

Article

# Improvement of photocatalytic H<sub>2</sub>-generation under visible light irradiation by controlling band gap of ZnIn<sub>2</sub>S<sub>4</sub> with Cu and In

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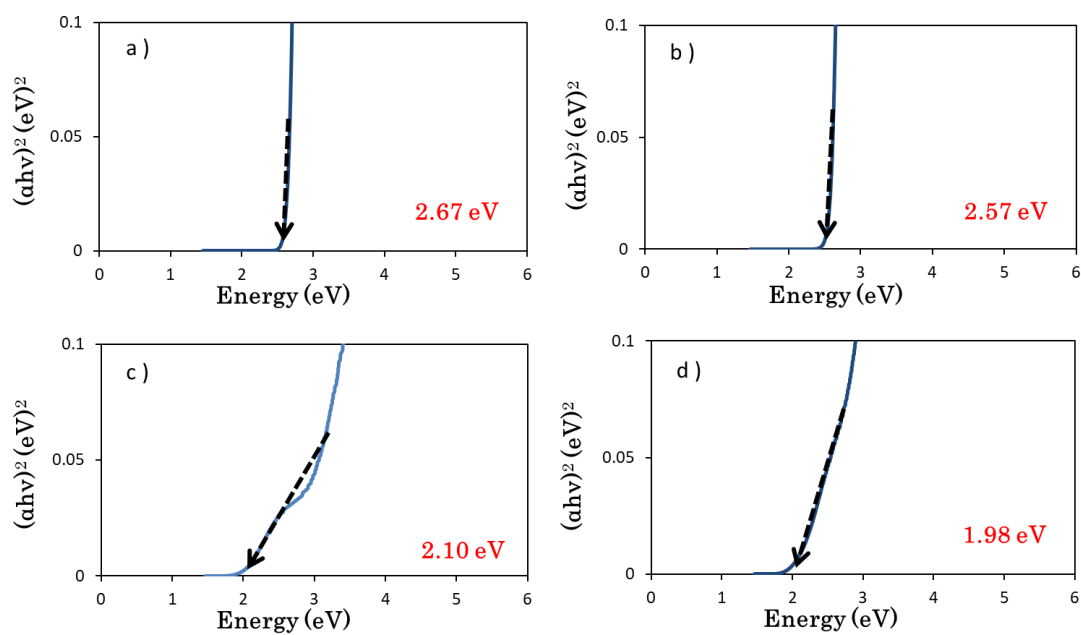
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**Table S1.** Expected composite components of photocatalyst (molar ratio).

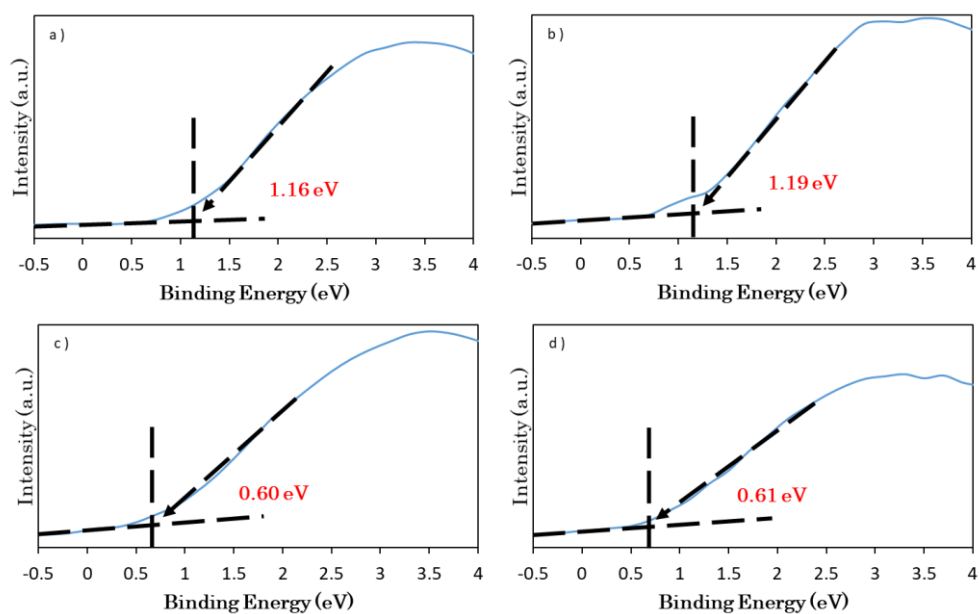
	ZnIn <sub>2</sub> S <sub>4</sub>	In <sub>2</sub> S <sub>3</sub>	CuInS <sub>2</sub>
ZnIn <sub>2</sub> S <sub>4</sub>	1	0	0
Zn <sub>0.87</sub> Cu <sub>0.13</sub> In <sub>2</sub> S <sub>3.935</sub>	0.87	0.065	0.13
Zn <sub>0.87</sub> In <sub>2</sub> S <sub>3.87</sub>	0.87	0.13	0
Zn <sub>0.74</sub> Cu <sub>0.13</sub> In <sub>2</sub> S <sub>3.805</sub>	0.74	0.195	0.13

