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Article

The Effect of Cu and Ga Doped $ZnIn_2S_4$ under Visible Light on the High Generation of H_2 Production

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Table S1. Starting material for the preparation of photocatalyst.

Catalyst	Starting Material (mmol)				
	$ZnSO_4 \cdot 7H_2O$	$GaCl_3$	CuCl	$InCl_3$ $4H_2O$	TAA
$ZnIn_2S_4$	1	0	0	2	8
$Zn_{0.87}Cu_{0.13}In_2S_{3.935}$	0.87	0	0.13	2	8
$Zn_{0.87}Ga_{0.13}In_2S_{4.065}$	0.87	0.13	0	2	8
$Zn_{0.86}(CuGa)_{0.07}In_2S_4$	0.86	0.07	0.07	2	8
$Zn_{0.80}(CuGa)_{0.10}In_2S_4$	0.80	0.1	0.1	2	8
$Zn_{0.74}(CuGa)_{0.13}In_2S_4$	0.74	0.13	0.13	2	8
$Zn_{0.68}(CuGa)_{0.16}In_2S_4$	0.68	0.16	0.16	2	8
$Zn_{0.62}(CuGa)_{0.19}In_2S_4$	0.62	0.19	0.19	2	8

Table S2. Expected photocatalyst components (molar ratio).

	$ZnIn_2S_4$	In_2S_3	$CuInS_2$	Ga_2S_3
$ZnIn_2S_4$	1	0	0	0
$Zn_{0.87}Cu_{0.13}In_2S_{3.935}$	0.87	0.065	0.130	0
$Zn_{0.87}Ga_{0.13}In_2S_{4.065}$	0.87	0.130	0	0.065
$Zn_{0.86}(CuGa)_{0.07}In_2S_4$	0.86	0.105	0.070	0.035
$Zn_{0.80}(CuGa)_{0.10}In_2S_4$	0.80	0.150	0.100	0.050
$Zn_{0.74}(CuGa)_{0.13}In_2S_4$	0.74	0.195	0.130	0.065
$Zn_{0.68}(CuGa)_{0.16}In_2S_4$	0.68	0.240	0.160	0.080
$Zn_{0.62}(CuGa)_{0.19}In_2S_4$	0.62	0.285	0.190	0.095

Table S3. Elemental ratios of $Zn_{(1-2x)}(CuGa)_xIn_2S_4$ from XPS result.

Catalyst	Elemental Component (Mole Ratio)				
	Zn	Ga	Cu	In	S
$ZnIn_2S_4$	1	-	-	2.25	3.99
$Zn_{0.86}(CuGa)_{0.07}In_2S_4$	0.86	0.06	0.06	2.09	4.11
$Zn_{0.80}(CuGa)_{0.10}In_2S_4$	0.74	0.09	0.09	1.91	3.77
$Zn_{0.74}(CuGa)_{0.13}In_2S_4$	0.74	0.11	0.12	2.31	3.88
$Zn_{0.68}(CuGa)_{0.16}In_2S_4$	0.68	0.15	0.14	2.09	3.61
$Zn_{0.62}(CuGa)_{0.19}In_2S_4$	0.62	0.19	0.19	1.83	3.70

Table S4. Specific surface area of photocatalysts.

Photocatalyst	Specific Surface Area [$m^2 \cdot g^{-1}$]
$ZnIn_2S_4$	5.5
$Zn_{0.74}(CuGa)_{0.13}In_2S_4$	32.7
$Zn_{0.62}(CuGa)_{0.19}In_2S_4$	18.6

