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Efficient Solar Hydrogen Production from Neutral Electrolytes Using Surface-Modified Cu(In,Ga)Se$_2$ Photocathodes

Hiromu Kumagai$^1$, Tsutomu Minegishi$^1$, Naotoshi Sato$^{2,3}$, Taro Yamada$^4$, Jun Kubota$^1$, Kazunari Domen$^1$*

1) Department of Chemical System Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
2) Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8589, Japan
3) FUJIFILM Corporation, 577, Ushijima, Kaisei-Machi, Ashigarakami-gun, 258-8577 Kanagawa, Japan
4) Department of Chemical System Engineering, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, 277-8589 Chiba, Japan

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 contain 0.5 M Na$_2$SO$_4$ and 0.5 M Na$_x$H$_{3-x}$PO$_4$ in total and pH were varied by mixing ratio of H$_3$PO$_4$, NaH$_2$PO$_4$, Na$_2$HPO$_4$ and Na$_3$PO$_4$ and adjusted by adding small amount of H$_2$SO$_4$ or NaOH aqueous solution. The potential was swept toward the positive direction at 10 mV s$^{-1}$. 

$I$ / mA cm$^{-2}$ (geometric)
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Fig. S4 Current–potential curves for Pt/Mo/Ti/CdS/CIGS electrodes with various thickness of Mo and Ti in 0.5 M Na$_2$SO$_4$, 0.25 M Na$_2$HPO$_4$ and 0.25 M NaH$_2$PO$_4$ (aq) (pH adjusted to 6.8 by NaOH addition) under AM 1.5G irradiation. The potential was swept toward the positive direction at 10 mV s$^{-1}$.
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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) CdS/CIGS, (B) Mo/Ti/CdS/CIGS, (C) Pt/Mo/Ti/CdS/CIGS just after Pt deposition and (D) after PEC test.
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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\textsubscript{RHE}. According to XPS results, Ti and Mo layer were described as TiO\textsubscript{x} and Mo/MoO\textsubscript{2}, respectively. The band diagram at solid-liquid interface was calculated using the water/TiO\textsubscript{x}/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\textsuperscript{1}, while that the CBM offset between CdS and TiO\textsubscript{x} was assumed to be 0.23 eV\textsuperscript{2}. The thickness of Mo layer was set as 1 nm because of partially removal through Pt electro-deposition. Carrier concentrations and relative permittivities are supposed to be 10\textsuperscript{17} cm\textsuperscript{-3} and 10, respectively. We note that MoO\textsubscript{2} could be reduced metallic state by photo-excited electron because of its redox potential of MoO\textsubscript{2}/Mo at approx. -0.15V\textsubscript{RHE}.\textsuperscript{3}
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Fig. S11 Current−time plot for a Pt/Mo/Ti/CdS/CIGS electrode at an applied potential of 0 V<sub>RHE</sub> 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

