

Development of visible light driven photocatalysts for water-splitting and environmental purification

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Photocatalytic or Photoelectrochemical Water Splitting under Visible Light

Photocatalytic water splitting into H_2 and O_2 using a semiconductor photocatalyst has received much attention recently due to the potential of this method for the clean production of H_2 from water utilizing solar energy. Although a number of metal oxides have been reported to be active photocatalysts for the water-splitting reaction, most only function under ultraviolet (UV) light ($\lambda < 400$ nm) owing to the large band gap energy of the materials (> 3 eV). Because almost half of all incident solar energy at the Earth's surface falls in the visible region ($400 < \lambda < 800$ nm), the efficient utilization of visible light remains indispensable for realizing practical H_2 production based on photocatalytic water splitting. We have recently developed a new type of photocatalytic water splitting system (Fig. 1), mimicking the mechanism of photosynthesis in green plants [1-5]. This system reduces the energy required to drive each photocatalysis process, allowing visible light to be utilized more efficiently than in conventional water splitting system. We have achieved overall water splitting using various visible light responsive photocatalysts, such as $SrTiO_3$ doped with Cr [1], tantalum oxynitrides (TaON or $BaTaO_2N$) [2, 3, 4], and organic dyes [5], which work as a H_2 evolution photocatalyst, combined with tungsten oxide (WO_3) for O_2 evolution in the presence of a shuttle redox mediator such as iodate/iodide. The use of $BaTaO_2N$ or coumarin organic dye was demonstrating to be photoactive at wavelength up to ca. 700 nm. These results demonstrate the potential of a two-step water-splitting system for utilizing a broader band of visible spectrum.

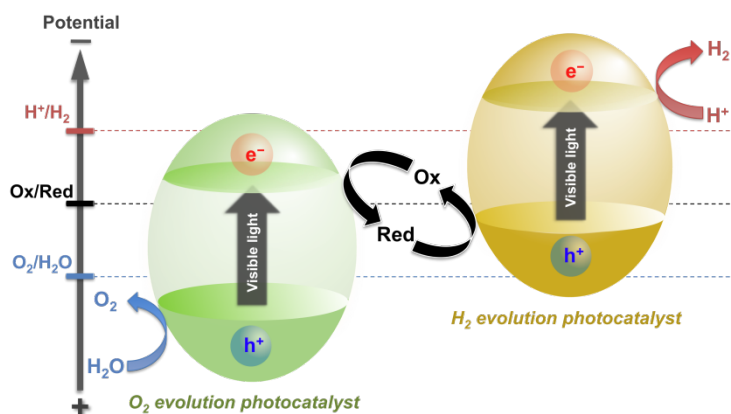


Figure 1. Photocatalytic water splitting under visible light through two-step photoexcitation

We have also demonstrated that the porous oxynitride TaON film electrode prepared on conducting glass (FTO) showed significantly high quantum efficiency (IPCE = ca. 76% at 400 nm at 0.6 V vs. Ag/AgCl) in an aqueous Na_2SO_4 solution, after loading of IrO_2 nanoparticles as a cocatalyst for water oxidation [6]. Overall water splitting into H_2 and O_2 under visible light was demonstrated using an IrO_2 -loaded TaON photoanode combined with a Pt electrode under an externally applied bias (0.6 ~ 1 V).

Highly Efficient Decomposition of Organic Compounds over Platinum-loaded Tungsten Photocatalyst under Visible Light Irradiation

The development of visible-light responsive photocatalysts for environmental purification has also been an active research field in recent years, with most research focused on achieving the efficient decomposition of environmental organic contaminants under sunlight or indoor light. Tungsten oxide (WO_3) has so far been regarded as inactive photocatalyst for the oxidative decomposition of organic compounds in air, due to the much lower level of CB (ca. +0.5 V) compared to the O_2 reduction. Recently, we have reported that crystalline WO_3 loaded with nanoparticulate platinum (Pt) exhibits significantly high photocatalytic activity for the decomposition of various organic compounds under visible light [7, 8]. Figure 2 shows the change in the amount of acetaldehyde (AcH) and CO_2 in the gas phase during reaction over Pt(0.1 wt%)-loaded WO_3 , a commercial titanium oxide (TiO_2 , P25), and a nitrogen-doped TiO_2 (N- TiO_2) under visible light irradiation ($\lambda > 400$ nm). With the onset of visible light irradiation, the amount of AcH in gas phase over Pt- WO_3 decreased rapidly accompanied by an increase in CO_2 generation. Stable CO_2 generation was observed over the conventional visible light-responsive photocatalyst N- TiO_2 , although at a rate much lower than that over Pt- WO_3 . It is known that the potential of multielectron reduction of O_2 is more positive (e.g., $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$, +0.682 V) than for the single-electron processes ($\text{O}_2 + \text{e}^- = \text{O}_2^-$ (aq), -0.284 V; $\text{O}_2 + \text{H}^+ + \text{e}^- = \text{HO}_2$, -0.046 V). It seems reasonable to consider that such multielectron reductions more readily proceed on the surface of Pt that works as electron pool and catalyze O_2 reduction. We actually confirmed the production of H_2O_2 over Pt- WO_3 during the decomposition of aqueous acetic acid. The high activity of Pt- WO_3 is therefore likely to be due to the promotion of multielectron reduction of O_2 on the Pt rather than single-electron reduction, which is generally considered as the main pathway for electron consumption over TiO_2 and N- TiO_2 photocatalysts, as shown in Fig. 3.