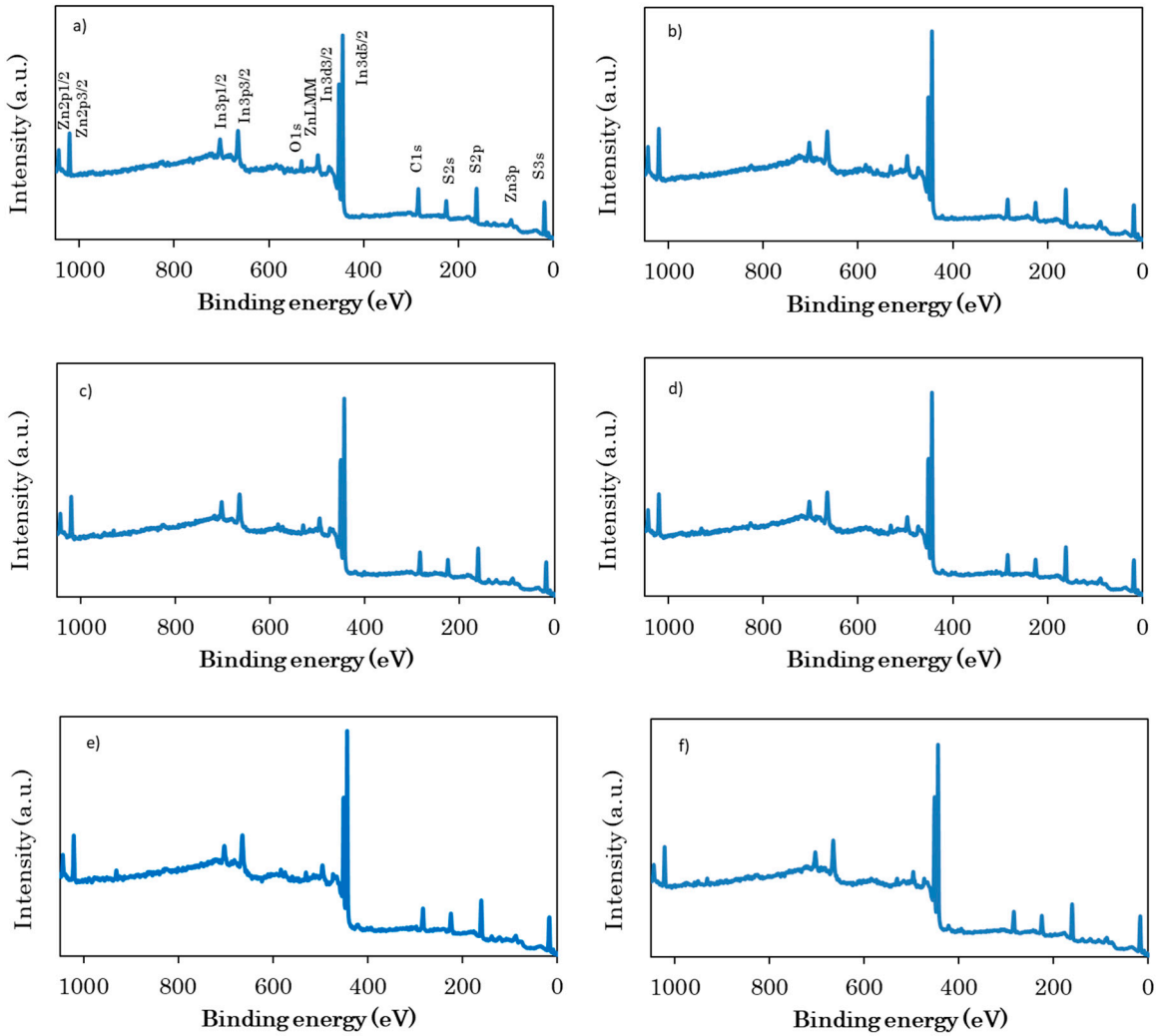

Figure S1. XPS survey spectra of $Zn_{(1-2x)}(CuGa)_xIn_2S_4$. (**a**) x = 0, (**b**) x = 0.07, (**c**) x = 0.10, (**d**) x = 0.13, (**e**) x = 0.16 and (**f**) x = 0.19.

