

## 論文の内容の要旨

論文題目 Evaluation and Enhancement of Photoelectrochemical Activity of SrTiO<sub>3</sub>

Based on a Model Photocatalyst Approach

(モデル光触媒研究を基礎としたSrTiO<sub>3</sub>の光電気化学特性の評価と高効率化)

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### 1. Introduction

Photoelectrochemical water splitting using a photoelectrochemical cell or powdered photocatalysts in water is a potentially useful way to convert solar energy into chemical energy. This artificial analogue of photosynthesis has been widely studied since the discovery of photoelectrochemical properties of TiO<sub>2</sub> in 1972 [1] to create a new sustainable energy infrastructure. Fig.1 illustrates the basic principle of water splitting using an *n*-type semiconductor photoelectrode, where photoexcited holes in a semiconductor (SC) are transported to the photoelectrode surface to oxidize H<sub>2</sub>O to O<sub>2</sub>, while photoexcited electrons flow to a metal counter electrode to reduce H<sub>2</sub>O to H<sub>2</sub>. The photocurrent density ( $J_{ph}$ ) is given by

$$J_{ph} = e J_{ab} \times \eta_{ct} \times \eta_{sr},$$

where  $e$  is the elementary charge and  $J_{ab}$ ,  $\eta_{ct}$ , and  $\eta_{sr}$  are the absorbed photon flux, and the carrier transport and the surface reaction efficiencies, respectively. Stability of semiconductors to photocorrosion is also a critical issue for a practical long-term operation [2].

Various types of semiconductors have been found to show photoelectrochemical activity for water splitting, among them SrTiO<sub>3</sub> is a good starting point for studying fundamental aspects of photocatalysts. Non-doped SrTiO<sub>3</sub> has a cubic perovskite structure (ABO<sub>3</sub>) with a band gap of 3.2 eV and shows stable photocatalytic water splitting activity under ultraviolet (UV) light. Since perovskites can accommodate a diverse selection of dopant elements, doped SrTiO<sub>3</sub> can be used to modify a variety of material properties such as the light absorption spectrum, carrier density, and magnetism. In particular, Rh<sup>3+</sup>- and Cr<sup>3+</sup>-doped and Rh<sup>3+</sup>/Sb<sup>5+</sup>- and Cr<sup>3+</sup>/La<sup>3+</sup>-co-doped SrTiO<sub>3</sub> have been reported to show relatively high photoelectrochemical activity under visible light [3].

Well-defined single crystal substrates and epitaxial thin films can be used as “model photocatalysts” to investigate the detailed physical and chemical properties of photocatalysts by the analytical methods in surface science and semiconductor device physics. In this study, SrTiO<sub>3</sub> single crystal substrates and doped SrTiO<sub>3</sub> epitaxial thin films were used to clarify the mechanism of photo-induced superhydrophilicity and the relationship between the electronic structure (especially the impurity level positions) and photoelectrochemical activity. Theoretical limitations of solar conversion efficiency in doped SrTiO<sub>3</sub> were analyzed and a material design using self-assembled

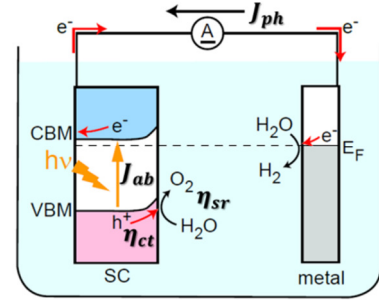


Fig.1 A schematic illustration of a photoelectrochemical cell.

nanopillar structure was proposed for improving the efficiency of solar water splitting.

## 2. Mechanism of Photo-induced Superhydrophilicity

Photocorrosion is a severe problem in most of semiconductors particularly in non-oxides [2,3]. Here, I investigated the water stability of single crystal oxide surfaces and also clarified the mechanism of photo-induced superhydrophilicity. Photo-induced superhydrophilicity is a phenomenon where the hydrophilicity of a surface increases and the water contact angle decreases to nearly  $0^\circ$  by light irradiation. The effect has been known since the original discovery on a  $\text{TiO}_2$  surface in 1997 [3]. However, the mechanism of photo-induced superhydrophilicity has not been fully understood yet. Two competing hypotheses have been proposed; one is the “surface reconstruction model”, which explains the strong hydrophilicity by the appearance of a surface reconstruction induced by a reaction with water under light [5]. The other is a “contamination model”, which considers photocatalytic decomposition of organic contaminants on a surface as the mechanism for the photo-induced increase of hydrophilicity, since the hydrophilicity of most oxide surfaces should be intrinsically very high due to the large surface energy [6,7].

