Evidence for Visible Light Photochromism of V$_2$O$_5$

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A binary oxide, polycrystalline V$_2$O$_5$, has been demonstrated to exhibit visible-light photochromism virtually for the first time. The oxide turns blue-black upon irradiation with visible laser light (514.5 nm) in air due to photoreduction of V^{5+}, and this effect is confirmed to be irradiation-induced, not heat-induced. This visible-light photochromism is also demonstrated to be repeatable without significant degradation of the effect.

Introduction

Photochromism is a reversible change of a single-chemical species between two states having distinguishably different absorption spectra, induced in at least one direction by irradiation.[1] This mechanism has received considerable attention because of its potential application for novel photofunctional materials.

Although many systems have been found to exhibit photochromism, very few are sensitive to visible light. Visible-light photochromism will be useful in the design of compact storage devices consisting of very small laser diodes that cover a broad wavelength from mid-IR to blue (typically 100–300 μm, not achievable by UV lasers) in which the photochromic material will function within its emission wavelength. Such visible-light photochromism is also expected to have applications in solar energy conversion because photochromism is often accompanied by the decomposition of water.[2] Thus, the development of photochromic materials that are sensitive to visible light is highly anticipated.

Metal-oxide photochromic materials have an advantage over other photochromic materials in that they are highly resistant to corrosion and heat. However, to the best of our knowledge, no binary oxides have been identified as exhibiting visible-light photochromism. The discovery of a binary oxide, the simplest oxide material, that features visible-light photochromism will greatly encourage development of devices based on photochromic materials. In this paper, we present evidence for visible-light photochromism of V$_2$O$_5$, which has an energy gap in the visible range (560–580 nm).[3] This is virtually the first report of visible light photochromism in binary oxides.

Experimental Section

V$_2$O$_5$ (99.99%) powder was obtained commercially. The powder was ground and pressed into a 1-mm-thick disk under a load of 20 MPa. The disk sample was then sintered at 500 °C for 15 h under flowing O$_2$ to remove adsorbates and to completely oxidize the V$_2$O$_5$. The sample had a density of 1.9 g/cm^3.

A continuous wave (CW) argon ion laser (514.5 nm) was used as the light source for inducing photochromism. All samples were irradiated in air at 0.5 mW with a spot diameter of 1 μm. The optical properties of the sample were examined using a conventional optical microscope and a diffuse reflectance microscope consisting of a 150-W lamp, a single-stage spectrometer, and a CCD multichannel detector. The field size according to the system geometry was 4-μm square; however, the actual field may be larger due to the collection of diffuse-reflected light. Finely ground BaSO$_4$ powder (99.999%) was used as a reference.

Reproducibility of the photochromic effect was evaluated based on the relationship between irradiation time and the intensity of photoluminescence (PL) at around 670 nm excited by the irradiation. PL is a good indicator of reproducibility in this case because the peak intensity changes in response to the electronic states of a material and the measurement of PL does not require irradiation to be interrupted. As the coloration reverts when heated without irradiation, measurement of material properties without interrupting irradiation is quite helpful for quantitative measurement of the coloration. The PL spectra were measured using the spectrometer and detector used for the diffuse reflectance microscope. The exposure time for a single measurement was 0.5 s.

Results and Discussion

An optical micrograph of the polycrystalline V$_2$O$_5$ sample after illumination for 60 min is shown in Figure 1a. The irradiated area turned blue-black. As lower valence vanadium oxides are known in general to appear blue or black,[4] and there are no other elements present, this coloration is attributed to the reduction of V^{5+}.

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(1) Brown, G. H. in *Photochromism*; Brown, G. H., Ed.; Wiley-Interscience: NewYork, 1971.

(2) Bechinger, C.; Oefinger, G.; Herminghaus, S.; Leiderer, P. *J. Appl. Phys.* **1993**, *74*, 4527.

