Mini-review

Pedro Migowski*, Adriano F. Feil **Uses of Physical Vapor Deposition Processes** in Photoelectrochemical Water Splitting Systems

DOI 10.1515/recat-2016-0001 Received May 15, 2015; accepted January 15, 2016

Abstract: Most of the hydrogen on planet earth is found bound to oxygen atoms in water, making H₂O one of the most promising H₂ storage molecules. Large availability, non-toxicity and low cost are among the advantages of using H₂O as a H₂ gas source. However, the decomposition of water into H₂ and O₂, called water splitting, needs a large amount of energy, increasing the final cost per kg of hydrogen produced. In this context, the energy provided by the sun may be used to power photoelectrochemical cells (PEC) for water splitting to produce cheap and high purity H₂. This mini-review will show recent advances on the use of physical vapor deposition (PVD) methods to improve semiconducting electrode performance. PVD enables the preparation of thin layers of expensive materials over photoelectrodes, therefore decreasing PEC systems manufacture costs. Moreover, the interface of between the semiconductor and the evaporated materials can be optimized under high vacuum conditions used in PVD processes and more efficient PEC systems can be obtained.



Keywords: Hydrogen, semiconductor, renewable energy, water splitting, nanomaterials, nanoparticles, sputtering, physical vapor deposition, thin films, photoelectrochemical cells, PEC

1 Introduction

The development of technologies aiming to decrease the emission of greenhouse gases in the atmosphere is a key feature for a sustainable economy. Solar cells and wind generators are the successful examples of such technologies. In the frontiers of fuel market, hydrogen emerges as a promising "green" alternative to fossil sources. Currently, low cost H₂ is produced from natural gas steam reforming and generates large amounts of CO₂ [1]. Therefore, the development of methodologies for H₂ generation with competitive prices is very important. In this context, solardriven photoelectrochemical water splitting (WS) to produce H, has emerged as a promising technology [2].

The working principle of photoelectrochemical cells (PEC) differs from photovoltaic-electrolysis cells [3]. Photovoltaic-electrolysis systems use the electrical power generated by the photovoltaic module to perform electrolysis of water, Figure 1a. On the other hand, PECs are characterized by a semiconductor-electrolyte junction where an electric field is created, facilitating the spatial separation of the photoexcited electron/hole pairs, Figure 1b [4]. The isolated minority charge carrier migrates to surface sites at the electrolyte-semiconductor interface where redox reaction occurs. The conduction band-edge (E_{CR}) and valence band-edge (E_{VR}) energy values determine if a semiconductor is suitable for non-biased WS reaction, Figure 1c [2]. In an ideal scenario, semiconductors E_{CR} should be more positive than the H₂/H⁺ electrochemical potential and E_{vB} should me more negative than H_2O/O_2 electrochemical potential, Figure 1c. Consequently, the minimum theoretical band-gap (E_{a}) that a semiconductor must have to perform non-biased WS is 1.23 eV (water splitting E°= 1.23 V), Figure 1c. However, the oxygen evolution reaction (OER) performed by photogenerated positive charge carriers (holes) in the semiconductor valence band (VB) and hydrogen evolution reaction (HER) performed by photoexcited electrons in the conduction band (CB) need an overpotential to overcome concentration and kinetic barriers. The estimated E_a needed to overcome these losses is in the range of 1.6-2.4 eV [2].

Download Date | 8/3/18 7:21 PM

^{*}Corresponding authors: P. Migowski, A. F. Feil, PUCRS, Faculdade de Física, Av. Ipiranga, 6681 90619-900 Porto Alegre - Brazil, E-mail: pedro.migowski@pucrs.br, adriano.feil@pucrs.br

CO BYANG-ND © 2016 Pedro Migowski, Adriano F. Feil, published by De Gruyter Open.

This work is licensed under the Creative Commons Attribution-NonCommercial-NonDerive 3-0 License Authenticated

The work published by Fujishima and Honda [5] on the light-driven photoelectrochemical WS using TiO, photoanodes stimulated the scientific community to investigate semiconductors for WS. Since then, metal oxides as TiO₂ [6], Fe₂O₂ [7], BiVO₄ [8], WO₂ [9], metal nitrides as Ta₃N₅ [10], metal phosphides as InP [11,12] and Si [13] semiconductors have been investigated aiming to develop photoelectrochemical systems with better solarto-hydrogen (STH) efficiencies. Wide band-gap oxide semiconductors show good stability under illumination in aqueous electrolytes, but poor visible radiation absorption resulting in low overall efficiency [14]. Visible light active non-oxide semiconducting materials present good STH efficiency, but low stability under illumination in aqueous solutions [15]. The current benchmark water splitting PEC, made by Turner group at NREL, has 12.4% STH efficiency and is based on a p-type GaInP, powered by a GaAs p-n junction [16].

Several strategies have been developed to improve PEC system performances. Most of them involve the semiconductor surface coverage with a functional material that increases the photoelectrochemical cells efficiency and stability. The function of the modifying materials can be divided into 3 different categories: i) Formation of a semiconductor-semiconductor junction [17], ii) sensitization [18] and iii) water reduction or oxidation electrocatalyst [19].

A semiconductor-semiconductor junction is characterized by a built-in voltage created at the interface between two semiconducting materials in physical contact. The strength of the electric field depends on the nature of the junction type (N-n, P-p or p-n), on the doping density difference and the composition of both semiconductors (homojunctions or heterojunctions) [20]. The electric field at the materials interface directs the majority of the electrical carriers flow, decreasing the recombination rates, and may increase the water splitting efficiency [4].

Sensitisation is the extension of the light absorption range of wide band-gap semiconductors by compounds adsorbed/deposited at its surface. Molecular dyes, metal nanoparticles that possess surface plasmon resonance (SPR) [21] or visible light absorbing semiconductors that absorb light with wavelengths longer than the base semiconductor are classified as sensitisers. Examples are the adsorption of Ru bypiridine complexes in TiO_2 [22] and CdSe nanoparticles deposited over ZnO electrodes [23]. Indeed the sensitisation made by semiconductors is a specific case of the formation of a semiconductorsemiconductor junction, but it deserves a special classification due to a number of such sensitisation examples shown in literature.

