Niobium-based Semiconductor Electrodes for Hydrogen Evolution Reaction

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ABSTRACT. This contribution focusses on the use of Nb-based materials-for the preparation of hybrid nickel-semiconductor electrodes for use in the electrochemical generation of hydrogen. The Nb-based semiconductors (*i.e.*, Nb_2O_5 and $\text{Nb}_3(\text{PO}_4)_5$) show good performance for the H_2 evolution reaction (HER) using a non-toxic electrolyte (K_2CO_3) under true water-splitting conditions. In particular, Nb_2O_5 shows HER efficiency two-orders-of-magnitude higher than its TiO_2 counterparts. Tafel analysis suggests the HER mechanism is the same for all type of electrodes studied and electrochemical impedance spectroscopy indicates these hybrid Ni-Nb-semiconductor electrodes are sensitive to light exposure, unlike TiO_2 . We propose that the differences in impedance upon irradiation are due to the band structure of these hybrid electrodes, which have lower Schottky barrier heights and show smaller work function values.

KEYWORDS. Hybrid-nickel electrodes, niobium oxide, hydrogen evolution reaction, renewable energy.

1. INTRODUCTION

The production of hydrogen as a fuel is an attractive approach to store clean energy from renewable resources, such as water. One of the main limitations of using water splitting to generate H_2 is that the process is rather inefficient as the simultaneous reduction and oxidation of water is an uphill reaction involving multiple steps.[1] In order to overcome this problem, sacrificial electron donors (SED) are often used to improve the efficiency of both photochemical or photoelectrochemical processes.[2] We have recently demonstrated that, although the use of SED greatly improve the H_2 formation efficiency, this cannot help to determine the efficiency of the materials towards true water splitting (i.e., H_2 formation from water in the absence of SEDs).[3] Electrochemical splitting of water is a promising technology for production of H_2 from renewable resources and, depending on the electrical source used, under green conditions (no green-house-gas generation).[4, 5] Platinum electrodes – typically used in acid electrolyzers – have excellent electrocatalytic properties; however, their high price is one of the major disadvantages that prevents their wide use for this application. In contrast, alkaline electrolyzers employing nickel electrodes are the preferred method for massive production of H_2 . [6, 7] However, Ni electrodes present low catalytic activity and experience fast deactivation processes such as formation of hydroxides, hydrides and other oxygenated species.[8, 9] Different strategies have been developed in order to enhance the catalytic efficiency of these electrodes; such as increasing electrode surface –i.e., increase porosity,[10] preparing metal alloys,[11] bifunctional materials, [12] or developing metal-semiconductor hybrid electrodes –specially using TiO_2 , which can greatly enhance the HER efficiencies in electrochemical systems. [13-18] The use of hybrid Ni-semiconductor (Ni-SC) type of electrodes opens the possibility to use a photo-electrochemical process in addition to conventional electrochemistry.[19] Thus, the formation of semiconductor-metal heterojunctions is

a very promising strategy that can broaden the light harvesting properties, improve chemical stability, and enhance the photoexcited charge separation of the SC.^[20] Moreover, several reports account for the protective role of TiO₂ films on photocathodes, where, in addition to the TiO₂ high stability and good conductivity, the favorable position of the TiO₂ conduction band can increase the HER efficiencies. [21-25]

Here, we select Ni-TiO₂ as the reference electrocatalyst and introduce the use of Nb-based SC, as alternatives to TiO₂, to construct hybrid Ni-SC electrodes for generation of H₂. Niobium has been extensively used in the metallurgic industry due to the multiple properties it can incorporate to the material, such as malleability, ductility, and high resistance to corrosion. More recently, few reports are based on the use of Nb in Li-ion batteries,[26-29] as it has demonstrated to increase the materials conductivity properties enhancing performance whereas extending the materials lifetime. Furthermore, Nb-based semiconductors are also used as photocatalysts for water splitting and fuel cells [30-36]. Although Nb-based SC have shown similar photocatalytic properties compared to titania,[37] including good chemical stability and acidity properties,[38] they have different optical band gap and crystalline structure (*vide infra*). This can drastically change the properties of the heterojunctions involving Nb-based semiconductors, giving, for instance, better electronic interactions.[39, 40] Here we show the preparation of two different hybrid Ni electrodes based on Nb-SC (i.e., Nb₂O₅ and Nb₃(PO₄)₅) and explore their reaction mechanism and electrochemical activity compared to commercial P25 TiO₂ under true water splitting conditions (no SED added). Thus, using an industrially optimized technique to prepare the electrodes,[41, 42] we are able to obtain reproducible results for the (photo)electrochemical production of H₂ in the presence of potassium carbonate as electrolyte.

