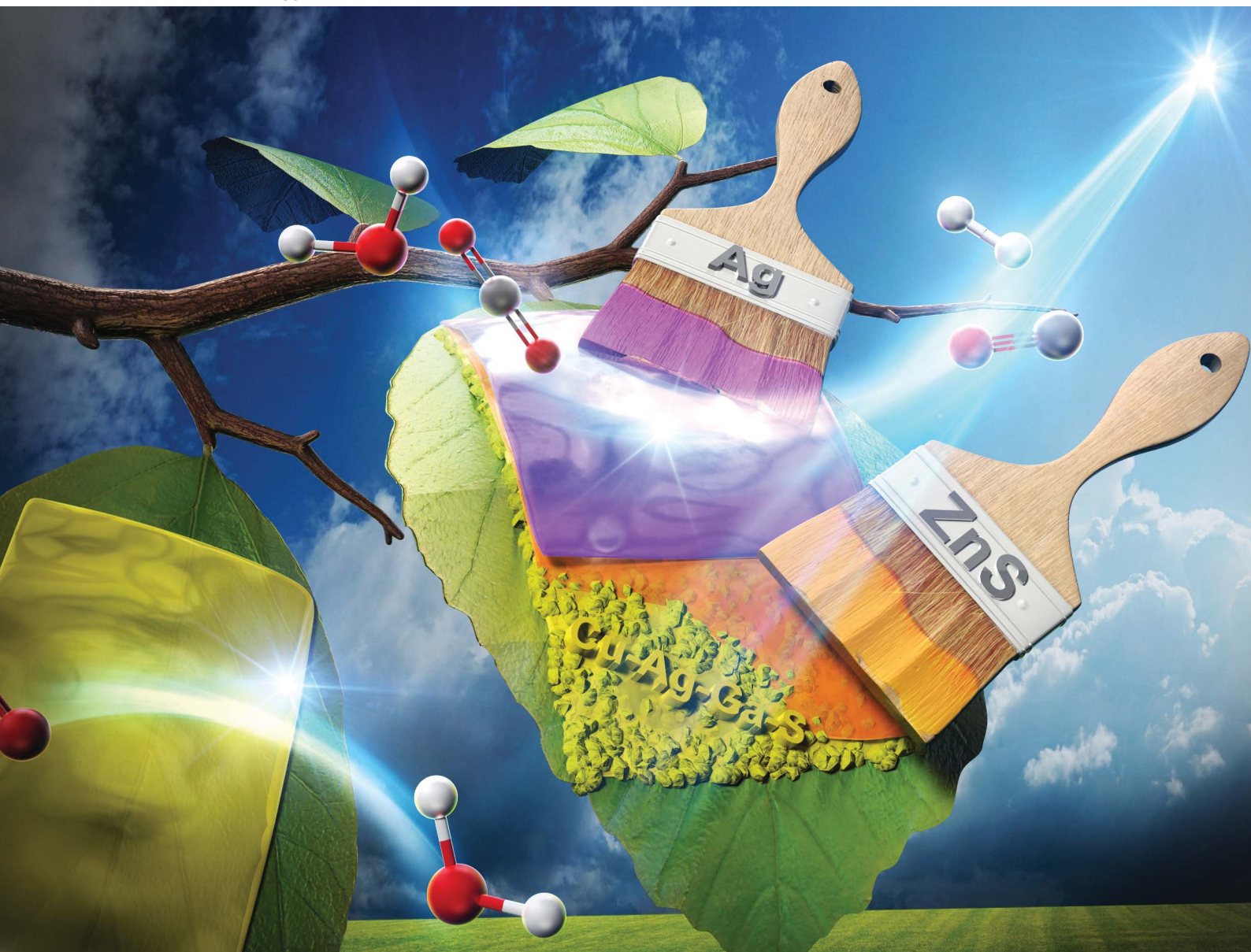


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PAPER

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Improvement of performance to form syngas utilizing water and CO₂ over a particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode by surface co-modification with ZnS and Ag[†]

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Surface of a particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode was co-modified with ZnS and Ag, resulting in improvement in the performance of the Cu_{0.8}Ag_{0.2}GaS₂ photocathode for syngas (H₂ + CO) formation through photoelectrochemical H₂O and CO₂ reduction under visible light in an aqueous electrolyte. Bubbles of the syngas were visually observed over the developed Ag and ZnS-co-modified Cu_{0.8}Ag_{0.2}GaS₂ photocathode at 0 V vs. RHE at the applied potential using a 300 W Xe-arc lamp ($\lambda > 420$ nm). Based on various control experiments and characterization studies, the following two crucial factors have arisen: (1) formation of a (ZnS)-(Cu_{0.8}Ag_{0.2}GaS₂) solid-solution near the surface of Cu_{0.8}Ag_{0.2}GaS₂ particles was vital for enhancing the separation of the photogenerated carriers, (2) the Ag cocatalyst loaded on the solid-solution worked as an active site for photoelectrochemical CO₂ reduction. Moreover, artificial photosynthetic syngas formation using water as an electron donor under simulated sunlight without any external bias was demonstrated by combining the developed Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode with a CoO_x-loaded BiVO₄ photoanode.

