

Supporting Information

Enhanced photoelectrochemical properties of CuGa₃Se₅ thin films for water splitting by the hydrogen mediated co-evaporation method

List of authors

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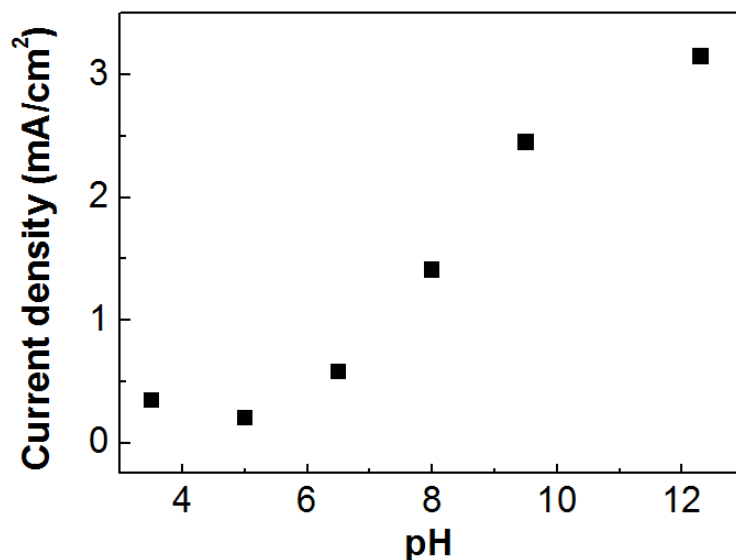
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Figure S1. Dependence of photocurrent density at 0 V_{RHE} of Pt/CGSe photocathode on pH values of electrolyte under AM 1.5G irradiation.



The experimental about the dependence of the photocathodic current of CGSe film on pH value as shown in Fig. S1 was conducted. The variance of photocurrent in different pH can be explained by following; (1) The evolution of hydrogen caused a decrease in the concentration of H^+ ion (increase OH^- concentration) around CGSe photoelectrode, and the resulting gradient in concentration may have interfered with the hydrogen evolution, especially in the neutral solution which had the lowest total concentration of H^+ and OH^- . (2) The band bending of CGSe film became steeper with increasing pH, judging from positive shift of the flat band potential (E_{FB}) with increasing pH. (By Mott-Schottky measurement, E_{FB} values of Pt/CGSe in solution with pH 5.0, 9.5 and 12.5 were 0.95, 1.21 and 1.39 V_{RHE} .) However, from consideration of $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CuInSe_2 photoelectrode in high pH solution, degradation of the electrode due to the release of Se in CGSe film as H_2Se was expected at $\text{pH} > 10$.^{1,2}

Figure S2. Current-time curve of Pt/CGSe and Pt/ZnS/CGSe at 0.1 V_{RHE} under continuous irradiation of 420-800 nm light in 0.1 M Na₂SO₄ solution (pH=9.5) with stirring.

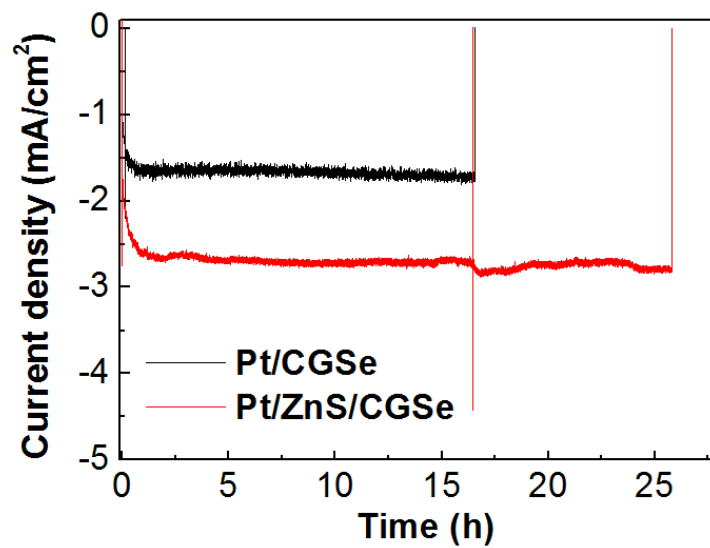


Table S1. Summarization of IPCE values for Pt/CGSe and Pt/ZnS/CGSe photoelectrodes at various hydrogen pressure.

	STH (%)*	Photocurrent density at 0 V _{RHE} (mA/cm ²)*	IPCE at 0 V _{RHE} (%)**
Pt/CGSe ^a	0.06	1.25	9.5
Pt/ZnS/CGSe ^a	0.10	2.21	13.2
Pt/CGSe ^b	0.09	1.80	9.9
Pt/ZnS/CGSe ^b	0.25	4.35	25.4

CGSe^a : CGSe film grown without hydrogen introduction.

CGSe^b : CGSe film grown with hydrogen introduction of 5×10^{-3} Pa.

*: under AM 1.5G irradiation.

** : under monochromatic light (520 nm).

In case of Pt/ZnS/CGSe^b, the expected photocurrent at 0 V_{RHE} from absorbable photons (1.4×10^{17} cm⁻²s⁻¹) in AM 1.5G, as estimated from the absorption edge of the CGSe (730 nm) and IPCE value, was 5.7 mA/cm². We suggest that a difference between expected and measured photocurrents can be reduced by more elaborating efforts to find a well matching overlayer with CGSe.

References

1. D. Yokoyama, T. Minegishi, K. Maeda, M. Katayama, J. Kubota, A. Yamada, M. Konagai and K. Domen, *Electrochem. Comm.*, 2010, **12**, 851-853.
2. O. Savadogo, *Sol. Energy Mater. Sol. Cells*, 1998, **52**, 361-388.