2. EXPERIMENTAL

2.1. Materials and Instruments

Ni plates were purchased from Cordes SA Argentina. Nafion and 2-propanol were purchased from Sigma and used as received. DI H₂O was obtained by purification of deionized water using a Thermo Scientific™ Barnstead™ GenPure™ water purification system (conductivity $\geq 18 \text{ M}\Omega \text{ cm}^{-1}$) and TiO₂ P25 was purchased from Univar Canada. Niobium oxide (Nb₂O₅) and niobium phosphate (Nb₃(PO₄)₅) were generously provided by CBMM (Companhia Brasileira de Metalurgia e Mineração) and used as received.

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO diffractometer operating at 40 kV and 40 mA using $\lambda = 1.5406 \text{ \AA}$ Cu K α radiation employing in the θ -2 θ Bragg-Brentano geometry. All measurements were carried out at room temperature. The 2 θ range used was 10–90°, with 0.02° steps and counting time of 5 s per step. The Rietveld method was used to refine the crystal structure employing the FullProf program.[43] A pseudo-Voigt shape function was used to fit the experimental data. The data refined were lattice parameters, atomic positions, isotropic thermal parameters, peak shape, and occupation factors. Raman spectra of the electrode surface were acquired with a LABRAM-HR 800, HORIBA Jobin-Yvon Raman microscope with a 100 $\times$ objective lens (NA = 0.9). The laser excitation used was 633 nm at 3.5 mW. The instrument allows recording spectra with a resolution of 1.5 cm⁻¹. The illuminated area in all Raman experiments was 1.0 μm^2 . At least five different zones on each sample were analyzed to confirm the homogeneity of the catalysts. AIST-NT Scanning Probe Microscope (SPM) SmartSPM-1000 was utilized to record topography and non-contact potential measurements using Au-coated tips purchased from MikroMasch with a radius <35 nm, a stiffness of 1.8–13 N m⁻¹, and a resonant frequency of 110 - 220 kHz. All measurements were performed in non-contact AFM mode and single pass Kelvin Probe Force Microscopy (KPFM) in the dark or under visible

light irradiation. The $5 \times 5 \mu\text{m}$ area of study was scanned at $1 \mu\text{m s}^{-1}$. For each scan line, the height profile was recorded in the first pass and then the tip was lifted 10 nm away from the surface and the potential offset was measured. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-1600 SE microscope working at an accelerating voltage of 2 kV. Electrochemical measurements were carried out using the Parstat 2273 advanced electrochemical system in a conventional three-electrode electrochemical cell. A Pt wire was used as counter electrode and saturated calomel electrode (SCE) as reference electrode (0.243 V vs. RHE).

2.2. Preparation of materials

2.2.1. Preparation of the electrodes

The electrodes were prepared by the painting method.[42] In brief, the standard Nafion-based inks were prepared by mixing 5 mg of the semiconductor catalysts – unless otherwise stated – with 30 mg of DI H_2O , 300 mg of 2-propanol and 15 mg of a 5 wt% Nafion solution; and sonicated for 30 min. Subsequently, 350 μL aliquots of the inks were pipetted onto a square-shaped Ni electrode of $\sim 1 \text{ cm}^2$ (surface previously polished with #600 sandpaper) and air-dried at room temperature for 2 h. The Ni-SC electrodes were electrochemically tested in a conventional three-electrodes electrochemical cell as is showed in Figure 1.

Figure 1. *Top*: preparation of the electrodes. *Bottom*: representative diagram of the electrochemical cell using Ni-SC as working electrode. *Inset*: representative diagram of the working electrodes composed of a Ni substrate and the SC particles imbedded in a Nafion matrix. Interstices between particles could be responsible for the porosity behavior of the catalyst (*vide infra*).

2.2.2. Hydrogen Evolution Reactions (HER)

The photogeneration of H₂ under water splitting conditions (absence of SED) was carried out in a 0.5 M aqueous solution of K₂CO₃ (pH = 11). The electrodes were immersed in the aqueous solution and irradiated for 4 h under UVA-Vis light irradiation (See Figure S5).