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1 Introduction

Photoelectrochemical systems which consist of a photocathode and a photoanode have been extensively studied not only for water splitting^{1,2} but also for CO₂ reduction^{3–5} using water as an electron donor. This is because these systems possess a potential to produce H₂ and CO as reduction products of water and CO₂ separately from O₂ as an oxidation product of water. The mixture of H₂ and CO is called syngas that can be used as a raw chemical for liquid fuels, lower olefines and aromatics synthesis.⁶ In this context, it is important to explore highly active photocathodes for syngas formation in terms of utilization of CO₂ and solar energy.

From the viewpoint of the construction of highly efficient photoelectrochemical cells,^{4,7} metal sulfide photocathodes are attractive because of their narrow band gaps and positive onset

potentials for the cathodic photocurrent.⁸ In particular, particulate-metal-sulfide-based photocathodes are advantageous because they can easily be fabricated as compared with a thin film photocathode using a vacuum process. We have reported that a particulate solid-solution of CuGaS₂ and AgGaS₂ (e.g., Cu_{0.8}Ag_{0.2}GaS₂) provides higher photocathodic performance than that of pristine CuGaS₂ in photoelectrochemical water reduction to form hydrogen under visible light.⁹ Moreover, the report¹⁰ that a particulate-(CuGa)_{0.5}ZnS₂-based photocathode is active for syngas formation under visible light motivated us to use a particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode for syngas formation. However, the photoelectrochemical performance of such a particulate-based photocathode is generally not yet enough to build photoelectrochemical cells that work under solar light if modifications such as loading cocatalysts are not performed. Therefore, it is important to discover a surface modification method being effective for improving the performance of Cu_{0.8}Ag_{0.2}GaS₂ in order to apply Cu_{0.8}Ag_{0.2}GaS₂ to a photocathode for syngas formation utilizing water and CO₂ under sunlight.

Various surface modifications of photocathodes have been investigated to develop highly active photocathodes. To date, Cu₂ZnSnS₄,^{11,12} Cu₂ZnGeS₄,¹³ CuInS₂,¹⁴ Cu(In,Ga)Se₂,¹⁵ *p*-InP,^{16,17} *p*-ZnTe,¹⁸ *p*-Si,^{19,20} N-doped Ta₂O₅,¹⁶ CuFeO₂,²¹ Cu₂O,²² CuGaO₂,²³ and *p*-Fe₂O₃ (ref. 24) have emerged to showcase their performances for CO₂ reduction to form CO and HCOOH in aqueous solutions under visible light irradiation, which have been

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improved by surface modifications. Specifically, n-type semiconductors, metal complexes, or metal nanoparticles have been investigated as the modifications. Furthermore, judging from the progress in photoelectrochemical water splitting,^{1,8} co-modification of metal sulfide photocathodes with n-type semiconductors and metallic cocatalysts is expected to bring highly efficient photocathodes for CO₂ reduction. This is because co-modifications with n-type semiconductors and noble cocatalysts are frequently employed to enhance the separation of photogenerated electron-hole pairs and introduce active sites for water reduction.

Herein, we focused on the combination of ZnS with metallic cocatalysts as a co-modification. This is because ZnS is an n-type semiconductor being effective in improvement of syngas formation on the Cu₂ZnGeS₄ thin film photocathode¹³ of which the crystal structure is similar to the chalcopyrite structure of Cu_{0.8}Ag_{0.2}GaS₂. ZnS is expected to be easily formed on the surfaces of particulate-metal-sulfide-based photocathodes by a chemical deposition method.²⁵ Additionally, the toxicity of ZnS is lower than that of CdS, which is another typical n-type semiconductor. We first investigated the effects of modification conditions to deposit ZnS over particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathodes on their photocathodic performances for CO₂ reduction. Sequentially, we investigated additional modifications of the ZnS-modified photocathodes with various cocatalysts. Then, we discovered a co-modification for fabricating an active photocathode for CO₂ reduction to form syngas under simulated solar light, resulting in artificial photosynthetic syngas formation upon combining the developed photocathode with a CoO_x-loaded BiVO₄ photoanode.

2 Experimental methods

2.1 Preparation and characterization of a particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode

A particulate Cu_{0.8}Ag_{0.2}GaS₂ photocatalyst was prepared by a solid-state reaction according to a previous report.⁹ Starting materials Cu₂S (Kojundo; 99%), Ag₂S (Rare Metallic; 99.9%), and Ga₂S₃ (Kojundo; 99.99%) were ground using an agate mortar. A 10% excess amount of Ga₂S₃ was added to the starting materials. This Ga₂S₃-rich condition is effective in improving performance of Cu_{0.8}Ag_{0.2}GaS₂.⁹ The mixture sealed in a quartz ampoule tube after evacuation (<0.1 Pa) was heated at 1073 K for 10 h to obtain Cu_{0.8}Ag_{0.2}GaS₂ powder. The obtained powder was identified to be an almost single-phase by powder X-ray diffraction (Rigaku; Miniflex, X-ray source; Cu K α). Diffuse reflectance spectra of powder and photocathode samples were obtained using a UV-vis-NIR spectrometer (Jasco; UbestV-570) with an integrating sphere, and were converted to absorbance spectra from the reflection by the Kubelka-Munk function. As the reference samples, (ZnS)_{2x}-(Cu_{0.8}Ag_{0.2}GaS₂)_x solid-solutions were prepared by the same procedure above. ZnS (Sigma-Aldrich, 99.99%) was used as the starting material.

