Vanadium oxide-based photochromic composite film

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V2O5-based composite films were fabricated using peroxy-iso-poly vanadic acid as the filler and transparent urethane resin as the matrix. The size of the V2O5 particles in the films was around 60–80 nm and the fabricated composite films exhibited photochromic properties when irradiated with ultraviolet (UV) light. The composite films displayed multichromism (yellow ↔ green ↔ pale blue) under UV irradiation. The absorption edge of the films shifted to lower wavelengths (Bürrstein Moss effect) with the increase of the coloring degree of the films. Almost all the colors of the composite film bleached when placed in a dark room.

2. Experimental procedure

Vanadium powder (1.0 g, Wako, Osaka, Japan) was mixed with 30%aq. H2O2 solution (100 mL) in an ice bath for 15 h. After reaction, the excess H2O2 was removed catalytically using Pt nets. The resulting orange solution was dried using a rotary evaporator with 60 rpm, placed in a water bath maintained at 40 °C for 1 h, to obtain V-IPA powder.

V-IPA powder was then dissolved in ion-exchanged water to form a vanadium solution, with a final concentration of 0.2 M. The obtained solution (0.15 mL) was mixed with 3.2 g of liquid urethane resin (M-40; Asahi Kasei Chemicals Corp., Japan). The liquid urethane resin was used as the matrix material in the synthesis of the composite films, and it was cured by irradiation with UV light. The precursor mixture (slurry state) was degassed at 1 kPa for 60 min. The precursor was first placed between two glass slides such that a 150 µm thick film could be formed and irradiated with UV light for 5 min before removing it from the glass. The resulting films were pale blue in color because of the effects of the UV radiation and hence, the composite films were placed in a dark room for three days for clarification.

The structure of the V-IPA powder was characterized by X-ray diffraction (XRD) using a Rigaku Miniflex with CuKα radiation. The microstructure and the crystallographic structure of the particles in the composite film was characterized by transmission electron microscopy (TEM, EM-002B; Topcon Corp., Japan) and selected area electron diffraction (SAED, ibid.). The photochromic properties of the films were evaluated at room temperature with a UV-Vis spectrophotometer (UV-1600; Shimadzu Corp., Japan). Throughout the investigation, a 1 kW high-pressure Hg lamp was used for curing the resin and for color manipulation of the composite films. The coloring properties of the films were evaluated by UV irradiation, while the film bleaching properties were observed by placing the films in a darkened room.
3. Results and discussions

A direct reaction between vanadium metal and hydrogen peroxide was carried out and the resulting precursor solution was dried by evaporation to obtain V$_2$O$_5$ powder. Fig. 1 depicts the XRD pattern of the resulting powder. The resulting powder displayed (110), (410), (310) and (600) planes of the V$_2$O$_5$ peaks, thus exhibiting only the (h00) planes. The results were in good agreement with previous studies of V-IPA. The V-IPA (2D-V$_2$O$_5$) powder, thus synthesized, was further used in our study.

Vanadium oxide-based composite films were fabricated using the synthesized V-IPA and the cured urethane resin. Fig. 2 shows the TEM bright field image and the selected area electron diffraction (SAED) image of a composite film. The V$_2$O$_5$ particle size in the composite film was about 60–80 nm and the particles were dispersed homogeneously throughout the film. Using the electron diffraction pattern, the crystallographic structure of the particles in the resulting composite film were confirmed to be V$_2$O$_5$. Photochromic properties of the films were evaluated by UV irradiation. Fig. 3 illustrates the UV-Vis spectra of the composite film before and after UV irradiation and the inset photographs shows the overview of the same. From the overview, it is evident that the initial color of the resultant film was yellow, which color was close to V$_2$O$_5$ film. However, the color of the film changed gradually from yellow to green to pale blue after exposure to UV light and had a weak, but broad absorption spectrum with peak at around 700 nm. After 60 min of UV irradiation the film displayed a higher transmittance in the wavelength region of 1000–1100 nm than the film exposed to 10 min of UV irradiation. Though the colored film bleached when placed in a dark room, complete bleaching did not occur until 48 h. In the previous investigation of V$_2$O$_5$ electrochromism, it was observed that the V$_2$O$_5$ film color changed from yellow ~ green ~ pale blue because of Li ion insertion and the previous results of color changing on the V$_2$O$_5$ electrochromism agreed well with the present investigation. Significantly, the composite film in the present study showed a semi-reversible photochromic property, similar to the electrochromic V$_2$O$_5$ film.

