Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Aluminum Incorporated *p*-CuO/*n*-ZnO Photocathode Coated with Nanocrystal Engineered TiO_2 Protective Layer for Photoelectrochemical Water Splitting and Hydrogen Generation

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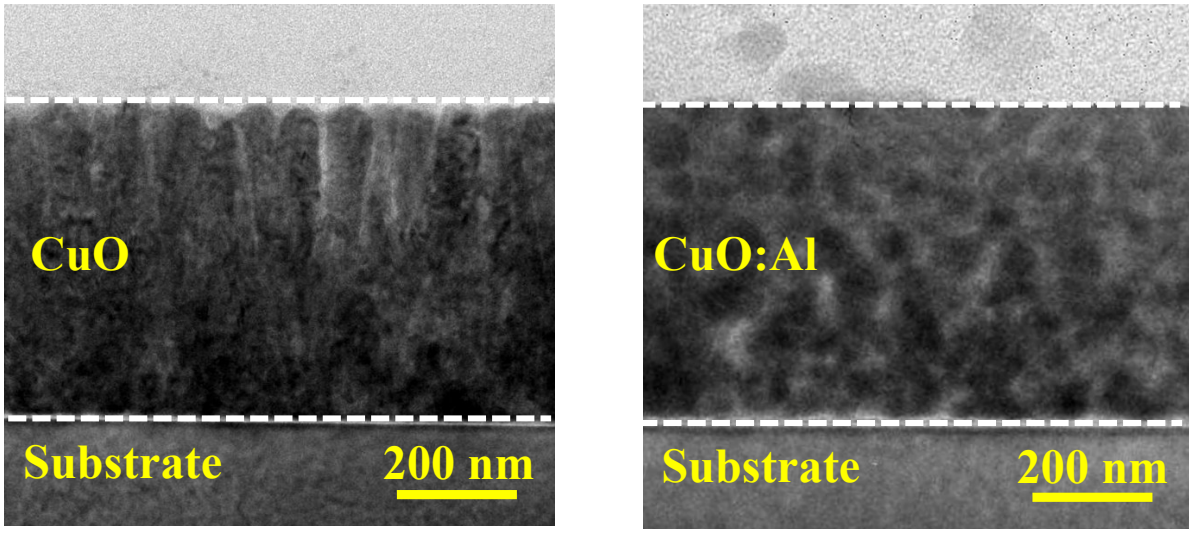


Figure S1. Cross-sectional TEM images of (a) CuO and (b) CuO:Al thin films deposited at CuO sputtering power of 300 W and Al sputtering power of 12 W. The thickness of the CuO and CuO:Al is ~500 nm.

