Development of hybrid photocathodes with Ru(II)-Re(I) metal complex photocatalyst for photoelectrochemical CO_2 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 $CuGaO_2$) were developed for photoelectrochemical CO_2 reduction in aqueous solution. The synthesized hybrid photocathodes showed photoelectrochemical activity for the conversion of CO_2 to CO with relatively high selectivity in an aqueous electrolyte solution. The photoelectrochemical cells consisting of these hybrid photocathodes and a CoO_x/TaON photoanode enabled the visible-light-driven catalytic reduction of CO_2 with water oxidation to obtain CO and O_2.
Keywords: CO_2 reduction, photoelectrochemisty, metal complex-semiconductor hybrid.

1. Introduction

Photochemical reduction of CO_2 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 CO_2 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 CO_2 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 CO_2 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 $Ni(NO_3)_2{\cdot}6H_2O$ and Pluronic F-88. $CuGaO_2$ electrode was prepared by the drop casting on FTO substrate using $CuGaO_2$ 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 CO_2 reduction reaction were conducted using a three-electrode setup with using CO_2-saturated 50 mM $NaHCO_3$ 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 ($\lambda_{ex} > 460$ 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 CO_2-purged 50 mM $NaHCO_3$ aqueous solution. Photoelectrochemical CO_2 reduction using the **RuRe**/NiO photocathode was conducted under the continuous irradiation and the catalytic amount of CO was observed, while little amount of H_2 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 CO_2 with using electrons supplied from the NiO electrode (Figure 1 (A)).

As an alternative of NiO, p-type $CuGaO_2$ electrode was developed for constructing hybrid photocathode with **RuRe**.[3] The synthesized **RuRe**/$CuGaO_2$ photocathode also shows photoelectrochemical activity for CO_2 reduction under visible light irradiation. Current-potential curves of the **RuRe**/$CuGaO_2$ 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 $CuGaO_2$ as an electrode material enabled to enlarge the region of working potential for CO_2 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**/$CuGaO_2$ 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 $CuGaO_2$ 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 CoO_x/TaON photoanode for the oxidation of water.[4] The constructed photoelectrochemical cells consisting of these hybrid photocathodes and the CoO_x/TaON photoanode enabled the visible-light-driven catalytic reduction of CO_2 with water oxidation to obtain CO and O_2 as the products. These systems successfully demonstrated CO_2 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 $CuGaO_2$ as an electrode material for the photocathode (**RuRe**/$CuGaO_2$−CoO_x/TaON) drove the reaction with no need of external bias, possibly with the aid of the positive onset potential of **RuRe**/$CuGaO_2$.

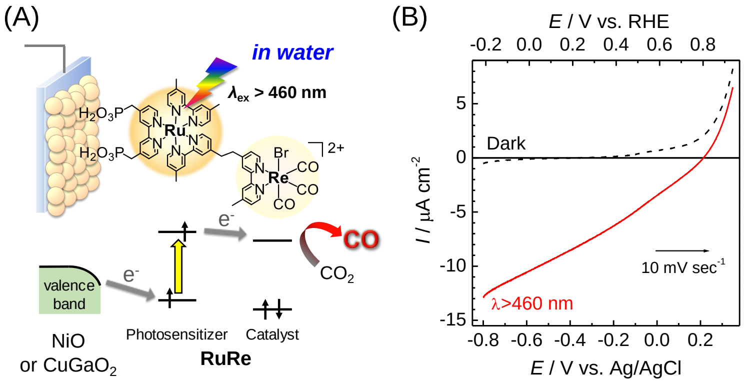

Figure 1. Reaction scheme of hybrid photocathodes (A) and *I-E* curves of **RuRe**/$CuGaO_2$ in CO_2-saturated 50 mM $NaHCO_3$ aqueous solution (B).

4. Conclusions

The hybrid photocathodes of **RuRe**/NiO and **RuRe**/$CuGaO_2$ displayed photoelectrochemical activity for the conversion of CO_2 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 CoO_x/TaON photoanode to demonstrate the visible-light-driven catalytic reduction of CO_2 with water oxidation to obtain CO and O_2.

References

1. Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol. C* 25 (2015) 106.; A. Nakada, K. Koike, K. Maeda, O. Ishitani, *Green Chem.* 18 (2016) 139.
2. G. Sahara, R. Abe, M. Higashi, T. Morikawa, K. Maeda, Y. Ueda, O. Ishitani, *Chem. Commun.* 51 (2015) 10722.; G. Sahara, H. Kumagai, K. Maeda, N. Kaeffer, V. Artero, M. Higashi, R. Abe, O. Ishitani, *J. Am. Chem. Soc.* 138 (2016) 14152.
3. H. Kumagai, G. Sahara, K. Maeda, M. Higashi, R. Abe, O. Ishitani, *Chem. Sci.*, 8 (2017) 4242.
4. M. Higashi, K. Domen, R. Abe, *J. Am. Chem. Soc.*, 134 (2012) 6968.