Efficient Solar Hydrogen Production from Neutral Electrolytes Using Surface-Modified Cu(In,Ga)Se<sub>2</sub> Photocathodes

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Fig. S1 Light transmission spectrum of a CIGS film grown directly on soda-lime glass. The

absorption edge is located at approximately 1050 nm.



Fig. S2 XRD pattern of as prepared CIGS film on Mo-coated soda-lime glass. It indicates that the

film has chalcopyrite structure. The reference pattern is for CIGS from ICSD No.190354.



Fig. S3 Current-potential curves of Pt/Mo/Ti/CdS/CIGS photoelectrodes in various pH solutions under AM 1.5G irradiation. The solutions contains 0.5 M Na<sub>2</sub>SO<sub>4</sub> and 0.5 M Na<sub>x</sub>H<sub>3-x</sub>PO<sub>4</sub> in total and pH ware varied by mixing ratio of H<sub>3</sub>PO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> and adjusted by adding small amount of H<sub>2</sub>SO<sub>4</sub> or NaOH aqueous solution. The potential was swept toward the positive direction at 10 mV s<sup>-1</sup>.



Fig. S4 Current–potential curves for Pt/Mo/Ti/CdS/CIGS electrodes with various thickness of Mo and Ti in 0.5 M Na<sub>2</sub>SO<sub>4</sub>, 0.25 M Na<sub>2</sub>HPO<sub>4</sub> and 0.25 M NaH<sub>2</sub>PO<sub>4</sub> (aq) (pH adjusted to 6.8 by NaOH addition) under AM 1.5G irradiation. The potential was swept toward the positive direction at  $10 \text{ mV s}^{-1}$ .



Fig. S5 XPS spectra of a Mo/Ti/CdS/CIGS electrode before and after Pt photo-assisted electrodeposition. The intensities of the Mo peaks are reduced and Ti and Cd peaks appear following

deposition.



Fig. S6 SEM image of the surface of a Pt/Mo/Ti/CdS/CIGS electrode. Pt particles with sizes less

than 50 nm cover the surface.



Fig. S7 Cross sectional SEM images of the surface of a (A) CdS/CIGS, (B) Mo/Ti/CdS/CIGS, (C)

Pt/Mo/Ti/CdS/CIGS just after Pt deposition and (D) after PEC test.



Fig. S8 Transmittance (*T*) and reflectance (*R*) spectra of Mo/Ti layers on glass plate. It should be noted that relatively high reflectance was observed when these layers were deposited on smooth substrate. Using the value of T/(1-R)(1-R) according to Lambert's law to evaluate transparency without reflectance, its transparency may be enough for light absorption of CIGS film.



Fig. S9 XPS spectra of a Mo/Ti/CdS/CIGS electrode after Pt deposition and PEC measurement. The correction of binding energy is carried out using C 1s peak. The Ti layer is partially oxidized even before PEC to oxygen deficient  $TiO_2$  ( $TiO_x$ ) and the remaining oxygen is provided during the PEC trial. In contrast, metallic Mo (ca. 227.7 eV for Mo  $3d_{5/2}$ ) remains undisturbed between the Pt and  $TiO_x$  following both Pt deposition and PEC measurement.



Fig. S10 (A)The schematic band diagram and (B)magnified drawing at electrode-electrolyte interface for Pt/Mo/Ti/CdS/CIGS electrode at 0  $V_{RHE}$ . According to XPS results, Ti and Mo layer were described as TiO<sub>x</sub> and Mo/MoO<sub>2</sub>, respectively. The band diagram at solid-liquid interface was calculated using the water/TiO<sub>x</sub>/CdS/CIGS structure and Mo was regarded as the charge transfer layer, since there was no big difference between their onset potential while the photocurrent significantly changed with/without existence of Mo layer. The value of the VBM offset between CIGS and CdS was 0.88 eV<sup>1</sup>, while that the CBM offset between CdS and TiO<sub>x</sub> was assumed to be 0.23 eV<sup>2</sup>. The thickness of Mo layer was set as 1 nm because of partially removal through Pt electrodeposition. Carrier concentrations and relative permittivities are supposed to be 10<sup>17</sup> cm<sup>-3</sup> and 10, respectively. We note that MoO<sub>2</sub> could be reduced metallic state by photo-excited electron because of its redox potential of MoO<sub>2</sub>/Mo at approx. -0.15V<sub>RHE</sub>.<sup>3</sup>



Fig. S11 Current–time plot for a Pt/Mo/Ti/CdS/CIGS electrode at an applied potential of 0  $V_{RHE}$  in 0.5 M Na<sub>2</sub>SO<sub>4</sub>, 0.25 M Na<sub>2</sub>HPO<sub>4</sub> and 0.25 M NaH<sub>2</sub>PO<sub>4</sub> (aq) (pH adjusted to 6.8 by NaOH addition) under AM 1.5G irradiation. The Pt/Mo/Ti/CdS/CIGS photocathode generated a cathodic photocurrent over 10 days, albeit with a decrease in the photocurrent.



Fig. S12 SEM image of the surface of a Pt/Mo/Ti/CdS/CIGS electrode after the long term durability

testing shown in Fig. S5. The electrode surface was roughened although the Pt particles remain.

#### Reference

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