# **Supporting Information**

## Improvement of Performance to form Syngas utilizing Water and CO<sub>2</sub> over Particulate-Cu<sub>0.8</sub>Ag<sub>0.2</sub>GaS<sub>2</sub>-Based Photocathode by Surface Comodification with ZnS and Ag

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Fig. S1 Linear sweep voltammograms of a series of  $Cu_{0.8}Ag_{0.2}GaS_2$  photocathodes prepared by various conditions for ZnS deposition. Open triangles indicate onset potentials. Electrolyte: 0.1 mol L<sup>-1</sup> of an aqueous K<sub>2</sub>SO<sub>4</sub> solution with phosphate buffer (pH7) saturated with 1 atm of N<sub>2</sub> gas, light source: a 300 W Xe-arc lamp with a cut-off filter ( $\lambda > 420$  nm).

#### **Comments on Fig. S1:**

For ZnS(NA)-CAGS, ZnS(473)-CAGS, ZnS(773)-CAGS, and ZnSO<sub>4</sub>-w/o-CAGS, their onsets were located at more positive potentials than that of CAGS. The point being similar to each other of these four samples was that the aqueous solution for CBD contained citric acid, ammonia, and thiourea. However, Citric acid(773)-CAGS, Ammonia(773)-CAGS, and Thiourea(773)-CAGS gave onsets at relatively negative potentials than that of CAGS. Onset of ZnSO<sub>4</sub>(773)-CAGS resembled that of CAGS. Although the onset potentials were affected by the difference in the condition of the CBD, relationship between the onset positions and the CBD conditions was somewhat unclear at the current stage.



**Fig. S2** Auger spectra of Zn-LMM observed in an X-ray photoelectron spectroscopy of (a) a CAGS powder, (b) CAGS, (c) ZnSO<sub>4</sub>-w/o-CAGS, (d) ZnSO<sub>4</sub>(NA)-CAGS, (e) ZnS(NA)-CAGS, (f) ZnS(473)-CAGS, (g) ZnS(773)-CAGS, and (h) ZnSO<sub>4</sub>(773)-CAGS photocathodes and (i) ZnS, (j) ZnO, and (k) Zn(OH)<sub>2</sub> powders. The intensities of ZnS, ZnO, and Zn(OH)<sub>2</sub> are one twentieth of that of their raw data. The dash lines indicate the positions of Zn-LMM peaks of ZnS (989.5 eV), ZnO (988.0 eV), and Zn(OH)<sub>2</sub> (986.7 eV), respectively.<sup>1</sup>

#### **Comments on Fig. S2:**

The intensities of Zn-LMM of (g) and (h) were not recognized despite post-modification with ZnS. This is most likely because of the low concentration of the Zn species in the surface by its diffusion through the annealing, as shown in Fig. S3.



**Fig. S3** X-ray photoelectron spectra of Zn 2p of (A) CAGS, (B) ZnS(NA)-CAGS, (C) ZnSO<sub>4</sub>(NA)-CAGS, (D) ZnS(473)-CAGS, (E) ZnS(773)-CAGS, and (F) ZnSO<sub>4</sub>(773)-CAGS photocathodes. Ar etching times: (a, e, i, m, q, and u) 0 s, (b, f, j, n, r, and v) 5 s, (c, g, k, o, s, and w) 20 s, (d, h, l, p, t, and x) 60 s.



Fig. S4 (A) X-ray diffraction patterns of  $Cu_{0.8}Ag_{0.2}GaS_2$  and  $(ZnS)_{2x}-(Cu_{0.8}Ag_{0.2}GaS_2)_{1-x}$  solidsolutions (x = 0.2 and 0.5) with references of CuGaS<sub>2</sub> and ZnS. (B) Diffuse reflectance spectra of  $Cu_{0.8}Ag_{0.2}GaS_2$ ,  $(ZnS)_{2x}-(Cu_{0.8}Ag_{0.2}GaS_2)_{1-x}$  solid-solutions (x = 0.2 and 0.5), and ZnS.



Fig. S5 Cross-sectional SEM-EDS analysis of a series of the ZnS-modified  $Cu_{0.8}Ag_{0.2}GaS_2$  photocathodes. Note that peak intensities of Zn species in EDS were few.



**Fig. S6** Analysis result of <sup>13</sup>CO as a reduction product of <sup>13</sup>CO<sub>2</sub> reduction on an Ag/ZnS/Cu<sub>0.8</sub>Ag<sub>0.2</sub>GaS<sub>2</sub> photocathode. Electrolyte: 0.1 mol L<sup>-1</sup> of an aqueous K<sub>2</sub>SO<sub>4</sub> solution saturated with 1 atm of <sup>13</sup>CO<sub>2</sub> gas, applied potential: -0.6 V vs. Ag/AgCl, light source: a 300 W Xe-arc lamp with a cut-off filter ( $\lambda > 420$  nm).

Applied potential	Reduction of the	Photocurrent density	Faradaic efficiency (%)	
/ V vs RHE	incident light density	$/ \mu A cm^{-2}$	$H_2$	СО
+0.3	0%	320	75	23
+0.3	50%	190	79	9
+0.3	90%	100	95	16
0	0%	690	78	22
0	50%	620	71	23
0	90%	360	69	27
-0.4	0%	950	74	28
-0.4	50%	690	72	18
-0.4	90%	210	77	18

**Table S1** Dependences of applied potentials and incident light densities on performances of  $Ag/ZnS/Cu_{0.8}Ag_{0.2}GaS_2$  photocathodes for CO<sub>2</sub> reduction.

Electrolyte: of 0.1 mol L<sup>-1</sup> of an aqueous KHCO<sub>3</sub> solution saturated with 1 atm of CO<sub>2</sub> gas (pH was *ca.* 7), light source: a 300 W Xe-arc lamp with a cut-off filter ( $\lambda > 420$  nm) and ND filters. The photocurrent densities and Faradaic efficiencies were recorded at 3 h of the reaction time by similar experiment procedures to that of Fig. 5.

### Reference

 M. Bär, A. Ennaoui, J. Klaer, T. Kropp, R. Sáez-Araoz, N. Allsop, I. Lauermann, H.-W. Schock, M. C. Lux-Steinerd, J. Appl. Phys., 2006, 99, 123503.