

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

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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.^[1, 2] 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 ($K_6[SiW_{11}O_{39}Mn^{II}(H_2O)]$, denoted as $SiW_{11}Mn$) with appropriate photocatalysts enabled a stoichiometric evolution of H_2 and O_2 under visible light.^[3] In the present study, V-substituted silicotungstate ($K_5[SiW_{11}O_{40}V^V]$, denoted as $SiW_{11}V$) was prepared and employed as redox mediator to pursue the availability of POM. 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.

The $SiW_{11}V^V$ was prepared according to a previously reported method.^[4] A reduced specie containing V^{IV} was prepared *via* a bulk electrolysis cell. Photocatalytic reactions were carried out using Ru/SrTiO₃:Rh particle^[5] as H_2 -evolving photocatalyst and PtO_x/WO₃ particle^[6] as O_2 -evolving photocatalysts. The 300 W Xe lamp was used as light source and the evolved gases were analyzed using on-line gas chromatograph.

Figure 1 shows the time course of H_2 evolution over Ru/SrTiO₃:Rh particles in aqueous KH₂PO₄ solution (0.5 M, 100 mL, pH 4.3) containing $SiW_{11}V^{IV}$ (100 μ mol) 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 μ mol of $SiW_{11}V^{IV}$ saturates at approximately 50 μ mol, 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 was almost same with the case of $SiW_{11}Mn^{II}$ 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/SrTiO₃:Rh photocatalysts in the absence of polyoxometalate within 15 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 finding indicates that photocatalytic H_2 evolution over the Ru/SrTiO₃:Rh photocatalysts 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/WO₃ 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/WO₃,

accompanied by an almost stoichiometric reduction of $\text{SiW}_{11}\text{V}^{\text{V}}$ to $\text{SiW}_{11}\text{V}^{\text{IV}}$. Thus, the $\text{SiW}_{11}\text{V}^{\text{V}}$ 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 $\text{Ru}/\text{SrTiO}_3:\text{Rh}$ photocatalyst^[5] and PtO_x/WO_3 photocatalyst^[6] suspended in an aqueous KH_2PO_4 solution (pH 4.5) containing $\text{SiW}_{11}\text{V}^{\text{V}}$ or $\text{SiW}_{11}\text{Mn}^{\text{II}}$ (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 $\text{SiW}_{11}\text{V}^{\text{V}}$ is reduced over PtO_x/WO_3 . The absorption derived from $\text{SiW}_{11}\text{V}^{\text{V}}$ in the solution after the 125 h of reaction was almost same with that in initial solution. Therefore $\text{SiW}_{11}\text{V}^{\text{V}}$ is the dominant component in the solution during reaction. In the case of $\text{SiW}_{11}\text{Mn}^{\text{II}}$, 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 $\text{SiW}_{11}\text{V}^{\text{V}}$ (100 μmol), at least 689.7 μmol of $\text{SiW}_{11}\text{V}^{\text{V}}$ is produced from $\text{SiW}_{11}\text{V}^{\text{IV}}$, 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 $\text{SiW}_{11}\text{V}^{\text{V}}/\text{SiW}_{11}\text{V}^{\text{IV}}$ redox couple functions as an shuttle redox mediator between the two photocatalysts $\text{Ru}/\text{SrTiO}_3:\text{Rh}$ and PtO_x/WO_3 .

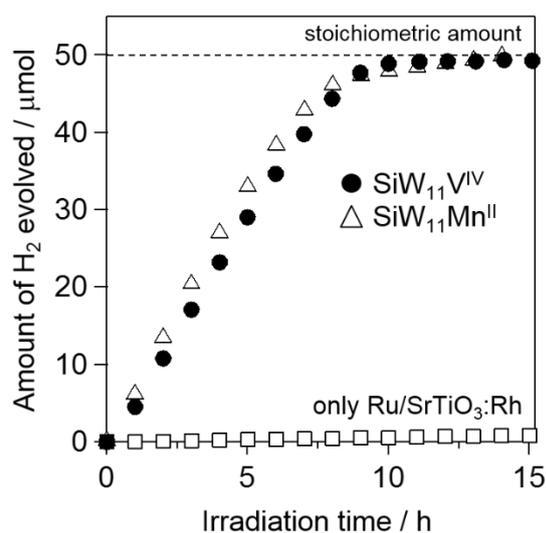


Fig. 1. Time courses of H_2 evolution over $\text{Ru}/\text{SrTiO}_3:\text{Rh}$ (0.1 g) from a KH_2PO_4 solution (0.5 M, 100 mL, pH 4.3) containing $\text{SiW}_{11}\text{V}^{\text{IV}}$ or $\text{SiW}_{11}\text{Mn}^{\text{II}}$ (1 mM).

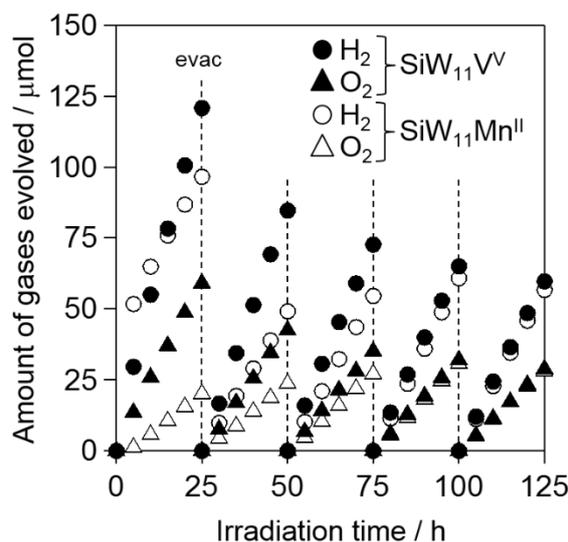


Fig. 2. Time courses of photocatalytic gases evolution using a mixture of $\text{Ru}/\text{SrTiO}_3:\text{Rh}$ (0.1 g) and PtO_x/WO_3 (0.1 g) suspended in a KH_2PO_4 (0.5 M) containing $\text{SiW}_{11}\text{V}^{\text{V}}$ or $\text{SiW}_{11}\text{Mn}^{\text{II}}$ (1 mM).

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