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Water oxidation with inhomogeneous metal-silicon interfaces

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Abstract

Si is a prime candidate for manufacturing water-splitting photoelectrochemical cells, however, the stability of this material remains a serious bottleneck. This is particularly true for the photoanode, subject to severe deactivation mechanisms. So far, thin film homogeneity has been the paradigm in the quest for stable and efficient Si-based photoanodes, which involved the use of vapor deposition methods to produce conformal thin films ensuring Si protection and efficient catalysis during operation. Recent reports on *n*-Si/metal thin film junctions have highlighted the benefits of the junction heterogeneity, generated *in situ*. In addition, results obtained from *n*-Si photoanodes partially covered with discontinuous films of Co and Ni nanoparticles lately suggested that homogeneity is not a prerequisite to reach efficiency and stability. Such findings may open new protection routes for Si-based photoanodes, breaking with classical strategies and allowing the use of liquid phase modification methods such as electrodeposition.

Abbreviations

ALD: atomic layer deposition

cocat: co-catalyst

MIS: metal-insulator-semiconductor

NP: nanoparticle

OER: oxygen evolution reaction

PEC: photoelectrochemical cell

SC: semiconductor

SCL: space charge layer

Si/pc: Si/co-catalytic protection layer

Si/p/c: Si/protection layer/co-catalyst

TCO: transparent conducting oxide

1-Introduction

Although the integration of solar and wind energies in electrical grids is considerably growing worldwide, a major concern in employing these energy sources to a much larger extent is their intermittency and their diffuse geographic distribution. A solution to solve these two issues is the conversion of renewables into a carbon-free energy carrier that would allow the storage of energy and its distribution on site and on demand.[1] Hydrogen (H₂) has long been considered as a highly promising energy carrier to fulfill this challenge in a carbon-neutral system, so-called the “hydrogen economy”.[2] In this view, solar and wind energies can be converted in H₂, which would ensure in a perfect manner: energy storage as well as distribution and conversion in fuel cells, devices that readily convert H₂ into electricity with water being the only by-product.[3] To this goal, H₂ needs to be generated by the conversion of renewable energies through a zero-emission process. This is possible by coupling water electrolysis to a renewable source of energy to yield a completely clean and scalable process that generates highly pure H₂ only from water, as described by the overall reaction (1).[4]

In water electrolysis, the electrical current that is applied between two electrodes, immersed in water, breaks the chemical bonds of the water molecule, thus generating H₂ at the cathode (reaction (2)) and O₂ at the anode (reaction (3)). The latter reaction, referred to as oxygen evolution reaction (OER), requires the transfer of four charge carriers (photogenerated holes when an *n*-type photoanode is used) and four protons and is often considered the bottleneck of water electrolysis as it requires a considerable amount of energy to be triggered. In the specific case of solar energy conversion, the transformation of sunlight energy *via* the electrolysis of water can be achieved by two strategies. First, conversion and electrolysis can be performed by two independent and separated commercial devices, *i.e.*, a photovoltaic panel and an electrolyzer.[5,6] The second strategy combines both aspects on a single device, which can be done by interfacing sunlight-absorbing semiconductors (SCs) with an aqueous phase.[7–10] These systems are referred to as photoelectrochemical cells (PECs; Fig.1a) and have the advantage of being based on a simpler design that induces less potential losses and no power conditioning. Under sunlight irradiation the SC absorbs photons and convert them into charge carriers that are driven at the solid-liquid interface to react with water, generating pure H₂ (reaction (2)) and O₂ (reaction (3)). If the operation of relatively efficient PECs has been already demonstrated by different research groups,[11] several key challenges, such as their cost and their stability, need to be tackled to enable their practical use.[12]

Fig.1. a) Scheme showing a PEC made of a SC photoanode and a SC photocathode connected by an ohmic contact. b) Scheme showing the deleterious mechanisms commonly occurring on Si photoelectrodes. c) Scheme of a conventional Si photoanode in the Si/protection layer/co-catalyst (Si/p/c) configuration. d) Scheme of an inhomogeneous MIS photoanode.