A pristine particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode was prepared by a drop-casting method. The Cu_{0.8}Ag_{0.2}GaS₂ powder was dispersed in ethanol (2–8 mg mL⁻¹). This suspension was dripped on a FTO substrate (Asahi Glass; F-doped

SnO₂) and thereby Cu_{0.8}Ag_{0.2}GaS₂ powder was accumulated on the substrate with 5 mg cm⁻². After drying up the ethanol at room temperature, the accumulated powder was annealed at 773 K for 2 h in N₂ gas to obtain a pristine particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode.

Modification of the pristine particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode (denoted as CAGS) with ZnS was conducted by a chemical bath deposition method according to the literature.²⁵ The notation of the photocathodes prepared under different conditions is summarized in Table 1. The detailed procedures of the experiments are explained as follows. ZnSO₄·7H₂O (Wako; 99.5%), thiourea (Wako; 98.0%) and citric acid (Wako; 98.0%) employed as the starting materials were dissolved in 270 mL of water at 353 K at concentrations of 0.033, 0.066 and 0.088 mol L⁻¹, respectively. After adding 30 mL of 25% of an aqueous ammonia solution (Wako) into the aqueous solution, a pristine particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode was immediately immersed into the final mixture for 10 minutes to deposit ZnS on the surface of the pristine photocathode. The ZnS-modified particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode was dried at room temperature and sequentially was annealed at 473 or 773 K for 2 h in N₂ gas. These are denoted as ZnS(473)-CAGS and ZnS(773)-CAGS. Then, the ZnS-modified particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode with non-annealing is denoted as ZnS(NA)-CAGS. A ZnSO₄-adsorbed particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode was prepared by dipping the pristine photocathode into an aqueous solution dissolving only ZnSO₄, followed by annealing at 773 K for 2 h under a N₂ gas. The obtained sample is denoted as ZnSO₄(773)-CAGS. The ZnSO₄-adsorbed Cu_{0.8}Ag_{0.2}GaS₂ photocathode with non-annealing is denoted as ZnSO₄(NA)-CAGS. A CAGS photocathode was dipped into the mixture of thiourea, citric acid and an aqueous ammonia solution (namely, without ZnSO₄) and then was annealed at 773 K for 2 h under N₂ gas. The obtained sample is denoted as ZnSO₄-w/o-CAGS. If a Cu_{0.8}Ag_{0.2}GaS₂ photocathode was immersed in an aqueous solution containing either thiourea, citric acid or an aqueous ammonia solution followed by annealing at 773 K for 2 h, the obtained photoelectrodes are denoted as thiourea(773)-CAGS, citric acid(773)-CAGS and ammonia(773)-CAGS, respectively.

Cocatalysts were loaded on the surfaces of photocathodes. AgNO₃, Cu(NO₃)₂, HAuCl₄, H₂PtCl₆, RuCl₃ and RhCl₃ were employed as the cocatalyst sources. An aqueous solution containing either one of the cocatalyst sources was dripped on a photocathode. The amount of the loaded cocatalyst was 100 nmol cm⁻². After drying off the aqueous solvent at room temperature, the photocathode was annealed at 773 K for 2 h in N₂ gas. Since it has been reported that RuCl₃ loaded on the surface of the Cu_{0.8}Ag_{0.2}GaS₂ photocathode through annealing in N₂ gas is reduced to metallic Ru by cathodic photocurrent during photoelectrochemical H₂ formation in an aqueous solution,⁹ various metal cocatalyst sources were loaded on the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode through the same procedure as that of the literature⁹ and could be reduced to the metallic state during the CO₂ reduction in our experiments. If necessary, the photocathode was immersed in a mixture of water and acetone (the ratio of 1 : 1 as volumes) for about 30 seconds



Table 1 Control experiments for deposition of ZnS on particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathodes^a

Entry	Sample notation	Conditions for ZnS deposition					Cathodic photocurrent density/ $\mu\text{A cm}^{-2}$
		Citric acid	Ammonia	Thiourea	ZnSO ₄	Anneal	
1	CAGS	No	No	No	No	None	130
2	ZnS(NA)-CAGS	Yes	Yes	Yes	Yes	None	200
3	ZnS(473)-CAGS	Yes	Yes	Yes	Yes	473 K	650
4	ZnS(773)-CAGS	Yes	Yes	Yes	Yes	773 K	1850
5	Citric acid(773)-CAGS	Yes	No	No	No	773 K	130
6	Ammonia(773)-CAGS	No	Yes	No	No	773 K	200
7	Thiourea(773)-CAGS	No	No	Yes	No	773 K	13
8	ZnSO ₄ -w/o-CAGS	Yes	Yes	Yes	No	773 K	220
9	ZnSO ₄ (773)-CAGS	No	No	No	Yes	773 K	400

^a Deposition time: 10 min. Photoelectrochemical measurement conditions; electrolyte: 0.1 mol L⁻¹ of an aqueous K₂SO₄ solution with a phosphate buffer (pH 7) saturated with 1 atm of N₂ gas, light source: a 300 W Xe-arc lamp with a cut-off filter ($\lambda > 420$ nm), applied potential: 0 V vs. RHE.

before dropping the aqueous solution containing the cocatalyst source in order to remove its water-repellency. Photocathode samples were analyzed using an X-ray photoelectron spectrometer (JEOL; JSP-9010MC; Mg anode). The binding energies of X-ray photoelectron spectra were corrected with the C 1s (284.3 eV) contamination peak on metallic Au foil. The binding energy of the Au foil was corrected using the reference datum of Au foil (Au 4f_{7/2}: 84.0 eV)²⁶ after a contamination and the oxide phase on the surface of the Au foil was carefully removed by Ar etching.

