

Electronic Supplementary Information

An Effect of Ag(I)-substitution at Cu sites in CuGaS₂ on Photocatalytic and Photoelectrochemical Properties for Solar Hydrogen Evolution

Hiroshi Kaga,^a Yuko Tsutsui,^a Akira Nagane,^a Akihide Iwase^{a,b} and Akihiko Kudo^{a,b*}

^a *Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1–3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan*

^b *Photocatalysis International Research Center, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan*

* Corresponding author: Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1–3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan.

TEL: +81-3-5228-8267

FAX: +81-3-5261-4631

E-mail: a-kudo@rs.kagu.tus.ac.jp (A. Kudo)

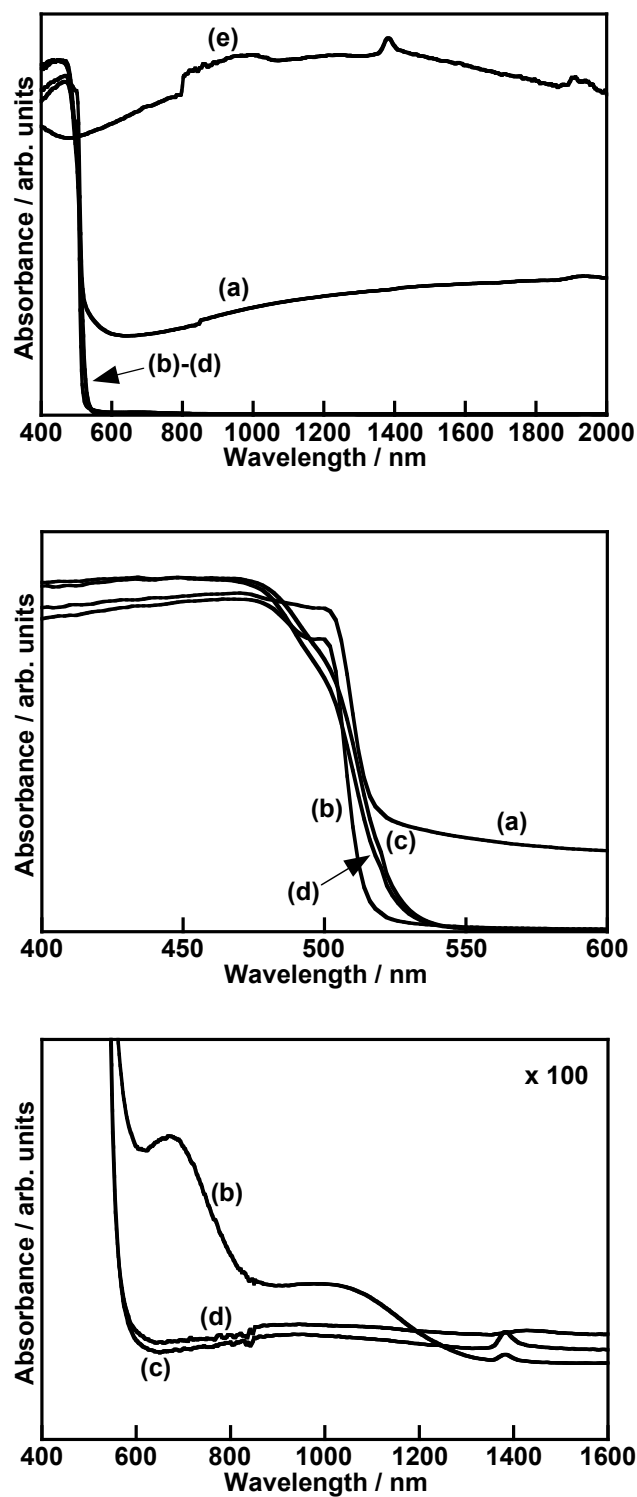


Figure S1. Diffuse reflectance spectra of (a)-(d) CuGaS_2 and (e) Cu_2S . CuGaS_2 samples were prepared (a) without and with (b) 10%, (c) 20% and (d) 30% excess Ga_2S_3 .