With respect to the electrochromism of V$_2$O$_5$, vanadium valence is electrochemically reduced from “+5” to “+4” and thus the color change is attributed to this change in the valence state. Similar to the photochromism of V$_2$O$_5$, it assumed that change...
in the valence state of vanadium and the change in color of V₂O₅ were caused by UV irradiation. The exact photochromic mechanism has been previously reported with regard to MoO₃-based composite films. Applying the similar theory to V₂O₅-based composite films; the photochromic mechanism can be explained as follows:

\[
\text{V}_2\text{O}_5 \xrightarrow{h^+} \text{V}_2\text{O}_5^+ + e^- + h^+ \\
\text{h}^+ + \text{H}_2\text{O} \text{ (as precursor solvent)} \rightarrow \text{H}^+ + \cdot\text{OH}
\]

\[
\text{V}_2\text{O}_5^+(\text{colored}) + x\text{H}^+ + xe^- (\text{bleached}) \rightarrow \text{H}_x\text{V}_{2-x}\text{O}_5^{4+} \text{O}_5 (\text{colored})
\]

where, * represents exited state, e⁻ is an electron, and h⁺ is a hole. From Fig. 3, it is clear that the absorption edge of the film shifted to lower wavelengths following an increase in UV irradiation time. We estimated the optical band gap, \(E_g\), of the film using a Tauc plot, as shown in Fig. 4. The \(E_g\) of the films before UV irradiation, after 10 min irradiation, and after 60 min irradiation were 2.52 eV, 2.57 eV, and 2.61 eV, respectively. Increasing the UV irradiation time caused an increase in the \(E_g\) of the films (Bürrstein Moss effect). However, in case of electrochromism of V₂O₅ with Li intercalation, an increase in the amount of intercalated Li caused an increase in the carrier concentration in V₂O₅, thus increasing the bandgap of V₂O₅ (Bürrstein Moss effect). It is assumed that the Bürrstein Moss effect is also seen in the current study because there is an increase in the carrier concentration in V₂O₅ due to the generation of photo-induced electrons. For the electrochromism of V₂O₅ films, the intercalated cation quantity in the V₂O₅ host caused the transmittance in the near-IR region to increase or decrease suitably. The transmittance change in the near-IR region at 1000–1100 nm (see Fig. 3) in the present film was also assumed to vary due to increased charge density caused by long time UV irradiation.

In order to evaluate the coloring and bleaching property of the films, time dependent studies on transmittance of the composite film were performed, as shown in Fig. 5. The colored films showed significant absorption around 700 nm and hence, transmittance at 700 nm was studied. Assuming the reaction to be of first order, the reaction rate constant \(k\) can be estimated as follows:

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

where \(A_0\) is the initial absorbance, \(t\) is the passing time and \(A\) is the absorbance at time \(t\). Fig. 6 shows a plot of \(-\ln([A]/[A_0])\) as a function of time. Plots for the coloring reaction were linear and the reaction rate constant of the composite film was calculated to be 0.084 min\(^{-1}\). However, plots for the bleaching reaction were nonlinear, and hence, were not first order reactions with a single rate determining step. The electron mobility in V₂O₅ clusters is assumed to be the rate-controlling factor, returning the electrons from \(V^{4+}\) to the matrix (hydroxyl function) and so on. However, the reaction constants of the bleached films could not be evaluated.

There have been few reports on the photochromism of V₂O₅ thin films or bulk ceramics. Nishio et al. reported the photochromism of V₂O₅ bulk ceramics that were colored by “Ar ion laser irradiation” and bleached by “oxidation at a high temperature of 400 °C”. Wan et al. fabricated V₂O₅ xerogel films by a sol–gel method; the film thickness was less than 10 µm. The V₂O₅ xerogel films exhibited photochromic property because of hydrogen atoms which were detached under the action of light from organic-molecules adsorbed on the “film surface”. However, these reports do not describe the bleaching property. Remarkably, in this study, 130 µm thick V₂O₅-based composite films with reversible photochromic properties were fabricated by just irradiating the films with UV light at room temperature. In addition, when the particle size in WO₃ and MoO₃-based composite film was in the order of sub nanometers, reversible photochromic properties were observed at room temperature. Similarly, the presence of these nanometer size V₂O₅ is considered to be responsible for the photochromic property of the composite film, in the present study. Furthermore, other nano-composite film fabrication methods have

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**Fig. 4** Plot of \((ahv)^2\) versus photon energy for the composite film.

**Fig. 5** The time dependence of transmittance change on coloring and bleaching of the composite film.
been reported.\textsuperscript{17,18} We should elucidate the photochromic properties of V\textsubscript{2}O\textsubscript{5} nano-composites fabricated by various methods in future research.

4. Conclusions

We fabricated vanadium oxide-based composite films with homogeneously dispersed sub-nanometer sized V\textsubscript{2}O\textsubscript{5} particles. The composite films upon irradiation with UV light showed a broad absorption peak at 700 nm. Furthermore, the optical band gap ($E_g$) of the film increased with increase in UV irradiation time because of the corresponding increase in carrier concentration. This increase in $E_g$ is assumed to be due to the Burstein-Moss effect. Moreover, the colored films bleached when kept in the dark. In conclusion, we successfully fabricated vanadium oxide photochromic composite films using V-IPA and urethane resin.

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