The third approach is the deposition of electrocatalysts for HER and OER. Semiconductors can have the band edges with proper energies to perform water oxidation and reduction but the electron transfer reactions may not be fast enough for a sustainable process. Addition of an electrocatalyst thin layer at the semiconductors surface not only decreases the overpotential required for high current densities, but also can act as a photocorrosion inhibitor. The most active known HER catalysts in PEC are noble metals (Pt, Pd, Rh and Ru) [24,25] nanoparticles or thin layers, meanwhile metal oxides like RuO₂, IrO₂, NiO or CoO are known to be the most effective OER [26] catalysts.

Chemical or physical methods can be used to cover the surface of a semiconductor with a functional material to improve the photoelectrochemical activity, Figure 2. Chemical methods such as electrodeposition [27], chemical bath deposition [28], successive ionic layer adsorption and reaction (SILAR) [29], adsorption of pre-made colloidal nanoparticles (NPs) [30] are widely employed to modify



Figure 1: Solar-driven electrochemical water splitting cells a) photovoltaic-electrolysis cell; b) photoelectrochemical water-splitting cell and c) working principle of and water splitting PEC with n-type semiconductor photoanode.



Figure 2: Methods to improve PEC by the use of physical or chemical methods. The emphasis of this review is centered on PVD methods to modify the semiconductor surface to form a semiconductor/semiconductor junction; sensitisation and; HER and OER electrocatalytic sites.

semiconducting photoelectrodes. However, physical vapor deposition methods are much less commonly reported on the preparation of PEC systems.

PVD techniques are already applied in the production of large-scale thin-film photovoltaic generators. Thermal evaporation, electron beam deposition, laser ablation and sputter deposition are widely used in the manufacture of high efficiency and low cost 2nd generation solar cells [31-34]. High-vacuum (HV) conditions normally used in PVD processes allow working with clean surfaces and thus obtain high quality interfaces between the substrate and the evaporated substance. Moreover, PVD permits one to obtain thin-films with controllable thickness down to a monolayer of the evaporated material.

The interest to use PVD methods has also been expanded to the H₂ fuel economy. Successful examples are fuel cell electrocatalysts [35], fuel cells bipolar plates [36] and water electrolyzer catalysts [37,38]. The paper published by Esposito and co-workers [37] shows how the use of PVD processes can be beneficial for H₂ formation from WS (photo)electrochemical systems. Based on model calculations, Figure 3, the cost for Pt HER catalyst in an electrolyzer was estimated as a function of the Pt loading and the current density (1) calculated using the Tafel equation. It can be seen that only a single Pt monolayer (black circles) on a flat surface would be enough to reach the typical currents of PEC systems (10-20 mA cm⁻²) [39]. Therefore, PVD can be used to prepare expensive material thin layers over photoelectrodes and decrease PEC systems manufactur costs.

In this mini-review, the use of PVD methods to modify the surface and improve the performance of PEC semiconducting electrodes will be described. The review is organized according to the function added to the semiconductor by the evaporated material: formation of a semiconductor-semiconductor junction; sensitisation and addition of electrocatalytic sites for HER and OER. Only reports in which the evaporated material is deposited



Figure 3: Platinum cost and the HER current density as a function of different morphology of Pt estimated using the Tafel equation: Spherical particles (; diameters in nm; a) 2 A cm⁻², b) 0.2 A cm⁻², c) 0.04 A cm⁻²), thin films (•; thicknesses given), and mesoporous supported Pt NPs (•). Reprinted with permission from [37]. Copyright 2013 John Wiley and Sons.

directly over the semiconductor will be considered, since the PVD HV conditions may benefit the interfacial properties among host semiconductor and functional material.

2 Semiconductor-Semiconductor junction formation by PVD

In a semiconductor-semiconductor junction, a build-in voltage is created at the interface between two semiconducting materials in physical contact. PEC efficiency may be improved by this electric field at the junction interface as it drives the majority of the carriers flow to the external circuit and decreases the photoexcited charge carrier recombination. Table 1 shows the examples of photoelectrodes at which a semiconductor-semiconductor junction was formed by the use of PVD.

From 2012 to 2013 Lai et al [40,43-46] published a sequence of 5 papers about water splitting PEC using TiO, nanotube (NT) arrays loaded with WO, by sputtering. The authors reported that the deposition of tungsten onto the TiO₂ NTs at a sputtering time of less than 1 min yielded the formation of hybrid WO₂-TiO₂ NTs, as manifested by the formation of W–O–Ti groups. Longer deposition times resulted in the accumulation of WO₂ on the top part of the nanotubes and initiated the growth of a cauliflower-like structure. The resultant hybrid NTs displayed higher visible light absorption and higher photoconversion efficiency as compared to the pure TiO₂ NTs. The best WO₃-TiO₂ NTs photoelectrode produced a 2.4 mA cm⁻² photocurrent that is 2 times higher than a pure TiO₂ NTs sample. This effect was attributed to better charge carrier separation and transportation in PEC WS by providing an effective way to address recombination losses due to the semiconductorsemiconductor junction formed.

Leroy et al. [41] synthesized LaTiO₂N photoanodes with a sputtered In₂O₃ overlayer. The authors reported that the coverage of LaTiO₂N with In₂O₃ multiplied the photocurrents by a factor of 2-3 when compared with pristine LaTiO₂N films. The enhancement could be attributed to: i) a better charge separation and lower charge recombination at the semiconductor-semiconductor junction and/or ii) to better charge extraction by the action of a surface dipole created between LaTiO₂N/ In₂O₃. The authors suggest additional studies on the interface to assess the actual mechanism. This study has shown the promising potential to combine In₂O₃ with oxynitrides for solar WS reaction. Shaheen et al. [42] fabricated a junction between TiO_2 and ZnO via the sputtering of ZnO layers on anodically grown TiO₂ NTs. The findings of this work indicate that longer sputtering times resulted in thicker ZnO shells, which in turn showed different morphologies and optical properties, Figure 4a-d. The TiO₂/ZnO heterojunctions were tested as photoelectrodes in WS PEC using Na₂SO₄ electrolyte, Figure 4e. The sample coated for 53 min with ZnO has shown the best photoelectrochemical response, showing 7.3 % photoconversion efficiency under UV radiation while pure TiO₂ NTs showed 4.1 % at the same conditions. This effect was confirmed via the incident photon to current efficiency (IPCE) measurements, Figure 4f.

