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Electronic and atomic structures of gasochromic $V_2O_5$ films

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Abstract – A gasochromic Pt/V$_2$O$_5$ film was fabricated by the sol-gel process and it exhibited excellent color change performance from yellow to gray/black upon exposure to hydrogen gas under ambient conditions. X-ray absorption spectroscopy was employed to study the unoccupied electronic states in detail and to explore the gasochromic effect and its coloration mechanism. Upon injection of hydrogen, gasochromism was revealed to correlate strongly with the change of both electronic and atomic structures. Since the hydrogen supplied an extra electron, the hybridization between vanadium 3$d$ and oxygen 2$p$ was modified, reducing the valence state of vanadium from 5$^+$ to 4$^+$. Linear polarized synchrotron X-rays were utilized to investigate the change in the structural symmetry and the orbital orientation. Along with the electronic structure, the geometric modulation of the VO$_6$ octahedron is crucial to the gasochromic mechanism, as also revealed in this study.

Introduction. – The development of gasochromic materials has drawn much attention in the areas of both academic research and technological application in recent years. The coloration of coated transition metal oxide films is of particular interest. These smart materials with noble metal catalysts can be used in optical hydrogen sensors [1] and gasochromic windows, owing to their transmittance over a wide range [2]. The gasochromic coloration of vanadium oxide films has been observed [3–6]. Vanadium pentoxide has attracted considerable interest as a hydrogen ion intercalation material because of its layered structure [7]. The alkali ions can be intercalated and de-intercalated between the adjacent layers of V$_2$O$_5$. The material is widely applied in energy storage devices, such as lithium batteries [8] and electrochemical super-capacitors [9]. The correlation between the modulation of the structural symmetry and the gasochromic property of vanadium oxide films is still not yet fully understood. Very few reports have adequately described the variations of the electronic and atomic structural properties as functions of hydrogen intercalation.

In this study, V$_2$O$_5$ films were successfully prepared by the sol-gel spin coating method. Gasochromic coloration was found in highly crystalline V$_2$O$_5$ films [10,11]. V$_2$O$_5$ films with a layered structure and orthorhombic Pmmm symmetry exhibited sharp anisotropic absorption spectra. Therefore, the unoccupied states of vanadium (V) 3$d$ and oxygen (O) 2$p$ band structures of these films is of particular interest and the electron-correlation effects of V-O hybridization are worth elucidating by X-ray absorption spectroscopy (XAS). Since the absorption cross-section of X-rays depends on the direction of the $E$ vector with respect to the crystallographic orientations and the orbital orientation of the unoccupied electronic states of transition-metal 3$d$ and oxygen 2$p$ states, information about the electron orbital orientation and structural information can be obtained by making linearly polarized XAS synchrotron radiation measurements. Generally, linearly polarized X-ray absorption yields abundant information on the orbital orientation of the unoccupied states.

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The orbital symmetry is probed by properly aligning the sample (in- and out-of-plane) with reference to the \( E \) vector of the incoming photon. EXAFS (extended X-ray absorption fine structure) is a powerful tool for local structural characterization.

**Experimental.** – The precursor sols for the preparation of \( V_2O_5 \) thin films consisted of a mixed solution of \( V_2O_5 \) powder, hydrogen peroxide, acetic acid, 95% ethanol and DI-water. Glass substrates with dimensions of \( 2.5 \times 2.5 \times 0.12 \text{ cm}^3 \) were spin-coated with the precursor sols at a speed of 2000 rpm for 20 s. The film was dried at 80 °C for one hour and then annealed at 200 °C for two hours to obtain high-quality films. The prepared film had a thickness of around 625 nm, as measured using a scanning electron microscope (SEM) (fig. 1(a)). The film was colored and bleached by exposure to hydrogen gas. A thin layer (2 nm) of Pt as catalyst was deposited on the back surface of the films to form Pt(2 nm)/\( V_2O_5 \)/Glass. Hydrogen gas is dissociated on the Pt catalyst into H atoms, which diffuse into, and color, the underlying \( V_2O_5 \) film. The quality of the sample was characterized using X-ray diffraction (XRD) and energy dispersive spectrometry (EDS). XRD was carried out at BL01C2 with a photon energy of 16 keV (\( \lambda = 0.774908 \text{ Å} \)) at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. V K-edge XAS were recorded in total fluorescence yield (TFY) mode at beamline BL17C and the \( V_L3,2 \)-edges and O K-edge were collected in total electron yield (TEY) mode at beamlines 20A1. All XAS spectra were normalized to unit step height of the absorption coefficient from well below to well above the edges. All data were collected \textit{in situ} in a vacuum with base pressure less than \( 5 \times 10^{-8} \text{ torr} \) using a simple gas cell, which contained the hydrogen.

