Photoelectrochemical Reduction of CO₂ to CO Using a CuGaS₂ Thin-film Photocathode Prepared by a Spray Pyrolysis Method

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A CuGaS₂ thin film was formed by annealing of spray-deposited precursor films in a sulfur atmosphere. The film worked as a photocathode for photoelectrochemical CO₂ reduction in a neutral aqueous solution saturated with CO₂ by applying a bias potential lower than that needed for inducing the reaction under a dark condition.

Keywords: CuGaS₂ thin film | Electron energy structure | Photoelectrochemical CO₂ reduction

Chemical transformation of carbon dioxide (CO₂) into chemical fuels and products has become an important means to solve the current problem of dwindling supply of fossil fuels. Photoelectrochemical (PEC) CO₂ reduction has been studied as one of the most attractive concepts because of the possible use of water (H₂O) as an electron source to drive the reaction.1,2 Separate production of reduced energy-rich chemicals from oxygen (O₂) produced from H₂O is also an important advantage in view of its practical use. Moreover, due to the efficient charge separation induced by band bending in the semiconductor electrode used, high performance for the CO₂ reduction can be expected by using the PEC system.

In order to induce the overall reaction of CO₂ reduction using H₂O as the electron source, application of a high voltage should be required. Therefore, in recent studies on PEC CO₂ reduction, a tandem system composed of a series connection between a photocathode for CO₂ reduction and a photoanode for H₂O oxidation has been used to obtain the necessary voltage to drive the reaction using only sunlight as an input without applying external bias. As possible candidates for the tandem system, there have been many studies on highly efficient photoanodes for H₂O oxidation, e.g., WO₃,§3 Fe₂O₃,∥4 BiVO₄,¶5 and TaON,∥6 while there are few reports on photocathodes that show appreciable production of CO₂.7 One of the difficulties associated with a photocathode for CO₂ reduction is preferential H₂ evolution in an aqueous solution. In order to overcome this problem, efficient catalysts and/or photocatalysts having selective catalytic activity for CO₂ reduction have been studied.8 Another simple strategy is the use of a photocathode consisting of a relatively negative conduction band minimum (CBM) energy level to gain the required overpotential for CO₂ reduction.

Copper gallium disulfide (CuGaS₂) is a p-type semiconductor crystallized in a chalcopyrite structure.⁹,¹⁰ Although its relatively large band gap energy (2.43 eV) compared to those of other substituents, such as CuInSe₂, CuGaSe₂ and CuInS₂, is not optimal for sunlight absorption, it has been studied as a host for intermediate band materials for solar cell applications.¹² Some of the co-authors have studied photocatalytic properties of modified CuGaS₂ powders for H₂O reduction into H₂.¹³ They also demonstrated CO₂ reduction using CuGaS₂ powder combined with an O₂ evolution photocatalyst powder (CoOₓ-loaded BiVO₄) and a reduced graphene oxide as an electron mediator.¹⁴ Regarding PEC CO₂ reduction, appreciable properties have also been observed for a photocathode obtained by dip-coating of photocatalyst powder composed of CuGaS₂ alloyed with Ag ((Ag/CuGaS₂)).¹⁵

For fabrication of chalcopyrite thin films with sufficient quality for photovoltaic and PEC applications, several vacuum and non-vacuum processes have been reported. Among them, we have studied spray pyrolysis as a promising technique in view of its cost effectiveness because a high deposition rate can easily be achieved and because the equipment for large-scale production is similar to that used for conventional spray coating in various industrial coating processes. Several chalcopyrite films, including CuiS₃ and CuiSn₂ alloyed with Ga (Cu(In,Ga)S₂) and Ag ((Ag/Cu)(In,Ga)S₂), have been successfully obtained and they have been shown to have efficient properties for photovoltaic¹⁶ and PEC water splitting.¹⁷ In regard to PEC CO₂ reduction, however, there has been no study on the spray deposition of a bare CuGaS₂ film for application to this system. Hence, we were motivated to explore the potential of a CuGaS₂ thin film as a photocathode for CO₂ reduction. In this study, we investigated the crystallographic structure, morphology, and electron energy structure of a CuGaS₂ thin film deposited by spray pyrolysis. We achieved PEC CO₂ reduction under simulated sunlight radiation (AM1.5G) by using the CuGaS₂ thin film as a photocathode for the first time.

