Electronic Supplementary Information

An Effect of Ag(I)-substitution at Cu sites in CuGaS$_2$ on Photocatalytic and Photoelectrochemical Properties for Solar Hydrogen Evolution

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Figure S1. Diffuse reflectance spectra of (a)-(d) CuGaS$_2$ and (e) Cu$_2$S. CuGaS$_2$ samples were prepared (a) without and with (b) 10%, (c) 20% and (d) 30% excess Ga$_2$S$_3$. 
Figure S2. X-ray diffraction patterns of CuGaS$_2$ prepared (a) without and with (b) 10%, (c) 20% and (d) 30% excess Ga$_2$S$_3$. Closed triangle indicates a peak due to an impurity phase.
Figure S3. Diffuse reflectance spectra of (a), (b) AgGaS$_2$ and (c) Ag$_2$S. AgGaS$_2$ samples were prepared with (a) 10% and (b) 20% excess Ga$_2$S$_3$. 
Figure S4. X-ray diffraction patterns of AgGaS$_2$ prepared with (a) 10% and (b) 20% excess Ga$_2$S$_3$. 
Figure S5. Diffuse reflectance spectra of (a)-(d) Cu$_{0.8}$Ag$_{0.2}$GaS$_2$, (e) Cu$_2$S and (f) Ag$_2$S. Cu$_{0.8}$Ag$_{0.2}$GaS$_2$ samples were prepared (a) without and with (b) 5%, (c) 10% and (d) 20% excess Ga$_2$S$_3$. 
Figure S6. X-ray diffraction patterns of Cu$_{0.8}$Ag$_{0.2}$GaS$_2$ prepared (a) without and with (b) 5%, (c) 10% and (d) 20% excess Ga$_2$S$_3$. Closed triangle indicates a peak due to an impurity phase.
Figure S7. XPS spectra of Ru in (a) a mixture of RuCl$_3$ and Cu$_{0.8}$Ag$_{0.2}$GaS$_2$, (b) Ru(1.0 wt%)-loaded Cu$_{0.8}$Ag$_{0.2}$GaS$_2$ powder and (c) Ru(0.5 wt%)-loaded Cu$_{0.8}$Ag$_{0.2}$GaS$_2$ electrode. The binding energy for each sample was calibrated using Cu2p.