Electrochemical measurements were performed in a three-electrode electrochemical cell using as aqueous electrolyte 0.5 M K₂CO₃ solution (pH = 11). A large area platinum foil was used as

counter electrode and a saturated calomel electrode (SCE) as reference electrode (0.243 V vs. RHE). The system was placed inside of a homemade-photoreactor setup (Figure S6) in order to perform photoelectrochemical measurements. The electrochemical experiments were carried out employing a Parstat 2273 potentiostat/galvanostat with a FRA2 module.

2.2.3. Cyclic voltammetry

Cyclic voltammograms (CVs) of all catalysts were recorded between -1.5 V and 0.1 V (vs. SCE) at a scan rate of 5 mV/s until stabilization. The CVs were performed in the dark and under UVA-Vis light irradiation. The CVs were used to construct Tafel curves and get mechanistic information of HER using the three different electrodes and under different conditions. The onset potential (OP) is determined as the potential at which current starts to increase, indicating the starting point of a process –i.e., H₂ generation.

2.2.4. Open Circuit Potential (OCP).

Measurements were performed using a pre-built method consisting on applying a close-to-zero current and measure the potential transient with time in the same three electrodes configuration. The OCP experiments were performed in the dark and under UVA, Vis, or a combination of UVA and Vis light irradiation.

2.2.5. Electrochemical Impedance Spectroscopy (EIS).

EIS experiments were performed at frequencies between 10 mHz and 200 kHz using a 10 mV bias potential at different electrode potentials: Ni open-circuit potential (OCP, -0.36 V), HER onset potential over pure Ni (OP, -1.1 V),^[44] -1.2 V, and -1.4 V (vs SCE) in order to cover the potential range where the HER occurs.^[43] The ZView 3.3 software (Scribner Associates, Inc.) was used to fit the measured data with different equivalent circuit models.

3. RESULTS AND DISCUSSION

3.1. Characterization of the semiconductors (SC)

Hybrid Ni electrodes based on SC are explored for Nb₂O₅ and Nb₃(PO₄)₅, and their catalytic activities are compared to P25 TiO₂. Before preparation of the electrodes, we characterize the SC used by means of UV-Vis diffuse reflectance (DR) spectroscopy and Raman spectroscopy, XRD, and SEM. DR spectra (Figure 2) show the absorption profile of the SC and are used to estimate their optical band gap (OBG) shown in Table 1. Briefly, Tauc plots are generated from Figure 2 and the OBG is obtained by linear extrapolations as shown in Figure S1[46]. Raman spectra (Figure S2) show the characteristic peaks for Nb₂O₅[45] and TiO₂ anatase form[46], whilst no signals are detected for Nb₃(PO₄)₅. Specifically, for Nb₂O₅ the Raman spectrum (Figure S2A) has peaks between 80 – 300 cm⁻¹ attributed to bending modes of Nb–O–Nb linkages as well as to the vibrations of the NbO₆ octahedra in Nb₂O₅. [45]. Additionally, Raman signals located in the region between 400 – 800 cm⁻¹ are usually assigned to the symmetric and antisymmetric stretching mode of the Nb-O-Nb group. Similarly, TiO₂ Raman spectrum (Figure S2C) shows signals located at 190, 390, 512 and 636 cm⁻¹ typically assigned to the anatase phase [13, 47, 48].

The XRD analyses (Figure S3) of the materials show Nb₂O₅ as a mixture of monoclinic and orthorhombic crystalline structures, TiO₂ P25 as a mixture of anatase and rutile, whereas Nb₃(PO₄)₅ is in its amorphous form. All diffraction parameters are summarized in Table S1. Especially, we observe the Nb₂O₅ crystal size — calculated using the Scherrer equation — is bigger than in TiO₂, which agrees with the particle size observed by SEM (*vide infra*).

Lastly, SEM imaging (Figure S4) shows that all semiconductors used have granular structure and, particularly, both Nb-based SC particle sizes are within the micrometer scale; thus, several orders of magnitude bigger than TiO₂ P25 particle size. Different particle sizes are directly related to the electrode porosity and exposed area.

Figure 2. UV-Vis diffuse reflectance spectra of the semiconductors (A) $\text{Nb}_3(\text{PO}_4)_5$, (B) Nb_2O_5 , and (C) TiO_2 .