The decrease in the band gap (3.06 eV), the higher surface area, and the relative band positions between ZnO and TiO_2 are thought to be the main reasons for the observed enhancement in the PEC efficiency.

3 Sensitization of semiconducting electrodes using PVD

The sensitisation is typically used to extend the light absorption of wide band-gap semiconductors to the visible light range. PVD processes were used to deposit metal nanoparticles that possess SPR or visible light absorbing semiconductors to sensitize wide band-gap semiconductors. Table 2 summarizes the examples of photoelectrodes sensitized by PVD methods found in literature.

Table 1: Literature reports of water splitting PEC photoelectrodes in which a semiconductor-semiconductor junction was formed by PVD. The results shown are for the best conditions described in each article.

Photoelectrode design	PEC experiment		PEC results		ref
	Electrolyte comp.	LPD (W m ⁻²)	pure semicon.	modified semicon.	
			J _{sc} (mA cm ⁻²)* / E _{oc} (V)	J _{sc} (mA cm ⁻²)* / E _{oc} (V)	-
n-TiO ₂ NTs were produced by anodization of Ti foil. Metallic W was deposited 30 s over NTs by RF sputtering system with 150 W and subsequently the pure n-TiO ₂ NTs and the n-W/TiO ₂ NTs samples were annealed at 400°C in Ar atmosphere for 4 h.	1 M KOH with 1wt% ETG, pH=14	800, no filter	~0.7/~0.37	1.3/~0.29	40
n-LaTiO ₂ N powder was deposited on FTO by electrophoretic deposition followed by TiCl ₄ treatment with subsequently annealing under vacuum for 30 min in 773 K. A 14 nm \ln_2O_3 layer was deposited by RF sputtering over LaTiO ₂ N film.	0.1 M Na ₂ SO ₄ pH=7	,1000, AM 1.5G	0.24/-	0.61/-	41
n-TiO ₂ NTs were produced by an odization of Ti foil. The ZnO was deposited over NTs by RF sputtering of ZnO targets system at 125 W for 53 min.	0.5 M Na ₂ SO ₄ pH=7	,1000, 320 < λ < 400 nm	\$9/0.11	13/0.01	42

LPD=Light power density; ETG= ethylene glycol; NRAs=nanorods arrays; QDs=quantum dots;

* at 1.23 V vs. RHE; ^{\phi} amorphous TiO, NTs,



Figure 4: SEM top-view images of (a) pure TiO_2 NT after annealing at 450°C, and the ZnO/TiO_2 NT formed via the sputtering of ZnO for (b) 18, (c) 35 and (d) 53 min, respectively. (e) Shows the photocurrent density vs. potential under intense UV illumination for the pure TiO_2 NT and the ZnO/TiO_2 heterojunction and the (f) IPCE data of pure TiO_2 NT and the 53-min ZnO/TiO_2 photoelectrodes under a constant bias of 1.23 vs. RHE.⁴²Adapted with permission from (B. S. Shaheen, H. G. Salem, M. A. El-Sayed, N. K. Allam, *J. Phys. Chem. C* **2013**, *117*, 18502-18509). Copyright (2013) American Chemical Society.

Table 2: Examples found in literature concerning the use of PVD methods to sensitise semiconductors applied in PEC water splitting reac
tions. The results shown are for the best photoelectrodes described in each article.

Photoelectrode design	PEC experiment		PEC results		ref
	electrolyte comp.	LPD (W m ⁻²)	pure semicon.	modified semicon.	
			J _{sc} (mA cm ⁻²)* / E _{oc} (V)	J _{sc} (mA cm ⁻²)* / E _{oc} (V)*	-
100 nm - TiO ₂ thin film on FTO glass substrate was deposited by RF magnetron sputtering. At the same procedure was applied to deposit 10 nm of Au on TiO ₂ surface. Then the as-prepared films were annealed in air at 400°C for 3 h.	1 mol/L KOH, pH=14	4700 for λ > 550 nm	0.0003** / -	0.0022** / -	[47]
n-TiO ₂ NT was fabricated by electrochemical anodization of Ti sheet. The CdSe was deposited onto TiO ₂ NT surface by DC magnetron sputtering for 30 min with subsequently annealing at 400°C for 30 min in vacuum (2 x 10 ⁻⁷ mbar).	0.24 M Na ₂ S and 0.35 M Na ₂ SO ₃ , pH=13	1000, λ > 400 nm	0 / 0	1.9 / 0.145	[48]
n-ZnO NWs were grown on glass substrate by hydrothermal process and a 15 nm of Au was subsequently sputtered on ZnO surface. Then the samples were annealed at 200°C for 1 h.	0.5 M Na ₂ SO ₄ , pH=7	1000, λ>400 nm	0.020 / 0.8	0.22 / 0.890	[49]

LPD=Light power density at 1.23 V vs. RHE, **under zero applied bias voltage

In 2014 Chen et al. [48] studied visible light responsive photoelectrodes composed of Au NPs deposited on TiO_2 (AuNPs-TiO₂) by RF magnetron sputtering. Composite structures where optimized by varying the Au film thickness. The photocurrents generated were increased 74 times for the best AuNPs-TiO₂ when compared with bare TiO₂ under visible light irradiation. The significant enhancement of PEC hydrogen generation observed on the composite structures was attributed to the process of the SPR excitation of the Au NPs. Our group [48] demonstrated the decoration of highly ordered TiO_2 NT arrays with CdSe via RF magnetron sputtering. Charge transfer across the TiO_2 -CdSe interface as well as high photocurrent generation were improved by controlling annealing temperature and CdSe film deposition time. The best PEC response was obtained from CdSe deposited for 30 min and annealed at 400°C in vacuum, presenting a photocurrent density of 1.9 mA cm⁻² at 1.23 V vs. RHE, resulting in 3 and 535 times enhancement when compared to pure TiO₂ NTs under 1 sun and visible light irradiation ($\lambda > 400$ nm) respectively, Figure 5a-c.

Kushwaha et al. [49] sensitized ZnO nanowires (NWs) by sputtering an Au layer followed by annealing at different temperatures, see Figure 6a-d. The tailored structure shows a maximum photocurrent of $300 \ \mu A \ cm^2$ under visible light illumination presenting a photon-to-current efficiency of 0.13 % at 1.23 V vs. RHE. The Au NPs tune the visible light absorption and utilize the SPR of the Au nanoparticle to boost the hot electron injection from Au nanoparticles to the ZnO conduction band. The Au NPs also suppress the hole trapping at surface defects of ZnO NWs and enhance the water splitting performance of the material under visible light, Figure 6e-g.

