**Abstract:** An efficient, stable and scalable hybrid photoelectrode for visible-light-driven \( \text{H}_2 \) generation in an aqueous pH 9.2 electrolyte solution is reported. The photocathode consists of a p-type Si substrate layered with a Ti and Ni-containing composite film, which acts as both a protection and electrocatalyst layer on the Si substrate. The film is prepared by the simple drop casting of the molecular single-source precursor, \([\text{[Ti}_2(\text{OEt})_9(\text{NiCl})]}_2\) (TiNi\(_{\text{pre}}\)), onto the p-Si surface at room temperature, followed by cathodic in situ activation to form the catalytically active TiNi film (TiNi\(_{\text{cat}}\)). The p-Si/TiNi\(_{\text{cat}}\) photocathode exhibits prolonged hydrogen generation with a stable photocurrent of approximately \(-5\, \text{mAcm}^{-2}\) at 0 V vs. RHE in an aqueous pH 9.2 borate solution for several hours, and serves as a benchmark non-noble photocathode for solar \( \text{H}_2 \) evolution that operates efficiently under neutral–alkaline conditions.

Photoelectrochemical (PEC) water splitting is an attractive strategy to generate the renewable energy carrier hydrogen (\( \text{H}_2 \))\(^{[1]}\). A solar energy conversion efficiency of greater than 20 % can theoretically be achieved in a PEC tandem cell with a 1.0 eV band-gap pair of semiconductor electrodes,\(^{[2]}\) there-by surpassing the current conversion targets for profitable solar \( \text{H}_2 \) generation of 15–20 %.\(^{[3]}\) However, the implementation of PEC water splitting can only be accomplished when such semiconductors are not only efficient, but also stable and scalable.

Crystalline silicon (Si) displays excellent light-harvesting and charge-separation properties, delivering cell efficiencies of up to 25 % in photovoltaic cells.\(^{[4]}\) Si is also among the most promising and advanced photocathode materials for fuel generation, in particular for PEC water splitting.\(^{[5]}\) p-Type Si (p-Si) possesses a small band-gap of 1.1 eV with a suitable conduction band potential of \(-0.6\, \text{V} \) vs. the reversible hydrogen electrode (RHE) for the reduction of aqueous protons. Thus, p-Si shows close-to-ideal solar light-harvesting properties and provides an overpotential (\( \eta \)) of 0.6 V for \( \text{H}_2 \) generation.

However, several drawbacks must be addressed before p-Si can be used in PEC devices. The surface of Si must be protected under ambient conditions to avoid the rapid formation of silicon oxide at the surface, which may lead to the complete quenching of its photoactivity. Furthermore, an electrocatalyst promoting the hydrogen evolution reaction (HER) must be introduced to its surface to overcome the kinetic barriers associated with proton reduction. Passivation of the semiconductor with a conformal layer of TiO\(_2\) has been shown to protect the electrode from photodecomposition and surface oxidation, and the further introduction of Pt was shown to promote HER in strongly acidic aqueous solution.\(^{[5a,b]}\) However, TiO\(_2\) layering requires costly sputtering\(^{[5a]}\) and atomic layer deposition (ALD)\(^{[5b]}\) techniques, whereas the use of noble metal catalysts is undesirable due to the scarce reserves and high costs. A simple and scalable method for preparing protected Si with an inexpensive and efficient electrocatalyst is therefore required to pave the way for p-Si in PEC devices.

Herein, we report a scalable procedure for protecting and catalytically activating p-Si under ambient conditions using the heterobimetallic single-source precursor \([\text{[Ti}_2(\text{OEt})_9(\text{NiCl})]}_2\) (TiNi\(_{\text{pre}}\)). Drop casting of the molecular TiNi\(_{\text{pre}}\) onto p-Si and in situ cathodic activation results in the formation of a protection layer for p-Si and a catalytically active film (TiNi\(_{\text{cat}}\), Figure 1). This hybrid p-Si/TiNi\(_{\text{cat}}\) photoelectrode contains only earth-abundant materials and demonstrates good photostabili-
ty for prolonged PEC $H_2$ generation in near-neutral pH aqueous solution.

