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Research Paper

Enhancement of CO_2 reduction activity under visible light irradiation over Zn-based metal sulfides by combination with Ru-complex catalysts

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ABSTRACT

Hybrid photocatalysts composed of metal sulfide semiconductors combined with various Ru-complex catalysts were synthesized for use during visible light-driven CO_2 reduction with powder suspension systems. A variety of Zn-based sulfides, including Ni-doped ZnS, $(CuGa)_{0.8}Zn_{0.4}S_2$ and $(AgIn)_{0.22}Zn_{1.56}S_2$, were adopted by conducting the CO_2 reduction reaction in acetonitrile containing an electron donor. The photocatalytic activities were found to be largely dependent on the basic characteristics of the Ru-complex and the metal sulfide. The results demonstrate that several of these sulfide semiconductors improve the CO_2 reduction selectivity when employed in the semiconductor/metal-complex system, and that $(AgIn)_{0.22}Zn_{1.56}S_2$ or Ni (0.2 mol%)-doped ZnS combined with a neutral Ru-complex incorporating a phosphonate ligand [Ru(4,4′-diphosphonate-2,2′-bipyridine)$(CO)_2Cl_2$] exhibit the highest CO_2 photoconversion activity when synthesizing formic acid, with a turnover number above 100, which catalysts were stable for 16 h irradiation. These results suggest that metal sulfides are potential candidates for use in powdered semiconductor/metal-complex systems for selective CO_2 photoreduction.

1. Introduction

The reduction of CO_2 to obtain useful energy-rich chemicals utilizing photocatalysts in water has attracted attention as a potential means of artificial photosynthesis operating under solar irradiation. As such, there have been many studies regarding photoelectrochemical systems incorporating photoelectrodes for both generation of H_2 [1] and organic substances [2], although relatively few assessments of powdered photocatalytic systems. These powdered photocatalysts are attractive as potential devices for the practical, cost-effective generation of H_2 by water splitting [3]. In contrast, the use of powdered systems for CO_2 reduction is challenging owing to the inherent difficulty in achieving the selective reaction of CO_2 in solution and obtaining efficient photoexcited electron transfer from the oxidation sites to the CO_2 reduction sites in a heterogeneous environment. The combination of a semiconductor photosensitizer and a metal complex catalyst is one promising approach to selective CO_2 reduction under visible light irradiation. A hybrid composed of *p*-type N-doped Ta_2O_5 (N-Ta_2O_5) [4] with $[Ru(dcbpy)_2(CO)_2]^{2+}$ (dcbpy: 4,4′-dicarboxy-2,2′-bipyridine, hereafter $[Ru(dcbpy)_2]$) suspended in acetonitrile (MeCN) has been shown to catalyze visible light-induced CO_2 reduction to formate using triethanolamine (TEOA) as an electron donor and proton source. This process is based on the efficient coordination of CO_2 molecules with the Ru-complex [5,6]. Interestingly, although N-Ta_2O_5 or $[Ru(dcbpy)_2]$ alone do not photocatalyze CO_2 reduction under visible irradiation, the CO_2 reduction reaction proceeds over a $[Ru(dcbpy)_2]$/N-Ta_2O_5 hybrid. Experimental and theoretical investigations have suggested that the energy difference, ΔG, between the conduction band minimum (E_{CBM}) of N-Ta_2O_5 and the LUMO of the Ru-complex is a very important factor that facilitates electron transfer from N-Ta_2O_5 in the photoexcited state to the Ru-complex [5–9], with the time constant of the electron transfer on the order of tens of picoseconds [10]. Ishitani and Maeda's group has reported powdered photocatalysts composed of a visible light-sensitive *n*-type oxynitride semiconductor (TaON) combined with Ru–Ru binuclear complex photocatalysts in MeOH [11] or aqueous solutions containing ethylenediaminetetraacetic acid disodium salt (EDTA) as an electron donor [12]. This same group has also demonstrated a carbon nitride (C_3N_4) semiconductor combined with Ru-complexes in various organic solvents (such as *N*, *N*-dimethylacetamide, MeCN, and MeOH/TEOA) [13,14] or aqueous solutions containing an electron donor [14], with the generation of formic acid from CO_2. Cowan and Durrant group demonstrated photocatalytic CO_2

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reduction in protic solvents using nickel cyclam catalysts immobilized on semiconductor materials including TiO_2 and $Ti_{1-x}Zr_xO_2$ [15].

