photonic crystal with a three-dimensionally ordered structure with a periodicity of optical wavelength, has attracted considerable attention from both fundamental and practical points of view, because new physical concepts such as the photonic band gap have been theoretically predicted and various applications of photonic crystals have been proposed. The three dimensional periodic structure can be realized by a self-assembly method, that is, by the sedimentation of nano-scale spheres of the order of optical wavelength in diameter, which is named synthetic opal.

Various organic functional materials such as conducting polymers, dyes and liquid crystals can be infiltrated in regular structure of nano-scale void space in these synthetic opals used as photonic crystals. We have infiltrated opals with several solutions of conducting polymers and dyes. As a material infiltrated into voids, solid is more desirable than liquid. In this study, opal was infiltrated with dye-doped polymer as a solid and we report its optical properties.

2.Experimental

Synthetic opals were fabricated by the sedimentation of the suspension of mono-dispersed silica spheres of 270 nm in diameter. Porous opals prepared by this procedure have a face-centered cubic crystal lattice structure and contain an interconnecting structure of tetrahedral and octahedral voids. The percolated porous structure permits the infiltration of dye molecules easily.

Dye-doped polymer was infiltrated into voids by the following procedure. The monomer of the infiltrated polymer and fluorescent dye were methyl methacrylate (MMA) and NK-3468, respectively. The molecular structure of NK-3468 is shown in Fig. 1. After the opal was dipped into MMA containing NK-3468 (1×10^{-4} mol/l), it was polymerized at 70℃ for about twelve hours.

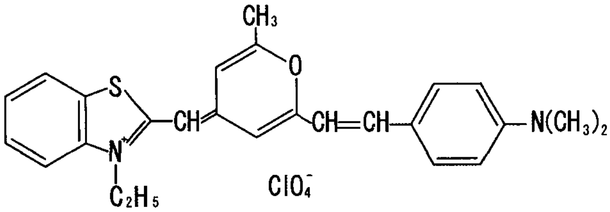


Fig. 1. Molecular structure of NK-3468.

Absorption and photoluminescence (PL) spectra of poly methyl methacrylate (PMMA) containing NK-3468 were measured using a Hewlett Packard HP8452 diode array spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer, respectively. The reflectance spectrum of the opal infiltrating with dye-doped polymer was measured by observing the light reflected from the sample surface irradiated with light of a wide spectrum in the visible range using a CCD multichannel photodetector PMA-11 (HAMAMATSU).

For the observation of spectral narrowing of the emission, second harmonic light (532 nm) of Nd-YAG laser (1064 nm) with 10-ns pulse width was used as an excitation light source. The PL from the infiltrated opals was measured.

By dipping the infiltrated opals in KOH solution and dissolving the silica spheres, the polymer replica was prepared. Scanning electron microscope (SEM) image of opal replica was taken with JSM-6320F (JEOL). The reflectance spectrum of opal replica was measured.

3.Results and Discussion

Figure 2 shows the absorption and PL spectra of PMMA containing NK-3468. Because the absorption spectrum has a peak at 530 nm, the excitation by second harmonic light of Nd-YAG laser is effective for the emission.

Figure 3 shows the PL spectrum of PMMA containing NK-3468 and reflectance spectrum of opal infiltrated with NK-3468-doped PMMA. The peak of reflectance spectrum is close to the PL peak of the NK-3468-doped PMMA.

Figure 4(a) shows the emission spectra of opal infiltrated with NK-3468-doped PMMA as a function of excitation light intensity. As is evident from this figure, spectral narrowing of emission was observed with increasing excitation intensity. In contract, PMMA containing NK-3468 did not exhibit such a spectral narrowing as shown in Fig 4(b). This indicates that the existence of the periodic structure of the opal plays an important role in the spectral narrowing of the emission from the dye.

A SEM image of the dye-doped polymer replica is shown in Fig. 5. It is confirmed that a regular three-dimensional periodic structure of the dye-doped PMMA is formed. The periodicity of the hole array estimated from the SEM image is 270 nm which coincides with the diameter of the SiO_2

sphere of the opal.

Figure 6 shows the reflectance spectrum of opal replica. Diffraction peaks are observed. These results indicate that this replica has a periodic nano-scale structure. Because difference between refractive index of polymer and air is large, it is expected that differ emission spectrum is measured.

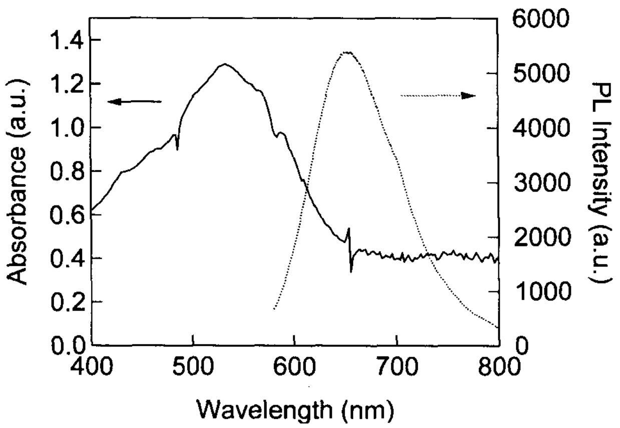


Fig. 2. The absorption and PL spectra of PMMA containing NK-3468.

