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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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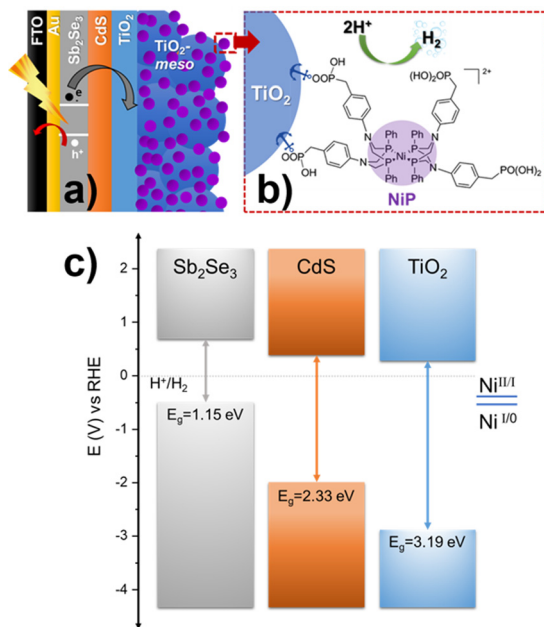


Fig. 1 (a) Schematic diagram of $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ hybrid photocathode. (b) Chemical structure of **NiP** catalyst molecular catalyst, panel a and b are not drawn to scale. (c) Equilibrium band alignment diagram of $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2$ 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$. 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 $7.08 \pm 0.43 \text{ nmol cm}^{-2}$ was achieved. All the photoelectrochemical tests were done under 100 mW cm^{-2} illumination (unless otherwise stated) and with $\lambda > 340 \text{ nm}$ 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 $-16 \mu\text{A cm}^{-2}$ at 0 V vs. RHE, which exceeds only slightly the current in the absence of any catalyst ($-3 \mu\text{A cm}^{-2}$ for $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2$, Fig. S2.4, ESI[†]). The spikes in the light chopped Linear Sweep Voltammetry (LSV) of $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$ 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$ 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

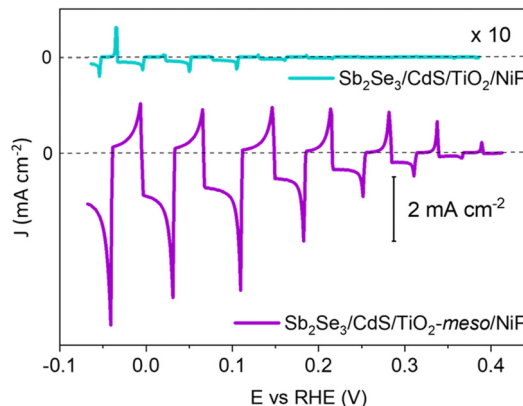


Fig. 2 Chopped light LSV of the hybrid photocathodes $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{NiP}$ (blue trace) and $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ (purple trace) at 10 mV s^{-1} . The TiO₂-meso enables a higher loading of the **NiP** catalysts and increased photocurrents. All experiments were carried out in 0.1 M Na₂SO₄ pH 3 at 100 mW cm^{-2} and $\lambda > 340 \text{ nm}$.

(TiO₂-meso). Typically, following deposition of a TiO₂ nanoparticle-organic binder paste, thermal annealing is carried out in air ($\sim 450 \text{ }^\circ\text{C}$) 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}$ also included the sputtered 100 nm TiO₂ layer since it was found to be essential during the UV curing to protect the $\text{Sb}_2\text{Se}_3/\text{CdS}$. The photocathode was then annealed at lower temperature ($350 \text{ }^\circ\text{C}$) 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ 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 $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2\text{-meso}/\text{NiP}$ 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[†])



