

Molecular Mechanism of Oxygen Photoevolution Reaction on TiO₂ (Rutile), Revealed by In-situ Spectroscopic Techniques

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Photo-oxidation of water and organic compounds at TiO₂ or related metal-oxide semiconductor surfaces has been attracting strong attention from the points of view of solar energy conversion (water splitting) as well as environmental cleaning (photodecomposition of dirt or harmful materials). Recently, this reaction has prompted new interest by the finding that doping of the metal oxides with nitrogen, sulfur, carbon, or other elements leads to an extension of the photoactive area from the UV to visible-light region. Further studies, in particular, mechanistic studies are now getting more important to search for highly photoactive and stable metal oxides under visible-light illumination.

For mechanistic studies, the application of in-situ spectroscopic techniques and the use of well-defined surfaces are of key importance. In the present work, we have applied in situ photoluminescence (PL)¹ and multiple internal reflection FTIR (MIR-FTIR) (Fig. 1)² techniques to detect primary intermediates of oxygen photoevolution reaction on TiO₂ (rutile) in contact with aqueous electrolyte solutions.

Figure 2 shows a time course of the FTIR spectrum for a TiO₂ (rutile) particulate film in contact with an acidic aqueous solution with 10 mM Fe³⁺ during UV illumination. We can see that a new peak at 838 cm⁻¹ and a shoulder at 812 cm⁻¹ gradually grow with the UV-illumination time. Detailed investigations of the effects of solution pH, the presence of methanol as a hole scavenger in the solution, and isotope labeling by use of H₂¹⁸O have shown that the 838- and 812-cm⁻¹ bands are assigned to the O-O stretching mode of surface TiOOH and TiOOTi groups, respectively, produced as primary intermediates of the oxygen photoevolution reaction.

A new reaction mechanism (scheme 1) was proposed², on the basis of the above results, for the oxygen photoevolution reaction on TiO₂ (rutile) in aqueous solutions, though it can only be applied to the case of solution pH less than 12. The scheme assumes that the oxygen photoevolution reaction produces a surface peroxy species of a bridge type, TiOOTi, as the first (stable) intermediate, which is followed by formation of surface hydroperoxy species, TiOOH, by protonation. The key of the mechanism is that the oxygen photoevolution reaction on TiO₂ is initiated by a nucleophilic attack of H₂O on a surface hole at lattice oxygen (Ti-O-Ti), not by oxidation of surface hydroxyl groups (Ti-OH) with photogenerated holes. In other words, we can say that the oxygen photoevolution reaction on TiO₂ is caused by a Lewis acid-base mechanism, not by an electron-transfer type mechanism.

We previously concluded the same mechanism as above from studies on directional and face-selective photoetching of TiO₂ (rutile) as well as the appearance of face-sensitive PL. The present mechanism is entirely different from the conventional mechanism of an electron-transfer type and will be helpful for studies to search for photoactive materials under visible-light illumination.

References

- [1] Ryuhei Nakamura, Akihito Imanishi, Kei Murakoshi and Yoshihiro Nakato. *J. Am. Chem. Soc.* **2003**, 125, 7443-7450.
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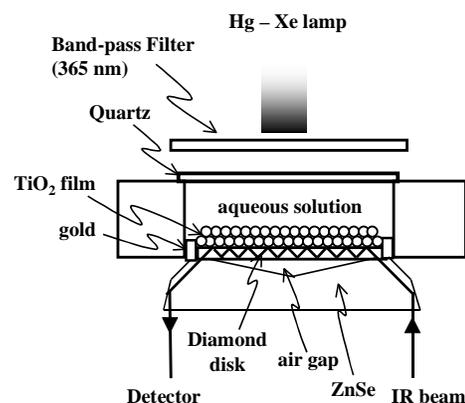


Fig. 1 Schematic illustration of a spectral cell used for in situ MIR FTIR absorption measurements.

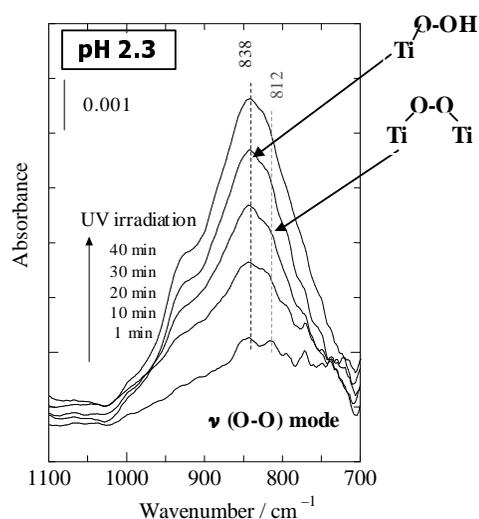
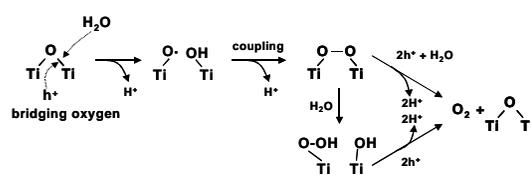


Fig. 2 A time course of the FTIR spectrum for a TiO₂ (rutile) particulate film in contact with an acidic aqueous solution with 10 mM Fe³⁺ during UV illumination.



Scheme 1 Reaction schemes for the oxygen photoevolution reaction on TiO₂