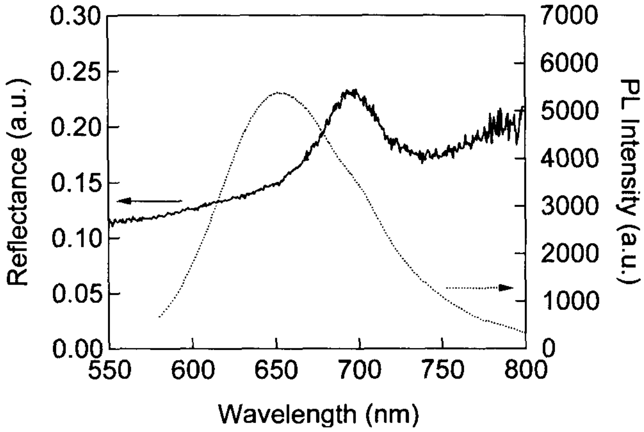
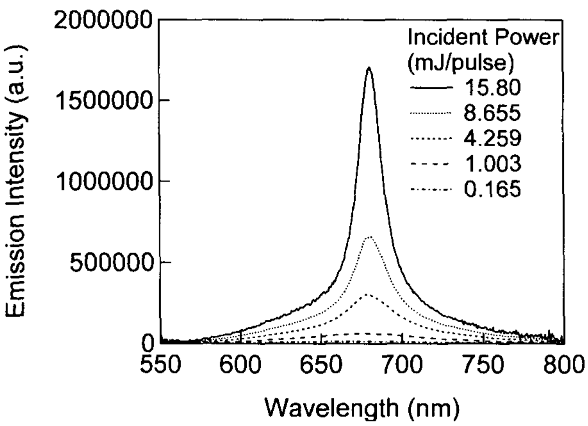


Fig. 3. The PL spectrum of PMMA containing NK-3468 and reflectance spectrum of opal infiltrated with NK-3468-doped PMMA.



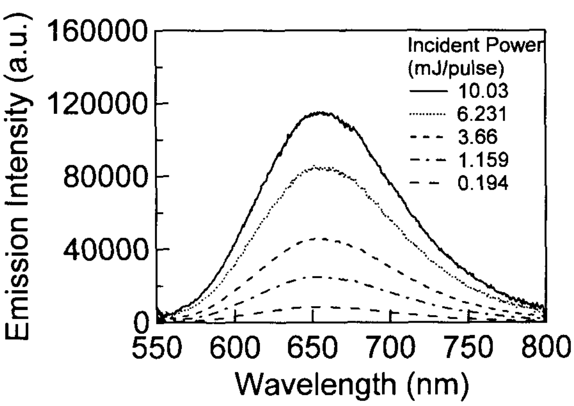


Fig. 4. (a) The emission spectra of opal infiltrated with NK-3468-doped PMMA at various excitation intensities.

(b) The emission spectra of PMMA containing NK-3468 at various excitation intensities.

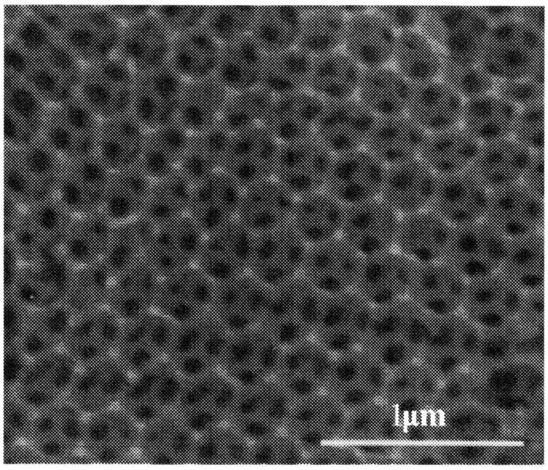


Fig. 5. A SEM image of the dye-doped polymer replica.

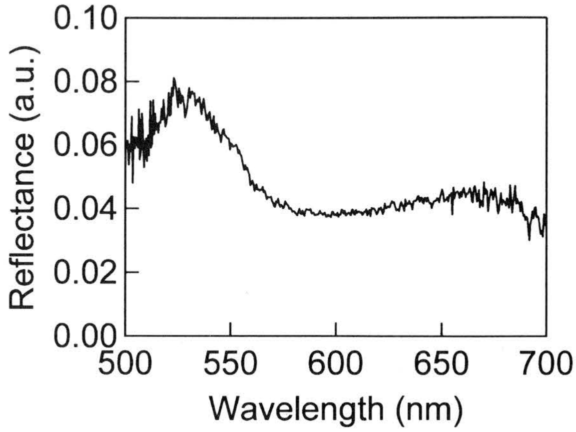


Fig. 6. The reflectance spectrum of opal replica.

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