

Valence Control of Rh Dopants in SrTiO₃ Water-Splitting Photocathodes

Doped transition metal oxides have been widely studied as potentially useful water-splitting photocathode materials for producing hydrogen from water under solar illumination. Rh:SrTiO₃ has received particular attention as it appears to be a reasonably efficient hydrogen evolution photocatalyst. In this project, we used high-resolution XPS to show that the Rh^{4+/3+} valence in the surface layer of epitaxial Rh:SrTiO₃ thin films can be controlled by changing the ambient oxygen pressure during synthesis. The photoresponse of the thin film photocathodes exceeded the efficiency of equivalent powder samples by an order of magnitude.

The phenomenon of photoelectrochemical water splitting has recently drawn renewed interest because the reaction can potentially be used to harvest solar energy and produce renewable hydrogen fuel from water. An ideal photocatalyst has to satisfy several conflicting constraints regarding the band gap, photocarrier dynamics, work function, and surface stability in water. Several transition metal oxides, particularly among the titanates, satisfy most of these conditions, except for the band gap, which tends to be above 3 eV (ultraviolet), while the optimal value is close to 2 eV (visible). One possible solution to the problem is to dope a wide-gap titanate, such as SrTiO₃, with additional cations that form in-gap impurity levels, effectively reducing the band gap of the parent material. Indeed, Rh:SrTiO₃ has been identified as a reasonably efficient hydrogen-evolution photocatalyst with a visible light water-splitting response.

For a hydrogen-evolution photocatalyst, it is important to choose a dopant that reduces the band gap primarily by raising the valence band edge, rather than reducing the energy of the conduction band bottom. Rhodium is a suitable dopant for SrTiO₃ in this regard, as the occupied Rh 4d levels form in-gap states just above the oxide valence band. As illustrated in Fig. 1, however, the precise location of Rh-related in-gap levels is dependent on the Rh valence [1]. The effect of the Rh dopant valence on the electronic structure of SrTiO₃ can

be seen visually as a color change between purple for Rh⁴⁺:SrTiO₃ and yellow for Rh³⁺:SrTiO₃.

In this work, the valence of the Rh dopant was studied in thin film samples, where the oxygen stoichiometry was controlled by changing the ambient oxygen pressure during thin film growth. High-resolution XPS was used to determine the valence state of Rh in the surface layer of the Rh:SrTiO₃ films. As shown in Fig. 2, the Rh valence dependent color change could be successfully reproduced in the thin film samples [2].

In a semiconducting photocatalyst, electron-hole pairs formed by light irradiation are separated and electrons or holes are transferred to the surface due to the presence of an internal electric field formed in the band bending region at the semiconductor-water interface. The electronically active region in the photocatalyst is therefore only a few tens of nanometers thick and it is important to determine the valence of Rh in this surface layer. Although the average valence of a dopant in a thick film or powder can be determined by optical absorption measurements, a surface-sensitive technique is needed to measure the dopant valence in the electronically active surface layer. For this purpose, high-resolution XPS was used at BL-13A to measure the 3d core-level spectra of Rh and determine the Rh valence in the thin film surface layer.

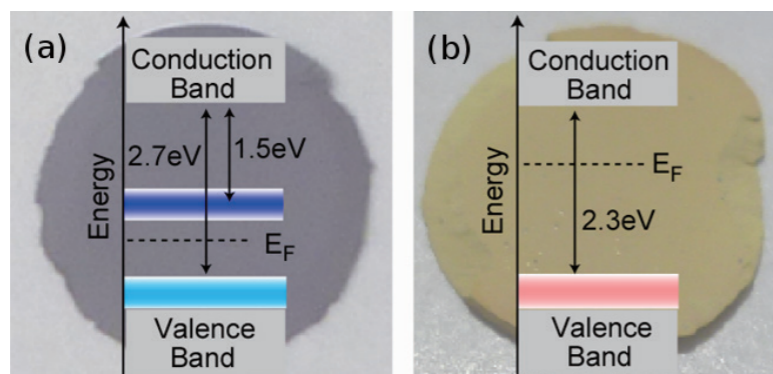


Figure 1: (a) Purple Rh⁴⁺:SrTiO₃ and (b) yellow Rh³⁺:SrTiO₃ pellets. Schematic energy level diagrams are shown for both cases.