Metal sulfide semiconductors, known to function as highly efficient visible light-driven hydrogen evolution photocatalysts in aqueous solutions in the presence of sacrificial hole scavengers, are also attractive for CO_2 photocatalysis. Metal sulfides generally have narrower band gaps than metal oxides due to the shallower valence bands formed by S 3p orbitals compared to those formed by O 2p orbitals [16]. Among the metal sulfides, both undoped CdS (with a band gap of 2.4 eV) [17–19] and ZnS (3.5 eV) [20] have been studied. ZnS in particular is recognized as an attractive host material for impurity doping and the formation of solid solutions for water splitting reactions. Because of its wide band gap, ZnS exhibits photoactivity only under UV irradiation [16,20], although doping with metal cations (Ni^{2+} [21], Cu^{2+} [22] or Pb^{2+} [23]) leads to efficient H_2 evolution activity in the presence of the electron donor species SO_3^{2-} under visible light irradiation, even without a metal cocatalyst. Doping with metals produces a new energy level in the band gap of ZnS due to the Ni 3d, Cu 3d, or Pb 3d orbitals. In addition, solid solutions based on ZnS such as $(CuGa)_{1-x}Zn_{2x}S_2$ [24], $(AgIn)_xZn_{2(1-x)}S_2$ [25–27] and $(CuIn)_xZn_{2(1-x)}S_2$ [27,28] can be formed by adding the narrow band gap semiconductors CuGaS, $AgInS_2$ and $CuInS_2$. These materials are attractive because the band position of the solid solution can be tuned by changing the semiconductor. The conduction and valence bands of $(CuGa)_{1-x}Zn_{2x}S_2$ primarily consist of Zn 4s4p + Ga 4s4p and Cu 3d + S 3p orbital combinations, respectively. The Zn 4s4p orbitals form a conduction band at a higher (more negative) level than the Ga 4s4p orbitals [24]. This orbital hybridization induces a redshift in the photo-response of the materials, such that photocatalytic hydrogen evolution has been demonstrated in aqueous sulfide and sulfite solutions containing the electron donor SO_3^{2-} at longer wavelengths than ZnS by Kudo's group [24–28]. Recently, CO_2 reduction using $CuGaS_2$ and Ni-doped ZnS in aqueous solution has also been reported [29]. In this work, HCOOH and CO were generated from CO_2 in aqueous solution in the presence of the electron donors K_2SO_3 and Na_2S without the loading of co-catalysts.

Based on the above, sulfide semiconductors are a strong candidate for use in complex/semiconductor hybrid systems having higher CO_2 reduction selectivity. Recently, Reisner et al. reported a photocatalytic CO_2 reduction system of a molecular Ni catalyst linked with CdS nanocrystals with CO selectivity of > 90% [30]. Among these, Zn-based sulfides are considered to be superior because ZnS possesses a relatively negative E_{CBM} as a result of the Zn 4s4p orbitals, which facilitates the electron transfer from the conduction band of the semiconductor in a photoexcited state to the metal complex catalyst. Cu_2ZnSnS_4 (CZTS) has been examined as a photocathode for CO_2 reduction by our own group, modified with polymerized [Ru{4,4′-di(1*H*-pyrrolyl-3-propylcarbonate)-2,2′-bipyridine}(CO)(MeCN)Cl_2] (hereafter [Ru(pypcbpy)]) [31]. Useable powdered hybrid systems have not yet been reported. Interestingly, powdered ZnS:Ni (0.1 mol% Ni) with [Ru(4,4′-dicarboxy-2,2′-bipyridine)(2,2′-bipyridine)$(CO)_2$]$^{2+}$ did not promote the photocatalytic CO_2 reduction reaction in a MeCN/TEOA solution, even though the ΔG driving the electron transfer should have been sufficient [5].

In the present study, the powdered Ni-doped ZnS semiconductors $(CuGa)_{0.8}Zn_{0.4}S_2$, and $(AgIn)_{0.22}Zn_{1.56}S_2$, which are active for sacrificial H_2 evolution, were investigated in combination with various Ru-complex catalysts with regard to the promotion of visible light induced CO_2 reduction. Working in MeCN/TEOA solutions, the effects of the anchoring groups and the charge of the Ru-complexes on photocatalytic CO_2 reduction were investigated using these ZnS:Ni materials. The results indicate that Zn-based sulfide semiconductors having various bandgaps and band positions are readily applicable as hybrid photocatalysts for CO_2 reduction under visible light irradiation.