3.2. Hydrogen Evolution Reaction (HER)

Using the SC described above, we prepare the electrodes as described in section 2.2.1 by means of a painting method previously reported.[42] Figure 1 shows a graphic representation of the obtained electrodes. The selection of Nafion –a sulfonated-tetrafluoroethylene-based fluoropolymer-copolymer– for the preparation of the electrodes is based on its excellent thermal and mechanical stability as well as its proton conduction properties.[49] After the electrodes preparation, we carry out a series of electrochemical measurements in order to establish the thermodynamic parameters that affect the mechanism of the hydrogen evolution reaction (HER) during water splitting. Thus, we first analyzed the cyclic voltammograms (CV) for the Ni electrode before and after modification with the SC (Figure 3) in the dark and under a combination of UV-vis light irradiation conditions (Figure S5) using the instrument setup shown in Figure S6. It is important to highlight, that the HER at the Ni electrode is not affected by the presence of Nafion, according to our control experiments. Notably, Ni-Nb₂O₅ catalyst presents a great decrease of the onset potential (OP) –*ca.* -0.42 V vs SCE– compared to those found in the bare Ni (*ca.* -1.1 V vs SCE[9]), Ni-TiO₂ or Ni-Nb₃(PO₄)₅ catalysts (Table 1). These results indicate the HER is greatly favored by the Ni/Nb₂O₅ heterojunction. This is further supported by the values of current density (*j*) obtained at -1.5 V (vs SCE), where *j* increases as follows: Ni < Ni-TiO₂ < Ni-Nb₃(PO₄)₅ << Ni-Nb₂O₅ (Table 2). In general, Nb-based semiconductors (Nb₂O₅ and Nb₃(PO₄)₅) perform better than TiO₂; with Ni-Nb₂O₅ system showing a two-order-of-magnitude enhancement in the HER compared to its TiO₂ or Nb₃(PO₄)₅ counterparts.

Figure 3. Cyclic voltammograms showing the response of the hybrid Ni-SC electrocatalysts under dark or UV-Vis irradiation conditions. Inset: Magnification of the cyclic voltammograms showing the behaviour of the least reactive electrodes. Note the roughness and porosity of the electrode upon gas generation can contribute to less smooth CV curves.[50]

Table 1. Summary of the properties of the SC used.

SC	Conditions	TiO ₂	Nb ₂ O ₅	Nb ₃ (PO ₄) ₅
^a OBG (eV)	--	3.19	2.99	3.5
OP (V)	Dark	-1.1	-0.42	-1.05
	UV-Vis	-1.1	-0.42	-1.05
^b V _{CPD} (mV)	Dark	774.1	9.9	133.7
	Vis	769.8	9.8	136.4

OBG: Optical Band Gap, OP: Onset Potential, V_{CPD}: Contact Potential Difference. ^aCalculated from the diffuse reflectance using the Tauc plots showed in Figure S1.[51] ^bDetermined by Kelvin Probe Force Microscopy using visible light irradiation shown in Figure S8. Values for Ni: OCP_{dark} = 360 mV, OP = -1.1 V, V_{CPD}(dark) = 586.9 mV, V_{CPD}(Vis) = 583.0 mV.

Table 2. Electrochemical and photoelectrochemical hydrogen generation using hybrid Ni-SC electrocatalysts.

SC	j (μA)		^a H ₂ (μmol g ⁻¹ h ⁻¹)	
	Dark	UV-Vis	Dark	UV-Vis
TiO ₂	1.02	1.01	6	6
Nb ₂ O ₅	520	521	298	299
Nb ₃ (PO ₄) ₅	7.02	7.00	40	40

^aHER rate ($\mathfrak{I}$) calculated as $\mathfrak{I} = jt/2em$; where j corresponds to the current density, t is time, e is the electron charge (96,485 C) and m is the mass of catalyst.