2.2 Photoelectrochemical measurement

Photoelectrochemical properties were evaluated using a potentiostat (Hokuto Denko; HSV-110). An H-type glass cell that consists of a working electrode cell and a counter electrode cell with a Nafion membrane (Dupont) to separate the compartment was used. A Pt wire and a saturated Ag/AgCl electrode (DKK-TOA) were used as counter and reference electrodes, respectively. 0.1 mol L⁻¹ of K₂SO₄ aq. with a phosphate buffer (each 0.025 mol L⁻¹ of KH₂PO₄ aq. and Na₂HPO₄ aq.) (pH 7) and 0.1 mol L⁻¹ of KHCO₃ aq. were employed as aqueous electrolytes, respectively. The electrolyte in the H-type glass cell was saturated with 1 atm of Ar, N₂ or CO₂ before measurements. pH of the aqueous KHCO₃ solution saturated with CO₂ was *ca.* 7. A 300 W Xe-arc lamp was employed as a light source. The wavelength of the irradiation light was controlled by a cut-off filter, an NIR-absorbing filter and band-pass filters. A solar simulator was employed as a light source of simulated sunlight (AM1.5G). The photocathode was irradiated with the light from the FTO side. The gaseous products were determined using gas chromatographs (Shimadzu; TCD, MS-5A, Ar and He carriers, detection of H₂ and O₂; FID with a methanizer, MS-13X, N₂ carrier, detection of CO). Formic acid was analyzed using an ion-chromatograph (TOSOH, IC-2000). An isotope experiment was conducted using ¹³CO₂ to confirm the carbon source of the product of the CO₂ reduction. ¹³CO of the reduction product of ¹³CO₂ was analyzed using GC-MS (Shimadzu; GCMS-QP2010 Plus, RESTEK; RT-Msieve 5A). For photoelectrochemical measurement using a two-electrode-type cell, the photocathode (3.3 cm²) was irradiated from the FTO side with the simulated

sunlight through a photoanode (1.0 cm²), resulting in that the total irradiation area was 3.3 cm².

3 Results and discussion

3.1 Surface modification with ZnS

Fig. 1 shows the effect of modification with ZnS on the photoelectrochemical properties of a particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode in an aqueous K₂SO₄ solution with a phosphate buffer (pH 7) saturated with 1 atm of N₂ gas under visible light irradiation. A pristine particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode gave a cathodic photocurrent under visible light irradiation as observed in a previous report (Fig. 1(a)).⁹ The cathodic photocurrent was increased by modification with ZnS on the surface of the particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode by chemical bath deposition (CBD) (Fig. 1(b)). The onset potentials of the linear sweep voltammograms were affected by the difference in the CBD conditions (Fig. S1†), though it was difficult to find the relationship between the onset positions and the CBD conditions. Onsets of action spectra of the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathodes almost agreed with the absorption edge of pristine Cu_{0.8}Ag_{0.2}GaS₂ powder (Fig. 2), indicating that the cathodic photocurrent was generated by the

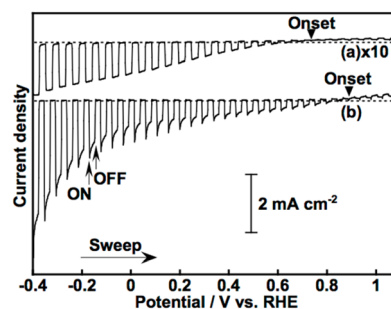


Fig. 1 Linear sweep voltammograms of (a) pristine and (b) ZnS-modified particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathodes under visible light irradiation. Electrolyte: 0.1 mol L⁻¹ of an aqueous K₂SO₄ solution with a phosphate buffer (pH 7) saturated with 1 atm of N₂ gas, light source: a 300 W Xe-arc lamp with a cut-off filter ($\lambda > 420$ nm).



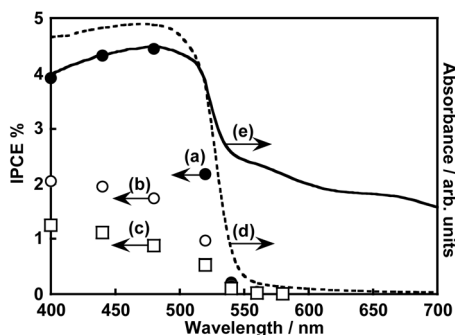


Fig. 2 Action spectra of ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathodes at (a) −0.4, (b) 0 and (c) 0.3 V vs. RHE and diffuse reflectance spectra of (d) pristine Cu_{0.8}Ag_{0.2}GaS₂ powder and (e) the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode. Electrolyte: 0.1 mol L^{−1} of an aqueous K₂SO₄ solution with a phosphate buffer (pH 7) saturated with 1 atm of N₂ gas, light source: a 300 W Xe-arc lamp with band-pass filters.

