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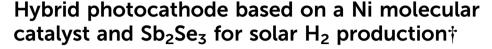


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We report a H₂ evolving hybrid photocathode based on Sb₂Se₃ and a precious metal free molecular catalyst. Through the use of a high surface area TiO2 scaffold, we successfully increased the Ni molecular catalyst loading from 7.08 \pm 0.43 to 45.76 \pm 0.81 nmol cm⁻², achieving photocurrents of 1.3 mA cm⁻² at 0 V vs. RHE, which is 81-fold higher than the device without the TiO₂ mesoporous layer.

Photoelectrodes for the production of solar fuels, for example by splitting water to generate H₂ and O₂, have the potential to play a key role in future energy systems. However, advances in both photoanodes for water oxidation² and photocathodes for hydrogen evolution (HER) are needed to improve the stability and to lower the cost for industrial scaling, since most longlasting devices rely on precious metals.³⁻⁵ Sb₂Se₃ has recently gained interest from the photovoltaic (PV) community due to its near-direct band gap of 1.18 eV, a high absorption coefficient across the visible region,⁶ and an unusual 1D nanoribbon structure that enables effective charge transport.7 These properties, combined with improvements in material processability and the use of earth-abundant elements, have led to the suggestion that Sb₂Se₃ could be a viable thin film PV material for use on a global scale.8 Sb₂Se₃ has also been studied as a photocathode for HER, the conduction band minimum at -0.5 V vs. RHE provides enough driving force for producing H_2 , and its band gap (E_g) is very close to the optimal calculated for the bottom electrode in dual absorber standalone device for water splitting. 10 Reported solar to hydrogen efficiencies, using state-of-the-art Sb₂Se₃ photocathodes, have now exceeded 10%. 11,12 These photocathodes consist of a Sb₂Se₃/CdS buried

The complete device FTO/Au/Sb₂Se₃/CdS/TiO₂/TiO₂-meso/ NiP is shown in Fig. 1a. Sb₂Se₃ (1.5 μm) was deposited on Au (70 nm) coated fluorine-doped SnO₂-glass (FTO) by a two-step fast-cooling close space sublimation process, which generates a compact preferentially orientated nanoribbon crystal structure that facilitates rapid hole transfer to the Au contact.^{7,11,12} Then, a thin sputtered CdS buffer layer (20 nm) was added which forms a Sb₂Se₃ heterojunction with a negligible conduction band offset, thereby allowing efficient charge separation and electron transfer towards TiO₂ (Fig. 1c).⁶ In this way, the onset potential and fill factor of the Sb₂Se₃ photocathodes are improved despite the parasitic absorption of photons below λ < 500 nm in the CdS causing a decrease in the photocurrent. 11,12 After, TiO₂ (100 nm) was sputtered to provide a physical barrier preventing contact between the light absorber

junction that is coated with a protective TiO₂ capping layer. The planar TiO₂ is then modified with a HER catalyst like Pt, 13,14 RuO₂, ^{12,15} and MoS₁, ¹⁶ Notably, even with state-of-the-art devices, reductive dissolution of TiO2 caused by photoelectron accumulation can occur. 11,13 C₆₀ between TiO₂ and the H₂-evolution catalyst can alleviate charge accumulation promoting the photoelectron transfer at the TiO₂/Pt interface, but device stabilities are still low. 11,13 Therefore, a need still exists to identify new active photoelectrode/catalysts systems that are able to keep up with the rate of photoelectron generation and to explore how the catalyst/TiO₂ interface can be modified to prevent the generation of highelectron densities. Earth abundant molecular electrocatalysts have not previously been explored on Sb₂Se₃ photocathodes, even though they are an alternative to precious metal electrocatalysts and could potentially offer improved rates of charge transfer at the semiconductor/molecular catalyst interface. 17,18 Here, NiP with a $[Ni(P_2^{R'}N_2^{R''})_2]^{2+}$ core $(P_2^{R'}N_2^{R''}) = bis(1,5-R'-diphospha-3,7-R''-diph$ diazacyclooctane)), shown in Fig. 1b, was chosen as model molecular catalyst. 19 The NiP catalyst mimics the hydrogenase intramolecular proton transfer to the Ni centre through the pendant amine groups in the second coordination sphere. 20 Furthermore, it can be covalently anchored to TiO₂ by the phosphonic acid groups in the outer coordination sphere, Fig. 1b.²¹