In this work,  $\text{SrTiO}_3(001)(\sqrt{13} \times \sqrt{13})\text{-R}33.7^\circ$  surface which has a  $\text{TiO}_2$  double layer on  $\text{SrTiO}_3(001)$  [8] was used as a model photocatalyst surface to investigate the intrinsic water stability and hydrophilicity of Ti-oxide surfaces. Although water exposure has been reported to destroy the atomic order on most reconstructed surfaces, the  $\text{SrTiO}_3(001)(\sqrt{13} \times \sqrt{13})\text{-R}33.7^\circ$  reconstruction was found to be stable even in water. The presence of a reconstruction-related RHEED pattern proves that the atomic order was not affected by water exposure (Fig.2(a)). The 1.4 nm lattice periodicity of the ideal  $(\sqrt{13} \times \sqrt{13})$  was observed even in water by FM-AFM (Fig.2(b)). DFT-MD simulations indicated that water molecules adsorb molecularly on this surface without dissociation (Fig.2(c)). Even this surface showed superhydrophilicity with  $<4^\circ$  water contact angle when the surface was not contaminated by air exposure (Fig.3), even without exposure to UV light irradiation. This clearly shows that  $\text{SrTiO}_3$ ,  $\text{TiO}_2$ , and other similar oxide surfaces are intrinsically superhydrophilic, favoring the contamination model as the mechanism of photo-induced superhydrophilicity.

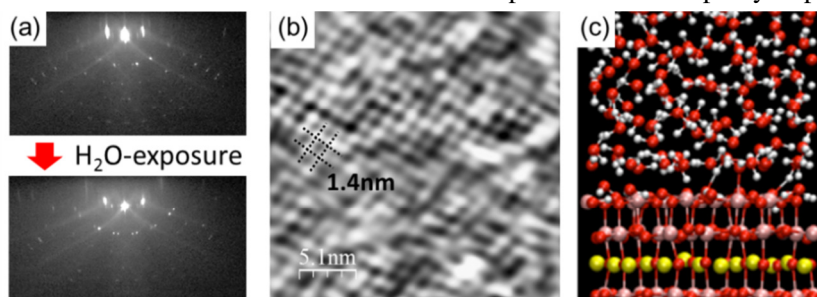


Fig.2 (a) RHEED patterns before and after  $\text{H}_2\text{O}$ -exposure. (b) Topography taken in water by FM-AFM. (c) A snapshot of a DFT-MD simulation of  $\text{H}_2\text{O}$  on a  $\text{SrTiO}_3(001)(\sqrt{13} \times \sqrt{13})\text{-R}33.7^\circ$  slab.

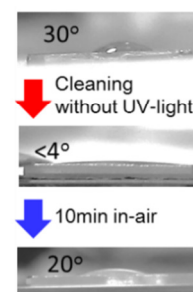


Fig.3 Water contact angle on a  $\text{SrTiO}_3(001)(\sqrt{13} \times \sqrt{13})\text{-R}33.7^\circ$  surface.

## 3. Electronic Structure and Photoelectrochemical Activity of Doped $\text{SrTiO}_3$

Chemical doping of  $\text{SrTiO}_3$  often creates impurity levels in the band gap, reducing the excitation