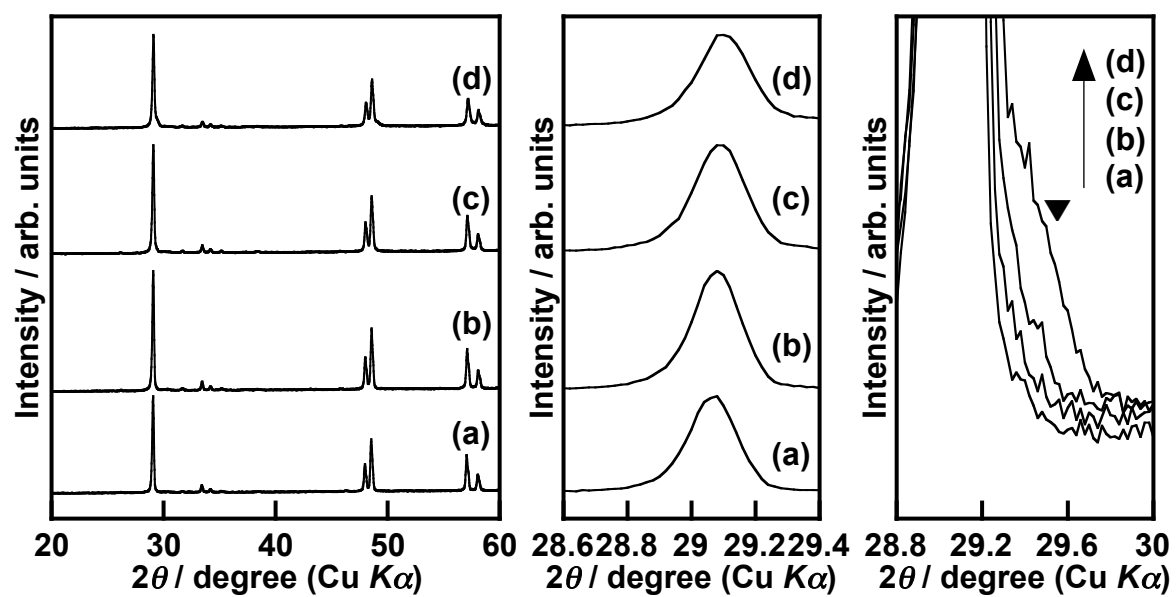


Figure S2. X-ray diffraction patterns of CuGaS_2 prepared (a) without and with (b) 10%, (c) 20% and (d) 30% excess Ga_2S_3 . Closed triangle indicates a peak due to an impurity phase.