The cathodically induced conversion of TiNi$_{pre}$ into the HER electrocatalyst TiNi$_{cat}$ was first investigated on a fluoride-doped tin oxide (FTO)-coated glass substrate by electrochemical methods. A TiNi$_{pre}$ solution ($2 \times 20 \mu L, 5 \text{ mm in toluene}$) was drop casted onto the FTO-coated glass ($1 \text{ cm}^2$ exposed surface area) to form the FTO|TiNi$_{pre}$ electrode. The theoretical amount of Ni atoms deposited on the FTO is approximately $0.4 \text{ mmolcm}^{-2}$ (see Supporting Information). The FTO|TiNi$_{pre}$ was subsequently used as the working electrode in a two-compartment electrochemical cell containing an aqueous borate (B) solution (0.1 M, pH 9.2). The electrochemical experiments were performed at room temperature under $N_2$ using a conventional three-electrode system, with Ag/AgCl/KCl$_{sat}$ as the reference electrode and Pt foil as the counter electrode.

The FTO|TiNi$_{pre}$ electrode requires chronoamperometric activation for 60 min at an applied potential of $-0.49 \text{ V vs. RHE}$ (see Supporting Information, Figure S1a). The current density increased initially and stabilized at $-1.45 \text{ mAm}^{-2}$ for the formation of $H_2$ bubbles (confirmed by gas chromatography). A similar activation process was observed in aqueous phosphate solution (0.1 M $P_2$, pH 7), but not in $Na_2SO_4$ (0.1 M, pH 9.2) or $NaNO_3$ solution (0.1 M, pH 9.2; see the Supporting Information, Figure S1). These experiments suggest that the buffer plays an important role in the activation of TiNi$_{cat}$ and its HER activity.

Figure 2a compares the electrocatalytic activity of different HER catalysts modified on FTO-coated glass in pH 9.2 B solution containing KCl (1 M) as the supporting electrolyte. It can be seen in the linear sweep voltammetry (LSV) scans (scan rate of 1 mV s$^{-1}$) that FTO|TiNi$_{pre}$ exhibits catalytic activity with a small $\eta$ of approximately 100 mV, catalyzing HER with a respectable current density of $-2 \text{ mAm}^{-2}$ at $\eta = 420 \text{ mV}$. Blank FTO and FTO|TiO$_2$ electrode (prepared by drop casting titanium isopropoxide in toluene on FTO followed by the same cathodic treatment as for FTO|TiNi$_{pre}$, see Supporting Information) exhibited negligible current densities. A metallic Ni HER catalyst (FTO|e-Ni) was electrodeposited on the FTO-coated glass using a B buffer solution containing Ni(NO$_3$)$_2\cdot$6H$_2$O (0.5 mm; see the Supporting Information and Figure S2). The resulting FTO|e-Ni electrode exhibited lower activity than FTO|TiNi$_{pre}$, generating a current density of $-2 \text{ mAm}^{-2}$ at $\eta = 490 \text{ mV}$, which is consistent with previously reported results.

The stability of the electrodes was tested by controlled potential electrolysis (CPE) in an aqueous pH 9.2 B/KCl electrolyte solution for 1 h at $\eta = 0.6 \text{ V}$ (Figure 2b). FTO|TiNi$_{cat}$ displayed good stability with a steady state current density of approximately $-5.5 \text{ mAm}^{-2}$. FTO|e-Ni showed decreased stability, with a current density of $-3.0 \text{ mAm}^{-2}$ remaining after 1 h CPE. Headspace product analysis by gas chromatography confirmed quantitative faradaic efficiency for FTO|TiNi$_{cat}$ (Table 1).

### Table 1. Summary of the amount of headspace $H_2$, the corresponding faradaic efficiency (FE) and TOF of electro- and photocatalytically generated $H_2$ with TiNi$_{cat}$ in a pH 9.2 B (0.1 M)/KCl (1 M) solution.

| Electrode | $E$ [V vs. RHE] | $H_2$ (mmol h$^{-1}$ cm$^{-2}$) | FE (%) | Ni amount (mmol cm$^{-2}$) | TOF (h$^{-1}$) |
|-----------|-----------------|-------------------------------|--------|---------------------------|----------------|
| FTO|TiNi$_{cat}$ | $-0.39$ | $26 \pm 4$ | $99 \pm 3$ | $0.4$ | $65$ |
| FTO|TiNi$_{cat}$ | $-0.6$ | $96 \pm 7$ | $97 \pm 2$ | $0.4$ | $240$ |
| p-Si|TiNi$_{cat}$ | $0$ | $74 \pm 4$ | $100 \pm 5$ | $1.2$ | $>62$ |

[a] Photocatalytic $H_2$ generation under simulated solar light irradiation (AM 1.5G). [b] The amount of Ni was estimated from the total amount of TiNi drop casted on the electrode (see Supporting Information). [c] The TOF of p-Si|TiNi$_{cat}$ is likely underestimated because significant amounts of TiNi solution leaked during the deposition.