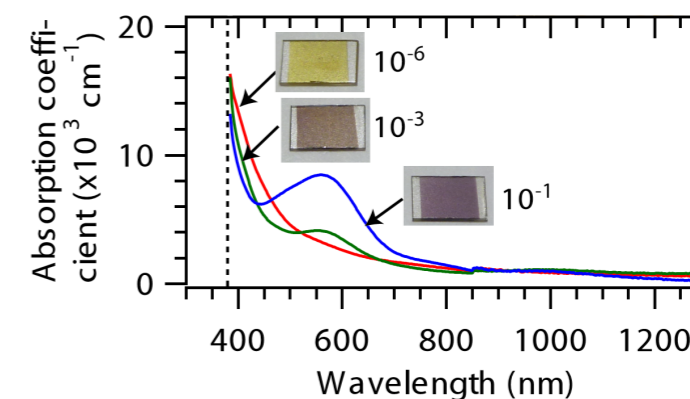


Figure 2: Optical absorption spectra and photographs of Rh:SrTiO₃ thin film samples grown at an oxygen pressure of 10⁻¹ Torr (purple, Rh⁴⁺), 10⁻³ Torr (brown, Rh^{4+/3+}), and 10⁻⁶ Torr (yellow, Rh³⁺).

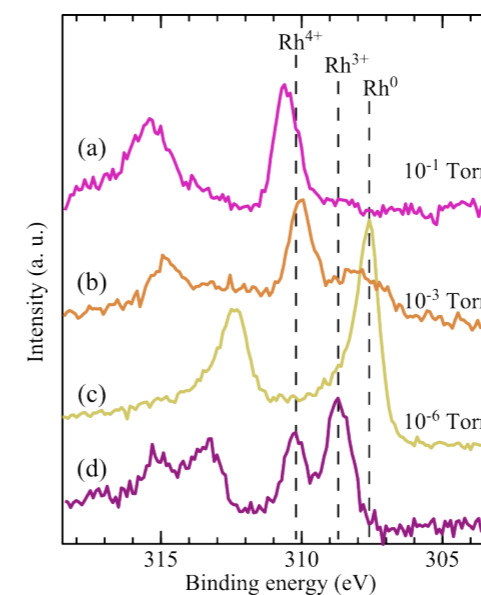


Figure 3: X-ray photoelectron spectra of Rh(5%):SrTiO₃ films grown at 700°C and various oxygen pressures: (a) 10⁻¹ Torr, (b) 10⁻³ Torr, and (c) 10⁻⁶ Torr. The film in (d) was grown at 10⁻¹ Torr and annealed at 10⁻⁶ Torr for 2 h.

The XPS results are shown in Fig. 3, comparing the Rh 3d core-level positions for films grown at various pressures. A pure Rh⁴⁺ valence state was obtained at the highest oxygen pressure and a systematic shift towards reduced species was seen for the lower growth pressures. As shown by plot (c), a reduction to metallic Rh occurs at the lowest growth pressure, which means

that the photocatalytic activity may be affected by the presence of a metallic co-catalyst on the surface. A better way of preparing a film with a stable Rh³⁺ valence is to reduce a film grown at high pressure, as shown by spectrum (d). In this case, no metallic Rh forms at the surface. It should be noted that the presence of metallic Rh may also occur in bulk powder samples, but this cannot be observed by optical absorption spectroscopy. These experiments show that surface-sensitive composition and valence state analysis is essential for accurately correlating the photocatalytic activity of a doped material with the assumed composition of a photocatalyst.

REFERENCES

- [1] S. Kawasaki, K. Akagi, K. Nakatsuji, S. Yamamoto, I. Matsuda, Y. Harada, J. Yoshinobu, F. Komori, R. Takahashi, M. Lippmaa, C. Sakai, H. Niwa, M. Oshima, K. Iwashina and A. Kudo, *J. Phys. Chem. C* **116**, 24445 (2012).
- [2] S. Kawasaki, K. Nakatsuji, J. Yoshinobu, F. Komori, R. Takahashi, M. Lippmaa, K. Mase and A. Kudo, *Appl. Phys. Lett.* **101**, 033910 (2012).

BEAMLINE

BL-13A

S. Kawasaki¹, K. Nakatsuji¹, J. Yoshinobu¹, F. Komori¹, R. Takahashi¹, M. Lippmaa¹, K. Mase² and A. Kudo³ (¹The Univ. of Tokyo, ²KEK-PF, ³Tokyo Univ. of Science)