Fabrication of Photochromic Tungsten Oxide Based Composite Film Using Peroxoisopolytungstic Acid

Hidetoshi Miyazaki,*[1] **Yuki Baba,**[1] **Masaya Inada,**[1]
Atsushi Nose,[1] **Hisao Suzuki,**[2] **and Toshitaka Ota**[3]

[1]Department of Material Science, Interdisciplinary Faculty
of Science and Engineering, Shimane University,
1060 Nishikawatsu, Matsue, Shimane 690-8504

[2]Graduate School of Science and Technology, Shizuoka
University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561

[3]Ceramic Research Laboratory, Nagoya Institute of
Technology, 10-6-29 Asahigaoka, Tajimi, Gifu 507-0071

Received August 1, 2011
E-mail: miya@riko.shimane-u.ac.jp

Tungsten-based photochromic composite films were fabricated using peroxoisopolytungstic acid aqueous solution and transparent urethane resin. UV–visible irradiation of the resulting composite films showed photochromic properties, indicating broad absorption with peaks at 650 and 900 nm. The coloring time was about 40 min. The colored composite films were transformed to clear film in a dark room in 90 h.

Amorphous tungsten trioxide (WO_3) films have been known to exhibit electrochromic[1,2] and photochromic properties.[3–7] Tungsten-based oxide photochromic films have been fabricated using EB evaporation,[3] vacuum evaporation,[4] sputtering,[5] and sol–gel coating.[6,7] Because tungsten oxide slightly dissolves in water (including water vapor), the films described above are difficult to apply for photochromic devices or windows in a deposited condition.

However, fabrication of a WO_3 base composite and hybrid photochromic films has been attempted.[8,9] Katayama et al. reported fabrication of tungsten oxide based hybrid films, which were synthesized using Na-WO_x heteropoly acid solution and GPTMS (3-glycidoxypropyltrimethoxysilane) as starting materials.[8] The film exhibited rapid coloration from a transparent state to colored state during coloration time of about 1 h.[8] Tungsten-based clusters were embedded into the resin matrix, thereby preventing erosion of the tungsten oxides in the film by liquid or vapor-phase water.

Kudo et al. reported fabrication of peroxoisopolytungstic acid (W-IPA, $W_{12}O_{38}(O_2)_6{}^{16-}$) using metal tungsten powder and H_2O_2.[10] The W-IPA powder is an "isopoly acid." Therefore, no cation or anion (e.g., Na, P) coexists in the powder. Furthermore, the W-IPA is water soluble, enabling easy treatment for synthesis of some devices.

In this report, the authors describe fabrication of a tungsten-based photochromic composite film using W-IPA and transparent urethane resin as starting materials. The urethane resin in this investigation, which was in a liquid state, can be cured by UV–visible light (UV–vis) irradiation. The transmittance of the cured urethane resin is extremely high. Therefore, the authors used it as matrix. Coloring and bleaching properties of the resulting composite films were evaluated.

Experimental

Metal tungsten powder (Mitsuwa Chemical Co., Ltd.) was used as a starting material. The tungsten powder was dissolved completely into an ice-cooled 15% H_2O_2 solution to achieve atomic tungsten concentration of 1 mol L^{-1}. After reaction, the excess H_2O_2 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 peroxoisopolytungstic acid powder (W-IPA). Peroxopolytungstic acid was prepared using the method reported by Kudo et al.[10]

W-IPA powder was dissolved to water to produce tungsten molar concentrations of 0.2 and 1.0 mol L^{-1}. The precursor W-IPA solution was mixed into urethane resin (Asahi Kasei Chemicals Corp., M-40) of 3.3 g (volume of 3 cm^3). The matrix resin quantity was fixed through investigation. The urethane resin can be cured by UV–vis light irradiation. First, the mixture was degassed at 10 Pa for 60 min to expel the dissolved air in the precursor slurry. Then the precursor slurry was put between the slide glasses with film thickness of 1 mm and the slurry was cured using UV–vis light irradiation for 10 min. The resulting film was colored because of the UV–vis light irradiation. Therefore, the composite film was put into a dark room to clarify the film for 7 days. The film photochromic properties were evaluated at room temperature using a UV–vis spectrophotometer (UV-1600; Shimadzu Corp.). Through the investigation, a 1 kW low-pressure Hg lamp was used for curing resin and for coloration of the composite films.

