Photoelectrochemical CO_2 reduction using a molecular photocathode prepared by polymerization of Ru(II)-Re(I) metal complexes on a NiO electrode

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Abstract: Novel molecular photocathodes consisting of a Ru(II)-Re(I) complex photocatalyst electropolymerized on a NiO electrode were successfully developed. The number of the immobilized metal complexes increased and its stability in adsorption on the NiO electrode was improved compared with those of the electrodes using the corresponding photocatalyst only with phosphonic acid anchors. The synthesized NiO-Ru(II)-Re(I) polymer electrodes succeeded in reducing CO_2 to CO at E = -0.7 V vs. Ag/AgCl under visible-light irradiation in aqueous solutions. The improved properties significantly contributed improving both activity for CO generation and its faradaic efficiency.

Keywords: CO_2 reduction, photoelectrochemical cell, metal complex-semiconductor hybrid.

1. Introduction

We recently reported that a photoelectrocatalytic activity of a Ru(II)-Re(I) binuclear complex immobilized on a NiO electrode with phosphonic acid anchoring groups.[1] The synthesized molecular photocathodes can catalytically reduce CO_2 to CO with relatively high selectivity under visible-light irradiation in an aqueous solution. However, the low adsorption amount and the low adsorption stability of the metal complex leaded to insufficient reaction efficiency and durability of the photocathode during the reaction.

In order to solve these problems, we applied the electropolymerization of vinyl groups to fix the Ru(II)-Re(I) binuclear complex or a Ru(II) complex (Second step in Figure (a)) after adsorbing another Ru(II) mononuclear complex with the phosphonic acid groups (First step in Figure (a)) on the NiO electrode. This method caused increase of the adsorbed amount of the metal complexes and improvement of their stability. In addition, the activity for photoelectrochemical CO_2 reduction was also improved.

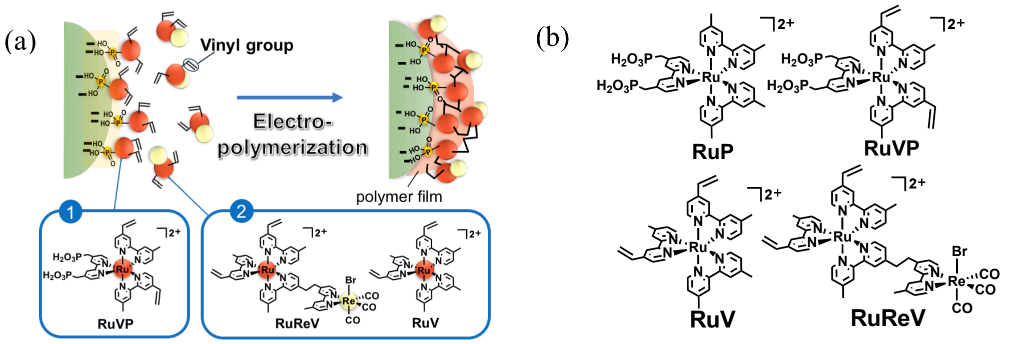

Figure. (a) Preparation of the electrode by using electropolymerization, and (b) metal complexes used in this study

2.Experimental

The NiO electrode was prepared by the squeegee method in the reported procedures[1]. The Ru(II) complex, which has both vinyl and phosphonic acid groups (**RuVP**, Figure (b)), was adsorbed onto the NiO electrode in an acetonitrile solution. Using this NiO-**RuVP** electrode as a working electrode, repeated sweeps of the voltage between E = 0 and -1.9 V vs. $Ag/AgNO_3$ were conducted in an acetonitrile solution containing **RuV**, which has only the vinyl groups, (Figure (b)) and Et_4NBF_4 as a supporting electrolyte under Ar atmosphere in order to obtain the photoelectrode with the electropolyemerized Ru(II) complex

