Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

Dynamic Article Links▶

ARTICLE TYPE

Platinum and Indium Sulfide-Modified CuInS$_2$ as Efficient Photocathodes for Photoelectrochemical Water Splitting

Gunawan,[a,b] Wilman Septina,[a] Shigeru Ikeda,*[a] Takashi Harada,[a] Tsutomu Minegishi,[c] Kazunari Domen[c] and

₅ Michio Matsumura[a]

A highly efficient CuInS$_2$-based photocathode for water reduction with maximum applied bias photon-to-current
₁₀ **efficiency of *ca*. 2% was prepared by using a novel In$_2$S$_3$ surface modifier.**

Hydrogen (H$_2$) production by photoelectrochemical (PEC) water splitting is an attractive concept for attaining a sustainable energy source. Since the first report of PEC water splitting over a single
₁₅ crystalline TiO$_2$ photoelectrode,[1] various semiconductor electrodes have been investigated for this purpose.[2] Meanwhile, Cu-chalcopyrite p-type semiconductors such as CuInSe$_2$, CuGaSe$_2$, CuInS$_2$, CuGaS$_2$ and their mixed crystals are widely used as photoabsorbers in thin film solar cells.[3] Due to their high
₂₀ absorption coefficients, tunable band gap values (1.0-2.4 eV) by changing In/Ga and/or Se/S ratios, and suitable band alignment for water reduction, these materials are also attractive for use as photocathodes for H$_2$ production from water.[4]

The insertion of n-type thin layers on photocathodes to
₂₅ improve their performance of PEC water splitting has been studied by several researchers using various p-type materials.[4b-h,5] This modification is widely employed to facilitate efficient charge separation due to the modulated built-in field at solid-solid interface by the formed p-n junction. For the Cu-chalcopyrite
₃₀ system, surface modification with an n-type CdS layer using a chemical bath deposition (CBD) technique was typically employed; this resulted in apreciable improvement of photocurrent as well as onset potential compared to those of unmodified films. However, due to the high toxity of CdS,
₃₅ replacement with alternative environment-friendly n-type layers would be advantageous for practical use.

In the present study, we investigated surface modification of a CuInS$_2$ thin film with a novel n-type surface modifier, In$_2$S$_3$, for PEC water splitting. In$_2$S$_3$ possesses an indirect gap
₄₀ characteristic: it exhibits favorable transparency over the solar spectrum due to the weak absorption in the blue region, despite its relatively narrow band gap (2.1 eV) compared to that of CdS.[6] Herein we show that the In$_2$S$_3$-modified CuInS$_2$ thin film worked more efficiently than the CdS-modified one as a photocathode for
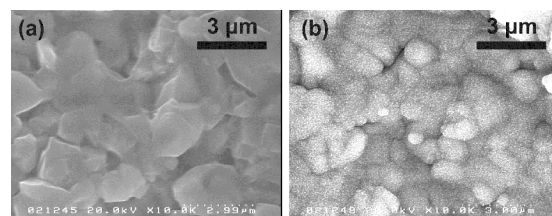₄₅ PEC water splitting.

Fig. 1 Surface SEM images of (a) a CuInS$_2$ thin film and (b) that modified with In$_2$S$_3$.

₅₀ A CuInS$_2$ thin film was fabricated from electrochemically stacked layers of metallic Cu and In followed by sulfurization. The XRD pattern of the thus-obtained thin film showed typical diffraction peaks assignable to the CuInS$_2$ with a chalcopyrite structure without any other phases (Fig. S1). The film consists of
₅₅ angular-shaped grains with sizes ranging from 1.5 to 3 μm, as shown in a top-view FE-SEM image (Fig. 1a). When the CuInS$_2$ thin film was modified with a *ca*. 50-nm thick In$_2$S$_3$ deposited by a chemical bath deposition method, the smooth surface of each CuInS$_2$ grain became granular (Fig. 1b). Appreciable lowering of
₆₀ the Cu/In atomic ratio after the In$_2$S$_3$ deposition as confirmed by EDX analysis (Table S1) also indicated overall surface coverage

of the CuInS$_2$ thin film by the In$_2$S$_3$ layer. It should be noted that we could not exclude the possibility of the presence of In(OH)$_3$ and In$_2$O$_3$ components in the In$_2$S$_3$ layer because of the observation of appreciably high EDX signals derived from 5 oxygen on the In$_2$S$_3$-modified sample.