Results and Discussion

The composite films were fabricated using pure water (ion-exchanged water) and urethane resin to conduct a blank test. Figure 1 portrays transmittance spectra of the resulting composite films with water contents of 0–0.25 mL in urethane resin (3.3 g, 3 cm^3). The transmittance of the composite film without mixing water was higher than 90% for wavelengths of 400–1100 nm. The transmittance of the composite film with water contents of less than 0.15 mL was also higher than 90% for

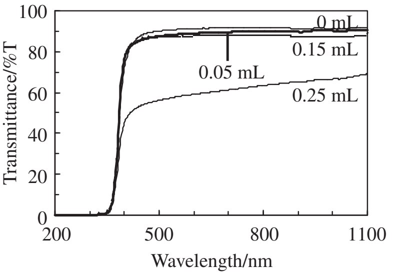

Figure 1. Transmittance spectra of composite films with water content of 0–0.25 mL.

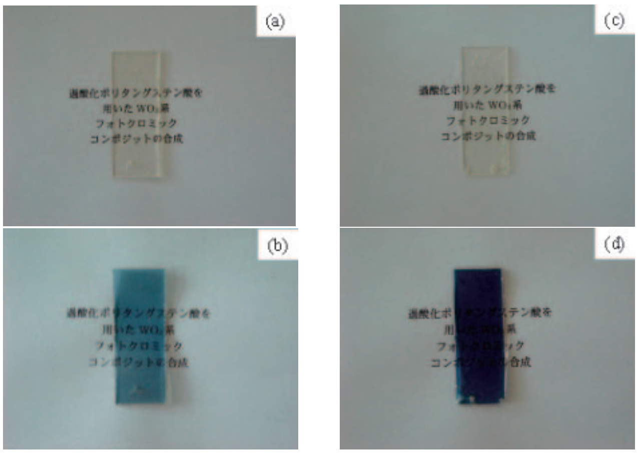

Figure 2. Photographs of the resulting films (a) before and (b) after UV–vis light irradiation with W-IPA concentration of 0.2 mol L^{-1}, and (c) before and (d) after UV–vis light irradiation with W-IPA concentration of 1.0 mol L^{-1}.

wavelengths of 400–1100 nm, and their transmittance properties were similar to those of the composite film without mixing with water. However, the transmittance of the composite film with water contents of 0.25 mL was about 60% for wavelengths of 400–1100 nm. These results show that increasing the added water quantity in the composite film decreased the transmittance of the resulting films. Therefore, adding water (or W-IPA solution) to the composite film was fixed at 0.05 mL for this investigation.

Tungsten–urethane composite films were fabricated with the W-IPA aqueous solution with concentrations of 0.2 and 1 mol L^{-1} in quantities of 0.05 mL. Figure 2 depicts photographs of the resulting films taken before and after UV–vis light irradiation. Here, the irradiation time was 60 min. Composite films were placed onto a paper, on which some words had been printed. Photographs taken before irradiation showed sufficient transparency of both films. Nevertheless, both composite films became blue during UV–vis irradiation.

Figure 3 presents transmittance spectra for the composite films described above (with W-IPA concentrations of (a) 0.2 and (b) 1.0 mol L^{-1}) before and after UV–vis light irradiation. Before UV–vis light irradiation, both composite films transmitted visible and near-IR wavelength light with wavelengths of 400–1100 nm. The composite films after UV–vis light irradiation showed two broad absorption peaks with peaks at 650 and 900 nm. For each film, increasing the irradiation time increased the degree of absorption.

Figure 4 presents coloring and bleaching of the composite films at 650 nm irradiation and the remarkable absorption of the composite films during coloring. For each film (precursor solution concentrations of 0.2 and 1.0 mol L^{-1}), the time until color saturation was about 40 min, with bleaching times from the colored state of about 90 h. The bleaching time was much longer than the coloring time. For the film using the 0.2 mol L^{-1} solution, the transmittance of the sample before UV–vis irradiation was 90%, while that after irradiation was 35%. However, for the film using the 1.0 mol L^{-1} solution, transmittance of the sample before UV–vis irradiation was 60%, whereas that after irradiation was 5%.

