

# Molybdenum doping effects on photochromic properties of WO<sub>3</sub> based composite films

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Mo-doped tungsten-based photochromic composite films were fabricated using a peroxoisopolytungstic acid methanol solution, peroxoisopolymolybdenum acid methanol solution, and transparent urethane resin. The non-doped composite films showed photochromic properties by UV–Vis light irradiation. The reaction rate constant was  $2.68 \times 10^{-2} \text{ min}^{-1}$ . The increasing Mo/W ratio in the film caused a blue shift of the absorption peak of the film. The reaction rate constants  $k$  of films with Mo/W rates of 0.1, 0.5, and 1.0 were 3.00, 4.23, and  $3.53 \times 10^{-2} \text{ min}^{-1}$ . Those values were larger than that of a non-doped film. All composite films showed a reversible photochromic property, which was the coloring and bleaching property.

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## 1. Introduction

Tungsten trioxide films have been studied widely for application in electrochromic materials,<sup>1),2)</sup> photochromic materials,<sup>3)–8)</sup> and sensor materials.<sup>9)</sup> Using WO<sub>3</sub> films as electrochromic or photochromic materials, the level of sunlight transmitted through the window materials can be controlled. Thereby, energy-efficient windows can be designed.

Photochromic properties of WO<sub>3</sub>-based materials show reduction of W<sup>6+</sup> to W<sup>5+</sup> in the WO<sub>3</sub> host by UV–vis light irradiation. Our previous report described fabrication of a WO<sub>3</sub>-based composite films using peroxoisopolytungstic acid [W-IPA, W<sub>12</sub>O<sub>38</sub>(O<sub>2</sub>)<sub>6</sub><sup>16–</sup>] and urethane resin as starting materials, and evaluation of a photochromic property of the films.<sup>8)</sup> The aims of this work are fabrication of WO<sub>3</sub>-based photochromic composite films using W-IPA and urethane resin, and controlling its photochromic property by doping other cations. Regarding WO<sub>3</sub>-based electrochromic and photochromic devices, another cation (Mo, V, etc.) was doped into the WO<sub>3</sub> matrix to control the photochromic property.<sup>2),7)</sup> In this investigation, Mo was doped into the WO<sub>3</sub>-based composite films, and the photochromic property of the Mo-doped films was evaluated.

## 2. Experimental procedures

Metal tungsten powder (Mitsuiwa Chemical Co. Ltd., Aichi, Japan) was used as a starting material to prepare W-IPA. The tungsten powder was dissolved completely into an ice-cooled 15% H<sub>2</sub>O<sub>2</sub> solution to achieve atomic tungsten concentration of 1 mol/L. After reaction, the excess H<sub>2</sub>O<sub>2</sub> was removed catalytically using Pt nets. The resultant solution was dried using a rotary evaporator with a 40°C water bath to obtain glassy solid matter as a W-IPA powder. Details of the W-IPA preparation were reported by Kudo et al.<sup>9)</sup> Similarly, peroxoisopolymolybdenum acid (Mo-IPA) was prepared using metal Mo (Kojundo Chemical Lab. Co.

Ltd., Saitama, Japan) and H<sub>2</sub>O<sub>2</sub>. Molybdenum powder of 4.0 g was dissolved completely into an ice-cooled 15% H<sub>2</sub>O<sub>2</sub> solution of 60 mL. After reaction, the excess H<sub>2</sub>O<sub>2</sub> was removed catalytically using Pt nets. The resulting solution was dried using a rotary evaporator with a 40°C water bath to obtain glassy solid matter as a Mo-IPA powder. Hinokuma et al. reported details of the Mo-IPA preparation.<sup>10)</sup>

W-IPA, Mo-IPA, and liquid type urethane resin (M-40; Asahi Kasei Chemicals Corp., Tokyo, Japan) were used as starting materials. The urethane resin can be cured by UV–Vis light irradiation. The W-IPA powder was dissolved into methanol with tungsten molar concentrations of 0.1 mol/L. The precursor W-IPA solution was mixed into liquid-type urethane resin, and the W atomic concentration in the matrix was 3.3 μmol/cm<sup>3</sup>. The tungsten concentration to the matrix was fixed through investigation. To dope Mo into a composite film, first the Mo-IPA and W-IPA methanol solution was mixed and stirred with the Mo/W ratio of 0.1 to 1.0. Then the mixed solution was added to the urethane resin.