**Results and discussion.** – Figure 1(a) shows the typical XRD patterns of the film at low 2\( \theta \) angles of 5°–50°. No peak of the impurity phase was observed in these samples. The broad peaks at 15°–40° correspond to the glass substrate. The well-defined peak at around 7° is the (001) peak of the \( V_2O_5 \) films [12,13]. The XRD and the cross-sectional SEM images shown in fig. 1(a) and (b) reveal that during the coating of the \( V_2O_5 \) film, the film grew along the c-axis with a layered structure. Furthermore, the peaks of the colored \( V_2O_5 \) film are shifted to a 2\( \theta \) value higher than those of the bleached film. This shift reflects a decrease in the lattice constant and a possible distortion of the lattice in the films that had been exposed to hydrogen. Figure 1(c) plots the transmittance curves of the bleached and colored states. The line profiles differ distinctly in the two cases. Similarly, as presented in the inset photographs, the color of the film changed from yellow to black upon exposure to 100% H\(_2\). Figure 1(d) (\( \Delta T = T_{\text{colored}} - T_{\text{bleached}} \), difference between transmittance in bleached and colored states) reveals a strong increase in the transmittance of the colored films from \( \lambda = 550 \text{ nm} \) to \( \lambda = 740 \text{ nm} \) with a maximum gasochromic performance of \( \Delta T \approx 39\% \).

Figure 2 shows the V L\(_{-}\) and O K-edge polarized XAS spectra of the films in bleached and colored states,
along with references. The V L-edge includes two main peaks, which are VL3 peaks (514–521 eV) and VL2 peaks (521–528 eV), which originate in the electron transitions, respectively, from the V 2p1/2 and 2p3/2 energy levels to the V 3d unoccupied states. The O K-edge is located in the energy range from 528 to 550 eV. Generally, many transition metal oxides exhibit MO6 octahedra as the basic building blocks of the crystalline structure. Hence, the O h crystal field 10Dq splits the M d orbitals into t2g and eg states. However, the vanadium atoms in V2O5 are displaced from their ideal positions in the octahedra, which are formed by two apical oxygen and four bridging oxygen atoms. One of the apical oxygen atoms is far from the equivalent site and the interaction along the long V-O axis is rather weak. This arrangement reduces the O h symmetry such that the V2O5 can be more appropriately described as forming a square-based pyramid VO5 as the main block, with one oxygen along the z-direction and four oxygen atoms in the square base. When the metal-ligand bond along the z-direction is stretched, the electrostatic repulsion between the electrons in the orbitals that have a component in the direction of the z-axis and the ligands on the z-axis falls. This gives rise to the C4v crystal field, specified by the Dq, Ds and Dt parameters, t2g (eg) is further split into e and b2 (a1 and b2) states [14,15]. The experimental result closely agrees with the calculation that was done by Mossanek et al. [14], as presented at the bottom of fig. 2. The spectrum of V2O5 is dominated by the 2p33d2L final state configuration, with a relative weight of 69%, whereas the relative contribution of the 2p33d1 final state configuration is approximately 25%.