(3) Kenny, N.; Kanneburf, C. R.; Whitmore, D. H. *J. Phys. Chem. Solids* **1966**, *24*, 1237.
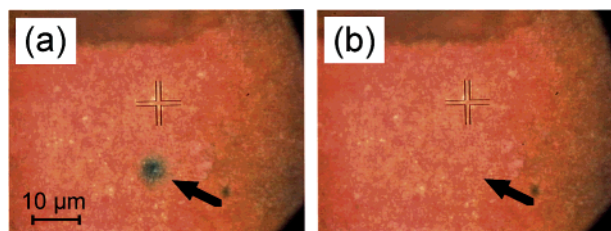
Figure 1. Optical micrographs of polycrystalline V₂O₅ after (a) irradiation for 60 min and (b) subsequent heating at 400 °C for 10 min. Target area is indicated by the arrow.
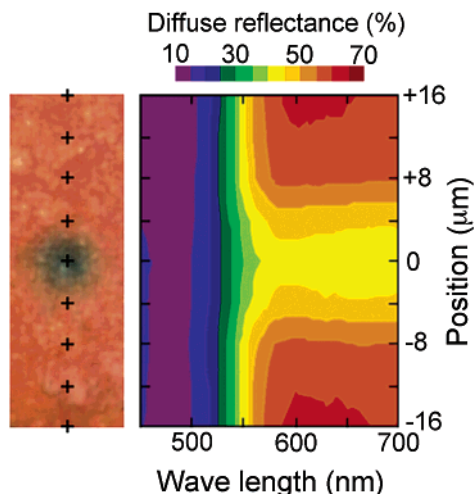

Figure 2. (Left) Optical micrograph of the blue-black spot of V₂O₅. (Right) Microdiffuse reflectance spectra for spot area corresponding to the measured points (+) on the optical micrograph.

The blue-black coloration was completely reverted by subsequent heating at 400 °C for 10 min, as shown in Figure 1b. After heating, the color change could be induced in the same region as the previous change. Microdiffuse reflectance spectra collected at and around the blue-black spot are shown in Figure 2. It was found that diffuse reflectance below the energy gap drops in the blue-black area. Similar spectral changes are observed when V₂O₅ is reduced by oxygen depletion[5] or lithium doping,[6] supporting the notion that the blue-black coloration shown in Figure 1a is due to reduction of V^{5+}.

As photochromism is often confused with thermochromism, it is important to strictly distinguish these two mechanisms. However, because heat is generated as a result of light absorption, verification of photochromism cannot be made based simply on the observation of a color change. It may also be argued that the effect is photoinduced thermochromism, as it is known that V₂O₅ tends to lose oxygen with increasing temperature.[7]

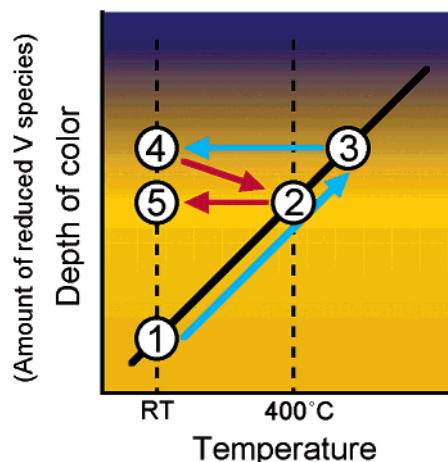Thermochromism occurs as indicated in the model in Figure 3. If the irradiation heats the sample to more

Figure 3. Model for light-induced thermochromism and bleaching of V₂O₅. Background color of the figure represents the color of the sample. Solid black line denotes total abundance of lower valence V species in thermal equilibrium, and blue and red arrows represent coloration and discoloration routes as described in the text. If the irradiation heats the sample to more than 400 °C (state 3), the coloration shown in Figure 1a can be explained by a light-induced thermochromic model.

than 400 °C, the sample is thermodynamically reduced as a result of the temperature rise. Removal of the irradiation allows the sample to cool rapidly, effectively fixing the reduced state (route 1 → 3 → 4). When the reduced sample is heated to 400 °C and allowed to equilibrate, the sample assumed the coloration characteristic of the material at 400 °C, which can again be fixed by rapidly cooling the sample to room temperature (route 4 → 2 → 5). Laser-induced coloration based on this thermochromic model is actually observed in WO₃.[8]

The sample was treated in two different ways to refute the possibility of thermochromism, as shown schematically in Figure 4. In the first treatment (Figure 4a), the sample was heated rapidly to 400 °C and held at that temperature while the sample was irradiated for 60 min. Irradiation was then cut off and the sample was cooled rapidly to room temperature. In the second treatment (Figure 4b), the sample was irradiated for 60 min at room temperature, then irradiation was ceased, and the sample was heated rapidly to 400 °C and maintained at that temperature for 30 s before being rapidly cooled to room temperature.