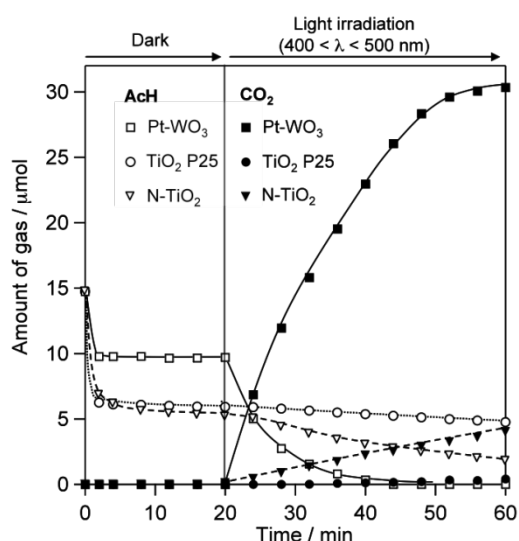


Figure 2. Time course of acetaldehyde decomposition over three photocatalysts under visible light irradiation

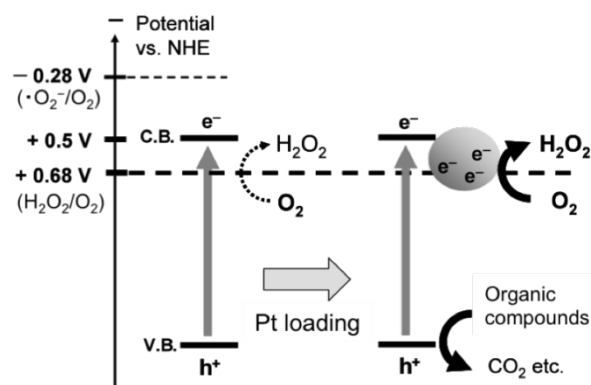


Figure 3. Speculated reaction mechanism on WO_3 and Pt- WO_3 photocatalysts

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Recent publications (selected)

1. **Abe, R.;** Sayama, K.; Sugihara, H., "Development of new photocatalytic water splitting into H₂ and O₂ using two different semiconductor photocatalysts and a shuttle redox mediator IO₃⁻/I⁻" *J. Phys. Chem. B*, 109, 16052-16061 (2005).
2. **Abe, R.;** Takata, T.; Sugihara, H.; Domen, K., "Photocatalytic overall water splitting under visible light irradiation by TaON and WO₃ with an IO₃⁻/I⁻ shuttle redox mediator", *Chem. Commun.*, 3829-3831 (2005).
3. Higashi, M.; **Abe, R.;** Takata, T.; Domen, K., "Photocatalytic overall water splitting under visible light using ATaO₂N (A = Ca, Sr, Ba) and WO₃ in a IO₃⁻/I⁻ shuttle redox mediated system", *Chem. Mater.*, 21, 1543-1549 (2009)
4. Maeda, K.; Higashi, M.; Lu, D.; **Abe, R.;** Domen, K. "Efficient Nonsacrificial Water Splitting through Two-Step Photoexcitation by Visible Light using a Modified Oxynitride as a Hydrogen Evolution Photocatalyst" *J. Am. Chem. Soc.*, 132, 5858-5868 (2010).
5. **Abe, R.;** Shinmei, K.; Hara, K.; Ohtani, B., "Robust Dye-sensitized Overall Water Splitting System with Two-step Photoexcitation of Coumarin Dyes and Metal Oxide Semiconductors", *Chem. Commun.*, 2009, 3577-3579 (2009).
6. **Abe, R.;** Higashi, M.; Domen, K., "Facile Fabrication of an Efficient Oxynitride TaON Photoanode for Overall Water Splitting into H₂ and O₂ under Visible Light Irradiation" *J. Am. Chem. Soc.*, DOI:10.1021/ja1016552 (2010).
7. **Abe, R.;** Takami, H.; Murakami, N.; Ohtani, B., "Pristine Simple Oxide as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-loaded Tungsten Oxide", *J. Am. Chem. Soc.*, 130, 7780-7781 (2008).

8. Sadakane, M.; Sasaki, K.; Kunioku, H.; Ohtani, B.; Ueda, W.; **Abe, R.**, "Preparation of Nano-Structured Crystalline Tungsten(VI) Oxide and Enhanced Photocatalytic Activity for Decomposition of Organic Compounds under Visible Light Irradiation", *Chem. Commun.*, 2008, 6552-6554 (2008).