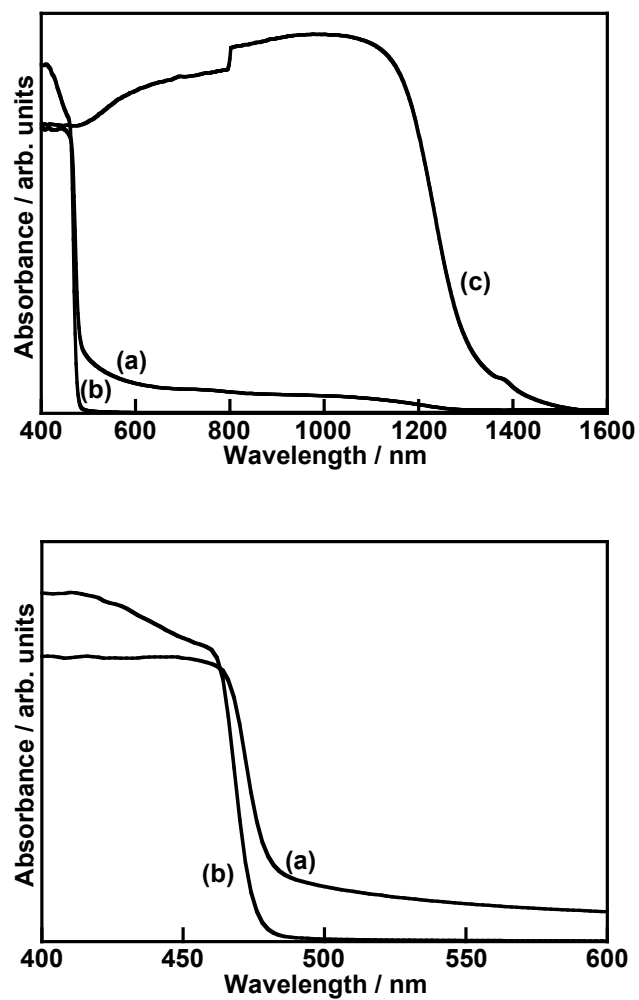


Figure S3. Diffuse reflectance spectra of (a), (b) AgGaS_2 and (c) Ag_2S . AgGaS_2 samples were prepared with (a) 10% and (b) 20% excess Ga_2S_3 .

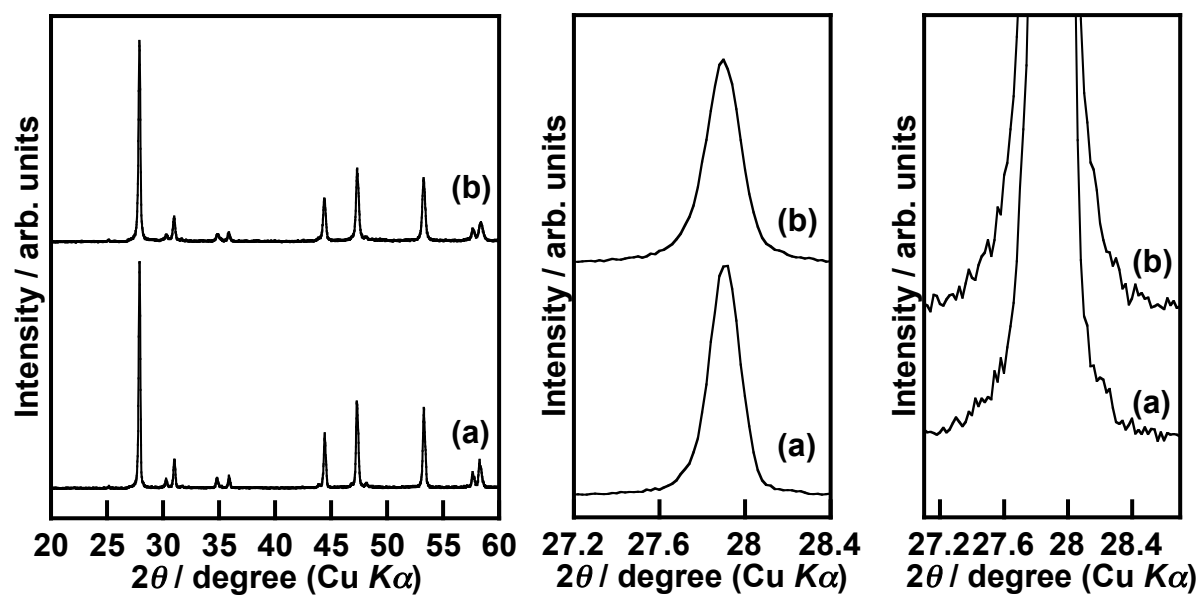


Figure S4. X-ray diffraction patterns of AgGaS_2 prepared with (a) 10% and (b) 20% excess Ga_2S_3 .