FTO|TiNi$_{cat}$ evolved approximately 26 and 96 mmol h$^{-1}$ cm$^{-2}$ of $H_2$ at $\eta = 0.39$ and $\eta = 0.6$, respectively. A turnover frequency (TOF; defined as mol $H_2$ per mol Ni estimated based on all Ni deposited on FTO) of approximately 65 h$^{-1}$ is reached at $\eta = 0.39$ V (see the Supporting Information), which is comparable with the reported TOF of the non-noble cobalt-based HER catalyst prepared by electrodeposition of a cobalt salt in P buffer (80 h$^{-1}$ at $\eta = 0.39$ V vs. RHE).

Scanning electron microscopy (SEM) showed a TiNi film thickness of approximately 3 to 4 $\mu$m and an unchanged surface morphology of agglomerated particles before and after catalysis (Figure 2 and Figure S3 in the Supporting Information). X-ray diffraction (XRD) studies confirmed an amorphous structure of TiNi$_{pre}$ and TiNi$_{cat}$ films (Figure S4). Both TiNi$_{pre}$ and TiNi$_{cat}$ films have no absorption in the visible light regions (Figure S5). X-ray photoelectron spectroscopy (XPS) confirmed that TiNi$_{cat}$ is composed of TiO$_2$ and Ni with a small amount of boron from B$_2$ (Figure S6). CI is only observable on the surface of TiNi$_{pre}$ and is absent from the surface after the activation process (Figures S6 and S7). In the Ni 2p region, two broad sets of signals at 855.7 eV (2p$_{3/2}$) and 873.3 eV (2p$_{1/2}$) core levels are present in TiNi$_{cat}$, which can be assigned to Ni(OH)$_2$/NiO$_x$. No metallic feature of Ni is visible on the surface of FTO|TiNi$_{pre}$, but this can be attributed to any surface metallic Ni being unstable in air, thus becoming oxidized during handling before the XPS measurement. However, a slightly lower binding energy in Ni 2p region is observed in Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ core levels is present in TiNi$_{cat}$, which can be assigned to Ni(OH)$_2$/NiO$_x$. The XPS survey of the Ni 2p region is observed for FTO|TiNi$_{cat}$, compared to FTO|TiNi$_{pre}$ (Figure S8), indicating that the composition of the film is likely changed after cathodic activation.

X-ray absorption spectroscopy (XAS) was performed to gain further insights into the average speciation, oxidation state, and local environments of the Ni and Ti atoms throughout the bulk of the amorphous TiNi material. Figure 3a presents the X-
ray absorption near-edge structure (XANES) of the Ni K-edge measured from FTO|TiNi-pre and FTO|TiNi-cat. For comparison, the XANES of Ni foil, Ni(OH)$_2$ and NiO were also measured. The absorption edge position and high peak intensity in the TiNi-pre XANES spectrum is consistent with the Ni species having a higher formal oxidation state than TiNi-pre and similar electronic characteristics to Ni(OH)$_2$ and NiO. The Fourier-transformed Ni extended X-ray absorption fine structure (FT EXAFS) $\chi(k)^2$ spectrum of hydrolyzed TiNi-pre shows a peak around 1.6 Å, corresponding to the presence of O in the first coordination shell of the Ni (Figure 3). In the case of TiNi-cat, the shape of the XANES spectrum is an intermediate between that of the Ni--O solids and metallic Ni. The Ni EXAFS $\chi(k)^2$ spectrum of TiNi-cat shows a peak of around 2 Å in the FT, with a small shoulder extending into the smaller reduced distances. This is consistent with the Ni having an average coordination environment more similar to that of Ni metal, with a small proportion of Ni--O species. Synergetic effects of NiO and Ni for HER under basic conditions have recently been demonstrated and may also be responsible for the higher activity of TiNi-cat compared to TiNi-pre and e-Ni.

