Z-schematic CO$_2$ reduction utilizing water as the sole electron donor employing visible-light-responsive metal oxides as a CO$_2$-reducing photocatalyst

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Abstract: Photocatalytic CO$_2$ reduction using water as an electron donor under visible light irradiation is an ultimate chemical reaction as artificial photosynthesis. In the present study, we have successfully constructed new Z-scheme systems for CO$_2$ reduction with suitable O$_2$ evolution under visible light irradiation. CO as a reduction product of CO$_2$ evolved steadily accompanied by H$_2$ and O$_2$ evolution due to water splitting, when Ag cocatalyst-loaded NaTaO$_3$:Ir,Sr and BaTa$_2$O$_6$:Ir were used as a CO$_2$-reducing photocatalyst in the Z-scheme system with BiVO$_4$ as an O$_2$-evolving photocatalyst and a Co-complex as an electron mediator.

Keywords: Z-schematic CO$_2$ reduction, Visible-light-responsive, Photocatalyst.

1. Introduction

Solar water splitting and CO$_2$ reduction over photocatalysts have attracted attention as a method of artificial photosynthesis.\cite{1} From the viewpoint of utilizing sun light, it is important to design a visible-light-driven photocatalyst system. We have reported Z-scheme systems for CO$_2$ reduction utilizing water as an electron donor using metal sulfide photocatalysts as a reducing photocatalyst and an RGO-metal oxide as an O$_2$-evolving photocatalyst.\cite{2,3} However, chemical stability still remains as a problem for the photocorrosive metal sulfides, and the selectivity for CO formation is low. In contrast, Ag-loaded tantalum metal oxides continuously reduce CO$_2$ to CO with high selectivity under UV irradiation.\cite{4} We also constructed a Z-scheme system for water splitting using Ir and La-codoped BaTa$_2$O$_6$ with visible light response up to 640 nm as an H$_2$-evolving photocatalyst, BiVO$_4$ as an O$_2$-evolving photocatalyst, and a Co-complex as an electron mediator.\cite{5} Thus, it is expected that Ag cocatalyst-loaded tantalum metal oxides doped with Ir function as a CO$_2$ and H$_2$O reducing photocatalyst in a Z-scheme system with a Co-complex. In the present study, we demonstrated the Z-schematic CO$_2$ reduction accompanied by suitable O$_2$ evolution under visible light irradiation using Ir-doped tantalum metal oxides as a reducing photocatalyst.

2. Experimental

An Ir and Sr-codoped NaTaO$_3$ (NaTaO$_3$:Ir,Sr) photocatalyst was synthesized by a solid-state reaction. An Ir and La-codoped BaTa$_2$O$_6$ (BaTa$_2$O$_6$:Ir,La) photocatalyst was synthesized by a borate-flux method. An Ag cocatalyst as an active site for CO$_2$ reduction was loaded by a liquid phase reduction method with NaPH$_2$O$_2$. BiVO$_4$ as an O$_2$-evolving photocatalyst was synthesized by a liquid-solid state reaction. Z-schematic CO$_2$ reduction was carried out in an atmosphere of CO$_2$. A 300 W Xe arc lamp with a cut-off filter was used as a light source. Gas products of H$_2$, O$_2$, and CO were determined using gas chromatographs with a thermal conductivity detector and a flame ionization detector with a methanizer.

3. Results and discussion

The obtained photocatalysts were identified using XRD. NaTaO$_3$:Ir,Sr was obtained as an almost single phase. BaTa$_2$O$_6$:Ir,La was a mixture of orthorhombic and tungsten bronze-tetragonal phases, as reported in the previous literature.\cite{5} Figure 1 shows the diffuse reflectance spectra of NaTaO$_3$:Ir,Sr and non-doped NaTaO$_3$. NaTaO$_3$:Ir,Sr showed new absorption bands with shoulders in the visible light region in addition to the band gap absorption of NaTaO$_3$. This shape of the diffuse reflectance spectrum was the
characteristics of a doped photocatalyst, indicating that impurity levels were formed by the doped Ir in the forbidden band.\(^6\)

![Figure 1](image)

Figure 1. Diffuse reflectance spectra of NaTaO\(_3\) and NaTaO\(_3\):Ir(1%),Sr(2%).

\(Z\)-schematic \(\text{CO}_2\) reduction under visible light was carried out by employing Ag cocatalyst-loaded NaTaO\(_3\):Ir,Sr and Ag cocatalyst-loaded BaTa\(_2\)O\(_6\):Ir,La as a \(\text{CO}_2\) and \(\text{H}_2\text{O}\)-reducing photocatalyst, BiVO\(_4\) as an \(\text{O}_2\)-evolving photocatalyst, and a Co-complex as an electron mediator. \(\text{CO}\) evolved steadily as a reduction product of \(\text{CO}_2\) accompanied by \(\text{H}_2\) and \(\text{O}_2\) evolution due to water splitting. Importantly, the ratio of reacted electrons to holes estimated from the evolved \(\text{CO}\), \(\text{H}_2\), and \(\text{O}_2\) was unity. This clearly indicates that water was used as the sole electron donor in the present \(Z\)-schematic \(\text{CO}_2\) reduction. The selectivity for \(\text{CO}\) evolution was almost 50% over an irradiation time of 40 hours, when Ag/NaTaO\(_3\):Ir,Sr was used.

4. Conclusions

Ag cocatalyst-loaded NaTaO\(_3\):Ir,Sr and BaTa\(_2\)O\(_6\) doped with Ir functioned as a reducing photocatalyst in the \(Z\)-scheme system for \(\text{CO}_2\) reduction under visible light irradiation by combining together with BiVO\(_4\) as an \(\text{O}_2\)-evolving photocatalyst and a Co-complex as an electron mediator. The unity of the ratio of the reacted electrons to holes clearly indicates that water was used as the sole electron donor. It is noteworthy that the selectivity for \(\text{CO}\) evolution was almost 50%. Thus, we have successfully constructed new \(Z\)-scheme systems for \(\text{CO}_2\) reduction under visible light irradiation.

References