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 ($K_5[SiW_{11}O_{39}V^{V}O]$, denoted as $SiW_{11}V$) was prepared and employed as redox mediator to pursue the availability of polyoxomeatalate. The $SiW_{11}V^{V}/SiW_{11}V^{IV}$ was confirmed to function as electron donor in H_2-evolution system or as electron acceptor in O_2-evolution system. The $SiW_{11}V^{V}/SiW_{11}V^{IV}$ 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,[1-4] 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 simple redox ion couples for use in Z-scheme 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. 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 {$K_6[SiW_{11}O_{39}Mn^{II}(H_2O)]$,[3] denoted as $SiW_{11}Mn$} or Mo-substituted one {$K_4[SiW_{11}O_{39}Mo^{VI}O]$, denoted as $SiW_{11}Mo$}[4] with appropriate photocatalysts enabled a stoichiometric evolution of H_2 and O_2 under visible light. Here, we paid attention to the use of Vanadium-substituted silicotungstate ($K_6[SiW_{11}O_{39}V^{V}O]$), denoted as $SiW_{11}V$), employed as shuttle redox mediator to pursue the availability of transition metal-substituted polyoxomeatalates.

2. Experimental

The $SiW_{11}V^{V}$ was prepared according to a previously reported method.[5] A reduced specie containing V^{IV} was prepared via a bulk electrolysis cell. Photocatalytic reactions were carried out using Ru/$SrTiO_3$:Rh particles[6] as H_2-evolving photocatalyst and PtO_x/WO_3 particles[7] as O_2-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 H_2 evolution over Ru/$SrTiO_3$:Rh particles in aqueous KH_2PO_4 solution (0.5 M, 100 mL, pH 4.3) containing $SiW_{11}V^{IV}$ (100 μmol) under visible light ($400 < \lambda < 800$ nm). The H_2 evolution is observed at an almost steady rate during irradiation. The H_2 evolution initialized with 100 μmol of $SiW_{11}V^{IV}$ saturates at approximately 50 μmol, which is in fairly good agreement with the stoichiometric value (assuming the oxidation of $SiW_{11}V^{IV}$ to $SiW_{11}V^{V}$ by one photogenerated hole, accompanied by the reduction of H^+ to H_2 with two photoexcited electrons). The rate of H_2 evolution on $SiW_{11}V$ was slightly lower than that on $SiW_{11}Mn^{II}$ that was confirmed to generate the stoichiometric amount of H_2 in our previous study.[3] No H_2 evolution occurs in the aqueous solution of Ru/$SrTiO_3$:Rh photocatalysts in the absence of polyoxometalate within 12 h. The absorption spectra of solution filtered after reaction can be assigned to the oxidized $SiW_{11}V^{V}$. The amount of $SiW_{11}V^{V}$ estimated from the absorbance is approximately consistent with the value estimated from the amount of H_2 evolved. These findings indicate that photocatalytic H_2 evolution over the $Ru/SrTiO_3:Rh$ photocatalyst proceeds accompanied by oxidation of $SiW_{11}V^{IV}$.

When the reaction is initiated with a $SiW_{11}V^{V}$ in the presence of PtO_x/WO_3 as O_2-evolving photocatalysts, almost stoichiometric amount of O_2 generation is observed. This finding indicates that photocatalytic water oxidation to O_2 proceeds over the PtO_x/WO_3, accompanied by an almost stoichiometric reduction of $SiW_{11}V^{V}$ to $SiW_{11}V^{IV}$. Thus, the $SiW_{11}V^{V}$ was confirmed to function as electron acceptor in the O_2-evolving system.