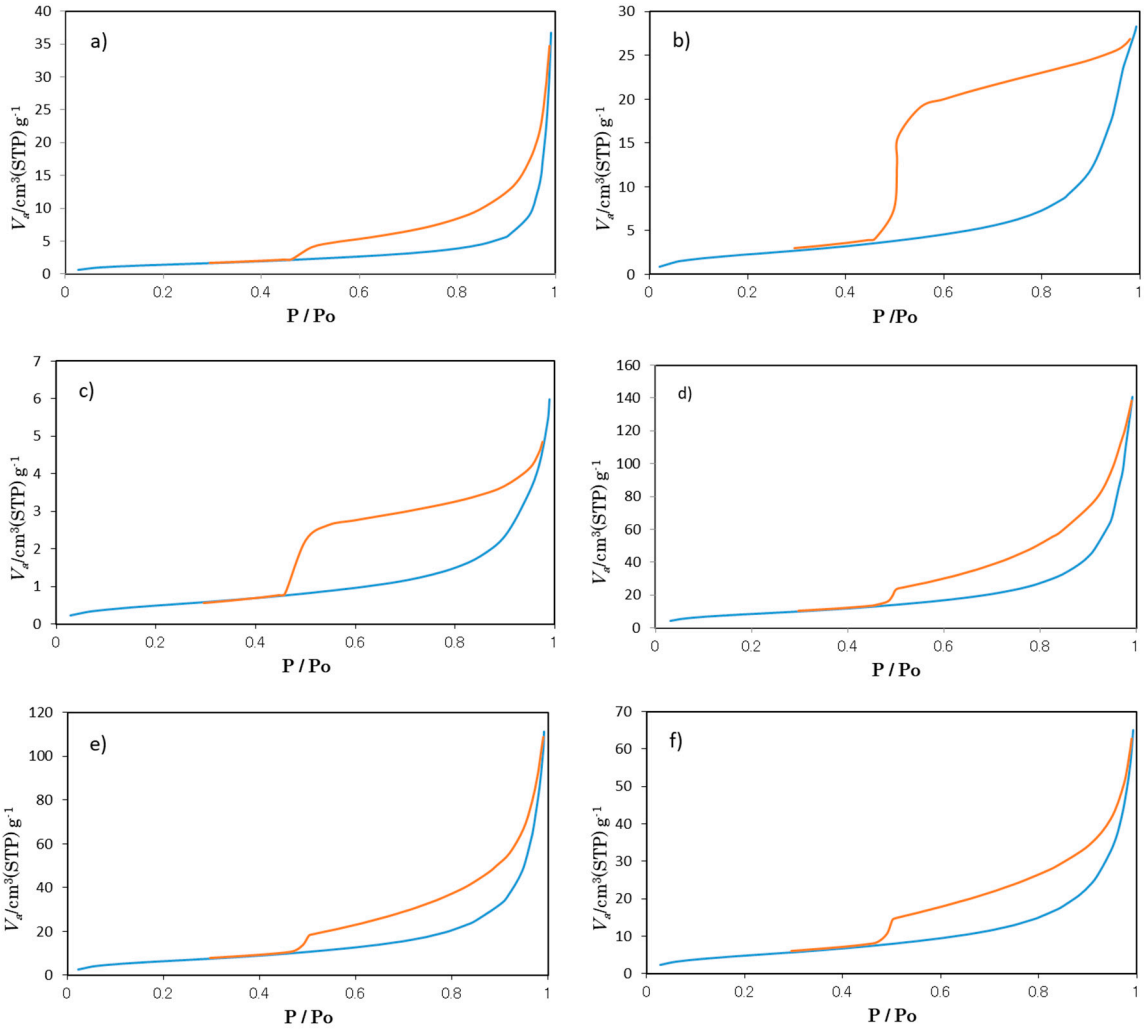

Figure S2. Adsorption/desorption isotherm of $Zn_{(1-2x)}(CuGa)_xIn_2S_4$. (**a**) x = 0, (**b**) x = 0.07, (**c**) x = 0.10, (**d**) x = 0.13, (**e**) x = 0.16 and (**f**) x = 0.19. Blue line: adsorption, orange line: desorption.

