

Electronic Supporting Information (ESI) for

**Platinum and indium sulfide-modified Cu₃BiS₃ photocathode for
photoelectrochemical hydrogen evolution**

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ESI. Fig. S1 Time course data for applied voltage during electrodeposition.

ESI. Fig. S2 Current-potential curves for Pt-Cu₃BiS₃, Pt-CdS/Cu₃BiS₃ and Pt-In₂S₃/Cu₃BiS₃.

ESI. Fig. S3 Current-potential curves for Cu₃BiS₃, Pt-Cu₃BiS₃, In₂S₃/Cu₃BiS₃ and Pt-In₂S₃/Cu₃BiS₃.

ESI. Table S1 ICP-AES analysis for aqueous electrolyte before and after photoelectrochemical reaction.

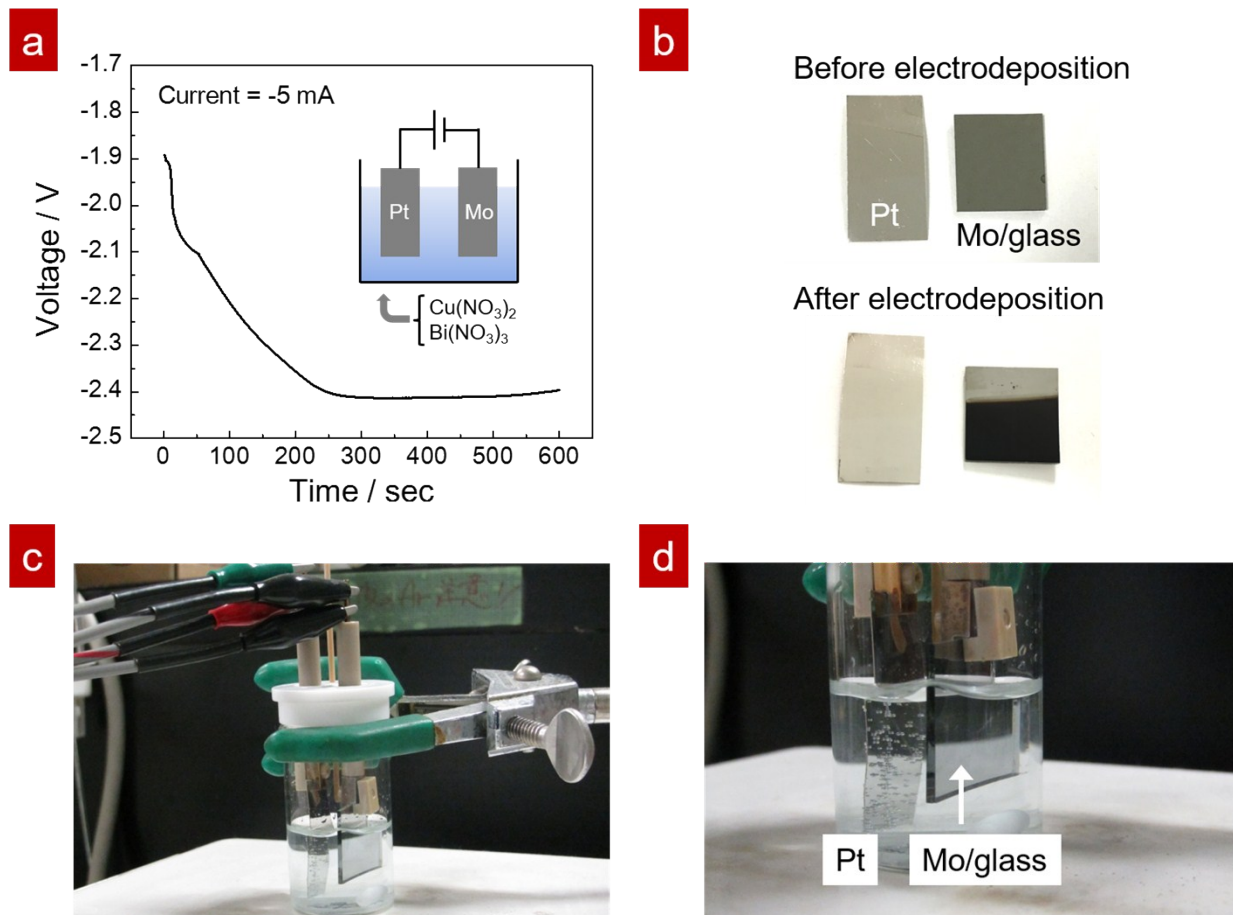


Fig. S1 (a) Time course data for applied voltage during electrodeposition. (b) Photographs of each electrodes before and after electrodeposition. As seen in these photographs, black Cu/Bi layer was deposited over Mo/glass substrate after electrodeposition, while Pt was no notable difference in the appearances. (c) Experimental photograph during electrodeposition. (d) Enlarged photograph. The small bubble was clearly observed over Pt electrode, which attributed to the oxygen gas.

