

# Water Splitting and CO<sub>2</sub> Fixation on Visible-Light-Responsive Rutile TiO<sub>2</sub>-based Photocatalysts

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Water splitting and CO<sub>2</sub> fixation using semiconductor photocatalysts are of particular importance from the viewpoint of solar-to-fuel energy conversion toward artificial photosynthesis. To achieve these reactions, it is important to improve both bulk and surface properties of a photocatalyst so as to suppress electron-hole recombination and promote surface redox catalysis. In this talk, recent progress on the development of new photocatalysts that are active for such artificial photosynthetic reactions will be given.

Metal oxides such as TiO<sub>2</sub> are well-known semiconductor photocatalysts, but the wide band-gap restricts their application to solar energy conversion. Since the nitrogen 2p orbital has a higher potential energy than the oxygen 2p orbital, nitrides and oxynitrides are of interest as visible-light-driven photocatalysts [1]. We developed Ta/N-codoped rutile TiO<sub>2</sub> for visible-light-driven water oxidation. TiO<sub>2</sub>:Ta/N powders modified with a RuO<sub>2</sub> cocatalyst were active under visible light up to 540 nm for water oxidation to produce O<sub>2</sub> in the presence of reversible electron acceptors (IO<sub>3</sub><sup>-</sup> or Fe<sup>3+</sup>), while TiO<sub>2</sub>:N exhibited negligible activity. Results of time-resolved infrared absorption spectroscopy revealed that the codoping Ta with N into TiO<sub>2</sub> prolonged the lifetime of photogenerated free electrons, leading to high photocatalytic activity. We demonstrated that overall water splitting into H<sub>2</sub> and O<sub>2</sub> was achieved using TiO<sub>2</sub>:Ta/N, in combination with a H<sub>2</sub>-evolution photocatalyst of SrTiO<sub>3</sub>:Rh and an Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple (Fig.1) [2]. TiO<sub>2</sub>:Ta/N also served as a stable photoanode to oxidize water under visible light, and could be coupled

to not only a H<sub>2</sub> evolution cathode but also a molecular photocathode for CO<sub>2</sub> reduction.

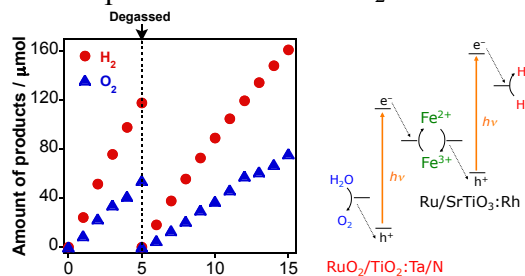


Fig.1 Typical time course of H<sub>2</sub> and O<sub>2</sub> evolution from mixtures of RuO<sub>2</sub>-loaded TiO<sub>2</sub>:Ta/N (50 mg) and Ru/SrTiO<sub>3</sub>:Rh (25 mg) dispersed in an aqueous solution (100 mL) containing FeCl<sub>3</sub> (1 mM) under visible light.

As another TiO<sub>2</sub>-based new photocatalyst, we explored that rutile TiO<sub>2</sub> modified with cobalt hydroxide nanoclusters was capable of harvesting visible light with wavelengths of up to 850 nm, and photocatalyzing water oxidation to produce molecular O<sub>2</sub> (Fig.2) [3]. To our knowledge, this system provides the first case of a photocatalytic material capable of water oxidation upon excitation by visible light up to such a long wavelength, even with the use of earth-abundant elements only.

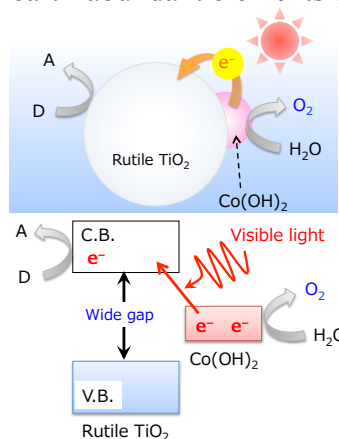


Fig. 2 Water oxidation under visible light using Co(OH)<sub>2</sub>-modified rutile TiO<sub>2</sub>.

## REFERENCES

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