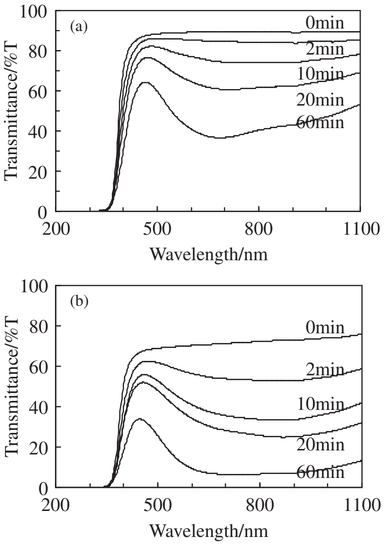

Figure 3. Transmittance spectra of composite films with the precursor aqueous solution concentrations of (a) 0.2 and (b) 1.0 mol L^{-1}.

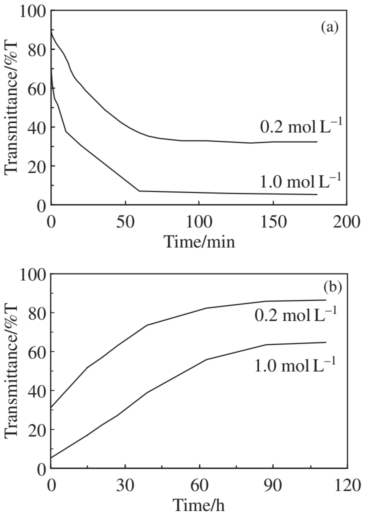

Figure 4. Photochromic properties of composite films with tungsten concentrations of 0.2 and 1.0 mol L^{-1}: (a) coloring and (b) bleaching properties.

The colored films, which were fabricated using precursor solution with 0.2 and 1.0 mol L^{-1}, were bleached in a dark room. The bleaching time from the colored state to the clear state was 90 h, and the transmittance of each bleached film was nearly equal to its initial transmittance. These results proved that the composite films in this investigation show reversible photochromism.

In an earlier study, Katayama et al. reported fabrication of tungsten-based photochromic hybrid films and their photochromic properties.[8] In this report, the film displayed photochromism (with color changed from transparent to blue) by UV light irradiation, the colored film showed broad absorption at absorption peaks of 650 and 900 nm, and the film turned blue in 40 min. The two absorption peaks were d–d bond intervalence transition states. The composite film in this investigation

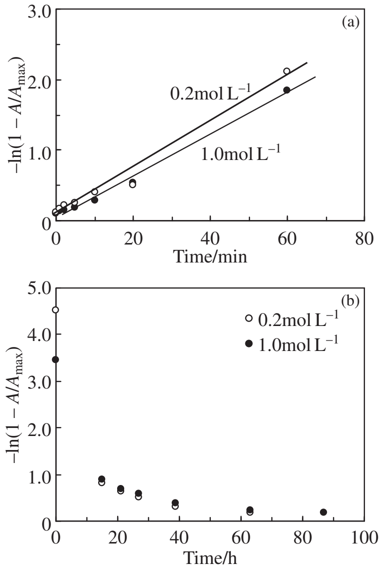

Figure 5. Plot of $-\ln(1 - A/A_{\max})$ as a function of (a) UV–vis irradiation time and (b) bleaching time after 60 min UV–vis irradiation.

showed similar photochromic properties corresponding to the sample described in that report.[8]

Using the optical properties of the composite films, the reaction rate constant *k* was estimated. The method of calculating the photochromic reaction rate constant was described an earlier report.[8] The reaction rate equation is described as

$$-\ln([A]/[A_0]) = kt \qquad (1)$$

where *A* is the initial absorbance and *t* is the time. Figure 5 shows the plot of $-\ln(1 - A/A_{\max})$ as a function of the coloration and bleaching time, where *A* is the absorbance, as calculated using transmittance. For the coloring, both plots show a linear relation. The reaction should be estimated as first-order. The constants *k* of the films using 0.2 and 1.0 mol L^{-1} W-IPA solutions were calculated as 0.029 and 0.032 min^{-1}. The reported value was 0.19 min^{-1};[8] the constant *k* in this investigation is much smaller. Itoh et al. reported that existence of the OH system group in the WO_3 base film engendered a remarkable photochromic property.[11] In an earlier investigation,[8] the WO_3 base photochromic composite was fabricated using an organosiloxane-based matrix containing many OH system groups. In contrast, the authors used urethane resin as matrix, which included a few OH system groups. The OH system group in the composite specimen in the present study included only aqueous water and hydrated water originating from the precursor W-IPA solution. Therefore, it is assumed that the photochromic reaction rate of the specimen fabricated by Katayama et al. was much higher than that for the composite film in this study. On the other hand, the lamp used in the present study was different from that of the previous study,[8] and it also caused the difference of coloration speed.