band gap excitation of Cu_{0.8}Ag_{0.2}GaS₂. Fig. 3 shows the time course of the photoelectrochemical H₂ formation using the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode. Although the photocurrent density was fairly high in the initial period (Fig. 3(a)), the value decreased with reaction time (Fig. 3(b)). This deactivation in the initial period could be attributed to the elution of the ZnS similar to the CdS deposited on chalcogenide photocathodes.^{12,27,28} The observed photocurrent of the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ in the later period almost corresponded to the H₂ evolution rates under visible light, indicating that the faradaic efficiency was almost 100% (Fig. 3(b)). In order to clarify the experimental factor affecting the H₂ formation rate over a ZnS-modified Cu_{0.8}Ag_{0.2}GaS₂ photocathode, control experiments were performed (Table 1). The annealing procedure after the ZnS modification with CBD was effective in improving the photocurrent density, while the photocurrent density of the pristine one was slightly enhanced by ZnS modification without annealing (Table 1, entries 1–4). Among them, annealing at 773 K was the most effective here. This is because, considering the heat resistance of FTO glass substrates, 773 K is close to the limit temperature. In contrast, significant improvement was not observed in the absence of ZnSO₄ in the starting materials for CBD with annealing at 773 K (Table 1, entries 5–8). The

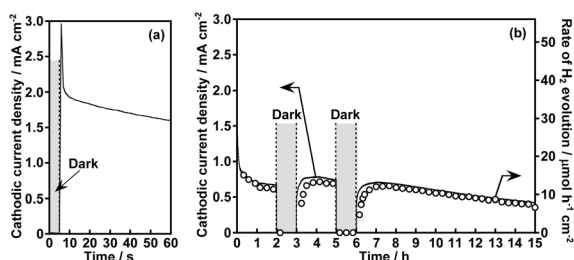


Fig. 3 Photoelectrochemical H₂ evolution using a ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode under visible light irradiation in (a) the initial and (b) the whole period of the reaction time. Electrolyte: 0.1 mol L^{−1} of an aqueous K₂SO₄ solution with a phosphate buffer (pH 7) saturated with 1 atm of Ar gas, light source: a 300 W Xe-arc lamp with a cut-off filter ($\lambda > 420$ nm), applied potential: 0 V vs. RHE.

photocurrent density of a ZnSO₄-modified Cu_{0.8}Ag_{0.2}GaS₂ photocathode was larger than that of the pristine one (Table 1, entry 9). Thus, the cathodic photocurrent of Cu_{0.8}Ag_{0.2}GaS₂ was significantly improved when all of ZnSO₄, thiourea, citric acid and ammonia were used for CBD with annealing at 773 K.

The surface configuration of the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode was examined using X-ray photoelectron spectra (XPS), Auger spectra and additional control experiments. Auger spectra indicated that the deposited ZnS partly included ZnO and Zn(OH)₂ (Fig. S2†). The ZnO and Zn(OH)₂ still existed at the surface even after annealing at 473 K. Such auger spectra disappeared after annealing at 773 K. Moreover, intensities of Zn 2p XPS peaks decreased with the increase in the annealing temperature, and annealing at 773 K drastically decreased the intensities (Fig. S3†). These auger and XPS measurements indicated the following two points; (i) deposited ZnS including ZnO and Zn(OH)₂ existed at the surface of ZnS(473)–CAGS, (ii) deposited Zn species were diffused in the surface of Cu_{0.8}Ag_{0.2}GaS₂ particles in ZnS(773)–CAGS. In other words, an annealing at 773 K is crucial to diffuse the ZnS deposited on the Cu_{0.8}Ag_{0.2}GaS₂ particles into the neighbourhood in the surface of the Cu_{0.8}Ag_{0.2}GaS₂ particles as summarized in Fig. 4(A). Specifically, the surface of the Cu_{0.8}Ag_{0.2}GaS₂ particles was covered with ZnS either of particles or film (Fig. 4(A)(a) and (b)). Afterwards, the ZnS was diffused into the Cu_{0.8}Ag_{0.2}GaS₂ particles by annealing at 773 K, though almost all of the ZnS existed in the neighbourhood in the surface (Fig. 4(A)(c)). This diffusion made the solid-solution of (ZnS)–(Cu_{0.8}Ag_{0.2}GaS₂) in the neighbourhood in the surface. The concentration of the diffused ZnS was gradually diluted from the surface to the bulk. Therefore, a crucial factor of the improvement was formation of

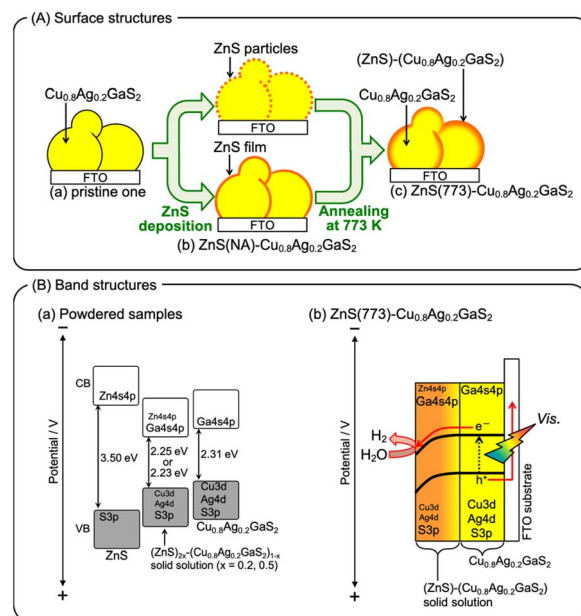


Fig. 4 (A) Proposed surface structures of the particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode, and (B) proposed band structures of (ZnS)_{2x}–(Cu_{0.8}Ag_{0.2}GaS₂)_x powders and the ZnS(773)–Cu_{0.8}Ag_{0.2}GaS₂ photocathode. The band gaps were estimated from the adsorption edges shown in Fig. S4†.