4 Deposition of HER and OER electrocatalysts by PVD methods

Theoretically a semiconductor owning the E_{CB} and E_{VB} that straddle the electrochemical potentials $-qEO(H^+/H_2)$ and $-qEO(O_2/H_2O)$, Figure 2c, can perform non-biased photoelectrochemical water splitting. Nevertheless, water redox reactions at bare semiconductor surfaces are usually not fast enough for a useful process and the employment of HER or OER electrocatalyst is necessary. Besides reducing the overpotentials needed to run

the PEC water splitting, the semiconductor coverage with electrocatalysts can reduce the photoelectrodes deactivation due to photocorrosion. PVD has been used to decorate semiconductors with a number of metal and metal oxides that act as HER or OER electrocatalysts. Table 3 summarizes a list of examples found in the recent literature.

4.1 Hydrogen evolution catalysts

There are few examples of p-type semiconductors modification with HER by means of PVD. Early examples found are the coverage of p-GaP and p-Si with Ag films obtained by thermal evaporation reported by Nakato et al. [57] and the deposition of Ru, Rh and Pt over p-InP using electron beam (e-beam) evaporation described by Heller and co-workers [58]. However, neither article is clear whether the PEC measurements were made with the PVD modified samples or obtained by chemical methods, and there is a lack of some electrochemical characterization.

Beyond the early works published, just two recent reports were found. The first example reports the sputter deposition of gold over p-GaN as a HER catalyst [50]. The Au layer covered 40% of the surface, forming 7.6 nm Au NPs. The STH efficiency of the bare p-GaN photoelectrodes increased from 0.02 to 0.59 % after gold deposition in nonbiased PEC using HCl as electrolyte. Moreover, the presence



Figure 5: (a) SEM images of samples obtained with different CdSe on TiO₂ NTs sputtering deposition times. (b) and (c) shows the current vs potential curves of samples with different annealing, measured under 1 sun irradiation and visible light irradiation (λ > 400 nm), respectively. Reproduced with permission from [48] with permission of the PCCP Owner Societies.



Figure 6: SEM images of Au NPs functionalized ZnO NWs. (a) As sputtered Au layer (15 nm) over ZnO NWs film, (b) Au–ZnO NWs film annealed at 200, (c) 400 and (d) 600°C, respectively. (e) Time dependent photoresponse of Au NP functionalized ZnO NWs, (f) linear seep scans of as grown ZnO NWs vs. size dependent Au NP coated ZnO NWs. (g) Solar to hydrogen conversion efficiency (n) of Au–ZnO NWs and (h) stability test of photoelectrodes. Reproduced with permission from [49] with permission of The Royal Society of Chemistry.

Table 3: Examples found in literature concerning the use of PVD methods to deposit HER or OER catalysts over semiconductor for applied in
water splitting PEC. The results shown are for the best conditions described in each article.

Photoelectrode design	PEC experiment		PEC results		ref
	Electrolyte comp.	LPD (W m ⁻²)	pure semicon.	modified semicon.	
	•		J _{sc} (mA cm⁻²)* / E _{oc} (V)	J _{sc} (mA cm⁻²)* / E _{oc} (V)	
p-GaN coated with gold by sputtering deposition. Au NPs with 7.6 nm were formed after deposition.	1 M HCl	1000, no filter	-0.5/1.76	-0.52/2.20	[50]
Planar p-Si and p-Si microwires were coated with 1 nm Pt by e-beam deposition.	Potassium biphtalate buffer pH 4.5	1000, no filter	0/0	0/-	[51]
n-TiO ₂ 1D columnar nanostructures were decorated with Pt by RF-sputtering. The best samples were obtained after 20 s of deposi- tion, in which 1.15 nm Pt NPs were observed.	1M KOH, pH=14	400, λ <400nm	-/-	9.49/-0.07	[52]
n-TiO ₂ nanorods were decorated with Pt by RF-sputtering. The best samples were obtained after 20 s of deposition, in which 4 nm Pt NPs were observed after annealing at 450°C for 2h.	0.05 М КОН, pH=12	2000, AM 1.5G	7.5 x 10 ⁻⁴ / 0.72	3.3/0.5	[53]
Nanotextured n-Si coated with NiRuO _x OER catalyst by co-sputtering NiO and Ru targets.	0.25 M Na ₂ SO ₄ / phos phate buffer, pH 7.2	1000, -AM 1.5G	0.01/0.25**	1.34/1.08	[54]
Passivated n-Si wafer was coated with 2 nm Ni film by e-beam deposition.	K ₃ BO ₃ buffer, pH 9.5	2250, no filter	-/-	~2/1.18	[55]
n-WO ₃ thin films deposited over FTO were covered with 10 nm of IrO ₂ formed by reactive sputtering of Ir targets.	1M H ₂ SO ₄ , pH=0	1000, AM 1.5G	0.91/0.4	0.5/0.4	[56]

LPD=Light power density, *at 1.23 V vs. RHE for n-type semiconductor and 0.00 V vs. RHE for p-type semiconductor, ** Si oxidation

of Au HER catalysts improved the photoelectrodes stability and just 25 % loss of current density was observed after 6 h under one sun illumination.



Figure 7: Current density as function of the applied potential (vs. RHE) profiles of planar p-Si samples with various HER under illuminated condition [51]. Note that Pt film obtained by e-beam showed ohmic behavior (resembling pure Pt wire) meanwhile Pt HER catalysts obtained by electroless deposition showed the best PEC performance. Reproduced with permission from [51] with permition of The Royal Society of Chemistry.

In the second article found, McKone et al. [51] studied the PEC performance of planar p-Si and p-Si microwires decorated with Pt HER catalysts obtained by e-beam evaporation. The deposition of Pt by e-beam created an ohmic contact with bi-phthalate electrolyte and no photocurrents were observed, Figure 7, whereas Pt deposited by electroless chemical methods have shown the highest photovoltages observed in all samples measured in their work.