To be employed in PECs, SC absorbers must have: a short band gap to absorb a considerable part of the sunlight and a high minority carrier lifetime. In this regard, silicon (Si) is particularly appealing because it meets these standards. Moreover, it is very abundant (the 2nd element in the earth crust) and widely used in the microelectronics and photovoltaic industries, which would be a great advantage for technology transfer.[13] However, using Si as a photoelectrode, and particularly as a photoanode is very challenging, because of *i*) its slow charge transfer kinetics for OER (reaction (3)) and *ii*) its instability. The first problem is usually solved by integrating a high-efficiency co-catalyst (*cocat*) on the Si surface which collects the photogenerated holes and improves OER kinetics. In this frame, a particular interest is currently given to water electrolysis in alkaline medium because it allows employing highly efficient OER *cocats*, based on cheap and abundant materials such as Fe, Mn, Co, and Ni.[14] The latter issue (stability) has been the bottleneck for PEC manufacturing for long and is still the subject of intense research.[15–17] As shown in Fig.1b, Si is subject to two main deleterious mechanisms. The first one is the thermodynamic instability of Si, which passivates upon immersion in

aqueous solutions or when exposed to air with the spontaneous formation of an insulating native surface oxide. The anodic polarization of Si in aqueous medium intensifies this phenomenon which strictly prohibits the use of bare Si surface for OER.[18] The second degradation mechanism is Si etching, which happens readily at high pH, and prevents its use in alkaline solutions.[18] Over the last decades, tremendous progress has been made on developing modification strategies to fabricate efficient and stable Si-based photoanodes.[15,16] In this short review, we will first briefly present the classical protection strategies based on the use of conformal layers and we will then focus on an emerging type of Si-based photoanodes, referred to as inhomogeneous metal-insulator-semiconductor (MIS). We will present the recent research on that topic and discuss the advantages and drawbacks of such systems.

2- Conformally coated Si photoanodes

2-1- One layer for stability, the other one for activity

The protection of Si-based photoanodes implies, in most cases, the introduction of a conformal protection layer between the SC and the *cocat*, [15,16] deposited by means of chemical vapor deposition, physical vapor deposition or atomic layer deposition (ALD).[19] In order to design an efficient protection layer, drastic considerations must be taken into account. First, the coating should allow a charge flow by means of its intrinsic conductivity or by tunneling, it should not deteriorate the energetics of the interface and it should not impede light absorption. It is worth noting that several interesting examples of Si-based tandem photoanodes operating with a wide band gap SC acting as the same time as an absorber and as a Si protection coating have been reported but fall outside our scope.[20–23] In contrast, this short review focuses on the most commonly-employed Si protection strategies, implying oxide layers that absorb a minimal portion of the incident light but ensure protection and promote charge transfer from Si to the *cocat*. We herein refer to this construct as the Si/protection layer/co-catalyst (*Si/p/c*) configuration (Fig.1C). Note that in most of the cases, a thin (<2 nm) interfacial SiO_x layer is also present at the Si surface. So far, TiO₂ has been the most employed material for Si protection. Several types of TiO₂, prepared by different techniques and operating through different mechanisms, have been reported to be effective. Thick (up to 140 nm) layers of amorphous[24] and crystalline[25] TiO₂, deposited by ALD on *n*-Si and interfaced with Ni-based *cocats* exhibit typical photovoltages of ~400 mV and could achieve OER with an unprecedented stability of 2,200 h.[26] In these systems, the solid Si/TiO₂ interface forms a buried junction[27] which controls the photovoltage and photogenerated holes are efficiently promoted through the “leaky” TiO₂ *via* electronic defects to the Ni which forms an ohmic contact with TiO₂ (Fig.2a).[24] Conversely, sputter-deposited crystalline Ti(5 nm)/TiO₂(100 nm) protection layers were reported to only conduct electrons and to form ohmic contacts with *np*⁺-Si homojunction.[28] Furthermore, thin (~1-2 nm)