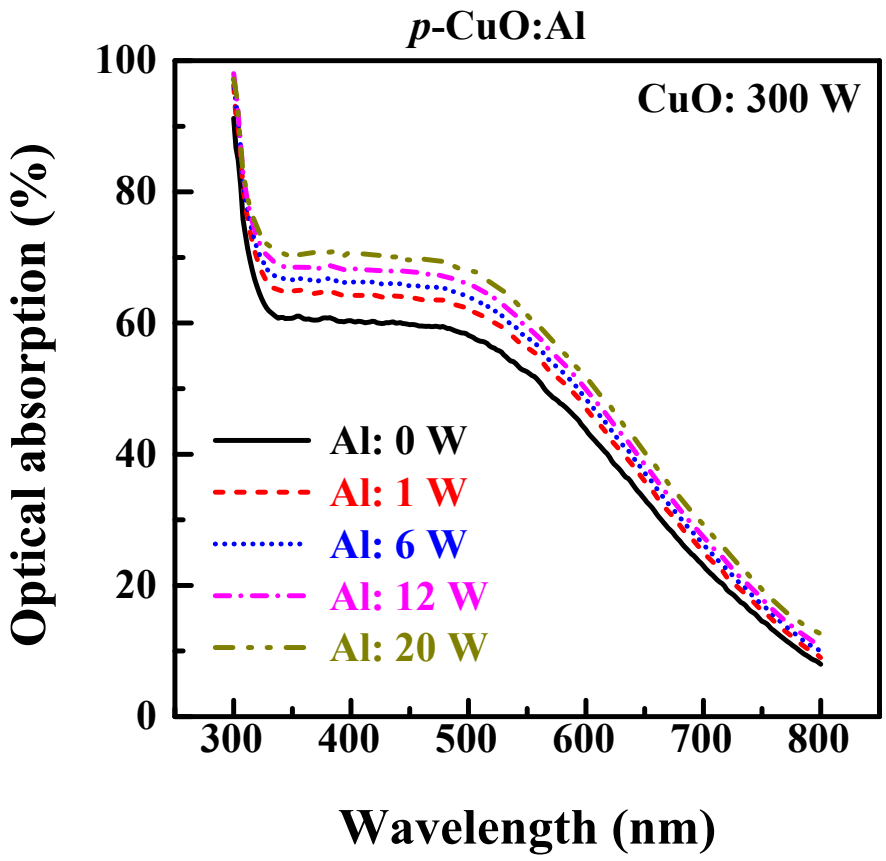


Figure S2. Absorption spectra of *p*-CuO:Al thin films deposited with Al sputtering power of 0-20 W. Optical absorption is enhanced with increasing Al incorporation.

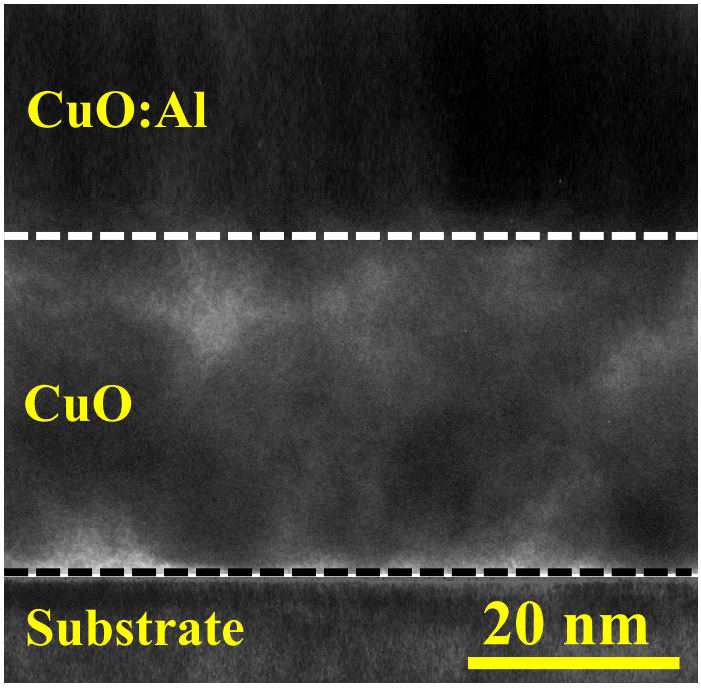


Figure S3. Cross-sectional TEM image of the 30-nm-thick CuO interfacial layer inserted below the CuO:Al film in a *p*-(CuO/CuO:Al) photocathode.

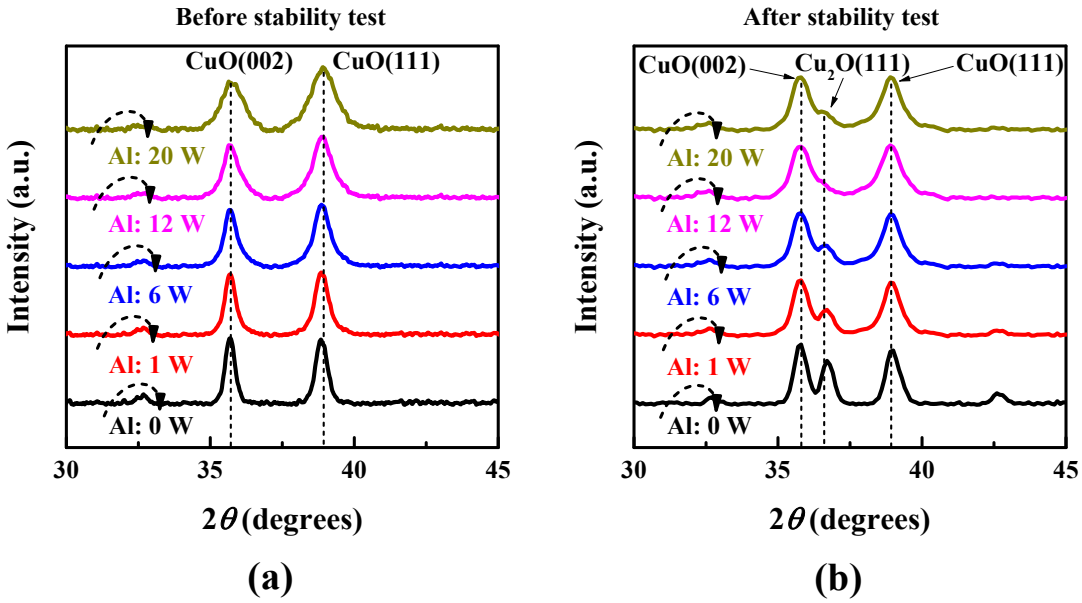


Figure S4. XRD spectra of *p*-(CuO/CuO:Al) photocathodes (a) before and (b) after photocorrosion stability test. An additional $Cu_2O(111)$ XRD peak at 2θ of 36.45 degrees can be found for both CuO and CuO:Al photocathodes after photocorrosion stability test, but the intensity of this peak is weaker in the CuO:Al photocathodes.

