Controlling the photochromic properties of tungsten oxide based photochromic composite films using boron-, carbon-, and sulfur-tungstic heteropoly acids

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Boron, carbon and sulfur conjugated heteropoly tungsic-acid (BW-HPA, CW-HPA and SW-HPA) was synthesized using peroxo-iso-poly tungstic acid (W-IPA) and B2O3, CO2 and H2SO4 solutions, and the photochromic composite films were fabricated using these W-IPA, BW-HPA, CW-HPA and SW-HPA as filler and transparent urethane resin as matrix. All the composite films showed reversible photochromic properties (coloring and bleaching), and the spectra of all the composite films showed two broad absorptions with the peaks at 650 and 900 nm. The composite film using SW-HPA showed a high coloring speed and a low bleaching speed, and the composite films using BW-HPA and CW-HPA showed a slight high coloring speed and a high bleaching speed.

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1. Introduction

Tungsten trioxide (WO₃) based films or composites showed a photochromic property,¹⁻⁷ thus the WO₃ based composites have widely been studied. The photochromic properties of WO₃-based composites result in the reduction of W⁶+ in the WO₃ host upon UV–Vis irradiation. In previous investigations, we fabricated WO₃-based photochromic composite films from peroxo-iso-poly tungstic acid [W-IPA, W₁₂O₃₆(O₂)₆]⁸) and transparent urethane resin.⁴),⁵),⁹) Where, W-IPA is soluble in water, methanol and ethanol, enabling easy treatment for synthesis of some devices.

W-IPA is Keggin-like structure, and the structure is close to that of a general dodeca tungstic acid (W₁₂O₃₆⁷⁺). The dodeca tungstic acid can be conjugated with the other elements and forms a heteropoly tungstic acid.¹⁰),¹¹) Thereby, it expected that W-IPA can be also conjugated with the other elements. Figure 1 illustrates a structural illustration of W-IPA and peroxo-heteropolytungstic acid. When the hetero element is conjugated in W-IPA, the hetero element sited at the center of the Keggin-like structure. Where, the ideal x/W ratio is 0.083 in the heteropoly acid. Previously, we prepared phosphorus-tungstic heteropoly acid using W-IPA and P₂O₅, and fabricated composite films (P-W composite) using the heteropoly phosphorus-tungstic acid (PW-HPA) and transparent urethane resin.⁵) A bleaching speed of the P-W composite film was much faster than that of a non-doped WO₃ based composite film. As well as improvement of the photochromic property of the composite film using PW-HPA, it is expected that the photochromic property of the WO₃ based composite films could be controlled using the other heteropolytungstic acids.

Fig. 1. Schematic illustration of (a) W-IPA and (b) the other element conjugated in a W-HPA framework structure.

In this investigation, we carried out a research for two purposes; one is synthesizing heteropoly tungstic acid with the other elements, and the second we fabricate photochromic composite films using the heteropoly tungstic acid to control a photochromic property and evaluate the photochromic property for the resulting composite films.
2. Experimental procedure

2.1 Preparation of W-IPA
Metal tungsten powder (Mitsuw Chemical Co. Ltd., Japan) was dissolved completely in an ice-cooled 15% H2O2 solution with an atomic tungsten concentration of 1 mol/L. After reaction, the excess H2O2 was removed catalytically by using Pt nets. The resulting solution was dried on a rotary evaporator with a 40°C water bath to obtain W-IPA powder as a glassy solid matter. Details of the W-IPA preparation were described in the previous investigations.4,5,9

2.2 Preparation of BW-HPA
W-IPA EtOH solution with 0.1 M was prepared, and B2O3 powder (Wako Pure Chemical Industries, Ltd., Japan) was dissolved into the solution with the B/W ratio of 0.083. The mixture solution was stirred for 2 h at room temperature. The resulting solution was dried on a rotary evaporator with a 40°C water bath, and the BW-HPA powder with yellow color was obtained.

