Electrochemical Change of the Photonic Stop Band of the Ordered Macroporous WO_3 Films

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Three-dimensional macroporous tungsten trioxide (WO_3) was electrochemically prepared by using the polystyrene opal as a template. The photonic stop band of the porous WO_3 film could be changed when the WO_3 was intercalated with lithium cation by the electrochemical method. The change of the stop band was attributed to the change of the refractive indices accompanied with the electrochromism of WO_3.

Photonic crystals are spatially ordered dielectric structures with the periodicity comparable to the wavelength of electromagnetic waves.[1] Because of the periodic modulation of the refractive index, the structured materials give a photonic band gap (PBG), that is, a particular range of wavelengths in which the propagation of light is forbidden. The materials have attracted much attention because of the applications such as optical switches, filters, and high efficient light emitting devices. In particular, the PBG materials which can operate at the visible regions have been highly desired, whereas the fabrication of three-dimensional (3D) submicrometer structure required to attain such materials still remain challenging. Recently, the synthetic methods of an ordered macroporous material (so-called inverse opal) using the colloidal crystal (opal) as a template have been developed.[2] The inverse opals are comprised of the fcc arranged macropores and dielectric frameworks surrounding the macropores, of which structures are suitable for obtaining the complete PBG.[3] Hence, the many studies, which selected TiO_2[4,5] and Si[6] with high refractive indices as the materials of the frameworks, have been conducted.

On the other hand, the control of the PBG by the external perturbations such as temperature, electric field, pressure, and light, should be important for the applications described above. In fact, the theoretical[7] and experimental[8] pioneering works using the change of the index of liquid-crystals were reported. However, there have been a few reports on such tunable PBG of the 3D inverse opal. Very recently, it was also reported that the temperature-induced phase transition of the ferroelectric $BaTiO_3$[9] and photochromic dyes[10] filled in the voids of normal opals were available for tuning the PBG. Considering that the inverse opals containing air spheres show the significant photonic properties, it should be of high value that the framework itself possesses the variable optical constants.

As a candidate for such framework, it is believed that the electrochromic WO_3 would be suitable because the optical constants such as the refractive index and absorption of light can be easily changed by the electrochemical methods. In addition, WO_3 is one of the most promising inorganic electrochromic materials and often discussed in the context of "smart windows". Accordingly, the combination of PBG properties with the electrochromism should be interesting from the viewpoint of the novel optical devices.

Here, we report the electrochemically induced change of PBG of the macroporous WO_3 which is prepared by the electrodeposition of WO_3 using the polystyrene (PS) opals as the templates.

The macroporous oxide films were prepared according to our previous report.[11] Briefly, a F-doped SnO_2 coated glass (OTE) was vertically dipped into the PS spheres with 267 nm diameter ethanolic dispersion. After ethanol was evaporated for 5 days, an opalescent PS opal with 3.0 μm average thickness was deposited on the OTE. The cathodic electrodeposition of WO_3 was potentiostatically performed by the published method[12] with a BAS 100 W (Bioanalytical Systems, Inc). The electolyte solution was prepared as follows: 4.6 g of tungsten powder was dissolved in 25 mL 30% H_2O_2. Then excess H_2O_2 was decomposed by putting a large area Pt sheet into the solution until O_2 gas evolution had stopped. Finally, the solution was diluted to 0.25 M tungsten with 70/30 v/v water/isopropanol. The working electrode was a PS-opal/OTE (active area of 0.78 cm^2 exposed to the electrolyte). The counter electrode was a Pt wire and the reference electrode was Ag/AgCl immersed in a saturated KCl solution. After electrodeposition for 10 min at -0.9 V, the templates were removed by dissolving in toluene for 48 h. The WO_3 inverse opal/OTE was washed with deionized water and characterized by UV-vis spectrophotometry, scanning electron microscopy (SEM), and X-ray diffraction (XRD).

Figure 1 shows the typical SEM image of the WO_3 inverse opal. The hexagonal close-packed arrangement of the macropores could be observed in the WO_3 film, indicating the success in preparing the inverse opal using the PS template. The three channels in the WO_3 framework surrounding each macropore, which formed at the contact points between the PS spheres, were also clearly visible, and confirmed that the macropores in the structure were interconnected with each other. The center-to-center mean distance between the macropores was 262 nm, reflecting a shrinkage of ca. 2% (compared to the diameter of the PS spheres). This WO_3 film prepared by electrodeposition was probed to be amorphous by XRD measurement.

