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 $BaTa_2O_6$: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.[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.[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.[4] We also constructed a Z-scheme system for water splitting using Ir and La-codoped $BaTa_2O_6$ 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.[5] Thus, it is expected that Ag cocatalyst-loaded tantalum metal oxides doped with Ir function as a CO_2 and H_2O 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 $BaTa_2O_6$ ($BaTa_2O_6$: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 $NaPH_2O_2$. $BiVO_4$ 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. $BaTa_2O_6$:Ir,La was a mixture of orthorhombic and tungsten bronze-tetragonal phases, as reported in the previous literature.[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]

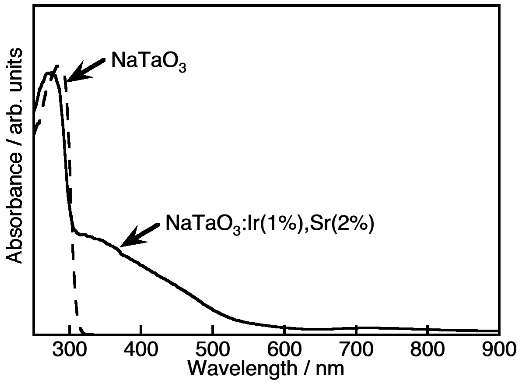

Figure 1. Diffuse reflectance spectra of $NaTaO_3$ and $NaTaO_3$:Ir(1%),Sr(2%).

Z-schematic CO_2 reduction under visible light was carried out by employing Ag cocatalyst-loaded $NaTaO_3$:Ir,Sr and Ag cocatalyst-loaded $BaTa_2O_6$:Ir,La as a CO_2 and H_2O-reducing photocatalyst, $BiVO_4$ as an O_2-evolving photocatalyst, and a Co-complex as an electron mediator. CO evolved steadily as a reduction product of CO_2 accompanied by H_2 and O_2 evolution due to water splitting. Importantly, the ratio of reacted electrons to holes estimated from the evolved CO, H_2, and O_2 was unity. This clearly indicates that water was used as the sole electron donor in the present Z-schematic CO_2 reduction. The selectivity for 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 $BaTa_2O_6$ doped with Ir functioned as a reducing photocatalyst in the Z-scheme system for CO_2 reduction under visible light irradiation by combining together with $BiVO_4$ as an 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 CO evolution was almost 50%. Thus, we have successfully constructed new Z-scheme systems for CO_2 reduction under visible light irradiation.

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