Now You See It

Smart window that modulates the heat and/or light transmission can reduce the energy consumption of buildings. Monitoring their operation with operando X-ray spectroscopic measurements reveals how the electronic and atomic structures of a smart film evolve when turning the knob.

A room with a window letting in light but not heat takes less energy to cool down in summer, but the smart window allowing independent control over its heat/light transmission can save energy all year long. After more than a decade of efforts, the so-called smart windows are making its way to market with its optical transmission adjusted simply by turning the knob or flicking a switch. The way a smart window works is to supply an external stimuli such as UV irradiation, temperature change, electric field, or gas exposure to modulate a glass's optical characteristics.[1] Under a given stimulation, the glass that responses stronger is considered the better candidate for smart windows. However, while the practical applications of smart glass are marching forward, fundamental problems continue to confront scientists. For example, there is little knowledge regarding if and how the atomic/electronic structure of a "glass" would change during its coloration.

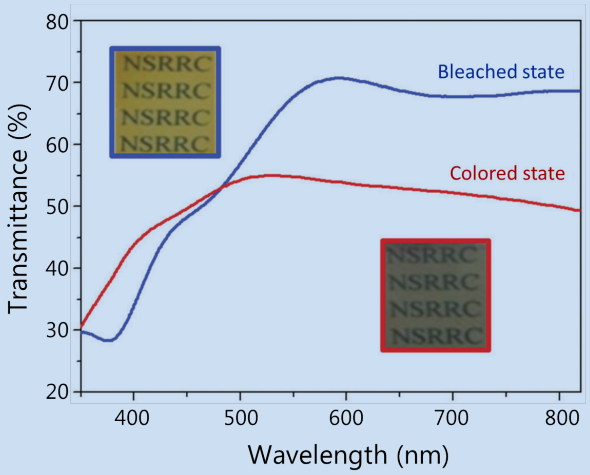

Fig. 1: Optical transmission of V_2O_5 film shows a significant modulation in the range of visible wavelengths (550–800 nm) when exposed to H_2/N_2 (10:90) gas at 760 torr. Photographs shows colors of film in colored and bleached states. [Reproduced from Ref. 2]

Conceptually, the light-matter interaction is where the optical property is rooted. It is therefore a good idea to monitor the evolution of electronic structure in real time so that any modifications introduced by a stimulus can be easily identified. That is exactly what Chung-Li Dong (Tamkang University) and his team did to investigate the gasochromic thin film of vanadium pentoxide (V_2O_5).[2] Using a home-made *in-situ* gas cell on at **TLS 20A1**, Dong's team was able to set up a reaction environment (a mixture of H_2 and N_2 gases at 760 torr) in the ultra-high vacuum condition (in the order of 10^{-10} torr). They acquired the V L-edge X-ray absorption spectra from a sol–gel spin-coated