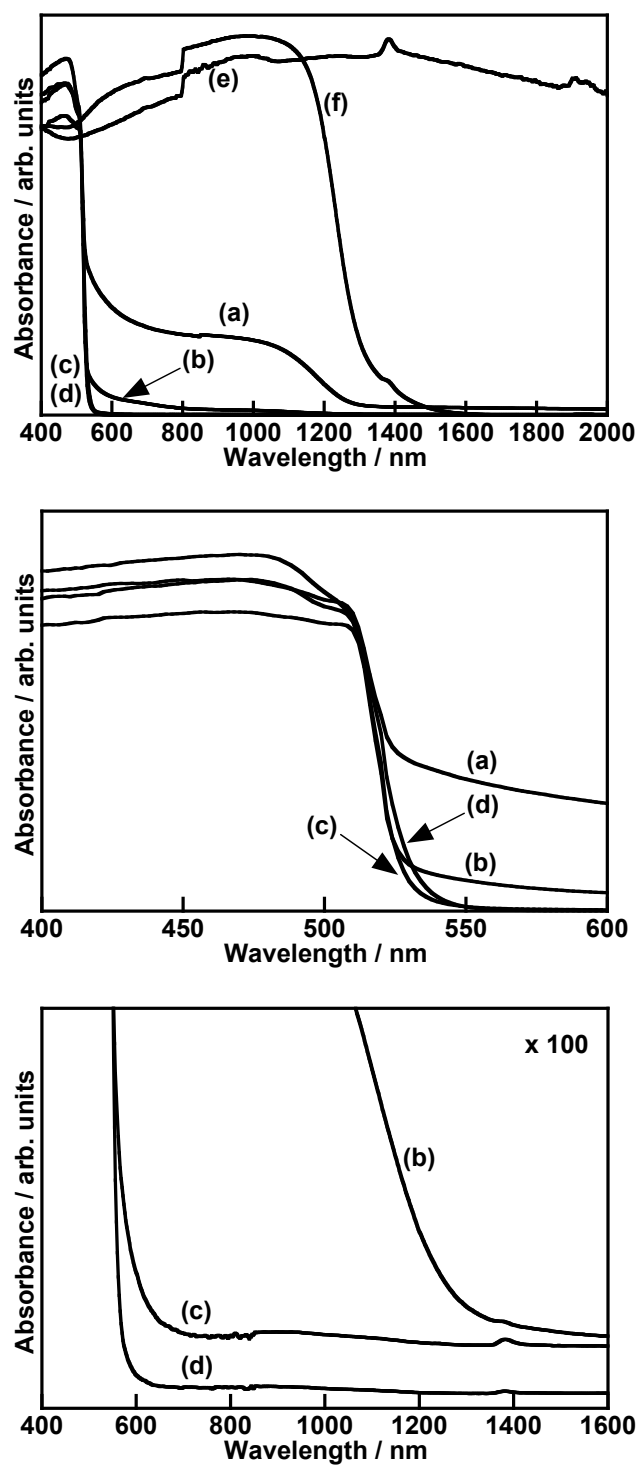


Figure S5. Diffuse reflectance spectra of (a)-(d) $\text{Cu}_{0.8}\text{Ag}_{0.2}\text{GaS}_2$, (e) Cu_2S and (f) Ag_2S . $\text{Cu}_{0.8}\text{Ag}_{0.2}\text{GaS}_2$ samples were prepared (a) without and with (b) 5%, (c) 10% and (d) 20% excess Ga_2S_3 .