4.2 Oxygen evolution catalysts

Photoanodes are more prone to photodecomposition as anodic potentials are applied to them and insulating oxides tend to be formed. The addition of OER catalysts not only increase the water oxidation rates but extend photoanodes lifetime by avoiding the photodecomposition or photocorrosion.

The coverage of n-Si electrodes by PVD with OER is a common example found in the literature [54,55,57,59,60]. In some cases, the OER catalyst was obtained during anodic polarization of metallic protecting overalyers deposited over n-Si. Kenney and co-workers have reported one of the most remarkable stability improvements of n-Si

photoanodes by using e-beam evaporation of Ni thin films [55]. The fine control over the Ni film thickness offered by the PVD methods enabled the development of an optimal device with Ni films over native oxide passivated single crystal (100) n-Si. It was found that photoelectrodes with 2 nm thick Ni films display higher built-in potentials than those with Ni films thicker than 5 nm. Two nanometer films do not neutralize all induced charge by the electrolyte. Meanwhile the built-in potential at the Ni-SiO_x-Si junction with films thicker than 5 nm is dictated by the Schottky barrier formed at the metal-insulator-semiconductor junction.

As a result, the Ni-SiO_x-Si electrodes with 2 nm Ni films need smaller applied potentials than the ones with films thicker than 5 nm to oxidize water under illumination, Figure 8a,b. Moreover, 2 nm Ni films are oxidized under anodic bias and formed an excellent OER catalyst layer providing impressive 80 h stability for n-type Si, Figure 8c.

Another recent example of n-Si corrosion protection by OER catalysts was made by Sun et al. [54]. Flat and nanotextured, Figure 9a,b, n-Si single crystals were coated with NiO_x and NiRuO_x using RF-sputtering. It was found that NiRuO_x films deposited over n-Si were better OER catalysts than pure NiO_x and voltages bellow 1.23 V vs. RHE were need to perform water oxidation in illuminated systems, Figure 9c. Moreover, the electrodes suffered a small current loss after 500 polarization cycles from open circuit to 430 mV anodic overpotential, decreasing from 7 to 5.95 mA cm² after 1.5 h, see Figure 9d.

Semiconducting oxide photoanodes were also modified with OER catalysts by PVD methods. Pt NPs were formed by sputtering Pt targets over TiO, nanorods [53] (NRs) and 1D columnar TiO₂ nanostructures [52]. Both works have shown that the deposition of Pt for 20 s has generated the most effective photoelectrodes. In the case of NRs the OER enhancement was more pronounced than in the 1D columnar photoanodes. Spurgeon and co-workers [56] studied PEC properties of WO₂ photoelectrodes covered with IrO₂ films made by spin coating, sputtering and electrodeposition. It was found that the reactive RF-sputtering deposition of Ir using an Ar/O_{2} mixture was the most effective method to attach the OER catalyst among all approaches tested. It was claimed that the porous nature of the sputtered films enabled the contact of the electrolyte with the WO₃ layer and thus J-E performances were similar to those of bare WO₃ in 1 mol L⁻¹ H₂SO₄ electrolytes. Moreover, the IrO₂ layers obtained by sputtering increased the Faradaic efficiency of O₂ evolution up to 99% meanwhile bare WO₃ electrodes did not produce O_2 due to the formation of $S_2O_8^{2}$.



Figure 8: Photoelectrochemical characterization of $n-Si/SiO_x/Ni$ photoanodes with different Ni thicknesses (2, 5, 10 and 20 nm) obtained by e-beam evaporation. a) *J-E* plots under illumination using in KOH electrolyte, b) *J-E* plots under illumination using in potassium borate buffer and c) 2 nm Ni photoelectrode degradation profile at constant current 10 mA cm⁻² using mixed electrolyte of Li⁺ and K⁺ borates (pH 9.5) [55]. From M. J. Kenney, M. Gong, Y. Li, J. Z. Wu, J. Feng, M. Lanza, H. Dai, *Science* **2013**, *342*, 836-840. Reprinted with permission from AAAS.

5 Final remarks

The use of PVD techniques to modify semiconductors aiming to improve the performance of water splitting PEC is relatively unexplored and only a few reports deeply studied the benefits of using such methodologies. Early examples of the use of PVD methods are difficult to find in the literature, principally because this method was used as a tool to prepare thin films over semiconductors and investigate effects other than the deposition method itself. Many examples described in this mini-review were found hidden in the results and discussion, therefore making a complete overview of the topic difficult.

The formation of semiconductor-semiconductor junction by PVD process has been explored very little up to this moment. The related works showed the necessity to obtain a thick semiconductor layer over the base semiconductor to improve PEC activity of photoelectrodes. In all cases, it was shown that the semiconductorsemiconductor interfaces play a key role in promoting charge separation and can shift the absorption slightly to the visible light region depending of the materials choice.

On the other hand, the semiconductor sensitisation through SPR of vaporized noble metals, such as Au, required a very short evaporation time when compared



Figure 9. Morphological and photoelectrochemical characterization of n-Si photoanodes modified with NiO_x and NiRuO_x OER catalysts by RF-sputtering. a) Top and b) side SEM images of nanotextured n-Si. c) *J-E* plots of the photoanodes containing OER catalysts and d) Current density as a function of voltage cycles from open circuit to 430 mV overpotentials [54]. Adapted with permission from (K. Sun, X. Pang, S. Shen, X. Qian, J. S. Cheung, D. Wang, *Nano Lett.* **2013**, *13*, 2064-2072.). Copyright (2013) American Chemical Society.

with semiconductor-semiconductor junction formation examples. The Au NPs sensitisers absorb light wavelengths longer than the base semiconductor, improving the PEC efficiency under visible light illumination. The authors claim two main mechanisms to explain the improvement of PEC efficiency due to the plasmonic effect: i) the interaction of localized electric field due to the SPR effect increases the visible light absorption and creates larger numbers of electron-holes pairs near the metalsemiconductor interface and ii) the noble metal NPs reduces the charge recombination on semiconductor surface in function of the NPs sites stabilizing the photogenerated charge leading to an improvement in the PEC water splitting reaction. When a semiconductor with small band gap acts as sensitizer, thick layers of this material over the wide band-gap semiconductor are necessary to maximize light absorption and enhance the transfer of photogenerated charge carriers in order to improve the PEC efficiency.