the (ZnS)-(Cu_{0.8}Ag_{0.2}GaS₂) solid-solution in the neighbourhood in the particulate Cu_{0.8}Ag_{0.2}GaS₂ surface. This crucial factor could provide the following effects. The surface incorporated with ZnS could work as an active site for photoelectrochemical water reduction, since ZnS is a well-known active photocatalyst for H₂ formation without loading of cocatalysts.^{29–32} Another aspect of the improvement may lie in the gradient of the band structure as shown in Fig. 4(B). The band gap of powdered Cu_{0.8}Ag_{0.2}GaS₂ was narrowed by forming the solid-solution of powdered (ZnS)-(Cu_{0.8}Ag_{0.2}GaS₂) (Fig. S4†). The same phenomenon to narrow the band gaps by homogeneously mixing with ZnS has been reported in the case of the (ZnS)-(CuGaS₂) solid-solution (namely, no Ag constituent).³³ These narrowed band gaps could be explained by the increase in the symmetries of MS₄ tetrahedrons (M = Zn, Cu, and Ga), implying that the conduction band minimum and valence band maximum both are shifted downwardly.³³ Again, XRD spectra of the (ZnS)-(Cu_{0.8}Ag_{0.2}GaS₂) (Fig. S4†) show that the MS₄ tetrahedrons (M = Zn, Cu, Ag, and Ga) tended to be close to the symmetrical tetrahedrons, judging from the peak splitting. Therefore, the conduction band minimum and valence band maximum of powdered (ZnS)-(Cu_{0.8}Ag_{0.2}GaS₂) might be located at more positive potentials than those of Cu_{0.8}Ag_{0.2}GaS₂ (Fig. 4(B)(a)). As for the structural information, no morphological changes in a series of ZnS-modified Cu_{0.8}Ag_{0.2}GaS₂ were observed using a scanning electron microscope (SEM), though it was difficult to clarify the structural configurations of the deposited ZnS in the observations using a SEM equipped with an energy dispersive X-ray spectrometer (SEM-EDS) (Fig. S5†). Although the quantitative consistency of the ZnS ratios between the photocathode and the powders was unclear, the aforementioned effect to alter the band positions implied that the conduction band minimum and valence band maximum of the neighbourhood in the surface gradually shifted downwardly due to the concentration gradient of the solid-solution of ZnS(773)-Cu_{0.8}Ag_{0.2}GaS₂ (Fig. 4(B)(b)). Assuming that the absorption coefficient of (ZnS)-(Cu_{0.8}Ag_{0.2}GaS₂) is similar to that of CuGaS₂ in the visible light region (20 000–50 000 cm⁻¹),³⁴ the ZnS-modified Cu_{0.8}Ag_{0.2}GaS₂ particles near FTO were mainly photoexcited. This is because the transmittance of incident photons would be at least 0.01% when the diameters of ZnS(773)-modified Cu_{0.8}Ag_{0.2}GaS₂ particles were *ca.* 2 μm (Fig. S5†). Indeed, we reported that CuGaS₂ particles being far from FTO have little contribution to the photocurrents of particulate-CuGaS₂-based photocathodes.^{35,36} Finally, the photogenerated electrons migrated to the surface region by the band bending of the ZnS-modified Cu_{0.8}Ag_{0.2}GaS₂ particles, resulting in enhancement of the separation of the photo-generated carriers (Fig. 4(B)(b)). These two aspects could be the crucial factors for the improvement by the ZnS modification.

3.2 Effect of cocatalysts loaded over ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathodes on CO₂ reduction performances

Table 2 shows the application of the ZnS(773)-Cu_{0.8}Ag_{0.2}GaS₂ photocathode (denoted as ZnS/Cu_{0.8}Ag_{0.2}GaS₂, hereafter) to CO₂ reduction under visible light and the effects of additional