2. Experimental

2.1. Preparation of the metal sulfide semiconductor

Ni-doped ZnS (0.2 mol% Ni) [21] was prepared by mixing an aqueous solution of $Zn(NO_3)_2$ and $Ni(NO_3)_2$ with an aqueous solution of Na_2S at room temperature. The resulting precipitate was washed with distilled water, filtered and dried in air, then heated at 773 K for 2 h under an Ar flow. Non-doped ZnS was also prepared using an aqueous $Zn(NO_3)_2$ solution and employing the same method. $(CuGa)_{0.8}Zn_{0.4}S_2$ [24] and $(AgIn)_{0.22}Zn_{1.56}S_2$ [25,26] were prepared according to previously reported procedures.

2.2. Synthesis of the Ru-complex

[Ru(4,4′-dicarboxy-2,2′-bipyridine)$_2$$(CO)_2$]$^{2+}$ ([Ru(dcbpy)$_2$]) [5], (4,4′-diphosphonate-2,2′- bipyridine)$(CO)_2$]$^{2+}$ ([Ru(dpbpy)-(bpy)]) [6], [Ru (4,4′-diphosphonate-2,2′-bipyridine)$(CO)_2$Cl ([Ru(dpbpy)]) [32], [Ru (4,4′-dicarboxy-2,2′-bipyridine)$(CO)_2$Cl ([Ru(dcbpy)]) [32], [Ru(2,2′-bipyridine)] and [Ru{4,4′-di(1H-pyrrolyl-3-propyl carbonate)-2,2′- bipyridine}(CO)(MeCN)Cl_2] ([Ru(pypcbpy)]) [33] were synthesized according to previously reported methods.

2.3. Preparation of the Ru-complex/metal sulfide hybrid photocatalysts (adsorption method)

Hybrid photocatalysts consisting of a Ru-complex ([Ru(dcbpy)$_2$], [Ru(dpbpy)(bpy)], [Ru(dpbpy)], or [Ru(dcbpy)]) and a metal sulfide were prepared by adsorption of the Ru-complex. A mixture of the metal sulfide powder (200 mg) and a solution of the Ru-complex (0.4 mg) in methanol (5 mL) was stirred overnight under dark conditions. The solution was subsequently filtered, washed with methanol and dried under vacuum at 313 K. The absorption spectra of these solutions after filtration were acquired using a UV/vis spectrophotometer (Shimadzu, UV-3600) and the amount of Ru-complex adsorbed on the metal sulfide was calculated from each spectrum.

2.4. Preparation of the [Ru(pypcbpy)]/ZnS:Ni hybrid photocatalyst (photopolymerization method)

A hybrid photocatalyst consisting of [Ru(pypcbpy)] and ZnS:Ni was prepared by photopolymerization of the Ru-complex. A mixture of ZnS:Ni powder and [Ru(pypcbpy)] (0.4 mg) in acetonitrile (5 mL) was stirred overnight under fluorescent lamp irradiation. The post-processing method was the same as that described above for the adsorption method.

2.5. Characterization

The crystal structures of the samples were assessed using X-ray diffraction (XRD, Rigaku, Ultima IV) with Cu Kα radiation at 40 kV and 40 mA. Surface areas were determined by BET measurement (Coulter, SA3100). The chemical structures of the hybrid photocatalysts were characterized using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS; JASCO, JNM-LA500). Diffuse reflection spectra were obtained using a UV–vis-NIR spectrometer (JASCO, V-780) and were converted from reflectance to absorbance by the Kubelka–Munk method. X-ray photoelectron spectroscopy (XPS; Ulvac-Phi Quantera SXM) was also conducted, with monochromated Al Kα radiation.

2.6. Photocatalytic reaction for CO_2 reduction in MeCN/TEOA

The photocatalytic activity of each hybrid photocatalyst was measured under ambient pressure in an 8 mL test tube containing 4 mL of a dry acetonitrile (MeCN)-triethanolamine (TEOA) mixture (5:1 by volume) and 8 mg of the photocatalyst. After purging with CO_2 for