1 ALD-deposited TiO_2 conformal coatings can behave as tunnel layers, allowing an efficient transfer of
 2 photogenerated charges when interfaced with an Ir *cocat* layer in a MIS configuration (Fig.2b).[29,30]
 3 Annealing these junctions with forming gas reduces the trap states density at the Si interface, which
 4 considerably increases the photovoltage.[31] In addition, a recent report revealed that integrating an
 5 np^+ -Si buried junction in such a MIS system allows to maintain a high interfacial hole density and to
 6 achieve an unprecedented photovoltage value of 630 mV.[32] Besides, thin (~ 2 nm) conformal
 7 dielectric films of ALD-deposited HfO_2 [33] and Al_2O_3 [31,34] have also been employed as dielectric
 8 layers in MIS photoanodes. In particular, Al_2O_3 , in contact with an Ir *cocat* film, behaves as a tunnel
 9 oxide, implying an exponential increase of the device resistance as a function of its thickness.[31] In
 10 another recent study, the introduction of a high work function metal layer between the Al_2O_3 tunnel
 11 layer and the Ni film allowed a considerable improvement of the barrier height, which resulted in
 12 photovoltages of ~ 530 mV for optimized photoanodes.[35] In this case, the authors found that the
 13 maximum photovoltage was not obtained for the thinnest dielectric layer and did not exclude the
 14 possibility of defect-mediated carrier transport through the Al_2O_3 film.[35] Finally, transparent
 15 conducting oxides (TCOs) have also been employed in the *Si/p/c* configuration. Only one example of a
 16 *p*-type TCO, NiCo_2O_4 , has been reported in the *Si/p/c* configuration. This TCO was combined with an
 17 np^+ -Si buried junction and a NiFe-based OER *cocat* to perform OER for 72 h.[36] Mainly, classical *n*-
 18 type TCOs such as indium tin oxide (ITO)[37] or fluorine-doped SnO_2 (FTO)[38] have been used for
 19 Si photoanode protection. In most of these reports, the TCOs have been employed with the aim of
 20 making non-rectifying electrical contact with a Si homojunction such as npp^+ -Si,[37,38] np^+ -Si [39] or
 21 with Si heterojunction cells,[40] in order to maintain the high photovoltage produced in the Si
 22 (Fig.2c). Thick (in the range of 100 nm) layers of sputtered ITO and FTO deposited by spray pyrolysis
 23 can protect the underlying Si when interfaced with OER *cocats*. These reports have however
 24 highlighted the disadvantages of this approach which are: *i*) the downward band bending at the ITO/Si
 25 interface that needs to be circumvented by employing a highly doped p^+ -Si layer at the interface in
 26 order to ensure an efficient hole collection,[37] *ii*) the low hole conductivity of these *n*-type oxides[39]
 27 and *iii*) the low stability of ITO at harsh pH.[41] A recent very interesting report demonstrates that
 28 thick (~ 100 nm) layers of spray-deposited SnO_x on *n*-Si produces a high barrier heterojunction that can
 29 be employed for promoting OER with a photovoltage of ~ 620 mV for 100 h when interfaced with
 30 highly-active OER *cocats*.[42]

Fig.2. Schematic band diagrams showing the charge transfer mechanisms occurring for the three main Si/p/c configuration reported, after equilibration in the dark (top row) and in photoelectrochemical operation (bottom row), the Fermi level (E_F) of each component, as well as the hole ($E_{F,p}$) and electron ($E_{F,n}$) quasi-Fermi levels are represented by dashed lines. a) The barrier height is imposed by the heterojunction formed between n -Si and the thick oxide protecting layer, the *cocat* forms an ohmic contact with the oxide. The charge transfer from Si to the *cocat* is achieved by charge conduction through the oxide layer (here, by hole conduction through defect bands). b) The barrier height is imposed by the Schottky junction between n -Si and the metal *cocat*. This configuration is referred to as MIS junction when the charge transfer from Si to the *cocat* occurs *via* tunneling through a thin dielectric film. c) The barrier height is controlled by the buried np^+ -Si homojunction. Efficient charge transfer at the Si/TCO interface is usually promoted by employing a highly doped Si interfacial layer to reduce the thickness of the interfacial space charge layer.

2-2- Combining protection and activity in a single layer

An alternative and highly beneficial strategy that has also been employed to decrease the manufacturing costs consists in employing a coating material that acts as a Si protection layer and, as the same time, as a *cocat*. We refer here to this configuration as Si/co-catalytic protection layer (*Si/pc*). Note that in such a configuration, even though only one layer is deposited over the Si surface, an additional conditioning step of the surface is often required to generate catalytic species on that layer, sometimes that step is spontaneously occurring during OER. Therefore, if the *Si/pc* is more attractive than the *Si/p/c* configuration in terms of fabrication, these systems are, *in fine*, relatively identical from a structural point of view. Interestingly, only one recent report has described a *Si/pc* photoanode operating at low pH (employing an Ir-based film on np^+ -Si).[43] In contrast, the use of the *Si/pc* configuration for photoanodes operating at high pH has been lately investigated by several groups. If this may first seem unexpected considering the fact that alkaline media are harsher for Si (Fig.1b) it can be explained by the fact that these conditions allow employing abundant OER-active materials (based on Fe, Mn, Co, and Ni).[14] So far, very little has been reported on FeO_x [44] and MnO_x [45] layers, which, when employed as films in the range of ~ 10 nm on n -Si, are known to promote OER