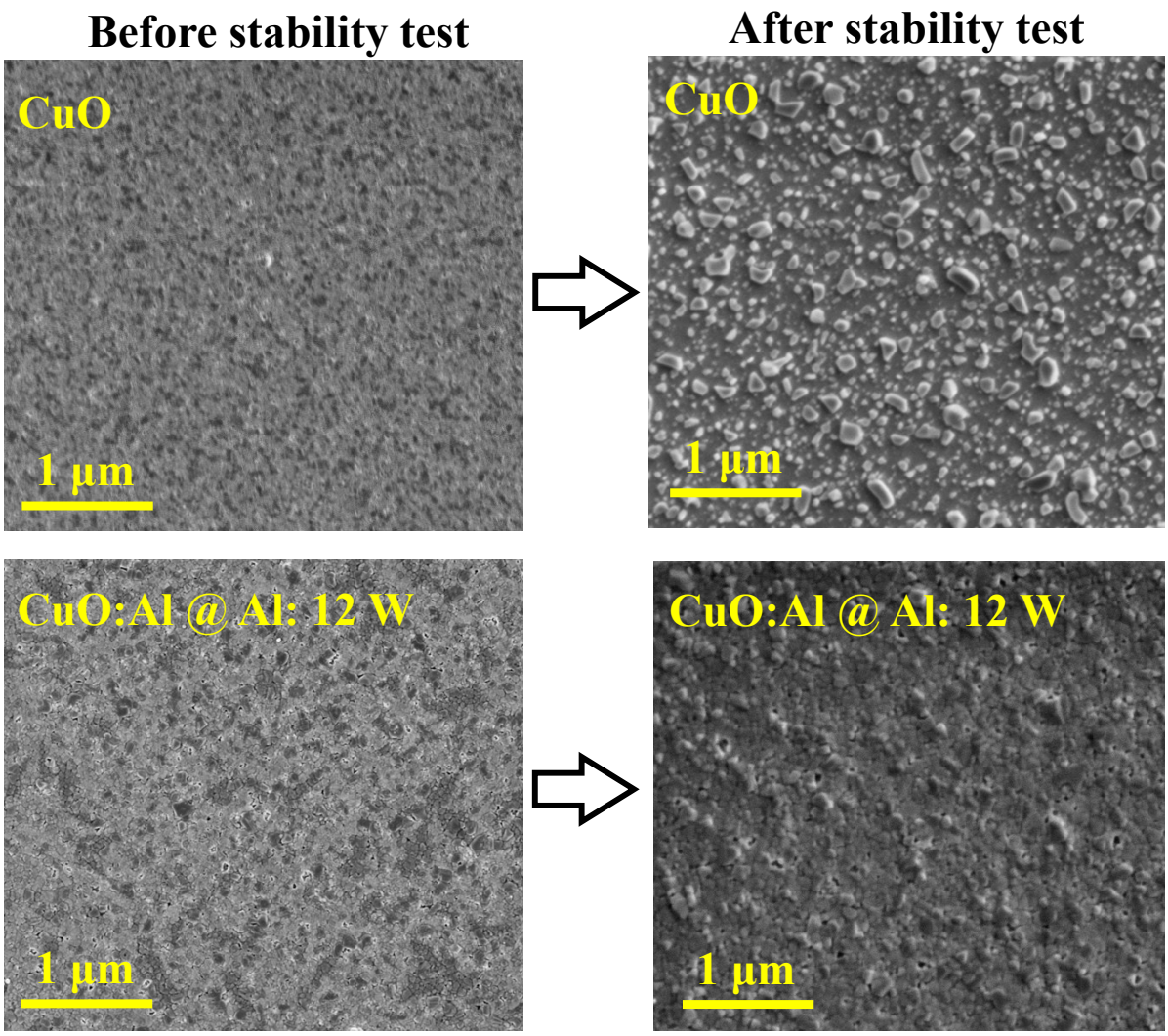


Figure S5. Top-view SEM images of the CuO and CuO:Al (@ Al: 12 W) photocathodes (a) before and (b) after photocorrosion stability test. Formation of small islands after the photocorrosion stability test, which is mainly caused by the reduction of CuO to Cu_2O, is reduced for the CuO:Al photocathode.