The addition of HER and OER catalysts over semiconducting electrodes by PVD is an important tool. It enables the precise control of the film thickness and homogeneity, ranging from disconnected islands (nanoparticles) to continuous films. The coverage, thickness and morphology of the films over the photoelectrode change the electrolyte-semiconductor junction behavior. For example, HER catalysts are usually noble metals and, if too thick, may form a metal-semiconductor Schottky junction and hinder the potential provided by the electrolytesemiconductor interface. Thick films of HER/OER materials also cause efficiency losses due to absorption or reflection of the incident light over the photoelectrode.

As could be seen in this mini-review, some reports emphasize the benefits of using PVD methodologies to improve PEC water splitting systems. The Ni deposition as a photocorrosion inhibitor/OER for n-Si photoanodes [55] example clearly shows that the precise control over the semiconductor-OER-electrolyte junction enabled by the use of physical vapor deposition might lead to the development of more efficient and long-lived electrodes. However, PEC water splitting cells measurements made by researchers using PVD to improve PEC systems have to be standardized in order to permit comparison among different groups. We suggest the measurement of, at least, the best sample following the recommendations described in references 61 and 62: three-electrode setup and one sun (100 mW cm² and AM 1.5G filter).

There is plenty of room for the improvement of water splitting PEC by using PVD methodologies. More detailed studies comparing PVD with different chemical methodologies allied to standardized PEC measurements will allow a deeper understanding of the benefits of depositing materials by physical methodologies. Moreover, the field of photocatalytic hydrogen production may also benefit from modifications with PVD techniques. Only two reports were found in the literature, one of our group⁶³ and another from Nam and Han,⁶⁴ and both show promising results.

Acknowledgements: We acknowledge the Brazilian agencies: CNPq (Universal n°. 443218/2014-5, PVE n°. 401449/2014-9 and BJT n°. 401063/2014-3) and FAPERGS (project 02/2014-PqG n°. 2227-2551/14-8 SIAFEM) for financial support.

References

- Ewan, B. C. R.; Allen, R. W. K. A figure of merit assessment of the routes to hydrogen. *Int. J. Hydrogen Energy* 2005, *30*, 809-819.
- [2] Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* 2010, 110, 6446-6473.
- [3] Bard, A. J.; Fox, M. A. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. Acc. Chem. Res. 1995, 28, 141-145.
- [4] Lewis, N. S. Chemical Control of Charge Transfer and Recombination at Semiconductor Photoelectrode Surfaces. *Inorg. Chem.* 2005, 44, 6900-6911.
- [5)Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 1972, 238, 37-38.
- [6] Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* 2014, *114*, 9987-10043.
- [7] Sivula, K.; Le Formal, F.; Grätzel, M. Solar Water Splitting: Progress Using Hematite (α-Fe2O3) Photoelectrodes. *ChemSusChem* 2011, 4, 432-449.
- [8] Park, Y.; McDonald, K. J.; Choi, K.-S. Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chem. Soc. Rev.* 2013, 42, 2321-2337.
- [9] Zhu, T.; Chong, M. N.; Chan, E. S. Nanostructured Tungsten Trioxide Thin Films Synthesized for Photoelectrocatalytic Water Oxidation: A review. *ChemSusChem* 2014, 7, 2974-2997.
- [10] Maeda, K. (Oxy)nitrides with d0-electronic configuration as photocatalysts and photoanodes that operate under a wide range of visible light for overall water splitting. *Phys. Chem. Chem. Phys.* 2013, *15*, 10537-10548.
- [11] Heller, A.; Aspnes, D. E.; Porter, J. D.; Sheng, T. T.; Vadimsky, R. G. Transparent metals preparation and characterization of light-transmitting platinum films. *J. Phys. Chem.* **1985**, *89*, 4444-4452.
- [12] Wang, G.; Ling, Y.; Wang, H.; Xihong, L.; Li, Y. Chemically modified nanostructures for photoelectrochemical water splitting. J. Photochem. Photobiol., C 2014, 19, 35-51.
- [13] Sun, K.; Shen, S.; Liang, Y.; Burrows, P. E.; Mao, S. S.; Wang,
 D. Enabling Silicon for Solar-Fuel Production. *Chem. Rev.* 2014, 114, 8662-8719.

- [14] Turner, J. A. Shining a Light on Solar Water Splitting-Response. *Science* **2014**, *344*, 469-470.
- [15] Gerischer, H. Photodecomposition of semiconductors thermodynamics, kinetics and application to solar cells. *Faraday Discuss. Chem. Soc.* **1980**, *70*, 137-151.
- [16] Khaselev, O.; Turner, J. A. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting. *Science* 1998, 280, 425-427.
- [17] Choudhary, S.; Upadhyay, S.; Kumar, P.; Singh, N.; Satsangi, V. R.; Shrivastav, R.; Dass, S. Nanostructured bilayered thin films in photoelectrochemical water splitting A review. *Int. J. Hydrogen Energy* 2012, *37*, 18713-18730.
- [18] Van Hieu, N.; Bich Ha, N. Visible light responsive titania-based nanostructures for photocatalytic, photovoltaic and photoelectrochemical applications. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 2012, *3*, 023001.
- [19] McKone, J. R.; Lewis, N. S.; Gray, H. B. <u>Will Solar-Driven Water-Splitting Devices See the Light of Day?</u> *Chem. Mater.* 2014, 26, 407-414.
- [20] Sze, S. M.; Ng, K. K.: Physics of semiconductor devices; John Wiley & Sons, 2006.
- [21] Warren, S. C.; Thimsen, E. Plasmonic solar water splitting. Energ. Environ. Sci. 2012, 5, 5133-5146.
- [22] Youngblood, W. J.; Lee, S.-H. A.; Maeda, K.; Mallouk, T. E. Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors. Acc. Chem. Res. 2009, 42, 1966-1973.
- [23] Chouhan, N.; Yeh, C. L.; Hu, S.-F.; Liu, R.-S.; Chang, W.-S.; Chen, K.-H. Photocatalytic CdSe QDs-decorated ZnO nanotubes: an effective photoelectrode for splitting water. *Chem. Commun.* 2011, 47, 3493-3495.
- [24] Trasatti, S. Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions. J. Electroanal. Chem. Interfacial Electrochem. 1972, 39, 163-184.
- [25] Miles, M. H. Evaluation of electrocatalysts for water electrolysis in alkaline solutions. J. Electroanal. Chem. Interfacial Electrochem. 1975, 60, 89-96.
- [26] Trasatti, S. Electrocatalysis by oxides Attempt at a unifying approach. J. Electroanal. Chem. Interfacial Electrochem. 1980, 111, 125-131.
- [27] Bindra, P.; Gerischer, H.; Kolb, D. M. Electrolytic Deposition of Thin Metal Films on Semiconductor Substrates. J. Electrochem. Soc. 1977, 124, 1012-1018.
- [28] Niitsoo, O.; Sarkar, S. K.; Pejoux, C.; Rühle, S.; Cahen, D.; Hodes, G. Chemical bath deposited CdS/CdSe-sensitized porous TiO₂ solar cells. *J. Photochem. Photobiol.*, A 2006, 181, 306-313.
- [29] Lee, H.; Wang, M.; Chen, P.; Gamelin, D. R.; Zakeeruddin, S. M.; Grätzel, M.; Nazeeruddin, M. K. Efficient CdSe Quantum Dot-Sensitized Solar Cells Prepared by an Improved Successive Ionic Layer Adsorption and Reaction Process. Nano Lett. 2009, 9, 4221-4227.
- [30] Zaban, A.; Mićić, O. I.; Gregg, B. A.; Nozik, A. J. Photosensitization of Nanoporous TiO₂ Electrodes with InP Quantum Dots. *Langmuir* **1998**, *14*, 3153-3156.
- [31] Paudel, N. R.; Yan, Y. Fabrication and characterization of high-efficiency CdTe-based thin-film solar cells on commercial SnO₂:F-coated soda-lime glass substrates. *Thin Solid Films* 2013, 549, 30-35.