As reported previously,[4c] a bare CuInS$_2$ thin film can not work as a photocathode for PEC water splitting. As shown in Fig. 2a, a current density-potential (*J-V*) curve of a CuInS$_2$ thin film measured in 0.1 M Na$_2$SO$_4$ (pH 9) under chopped irradiation of 10 AM 1.5 simulated solar light also exhibited almost no photoresponse. Surface modification of Pt deposits is a well-known technique to enhance H$_2$ production from water. As expected, the CuInS$_2$ thin film modified with Pt deposits (Pt-CuInS$_2$) exhibited appreciable cathodic photocurrents. By 15 applying the modification of Pt deposits to the In$_2$S$_3$-modified CuInS$_2$ thin film, significant increase of cathodic photocurrent was achieved. As shown in Fig. 2c, the CuInS$_2$ thin film modified with both In$_2$S$_3$ and Pt deposits (Pt-In$_2$S$_3$/CuInS$_2$) showed higher photocurrent density than that of CuInS$_2$ as well 20 as a large shift of the photocurrent onset to the positive region. As illustrated in Fig. S3, the p-n junction of the Pt-In$_2$S$_3$/CuInS$_2$ system resulted in the formation higher built-in potential than that of the semiconductor-electrolyte one of the Pt-CuInS$_2$ system.
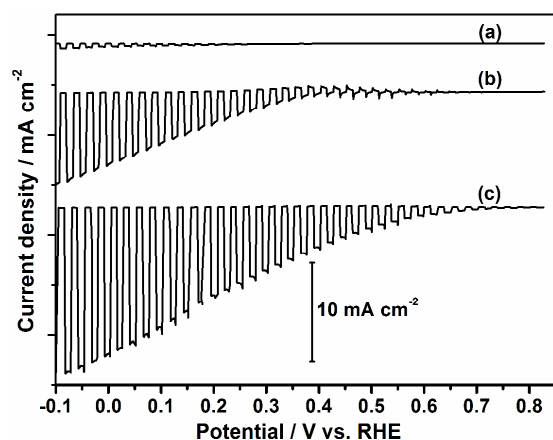

25

Fig. 2 *J-V* curves of (a) a CuInS$_2$ thin film, (b) Pt-CuInS$_2$, and (c) Pt-In$_2$S$_3$/CuInS$_2$ measured in 0.1 M Na$_2$SO$_4$ (pH 9) under chopped illumination from AM 1.5 simulated solar irradiation.

30 For quantitative analyses, the applied bias photon-to-current efficiency (ABPE) of Pt-In$_2$S$_3$/CuInS$_2$ was calculated by using the above *J-V* curve with assumption of 100% Faradic efficiency. As a result, the Pt-In$_2$S$_3$/CuInS$_2$ electrode exhibited photocurrent onset at 0.78 V (*vs*. RHE), and maximum ABPE of 1.97% was