The mixture precursor was degassed at 1 kPa for 60 min to expel the dissolved air in the precursor. Then the precursor was put between slide glasses with film thickness of 1 mm. The precursor was cured for 10 min using UV–Vis light irradiation. The resulting films were colored because of the effects of the UV–Vis light irradiation. Therefore, the composite films were put into a dark room for clarification for 7 days.

The photochromic property of the films was evaluated at room temperature using a UV–Vis spectrophotometer (UV-1600; Shimadzu Corp., Japan). Through the investigation, a 1 kW low-pressure Hg lamp was used for curing resin and for coloration of the composite films. The tungsten cluster in the composite films was characterized using transmission electron microscopy (TEM, EM-002B; Topcon Corp., Japan).

## 3. Results and discussion

A non-doped film was fabricated using the W-IPA methanol solution with concentrations of 0.1 mol/L. **Figure 1** presents

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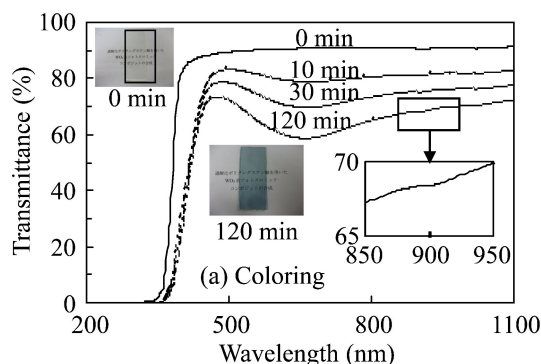


Fig. 1. (Color online) Transmittance spectra for the composite film with the precursor W-IPA methanol solution with concentrations of 0.1 mol/L: (a) the coloring property depending on UV-Vis light irradiation time, and (b) the bleaching property of the film in a dark room. Inset photographs in the coloring property [Panel (a)] are those before (0 min) and after (120 min) UV-Vis irradiation.

transmittance spectra for the composite film measured before and after 10–120 min UV-Vis light irradiation. The inset photographs in the coloring property [Panel (a)] show the film before (0 min) and after (120 min) UV-Vis irradiation. The film showed a coloring property by UV-Vis irradiation corresponding to reduction from  $W^{6+}$  to  $W^{5+}$  in  $WO_3$  based cluster in the film. The colored film was bleached by stoppage of light irradiation for 40 h. The colored film showed broad absorption at absorption peaks of 650 and 900 nm.

Using the optical property of the composite films, the reaction rate constant  $k$  was estimated at the wavelength of 650 nm: the remarkable absorption peak of the film in the coloring condition. The method of calculating the photochromic reaction rate constant was described in an earlier report.<sup>8)</sup> The reaction rate equation is

$$-\ln([A]/[A_0]) = kt,$$

where  $A_0$  represents the initial absorbance and where  $t$  denotes the time. The calculated reaction rate constant was  $2.68 \times 10^{-2} \text{ min}^{-1}$ . In this investigation, the absorbance of the films was calculated using the value of the transmittance. The reaction constant rates of the other samples were also calculated using this method. Regarding the bleaching property, plots of the reactions on the equation above showed no linear property. Therefore, the bleaching reaction was not first-order. The reaction constant of the bleaching property could not be evaluated. The resulting film showed a reversible photochromic property, which was coloring and bleaching.