modification of ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathodes with various cocatalysts. In this measurement, an aqueous KHCO₃ solution saturated with 1 atm of CO₂ gas (pH was *ca.* 7) was used as an electrolyte and 0 V *vs.* RHE was constantly applied to the photocathodes. Again, the pristine particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode gave a cathodic photocurrent in the aqueous KHCO₃ electrolyte (Table 2, entry 1). Partial cathodic photocurrent densities (*J*_{partial}) for H₂ and CO formations were certainly estimated. The surface modification with ZnS was effective for improving both *J*_{partial} and FE_{CO} (Table 2, entry 2). Considering the literature about photoelectrochemical CO₂ reduction to form CO over surfaces of (CuGa)_{0.5}ZnS₂ (ref. 10) and ZnS-modified Cu₂ZnGeS₄ (ref. 13) photocathodes, the surface of ZnS/Cu_{0.8}Ag_{0.2}GaS₂ seems to be effective for CO formation. No cathodic photocurrents for H₂ and CO formation were observed under darkness (Table 2, entry 3). In an aqueous K₂SO₄ solution with a phosphate buffer (pH 7) saturated with 1 atm of N₂ gas under visible light irradiation instead of the KHCO₃ electrolyte, photocurrent density only for H₂ formation was observed (Table 2, entry 4). Various cocatalysts were further loaded on the surfaces of the ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathodes (Table 2, entries 5–13). Noble metal cocatalysts of Pt, Rh and Ru were not effective for CO₂ reduction (Table 2, entries 5–7). Although the faradaic efficiencies of Pt- and Ru-loaded ones were beyond 100%, this is most likely because of experimental errors associated with usage of a syringe (1 mL) to extract the gaseous products. Au, Cu and Ag cocatalysts improved the partial current densities not only for H₂ formation but also for CO formation (Table 2, entries 8–10). The Ag-loaded ZnS/Cu_{0.8}Ag_{0.2}GaS₂ (Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂) photocathode showed the highest partial cathodic photocurrent densities for H₂ and CO formation. This sufficient performance was only obtained when the surface was modified with both ZnS and Ag accompanied by annealing (Table 2, entries 10–13). Considering the following three insights: (1) RuCl₃ loaded on the surface of the Cu_{0.8}Ag_{0.2}GaS₂ photocathode through annealing in N₂ gas is reduced to metallic Ru by cathodic photocurrent during photoelectrochemical H₂ formation in an aqueous solution,⁹ (2) In₂S₃ modified on a Cu₂ZnSnS₄ photocathode is reduced to metallic In during the photoelectrochemical reduction reaction,¹² (3) powdered Ag-containing metal sulfide photocatalysts with high apparent quantum yield for H₂ formation may reduce silver sulfide to metallic Ag during H₂ formation in an aqueous solution,^{37,38} it was suggested that the cathodic photocurrent was partly used to reduce the silver species loaded on the surface to metallic silver at the beginning stage. This metallic silver could be electrochemically active for CO₂ reduction as reported in the literature about an Ag metal electrode.^{39,40} The bubbles mixed with H₂ and CO gases were visually generated on the Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode accompanied by O₂ production on a Pt counter electrode when 0 V *vs.* RHE was applied to the photocathode under visible light irradiation (see an attached movie file). The Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode was active even under simulated sunlight (Fig. 5). An isotope experiment using ¹³CO₂ was conducted to confirm the carbon source of CO obtained. An aqueous K₂SO₄ solution saturated with 1 atm of ¹³CO₂ was employed as the electrolyte



Table 2 Effects of various surface modifications of particulate Cu_{0.8}Ag_{0.2}GaS₂-based photocathodes on photoelectrochemical CO₂ reduction under visible light^a

Entry	Cocatalyst	Annealing ^b	ZnS	Light	Gas	$J_{\text{partial}}/\mu\text{A cm}^{-2}$		FE _{CO} %	FE _{Total} %
						H ₂	CO		
1	None	—	No	Yes	CO ₂	10	0.3	3	98
2	None	—	Yes	Yes	CO ₂	430	70	14	95
3	None	—	Yes	No	CO ₂	0	0	—	—
4	None	—	Yes	Yes	N ₂	1200	0	0	97
5	Pt	773 K	Yes	Yes	CO ₂	790	10	1	117
6	Rh	773 K	Yes	Yes	CO ₂	420	30	7	100
7	Ru	773 K	Yes	Yes	CO ₂	90	5	5	127
8	Au	773 K	Yes	Yes	CO ₂	890	200	17	100
9	Cu	773 K	Yes	Yes	CO ₂	620	200	24	92
10	Ag	773 K	Yes	Yes	CO ₂	1600	330	17	100
11	Ag	773 K	No	Yes	CO ₂	190	5	3	96
12	Ag	None	No	Yes	CO ₂	60	1	2	98
13	Ag	None	Yes	Yes	CO ₂	130	7	5	91

^a Electrolyte: 0.1 mol L⁻¹ of an aqueous KHCO₃ solution saturated with 1 atm of CO₂ gas (pH was *ca.* 7), light source: a 300 W Xe-arc lamp with a cut-off filter ($\lambda > 420$ nm), applied potential: 0 V vs. RHE, reactor: a closed H-type glass cell (namely, a batch-type reactor). J_{partial} indicates an average of a partial cathodic photocurrent density for 3 h. For quantification of the gaseous products, a syringe (1 mL) was used to extract the gas. ^b Annealing was performed under a N₂ atmosphere for loading cocatalysts. FE_{CO} = (sum of the number of electrons consumed for CO formation)/(sum of the number of electrons passing through the outer circuit) × 100. FE_{total} = (sum of the number of electrons consumed for H₂ and CO formation)/(sum of the number of electrons passing through the outer circuit) × 100.

(Fig. S6†). Not ¹²CO but ¹³CO was obtained as the reduction product of ¹³CO₂ over the Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode, indicating that the carbon source of the obtained CO was a CO₂ molecule. When Ag, Cu and Au cocatalysts were employed, a small amount of formic acid was detected but it was difficult to quantify the formic acid. Thus, co-modification with ZnS and Ag using annealing has arisen as a new effective technique for improving the performance of the particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode for the CO₂ reduction to form CO accompanied by H₂ formation in an aqueous solution under simulated sunlight.