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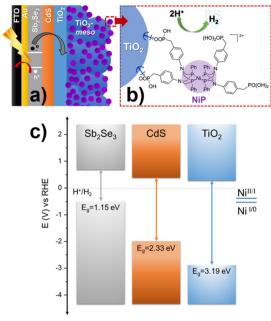


Fig. 1 (a) Schematic diagram of Sb₂Se₃/CdS/TiO₂-meso/NiP hybrid photocathode. (b) Chemical structure of NiP catalyst molecular catalyst, panel a and b are not drawn to scale. (c) Equilibrium band alignment diagram of Sb₂Se₃/CdS/TiO₂ heterojunction based on VBM¹¹ and E_{α} measured separately for each layer (Fig. S2.1, ESI†), note that NiP redox couple is pH independent.21

and the electrolyte.²² Full details of the synthetic procedures, the device characterisation and SEM images are provided in the ESI,† Fig. S2.1-3.

The molecular catalyst was first immobilized overnight onto the sputtered TiO2 (without the TiO2-meso) by soaking the photoelectrode in dry methanolic solution (0.5 mM NiP), 19,23,24 and from now on labelled as Sb₂Se₃/CdS/TiO₂/NiP. It was removed from the soaking solution, thoroughly washed in methanol to remove the non-chemisorbed catalyst and dried under vacuum. NiP loadings were determined by stripping the catalyst off using NaOH and then quantified by UV-vis spectroscopy, as shown in Table S1 (ESI†). When NiP was attached to the sputtered TiO2 layer, a loading of 7.08 \pm 0.43 nmol cm $^{-2}$ was achieved. All the photoelectrochemical tests were done under 100 mW cm⁻² illumination (unless otherwise stated) and with $\lambda > 340$ nm in 0.1 M Na₂SO₄ at pH 3. pH 3 was chosen due to past studies that showed NiP was most active at this pH.23,25 Fig. 2 shows a photocurrent of only -16 µA cm⁻² at 0 V vs. RHE, which exceeds only slightly the current in the absence of any catalyst $(-3 \mu A cm^{-2} for Sb_2Se_3/CdS/TiO_2, Fig. S2.4, ESI^{\dagger})$. The spikes in the light chopped Linear Sweep Voltammetry (LSV) of Sb₂Se₃/CdS/ TiO2/NiP demonstrated that the photoelectrons are not being utilised at a fast-enough rate by the catalyst, instead recombination is dominating.26

The low photocurrent of the Sb₂Se₃/CdS/TiO₂/NiP electrode is due to the low loading of NiP compared with previous devices.^{23,24} A common approach to achieve higher catalyst loadings on a photoelectrode is to increase the available surface area for catalyst binding by using a mesoporous TiO2 layer

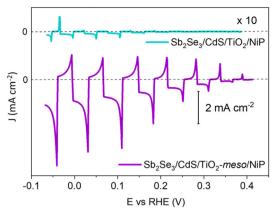


Fig. 2 Chopped light LSV of the hybrid photocathodes Sb₂Se₃/CdS/TiO₂/ NiP (blue trace) and Sb₂Se₃/CdS/TiO₂-meso/NiP (purple trace) at 10 mV s⁻¹. The TiO₂-meso enables a higher loading of the **NiP** catalysts and increased photocurrents. All experiments were carried out in 0.1 M Na_2SO_4 pH 3 at 100 mW cm⁻² and $\lambda > 340$ nm.