The Mo-doped composite films were fabricated by altering the Mo concentration (Mo/W ratio of 0.1–1.0). The films were also evaluated for their photochromic properties. **Figure 2** shows transmittance spectra for composite films obtained before and after UV-Vis light irradiation. The inset photographs in each graph show films after 120 min UV-Vis irradiation. The absorption peak position of the film shifted to the low wavelength (blue shift) with the increase of the Mo/W ratio in the films. In previous investigations of  $WO_3/MoO_3$  film electrochromism, the absorption peak of the films shifted to a lower position with increased  $MoO_3$  contents in the  $WO_3$  host.<sup>11)</sup> In the present study, similarly to the electrochromic property of  $WO_3/MoO_3$  film, the absorption peak of films was shifted to a lower position with increased  $MoO_3$  contents in  $WO_3$ . The coloring reaction rate constants  $k$  were also calculated using the optical property of the

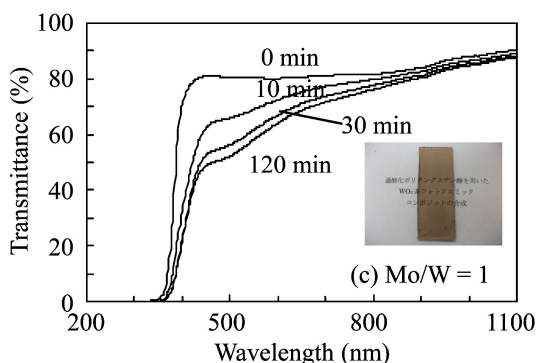
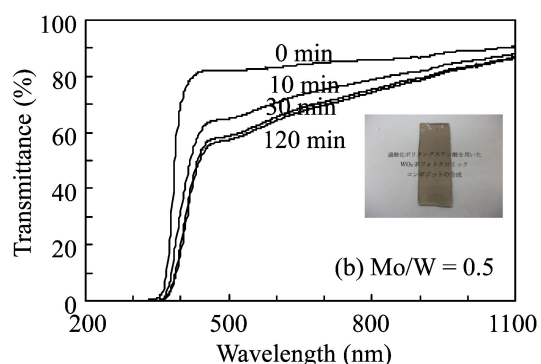
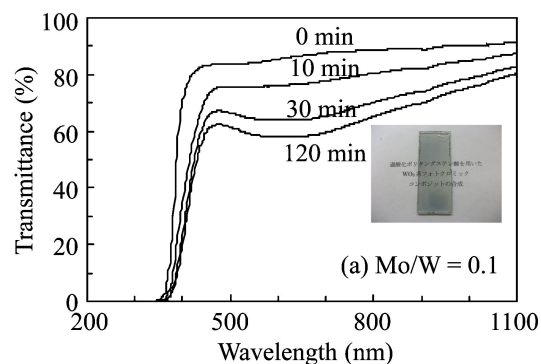


Fig. 2. (Color online) Transmittance spectra for composite films with various Mo/W ratios before and after UV-Vis light irradiation. Inset photographs in respective graphs show films after 120 min UV-Vis irradiation.

films. The wavelength used to estimate the constants was each peak position of the films. The respective reaction rate constants of the films with Mo/W rates of 0.1, 0.5, and 1.0 were 3.00, 4.23, and  $3.53 \times 10^{-2} \text{ min}^{-1}$ , respectively. The values were larger than that of the non-doped film. In short, the film coloring speed was increased by Mo doping.

When Mo was doped to a  $WO_3$ -based composite film, a blue shift of the absorption peak was observed along with increased coloring speed. In a previous report, He et al. described that a photochromic absorption peak of the  $WO_3$  thin film indicated a blue shift by Mo doping.<sup>7)</sup> In this investigation, although the fabricated sample was the  $WO_3$ -based composite film and differed from the sample reported by He et al., the blue shift of the photochromic absorption peak occurred as described in previous reports.<sup>7)</sup> **Figure 3** portrays a TEM bright field image of the composite film with Mo/W ratio of 1.0 (e). The mean particle size was estimated using the TEM micrographs. We investigated a correlation between the microstructure of the non-doped and the Mo-doped film. The Mo-doped film cluster size was 19.8 nm,