35 achieved at 0.28 V (*vs*. RHE) (Fig. 3a). When the same analysis was performed for the CuInS$_2$ thin film modified with both an n-type CdS layer and Pt deposits (Pt-CdS/CuInS$_2$) (Fig. 3b), the photocurrent onset potential was estimated to be 0.65 V (*vs*. RHE), and maximum ABPE of 1.63% at 0.2 V (vs. RHE) was 40 obtained. Hence, it is obvious that the present Pt-In$_2$S$_3$-CuInS$_2$ electrode was more advantageous than the Pt-CdS/CuInS$_2$ electrode for use as a cathode for PEC water splitting. The results suggest that the In$_2$S$_3$-CuInS$_2$ interface forms a favorable p-n junction for suppressing recombination of photogenerated 45 carriers at the heterointerface compared to that of the CdS-CuInS$_2$ interface. A possible explanation is the homogeneous coverage of CuInS$_2$ with In$_2$S$_3$, leading to efficient utilization of the heterointerface for charge separation. Another possibility is the limited interdiffusion of In and Cu from In$_2$S$_3$ and CuInS$_2$ 50 layers to form a p-n homojunction; this should suppress interface recombination, resulting in higher attainable photovoltage compared to the use of the CdS/CuInS$_2$ heterojunction. In order to clarify the interface structure, detailed structural characterizations are now underway.
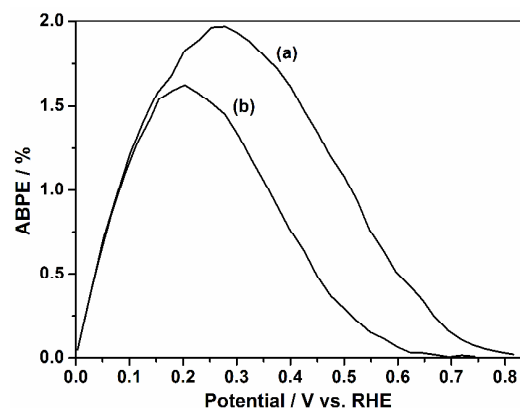

55

Fig. 3 ABPE curves of (a) Pt-In$_2$S$_3$/CuInS$_2$ and (b) Pt-CdS/CuInS$_2$ obtained from *J-V* curves of these samples measured in 0.1 M Na$_2$SO$_4$ (pH 9) under chopped illumination from AM 1.5 simulated solar irradiation.

60 The incident photon-to-current conversion efficiency (IPCE) spectra of Pt-In$_2$S$_3$/CuInS$_2$ and Pt-CdS/CuInS$_2$ measured at 0 V (*vs*. RHE) showed the same onset at photon energy of 1.45 eV, which is close to the band gap of CuInS$_2$ (1.5 eV)[7] (Fig. S2). Both 65 of the spectra reached around 37-41% in the range of 520-700 nm and then dropped in the relatively large photon energy region. The drop was greater for the Pt-CdS/CuInS$_2$ sample. Since this energy region corresponds to the band gap of bulk CdS (2.4 eV),[8] the observed drop in the spectra of Pt-CdS/CuInS$_2$ should be

caused by photon absorption of the top CdS layer. The drop was obviously suppressed for Pt-In$_2$S$_3$/CuInS$_2$, i.e., the sample had a higher IPCE gain at this high photon energy region than that of Pt-CdS/CuInS$_2$. As shown in Fig. S4, transmitance spectra of CdS

5 and In$_2$S$_3$ layers deposited on a fluorine doped tin oxide (FTO) glass substrate indicated appreciably higher transparency of the In$_2$S$_3$ layer than that of the CdS layer at this energy region. The better transparency of In$_2$S$_3$ led to the advantageous feature for PEC water splitting.

10   Fig. 4 shows time course curves of H$_2$ and O$_2$ evolution over the Pt-CdS/CuInS$_2$ photocathode and the Pt counter electrode in the three-electrode system with applied bias of 0 V (*vs*. RHE) under light irradiation from a 300 W xenon lamp. While a slight induction preriod was observed for the O$_2$ time course curve, H$_2$

15 evolution and O$_2$ evolution were monotonically observed close to the stoichiometric ratio. A slight deviation of the amount of H$_2$ evolved from half of the electrons passing through the outer circuit (e$^-$/2, shown as a solid line in Fig. 4) is likely to be due to the occurance of backward reaction, i.e., water formation from

