

Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

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Education

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Professional Employment

1989 Assistant Professor, The University of Tokyo
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1999 Project Leader, Kanagawa Academy of Science and Technology
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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
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We are proud of our internationally 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 look forward to collaborating with researchers in academic and industrial organizations to unravel the science behind material conversion and energy dissipation at liquid–solid interfaces.

A new era of molecular science will be revealed at liquid–solid interfaces of finite thickness (Figure 1). The molecular interface is the site of reaction where molecules of interest collide or interact with other molecules. We need to observe individual molecules there. On the other hand, the molecular interface is connected to the liquid and solid. Materials and

energy come from/to the two condensed phases, since functional interfaces are always open to the environment. Operando characterization is absolutely necessary to study the interface in its working state.

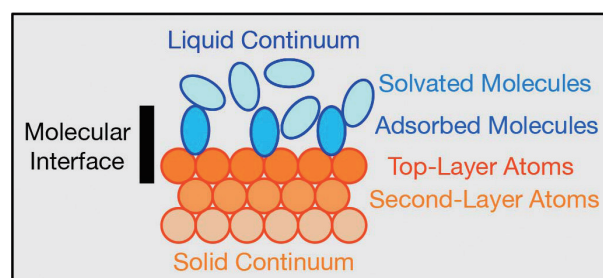


Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- Z. Fu, T. Hirai and H. Onishi, “Long-Life Electrons in Metal-Doped Alkali-Metal Tantalate Photocatalysts Excited under Water,” *J. Phys. Chem. C* **125**, 26398–26405 (2021).
- T. Kosaka, T. Ando, T. Hisatomi, H. Nishiyama, Y. Zhou, K. Domen, Y. Takahashi and H. Onishi, “Microelectrode-Based Transient Amperometry of O₂ Adsorption and Desorption on a SrTiO₃ Photocatalyst Excited under Water,” *Phys. Chem. Chem. Phys.* **23**, 19386–19393 (2021).
- T. Minato, K. Umeda, K. Kobayashi, Y. Araki, H. Konishi, Z. Ogumi, T. Abe, H. Onishi and, H. Yamada, “Atomic-Level Nature of Solid/Liquid Interface for Energy Conversion Revealed by Frequency Modulation Atomic Force Microscopy,” *Jpn. J. Appl. Phys.* **60**, SE0806 (2021).
- T. Kosaka, Y. Teduka, T. Ogura, Y. Zhou, T. Hisatomi, H. Nishiyama, K. Domen, Y. Takahashi and H. Onishi, “Transient Kinetics of O₂ Evolution in Photocatalytic Water-Splitting Reaction,” *ACS Catal.* **10**, 13159–13164 (2020).
- S. Xue, A. Sasahara and H. Onishi, “Atom-Scale Imaging of TiO₂(110) Surface in Water by Frequency-Modulation Atomic Force Microscopy,” *J. Chem. Phys.* **152**, 054703 (7 pages) (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).

1. Infrared and Near-Infrared Spectrometry of Anatase and Rutile Particles Bandgap Excited in Liquid

The chemical transformation of materials is accomplished in milliseconds or seconds by assembling atoms over semiconductor photocatalysts. Bandgap-excited electrons and holes, which are reactive on this time scale, are key to the efficient assembly of atoms to yield the desired products. In this study,¹⁾ attenuated total reflection of infrared and near-infrared light was used to characterize and quantify the electronic absorption of TiO₂ photocatalysts excited under liquid. Nanoparticles of rutile or anatase were placed on a diamond prism, covered with liquid, and irradiated with continuous UV light through the prism. Electrons excited in rutile particles (JRC-TIO-6) formed small polarons characterized by a symmetric absorption band spread over 10000–700 cm⁻¹ with a maximum at 6000 cm⁻¹ (Figure 2). Electrons in anatase particles (JRC-TIO-7) formed large polarons and produced an asymmetric absorption band that gradually strengthened at wave numbers below 5000 cm⁻¹ and weakened sharply at 1000 cm⁻¹. The absorption spectrum of large electron polarons in TIO-7 was compared with the absorption reported in a Sr-doped NaTaO₃ photocatalyst, and it was suggested that excited electrons were accommodated as large polarons in NaTaO₃ photocatalysts efficient for artificial photosynthesis. The UV light power dependence of the absorption bands was observed in N₂-exposed decane liquid to derive the electron–hole recombination kinetics. At light power densities P greater than 200 W m⁻² (TIO-6) and 2000 W m⁻² (TIO-7), the polaron absorptions were enhanced with the absorbance proportional to $P^{1/2}$. The observed 1/2 power law suggested recombination of multiple electrons and holes moving randomly in each particle. Upon excitation with smaller P , the power law order increased to unity. The unity-order power law was interpreted as the recombination of an electron and a hole excited by the same photon. Furthermore, an average lifetime of 1 ms was estimated for electron polarons in TIO-6 when weakly excited at $P = 20 \text{ W m}^{-2}$ to simulate solar light irradiation.