with photovoltages partially controlled by the liquid phase. [44,45] More work has been focused on CoO_x layers, for instance, thin ($\sim 2\text{-}5$ nm) CoO_x layers deposited by plasma-enhanced ALD or sputtering have been employed to protect crystalline[46] or amorphous Si homojunctions.[47] In particular, annealing these films allowed to generate a catalytically-active $\text{Co}(\text{OH})_2$ outer layer on the top of a dense and highly impermeable Co_3O_4 which was very efficient on np^+ -Si.[48] Thicker (~ 50 nm), ALD-deposited CoO_x coatings have been also employed on n -Si with which they form a heterojunction affording a ~ 570 mV photovoltage and can protect the system for 100 days of continuous electrolysis.[49] Most of the Si/pc systems are based on Ni layers. It has been reported that ~ 75 nm-thick transparent and antireflective NiO_x layers (deposited by reactive sputtering) generate a rather low barrier heterojunction with n -Si (and can only afford a ~ 200 mV photovoltage for OER),[50] it can be considerably improved by incorporating a CoO_x interlayer.[51] Such NiO_x coatings can be employed as conductive, protective and catalytic layers for crystalline[50] and amorphous[52] Si homojunctions as well as Si heterojunctions.[52] In addition, sputtered, ~ 50 nm-thick NiO [53] and NiCoO_x [54] have been used as p -type conductive catalytic layers to protect np^+ - and back-illuminated n^+pp^+ -Si homojunctions. It has been clearly shown that the electrochemical performance of these layers is affected by the presence of Fe in solution and have been employed for 300[53] and 72 h[54] of operation, respectively. It is worth noting that the deliberate or unintentional doping of Ni-based coatings with Fe atoms (that can originate from the materials employed during water electrolysis experiments) is quite important as Fe is known to strongly affect the catalytic performance of Ni-based catalysts, for instance, it integrates into the highly-active OER phase NiOOH to produce $\text{Ni}(\text{Fe})\text{OOH}$, that can lead to an improvement or a degradation of the OER thermodynamics and kinetics, depending on the Fe content.[77] Thin Ni metal layers, deposited by e-beam or thermal evaporation on n -Si, have also been employed for manufacturing Si/pc photoanodes. The first publication on this system reported the considerable effect of the layer thickness on the photoelectrochemical properties as well as the importance of the interfacial SiO_x layer.[55] Optimal performance was obtained for 2 nm-thick films which afforded ~ 500 mV photovoltage and 12 h stability at pH 14. This photovoltage value is much higher than the one expected for a classical n -Si/ SiO_x /Ni Schottky barrier and this striking behavior, obtained for such a simple system, has triggered a broad interest. In particular, it has been recently shown that the failure is caused by the thickening of the SiO_x ,[56] associated with the permeation of the Ni/ NiO_x during operation. The n -Si/ SiO_x /Ni photoanodes have been first described as a classical MIS device (Fig.2b) where the partially oxidized Ni layer homogeneously coat Si, but, with a particular case for ultrathin layers (2 nm) where n -Si equilibrates with both the Ni and the liquid phase, affording the higher built-in potential.[55] If this description has been confirmed for thick Ni layer,[57,58] a recent study employing the dual working electrode technique (which allows decoupling the electrochemical activity of the coating from the overall photoanode response) allowed to get more insights on the operating mechanism of n -Si photoanodes coated with ultrathin Ni layers.[58] First, it revealed that the junction controlling the

photovoltage is buried and dynamic as it is not influenced by the solution potential but evolves during electrochemical conditioning. However, it clearly pointed out that the activity of this system was not entirely controlled by the chemical transformation of Ni to a more active *cocat* phase during conditioning, but is mostly due to a structural change at the solid/solid interface.[58] It was proposed that during activation the majority of the Ni⁰ layer was converted into Ni(OH)₂ which is OER active, but, more importantly, permeable to the electrolyte, causing the anodization of Si to insulating SiO_x in the regions of contact with the electrolyte. Besides, X-ray photoelectron spectroscopy revealed the presence of Ni⁰ remaining in the film. These elements allowed a better understanding of this surface, considered now as an inhomogeneous buried junction operating in the pinch-off regime, as shown in Fig.3c (note that pinch-off will be described in section 3-2).