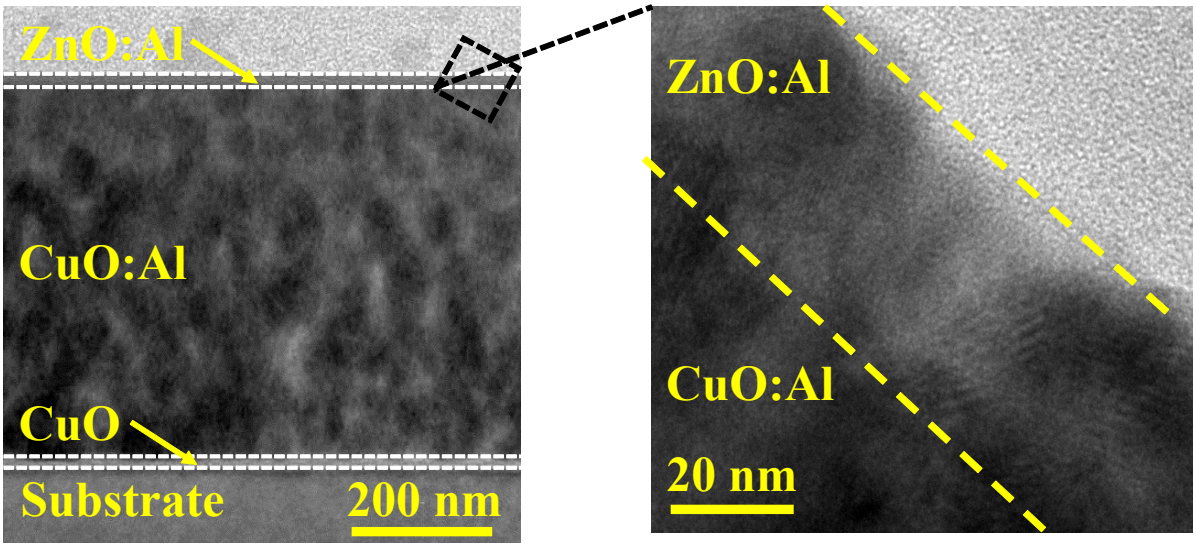
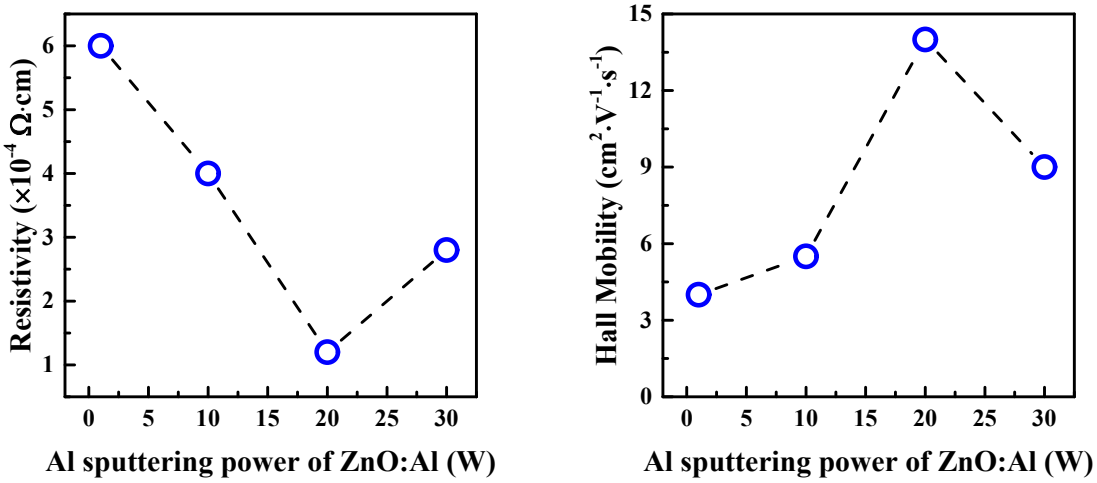


Figure S6. (a) Cross-sectional and (b) high-resolution TEM images of a *p*-(CuO/CuO:Al)/*n*-ZnO:Al photocathode fabricated with Al sputtering power of 20 W during ZnO:Al deposition. The thickness of the ZnO:Al layer is ~20 nm.