- [32] Wada, T.; Kohara, N.; Nishiwaki, S.; Negami, T. Characterization of the Cu(In,Ga)Se₂/Mo interface in CIGS solar cells. *Thin Solid Films* 2001, *387*, 118-122.
- [33] Repins, I.; Contreras, M. A.; Egaas, B.; DeHart, C.; Scharf,
 J.; Perkins, C. L.; To, B.; Noufi, R. 19.9%-efficient ZnO/CdS/
 CulnGaSe₂ solar cell with 81.2% fill factor. *Prog. Photovoltaics Res. Appl.* 2008, *16*, 235-239.
- [34] Bosio, A.; Romeo, A.; Menossi, D.; Mazzamuto, S.; Romeo, N. The second-generation of CdTe and CulnGaSe₂ thin film PV modules. *Cryst. Res. Technol.* 2011, 46, 857-864.
- [35] Dameron, A. A.; Olson, T. S.; Christensen, S. T.; Leisch, J. E.; Hurst, K. E.; Pylypenko, S.; Bult, J. B.; Ginley, D. S.; O'Hayre, R. P.; Dinh, H. N.; Gennett, T. Pt–Ru Alloyed Fuel Cell Catalysts Sputtered from a Single Alloyed Target. ACS Catal. 2011, 1, 1307-1315.
- [36] Cooke, K. E.; Sun, H. Physical vapour deposition coatings for demanding applications in the new hydrogen economy. *Trans. Inst. Met. Finish.* 2013, *91*, 294-297.
- [37] Esposito, D. V.; Hunt, S. T.; Stottlemyer, A. L.; Dobson, K. D.; McCandless, B. E.; Birkmire, R. W.; Chen, J. G. Low-cost hydrogen-evolution catalysts based on monolayer platinum on tungsten monocarbide substrates. Angew. Chem. Int. Ed. 2010, 49, 9859-9862.
- [38] Stephens, I. E.; Chorkendorff, I. Minimizing the use of platinum in hydrogen-evolving electrodes. Angew. Chem. Int. Ed. 2011, 50, 1476-1477.
- [39] van de Krol, R.; Grätzel, M.: *Photoelectrochemical Hydrogen Production*; Springer, 2011.
- [40] Lai, C. W.; Sreekantan, S.; E, P. S.; Krengvirat, W. Preparation and photoelectrochemical characterization of WO₃-loaded TiO₂ nanotube arrays via radio frequency sputtering. *Electrochim. Acta* **2012**, *77*, 128-136.
- [41] Leroy, C. M.; Maegli, A. E.; Sivula, K.; Hisatomi, T.; Xanthopoulos, N.; Otal, E. H.; Yoon, S.; Weidenkaff, A.; Sanjines, R.; Gratzel, M. LaTiO₂N/In₂O₃ photoanodes with improved performance for solar water splitting. *Chem. Commun.* **2012**, *48*, 820-822.
- [42] Shaheen, B. S.; Salem, H. G.; El-Sayed, M. A.; Allam, N. K. Thermal/Electrochemical Growth and Characterization of One-Dimensional ZnO/TiO₂ Hybrid Nanoelectrodes for Solar Fuel Production. J. Phys. Chem. C 2013, 117, 18502-18509.
- [43] Lai, C. W.; Sreekantan, S. Study of WO₃ incorporated C-TiO₂ nanotubes for efficient visible light driven water splitting performance. *J. Alloys Compd.* **2013**, *547*, 43-50.
- [44] Lai, C. W.; Sreekantan, S. Effect of heat treatment on WO₃-loaded TiO₂ nanotubes for hydrogen generation via enhanced water splitting. *Mater. Sci. Semicond. Process.* 2013, 16, 947-954.
- [45] Lai, C. W.; Sreekantan, S.; San E, P. Effect of radio frequency sputtering power on W–TiO₂ nanotubes to improve photoelectrochemical performance. J. Mater. Res. 2012, 27, 1695-1704.
- [46] Lai, C. W.; Sreekantan, S. Optimized Sputtering Power to Incorporate WO₃ into C–TiO₂ Nanotubes for Highly Visible Photoresponse Performance. *Nano* 2012, 07, 1250051.
- [47] Chen, W.; Lu, Y.; Dong, W.; Chen, Z.; Shen, M. Plasmon mediated visible light photocurrent and photoelectrochemical hydrogen generation using Au nanoparticles/TiO₂ electrode. *Mater. Res. Bull.* **2014**, *50*, 31-35.
- [48] Fernandes, J. A.; Migowski, P.; Fabrim, Z.; Feil, A. F.; Rosa, G.; Khan, S.; Machado, G. J.; Fichtner, P. F.; Teixeira, S. R.; Santos,

M. J.; Dupont, J. TiO₂ nanotubes sensitized with CdSe via RF magnetron sputtering for photoelectrochemical applications under visible light irradiation. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9148-9153.

