Design of metal-to-metal charge transfer chromophores for visible light activation of oxygen evolving Mn oxide catalysts in a polymer film

Developing effective solar to energy conversion system is highly demanding for sustainable society, and one of the challenges is the management of the charge transfer between photo-absorption center and catalysts. In this work, to construct photo-responsive unidirectional charge transfer units for the activation of oxygen-evolving manganese oxide (MnOₓ) catalyst, metal-oxide nanoclusters consisting of cerium (Ce³⁺) or cobalt (Co²⁺) ions and Keggin-type polyoxotungstate (PW₁₂O₄₀³⁻) were synthesized in a polymer matrix as visible-light-absorbing chromophores. The utilization of the polymer matrix enabled the molecularly-dispersed PW₁₂O₄₀³⁻ states and was advantageous to achieve product separable energy conversion systems. The reaction of PW₁₂O₄₀³⁻ with Ce or Co ions in the polymer matrix generated the new broad absorption tails extending from UV to visible region assignable to metal-to-metal charge transfer (MMCT) transitions of oxo-bridged binuclear W⁶⁺–O–Ce³⁺ and W⁶⁺–O–Co²⁺ units. Although visible light irradiation of the polymer membrane having W⁶⁺–O–Co²⁺ units generated negligible photocurrent, a clear anodic photocurrent response assigned to photo-induced W⁶⁺–O–Co²⁺ → W⁵⁺–O–Co³⁺ transition was observed after the coupling of MnOₓ catalysts to W⁶⁺–O–Co²⁺ units. This finding demonstrated that the generation of anodic photocurrent is derived from the activation of MnOₓ catalyst by the photo-generated Co³⁺ through confined W⁶⁺–O–Co²⁺ linkages. The system in this work based on POM and polymer, and its synthetic method provide us a novel methodology to develop artificial photosynthetic systems with spatially and energetically-optimized components.

Recent Publications


Biography

Akira Yamaguchi received his Doctor of Engineering degree at the University of Tokyo in 2015 for the work on functionalization of metal-oxide and sulfide minerals toward efficient multi-electron transfer catalysis with abundant elements under the direction of Prof. Kazuhito Hashimoto. After his Postdoctoral research in Dr. Ryuhei Nakamura’s laboratory of RIKEN from April 2015 to March 2016, he joined Tokyo Institute of Technology as an Assistant Professor. His particular field is Electrochemistry and his research interest includes the development of catalysts and the primordial carbon fixation on the Earth. Recently, he developed MnOₓ-based water oxidation catalysts inspired by the natural photosynthesis. Now he is aiming at the solar to chemical energy conversion system, called artificial photosynthesis, and his experience in developing water oxidation catalysts will contribute to this research fields.

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