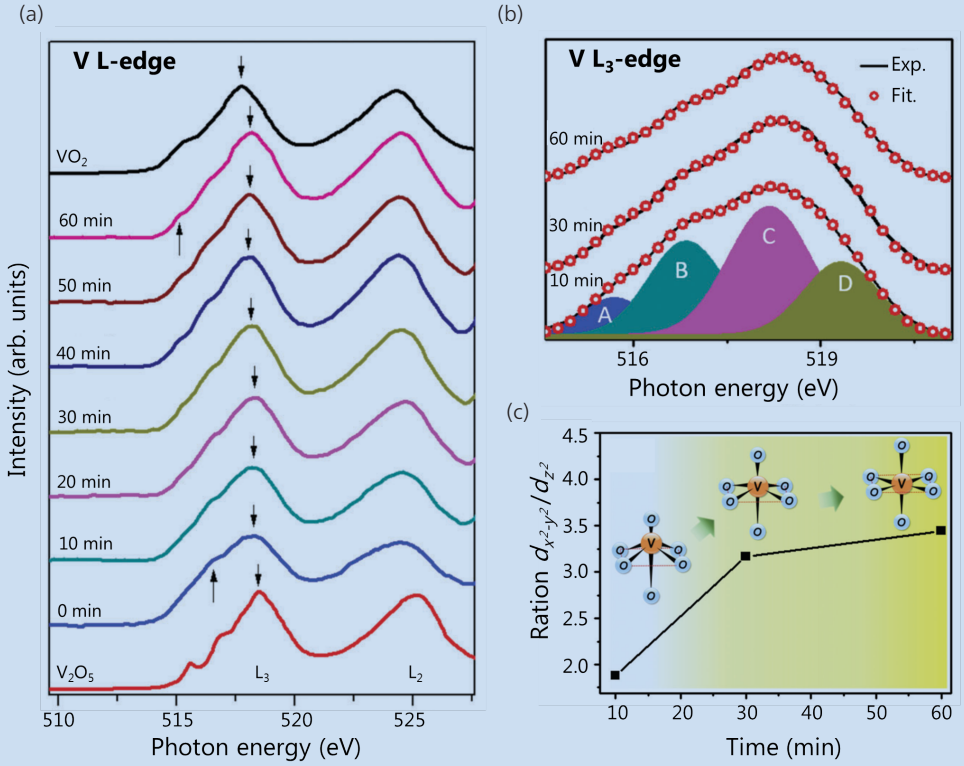

Fig. 2: (a) *In situ* V L-edge XAS spectra recorded in real time with the V_2O_5 film exposed to H_2/N_2 (1:9) gas. (b) Spectral deconvolution using four different 3*d* orbital symmetries. Three spectra taken at 10, 30, and 60 min after gasochromic reaction are presented, (c) $d_{x^2-y^2}/d_{z^2}$ ratios in spectra shown in (b). [Reproduced from Ref. 2]

vanadium oxide (V_2O_5) thin film placed inside the gas cell. V_2O_5 thin film has been used in electrochromic coloration, but little is known regarding if, and how, the atomic/electronic structures of a V_2O_5 thin film were modulated at the same time.

Figure 2(a) illustrates the L-edge spectra taken from gasochromic V_2O_5 under color switching. Two more spectra recorded from VO_2 and V_2O_5 crystals were added in to serve as references. A typical V L-edge spectrum has two broad peaks centered at about 518 and 525 eV that feature the transitions from two spin-orbit split 2*p* states to 3*d* states. Considering the 2*p* orbital is localized on V, the L-edge intensity is directly proportional to the unoccupied *d*-character. As shown in **Fig. 1(a)**, the main peak of the V L_3-edge shifts to a lower energy as the reaction proceeds (marked by arrows). This is an indication of vanadium receiving charge upon hydrogen absorption.

In addition to the change of absorption resonance energy, the profile of a XAS spectrum is informative too. As shown in **Fig. 2(b)**, V L_3 peak is decomposed into four components that each of them corresponds to a specific V 3*d* orbital symmetry (A: $3d_{xz}$ & $3d_{yz}$, B: $3d_{xy}$, C: $3d_{x^2-y^2}$ and D: $3d_{z^2}$). A fit of these spectra recorded at three coloration stages (10, 30 and 60 min) returns with the findings that the coloration leads to different intensity variation among the four sub-components of L_3-edge. In particular, with the increase of intensity at component A (more empty *d* states, weaker hybridization along *z*-axis) and decrease of intensity at component B (less empty *d* states, stronger hybridization at basal plane), it is apparent that coloration leads to a strengthened interaction between V atoms and basal oxygen. This finding is consistent with the intensity variation found between components C and D that count the electron density distributed along all three axes (*x,y,z*). According to **Fig. 2(c)**, the increase of intensity ratio between $d_{x^2-y^2}$ and d_{z^2} is a consequence of the central V atom moving closer to the basal plane after the gasochromic coloration.

In summary, Dong used operando XAS measurements to reveal that, for a V_2O_5 film going through the gasochromic coloration process, there are not only changes on the charge state of vanadium, but also modification on the local atomic symmetry of V_2O_5. The injected hydrogen atoms cause a structural deformation from pyramid-like to octahedral-like symmetry. (Reported by Der-Hsin Wei)

This report features the work of Chung-Li Dong and his collaborators published in Phys. Chem. Chem. Phys. ***19****, 14224 (2017).*

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- XANES, XFS, PSD, XPS, AES
- Materials Science, Chemistry, Surface, Interface and Thin-film Chemistry, Condensed Matter Physics

References

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Novel Route to Effective Doping at Heterostructure Interfaces

Doping carriers across interfaces of thin film heterostructures is an extremely sensitive and important requirement for controlling their emergent properties. Atomically precise termination is now shown to be a novel route to effectively dope superconductor/ferromagnet ($YBa_2Cu_3O_{7-x}/La_{0.7}Ca_{0.3}MnO_3$) heterostructures.

Heterostructures hold tremendous potential for creating emergent properties not seen in single phase bulk materials. Since the discovery of a 2-D (2-dimensional) electron gas at the $LaAlO_3$-$SrTiO_3$ interface,[1,2] there have been several important results revealing unexpected properties of interfaces: controlling a 2D electron gas with a ferroelectric,[3] orbital reconstruction at superconductor-ferromagnet interfaces,[4] *etc*.

In this article, we discuss the work carried out by Ying-Hao Chu (National Chiao Tung University) and his co-workers,[5] which reported on the successful development and observation of termination control for effectively dop-