3- Inhomogeneously coated Si photoanodes

3-1- Inhomogeneous photoanodes not in the pinch-off regime

3-1-1- Photoanodes patterned by vapor deposition

Using arrays of micrometer-sized *cocat* patterns in contact with Si instead of conformal films can be advantageous for reducing optical losses and improving light absorption by the SC. Furthermore, the protection of the uncoated surface can be addressed quite conveniently by oxidizing the uncovered Si to generate a passive SiO_x layer. Several interesting examples of inhomogeneous Si photoanodes patterned with arrays of micrometer-sized *cocat* patches (larger than the SCL, thus not exhibiting pinch-off, see section 3-2), fabricated by a combination of clean room and physical vapor deposition techniques have been reported. For instance, Ni deposited directly on *n*- or *np*⁺-Si(111), can be employed as micro-sized catalytic patches to promote OER for durations exceeding 100 h at pH 14.[59] In this case, the anodic SiO_x generated *in situ* protects the uncoated Si during operation. This design has been employed for monitoring the local O₂ production and identifying the photoanode failure modes. Another strategy consists in patterning a Si surface that is initially passivated with a thick SiO₂ thermal oxide layer to ensure a long-term stability. This concept has been employed with arrays of Pt and Ti/Ni planar disks[60] as well as nanostructured Au/Ni and Au/NiFe micro-sized islands[61] on *np*⁺-Si for OER at alkaline pH. In these cases, however, the use of reactive ion etching is required to regioselectively remove the SiO₂ before metal deposition. An attractive and original method based on localized dielectric breakdown can be employed to circumvent this technical issue. It has been shown that micrometer-sized islands of a NiFe-based *cocat*, deposited by e-beam evaporation directly on a 30 nm-thick thermally grown SiO₂, can be electrically contacted to the underlying *n*-Si by exceeding the breakdown voltage. Such a procedure allows creating a conducting filament between the *cocat* island and the SC that promotes the conduction of photogenerated holes through the dielectric.[62]

3-1-2- Photoanodes prepared by electrochemical methods

Almost all photoanode designs discussed in the previous sections require high vacuum deposition techniques. Alternative solution-based methods would not be only attractive from a financial point of view but also because they may offer new possibilities in terms of coating composition or morphology. Pioneer research has been carried out in that direction using sol-gel processes to protect *n*-Si but resulted in limited stability.[63] Modification techniques based on electrochemistry, such as electrodeposition, seems particularly attractive because they are usually low-cost, can be employed to deposit a wide variety of materials on conductors or SCs and they usually allow a precise control over the film thickness. Even though electrochemical techniques such as electrodeposition and anodization were early suggested to prepare Si-based photoanodes,[64] they have been scarcely employed so far, probably due to the well-established instability of Si surfaces in liquid electrolytes and the fear of generating a fully-insulating SiO_x layer during surface modification (section 1). In addition, high vacuum techniques are usually preferred as they typically produce high density and pinhole-free coatings, which is not always the case for electrodeposited layers, at the expense of long-term stability. However, in view of the recent knowledge on the Si/electrolyte interface and the interest given on the pinch-off effect (see section 3-2), it does not seem worthless to explore the use of electrochemical processes applied to the manufacturing of Si-based photoanodes, and experimental works readily revealed that such methods could lead to photoanodes with remarkable performance. In the following, we will first describe the very few examples using electrochemical methods (mostly electrodeposition) to fabricate Si-based photoanodes that are not operating in the pinch-off regime and we then will discuss the fabrication of pinched-off photoanodes (next section). Recently, electrodeposition of inhomogeneous metal layers has been employed to produce photoanodes in the *Si/pc* configuration to protect Si buried homojunctions. Thin (~6 nm) and discontinuous NiFe metal films exhibited great performance on *np*⁺-Si, which afforded a photovoltage of 620 mV and a stability >12 h at pH 14.[65] In addition, the scalability of electrochemical processes applied to Si-based materials has been demonstrated by a recent publication that reported the electrodeposition of large and flexible NiFe films and their subsequent anodization via a continuous roll-to-roll process to form a highly active OER *cocat* layer. Its integration to an amorphous Si solar cell has allowed oxidizing water in 1 M KOH from on onset potential as low as +0.6 V vs RHE and an operation time of 12 h.[66]