Onto a Mo-coated glass substrate, an aqueous solution containing Cu²⁺ and Ga³⁺ ions and thiourea (as a sulfur source) was sprayed at 290°C. Figure 1A shows XRD patterns of the as-deposited film. The film showed weak reflections assignable to a divalent CuS compound (CSD: CR881601) in addition to an intense reflection of the Mo substrate. Corresponding Raman spectra also indicated the presence of the CuS crystal in the film (Figure S1A).¹⁸ No appreciable signal appeared for a Ga-containing compound(s) in either the XRD pattern or Raman spectrum of the film, indicating an amorphous nature of the component. For the growth of a CuGaS₂ crystallite, the as-deposited film was sulfurized in the presence of 12 mg of elemental sulfur powder in an evacuated Pyrex ampoule at 600°C for 30 min. The XRD pattern of the film after the annealing gave appreciable reflections other than that of Mo.
Figure 1. XRD patterns of (A) the as-deposited film and (B) that annealed at 600 °C in a sulfur atmosphere. (C) CSD data of CuGaS$_2$ (KE110102).

(Figure 1B). Most of the peaks were assignable to a chalcopyrite CuGaS$_2$ crystal (CSD: KE110192, Figure 1C).$^{9,10}$ Broad weak reflections derived from CuS (CSD: 2310609) were also included in the XRD pattern. The Raman spectrum of the film showed an intense peak at 307 cm$^{-1}$ that was assigned to the A1-band for chalcopyrite CuGaS$_2$; other peaks except for an unknown shoulder that appeared at 321 cm$^{-1}$ were also typically observed for the chalcopyrite CuGaS$_2$ compound (Figure S1B).$^{10}$ Hence, we could confirm the formation of a chalcopyrite CuGaS$_2$ film in the present process, though the film still has secondary components probably due to the short annealing duration and/or low temperature. Since further annealing or increment of the annealing temperature induced peeling off of the film as well as severe damage to the Mo/glass substrate, we used CuGaS$_2$ films obtained under the present annealing conditions for further studies.

Figure 2 shows cross-sectional SEM images of the as-deposited film and the CuGaS$_2$ film obtained after sulfur annealing. The as-deposited film showed formation of a ~1.5-μm-thick thin film composed of plate-shaped grains (Figure 2A). Based on the above XRD and Raman results, these grains would be derived from the CuS compound. The annealing induced the formation of submicron-sized particulate grains (Figure 2B). In addition to the change in grain shape, reduction on voids was also seen, though the film retained a porous nature, as shown in the corresponding top-view SEM image (Figure S2). Such a morphology is not suitable for application in photovoltaics because it would induce shunts. However, the morphology would be applicable for a PEC system; in some way, the rough morphology is beneficial because it increases contact area between the surface of photoelectrode and the reaction solution.

Linear sweep voltammetry (LSV) measurements in the dark and with photonirradiation of simulated sunlight (AM1.5G) were performed for the CuGaS$_2$ film by using a Eu(NO$_3$)$_3$ solution as an electron scavenging electrolyte.$^{17a}$ The film showed appreciable cathodic photocurrents, indicating a p-type semiconductive feature (Figure S3). An IPCE spectrum of the photocathode measured at −0.6 V (vs Ag/AgCl) is shown in Figure 3A. After a plateau region at wavelengths shorter than ~500 nm, the spectrum showed a steep drop up to a wavelength of ~530 nm; an appreciable Urbach tail was observed at longer wavelengths up to ~600 nm, suggesting the presence of defect states in the sample. By deformation of the spectrum into [$-h\nu\ln (1 - \text{IPCE})$]$^2$ vs. $h\nu$ (eV) plots at onset regions and application of extrapolation to the energy axis (inset in Figure 3A), the band gap energy of the film was estimated to be 2.37 eV, slightly smaller than with that reported in the literature (2.43 eV)$^{6,11}$ probably due to the influence of tail states.

The ionization potential of the CuGaS$_2$ film was analyzed by photoelectron spectroscopy (PES) to investigate the electron energy position of the valence band maximum (VBM) of the film. A cubic root of the photoelectron yield ($Y_p$) as a function of the energy of the incident light ($E_i$) is shown in Figure S4. The empirical functional form of photoemission from the semiconductor material is given by

$$Y_p \propto (E_i - E_{\text{ioniz}})^3,$$

where $E_{\text{ioniz}}$ is ionization potential.$^{19}$ Hence, $E_{\text{ioniz}}$ of the present film can be estimated from extrapolation of the plot toward the baseline: the $E_{\text{ioniz}}$ value thus-obtained was 5.37 eV. Assuming that there is no contribution of surface states, the thus-obtained $E_{\text{ioniz}}$ value corresponds to the VBM energy of the CuGaS$_2$ film. Moreover, when no pH dependence of the VBM energy of the
CuGaS₂ film is also assumed, the potential of VBM with respect to the Ag/AgCl electrode was 0.73 V (vs Ag/AgCl).