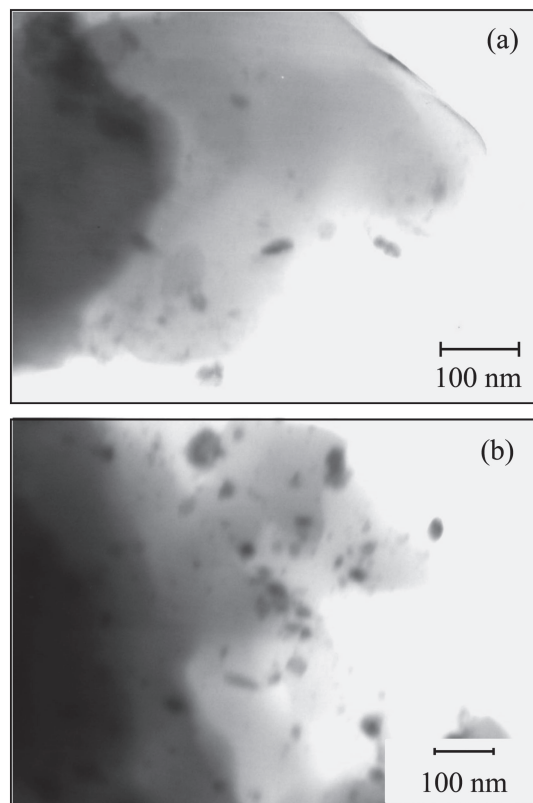


Fig. 3. TEM bright field images of the composite films with the Mo/W ratio of 0 (a) and 1.0 (b).

which was slightly smaller than that of the non-doped film of 21.8 nm [c.f. Figs. 3(a) and 3(b)]. We confirmed that the clusters of all the Mo-doped films were slightly smaller than that of the non-doped film. Results show that the coloring speed of the Mo-doped films was greater than that of the non-doped film. The difference of cluster sizes between Mo-doped and non-doped film was not great. Thereby, it is assumed that the doped Mo affected

the photochromic property of the WO<sub>3</sub>-based film as a sensitizer. Ishikawa et al. reported that the optical sensitivity of MoO<sub>3</sub> film is 18 times larger than that of WO<sub>3</sub> films.<sup>12)</sup> For this investigation, as in that report, it was assumed that increased MoO<sub>3</sub> contents increased the coloring speed of the films. All Mo-doped films showed a bleaching property. Moreover, the film bleaching speed was not increased by Mo doping.

#### 4. Conclusion

Using WO<sub>3</sub>-based photochromic composite films fabricated using W-IPA and urethane resin, Mo doping effects on the photochromic property of the composite films were investigated. When Mo was doped into the WO<sub>3</sub>-based composite films, the increasing Mo/W ratio in the film caused a blue shift of the absorption peak. Furthermore, the coloring speed of the WO<sub>3</sub>-based films was increased by Mo doping. The doped Mo was effective as a sensitizer for the WO<sub>3</sub>-based photochromic films.

#### References

- 1) C. G. Granqvist, *Sol. Energy Mater. Sol. Cells*, **60**, 201 (2000).
- 2) X. L. Sun, A. H. Chen, H. Z. Zhang and H. T. Cao, *Adv. Mater. Res.*, **79–82**, 843 (2009).
- 3) Y. Shigesato, *Jpn. J. Appl. Phys.*, **30**, 1457 (1991).
- 4) Y. A. Yang, Y. W. Cao, P. Chen, B. H. Loo and J. N. Yao, *J. Phys. Chem. Solids*, **59**, 1667 (1998).
- 5) C. Bechinger, M. S. Burdis and J.-G. Zhang, *Solid State Commun.*, **101**, 753 (1997).
- 6) N. Xu, M. Sun, Y. W. Cao, J. N. Yao and E. G. Wang, *Appl. Surf. Sci.*, **157**, 81 (2000).
- 7) T. He and J. Yao, *Prog. Mater. Sci.*, **51**, 810 (2006).
- 8) H. Miyazaki, Y. Baba, M. Inada, A. Nose, H. Suzuki and T. Ota, *Bull. Chem. Soc. Jpn.*, **84**, 1390 (2011).
- 9) T. Kudo, H. Okamoto, K. Matsumoto and Y. Sasaki, *Inorg. Chim. Acta*, **111**, L27 (1986).
- 10) K. Hinokuma, K. Ogasawara, A. Kishimoto, S. Takano and T. Kudo, *Solid State Ionics*, **53–56**, 507 (1992).
- 11) B. W. Faughnan and R. S. Crandall, *Appl. Phys. Lett.*, **31**, 834 (1977).
- 12) A. Ishikawa and T. Yoshimura, *Denki Kagaku*, **60**, 416 (1992).