(TiO2-meso). Typically, following deposition of a TiO2 nanoparticleorganic binder paste, thermal annealing is carried out in air (~450 °C) to remove the binder and sinter the TiO₂ nanoparticles forming conductive pathways.26 Sb2Se3 is unstable at these temperatures in air,8 therefore we modified a UV curing approach successfully developed by the Grätzel group for CuO2/AZO/TiO2 photocathodes.²⁷ Following doctor blading of an anatase TiO₂ paste (av. particle size 20 nm diameter) the sample was UV cured for 68 h using a 365 nm LED, Fig. S2.5 (ESI†). Note that the Sb₂Se₃/ CdS/TiO2-meso also included the sputtered 100 nm TiO2 layer since it was found to be essential during the UV curing to protect the Sb₂Se₃/CdS. The photocathode was then annealed at lower temperature (350 °C) under N₂ to improve the electrochemical properties of the TiO₂-meso layer (Fig. S2.6-7, ESI†) without hindering the light absorber capabilities (Fig. S2.9, ESI†). The TiO₂-meso was ca. 4-6 µm thick determined by profilometry, the cross-sectional image and energy-dispersive X-ray spectroscopy (EDX) maps are shown Fig. 3a and Fig. S2.10 (ESI†), respectively. Neither the UV curing nor the N2 annealing alone resulted in a TiO2-meso layer with electrical and mechanical features suitable for a molecular catalyst scaffold (Fig. S2.5 and S2.8, ESI†). The NiP immobilization on the TiO2-meso device was carried out using the same experimental protocol as for the planar structure. The resultant Sb₂Se₃/ CdS/TiO2-meso/NiP photocathode achieved an increased NiP loading $(45.76 \pm 0.81 \text{ nmol cm}^{-2})$, in line with the literature. ²⁴ Top view EDX mapping shows the catalyst is evenly distributed on the photocathode surface (Fig. S2.11, ESI†). X-Ray photoelectron spectroscopy (XPS) analysis of the NiP on the Sb₂Se₃/CdS/TiO₂meso/NiP electrode is shown in Fig. 3b-d. The energies of the Ni 2p (Fig. 3b, 1/2 at 872.1 eV and 3/4 at 854.6), P 2p (Fig. 3c, 132.6 eV) and N 1s (Fig. 3d, 399.6 eV) peaks are in good agreement with the NiP catalyst prior to immobilisation (all the XPS peak positions are shown in Table S2, ESI†). 23-25 The complete Sb₂Se₃/CdS/TiO₂-meso/ **NiP** photocathode achieves a photocurrent of -1.3 mA cm⁻² at 0 V vs. RHE with an onset potential of ca. +0.37 V vs. RHE (Fig. 2). The photocurrent for this electrode structure is amongst the highest reported for a NiP decorated photocathode, Table S3 (ESI†)

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Ni post-CPP b) Ni pre-CPP $2p_{3/2}$ $2p_{1/2}$ 870 860 850 Binding energy (eV) P nost-CPF d) P pre-CPP N pre-CPP P NiP N NiP

Fig. 3 (a) Cross-sectional SEM image of Sb₂Se₃/CdS/TiO₂-meso/NiP. (b-d) XPS spectra of NiP molecular catalyst (blue trace) after it is immobilized on TiO2 (pre-CPP,black trace), and after 5 h of CPP test at 0 V vs. NHE (post-CPP, red trace) with light intensity of 100 mW cm⁻² and $\lambda > 340$ nm in 0.1 M Na₂SO₄ at pH 3. (b-d) XPS spectra showing Ni 2p, P 2p and N 1s regions respectively.