Based on results of the above electrostructural analyses, an estimated electron energy structure of the CuGaS₂ film is illustrated in Figure 3B. Equilibrium potentials of CO₂ and several reduction products with respect to the Ag/AgCl electrode at pH 6.8 are also shown in this figure. It is clear from the figure that the compound has sufficient overpotentials to induce CO₂ reduction into various products.

Figure 4A shows time course curves of gaseous products over the CuGaS₂ film immersed in a 0.1 M KHCO₃ solution saturated with CO₂ at pH 6.8 using the three-electrode setup at −0.6 V (vs Ag/AgCl) under illumination by simulated sunlight (AM1.5G). Although the main product was molecular hydrogen (H₂), appreciable amounts of carbon monoxide (CO) was liberated and accumulated monotonically with time. Other gaseous products were not detected. In addition, no CO production was observed when the photoelectrochemical reaction was performed in a 0.1 M Na₂SO₄ (pH 6.8) under N₂, indicating that the observed CO in this study was derived from CO₂. The total amounts of H₂ and CO liberated after illumination for 7.5 h reached ~6.49 μmol and ~0.07 μmol, respectively. The total amounts of evolved gasses exceeded the molar amount of CuGaS₂, which was ~1.8 μmol, as estimated by the density of CuGaS₂ (4.4 g cm⁻³), estimated from its lattice constant⁹,¹⁰, thickness (1.5 μm, see above), and area of the used film (0.56 cm²). It should be noted that analyses of the aqueous phase after the 7-h illumination indicated no probable products like formic acid, formaldehyde, and methanol. The trend in these product distributions was similar to that observed in the powder photocatalytic system based on the CuGaS₂ compound.¹⁴

Figure 4B shows the photocurrent stability profile during the reaction. The fact that there was no current flow when the light was turned off indicates that the observed currents (i.e. H₂ and CO liberations) are derived from PEC processes at the present applied potential. The photocurrent showed gradual increase from ~0.05 mA cm⁻² (initial) to ~0.18 mA cm⁻² (after 7.5-h reaction). It should be noted that there is no appreciable change in the structure of the CuGaS₂ film after the reaction (Figure S5). Although causes of the gradual activation are not clarified, we can confirm the stability of the CuGaS₂ film under the present reaction conditions. In our previous study,¹⁷,³⁰ we have discussed decay of the photocurrent with time for chalcogenide-based photocathodes used in water reduction to H₂. In these cases, photocathodes were modified with secondary components and/or catalysts on their surfaces; the photocurrent decay was often attributed to deteriorations of such surface components. Present results suggest sufficient stability of chalcogenide-based photocathodes and requirements to find highly stable surface modifier for improving the activity and the selectivity for CO₂ reduction are satisfied.

The Faradaic efficiencies (FEs) for H₂ and CO₂ productions after 7.5-h reaction were estimated to be 69.2% and 0.7%, respectively. Although there is no other detectable product (see
above), occurrences of side reactions should be considered. Reduction/re-oxidation of molecular O₂ generated on the counter electrode would be the other probable cause of lower FE values. Further studies are needed to clarify the product distribution after achieving further improvements of the overall reaction efficiency.

In conclusion, we have shown the possible application of a CuGaS₂ film to PEC CO₂ reduction using solar energy and H₂O as the electron source. Although the selectivity for water reduction and the activity for efficient utilization of sunlight energy are still insufficient, the high stability of the mixed chalcogenide film during the reaction is promising for future practical use. Inclusion of the Cu₂S impurity phase in the present film might fail to suppress PEC properties; we can expect improvements when a pure CuGaS₂ film having sufficient crystallinity is obtained. Moreover, since the present spray pyrolysis protocol is advantageous for the survey of new materials, we can also expect to find efficient mixed chalcogenide materials for induction of highly selective and active PEC CO₂ reduction with relatively low overpotentials by using this technique.

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