Osamu Tomita

Graduate School of Engineering, Kyoto University
Assistant Professor

tomita.osamu.6s@kyoto-u.ac.jp

http://www.ehcc.kyoto-u.ac.jp/eh41/home/abe/index.html

Research keywords: Redox mediator, Transition metal-substituted polyoxometalate, Two-step water splitting, Hydrogen production

Transition Metal substituted Polyoxometalate as an Effective Shuttle Redox Mediator in Z-scheme Water Splitting into H2 and O2 under Visible Light

Water splitting systems based on two-step photoexcitation, so-called Z-scheme systems, have recently been developed and proven as a promising approach to harvesting a wider range of visible light,[1,2] because the water splitting reaction is separated into two parts, i.e., H_2- and O_2-evolving systems. Although the introduction of Z-scheme systems enables us to employ various visible-light responsive photocatalysts, the choice of redox has been limited to simple ion couples such as IO_3^-/I^- and Fe^{3+}/Fe^{2+}. This is mainly due to the problems with mismatching redox potentials and/or irreversibility presented by other materials. Therefore the suitable properties of redox couple for Z-scheme water splitting is still unclear in this research field, and also the development of new redox couples is strongly desired in order to widen the available choice of Z-scheme photocatalyst materials and achieve highly efficient water splitting under visible light. Here, we have paid attention to the use of transition metal-substituted-polyoxometalates,[3] most of which are known to exhibit reversible redox behavior derived from valence differences between the incorporated transition metals, as effective shuttle redox mediators. We have recently reported a new Z-scheme water splitting system using a polyoxometalate as a redox mediator; the use of a Mn-substituted silicotungstate or Mo-substituted one ($K_6[SiW_{11}O_{39}Mn^{II}(H_2O)]$ or $K_4[SiW_{11}O_{40}Mo^{VI}]$) with appropriate photocatalysts enabled a stoichiometric evolution of H_2 and O_2 under visible light.[4, 5]

In the present study, various kinds of metal substituted polyoxometalate will be prepared and employed as redox mediator between the two photocatalysts in order to obtain the knowledge toward the preparation of redox mediator with suitable properties for efficient Z-scheme water splitting.

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