- [49] Kushwaha, A.; Aslam, M. Defect controlled water splitting characteristics of gold nanoparticle functionalized ZnO nanowire films. *RSC Adv.* 2014, *4*, 20955.
- [50] Tu, W. H.; Hsu, Y. K.; Yen, C. H.; Wu, C. I.; Hwang, J. S.; Chen, L. C.; Chen, K. H. Au nanoparticle modified GaN photoelectrode for photoelectrochemical hydrogen generation. *Electrochem. Commun.* 2011, 13, 530-533.
- [51] McKone, J. R.; Warren, E. L.; Bierman, M. J.; Boettcher, S. W.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. Evaluation of Pt, Ni, and Ni-Mo electrocatalysts for hydrogen evolution on crystalline Si electrodes. *Energ. Environ. Sci.* 2011, *4*, 3573-3583.
- [52] An, W. J.; Wang, W. N.; Ramalingam, B.; Mukherjee, S.; Daubayev, B.; Gangopadhyay, S.; Biswas, P. Enhanced water photolysis with Pt metal nanoparticles on single crystal TiO₂ surfaces. *Langmuir* **2012**, *28*, 7528-7534.
- [53] Wang, F.; Zheng, Z.; Jia, F. Enhanced photoelectrochemical water splitting on Pt-loaded TiO₂ nanorods array thin film. *Mater. Lett.* 2012, *71*, 141-144.
- [54] Sun, K.; Pang, X.; Shen, S.; Qian, X.; Cheung, J. S.; Wang, D.
 Metal oxide composite enabled nanotextured Si photoanode for efficient solar driven water oxidation. *Nano Lett.* 2013, *13*, 2064-2072.
- [55] Kenney, M. J.; Gong, M.; Li, Y.; Wu, J. Z.; Feng, J.; Lanza, M.; Dai, H. High-Performance Silicon Photoanodes Passivated with <u>Ultrathin Nickel Films for Water Oxidation.</u> *Science* 2013, *342*, 836-840.
- [56] Spurgeon, J. M.; Velazquez, J. M.; McDowell, M. T. Improving O₂ production of WO₃ photoanodes with IrO₂ in acidic aqueous electrolyte. *Phys. Chem. Chem. Phys.* **2014**, *16*, 3623-3631.
- [57] Nakato, Y.; Ohnishi, T.; Tsubomur<u>a, H. Photoelectrochemical</u> <u>Behaviors of Semiconductor Electrodes Coated with Thin Metal</u> <u>Films. Chem. Lett. 1975, 4</u>, 883-886.
- [58] Heller, A.; Aharon-Shalom, E.; Bonner, W. A.; Miller, B. <u>Hydrogen-evolving semiconductor photocathodes: nature of</u> <u>the junction and function of the platinum group metal catalyst</u>. J. Am. Chem. Soc. **1982**, *104*, 6942-6948.
- [59] Fan, F. R. F.; Keil, R. G.; Bard, A. J. Semiconductor electrodes.
 48. Photooxidation of halides and water on n-silicon protected with silicide layers. J. Am. Chem. Soc. 1983, 105, 220-224.
- [60] Li, G.; Wang, S. Photoelectrochemical characteristics of metal-modified epitaxial n-Si anodes: Part I. NiO(OH)-coated n+/p-Si and n+/n-Si electrodes for catalytic oxygen evolution. J. Electroanal. Chem. Interfacial Electrochem. 1987, 227, 213-221.
- [61] Chen, Z.; Jaramillo, T. F.; Deutsch, T. G.; Kleiman-Shwarsctein, A.; Forman, A. J.; Gaillard, N.; Garland, R.; Takanabe, K.; Heske, C.; Sunkara, M.; McFarland, E. W.; Domen, K.; Miller, E. L.; Turner, J. A.; Dinh, H. N. Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols. J. Mater. Res. 2010, 25, 3-16.
- [62] Chen, Z.; Dinh, H.; Miller, E.: Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols; Springer Science & Business Media, 2013.

- [63] Languer, M. P.; Scheffer, F. R.; Feil, A. F.; Baptista, D. L.;
 Migowski, P.; Machado, G. J.; de Moraes, D. P.; Dupont, J.;
 Teixeira, S. R.; Weibel, D. E. Photo-induced reforming of alcohols with improved hydrogen apparent quantum yield on TiO₂ nanotubes loaded with ultra-small Pt nanoparticles. *Int. J. Hydrogen Energy* 2013, *38*, 14440-14450.
- [64] Nam, W.; Han, G. Y. Preparation and characterization of anodized Pt-TiO₂ nanotube arrays for water splitting. *J. Chem. Eng. Jpn.* 2007, 40, 266-269.

Biographies



Adriano Friedrich Feil, born in Porto Alegre-RS (Brazil), in 1983, graduated in Physics from Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS) in 2004. He has received his Ph.D in Materials Science from Universidade Federal do Rio Grande do Sul (UFRGS), Brazil in 2009. After his post-doctoral tenure in the National Renewable Energy

Laboratory (NREL) Golden-CO, as a CNPq fellow (2012-2013) in the John A. Turner group, he joined at PUCRS as an assistant Professor at Physics faculty. Presently, he is full Professor there. His current research includes the development of new nanostructured materials for renewable energy systems, such as solar cells and watersplitting reactions. He is currently fellow of technological development and innovative extension: energy program of the CNPq agency.



Pedro Migowski received his Ph.D. degree in Chemistry at theUniversidade Federal do Rio Grande do Sul (UFRGS) (Porto Alegre, Brazil) in 2013. After his first post-doctoral tenure in the Institute of Physics at UFRGS (2013), he joined the group of Prof. Leitner at RWTH Aachen University in 2014 as a Capes-Alexander von Humboldt

postdoctoral fellow. Currently, he is developing his research in a post-doctoral tenure at PUCRS-Brazil with a Young Talent Fellowship (CNPq). His research interests are in the development of nanomaterials for water-splitting reaction and nanocatalysts for biomass conversion.