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Hybrid photocathode based on a Ni molecular catalyst and Sb₂Se₃ for solar H₂ production†

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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 ± 0.43 to 45.76 ± 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 O₂,¹ 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 long-lasting 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 H₂,⁹ 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

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 MoS_x.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 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 high-electron 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(P₂^RN₂^{R'})₂]²⁺ core (P₂^RN₂^{R'} = bis(1,5-R'-diphospha-3,7-R''-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

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

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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_g 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 ± 0.43 nmol cm⁻² was achieved. All the photoelectrochemical tests were done under 100 mW cm⁻² illumination (unless otherwise stated) and with λ > 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 μA cm⁻² for Sb₂Se₃/CdS/TiO₂, Fig. S2.4, ESI[†]). 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 Na₂SO₄ pH 3 at 100 mW cm⁻² and λ > 340 nm.

(TiO₂-meso). Typically, following deposition of a TiO₂ nanoparticle-organic 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 ± 0.81 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/TiO₂-meso/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[†])





Fig. 3 (a) Cross-sectional SEM image of $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$. (b–d) XPS spectra of **NiP** molecular catalyst (blue trace) after it is immobilized on TiO_2 (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 $\lambda > 340 \text{ nm}$ in 0.1 M Na_2SO_4 at pH 3. (b–d) XPS spectra showing Ni 2p, P 2p and N 1s regions respectively.

provides the state-of-the-art hybrid photocathodes for H_2 production. **NiP** has been previously used with a $\text{Si}/\text{TiO}_2\text{-meso}$ 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 $\text{La}_5\text{Ti}_2\text{Cu}_{0.9}\text{Ag}_{0.1}\text{S}_5\text{O}_7/\text{TiO}_2$ photocathode.²³ A control experiment without the catalyst ($\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}$, 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 Sb_2Se_3 .^{6,7}

Controlled potential photoelectrolysis (CPP) carried out at 0 V vs. RHE assessed the stability of the $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ electrode, results shown in Fig. 4. The H_2 faradaic efficiency after 1 h was $77.5 \pm 9.1\%$, giving a TON_{NiP} of 12.8 ± 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 TiO_2 .^{23,24} XPS analysis of the hybrid photocathode post CPP shows the loss of the Ni^{2+} 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$ (a) and $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ (b) in 0.1 M Na_2SO_4 pH 3 at 100 mW cm^{-2} and $\lambda > 340 \text{ nm}$.

To explore the mechanism of the hybrid photocathode decay here, we examined the $\text{TiO}_2\text{-meso}/\text{NiP}$ interface (without $\text{Sb}_2\text{Se}_3/\text{CdS}$). 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 $\text{TiO}_2\text{-meso}/\text{NiP}$ interface is stable at this potential and capable of dealing with low current density. However, the current spikes observed with $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ when the light is turned off in Fig. 2 are typical features of electron accumulation in the TiO_2 , 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** ($45.76 \pm 0.81 \text{ nmol cm}^{-2}$), and the highest reported turnover frequency of **NiP** ($460 \pm 5 \text{ h}^{-1}$),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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}$, we used Pt as co-catalyst (see ESI[†] for synthetic details, Fig. S2.14). The $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{Pt}$ 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 $\text{Sb}_2\text{Se}_3/\text{CdS}$ interface greatly exceeds the maximum current density that **NiP** can sustain. The catalytic mechanism of **NiP** is shown in Fig. S2.15 (ESI[†]),²⁰ H_2 production occurs following the $\text{Ni}^{\text{III/I}}$ 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 Sb_2Se_3 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 TiO_2 coated Sb_2Se_3 photocathodes have noted that