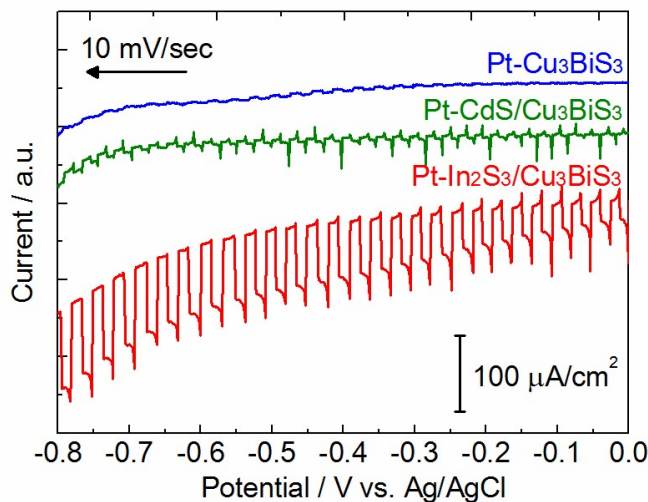


Fig. S2. Comparison of current-potential curves for Pt-Cu₃BiS₃, Pt-CdS/Cu₃BiS₃ and Pt-In₂S₃/Cu₃BiS₃ in 0.1M Na₂SO₄ aqueous solution (pH 6) under AM1.5G simulated solar light. The CdS buffer layer was deposited over the Cu₃BiS₃ electrode by chemical bath deposition method, which procedure has been reported in our previous work (S. Kamimura *et al.*, RSC advances, 2016, 6, 112594-112601).

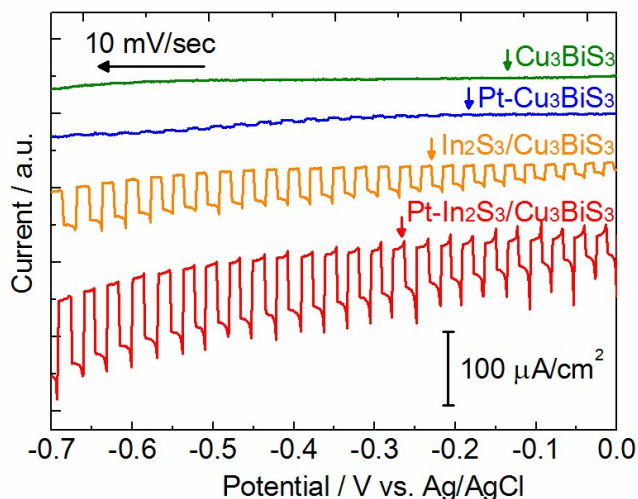


Fig. S3. Current-potential curves for Cu₃BiS₃, Pt-Cu₃BiS₃, In₂S₃/Cu₃BiS₃ and Pt-In₂S₃/Cu₃BiS₃ in 0.1M Na₂SO₄ aqueous solution (pH 6) under an irradiation of AM1.5G simulated solar light.

Table 1. ICP-AES analysis for aqueous electrolyte before and after photoelectrochemical reaction.

	Emission intensities of elements (a.u.)			
	Cu	Bi	In	S
Before ^a	0.027	0.0077	0.22	--
After ^b	0.028	0.0063	0.25	--

(a) As-prepared 0.1 M Na₂SO₄ aqueous electrolyte. (b) 0.1 M Na₂SO₄ aqueous electrolyte after photoelectrochemical reaction by using Pt-In₂S₃/Cu₃BiS₃ electrode.