20 the evolved H$_2$ and O$_2$. After 150-min photoirradiation, 407 μmol of H$_2$ gas and 185 μmol of O$_2$ gas were evolved: the amount of evolved H$_2$ significantly exceeded the molar amount of CuInS$_2$ used (approximately 2 μmol was deposited on the sample used with a total area of 0.7 cm^{-2}), indicating catalytic function of the
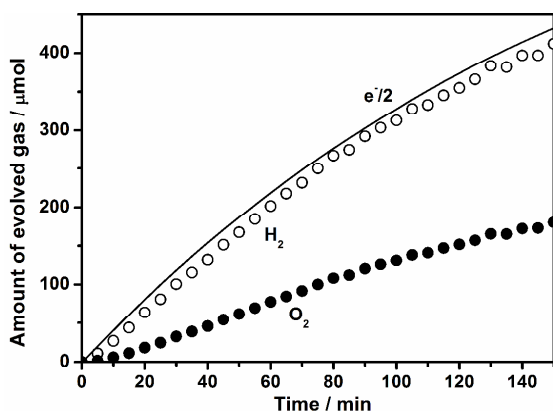
25 electrode.

Fig. 4 Time course curves of gas evolution from the Pt-In$_2$S$_3$/CuInS$_2$ photocathode (H$_2$: open circle) and the Pt counter electrode (O$_2$: closed circle) in a 0.1 M Na$_2$SO$_4$ solution (pH 9) at 0 V (*vs*. RHE) under

30 irradiation from a 300 W xenon lamp. The solid line denotes a time course curve of half of electrons passing through the outer curcuit (e$^-$/2).

   The formation of a p-n junction by surface modification of the CuInS$_2$ film with an n-type In$_2$S$_3$ layer followed by loading of Pt

35 deposits made it an efficient H$_2$-evolving photoelectrode:

maximum ABPE of 1.97% at 0.28 V (*vs*. RHE) measured at 0.1 M Na$_2$SO$_4$ (pH 9) under simulated AM 1.5 solar irradiation. To our knowledge, the observed PEC water splitting activity is the highest among chalcopyrite-based photocathodes reported so far.[9]

40 This modification also effectively shifted the onset potential a lower applied bias (*ca*. 0.78 V *vs*. RHE), which is promising for a tandem PEC system without any bias voltage. However, one of the critical issues encountered in the present system is stability, *e.g.*, prolonged illumination in a 0.1 M Na$_2$SO$_4$ solution (pH 9) at

45 0 V (*vs*. RHE) for 3 h resulted in 63% reduction of photocurrent from the initial amount (Fig. S5). Thus, further studies to improve it are now in progress.

Notes and references

^{a}Research Center for Solar Energy Chemistry, Osaka University, 1–3 Machikaneyama, Toyonaka Campus, Osaka 560–8531, Japan. E-mail: sikeda@chem.es.osaka-u.ac.jp; fax:81 6 6850 6699.

60 ^{b}Chemistry Department, Faculty of Sciences and Matematics, Diponegoro University, Semarang, Indonesia. ^{c}Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, 113-8656 Tokyo, Japan.

65 † Electronic Supplementary Information (ESI) available: Experimental details and additional figures and table. See DOI: 10.1039/b000000x/

