# **Operando Molecular Science in Liquid–Solid** Interfaces of Finite Thickness

# Division of Advanced Molecular Science (Department of Materials Molecular Science, Electronic Structure)



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#### Education

- 1985 B.S. The University of Tokyo
- 1993 Ph.D. The University of Tokyo

## Professional Employment

- 1989 Assistant Professor, The University of Tokyo
- 1997 Associate Professor, The University of Tokyo
- 1999 Project Leader, Kanagawa Academy of Science and Technology
- 2004 Professor, Kobe University
- 2021 Professor (Cross Appointment), Institute for Molecular Science

#### Awards

- 2001 Young Scientist Award , Catalysis Society of Japan
- 2002 Nano-Probe Technology Award, Nano-Probe Technology Committee, JSPS
- 2003 Technical Award, Surface Science Society of Japan
- 2004 Yazaki Award, Yazaki Foundation
- 2019 Society Award, Japan Society of Vacuum and Surface Science

Keywords

Reactions at Interfaces, Catalysis, Energy-Related Chemistry

We are proud of our international-compatible studies of liquid–solid interfaces, *e.g.* photocatalysts for artificial photosynthesis and lubricants for smooth tribology. Characterization with frequency-modulation AFM, time-resolved ATR-IR spectroscopy, soft X-ray absorption, and microelectrode-based amperometry are being developed. We are pleased to collaborate with researchers in academic and industrial organizations to reveal science behind material conversion and energy dissipation at liquid–solid interfaces.

A new era of molecular science should be revealed in liquid–solid interfaces of finite thickness (Figure 1). The molecular interface is the place of reaction where molecules of interest collide with or interact with other molecules. We need to observe individual molecules there. On the other hand, the molecular interface is connected to liquid and solid. Materials and energy come from/to the two condensed phases, since functional interfaces are always open to the environment. In addition, operando characterization is definitely required for investigating the interface in its working state.

Member Secretary

> ISHIKAWA, Azusa KURITA, Yoshiko





#### Selected Publications

- T. Kosaka, Y. Teduka, T. Ogura, Y. Zhou, T. Hisatomi, H. Nishiyama, K. Domen, Y. Takahashi and H. Onishi, "Transient Kinetics of O<sub>2</sub> Evolution in Photocatalytic Water-Splitting Reaction," *ACS Catal.* 10, 13159–13164 (2020).
- S. Xue, A. Sasahara and H. Onishi, "Atom-Scale Imaging of TiO<sub>2</sub>(110) Surface in Water by Frequency-Modulation Atomic Force Microscopy," *J. Chem. Phys.* **152**, 054703 (7 pages) (2020).
- T. Fujiwara, A. Sasahara, N. Happo, K. Kimura, K. Hayashi and H. Onishi, "Single-Crystal Model of Highly Efficient Water-Splitting Photocatalysts: A KTaO<sub>3</sub> Wafer Doped with Calcium Cations," *Chem. Mater.* 32, 439–1447 (2020).
- S. Moriguchi, T. Tsujimoto, A. Sasahara, R. Kokawa and H. Onishi, "Nanometer-Scale Distribution of Lubricant Modifier on Iron Films: A Frequency-Modulation Atomic Force Microscopy Study Combined with Friction Test," ACS Omega 4, 17593–17599 (2019).
- H. Onishi, "Sodium Tantalate Photocatalysts Doped with Metal Cations: Why Are They Active for Water Splitting?" *ChemSusChem* 12, 1825–1834 (2019).
- H. Imada, K. Kimura and H. Onishi, "Water and 2-Propanol Structured on Calcite (104) Probed by Frequency-Modulation Atomic Force Microscopy," *Langmuir* 29, 10744–10751 (2013).