3-2- Pinched-off photoelectrodes

The pinch-off phenomenon has been first introduced in the field of solid state physics as a way to explain the behavior of inhomogeneous Schottky junctions.[67] In such a typical system, the SC surface is brought in contact with two phases leading to an inhomogeneity of the depletion region. If these systems were previously typically considered as separated heterojunctions operating in parallel, several results revealed the non-validity of this model when the characteristic size of one junction became comparable or fell below the thickness of the space-charge layer (SCL).[68] This size effect

has been attributed to the pinch-off effect in the early eighties,[69] and was rationalized in the nineties.[70] The pinch-off effect is illustrated by Fig.3b in the case of a low-doped n -Si surface that contains two interfaces of different barrier heights: a low barrier region, spatially distributed in areas of a characteristic size smaller than the SCL and a high barrier region that covers the rest of the Si surface. In this size regime, the depletion of majority carriers required to reach equilibrium at the high barrier contact extends under the low barrier contact, affecting the local band bending (creating a “saddle point” under the high barrier-region) and increases the overall barrier height (Fig.3a vs Fig.3b).[67] The pinch-off effect has been early observed in the case of inhomogeneous n -Si/metal junction in contact with liquid phases.[71,72] Notably, a study has shown that the behavior of n -Si covered with Ni patches immersed in an organic electrolyte containing a reversible redox couple (to create a high barrier Si/electrolyte region at the Ni-free regions) behaves in good agreement with the pinch-off theoretical predictions when the Ni patch size was below 100 nm.[73] It is obvious that the pinch-off effect can be very advantageous to fabricate Si-based OER photoanodes and compensate the losses caused by Fermi-level pinning, often generated at SC/metal junctions. In addition, it combines very well with the hydrogenated Si (Si-H) surface for which surface energetics can be finely tuned by chemical surface functionalization.[74] More importantly, interfacial SiO_x can be easily employed to passivate Si and generate a high barrier region with a low density of interface states. Thus, pinched-off photoelectrodes could be, in principle, easily fabricated by partially modifying Si with small particles of an appropriate metal and oxidizing the non-coated area. In addition to the high photovoltage generated by the effect, in this configuration, the photogenerated holes will mainly flow through the less resistive pathway and will be collected at the metal particles where they can be employed for OER.

Fig.3. a,b) Schematic energy diagrams, adapted from Nakato *et al.* (reference[72]), for a *n*-type SC in contact with a metal patch that produces a low barrier height (ϕ_B^M) region and a second phase that produces a high barrier height (ϕ_B^E) region (q is the elementary charge). In a) the metal patch is large and in b) the metal patch is small with respect to the depletion width. In blue are represented the energies of the Fermi level (E_F dotted line), the valence band (E_{VB}) and the conduction band (E_{CB}) of the SC and in red is represented the E_F of the metal. The full black lines represent the distribution of the potential barrier inside the SC, the dotted black line represent the potential distribution under a metal patch and the dark yellow line represent the depletion region. In Fig.3b, because of the small size of the metal patches, the surface is pinched-off and the effective barrier height (ϕ_{Beff}) is much higher than ϕ_B^M . c) Scheme, adapted from Boettcher *et al.* (reference [58]), showing the interface of an *n*-Si/SiO_x/Ni, where the Ni is ultrathin. During operation, the Ni surface is partially converted in catalytic and permeable Ni(OH)₂/NiOOH, allowing Si to oxidize and to form a SiO_x passive layer. This surface is thought to be pinched-off (as in Fig.3b), explaining the high value of obtained photovoltages. d) Scheme showing the interface of a pinched-off inhomogeneous MIS photoanode fabricated by electrodeposition of Ni⁰ on *n*-Si (section 3-3).