1.   A. Fujishima and K. Honda,*Nature,* 1972, **238**, 37.
2.   a) K. Domen, J. N. Kondo, M. Hara and T. Takata, *Bull.. Chem. Soc.*
      Jpn., 2000, **73**, 1307-1331; b) J. Sato, N. Saito, Y. Yamada, K.
70   Maeda, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen,
      and Y. Inoue, *J. Am. Chem. Soc*. 2005, **127**, 4150-5151; c) K. Maeda,
      K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen,
      Nature, 2006, **440**, 295; d) K. Maeda and K. Domen, *J. Phys. Chem.*
      C, 2007, **111**, 7851-7861; e) F. E. Osterloh, *Chem. Mater*., 2008, **20**,
75   35-54.
3.   a) J. Klaer, J. Bruns, R. Henninger, K. Siemer, R. Klenk, K. Ellmer
      and D. Bräunig, *Semicond. Sci. Technol*., 1998, **13**, 1456-1458; b) H.
      W. Schock and R. Noufi, *Prog. Photovolt. Res. Appl.* 2000, **8**, 151-
      160; c) K. Siemer, J. Klaer, I. Luck, J. Burns, R. Klenk and D.
80   Braunig, *Sol. Energy Mater. Sol. Cells*, 2001, **67**, 159-166; d) A.
      Ennaoui, M. Bär, J. Klaer, T. Kropp, R. Sáez-Araos and M. C. Lux-
      Steiner, *Prog. Photovol. Res. Appl*. 2008, **16**, 235-239.
4.   a) M. Tabata, K. Maeda, T. Ishihara, T. Minegishi, T. Takata and K.
      Domen, *J. Phys. Chem. C*, 2010, **114**, 11215-11220; b)   D.
85   Yokoyama, T. Minegishi, K. Maeda, M. Katayama, J. Kubota, A.
      Yamada, M. Konagai and K. Domen, *Electrochem. Commun.*, 2010,
      12, 851-853; c) S. Ikeda, T. Nakamura, S. M. Lee, T. Yagi, T.
      Harada, T. Minegishi and M. Matsumura, *ChemSusChem.*,2011, **4**,
      262-268; d) J. Kim, T. Minegishi, J. Kubota and K. Domen, *Energy*
90   *Environ. Sci*., 2012, **5**, 6368; e) L. Djellal, B. Bellal and M. Trari,
      Mater. Chem. Phys., 2012, **137**, 340-345e) S. Ikeda, M. Nonogaki, W.
      Septina, G. Gunawan, T. Harada and M. Matsumura, *Catal. Sci.*

Tecnol., 2013, **3**, 1849-1854; f) M. Moriya, T. Minegishi, H. Kumagai, M. Katayama, J. Kubota and K Domen, *J. Am. Chem. Soc*., 2013, **135**, 3733-3735; g) L. Zhang, T. Minegishi, J. Kubota and K Domen, *Phys. Chem. Chem. Phys*., 2014, **16**, 6167-6174; h) H.
5 Kumagai, T. Minegishi, Y. Moriya, J. Kubota, K. Domen, *J. Phys. Chem. C*, dx.doi.org/10.1021/jp409921f .

5. a) D. Yokoyama, T. Minegishi, K. Jimbo, T. Hisatomi, G. Ma, M. Katayama, J. Kubota, H. Katagiri and K. Domen, *Appl. Phys. Express*, 2010, **3**, 101202; b) G. Ma, T. Minegishi, D. Yokohama, J.
10 Kubota and K. Domen, *Chem. Phys. Lett*., 2011, **501**, 619-622; c) L. Rovelli, S. D. Tilley and K. Sivula, *ACS Appl. Mater. Interfaces,* 2013, **5**(16), 8018-8024.

6. M. G. Sandoval-Paz, M. Sotelo-Lerma, J. J. Valenzuela-Jáurequi, M. Flores-Acosta, and R. Ramirez-Bon, *Thin Film Solids*, 2005, **472**, 5-
15 10.

7. R. Klenk, J. Klaer, R. Scheer, M. C. Lux-Steiner, I. Lux, N. Meyer and U. Ruhle, *Thin Solid Films*, 2005, **480**, 509.

8. M. Sardova, M. Weinstein and G. A. Wolf, *Physical review*, 1965, **140**, 633.

20 9. a) F. Yang, V. Kuznietsov, M. Lublow, C. Merschjann, A. Steigert, J. Kher, A. Thomas and T. Schedel-Niedrig, *J. Mater. Chem. A*, 2013, **1**, 6407-6415; b) M. Malizia, B. J. Seger, I. Chorkendorff and P. C. K. Vesborg, *J. Mater.Chem. A*, 2014, DOI:10.1039/C4TA00752B; c) M. Higashi, K. Domen and R. Abe, *J. Am. Chem. Soc*., 2013, **135**,
25 10238-10241.