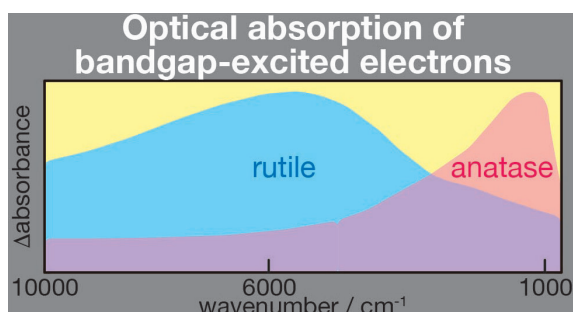


Figure 2. Optical absorption of electrons photoexcited in rutile and anatase TiO₂.

2. Three Dimensional Atom Imaging in KTaO₃ Photocatalysts Doped with Metal Cations

Potassium tantalate, KTaO₃, is a highly efficient semi-

conductor photocatalyst for the overall water splitting reaction. Doping a semiconductor photocatalyst with foreign metal cations typically increases the apparent quantum yield of the splitting reaction. In this study,²⁾ we constructed a single-crystal model of cation-doped photocatalysts that would be suitable for future investigation using advanced surface-sensitive methods. Centimeter-sized (001)-oriented KTaO₃ wafers were doped with Sr or La cations in KCl flux. X-ray diffraction revealed Sr- and La-containing perovskite-structured layers epitaxially covering the bulk KTaO₃. On the Sr-doped wafer, the surface layer lattice was expanded by 2% relative to the bulk lattice. X-ray fluorescence holography was used to determine the three-dimensional short-range ordered structure around the K and Sr cations (Figure 3). Holograms obtained with Sr K α fluorescence confirmed the simultaneous placement of Sr cations in the A and B sites. The placement of the Sr cations in the B sites was supported by the TaO₆ breathing vibration observed in Raman scattering. These experimental results suggest that a KTaO₃-Sr(Sr_{1/3}Ta_{2/3})O₃ solid solution is generated by doping. Two La-containing phases, one with a 2% lattice contraction and the other with a 0.4% expansion, were detected on the La-doped wafer. La L α fluorescence holograms indicated a complex type of doping. The obtained atom distribution around La cations was interpreted by the simultaneous La cation occupancy at the A site, B site and an interstitial site. Local lattice deformation was quantitatively deduced around the La cations occupying the interstitial site. Elemental composition determined by X-ray photoelectron spectroscopy revealed the enrichment of dopant elements on the wafer surface. Nanometer-scale topography observed by atomic force microscopy suggested that doping concentrations should be optimized to obtain flat, crystalline surfaces.

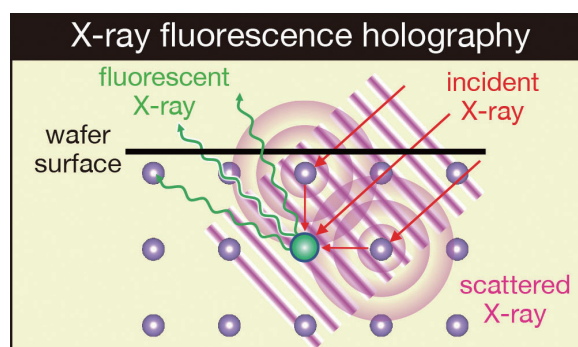


Figure 3. X-ray fluorescence holography.

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- 2) A. Sasahara, K. Kimura, H. Sudrajat, N. Happo, K. Hayashi and H. Onishi, *J. Phys. Chem. C* **126**, 19745–19755 (2022).