Figure 2 shows the time course of photocatalytic evolution of H_2 and O_2 under visible-light irradiation using a mixture of $Ru/SrTiO_3:Rh$ photocatalyst and PtO_x/WO_3 photocatalyst suspended in an aqueous KH_2PO_4 solution (pH 4.5) containing $SiW_{11}V^{V}$ or $SiW_{11}Mn^{II}$ (100 μmol). Although the rate of gases evolution gradually decreases, the generation of ca. 197.4 μmol of O_2 (total amount) indicates that ca. 789.7 μmol of $SiW_{11}V^{V}$ is reduced over PtO_x/WO_3. The absorption derived from $SiW_{11}V^{V}$ in the solution after the 125 h of reaction was almost same with that in initial solution. Therefore $SiW_{11}V^{V}$ is the dominant component in the solution during reaction. In the case of $SiW_{11}Mn^{II}$, the oxidized specie is also the dominant one.[3] Therefore, the O_2-evolving systems are considered to be the rate-determining step in both cases. Considering the initial amount of $SiW_{11}V^{V}$ (100 μmol), at least 689.7 μmol of $SiW_{11}V^{V}$ is produced from $SiW_{11}V^{IV}$, indicating the sufficient turn-over number in the redox cycle. These results demonstrated that the water splitting into H_2 and O_2 proceeds photocatalytically, and that the $SiW_{11}V^{V}/SiW_{11}V^{IV}$ redox couple functions as an shuttle redox mediator between the two photocatalysts $Ru/SrTiO_3:Rh$ and PtO_x/WO_3.

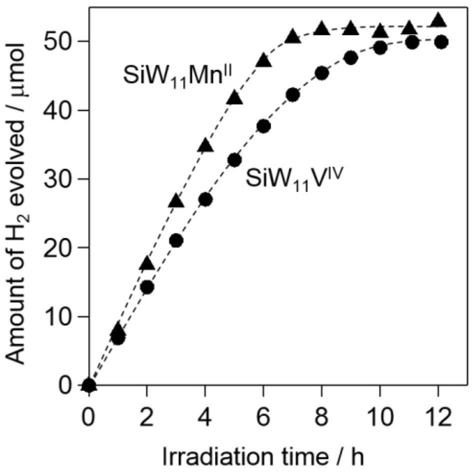

Figure 1. Time courses of H_2 evolution over $Ru/SrTiO_3:Rh$ (0.1 g) from a KH_2PO_4 aq. solution (0.5 M, 100 mL) containing $[SiW_{11}O_{39}V^{IV}O]^{6-}$ or $[SiW_{11}O_{39}Mn^{II}(H_2O)]^{6-}$ (100 μmol).

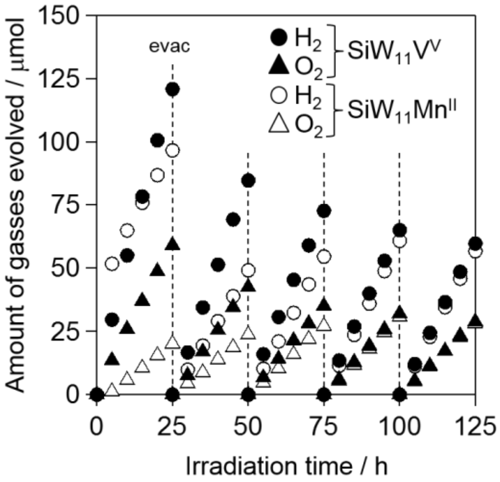

Figure 2. Time courses of gasses evolution over $Ru/SrTiO_3:Rh$ (0.1 g) and PtO_x/WO_3 (0.1 g) from a KH_2PO_4 aq. solution (0.5 M, 100 mL) containing $[SiW_{11}O_{39}V^{V}O]^{5-}$ or $[SiW_{11}O_{39}Mn^{II}(H_2O)]^{6-}$ (100 μmol).

4. Conclusions

A vanadium-substituted silicotungstate, $[SiW_{11}O_{39}V^{V}O]^{5-}$, was revealed to function as stable shuttle redox mediator, affording simultaneous and stoichiometric generation of H_2 and O_2 under visible light with an appropriate combination of photocatalysts.

References

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