406 404 402 400 398 396 394

Binding energy (eV)

140

135

Binding energy (eV)

provides the state-of-the-art hybrid photocathodes for H2 production. NiP has been previously used with a Si/TiO2-meso photocathode to achieve a photocurrent of -0.3 mA cm⁻² at 0 V vs. RHE²⁴ and -0.6 mA cm⁻² at 0 V vs. RHE for a La₅Ti₂Cu_{0.9}Ag_{0.1}S₅O₇/ TiO₂ photocathode.²³ A control experiment without the catalyst (Sb₂Se₃/CdS/TiO₂-meso, Fig. S2.4. ESI†) demonstrates the importance of the NiP catalyst, it showed a photocurrent of only -0.12 mA cm⁻² at 0 V vs. RHE. Incident photon to current efficiency (IPCE, Fig. S2.12, ESI†) demonstrates the device is active at wavelengths up to 900 nm (at 0 V vs. RHE), in-line with the E_{g} of Sb₂Se₃.6,7

Controlled potential photoelectrolysis (CPP) carried out at 0 V vs. RHE assessed the stability of the Sb₂Se₃/CdS/TiO₂-meso/ NiP electrode, results shown in Fig. 4. The H₂ faradaic efficiency after 1 h was 77.5 \pm 9.1%, giving a TON_{NiP} of 12.8 \pm 2.8. However, the photocurrent decreased significantly in the first hour reaching $-40 \,\mu\text{A cm}^{-2}$ and by 5 hours, it decreased to only $-15 \,\mu\text{A cm}^{-2}$ (Fig. S2.13, ESI†). The loss of photoactivity of **NiP** photoelectrodes has previously been attributed to the hydrolysis of the phosphonic anchoring group from the TiO₂. ^{23,24} XPS analysis of the hybrid photocathode post CPP shows the loss of the Ni²⁺ bands (red trace, Fig. 3b). However, it is clear that both the N 1s and P 2p signals are still present, although significantly shifted. A broadening of the N 1s band has previously been assigned to protonation of the amine in the acidic electrolyte²³ and the shifting of the P band is due to the loss of the metal centre.28 The XPS results suggest the phosphonate linkage has been retained but the Ni is no longer coordinated to the ligand, in-line with the stability of the phosphonate linkage at pH < 7.29 Past studies have shown that NiP degradation occurs on photocathodes but with a slower decay rate. 23,24

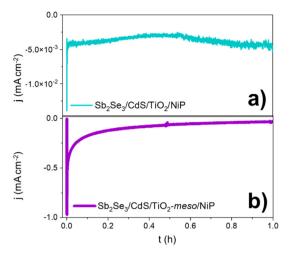


Fig. 4 CPP at 0 V vs. RHE of the hybrid photocathodes Sb₂Se₃/CdS/TiO₂/ NiP (a) and Sb₂Se₃/CdS/TiO₂-meso/NiP (b) in 0.1 M Na₂SO₄ pH 3 at 100 mW cm⁻² and $\lambda > 340$ nm.