The coloration routes expected for thermochromism are shown in Figure 4c. If the color change is due to light-induced thermochromism, the coloration produced by the first treatment should be deeper than that by the second treatment because the sample in the first treatment is heated by both conduction and irradiation, and the first treatment does not include bleaching by heating after irradiation. It should also be noted that the irradiated area in the second treatment must be heated to more than 400 °C if thermochromism is assumed, although the temperature will still be lower than that in the first treatment.

Optical micrographs of polycrystalline V₂O₅ after these two treatments are shown in Figure 5. The

(4) Clark, R. J. H. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeleus, H. J., Nyholm, R., Trotman-Dickerson, A. F., Eds.; Pergamon: Oxford, 1973.
(5) Ramana, C. V.; Hussain, O. M.; Srinivasulu Naidu, B.; Reddy, P. J. *Thin Solid Films* **1997**, *305*, 219.
(6) Ashrit, P. V.; Benaissa, K.; Bader, G.; Girouard, F. E.; Truong, V.-V. *Solid State Ionics* **1993**, *59*, 47, and references therein.
(7) Dziembaj, R.; Piwowarczyk, J. *J. Solid State Chem.* **1977**, 21, 387. Dziembaj, R. *J. Solid State Chem.* **1978**, *26*, 159.

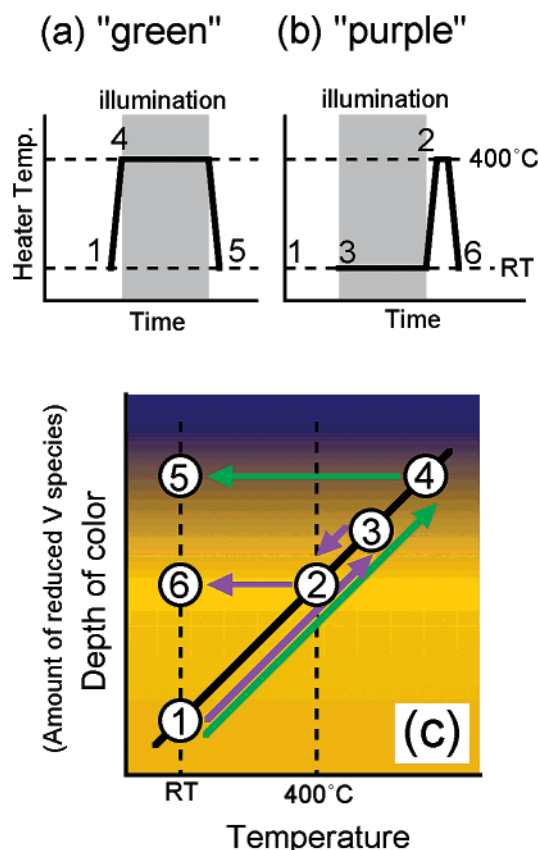(8) Zhao, Y.; Feng, Z. C.; Liang, Y.; Sheng, H. W. *Appl. Phys. Lett.* **1997**, *71*, 2227.

Figure 4. Model for light-induced thermochromism and bleaching of V_2O_5. (a,b) Schematics of two treatment methods to disprove the light-induced thermochromic model. (c) Routes of the two treatment methods assuming light-induced thermochromism. The numbers in (a) and (b) correspond to those in (c). Background color in (c) represents the color of the sample. If the color change in Figure 1a is due to light-induced thermochromism, the coloration produced by treatment (a) (green arrows in (c)) should be deeper than that by treatment (b) (purple arrows in (c)) because the sample in treatment (a) is heated by both conduction and irradiation and does not include bleaching by heating after irradiation.
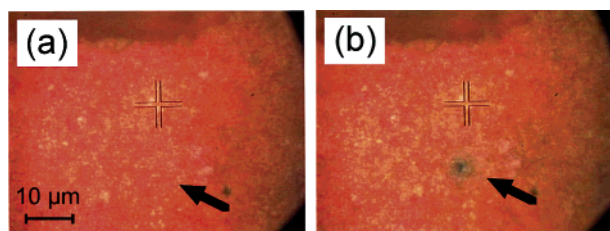

Figure 5. Optical micrographs of polycrystalline V_2O_5 after treatments (a) and (b) in Figure 4. The observed changes are opposite those predicted by the thermochromic model (Figure 4c): no coloration was observed after treatment (a), while significant coloration can be seen after treatment (b).

observed changes are opposite to those predicted by the thermochromic model: no coloration was observed after the first treatment, while significant coloration can be seen after the second treatment. It is clear that the laser-induced chromism of V_2O_5 is suppressed by heat, confirming that the color change is due to photochromism and not thermochromism. Thus, we have for the first time evidence of visible-light photochromism for a binary oxide.