The VL3,2-edge at normal incidence (ϕ = 90°, E ⊥ ĉ) in the bleached state exhibits multiple features that are consistent with the V2O5 electronic and band structure calculations based on the C4v symmetries [14,15]. The 3d orbital is normally empty in V5+ and the t2g (dxy, dxz, and dyz) and eg (dz2, dxy2−y2, and dzz) bands exhibit multiple scattering in the VL3-edge. At glancing incidence (ϕ = 30°, E // ĉ), the intensity of the L3-edge is lower than that of the spectrum obtained at an incident angle of 90°, implying the anisotropic character of the film. The multiplet structure of the L-edge spectra is usually sensitive to the C4v crystal field splitting. Notably, at the V L3-edge, the spectra depend weakly ϕ, but at the O K-edge, a strong dependence is evident. Theory indicates that, subject to the dipole selection rule Δl = ±1 and Δm = 0, ±1, transitions from s orbitals have a single initial state, m = 0, while those from p orbitals have three...
initial states, \( m = 0, \pm 1 \). The polarization dependences of the absorptions in each of the initial states compensate for each other such that the total polarization dependence of the V L-edge is very weak [16]. This fact explains the weaker dependence of the V L3-edge than that of the O K-edge. Accordingly, the anisotropy in the O K-edge is analyzed in detail below. The insertion of hydrogen causes the film to undergo a color change and its spectral features to exhibit a chemical shift to lower energy as its line shapes become more similar to those of the VO\(_2\) phase. The calculation of the band structure by Hébert et al. suggested that a reduction in valence and a change in the spatial structure influence the crystal-field effect [16]. In the colored state, the spectrum at either \( \varphi = 30^\circ \) or \( 90^\circ \) is less intense than the spectrum at the same angle in the bleached state. This reduction in intensity can be interpreted as a decrease in the number of 3d unoccupied states, which implies an increase in charge in the \( t_{2g} \) state of the \( d \) orbital upon coloration process. The additional electron lowers the charge state of the vanadium ions, causing the main peak of the V L3-edge to shift to a lower energy. The change of the intensity also indicates a modulation in the relative weight of the \( xy \) (in-plane) and \( z \) (out-of-plane) characteristics of the 3d orbital transitions in \( C_{4v} \) symmetry, since the film has a highly anisotropic layered structure. Therefore, the difference between the 3d band splitting in the bleached and colored films is related to the variations in the structural geometry and electronic configuration, which alter the line profile of the polarized XAS spectra.

Figure 2 also shows that the pre-edge features of the O K-edge at 528–534.2 eV exhibit a large change in structural symmetry between the colored and bleached films owing to changes in the hybridization between the oxygen 2p and the vanadium 3d orbital. These multi-feature absorption spectra correspond to the transition from oxygen 1s to 2p\(_x\) or 2p\(_y\) and 2p\(_z\) electronic orbital states [17]. Owing to the hybridization with different orientations of the oxygen 2p and V 3d orbitals in the distorted octahedrally symmetric structure \( C_{4v} \), two broad structures of the pre-edge absorption, separated by about 2.1 eV, are attributable to the \( t_{2g}\)-like (\( \sim 529.4 \) eV) and \( e_g\)-like (\( \sim 531.5 \) eV) structures [15]. In a \( C_{4v} \) crystal field, the \( t_{2g} \) orbital is split into \( e \) (\( d_{xz}, d_{yz} \)) and \( b_2 \) (\( d_{xy} \)) states, and the \( e_g \) orbital is split into \( a_1 \) (\( d_{x^2} \)) and \( b_1 \) (\( d_{z^2} \)) states. Generally, 10\( D_q \) gives the energy splitting between \( t_{2g} \) and \( e_g \) orbitals, whereas 4\( D_s \) + 5\( D_t \) and 3\( D_s \) − 5\( D_t \) yield the energy splits of \( \Delta E_{t_{2g}} \) (\( e \) and \( b_2 \)) and \( \Delta E_{e_g} \) (\( a_1 \) and \( b_1 \)). Hence, the energies of the \( e \), \( b_2 \), \( a_1 \) and \( b_1 \) levels in \( C_{4v} \) symmetry are 6\( D_s \) + 2\( D_t \) − 6\( D_t \), 6\( D_q \) + 2\( D_s \) − 1\( D_t \), −4\( D_q \) + 2\( D_s \) − 1\( D_t \), and −4\( D_q \) − 1\( D_s \) + 4\( D_t \), respectively [14]. The energy separations of these transitions are too small to be resolved in the X-ray absorption spectrum, but they can be identified by the cluster model calculation with a single-particle approximation [14], as shown at the bottom of fig. 2. They are sensitive to the local structure and the atomic species of the nearest neighbors [18]. At a glance, both bleached and colored films yielded significant changes in the relative weights of the \( t_{2g}\)- and \( e_g\)-like structures in the angle-dependence spectra, suggesting the anisotropic character of these films. The lower peak \( \sim 529.4 \) eV is essentially generated by O 2p\(_x\) and 2p\(_y\) contributions to the \( t_{2g}\)-like final state, while the higher \( e_g\)-like peak at \( \sim 531.5 \) eV is associated with orbitals with O 2p\(_z\) character. This result is consistent with the local geometry of vanadyl oxygens, which point along the normal to the \( xy \)-plane. At normal incidence (\( \varphi = 90^\circ \)), \( E \) is parallel to the \( xy \)-plane and electrons are excited to the unoccupied states of O 2p\(_x\) and 2p\(_y\) symmetry that are oriented within the in-plane. The \( t_{2g}\)-like (\( e \) and \( b_2 \) bands) structure of the colored film has a lower intensity than that of the bleached film, indicating the extra electron occupancy due to the incorporation of hydrogen atoms and a slight distortion of the VO\(_5\) pyramid in \( C_{4v} \) symmetry, which corresponds to the variation in the V 3d\(_{x^2-y^2}\)O 2p\(_z\) hybridized band in the O-V-O plane. As the \( \varphi \) angle goes from normal to \( 30^\circ \), \( E \) becomes closer to the z-axis of the film, such that electronic transitions to the unoccupied states of the vanadium 3d \( e_g\)-like band (\( a_1 \) band with \( d_{z^2} \) character) [14] hybridized with O 2p\(_z\) symmetry oriented tended to dominate. Notably, the intensity of the \( t_{2g}\)-like (\( e_g\)-like) structure is lower (higher) in the colored film than in the bleached films, because the orbital symmetry of the 2p\(_z\) state is greater in the colored film. The above results suggest that the changes in orbital orientation are caused by the modification of the lattice structure from the distorted \( O_h \) (\( C_{4v} \)) of the V\(_2\)O\(_3\) thin film in the bleached state to the more symmetrical \( O_h \) of the film in the colored state, as will be discussed in more detail in the section on the EXAFS results.

