Visible Light Driven Z-scheme Water Splitting with Transition Metal Substituted Polyoxometalates as Shuttle Redox Mediators

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Abstract: Water splitting systems based on Z-scheme mechanism have been developed and proven as a promising approach to harvesting a wider range of visible light. In the present study, V-substituted silicotungstate (K₅[SiW₁₁O₃⁹V³O], denoted as SiW₁₁V) was prepared and employed as redox mediator to pursue the availability of polyoxometalate. The SiW₁₁V/SiW₁₁IV was confirmed to function as electron donor in H₂-evolution system or as electron acceptor in O₂-evolution system. The SiW₁₁V/SiW₁₁IV was revealed to function as effective shuttle redox mediator between the two photocatalysts under visible light irradiation.

1. Introduction

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 because the water splitting reaction is separated into two parts, i.e., H₂- and O₂-evolving systems. Although the introduction of Z-scheme systems enables us to employ various visible-light responsive photocatalysts, the choice of simple redox ion couples for use in Z-scheme has been limited to simple ion couples such as IO³⁻/I⁻ and Fe³⁺/Fe²⁺. This is mainly due to the problems with mismatching redox potentials and/or irreversibility presented by other materials. The development of redox couples with appropriate redox potentials and sufficient reversibility under mild pH conditions is thus required in order to achieve highly efficient Z-scheme systems. We have recently reported a new Z-scheme water splitting system using a polyoxometalate (POM) as a redox mediator; the use of a Mn-substituted silicotungstate {K₆[SiW₁₁O₃⁹Mn⁴⁺(H₂O)]}, denoted as SiW₁₁Mn} or Mo-substituted one {K₆[SiW₁₁O₃⁹Mo⁴⁺O]}, denoted as SiW₁₁Mo} with appropriate photocatalysts enabled a stoichiometric evolution of H₂ and O₂ under visible light. Here, we paid attention to the use of Vanadium-substituted silicotungstate (K₆[SiW₁₁O₃⁹V³O]), denoted as SiW₁₁V), employed as shuttle redox mediator to pursue the availability of transition metal-substituted polyoxometalates.

2. Experimental

The SiW₁₁V was prepared according to a previously reported method. A reduced specie containing V⁴⁺ was prepared via a bulk electrolysis cell. Photocatalytic reactions were carried out using Ru/SrTiO₃:Rh particles as H₂-evolving photocatalyst and PtO₃/WO₃ particles as O₂-evolving photocatalysts. A 300 W Xe lamp was used as light source and the evolved gases were analyzed using on-line gas chromatograph.

3. Results and discussion

Figure 1 shows the time course of H₂ evolution over Ru/SrTiO₃:Rh particles in aqueous KH₂PO₄ solution (0.5 M, 100 mL, pH 4.3) containing SiW₁₁IV (100 μmol) under visible light (400 < λ < 800 nm). The H₂ evolution is observed at an almost steady rate during irradiation. The H₂ evolution initialized with 100 μmol of SiW₁₁IV saturates at approximately 50 μmol, which is in fairly good agreement with the stoichiometric value (assuming the oxidation of SiW₁₁IV to SiW₁₁V by one photogenerated hole, accompanied by the reduction of H⁺ to H₂ with two photoexcited electrons). The rate of H₂ evolution on SiW₁₁V was slightly lower than that on SiW₁₁Mn that was confirmed to generate the stoichiometric amount of H₂ in our previous study. No H₂ evolution occurs in the aqueous solution of Ru/SrTiO₃:Rh photocatalysts.
in the absence of polyoxometalate within 12 h. The absorption spectra of solution filtered after reaction can be assigned to the oxidized SiW\textsubscript{11}V\textsuperscript{V}. The amount of SiW\textsubscript{11}V\textsuperscript{V} estimated from the absorbance is approximately consistent with the value estimated from the amount of H\textsubscript{2} evolved. These findings indicate that photocatalytic H\textsubscript{2} evolution over the Ru/SrTiO\textsubscript{3}:Rh photocatalyst proceeds accompanied by oxidation of SiW\textsubscript{11}V\textsuperscript{IV}.

When the reaction is initiated with a SiW\textsubscript{11}V\textsuperscript{V} in the presence of PtO\textsubscript{2}/WO\textsubscript{3} as O\textsubscript{2}-evolving photocatalysts, almost stoichiometric amount of O\textsubscript{2} generation is observed. This finding indicates that photocatalytic water oxidation to O\textsubscript{2} proceeds over the PtO\textsubscript{2}/WO\textsubscript{3}, accompanied by an almost stoichiometric reduction of SiW\textsubscript{11}V\textsuperscript{V} to SiW\textsubscript{11}V\textsuperscript{IV}. Thus, the SiW\textsubscript{11}V\textsuperscript{V} was confirmed to function as electron acceptor in the O\textsubscript{2}-evolving system.

Figure 2 shows the time course of photocatalytic evolution of H\textsubscript{2} and O\textsubscript{2} under visible-light irradiation using a mixture of Ru/SrTiO\textsubscript{3}:Rh photocatalyst and PtO\textsubscript{2}/WO\textsubscript{3} photocatalyst suspended in an aqueous KH\textsubscript{2}PO\textsubscript{4} solution (pH 4.5) containing SiW\textsubscript{11}V\textsuperscript{V} or SiW\textsubscript{11}Mn\textsuperscript{II} (100 \textmu mol). Although the rate of gases evolution gradually decreases, the generation of ca. 197.4 \textmu mol of O\textsubscript{2} (total amount) indicates that ca. 789.7 \textmu mol of SiW\textsubscript{11}V\textsuperscript{V} is reduced over PtO\textsubscript{2}/WO\textsubscript{3}. The absorption derived from SiW\textsubscript{11}V\textsuperscript{V} in the solution after the 125 h of reaction was almost same with that in initial solution. Therefore SiW\textsubscript{11}V\textsuperscript{V} is the dominant component in the solution during reaction. In the case of SiW\textsubscript{11}Mn\textsuperscript{II}, the oxidized specie is also the dominant one.\textsuperscript{3} Therefore, the O\textsubscript{2}-evolving systems are considered to be the rate-determining step in both cases. Considering the initial amount of SiW\textsubscript{11}V\textsuperscript{V} (100 \textmu mol), at least 689.7 \textmu mol of SiW\textsubscript{11}V\textsuperscript{V} is produced from SiW\textsubscript{11}V\textsuperscript{IV}, indicating the sufficient turn-over number in the redox cycle. These results demonstrated that the water splitting into H\textsubscript{2} and O\textsubscript{2} proceeds photocatalytically, and that the SiW\textsubscript{11}V\textsuperscript{V}/SiW\textsubscript{11}V\textsuperscript{IV} redox couple functions as a shuttle redox mediator between the two photocatalysts Ru/SrTiO\textsubscript{3}:Rh and PtO\textsubscript{2}/WO\textsubscript{3}.

4. Conclusions

A vanadium-substituted silicotungstate, [SiW\textsubscript{11}O\textsubscript{39}V\textsuperscript{V}O\textsuperscript{V}]\textsuperscript{5−}, was revealed to function as stable shuttle redox mediator, affording simultaneous and stoichiometric generation of H\textsubscript{2} and O\textsubscript{2} under visible light with an appropriate combination of photocatalysts.

References