energy required to generate photocarriers, and inducing the visible light response that is important for utilizing the energy of sunlight. However, the role of different dopants in determining the photoelectrochemical activity of SrTiO<sub>3</sub> has not been comprehensively studied. In this work, I investigated the photoelectrochemical activity and the electronic structure of Rh- and Ir-doped SrTiO<sub>3</sub>. Epitaxial thin film samples were fabricated by pulsed laser deposition (PLD). The electronic structure was experimentally determined by various forms of synchrotron x-ray spectroscopy: XAS, XES, and XPS, measured at SPring-8 and Photon Factory and supported by first-principles calculations using the VASP code with the HSE06 functional (Fig.4). The photoelectrochemical properties were evaluated in a conventional 3-electrode cell. The saturated photocurrent density ( $J_{sc}$ ) can be used to evaluate the performance of a semiconductor independently of the surface properties ( $\eta_{sr}$ ), with  $J_{sc} = e J_{ab} \times \eta_{ct}$  being mostly determined by the bulk semiconductor parameters: the energy gap ( $E_g$ ), absorption coefficient ( $\alpha$ ), mobility ( $\mu$ ), and lifetime ( $\tau$ ). The  $J_{sc}$  measured under 300W Xe-lamp ( $\lambda > 420$  nm) is shown in Fig.4(b). The impurity level position from VB ( $\Delta E$ ) in Fig. 5 affects both light absorption (effective  $E_g$ ) and photocarrier dynamics (typically  $\mu$  and  $\tau$ ). The light absorption density ( $\Delta n$ ) under sunlight increases with increasing  $\Delta E$  (reducing  $E_g$ ), while the photocarrier diffusion ( $\mu\tau$ ) logarithmically decreases. Thus, the photoelectrochemical activity strongly depends on the impurity levels and explains the dopant dependence of the photoelectrochemical activity. These results indicated that both the low light absorption coefficient and the low photocarrier transport efficiency of doped SrTiO<sub>3</sub> significantly limit the photoelectrochemical activity. The discussion is not restricted to doped SrTiO<sub>3</sub> but can be extended to a variety of other semiconductors as well.

#### 4. Photoelectrochemical Activity Enhanced by Self-Assembled Metal Nanopillars

The study of doped SrTiO<sub>3</sub> indicated that the low  $\eta_{ct}$  is a critical problem that needs to be overcome to construct practical efficient photoelectrodes. Nanoscale material design of photoelectrodes is an effective method for improving photocarrier transport. Morphology control and

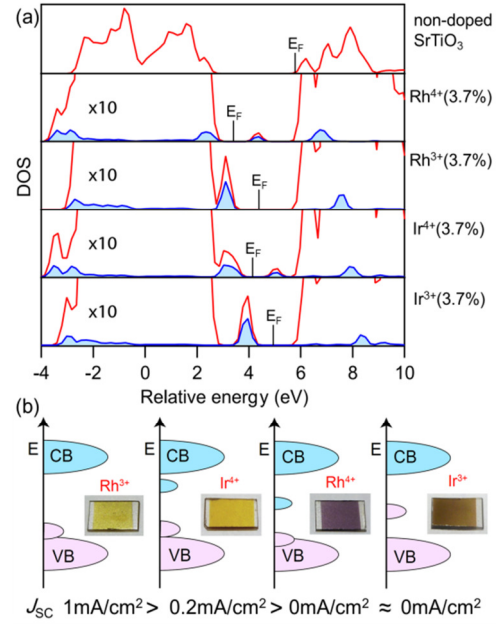


Fig.4 (a) DOS of SrTiO<sub>3</sub>, Rh:SrTiO<sub>3</sub> and Ir:SrTiO<sub>3</sub>. (b) Impurity levels and  $J_{sc}$  of Rh: SrTiO<sub>3</sub> and Ir:SrTiO<sub>3</sub>.

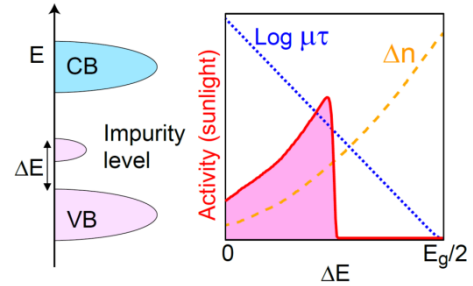


Fig.5 Relationship between impurity level positions and photoelectrochemical activity of doped SrTiO<sub>3</sub> under sunlight.