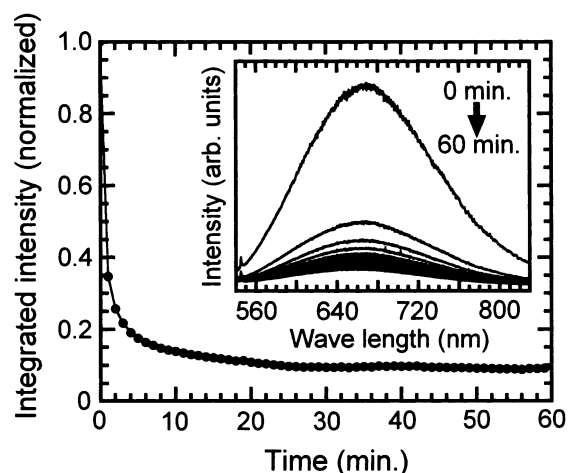The integrated PL intensity from 550 to 840 nm and the change in the PL spectrum during irradiation are

Figure 6. Relationship between irradiation time and integrated PL intensity (550−840 nm). (Inset) Change in PL spectrum during irradiation.
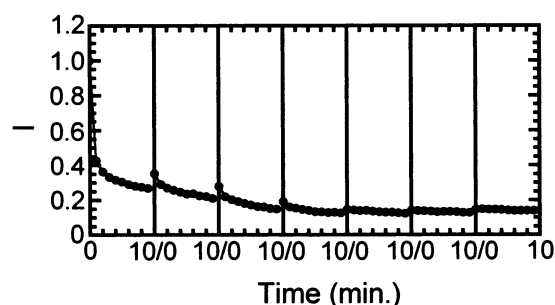

Figure 7. Change in normalized integrated PL intensity (540−840 nm) for repeated irradiation for 10 min followed by resting for 10 min at room temperature.
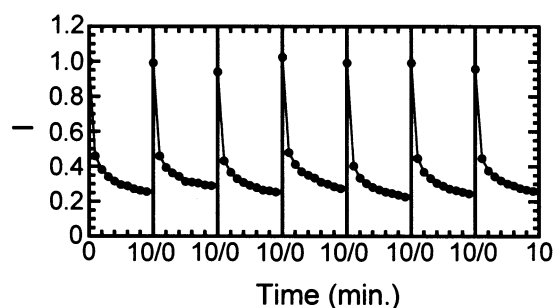

Figure 8. Change in normalized integrated PL intensity (550−840 nm) for irradiation for 10 min at room temperature followed by heating at 400 °C for 10 min without irradiation.

shown in Figure 6. The PL can be seen to be quenched by the irradiation. In general, both temperature increase and chemical reduction can quench PL. Therefore, the PL is expected to be quenched in this case as a result of a laser-induced temperature rise, the formation of lower valence V species with increasing temperature, and the formation of lower valence V species due to photochromism. The photoreduction of V can be used as an index of the coloration. The contribution of photoreduction to the quenching of the PL was evaluated by repeatedly irradiating the sample for 10 min and resting for 10 min at room temperature. As the irradiated area will cool to room temperature during the rest period, any contribution to PL quenching by thermal effects will weaken, allowing the PL intensity to recover during the rest period. However, as shown

in Figure 7, the PL intensity did not recover during the rest period, indicating that the PL quenching in V_2O_5 is primarily caused by photochromism. Therefore, the PL intensity was employed to investigate the reproducibility of the photochromatic effect.

The samples were repeatedly irradiated for 10 min at room temperature and then heated at 400 °C without irradiation for 10 min, and the change in the PL intensity during irradiation was observed. As shown in Figure 8, the PL intensity recovers during rest at 400 °C and decays consistently during irradiation. It appears from these results that this cycle can be repeated without significant degradation of the photochromic effect.

Conclusion

Vanadium oxide V_2O_5 has been confirmed to exhibit visible-light photochromism, representing the first report of visible-light photochromism for binary oxides. In addition, it was shown that the photochromic effect can be repeated without significant degradation of the effect, as indicated by photoluminescence measurements.