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Platinum and indium sulfide-modified $CuInS_2$ as efficient photocathodes for photoelectrochemical water splitting†

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A highly efficient $CuInS_2$-based photocathode for water reduction with a maximum applied bias photon-to-current efficiency of *ca.* 2% was prepared by using a novel In_2S_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 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 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 layers on photocathodes to 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 the solid–solid interface by the formed p–n junction. For the Cu–chalcopyrite system, surface modification with an n-type CdS layer using a chemical bath deposition (CBD) technique was typically employed; this resulted in appreciable improvement of photocurrent as well as onset potential compared to those of unmodified films. However, due to the high toxicity of CdS, 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_2S_3, for PEC water splitting. In_2S_3 possesses an indirect gap 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_2S_3-modified $CuInS_2$ thin film worked more efficiently than the CdS-modified one as a photocathode for PEC water splitting.

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 $CuInS_2$ film with a chalcopyrite structure without any other phases (Fig. S1, ESI†). The film consists of 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_2S_3 deposited by a chemical bath deposition method, the smooth surface of each $CuInS_2$ grain became granular (Fig. 1b). Appreciable lowering of the Cu/In atomic ratio after the In_2S_3 deposition as confirmed by EDX analysis (Table S1, ESI†) also indicated the overall surface coverage of the $CuInS_2$ thin film by the In_2S_3 layer. It should be noted that we could not exclude the possibility of the presence of $In(OH)_3$ and In_2O_3 components in

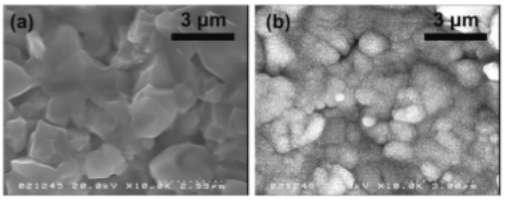

Fig. 1 Surface SEM images of (a) a $CuInS_2$ thin film and (b) that modified with In_2S_3.

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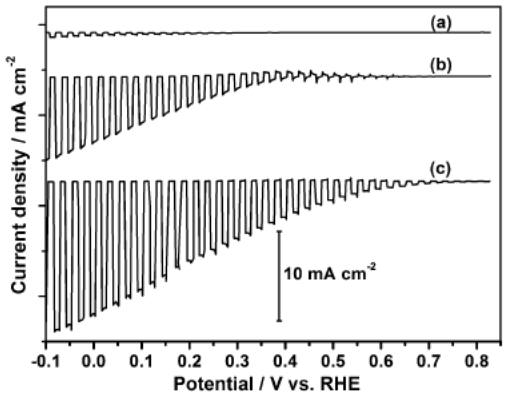

Fig. 2 *J–V* curves of (a) a $CuInS_2$ thin film, (b) Pt–$CuInS_2$, and (c) Pt–In_2S_3/$CuInS_2$ measured in 0.1 M Na_2SO_4 (pH 9) under chopped illumination from AM 1.5 simulated solar irradiation.

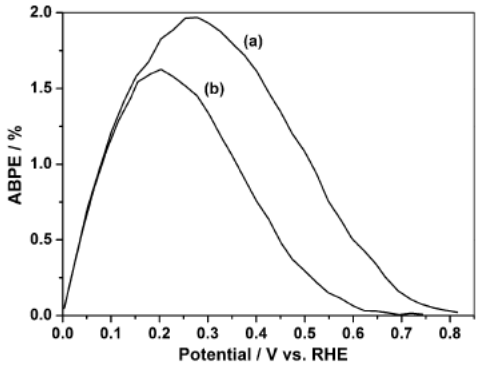

Fig. 3 ABPE curves of (a) Pt–In_2S_3/$CuInS_2$ and (b) Pt–CdS/$CuInS_2$ obtained from *J–V* curves of these samples measured in 0.1 M Na_2SO_4 (pH 9) under chopped illumination from AM 1.5 simulated solar irradiation.

the In_2S_3 layer because of the observation of appreciably high EDX signals derived from oxygen on the In_2S_3-modified sample.