Both the XANES and EXAFS of the Ti K-edge reveal that the dominant Ti species before and after cathodic activation of TiNi closely resembles the oxidation state and coordination environment of TiO$_2$ (see the Supporting Information, Figure S9). This is consistent with the formation of TiO$_2$ after TiNi-pre hydrolysis. Following cathodic activation, the Ti species within TiNi-cat remains as TiO$_2$ trapped in an amorphous mixture containing the Ni--O and Ni metal species.

TiNi-cat was subsequently investigated as a dual stabilizing and HER electrocatalyst layer on a planar p-Si substrate. Commercial p-Si wafers were employed as the light-absorbing semiconductor, and TiNi-pre was coated onto the p-Si electrode (p-Si|TiNi) by drop casting the TiN solution (8 $\times$ 12.6 μL, 2.5 mM in toluene) on p-Si (0.42 cm$^2$ exposed surface area). The activation process for p-Si|TiNi involved holding p-Si|TiNi at 0 V vs. RHE under solar light irradiation in an aqueous Biso solution (0.1 M B$_2$O$_3$ and 1 M KCl) under chopped solar light irradiation (AM 1.5G) with a scan rate of 5 mV s$^{-1}$. Pt serves as a reference benchmark catalyst for the TiNi-cat HER catalyst.

The p-Si|TiNi-cat photocathode exhibited excellent photoresponse with an onset potential for HER of approximately 0.3 V vs. RHE, which is close to the valence band potential in p-Si of approximately 0.5 V vs. RHE. A photocurrent of $-5$ mA cm$^{-2}$ was observed at 0 V vs. RHE, which is approximately 10-fold higher than that of p-Si coated with separate layers of TiO$_2$ and Ni. The p-Si|TiNi-cat shows an incident photon-to-current conversion efficiency (IPCE) of 40–50% and an absorbed photon-to-current conversion efficiency (APCE) of 55–74% when irradiating with $\lambda$ = 400 to 800 nm (0.2–0.6 mW cm$^{-2}$) at an applied potential of 0 V vs. RHE (see the Supporting Information, Figure S12). A bare p-Si electrode (without electrocatalyst), p-Si with electrodeposited Ni or a drop-casted TiO$_2$ layer exhibited comparably poor photocactivity, producing photocurrents of less than $-0.4$ mA cm$^{-2}$ at 0 V vs. RHE (Figure 4).

The benchmark p-Si|Pt photocathode has a more positive onset potential than p-Si|TiNi-cat; a photocurrent onset potential of approximately 0.4 V with a current density of $-9$ mA cm$^{-2}$ at 0 V vs. RHE was observed. Both p-Si|TiNi-cat and p-Si|Pt exhibit an anodic shift in onset potential, which indicates reduced surface recombination due to a reduced kinetic/electron-transfer barrier at the photocathode surface, and the increased electrochemical activity on the p-Si substrate. A more positive onset potential may be achieved by using different strategies, for example, by using very thin insulating layers between TiNi-cat and p-Si to electrically decouple those two layers.

Photocathodes fabricated with TiNi-cat also exhibit good stability with a negligible decrease in the photocurrent after 4 h of continuous solar light irradiation (Figure 4b and S13). The p-
Si|TiNiCat electrode exhibited a half-life time of 12 h and displayed a comparable photostability to p-Si|Pt. We observed that the catalytic coatings flaked off from the vigorous H₂ bubbling and the long-term stability of both electrodes appears therefore to be compromised by physical instability. Without the protective layer of TiNiCat or Pt, the activity of bare p-Si significantly drops within a few minutes. To confirm that the photocurrent of p-Si|TiNiCat was due to HER, photoelectrolysis was performed at 0 V vs. RHE under solar light irradiation using headspace gas analysis by gas chromatography. After 1 h, 6.1 ± 0.8 C passed through the outer circuit and 31 ± 4 μmol of H₂ were detected with an exposed area of 0.42 cm², corresponding to quantitative faradic efficiency (Table 1).