3.3. Mechanistic studies

3.3.1. Tafel analysis

In order to explore the mechanisms in place we evaluate the Tafel plots obtained for each electrocatalyst. It is well known that the HER mechanism can involve at least two of the following steps:

which constitute the activation barrier of the reaction.[52] Therefore, we use the CV presented in Figure 3 to construct the Tafel plots for each electrocatalyst under different irradiation conditions and evaluated their slopes (Figure S9). The Tafel slope values are similar to that reported for conventional Ni electrodes in alkaline medium (-0.13 V dec⁻¹),[9, 53] and are consistent with the Volmer step reaction as the rate-determining step. This corresponds to 1 electron transfer with a

theoretical Tafel slope of $\sim -0.12 \text{ V dec}^{-1}$, [53] indicating that the presence of the different SC does not affect the reaction mechanism compared to bare Ni electrodes. Additionally, we found no substantial changes in the values of equilibrium potential (E_r) or in the exchange current (j_0) in the dark or under irradiation conditions, as it has been also seen for OP values under different conditions (Table S1).

3.3.2. Electrochemical Impedance Spectroscopy (EIS)

We perform a series of Electrochemical Impedance Spectroscopy (EIS) measurements under dark –or under light– conditions, at four different electrode potentials (vs SCE): *i*) the pure Ni open circuit potential (OCP) reported as -0.36 V ,⁶ *ii*) pure Ni HER OP reported as -1.1 V ,⁶ *iii*) -1.2 V , and *iv*) -1.4 V . The potentials selected are the same as those commonly used in pure Ni electrodes, normally used in alkaline electrolysis.[54, 55] Figure 4 shows the impedance spectra obtained for each three catalysts under dark –or under light– conditions at -1.2 V . The Ni-Nb₂O₅ impedance spectra show two semicircles, describing at least two processes occurring over the surface of the electrodes, as predicted by the impedance theory for HER. [56, 57] One of the processes occurs at high frequencies (Figure 4A), corresponding to the capacitive processes occurring at the surface of the catalyst; and another one at low frequencies, associated with the HER –which clearly depends on the applied potential (*cf.* Figure S10). The impedance spectra obtained for Ni-Nb₃(PO₄)₅ and Ni-TiO₂ shows only one semicircle (Figure 4B-C), although the EIS theory indicates that a second semicircle should be observed. This effect is commonly founded in systems where the charge transfer resistance (R_{ct}) values are high (Table 3), and the HER kinetics prevails over other superficial processes.[56] The obtained data are adjusted by two equivalent circuit models (Scheme S1), the Randles model[57] and the Armstrong & Henderson equivalent circuit (AHEC), [58, 59] both modified with a constant phase element (CPE) to account for the electrode

porosity (Randles-CPE and AHEC1CPE, respectively).[60] The first one describes only one slow faradaic process, whereas the second model adjusts the HER to two processes –the high frequency semicircle related to the porosity, and the low-frequency semicircle related to the charge-transfer process.[13] Figure 4 shows both models fit the experimental data for each electrode obtaining in all cases fittings with errors less than 1%. Additionally, it can be seeing the porosity of the electrodes is different in the case of Ni-Nb₂O₅. Table 3 shows the values corresponding to the fittings with both models of the data measured at -1.2 V (vs. SCE). Note that all catalysts have markedly flattened semicircles, indicating high porosity, more likely originated by the interstices between the SC particles, as suggested in Figure 1. Noticeably, irradiation with UV-Vis light provokes a considerable decrease in the R_{ct} , particularly under potentials where the HER can take place (lower than -1.1 V vs. SCE). This confirms that there is a considerable positive effect of the SC on the catalytic activity of the hybrid Ni-SC electrodes, originated by the modification in the band structure of the catalysts, affecting the Fermi level of the electrodes and, therefore, the work function.

3.3.3. Kelvin Probe Force Microscopy (KPFM)

We use Kelvin Probe Force Microscopy (KPFM) to determine the changes in the work function of the materials. The KPFM technique proves to be an efficient way to determine the work function values of electrode surfaces by analyzing the contact potential difference (CPD) which is related to the concentration of electron-hole pairs. In particular, the study of illumination effects on various kinds of structures show that CPD can reflect the surface band structure of the sample.[61, 62] As it is shown in Table 1, there are large differences between the CPD values found among the three SC used and compared to bare Ni electrode. The Nb-based catalysts have a much lower CPD than would be observed in the Ni-TiO₂, indicating different work functions for each electrode.

This could explain the differences found in the catalytic activity of the Nb catalysts with respect to Ni-TiO₂. [62]

Figure 4. Electrochemical impedance spectra (EIS) under dark (black) or UV-Vis irradiation (red) conditions measured at 25 °C and −1.2 V (vs. SCE) adjusted with the equivalent circuit models AHEC1CPE (*left*) and Randles-CPE (*right*). (A) Nb₂O₅, (B) Nb₃(PO₄)₅, and (C) TiO₂.