As reported previously,[4c] a bare $CuInS_2$ thin film cannot 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_2SO_4 (pH 9) under chopped irradiation of 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 applying the modification of Pt deposits to the In_2S_3-modified $CuInS_2$ thin film, a significant increase of cathodic photocurrent was achieved. As shown in Fig. 2c, the $CuInS_2$ thin film modified with both In_2S_3 and Pt deposits (Pt–In_2S_3/$CuInS_2$) showed higher photocurrent density than that of $CuInS_2$ as well as a large shift of the photocurrent onset to the positive region. As illustrated in Fig. S3 (ESI†), the p–n junction of the Pt–In_2S_3/$CuInS_2$ system resulted in the formation of higher built-in potential than that of the semiconductor-electrolyte one of the Pt–$CuInS_2$ system.

For quantitative analyses, the applied bias photon-to-current efficiency (ABPE) of Pt–In_2S_3/$CuInS_2$ was calculated by using the above *J–V* curve with an assumption of 100% Faradic efficiency. As a result, the Pt–In_2S_3/$CuInS_2$ electrode exhibited a photocurrent onset of 0.7 V (*vs.* RHE), and a maximum ABPE of 1.97% was 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 a maximum ABPE of 1.63% at 0.2 V (*vs.* RHE) was obtained. Hence, it is obvious that the present Pt–In_2S_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_2S_3–$CuInS_2$ interface forms a favorable p–n junction for suppressing recombination of photogenerated 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_2S_3, leading to efficient utilization of the heterointerface for charge separation. Another possibility is the limited interdiffusion of In and Cu from In_2S_3 and $CuInS_2$ 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 characterization is now underway.

The incident photon-to-current conversion efficiency (IPCE) spectra of Pt–In_2S_3/$CuInS_2$ and Pt–CdS/$CuInS_2$ measured at 0.4 V (*vs.* RHE) showed the same onset at a photon energy of 1.45 eV, which is close to the band gap of $CuInS_2$ (1.5 eV)[7] (Fig. S2, ESI†). Both 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_2S_3/$CuInS_2$, *i.e.*, the sample has a higher IPCE gain at this high photon energy region than that of Pt–CdS/$CuInS_2$. As shown in Fig. S4 (ESI†), transmittance spectra of CdS and In_2S_3 layers deposited on a fluorine doped tin oxide (FTO) glass substrate indicated appreciably higher transparency of the In_2S_3 layer than that of the CdS layer at this energy region. The better transparency of In_2S_3 led to the advantageous feature for PEC water splitting.

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 an applied bias of 0 V (*vs.* RHE) under light irradiation from a 300 W xenon lamp. While a slight induction period was observed for the O_2 time course curve, H_2 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 occurrence of backward reaction, *i.e.*, water formation from the evolved H_2 and O_2. After 150 min photoirradiation, 407 μmol of H_2 gas and 185 μmol of O_2 gas

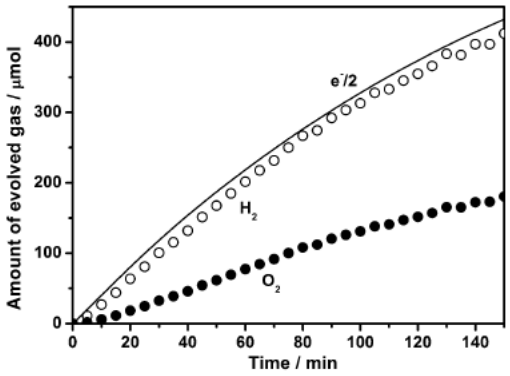

Fig. 4 Time course curves of gas evolution from the Pt–In_2S_3/$CuInS_2$ photocathode (H_2: open circle) and the Pt counter electrode (O_2: closed circle) in a 0.1 M Na_2SO_4 solution (pH 9) at 0 V (*vs.* RHE) under irradiation from a 400 W xenon lamp. The solid line denotes a time course curve of half of electrons passing through the outer circuit ($e^-/2$).

were evolved: the amount of evolved H_2 significantly exceeded the molar amount of $CuInS_2$ u[illegible] (approximately 2 μmol was deposited on the sample used with a total area of 0.7 cm^{-2}), indicating catalytic function of the electrode.

The formation of a p–n junction by surface modification of the $CuInS_2$ film with an n-type In_2S_3 layer followed by loading of Pt deposits made it an efficient H_2-evolving photoelectrode: a maximum ABPE of 1.97% at 0.28 V (*vs.* RHE) measured a[illegible] M Na_2SO_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] This modification also effectively shifted the onset potential to 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_2SO_4 solution (pH 9) at 0 V (*vs.* RHE) for 3 h resulted in 63% reduction of photocurrent from the initial amount (Fig. S5, ESI†). Thus, further studies to improve it are now in progress.

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