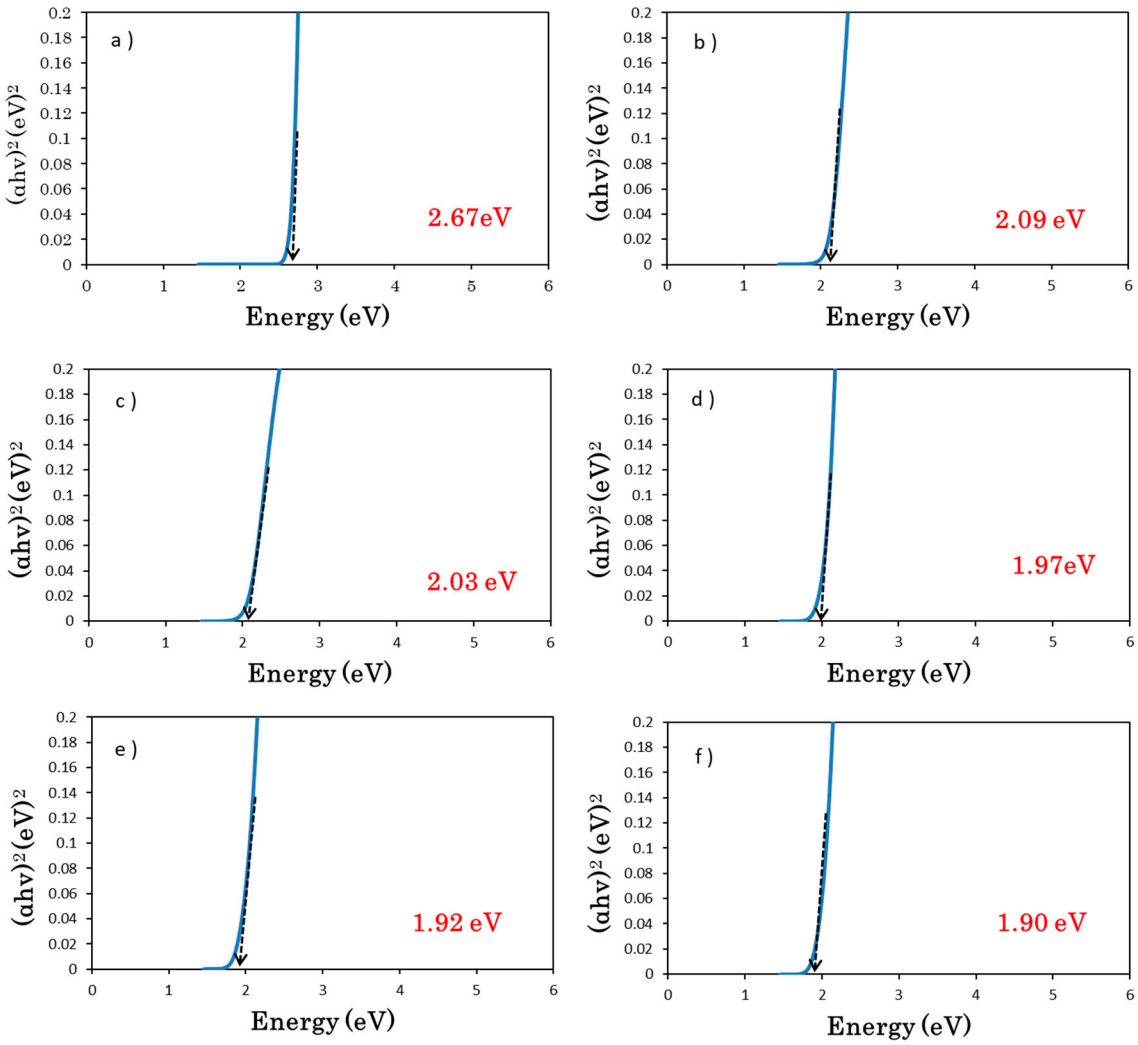

Figure S3. Tauc plots of $Zn_{(1-2x)}(CuGa)_xIn_2S_4$. (**a**) x = 0, (**b**) x = 0.07, (**c**) x = 0.10, (**d**) x = 0.13, (**e**) x = 0.16 and (**f**) x = 0.19.

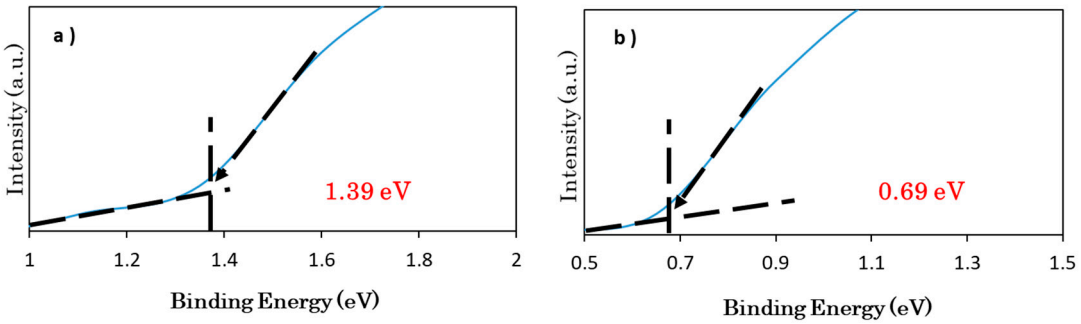

Figure S4. Valence-band edge XPS spectra of (**a**) $ZnIn_2S_4$ and (**b**) $Zn_{0.74}(CuGa)_{0.13}In_2S_4$.