To explore the mechanism of the hybrid photocathode decay here, we examined the TiO₂-meso/NiP interface (without Sb₂Se₃/ CdS). CPE at -0.24 V vs. RHE (Fig. S2.7b, ESI†), shows that following an initial drop in the current in the first 600 s, the electrode maintains a stable current of -0.24 mA cm⁻² for 1 h suggesting that the TiO2-meso/NiP interface is stable at this potential and capable of dealing with low current density. However, the current spikes observed with Sb₂Se₃/CdS/TiO₂-meso/NiP when the light is turned off in Fig. 2 are typical features of electron accumulation in the TiO2, suggesting that the NiP catalyst was unable to turnover at the rate of photoelectron generation under 100 mW cm⁻² illumination. Based on the concentration of immobilised NiP (45.76 \pm 0.81 nmol cm⁻²), and the highest reported turnover frequency of NiP (460 \pm 5 h⁻¹), ²¹ we calculate that the NiP on the surface could support a photocurrent of -1.15 mA cm $^{-2}$. This magnitude of photocurrent is achieved briefly in the LSV, but CPP shows the photocurrent decreases rapidly as the NiP catalyst degrades. To assess the photoelectron generation of Sb₂Se₃/CdS/TiO₂-meso, we used Pt as co-catalyst (see ESI,† for synthetic details, Fig. S2.14). The Sb₂Se₃/CdS/TiO₂-meso/ Pt electrode achieved a stable photocurrent of -3 mA cm⁻² at 0 V vs. RHE for 5 hours. It is clear that the rate of photoelectron generation at the Sb₂Se₃/CdS interface greatly exceeds the maximum current density that NiP can sustain. The catalytic mechanism of NiP is shown in Fig. S2.15 (ESI†), 20 H2 production occurs following the Ni^{II/I} reduction. Further reduction from Ni^I to Ni^{0} can also potentially occur deactivating the catalyst if the rate of photoelectron generation is too high.³⁰ To explore if limiting the photoelectron generation on the Sb₂Se₃ would be beneficial, experiments at 20 mW cm⁻² (Fig S2.16 and S17, ESI†) were carried out. Notably, only a small decrease in photocurrent was observed from 1.30 to 0.81 mA cm⁻² at 0 V vs. RHE, and 20% of photocurrent was retained after 1800 s compared with the 11% at 100 mW cm⁻².

Past studies using precious metal HER catalysts like Pt on planar TiO2 coated Sb2Se3 photocathodes have noted that Communication ChemComm

dissolution of TiO2 can also occur due to photoelectron accumulation. 11,13 The SEM images post-CPP Sb₂Se₃/CdS/ TiO₂-meso/NiP electrodes (tested at 100 mW cm⁻²) did not show significant change in the morphology of the device (Fig. S2.18, ESI†) despite the demonstration of electron accumulation in the device. XRD analysis of a post-CPP sample only showed the typical peaks of Sb₂Se₃ and TiO₂ (Fig. S2.19, ESI†) and no indication of Sb₂O₃ formation, which has been associated with the deactivation of the Sb₂Se₃ photoelectrodes (Fig. S2.20, ESI†). 12,13 However experiments where Sb₂Se₃/ CdS/TiO2-meso/NiP underwent (i) LSV and CPP at 0 V vs. RHE for 1 h, (ii) removal of any remaining NiP by NaOH stripping, and (iii) Pt addition and photoelectrochemical testing showed evidence of partial failure of the sputtered TiO2 layer due to photoelectron accumulation. Significantly higher dark currents $(<-5 \text{ mA cm}^{-2}, \text{ Fig. S2.21, ESI}^{\dagger})$ and decreased photocurrents were measured compared to a pristine platinized photoelectrode, reinforcing the importance of preventing photoelectron accumulation in the Sb₂Se₃/CdS/TiO₂-meso/**NiP** photocathode.

Emergent chalcogenide semiconductors such as Sb₂Se₃ are promising photocathodes due to their ability to achieve a high rate of photoelectron generation but they suffer from thermal instability limiting processing opportunities. Furthermore, Sb₂Se₃ interfaces need to be protected by metal oxide capping layers where corrosion could occur due to photoelectron accumulation. To prevent electron accumulation research has focused on the use of these absorbers with precious metal HER catalysts. Here we present an alternative approach using a Sb₂Se₃/CdS/TiO₂-meso photocathode. The high surface area TiO₂ support, prepared by a UV and low temperature N₂ annealing process that is compatible with Sb₂Se₃, enables a high loading of an earth abundant molecular HER catalyst, NiP. An 81-fold increase in the photocurrent was achieved when compared to a similar device without the mesoporous TiO₂. Despite the high catalyst loading, stability and activity under $100~\mathrm{mW~cm^{-2}}$ is still limited by the turnover frequency of the HER catalyst. However, initial experiments under low light intensities indicate that improved stability is achievable with further advances in the catalytic turnover frequency.

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Conflicts of interest

There are no conflicts to declare.

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