The limiting factor of the PEC activity in p-Si|TiNiCat can be understood by considering the (photo)electrochemical response of FTO|TiNiCat, FTO|Pt and p-Si|Pt in Figure 5. The photocurrent measured at a photoelectrode is limited by the reaction kinetics at the electrode surface, the electron–hole separation efficiency in the bulk semiconductor substrate and/or light absorption. FTO|TiNiCat shows a current density of approximately −6 mA cm⁻² at −0.6 V vs. RHE. This potential corresponds to the Si conduction band potential and the current of FTO|TiNiCat at −0.6 V vs. RHE is indeed close to the photocurrent of −5.0 mA cm⁻² at 0 V vs. RHE generated by the p-Si|TiNiCat electrode under AM 1.5 light irradiation (100 mW cm⁻²; Figures 2b and 5). This observation suggests that the performance of p-Si|TiNiCat is limited by the HER kinetics of TiNiCat.

In contrast, a current density of approximately −19 mA cm⁻² was generated by FTO|Pt at −0.6 V vs. RHE, which may correspond to the maximum current density obtainable with the conduction-band electrons of p-Si (Figure 5). However, a photocurrent of −9 mA cm⁻² was produced by the p-Si|Pt electrode at 0 V vs. RHE. This suggests that the performance of this photocathode was limited by the photoactivity of p-Si and not the HER kinetics of the Pt. Consistently, the photocurrent of p-Si|Pt is dependent on the light intensity (see the Supporting Information, Figure S14). Hence, despite Pt being a more efficient electrocatalyst than TiNiCat, the p-Si|Pt photocathode shows only a small improvement compared to p-Si|TiNiCat due to the intrinsic activity limitation of p-Si. Thus, TiNiCat shows good performance as a non-noble HER catalyst, operates under near-neutral conditions,⁷,⁸ and it can even show an activity close to Pt when deposited on p-Si.

Other promising non-noble HER catalysts that have been fabricated on crystalline p-Si to form a hybrid photocathode include nickel–molybdenum (Ni–Mo),⁹,¹⁰ molybdenum disulfide (MoS₂),¹¹–¹³ tungsten carbide (W₂C).¹⁴ Compared to these previously reported Si electrodes, p-Si|TiNiCat exhibits a favorable anodic onset potential and comparable photostability and does not require acidic conditions. The high photocactivity of p-Si|TiNiCat under neutral–alkaline conditions is important, because most non-noble metal-based O₂ evolution electrocatalysts and photoanodes are only functional in neutral or alkaline conditions. However, operating close to pH neutral conditions can give rise to a pH gradient at the electrode surface.¹¹ This may lead to a non-optimal fill factor, which would limit the HER photocurrent in the underpotential region (E > 0 V vs. RHE). Regardless, research close to pH 7 is still essential for eco-friendly future technologies, where abundant water supplies such as river water and seawater are employed. p-Si|TiNiCat is therefore an attractive non-noble metal photocathode with good compatibility with photoanodes for overall solar water splitting. Furthermore, unlike the preparation procedures of the aforementioned hybrid photocathodes, the preparation of p-Si|TiNiCat is very simple and scalable, without requiring costly equipment and procedures.

In summary, we report a novel, non-noble hybrid photocathode that operates at high efficiency and with good photostability under near pH neutral conditions. This p-Si|TiNiCat photocathode is very easy to prepare and makes use of single-source precursor chemistry, which gives much scope to explore other molecular precursors to further improve the performance of the hybrid electrodes in the future.¹⁹ The TiNiCat film is formed through a dual activation process—hydrolysis and in situ cathodic treatment. This novel composite phase consists of metallic Ni embedded in an amorphous NiO/Ni(OH)₂ and TiO₂ matrix and is difficult to access through conventional synthetic routes. This TiNiCat film forms an excellent interface with p-Si, simultaneously passivating the p-Si semiconductor and activating it for HER catalysis. The passivated p-Si|TiNiCat electrode displays a promising stability, which even allows it to be handled under ambient conditions. During operation, it generates photocurrents of approximately 5 mA cm⁻² in an aqueous pH 9.2 solution at 0 V vs. RHE with a quantitative faradic efficiency for several hours under 1 sun illumination. p-Si|TiNiCat therefore sets a novel benchmark for a H₂-evolving photocathode constructed solely from earth-abundant materials that operates efficiently under neutral–alkaline conditions.

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