Figure 2 compares the three transmission spectra of the bare PS opal and the macroporous WO_3 before and after applying bias -1.0 V vs Ag/AgCl for 1 min in a 0.1 M $LiClO_4$ aqueous solution. In all the spectra, the transmission dips (stop bands) due to the Bragg diffraction caused by the ordered structures were clearly observed. The dips appeared at 636 nm and 539 nm for bare PS opal and macroporous WO_3, respectively. Two main spectral

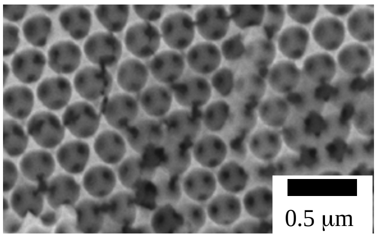

Figure 1. Typical SEM image of the macroporous WO_3.

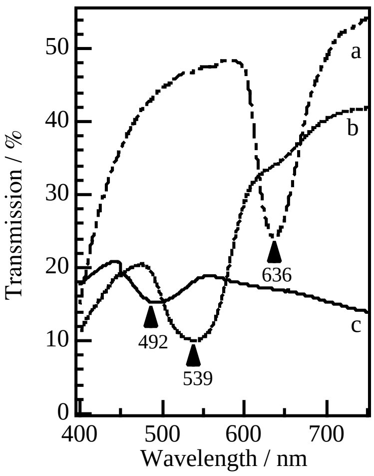

Figure 2. Transmission spectra of (a) the polystyrene opal, (b) the macroporous WO_3 and (c) the macroporous WO_3 doped with Li^+ at normal incidence.

changes could be observed between the macroporous WO_3 before and after applying the bias. Firstly, the decrease in transmission in the wide wavelength range from 600 nm to 800 nm, which was attributed to the characteristic absorption of WO_3 intercalated with Li^+. Secondly, the transmission dip appeared at 492 nm which was blue-shifted compared to 539 nm before the electrochromism. In case of applying the bias for longer time than 1 min, the further blue-shift could not be observed.

In order to investigate the reason of the shift of the dip positions, we analyzed the incidence angle dependency of the dip positions. The dip position of each sample blue-shifted with increasing the incidence angle. This angle dependency well obeyed the Bragg's law [eq (1)] as an approximate expression

$$\lambda = 2d_{111}({n_{\text{eff}}}^2 - \sin^2\theta)^{1/2}, \tag{1}$$

where λ is the wavelength of the dip position, d_{111} the spacing between the (111) planes of the oredered structure, n_{eff} the effective refractive index,[13] and θ is the angle measured from the normal to the planes as shown in the inset of Figure 3. By plotting $\sin^2\theta$ vs λ^2,[14] we could determine the d_{111} and n_{eff} because a linear fit to the experimental data has a gradient of $-1/(2d_{111})^2$ and an intercept equal to ${n_{\text{eff}}}^2$.

Figure 3 shows such plots. The d_{111} spacings were determined to be 220 nm and 219 nm for bare opal and macroporous WO_3, respectively. These values were in good agreement with the value of 218 nm estimated using the geometry of the structure.[15] The n_{eff} for the bare opal was 1.44, which decreased to 1.23 for the macroporous WO_3 because the polystyrene spheres were replaced by air. The calculated refractive indices of polystyrene and WO_3 were 1.56 and 1.72, which were in good agreement with the reported values of 1.59 and 1.75,[12] respectively.

The calculated value of d_{111} of the macroporous Li_xWO_3 was 221 nm and almost equal to 219 nm before applying the bias. This was also supported by the SEM observation (data not shown). In contrast, the n_{eff} of macroporous Li_xWO_3 decreased to 1.12 lower than that before the intercalation. In the literature,[16] it was reported that the refractive index of WO_3 significantly decreased in the wavelengh range over 300–900 nm when the intercalation of Li^+ occurred, supporting the results in our system. Therefore, it was concluded that the dip position was shifted toward the shorter wavelength region because of the change of the refractive index of WO_3.

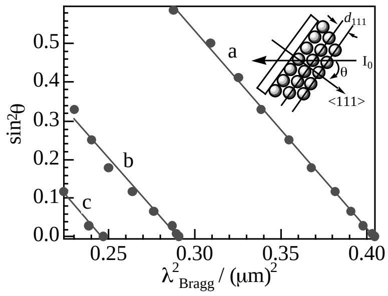

Figure 3. Plots of $\sin^2\theta$ vs the square of the Bragg peaks (λ^2 in case of (a) the original polystyrene opal, (b) the macroporous WO_3 and (c) the macroporous WO_3 after the electrochromism, where θ is the angle of incidence as shown in the inset.

In conclusion, we could electrochemically prepare the ordered macroporous WO_3 via the colloidal crystal templating. The stop band of the ordered porous WO_3 was found to vary through the refractive index change accompanied with the electrochromism. The reversibility of the electrochromism was not good, and therefore, the further studies on its improvement by thermal treatment and the use of organic solvents would be needed.

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