Table 3. AHEC1CPE and Randles-CPE models' parameters obtained for the HER in 0.5 M K₂CO₃ at 298 K for each electrode at -1.2 V (vs. SCE).

Ni-SC	Ni-TiO ₂		Ni-Nb ₃ (PO ₄) ₅		Ni-Nb ₂ O ₅	
Condition	dark	light	dark	light	Dark	light
AHEC1CPE						
R _s	6.515	15.55	28.65	51.73	19.72	13.32
C _{d11}	5.53 10 ⁻⁸	4.47 10 ⁻⁷	4.37 10 ⁻⁸	2.38 10 ⁻⁷	5.27 10 ⁻⁷	1.62 10 ⁻⁷
R _p	5.21	71.4	47.3	154	6.91	5.90
CPE ₁	2.09 10 ⁻⁵	1.14 10 ⁻⁵	8.51 10 ⁻⁶	2.67 10 ⁻⁵	6.26 10 ⁻⁴	9.15 10 ⁻⁴
R _{ct}	374410	237860	240540	101780	74.04	67.69
Randles-CPE						
R _s	9.535	12.32	24.12	17.99	26.96	19.88
CPE ₁	2.08 10 ⁻⁵	1.18 10 ⁻⁵	8.61 10 ⁻⁶	2.86 10 ⁻⁵	5.81 10 ⁻⁴	8.02 10 ⁻⁴
R _{ct}	343490	235400	255150	130860	72.97	65.44

3.3.4. Theoretical band gap

In order to understand the outstanding performance of Nb₂O₅ over the other SC, we also evaluate their theoretical band gap structures. Table S2 shows the conduction band (CB) and valence band (VB) potentials of the SC calculated as described in the SI.^[63] The presence of the fundamental SC band gap in the metal-semiconductor (MS) heterojunction originates that the lowest-lying states of the SC conduction band interact with electrons in the metal Fermi level. For the electronic transport across the MS interface, this energy offset, known as the Schottky barrier height (SBH), manifests as a potential energy barrier that leads to rectifying behaviour between the metal and the SC by which the electrons flux from the SC to the metal is favoured.^[64] Therefore, it is desirable that the SC used have an SBH barrier corresponding to the conduction band close to the Ni Fermi

level to facilitate the transfer of electrons to the metal mediated by an external potential (or light) favouring the reduction of water into H_2 . The results in table S2 show CB energy levels for both Nb-SC are closer to the Ni Fermi level compared to TiO_2 . Although this simplified theory overlooks the crystal surface of the SC and the interface chemistry, can explain the outstanding catalytic activity of Nb_2O_5 compared to TiO_2 .

4. CONCLUSIONS

In summary, we describe the use of hybrid Ni-SC electrodes for HER in the absence of SED, using Nb-based semiconductors as a superior alternative to TiO_2 . This is, to the best of our knowledge, the first use of Nb-based semiconductors as cathodes or photocathodes for hydrogen generation. These materials present better electrocatalytic activity than their TiO_2 counterpart, showing two-order-of-magnitude enhancement of the HER in the case of Nb_2O_5 . Additionally, we demonstrate the HER can be carried out using a non-toxic electrolyte (K_2CO_3); which increases the application span of the materials towards home and industrial uses.

Characterization of the SC — by DR spectroscopy — shows their OBG values are 2.99, 3.19 and 3.5 eV for Nb_2O_5 , $Nb_3(PO_4)_5$ and TiO_2 , respectively. XRD analysis displays the conventional crystal structure observed for TiO_2 and Nb_2O_5 , while the $Nb_3(PO_4)_5$ is clearly amorphous, also confirmed by Raman spectroscopy. Further, differences in the crystal size obtained from XRD diffractograms are in good agreement with the particle size seen by SEM, which suggest Nb-based SC are several orders of magnitude bigger than TiO_2 .

