

Development of Mixed-Anion Semiconductors for Visible Light Induced Water Splitting

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Photocatalytic and photoelectrochemical water splitting using semiconductors has received much attention recently due to the potential for the clean production of H₂ from water utilizing solar energy.^[1] Because almost half of all incident solar energy at the Earth's surface falls in the visible region, the efficient utilization of visible light remains indispensable for realizing practical H₂ production. We have recently developed Z-scheme type water splitting system (see Fig. 1), in which the water splitting reaction is broken up into two stages by using a shuttle redox couple (Red/Ox) in the solution.^[2] Over a H₂-evolving photocatalyst, the photoexcited electrons reduce water to H₂ and holes oxidize a reductant (Red) to an oxidant (Ox). The Ox is reduced back to the Red by photoexcited electrons over an O₂-evolving photocatalyst, where the holes oxidize water to O₂.

Z-scheme type water splitting have been for the first time demonstrated by using a combination of SrTiO₃ doped with Cr and tungsten oxide (WO₃) for H₂ and O₂ evolution, respectively, in the presence of an iodate/iodide (IO₃⁻/I⁻) redox couple.^[3] Introduction of such two-step photoexcitation mechanism can reduce the energy required to drive each photocatalysis process, allowing various visible light responsive semiconductors, even organic dye,^[4] to be utilized more efficiently than in conventional systems. Recently, various mixed-anion compounds such as oxynitrides, oxysulfides, and oxyhalides have been extensively studied as promising photocatalysts, because their valence band maximum (VBM) values are generally more negative than those of conventional oxides, due to the significant contribution of high-energy *p* orbitals of the non-oxide anions (e.g., N-2p, S-3p, Br-4p, and I-5p) mixed with O-2p. Indeed, some tantalum oxynitrides (TaON and BaTaO₂N) have been successfully employed as a H₂-evolving photocatalyst, combined with WO₃.^[5] However, most of mixed-anion compounds suffer from facile self-oxidative deactivation of non-oxide anions by photogenerated holes, thereby imposing surface modifications such as loading some cocatalysts to circumvent the oxidative deactivation. For example, we have demonstrated that the loading of IrO₂ or CoO_x

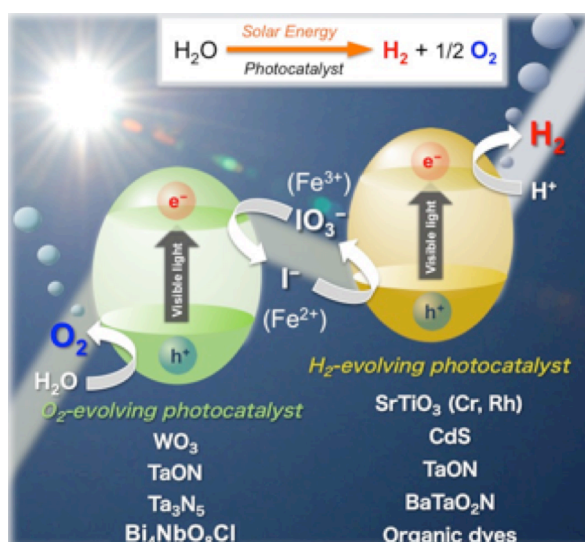


Figure 1 Conceptual scheme for photocatalytic water splitting under visible light through two-step photoexcitation.

nanoparticles as a cocatalyst for water oxidation on such oxynitrides suppress the self-oxidative deactivation to some extent, and thus enable us to employ such surface modified (oxy)nitrides (TaON and Ta₃N₅) as O₂-evolving photocatalysts in Z-scheme systems with (IO₃⁻/I⁻) redox.^[6] Such surface modification has been proven effective for the fabrication of (oxy)nitride-based photoanode. We have demonstrated that porous tantalum oxynitrides (TaON or BaTaO₂N) electrode prepared on conducting substrates showed stable O₂ evolution with significantly high quantum efficiency in an aqueous solution, after loading of effective cocatalyst nanoparticles for water oxidation; enabling water splitting into H₂ and O₂ under visible light with a Pt electrode under an externally applied bias.^[7]

We have recently demonstrated that an oxyhalide Bi₄NbO₈Cl, with single layer Sillen-Aurivillius perovskite structure, can stably and efficiently oxidize water under visible light even without any cocatalyst loading, enabling an efficient Z-scheme overall water splitting with Fe³⁺/Fe²⁺ redox.^[8] It is found that the valence band maximum of Bi₄NbO₈Cl is unusually high owing to highly dispersive O-2*p* orbitals (not Cl-3*p* orbitals), affording the narrow band gap and possibly the stability against water oxidation. The results have suggested that a family of Sillen-Aurivillius oxyhalides can be a promising system to allow an effective band level tuning for establishing efficient and stable water-splitting under visible light.

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References:

- [1] R. Abe, *J. Photochem. Photobiol. C: Photochemistry Reviews* **2011**, *11*, 179.
- [2] R. Abe, *Bull. Chem. Soc. Jpn. (Award account)* **2011**, *84*, 1000.
- [3] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* **2001**, 2416; b) R. Abe, K. Sayama, and H. Sugihara, *J. Phys. Chem. B* **2005**, *109*, 16052.
- [4] R. Abe, K. Shinmei, N. Koumura, K. Hara, and B. Ohtani, *J. Am. Chem. Soc.* **2013**, *135*, 16872.
- [5] a) R. Abe, T. Takata, H. Sugihara, and K. Domen, *Chem. Commun.* **2005**, 3829; b) M. Higashi, R. Abe, T. Takata, and K. Domen, *Chem. Mater.* **2009**, *21*, 1543; c) K. Maeda, M. Higashi, D. Lu, R. Abe, and K. Domen, *J. Am. Chem. Soc.* **2010**, *132*, 5858; d) R. Abe, M. Higashi, and K. Domen, *ChemSusChem* **2011**, *4*, 228.
- [6] a) M. Higashi, R. Abe, A. Ishikawa, T. Takata, B. Ohrani, K. Domen et al., *Chem. Lett.* **2008**, *37*, 138; b) M. Tabata, K. Maeda, M. Higashi, D. Lu, T. Takata, R. Abe, K. Domen et al., *Langmuir*, **2010**, *26*, 9161.
- [7] a) R. Abe, M. Higashi, and K. Domen, *J. Am. Chem. Soc.* **2010**, *132*, 11828; b) M. Higashi, K. Domen, and R. Abe, *Energy Environ. Sci.* **2011**, *4*, 4138; c) M. Higashi, K. Domen, and R. Abe, *J. Am. Chem. Soc.* **2012**, *134*, 6968; d) M. Higashi, K. Domen, and R. Abe, *J. Am. Chem. Soc.* **2013**, *135*, 10238.
- [8] H. Fujito, H. Kunioku, D. Kato, H. Suzuki, M. Higashi, H. Kageyama, and R. Abe, *J. Am. Chem. Soc.* **2016**, *38*, 2082.