# 1. Microelectrode-Based Transient Amperometry of O<sub>2</sub> Adsorption and Desorption on a SrTiO<sub>3</sub> Photocatalyst Excited under Water

Oxygen evolution at water–solid interfaces is a key reaction for sustainable energy production. Although some intermediate states have been detected in transient absorption spectroscopy, the O<sub>2</sub> evolution kinetics after the multi-step, four-electron oxidation of water remain unknown. In this study,<sup>1)</sup> transient amperometry with a microelectrode was applied to *operando* O<sub>2</sub> detection over Al-doped SrTiO<sub>3</sub> particles doubly loaded with RhCrO<sub>x</sub> and CoO<sub>y</sub> cocatalysts, an efficient photocatalyst for the overall water-splitting reaction. A platinum electrode (radius: 10 µm) was moved close to the particles in an electrolyte solution. Molecular oxygen was released on the particles, diffused across the electrode–particle gap, and converted to a current on the electrode (Figure 2).

Electrochemical O<sub>2</sub> detection at intervals of 0.1 s, which was thereby achieved, unexpectedly indicated instantaneous O<sub>2</sub> adsorption and desorption in addition to steady, photocatalytic O<sub>2</sub> evolution on the photocatalyst modified under intense light irradiation. We hypothesized that electrons excited in the conduction band were transferred to O2 in water thorough Ti cations neighboring an oxygen anion vacancy on the modified Al-doped SrTiO<sub>3</sub>. The negatively charged O<sub>2</sub> was then bound to the Ti cations. It was neutralized and released when shaded through electron back-transfer to the conduction band. The hypothesized mechanism for O<sub>2</sub> adsorption and desorption was compared with the photoinduced O2 desorption known to occur on anion vacancies of  $TiO_2(110)$ . The microelectrode-based transient amperometry demonstrated here will be applied to many other phenomena at liquid-solid interfaces.



Figure 2. Transient amperometry for detection of molecular oxygen released into water.

# 2. Long-Life Electrons in Metal-Doped Alkali-Metal Tantalate Photocatalysts Excited under Water

Conversion of materials for artificial photosynthesis is

completed in milliseconds or seconds by assembling atoms over semiconductor photocatalysts. Bandgap-excited electrons and holes reactive on this time scale are key for efficient atom assembly to yield the desired products. In this study,<sup>2)</sup> attenuated total reflection of infrared (IR) light was applied to characterize the electronic absorption of long-life charge carriers excited under water. This was a difficult task since water absorbs IR light for probing, while excitation light is absorbed by photocatalyst particles. An attenuated total reflection (ATR) assembly with a diamond prism is key for guiding the excitation light to the volume probed by IR light (Figure 3).

Under excitation, NaTaO3 and KTaO3 photocatalyst particles doped with Sr or La cations absorbed IR light. A broad absorption band appeared with a maximum at  $1400 \text{ cm}^{-1}$ , which was enhanced by the addition of hole scavengers (e.g., methanol and Na<sub>2</sub>SO<sub>3</sub>) and disappeared in the presence of electron scavengers (e.g., FeCl<sub>3</sub>, NaIO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>). This absorption corresponded to the electronic transition of bandgap-excited electrons accommodated in mid-gap states. In anaerobic *n*-decane, the electron absorption was enhanced by the excitation light power, P, with absorbance being proportional to  $P^{1/2}$ . The observed 1/2-order power law suggested de-excitation via recombination of electrons and holes. When the excitation light was stopped, the absorbance decreased as a function of time with a second-order rate law, as expected in the case of recombinative de-excitation. In addition, the 1/2order power law and second-order decay rate law were observed in anaerobic water, with an accelerated decay rate, which was possibly due to a water-related electron-consuming reaction. This study demonstrated that long-life electrons contribute to surface redox reactions over semiconductor photocatalysts for artificial photosynthesis.



**Figure 3.** An attenuated total reflection assembly with a diamond prism for guiding ultraviolet light to the volume probed by IR light.

### References

- T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, *Phys. Chem. Chem. Phys.* 23, 19386–19393 (2021).
- Z. Fu, T. Hirai and H. Onishi, J. Phys. Chem. C 125, 26398–26405 (2021).

## Award

ONISHI, Hiroshi; 2021 HOT PCCP article [T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, *Physical Chemistry Chemical Physics* 23, 19386–19393 (2021)] (2021).