(NiO-**RuVP**-**RuV** electrode). The NiO-**RuP** electrode was also prepared in the similar to the first part described above with **RuP** which has only the phosphonic acid anchors (**RuP,** Figure (b)**)**. The numbers of the immobilized electroactive metal complexes were evaluated by cyclic voltammetry in acetonitrile solutions with sweeping in the range between 0 to +1.3 V to observe a reversible oxidation-reduction wave of one electron oxidation of the Ru(II/III) complex. Desorption of the immobilized complexes from these electrodes was also investigated by soaking the electrode into 50 mM $NaHCO_3$ water solutions overnight. Photocurrent of the NiO-**RuVP**-**RuV** electrode was measured under irradiation at λ_{ex} = 460 nm in an acetonitrile solution containing Et_4NBF_4 as supporting electrolyte.

NiO-**RuVP**-**RuReV** electrode, where the Ru(II)-Re(I) binuclear complex with vinyl groups (**RuReV**, Figure (b)) was electropolymerized on the NiO-**RuVP** electrode, was prepared in the same manner descriged above. Photoelectrochemical CO_2 reduction was attempted by using the NiO-**RuVP**-**RuReV** electrode at E = -0.7 V vs. Ag/AgCl in a CO_2-purged aqueous solution containing 50 mM $NaHCO_3$.

3. Results and discussion

The Ru(II) mononuclear complex as a model of the photosensitizer of the Ru(II)-Re(I) photocatalyst was used to check the various property of the polymer electrode. In the electropolymerization process of **RuV** using the NiO-**RuVP** electrode as the working electrode, stepwise increase in the current was observed with repeating the potential sweep in an acetonitrile containing **RuV**. This suggests that immobilization of electroactive complexes proceeded on the electrode; anion radical generated by reduction of **RuV** probably nucleophilically attacked to another vinyl group[2]. The diffuse reflectance spectrum of the NiO-**RuVP**-**RuV** electrode showed clear increase of absorption at 464 nm during the electropolymerization, which should be the ^{1}MLCT absorption band of the Ru complexes on the electrode. These results support the adsorption of the Ru complexes on the electrode by the electropolymerization. The amount of the adsorbed Ru complex on the NiO-**RuVP**-**RuV** electrode was ca. 10 nmol cm^{-1} while that for the NiO-**RuP** electrode was ca. 3.6 nmol cm^{-1}. After soaking these electrodes into 50 mM $NaHCO_3$ aqueous solution overnight, 83% of the active complex was maintained for the NiO-**RuVP**-**RuV** electrode while 91% of the complex was desorbed in the case of the NiO-**RuP** electrode. Such high stability against desorption can be explained by the insolubility of the complex polymer into water. In addition, the NiO-**RuVP**-**RuV** electrode generated much higher photocurrent compared to the NiO-**RuP** electrode under visible light irradiation owing to the enhanced amount of active complexes on the electrode.

In order to apply the polymer-modified electrode to CO_2 reduction, the **RuReV** photocatalyst consisting of the Ru photosensitizer and Re catalyst units was electropolymerized onto the NiO-**RuVP** electrode instead of **RuV** giving the NiO-**RuVP**-**RuReV** electrode. The photoelectronchemically catalyzed CO_2 reduction giving CO at E = -0.7 V vs. Ag/AgCl in an aqueous solution. The amount of produced CO was 502 nmol for 5 h irradiation at λ_{ex} > 460, which was about 2.5 times higher compared to that by using the corresponding electrode adsorbing a Ru(II)-Re(I) complex with only phosphonic acid anchoring groups.

4. Conclusions

The novel preparation method of the stable and efficient moleculr photocathode for CO_2 reduction was developed by using the electropolymerization. This can increase the amount of the immobilized metal complexes and improved their stability. The synthesized NiO-**RuVP**-**RuReV** electrode showed high photoelectrochemical activity for CO_2 reduction giving CO under visible light irradiation in an aqueous solution.

References

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