Regarding bleaching, neither plot of the reactions showed a linear relation. Therefore, the bleaching reaction was not first-order. This suggests that the bleaching reaction differs from the coloring reaction. The resulting composite film was not subjected to heat treatment. Therefore, the tungsten oxide cluster in the film existed in an amorphous-like state. The band structure of an amorphous-like material is shown to have random potential, and an electron generated by the photochromic reaction exists at a deep potential site (Anderson localization).[12] The electron at the deep potential site is diffused by thermal hopping, known as "Mott's variable range hopping."[13] For that reason, the electron as the color center at the W^{5+} site needed much thermal energy to itinerant in the WO_3 cluster. For these reasons, we infer that the bleaching reaction did not show first-order kinetics.

To elucidate the condition of tungsten oxide clusters in the composite film, the authors used X-ray diffractometry (XRD) to clarify the crystallographic structure, X-ray photoelectron spectroscopy (XPS) to examine the valence of the tungsten before and after coloring, and IR and Raman spectroscopy to evaluate the W–O bond. The concentration of the tungsten in the film was extremely low (0.05 mL solution with 1.0 mol L^{-1} W-IPA was mixed into 3 cm^3 urethane resin, which has limited solubility). Therefore, the tungsten signal was not obtainable for all measurements. Furthermore, the composite film was prepared using 10 mol L^{-1} W-IPA solution, which was close to the limit of solubility. However, no signal was observed for any measurement. Further investigation is necessary to clarify the tungsten state in the composite films.

Conclusion

Tungsten-based photochromic composite films were fabricated using W-IPA aqueous solution and urethane resin. Both the composite films with the W-IPA concentration of 0.2 and 1.0 mol L^{-1} showed a photochromic property: the film color changed from transparent to blue during 40 min irradiation by UV–vis light. The composite films after UV–vis light irradiation showed broad absorption, with peaks at 650 and 900 nm. Both samples using 0.2 and 1.0 mol L^{-1} solutions showed bleaching. Therefore, the composite films in this investigation showed reversible photochromism. The coloring reaction rates of the composite films using 0.2 and 1.0 mol L^{-1} W-IPA solutions were calculated as 0.029 and 0.032 min^{-1}. The bleaching reaction rate was not estimated because the reaction was not first-order.

References

1 H. R. Zeller, H. U. Beyeler, *Appl. Phys. (Berlin)* **1977**, *13*, 231.
2 C. G. Granqvist, *Adv. Mater.* **2003**, *15*, 1789.
3 Y. Shigesato, *Jpn. J. Appl. Phys.* **1991**, *30*, 1457.
4 Y. A. Yang, Y. W. Cao, P. Chen, B. H. Loo, J. N. Yao, *J. Phys. Chem. Solids* **1998**, *59*, 1667.
5 C. Bechinger, M. S. Burdis, J.-G. Zhang, *Solid State Commun.* **1997**, *101*, 753.
6 C. O. Avellaneda, L. O. S. Bulhões, *Solid State Ionics* **2003**, *165*, 117.
7 X. Chen, Y. Lin, *J. Sol-Gel Sci. Technol.* **2005**, *36*, 197.
8 S. Katayama, N. Yamada, K. Kikuta, M. Awano, *J. Ceram. Soc. Jpn.* **2006**, *114*, 114.
9 T. He, J. Yao, *Prog. Mater. Sci.* **2006**, *51*, 810.
10 T. Kudo, H. Okamoto, K. Matsumoto, Y. Sasaki, *Inorg. Chim. Acta* **1986**, *111*, L27.
11 K. Itoh, K. Yamagishi, M. Nagasono, M. Murabayashi, *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 1250.
12 P. W. Anderson, *Phys. Rev.* **1958**, *109*, 1492.
13 N. F. Mott, *Philos. Mag.* **1969**, *19*, 835.