the use of composite materials have been shown to improve the photocarrier transport from bulk to surface either by decreasing the charge transport distance or by creating additional internal electric field regions [9]. In this study, I propose a new concept of nanoscale design to enhance the photoelectrochemical activity by embedding metal nanopillars in a semiconductor photoelectrode, where carrier transport efficiency is improved by the formation of 3-dimensional Schottky junction surrounding the metal nanopillars. The formation of self-assembled nanopillars by inducing thermodynamic phase separation during thin film deposition has been reported in several thin film systems [10]. In this work, I studied the spontaneous formation of Ir, Pt, Pd, Rh, Au and Ni metal nanopillars in SrTiO<sub>3</sub> films. For the nanopillar formation, metal-doped SrTiO<sub>3</sub> films were deposited by PLD at various temperatures and oxygen pressures. Ir nanopillar formation in a Ir:SrTiO<sub>3</sub> film was clearly observed by scanning transmission electron microscopy (STEM) (Fig.6(a)). Although the incident photon-to-current efficiency (IPCE) is lower than 10% due to the low light absorption, the absorbed photon-to-current efficiency (APCE) exceeded 80% in a wide visible spectral range of 400 to 600 nm (Fig.6(b)), meaning that  $\eta_{ct}$  was successfully enhanced by the formation of the metal nanopillars. The sample also showed long-term operational stability.

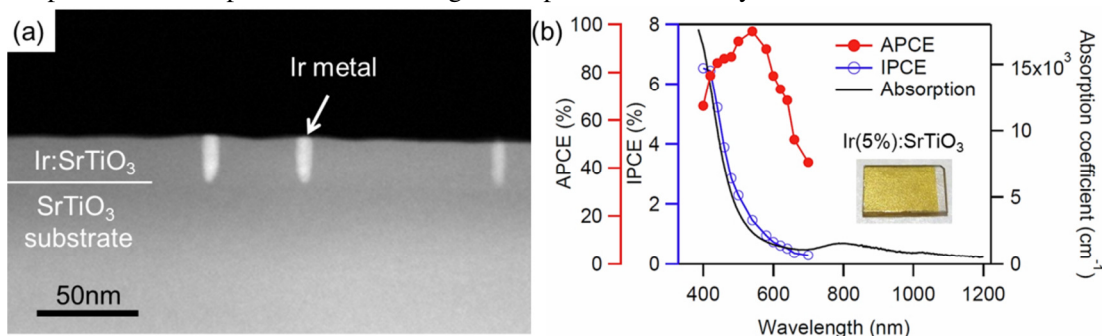


Fig.6 (a) Cross-sectional STEM image of an Ir(5%):SrTiO<sub>3</sub> film on a SrTiO<sub>3</sub>(001) substrate.

(b) APCE, IPCE, and absorption coefficient of Ir(5%):SrTiO<sub>3</sub> with embedded Ir nanopillars.

## 5. Conclusion

Based on the model photocatalyst studies, the mechanism of photo-induced superhydrophilicity and the relationship between the electronic structure and the photoelectrochemical activity of doped SrTiO<sub>3</sub> were clarified. I demonstrated a novel material design of embedding metal nanopillars in a thin film photoelectrode to enhance the photoelectrochemical activity. These results improve our understanding of the fundamental aspects of photocatalysts and will hopefully accelerate the development of practical photoelectrochemical energy systems in the future.

**References** [1] A. Fujishima *et al.*, *Nature* **238**, 37 (1972). [2] J.Manassen *et al.*, *Nature* **263**, 97 (1976). [3] A. Kudo *et al.*, *Chem. Rev.* **38**, 253 (2009). [4] R. Wang *et al.*, *Nature* **388**, 432 (1997). [5] N. Sakai *et al.*, *J. Phys. Chem. B* **107**, 1028 (2003). [6] M. Takeuchi *et al.*, *J. Phys. Chem. B* **109**, 15422 (2005). [7] T. Zubkov *et al.*, *J. Phys. Chem. B* **109**, 15454 (2005). [8] D.M. Kienzle *et al.*, *Phys. Rev. Lett.* **106**, 176102 (2011). [9] Y. Lin *et al.*, *Chem. Phys. Lett.* **507**, 209 (2011). [10] W. Zhang *et al.*, *MRS Bulletin* **40**, 736 (2015).