Figure 3 shows the V K-edge spectra, which are explained by a projection of the local electronic transition from the V inner 1s to the outer 4p state and are sensitive to the local structure as well as the valence states of the central atoms. The spectra exhibit a pre-peak at the photon energy of around 5470.5 eV, resulting from V-O hybridized states, which probes the unoccupied 3d states via the quadrupole transition. The absorption edge in the colored state with inserted H\(^+\) is shifted to lower energy (\( \sim 1.5 \) eV), owing to the transition from 1s to a new final state, as shown in the inset in fig. 3. The position of the absorption edge is related to the valence state. The electron occupies the empty 3d orbital of the colored film and the core level becomes more tightly bound. Extrapolating the energy of the V\(_2\)O\(_5\) (bleached and colored) films from the reference samples yielded a change from the formal charge of V\(^{5+}\) to V\(^{4.1+}\) in the colored state. Moreover, the significant drop in the pre-peak intensity was also caused by the electronic occupation of V 3d (\( t_{2g} \)) state.

As discussed above, local structural information is vital and can be revealed by EXAFS. Figure 4(a) shows the Fourier transform (FT) of the EXAFS k\(^3\)\( \chi \) data at the
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$V$ $K$-edge from $k=2$ to $10\,\text{Å}^{-1}$, which exhibit notable differences in radial distribution between the bleached and colored states. The FT profiles in real space provide direct evidence of the change in the V-O bond length in the first coordination revealed by the FEFF fitting of the results of interactive EXAFS analysis using the ARTEMIS program, as depicted in fig. 4(b). Two V-O split peaks of the first coordination in a strongly distorted VO$_6$ octahedron in orthorhombic $V_2O_5$ are observed in the bleached state [19]. From the curve fitting results, the bond lengths of V-O in the VO$_6$ octahedron (inset in fig. 4(a)) in the bleached state are $O(1)=1.61\,\text{Å}$, $O(2)=1.76\,\text{Å}$, and $O(3)=1.90\,\text{Å}$. The V-O length changes in the colored state to become similar to that of the monoclinic VO$_2$ bond, revealing a V-O bond in the symmetrical $O_h$ with V-O = 1.67 and 1.91 Å, consistent with the calculations of Hébert et al. [18]. Thus, coloration increase the symmetry of the VO$_6$ octahedra in the $V_2O_5$ film. Accordingly, the insertion of hydrogen into colored films changes the structure of the octahedra from strongly distorted symmetric in the bleached state to the more symmetric $O_h$, as shown in the inset in fig. 4(a). This finding is consistent with the above XAS analysis.

**Conclusion.** – In summary, layered Pt/$V_2O_5$ gasochromic films were successfully synthesized by the sol-gel process. Their optical properties revealed excellent gasochromic performance. The polarized XAS measurement of the films in bleached and colored states provided abundant information about the electron-orbital interactions in the films. The electron correlation effect and the orbital symmetries of hybridized unoccupied states before and after exposure to hydrogen gas are also examined. The insertion of hydrogen ions changed the valence of the vanadium ions and lattice structural distortion, which was evident in the local symmetry of the VO$_6$ octahedra. These results concerning gasochromic properties and the electronic/atomic structure may lead to significant improvements in the efficiency of gasochromism.

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