2.3 Preparation of CW-HPA
Excess dry ice (solid CO2) was dissolved in EtOH, and a saturated CO2-EtOH solution was prepared. W-IPA powder was dissolved into the resulting solution, and the solution was stirred for 24 h at room temperature. The solution was dried on a rotary evaporator with a 40°C water bath, and the CW-HPA powder with yellow color was obtained.

2.4 Preparation of SW-IPA
W-IPA aqueous solution with 0.1 M was prepared, and sulfuric acid was dissolved into the solution with the S/W ratio of 0.083. The mixture solution was stirred for 2 h at room temperature. The solution was dried on a rotary evaporator with a 40°C water bath, and the SW-HPA powder with yellow color was obtained.

2.5 Composite film preparation and characterization

The heteropoly-acid solution with a tungsten molar concentration of 0.1 mol/L and liquid-type urethane resin (M-40; Asahi Kasei Chemicals Corp., Japan) were used as starting materials for the formation of the composite films. The urethane resin can be cured by irradiation with UV–Vis light. The precursor solution of 0.2 mL was mixed into liquid urethane resin (3.2 g). The mixture precursor (slurry state) was degassed at 1 kPa for 60 min to remove the dissolved air. Subsequently, the precursor slurry was placed between slide glasses with a film thickness of 1 mm. The precursor was cured for 1 min through UV–Vis irradiation, and the resulting composite films were removed from the substrate glasses. The resulting films were colored because of the effects of the UV–Vis irradiation, so the composite films were placed in a dark room for two days for clarification in order to evaluate the photochromic properties.

The IR transmittance spectra of the heteropoly-acid precursor powders were measured with an infrared spectrometer (FT-IR 660 Plus; Jasco Inc., Japan) as KBr pellets, and the powders were obtained by evaporation of the precursor solution using a rotary evaporator. The photochromic properties of the composite films were measured with a UV–Vis spectrophotometer (UV-1600; Shimadzu Corp., Japan), and a 1 kW high-pressure Hg lamp was used for coloration of the composite films. The microstructure in the composite films was characterized by transmission electron microscopy (TEM, EM-002B; Topcon Corp., Japan).

3. Results and discussion

Each heteropoly-acid was synthesized by the above-mentioned method, and IR measurements were performed to identify the structures of the resulting heteropoly-acid powder samples. Figure 2 depicts the IR spectra for the samples of W-IPA, BW-HPA, CW-HPA, and SW-HPA. Peaks were observed at 870, 980, 1456, and 1623 cm⁻¹ for all the samples, which are attributed to W-O-W, W=O, the OH group in methanol, and the OH group in H2O, respectively.7,9 These results revealed that the Keggin-like structure was maintained in all the samples. The sample using BW-HPA showed an absorption peak at 1195 and 1450 cm⁻¹, which were attributed to the BW heteropoly-acid.12 The sample using CW-HPA showed an absorption peak at 780 and 1350 cm⁻¹, which were attributed to the CW heteropoly-acid and C–O absorption of excess CO2 in the samples. The samples using SW-HPA showed an absorption peak at 1186 and 1063 cm⁻¹, which were attributed to the heteropoly-acid.11 An S–O bond attributing to sulfonic acid was observed at 1115 cm⁻¹ in the SW heteropoly-acid, thus; it assumed that the excess sulfonic acid remained in the SW heteropoly-acid. These results suggested that Keggin-type BW, CW, and SW heteropoly-acid could be synthesized by the above-mentioned methods.

The composite films were fabricated using these heteropoly-acid and urethane resin, and Fig. 3 illustrates the representative UV–Vis spectra of the composite films before and after UV–Vis irradiation. All the films showed a coloring property by UV–Vis irradiation, and the colored film showed broad absorptions with the absorption peaks at 650 and 900 nm.