**Table S2.** Elemental ratios of ZnIn<sub>2</sub>S<sub>4</sub>, Zn<sub>0.87</sub>In<sub>2</sub>S<sub>3.87</sub>, Zn<sub>0.87</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.935</sub> and Zn<sub>0.74</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.805</sub> from XPS result.

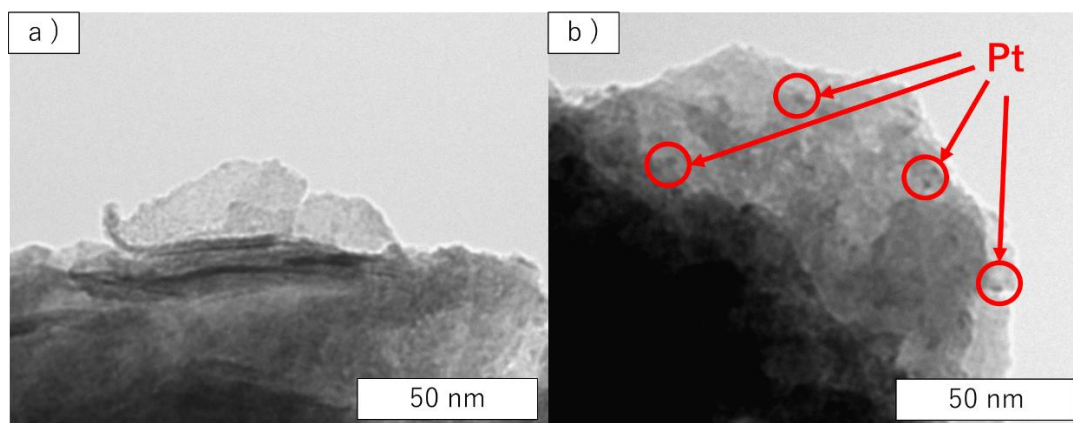
Catalyst	Elemental component (mole ratio)			
	Zn	Cu	In	S
ZnIn <sub>2</sub> S <sub>4</sub>	1	0	2.25	3.99
Zn <sub>0.87</sub> Cu <sub>0.13</sub> In <sub>2</sub> S <sub>3.935</sub>	0.86	0.13	2.09	4.11
Zn <sub>0.87</sub> In <sub>2</sub> S <sub>3.87</sub>	0.85	0	1.91	3.86
Zn <sub>0.74</sub> Cu <sub>0.13</sub> In <sub>2</sub> S <sub>3.805</sub>	0.74	0.12	1.83	3.7



**Figure S1.** Tauc plots of a) ZnIn<sub>2</sub>S<sub>4</sub>, b) Zn<sub>0.87</sub>In<sub>2</sub>S<sub>3.87</sub>, c) Zn<sub>0.87</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.935</sub> and d) Zn<sub>0.74</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.805</sub>.



**Figure S2.** Valence-band edge XPS spectra of a) ZnIn<sub>2</sub>S<sub>4</sub>, b) Zn<sub>0.87</sub>In<sub>2</sub>S<sub>3.87</sub>, c) Zn<sub>0.87</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.935</sub> and d) Zn<sub>0.74</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.805</sub>.



**Figure S3.** TEM images of Zn<sub>0.74</sub>Cu<sub>0.13</sub>In<sub>2</sub>S<sub>3.805</sub>. a) before and b) after irradiation.