3.3 Photoelectrochemical syngas formation using water as an electron donor under simulated sunlight

Fig. 6 shows CO₂ reduction using a photoelectrochemical cell consisting of a Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode and a CoO_x/BiVO₄ photoanode⁴¹ in an aqueous KHCO₃ solution saturated with 1 atm of CO₂ gas. This photoelectrochemical cell of which the structure was partly a tandem-type gave photocurrent under simulated sunlight irradiation without any external bias. This is due to an overlap between onset potentials of the photocathode and the photoanode in the CO₂-saturated KHCO₃ electrolyte, as shown in Fig. 7. Considering that the

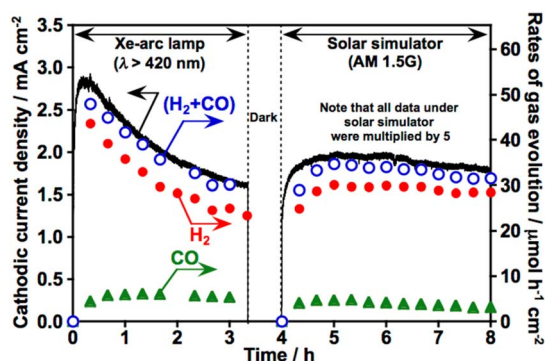


Fig. 5 Photoelectrochemical CO₂ reduction using the Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode under visible light and simulated sunlight irradiation. Electrolyte: 0.1 mol L⁻¹ of an aqueous KHCO₃ solution saturated with 1 atm of CO₂ gas, light source: a 300 W Xe-arc lamp with a cut-off filter ($\lambda > 420$ nm) and a solar simulator (AM1.5G), applied potential: 0 V vs. RHE. All of the observed current and the production rates under simulated solar light were multiplied by 5 for ease of the discussion of the performances.

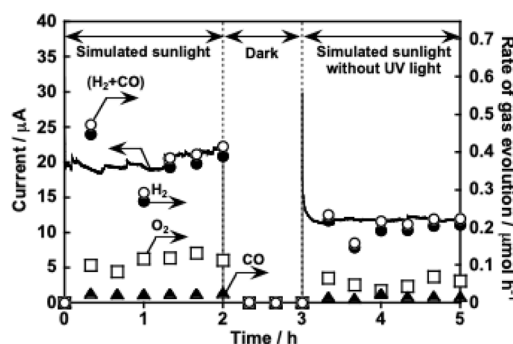


Fig. 6 CO₂ reduction utilizing water as an electron donor using a photoelectrochemical cell consisting of an Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode and a CoO_x/BiVO₄ photoanode under simulated sunlight without any external bias. Electrolyte: 0.1 mol L⁻¹ of an aqueous KHCO₃ solution saturated with 1 atm of a CO₂ gas, light source: a solar simulator (AM1.5G) without/with a cut-off filter ($\lambda > 420$ nm), area of electrodes: Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode; 3.3 cm² and CoO_x/BiVO₄ photoanode; 1.0 cm².



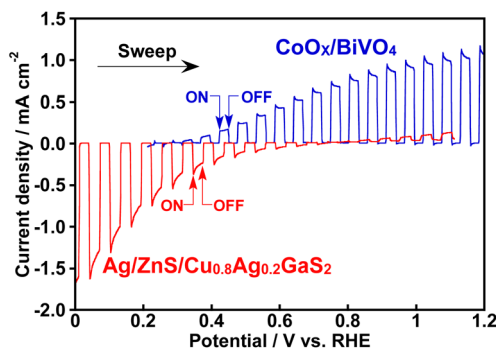


Fig. 7 Linear sweep voltammograms of an Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode and a CoO_x/BiVO₄ photoanode under visible light irradiation. Electrolyte: in 0.1 mol L⁻¹ of an aqueous KHCO₃ solution saturated with 1 atm of a CO₂ gas, light source: a 300 W Xe-arc lamp with a cut-off filter ($\lambda > 420$ nm).

absorption coefficient of BiVO₄ at 420 nm is 67 000 cm⁻¹,⁴² 1% of the incident photons could arrive at the Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode when the thickness of our BiVO₄ was regarded to be similar to the literature (*ca.* 300 nm).⁴¹ The faradaic efficiency for CO formation using the Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode was *ca.* 20% regardless of the decrease in the incident photons and change in the applied potentials (Table S1†). Therefore, the cell of which the structure was partly a tandem-type would hardly affect the selectivity for syngas formation. By paying attention to Fig. 6 again, observed photocurrent almost corresponded to the summation of CO and H₂ formation in the cathode cell, indicating that the photocurrent was used for syngas formation through photoelectrochemical reduction of water and CO₂. Most importantly, O₂ of the oxidation product of water was certainly obtained in the anode cell, whereas the rate of O₂ formation was slightly less than the stoichiometry due to an experimental error with the lower photocurrent. The photocurrent was continuously observed even under visible light included in simulated sunlight without any external bias. This indicated that this cell possessed an ability to utilize the visible light of sunlight. Thus, we successfully demonstrated solar syngas formation through the reduction of water and CO₂ separately from O₂ of the oxidation product of water upon constructing the photoelectrochemical cell consisting of the developed Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode and the CoO_x/BiVO₄ photoanode.

4 Conclusions

A co-modification with ZnS and Ag has been developed for improvement in H₂O and CO₂ reduction over a particulate-Cu_{0.8}Ag_{0.2}GaS₂-based photocathode to form H₂ and CO under visible light in an aqueous electrolyte. The faradaic efficiency and the partial cathodic photocurrent density for CO formation over the Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode achieved approximately 20% and 300 $\mu\text{A cm}^{-2}$, respectively, at 0 V vs. RHE. The Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS₂ photocathode was successfully combined with a CoO_x/BiVO₄ photoanode for constructing a photoelectrochemical cell. This photoelectrochemical cell

gave steady photocurrent under simulated sunlight irradiation without any external bias, resulting in syngas (H₂ and CO) formation using water as an electron donor. The knowledge in this work is expected to contribute to development of new particulate-photocatalyst-based photocathodes for highly efficient syngas production under sunlight.

Data availability

The data supporting this article have been included as ESI.†

Conflicts of interest

There are no conflicts to declare.

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