Development of hybrid photocathodes with Ru(II)-Re(I) metal complex photocatalyst for photoelectrochemical CO₂ reduction in aqueous solution

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Abstract: Hybrid photocathodes which consists Ru(II)-Re(I) metal complex photocatalyst (RuRe) and p-type semiconductor electrodes (NiO and CuGaO₂) were developed for photoelectrochemical CO₂ reduction in aqueous solution. The synthesized hybrid photocathodes showed photoelectrochemical activity for the conversion of CO₂ to CO with relatively high selectivity in an aqueous electrolyte solution. The photoelectrochemical cells consisting of these hybrid photocathodes and a CoOx/TaON photoanode enabled the visible-light-driven catalytic reduction of CO₂ with water oxidation to obtain CO and O₂.

Keywords: CO₂ reduction, photoelectrochemistry, metal complex-semiconductor hybrid.

1. Introduction

Photochemical reduction of CO₂ is one of the potential means for overcoming both the problem of global warming and the shortage of fossil resources. Metal complex photocatalysts can be attractive candidate in the CO₂ reduction system due to their high selectivity and efficiency under visible light even in aqueous solution.1 In these systems, however, the sacrificial reductants were needed to drive the reaction because of the low oxidizing power of the photosensitizer unit.

In this study, novel hybrid photocathodes consisting of Ru(II)-Re(I) metal complex photocatalyst (RuRe) and p-type semiconductor electrodes for visible-light-driven CO₂ reduction were developed (Figure 1). In such systems, it is expected that the photoexcited metal complex photocatalyst can receive the electron from an external circuit through semiconductor electrodes without requiring any sacrificial reagent. The activity of the hybrid photocathodes for photoelectrochemical CO₂ reduction in an aqueous solution was examined.

2. Experimental

RuRe metal complex photocatalyst, which consists of tris-diimine Ru(II) unit as a photosensitizer with methylphosphonate anchoring group to adsorb on the electrode surface and tricarbonyl diimine Re(I) unit as a catalyst, was synthesized as the reported procedure. NiO electrode was prepared by the doctor blade method on FTO substrate using precursor solution containing Ni(NO₃)₂·6H₂O and Pluronic F-88. CuGaO₂ electrode was prepared by the drop casting on FTO substrate using CuGaO₂ powder synthesized by the solid state reaction. The electrodes immersed in a solution of acetonitrile containing RuRe overnight to obtain hybrid photocathodes. Photoelectrochemical measurement and CO₂ reduction reaction were conducted using a three-electrode setup with using CO₂-saturated 50 mM NaHCO₃ aqueous solution (pH 6.6) as the electrolyte. A Pt wire and Ag/AgCl in saturated KCl aqueous solution were employed as the counter and reference electrodes, respectively.

3. Results and discussion

A p-type NiO electrode was hybridized with RuRe to obtain a hybrid photocathode (RuRe/NiO).2 The RuRe/NiO photocathode showed photocathodic responses under the visible light (λₑₓ > 460 nm), which selectively photoexcites Ru(II) photosensitizer in RuRe, without the need for any sacrificial additives. Its onset potential for cathodic photocurrent was approx. -0.1 V vs. Ag/AgCl in a CO₂-purged 50 mM NaHCO₃ aqueous solution. Photoelectrochemical CO₂ reduction using the RuRe/NiO photocathode was conducted under the continuous irradiation and the catalytic amount of CO was observed, while little amount of H₂ was
generated as byproduct. Its turnover number for CO formation, which was based on the amount of RuRe on the NiO, was 32 for 12 h irradiation at the potential of -0.7 V vs. Ag/AgCl. The selectivity of CO formation was 91%. These results clearly suggest that the immobilized metal complex photocatalyst (RuRe) functions to drive photoreduction of CO2 with using electrons supplied from the NiO electrode (Figure 1 (A)).

As an alternative of NiO, p-type CuGaO2 electrode was developed for constructing hybrid photocathode with RuRe.3 The synthesized RuRe/CuGaO2 photocathode also shows photoelectrochemical activity for CO2 reduction under visible light irradiation. Current-potential curves of the RuRe/CuGaO2 photocathode is shown in Figure 1 (B). The photocathodic responses was obtained from approx. +0.3 V vs. Ag/AgCl, which is equivalent to +0.9 V vs. RHE. This value of onset potential is around 0.4 V positive than that for RuRe/NiO, indicating that the utilization of CuGaO2 as an electrode material enabled to enlarge the region of working potential for CO2 reduction to positive direction. This tendency agreed well to the flat band potentials of these semiconductor electrodes obtained from the electrochemical impedance spectroscopy. The turnover number of CO formation using the RuRe/CuGaO2 photocathode reached to 125 for 15 h irradiation at the potential of -0.3 V vs. Ag/AgCl. The selectivity of CO formation was 61%. These results indicate the advantage of CuGaO2 for usage of an electrode material for molecular photocathode from the aspect of efficient interfacial electron injection.

Next these photocathodes were investigated to combine with a CoO2/TaON photoanode for the oxidation of water.4 The constructed photoelectrochemical cells consisting of these hybrid photocathodes and the CoO2/TaON photoanode enabled the visible-light-driven catalytic reduction of CO2 with water oxidation to obtain CO and O2 as the products. These systems successfully demonstrated CO2 reduction using water as an electron donor by means of combined photocatalytic abilities of both the molecular metal complex (RuRe) and the semiconductor material (TaON). Especially the cell which consists of CuGaO2 as an electrode material for the photocathode (RuRe/CuGaO2–CoO2/TaON) drove the reaction with no need of external bias, possibly with the aid of the positive onset potential of RuRe/CuGaO2.

![Figure 1. Reaction scheme of hybrid photocathodes (A) and I-E curves of RuRe/CuGaO2 in CO2-saturated 50 mM NaHCO3 aqueous solution (B).](image)

4. Conclusions

The hybrid photocathodes of RuRe/NiO and RuRe/CuGaO2 displayed photoelectrochemical activity for the conversion of CO2 to CO in an aqueous electrolyte solution. Their photoelectrochemical properties and activities were affected by the property of the semiconductor electrode. These hybrid photocathodes successfully combined with CoO2/TaON photoanode to demonstrate the visible-light-driven catalytic reduction of CO2 with water oxidation to obtain CO and O2.

References