The complete electrochemical characterization of the systems reveals the same HER mechanism found for bare Ni electrodes. Electrochemical impedance spectroscopy proves to be much more sensitive to irradiation effects than CV or KPFM; notably, a very powerful tool for the study of photosensitive systems. The results reveal that these SC, in particular Nb_2O_5 , could have promising

photocatalytic properties towards hydrogen generation and slight modifications to their electronic structure can furnish enhanced photoelectrochemical activity. Particularly, Nb₂O₅ semiconductor shows a superior catalytic activity with respect to the other semiconductors analyzed, even in comparison with TiO₂, a SC normally used for HER. These Nb-based materials would allow obtaining very simple and economical photocathodes with minimal modifications to the methods currently used for the production of catalysts for electrolyzers. We envision that the use of these alternative semiconductors could open new ways to efficiently produce H₂.

ASSOCIATED CONTENT

Supporting Information. Experimental details and additional results can be found in the Supporting Information.

Notes

The authors declare no competing financial interest.

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GRAPHICAL ABSTRACT

Ni cathodes can be easily modified by Nb-based semiconductors showing enhanced HER efficiency comparing to their hybrid Ni-TiO₂ counterparts.

Niobium-based Semiconductor Electrodes for Hydrogen Evolution Reaction

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Cyclic voltammetry and Tafel analysis

Table S1. Electrochemical and kinetic parameters for the HER in 0.5 M K₂CO₃ for each electrode (vs SCE).

	SC	b / (mVdec ⁻¹)	j ₀ / (mAcm ⁻²)	OCP / mV	E _r / V	j at -1.5 V / mAcm ⁻²
Dark	TiO ₂	-0.14	6.79 10 ⁻⁸	-82	-1.08	1.02 10 ⁻⁶
	Nb ₂ O ₅	-0.13	3.61 10 ⁻⁶	-109	-0.42	5.20 10 ⁻⁴
	Nb ₃ (PO ₄) ₅	-0.13	8.04 10 ⁻⁸	-148	-1.09	7.02 10 ⁻⁶
Light	TiO ₂	-0.13	5.75 10 ⁻⁸	-90	-1.05	1.01 10 ⁻⁶
	Nb ₂ O ₅	-0.12	5.61 10 ⁻⁶	-123	-0.46	5.21 10 ⁻⁴
	Np ₃ (PO ₄) ₅	-0.13	2.18 10 ⁻⁸	-143	-0.82	7.00 10 ⁻⁶

Tafel Slope (b), Exchange Current Density (*j*₀), Open-circuit Potential (OCP), Equilibrium potential (E_r) and Current Density (j).

Figure S9. Tafel plots for the HER on Ni-TiO₂, Ni-Nb₂O₅ and Ni-Nb₃(PO₄)₅ catalysts measured at 293 K in the dark and under UVA-Vis irradiation. Scan rate = 5 mV s⁻¹. Electrolyte: K₂CO₃ 0.5 M.

Electrochemical Impedance Spectroscopy (EIS)

As previous studies suggest for nickel electrodes in alkaline medium, we have used the Armstrong and Henderson Equivalent Circuit (AHEC) and the Randles model to describe the HER. [1-3] The addition of a constant phase element (CPE) accounts for high porosity or roughness on the electrode, denoted as AHEC1CPE and Randles-CPE, respectively (Scheme S1). All fittings showed χ^2 values below 0.01.

Scheme S1. Top: Randles-CPE model. Bottom: AHEC1CPE.

Figure S10. Electrochemical impedance spectra of all the catalysts at the different potentials used.

Theoretical band gap structures

The CB and VB of the SC were calculated using equations (1) and (2):

$$E_{VB} = \chi - E_e + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

where E_{VB} is the VB edge potential; χ is the electronegativity of the SC, which is the geometric average of the absolute electronegativity of the constituent atoms, E_e is the energy of free electrons on the hydrogen scale ($E_e \approx 4.5\text{eV}$); and E_g is the band gap energy of the SC (Table 1).

Table S2. Calculated VB and CB potentials for the materials studied (eV).

Support	Optical BG	χ_{SC}	E_{VB}	E_{CB}
TiO ₂	3.19	5.81	2.91	-0.28
Nb ₂ O ₅	2.99	6.29	3.29	0.30
Nb ₃ (PO ₄) ₅	3.5	6.68	3.93	0.43

Electronegativity of the semiconductors (χ_{SC}) calculated as the geometric average of the absolute electronegativity of the constituent atoms using the electronegativity of each element from reference.[4] Theoretical Ni Fermi level: 0.85 V vs NHE (Work Function of Ni(111): 5.35 eV.[5])

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