3-3- Pinched-off photoanodes prepared by electrochemical methods

Typical cathodic electrodeposition of metals occurs *via* a nucleation-growth mechanism which makes this method particularly relevant for the decoration of an *n*-Si surface with dispersed metal nanoparticles (NPs), causing a minimal light interference and inducing the pinch-off phenomenon. The first example of a rather stable (~2 h at pH 14 and 25 h at pH 9) photoanode composed of nanometer-sized metal electrodeposits on *n*-Si was reported in 2015. Here, inhomogeneous Co islands were reported to generate high photocurrents ($> 30 \text{ mA cm}^{-2}$) and surprisingly high photovoltages, greater than the one obtained with conformal *n*-Si/CoSi₂ and *n*-Si/SiO_x/Co solid junctions.[75] If the authors

could not ascribe this behavior to a precise physical phenomenon, they clearly demonstrated the importance of *i*) the Co inhomogeneity to generate different barrier heights and *ii*) the SiO_x layer, and, showed that the photovoltage was independent of the solution potential. In addition, they also suggested that the CoOOH catalytic layer, formed around the Co⁰ particles could play a role in the interface energetics and may improve charge extraction.[75] This report set an important landmark as it showed for the first time that electrodeposited inhomogeneous coatings can be used to fabricate photoanodes with remarkable performance without employing a buried Si homojunction and a homogeneous protection layer. Two years later, we have demonstrated that *n*-Si modified with dispersed hemispherical Ni NPs by cathodic electrodeposition can be employed to trigger OER in alkaline media with an onset potential more negative than the O₂/H₂O formal potential and a higher stability[76] than those previously reported for Co-based electrodes.[75] We have also evidenced a strong correlation between the Ni coverage and the photoelectrochemical performance. Indeed, the highest photovoltages and photocurrents were obtained for low Ni coverage while an increase of the Ni loading decreased the performances (but increased the stability). The electrodes fabricated using this method exhibit photovoltages that can exceed 400 mV and can operate for more than 10 h at pH 14.[76] Actually, the behavior of these photoanodes is very similar to that reported for ultrathin conformal layers of Ni (described in section 2-2, see Fig.3c), which suggests that both of them are operating in the pinch-off regime, as shown in Fig.3d.[55] We recently reported the effect of photoelectrochemical activation, which, by producing a catalytic Ni(OH)₂/NiOOH shell, doped with Fe (thus referred here as Ni(Fe)(OH)₂/Ni(Fe)OOH), around the Ni⁰ particles, can considerably improve the OER kinetics.[77] In addition, a stability study revealed that the protection originates from the oxidation of the uncoated Si which readily passivates the Si exposed to the solution and protects it, *in operando*, from alkaline etching. Besides, unexpected stability was reported at the open circuit potential and it was found that the presence of the Ni particles on the surface slowed down electrode deactivation with a more pronounced effect under illumination.[77] After our initial report, several groups have employed the same strategy to fabricate pinched-off photoanodes. For instance, the effect of annealing was studied and the thermal oxidation of the Ni particles was found to improve the photovoltage and the photocurrent, which was attributed to the partial conversion of Ni to a *p*-type NiO_x that increased the pinched-off barrier height underneath the Ni NPs.[78] An interesting study has reported the effect of the thickness of the Ni(OH)₂ layer grown on the Si NPs. In this case, the Ni(OH)₂ was electrochemically deposited over the Ni particles,[79] which produced essentially the same effect as electrochemical conditioning,[77] except that the Ni core remained unaffected during deposition. It was shown that the presence of the Ni(OH)₂ coating considerably improved the open circuit photovoltage and therefore the performance for OER. Ni(OH)₂ was assumed to be responsible for the increase in the overall barrier height due to a *p*-type nature,[79] which may be the subject of debate because Ni(OH)₂ is typically insulating and electrolyte permeable.[80] Also, this electrodeposition process has been applied to microstructured *n*-Si.[81] Recently, we have reported the

1 integration of these pinched-off photoanodes in an “all Si”-based monolithic photoelectrochemical cell
2 that quantitatively produced H_2 directly under solar illumination,[82] showing that this type of
3 photoanode can be employed for unassisted solar water splitting.

4 Furthermore, owing to the very negative redox potential of the SiO_2/Si couple, bare Si can be directly
5 employed to reduce certain metal salts at its surface without applying an external bias. Although being
6 of an electrochemical nature, this process, referred to as electroless deposition, is spontaneous and
7 does not require the use of a potentiostat. It has been recently employed to spontaneously modify n -Si
8 with Ni particles,[83] leading to photoanodes with a considerably different structure as, in this case, a
9 submicrometer-thick porous SiO_2 layer comprising conductive Ni filaments was formed between the
10 Si and the Ni *cocat* during the electroless deposition process. Interestingly, the reported
11 photoelectrochemical properties of these photoanodes were very similar to those obtained by Ni
12 cathodic electrodeposition, suggesting that the pinch-off effect might also happen at the
13 Si/inhomogeneous Ni- SiO_2 interface despite structural differences and the interface complexity.