Figure 4 presents the time dependences of transmittance change on (a) coloring and (b) bleaching for the composite films, and the employed wavelength was 650 nm, that is, the wavelength 650 nm of the remarkable absorption peak of the colored films. Using the coloring properties of the composite films, the reaction rate constants k were estimated, where the estimation method of the reaction rate constants k was described in our previous reports.5,9 The calculated reaction rate constants of the films using W-IPA, BW-HPA, CW-HPA, and SW-HPA were 5.68 × 10⁻², 7.31 × 10⁻², 7.22 × 10⁻², and 9.43 × 10⁻² min⁻¹, respectively. These were described on the Table 1. The coloring speed of the composites using BW-HPA and CW-HPA was slightly faster than that of the composite film using W-IPA, and the coloring speed of the composites using SW-HPA was much faster than that of the composite film using W-IPA. These results suggested that acidity and valence of the additions affected the coloring speed of the resulting composites, increasing acidity of the additions caused increase of the coloring speed of the composites.

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Fig. 2. IR spectra for the W-IPA, BW-IPA, CW-IPA, and SW-IPA.
Bleaching properties of the films were also evaluated using the absorption properties, and the time dependences of bleaching were also plotted on the Fig. 4(b). To compare the bleaching speeds of the films semiquantitatively, we calculated their half-life periods $\tau$ (h), where $\tau$ was considered to be the time required for the film transmittance to change from its initial colored state (obtained after 60 min UV-Vis irradiation) to half of its ultimate value in the bleached state (taken after 120 h in darkness). Table 1 depicts $\tau$ values of the composite films using W-IPA, BW-HPA, CW-HPA, and SW-HPA. The $\tau$ values of the composites using BW-HPA, CW-HPA decreased considerably comparing with that of W-IPA (no-addition. The $\tau$ value of the composite film using SW-HPA was as same as that of W-IPA. The bleaching speed was also affected on acidity and valence of the additions, decreasing acidity of the additions caused increase of the bleaching speed of the composites.

In previous reports, the WO$_3$ based cluster size in the films or composites affected to the photochromic property, and we confirmed the WO$_3$ based cluster size of the resulting composite films. Figure 5 shows TEM bright-field images of the composite films using W-IPA, BW-IPA, CW-IPA, and SW-IPA. The particle sizes of all the composites were about 20–40 nm, and the sizes of all the composites did not depend on the additions. In previous reports on tungsten oxide based photochromic composites, the size of the tungsten oxide clusters affected the coloring or bleaching speeds of the composite films; thus, the photochromic properties of the composite films depend on the cluster size. In the present study, the cluster sizes of the composite

Table 1. The reaction rate constants $k$ and the half-life periods $\tau$ of the composite films

| Filler  | W-IPA | BW-HPA | CW-HPA | SW-HPA |
|---------|-------|--------|--------|--------|
| $k$ (min$^{-1}$) | $5.68 \times 10^{-2}$ | $7.31 \times 10^{-2}$ | $7.22 \times 10^{-2}$ | $9.43 \times 10^{-2}$ |
| $\tau$ (h) | 28.0 | 17.3 | 18.5 | 27.0 |

Fig. 3. Transmittance spectra for the composite films using (a) W-IPA, (b) BW-IPA, (c) CW-IPA, and (d) SW-IPA before and after UV-Vis irradiation.

Fig. 4. The coloring and bleaching properties of the composite films using W-IPA, BW-IPA, CW-IPA, and SW-IPA. The coloring properties were observed by UV-vis irradiation, and the bleaching properties were observed in the dark room.
films did not vary much with the additions. Thus, it was assumed that the acceleration of the bleaching of the composite films was caused by the correlation between the additions and WO₃ host cluster.

4. Conclusion

Boron, carbon and sulfur conjugated heteropoly tungsic-acid (BW-HPA, CW-HPA and SW-HPA) was successfully synthesized using peroxoisopoly tungstic-acid (W-IPA) and B₂O₃, CO₂ and H₂SO₄ solutions. The photochromic composite films were fabricated using these W-IPA, BW-HPA, CW-HPA and SW-HPA as filler and transparent urethane resin as matrix, and all the composite films showed reversible photochromic properties. The composite film using SW-HPA (strong acid) showed a high coloring speed and a low bleaching speed. On the other hand, the composite film using BW-HPA and CW-HPA (weak acid) showed a slight high coloring speed and a high bleaching speed. These results suggested that the acidity of additions affected to the photochromic property of WO₃ based composite films.

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