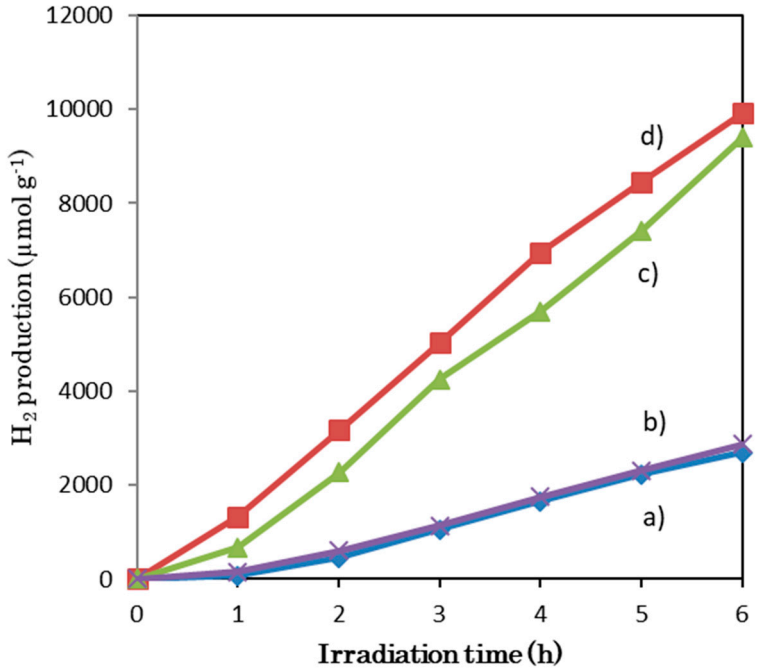

Figure S5. Photocatalytic hydrogen production with (**a**) $ZnIn_2S_4$ (rhombus), (**b**) $Zn_{0.87}Ga_{0.13}In_2S_{4.065}$ (cross), (**c**) $Zn_{0.87}Cu_{0.13}In_2S_{3.935}$ (triangle) and (**d**) $Zn_{0.74}(CuGa)_{0.13}In_2S_4$ (square). Pt doping: 1.0 wt%.

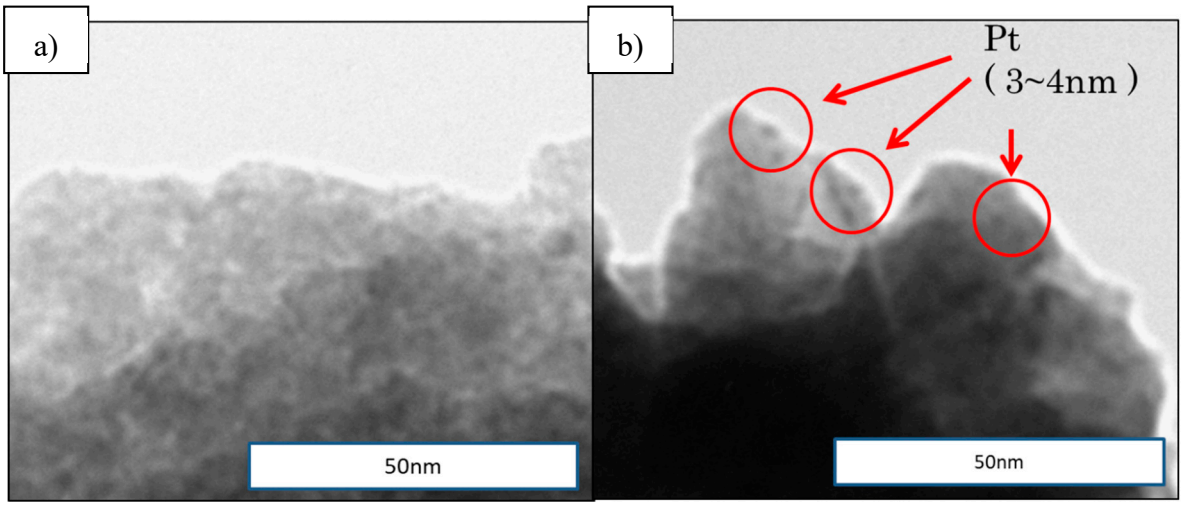

Figure S6. TEM images of $Zn_{0.74}(CuGa)_{0.13}In_2S_4$. (**a**) before and (**b**) after irradiation.