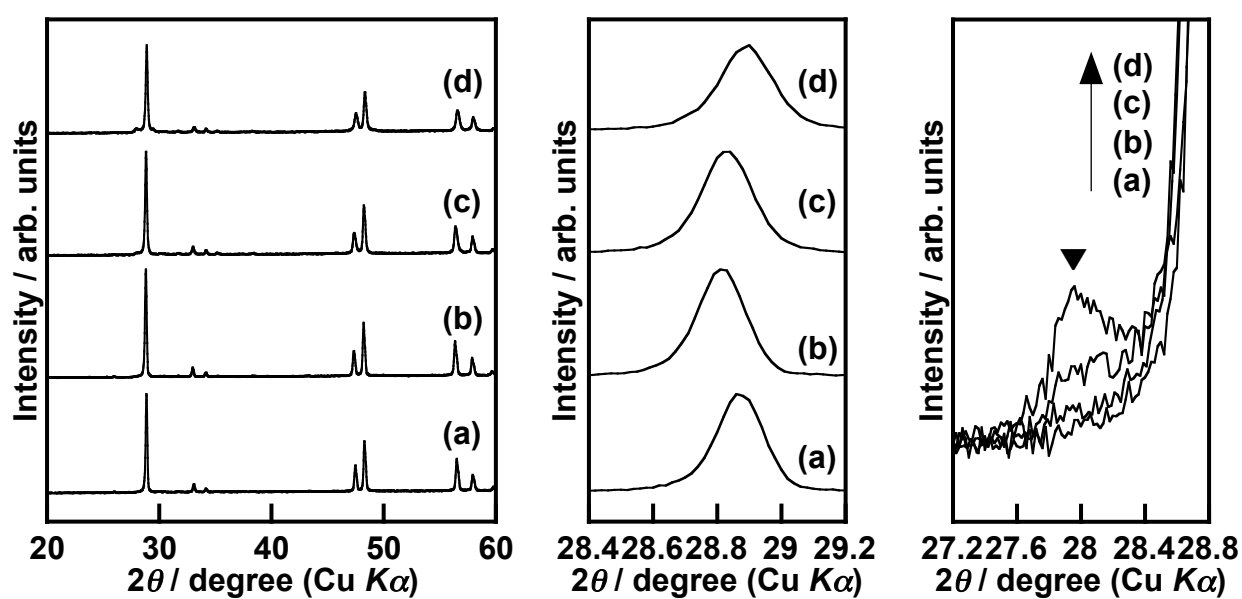


Figure S6. X-ray diffraction patterns of $\text{Cu}_{0.8}\text{Ag}_{0.2}\text{GaS}_2$ prepared (a) without and with (b) 5%, (c) 10% and (d) 20% excess Ga_2S_3 . Closed triangle indicates a peak due to an impurity phase.

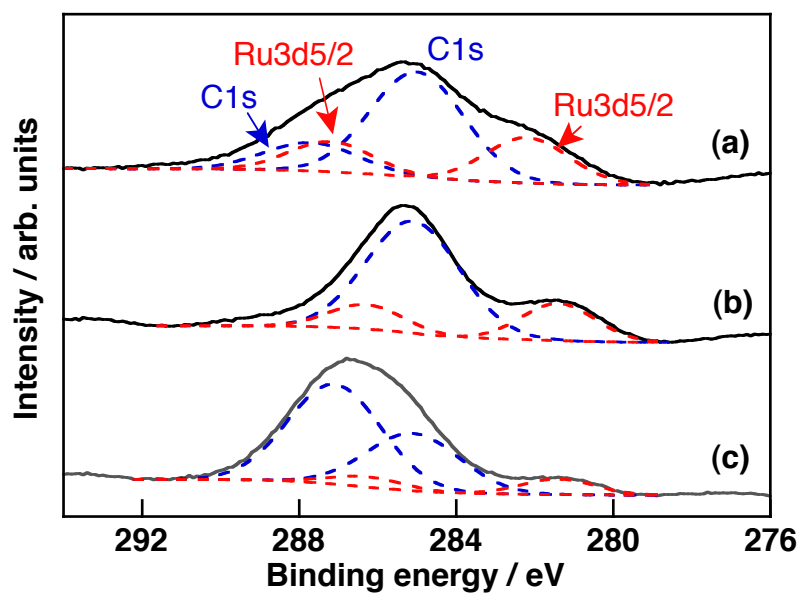


Figure S7. XPS spectra of Ru in (a) a mixture of RuCl_3 and $\text{Cu}_{0.8}\text{Ag}_{0.2}\text{GaS}_2$, (b) Ru(1.0 wt%)-loaded $\text{Cu}_{0.8}\text{Ag}_{0.2}\text{GaS}_2$ powder and (c) Ru(0.5 wt%)-loaded $\text{Cu}_{0.8}\text{Ag}_{0.2}\text{GaS}_2$ electrode. The binding energy for each sample was calibrated using Cu2p.