15 **4- Concluding remarks**

16 Si-based water-splitting PECs could potentially play a role in a sustainable energy economy, however,
17 this would be only feasible if the current bottlenecks that are: *i*) their cost and *ii*) their stability are
18 successfully addressed. In order to overcome this challenge, considerable research effort has been
19 made on Si-based photoanodes, that suffer from serious deleterious mechanisms, leading to their fast
20 deactivation (section 1). So far, homogeneity has been the paradigm in the search for stable and
21 efficient Si-based photoanodes, which involved the use of physical vapor deposition, chemical vapor
22 deposition or ALD to produce conformal, pinhole-free, oxide thin films ensuring Si protection and
23 efficient catalysis during operation (section 2). The recent progress in this area has been considerable,
24 as demonstrated by several reports showing the operation of highly stable Si-based photoanodes with
25 operation time in the range of 100 h and up to more than 2,000 h.[26]

26 On the other hand, recent reports on photoanodes based on the MIS configuration have shown that,
27 when properly engineered,[32,35] such interfaces can exhibit excellent OER performance,
28 approaching the one obtained with buried Si homojunctions. The interest of these studies is twofold as
29 they may potentially decrease the process costs related to the fabrication of Si-based photoanodes by
30 avoiding the need for homojunctions and also because they point out principles that may be transposed
31 to other SC materials, for which homojunctions cannot be created. A remarkable example in the frame
32 of Si/metal junction is the n -Si/Ni junction,[55] which is prepared by coating n -Si with an ultrathin
33 layer of Ni. Although this junction is initially homogeneous, a recent experimental study has shown
34 that its outstanding performance originates from its inhomogeneity, which is generated during
35 operation.[58] It is, thus, intriguing to note that considerable improvement can arise from the

transformation of a homogeneous phase to a highly inhomogeneous (and partially electrolyte-permeable) phase while keeping a decent stability. Such findings should trigger the interest in novel forms of protection, breaking with the classical strategies, which could involve simpler liquid-phase fabrication methods.

In this context, electrochemical modification methods may be perfect candidates for preparing efficient water-splitting photoanodes. This has been recently suggested by recent reports on randomly-dispersed Co[75] and Ni[76,77] NP arrays, generated by electrodeposition on *n*-Si. In these systems, a large portion of the Si is exposed to the electrolyte, which induces its anodic passivation under operation and favors pinch-off (section 3-2), promoting high built-in voltages. The simplicity of Ni electrodeposition has quickly driven several research groups to employ this method successfully which has led to stability in the range of 10 h at pH ~14[76] and up to 300 h at pH 9.[79] Such a stability could first seem unexpected considering such corrosive environments for Si, and that the largest Si part is covered by nothing but its anodic oxide. If these unexpected recent reports are exciting, the performance of inhomogeneous photoanodes manufactured this way is still far from their conformal, oxide-coated, counterparts in terms of photovoltage[42] but also stability.[26] Nevertheless, it is expected that considerable progress could be obtained through a better understanding of the pinch-off effect as well as a fine characterization of the Si/metal, Si/SiO_x and SiO_x/metal interfaces, that all seem to play an important role for photovoltage generation and stability.[77] A detailed comprehension of each component of these complex inhomogeneous surfaces may open doors for improvement of the photoanode lifetime. It is envisioned that ameliorations are within reach by applying simple chemical treatments, for instance, improving the oxide quality or generating interfacial silicides. Electrodeposition conveniently allows triggering layer by layer modifications at the *cocat* level (allowing the generation of core-shell structures) and thus, is expected to quickly lead to progress in the optimization the catalytic aspect of these photoanodes.[77,79,84] In addition, progress will probably arise from studying other important considerations such as *cocat* geometry, adhesion, and surface distribution. Attention should also be paid to a crucial but often neglected aspect that is the photoanode stability when unbiased. Indeed, all photoanodes described in this short review are expected to be integrated into water-spitting PECs where they will be subject to dark cycles (typically overnight) which may be strongly deleterious to, especially at high pH.

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Papers of special interest (•): refs [13],[16],[24],[32],[35],[58],[70],[73],[76],[79],[82]

Papers of outstanding interest (••): refs [55],[75]

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