(a) **(b)**

Figure S7. (a) Electrical resistivity and (b) hall mobility of thin sputter-deposited ZnO:Al films on glass substrate. The Al concentration in ZnO significantly influences its electrical resistivity and hall mobility.

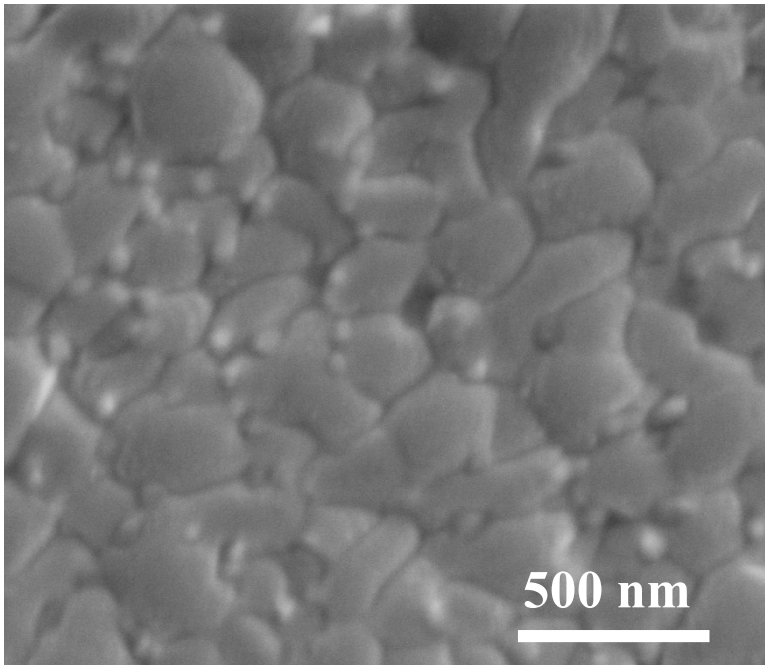
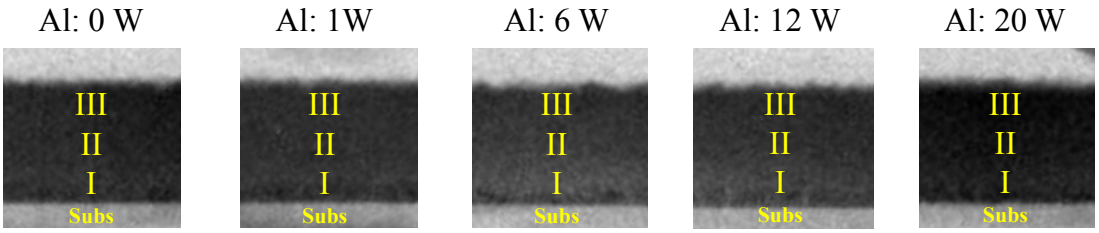


Figure S8. Top-view SEM image of a *p*-(CuO/CuO:Al)/*n*-ZnO:Al/TiO_2/Au-Pd photocathode. The Au-Pd nanoparticles are randomly and uniformly distributed on the TiO_2 protective layer.

Table SI. Results of energy-dispersive X-ray spectroscopy (EDS) analysis of the CuO:Al thin films prepared at CuO sputtering power of 300 W and different Al sputtering power.



Region	Al: 0 W			Al: 1 W			Al: 6 W			Al: 12 W			Al: 20 W		
	Cu	O	Al	Cu	O	Al	Cu	O	Al	Cu	O	Al	Cu	O	Al
I	51%	49%	0%	50.2%	49.3%	0.5%	49.5%	48.5%	2%	48.5%	47.5%	4%	47.5%	46.5%	6%
II	51%	49%	0%	50%	49.5%	0.5%	49%	49%	2%	48%	48%	4%	47%	47%	6%
III	50%	50%	0%	50%	49.5%	0.5%	49%	49%	2%	48%	48%	4%	47%	47%	6%

Table SII. Cu, O, and Al percentages in the CuO:Al (Al: 0, 1, 6, 12, and 20 W) samples, calculated from XPS analysis.

	Al: 0 W	**Al: 1 W**	**Al: 6 W**	**Al: 12 W**	**Al: 20 W**
Cu (%)	50	49.4	49.1	48.15	46.9
O (%)	50	49.2	49	48.1	46.8
Al (%)	0	0.4	1.9	3.75	6.3