Thin-Film Oxynitride Photocatalysts for Solar Hydrogen Generation: Separating Surface and Bulk Effects Using Synchrotron X-Ray and Neutron-Based Techniques

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1. Introduction to the Photoelectrochemical Water-Splitting Mechanism

The decomposition of water into H₂ and O₂ using electricity was first observed in 1800 by Anthony Carlisle and William Nicholson, fascinated and inspired by a letter that Alessandro Volta wrote on March 20, 1800, to the President of the Royal Society in London. However, it was not until the late 1970s that the photochemical splitting of water was discovered by Honda and Fujishima[1] using TiO₂ irradiated under ultraviolet (UV) light.

The photoelectrochemical (PEC) splitting of water[2] into molecular hydrogen and oxygen uses a solar light-responsive semiconductor able to absorb photons with energies in the visible and UV range to generate electron/hole (e/h) pairs. The photo-generated charges should possess an average lifetime longer than the time needed to reach the surface of the semiconductor, in contact with water. At the solid–liquid interface, the charge carriers should be easily extracted from the bulk to the surface where there should be sufficient catalytic activity to consume the holes and electrons in the water redox reactions. The overall process is schematically represented in Figure 1.

The electrochemical generation of molecular oxygen and hydrogen from water is described by the Equation (1) and (2), summarized in Equation (3).

\[ 2H_2O + 4h^+ \rightarrow O_2^+ + 4H^+ \]  
\[ 4H^+ + 4e^- \rightarrow 2H_2 \]  
\[ 2H_2O \rightarrow 2H_2 + O_2 \]  

The minimum energy needed for this four-electron transfer process is 1.23 eV. However, a semiconductor with a bandgap larger than 1.7 eV is typically considered to be a realistic value[3] to account for the presence of overpotentials, such as thermodynamic losses, electrodes and electrolyte resistance, mass transfer limitations, etc.

It is also worth mentioning here that semiconductor photocatalysts, under applied potential and/or photon irradiation, would...
also possess quasi-Fermi energy levels for electrons and holes in between the energy bandgap. In semiconductor photocatalysts for PEC application, this effect is normally considered to be not particularly relevant.

In general, 1.7 eV represents the minimum energy of the photogenerated charges for the water-splitting reaction to proceed. In addition, not only the width of the bandgap is important, but also the energy position of the band edges with respect to the water reduction and oxidation potentials. In other words, the valence band maximum (VBM) should be lower in energy than the hydrogen evolution potential, whereas the conduction band minimum (CBM) higher than the oxygen evolution potential (Figure 1). Finally, if we want to achieve efficient PEC water splitting using sunlight, the semiconductor should be able to absorb light in the visible energy range, ideally above 1.7 eV, as discussed earlier, and not only in the UV energy range because UV radiation accounts for less than 5% of the solar spectrum.

To summarize, these are the requirements a semiconductor material should fulfill to allow efficient solar hydrogen production:\[5,6\] bandgap in the visible energy range, band edges straddling the water redox potentials, high electron and electron/hole mobility, low recombination probability, easy bulk-to-surface charge extraction, and a high catalytic activity for the water oxidation/reduction reactions. Finally, suitable materials should also offer very good photoelectrochemical stability in operation conditions.

It is important to highlight that the PEC water splitting can be achieved not only using one semiconductor material through a one-step or single-photon excitation, as depicted in Figure 1, but also using two semiconductors each specifically engineered and optimized for each half of the reaction. In such a case, the two materials work in tandem with a shuttle redox mediator to allow the exchange of the photogenerated charges. This configuration is known as Z-scheme, two-step, and/or two-photon excitation mechanisms. The obvious disadvantage is that two materials and two photons are required; however, the possibility to optimize the semiconductor for a specific reaction can make this approach very attractive.

The catalytic activity for hydrogen and oxygen generation from water is not necessarily provided by the semiconductor photoabsorber; rather, it relies on engineered surface functionalization. The semiconductor surface is decorated, or functionalized, with cocatalyst nanoparticles. The role of these electrochemically active sites is to boost the bulk-to-surface charge extraction by favoring the utilization of electrons and holes for water reduction and oxidation, respectively.\[7-9\]

The simplest PEC setup consists of oxynitride semiconductor particulates decorated with cocatalyst nanoparticles and dispersed in water. Upon illumination with visible light, the amount of the evolving hydrogen and oxygen can be monitored by gas chromatography.

Alternatively, the typical three-electrode configuration shown in Figure 2 is widely adopted to characterize the PEC activity of oxynitrides.

In this latter case, the semiconductor particulate is deposited on an electronically conductive substrate, typically an indium tin oxide-coated glass. The current collector of the substrate is electrically connected to a second electrode that can be a Pt or Au wire. A third electrode, the reversible hydrogen electrode (RHE), is used to set the reference potential to the hydrogen reduction potential \(H^+/H_2\) at the selected pH of the electrolyte.

A potentiostat applies a variable potential difference between the oxynitride electrode (the counter electrode) and the Pt or Au wire (the working electrode), using the RHE as the potential reference (reference electrode).

When the semiconductor particulate absorbs light, the externally applied potential drives the photogenerate electrons toward the current collector of the substrate. The electrons are then transferred to the working electrode where they are consumed in the hydrogen evolution reaction (Equation (2)), reducing water molecules in the electrolyte and leaving \(OH^-\) ions free

![Figure 1. Schematic representation of the light-driven water-splitting process. In a semiconductor, the absorption of a photon with energies higher than 1.23 eV promotes an electron from the valence to the conduction band, leaving a hole behind. At the surface of the semiconductor, in contact with water, electrons and holes are consumed for the \(H_2\) and \(O_2\) evolution reactions, respectively.](image1)

![Figure 2. Schematic representation of the typical three-electrode configuration used to characterize the PEC properties of photoelectrodes for light-induced water splitting.](image2)
to migrate toward the counter electrode. The photogenerated holes instead migrate toward the surface of the counter electrode, where they are consumed with the OH− ions to form molecular oxygen (Equation (1)). With such an experimental set up, a simple measurement of the electron current, flowing from counter to working electrode, under illumination, as a function of the applied potential, provides the figure of merit of the PEC activity. This current, normalized to the illuminated area, is called photocurrent density. The measurement is typically performed under chopped illumination to distinguish between light- and voltage-induced effects (examples are shown later).

An advantage of this experimental setup is the possibility to separate the oxygen and the hydrogen evolution processes. This can be achieved by separating the counter and working electrodes using, for example, an ion exchange membrane that allows ionic transport but impedes oxygen and hydrogen mixing. Moreover, by engineering the solid/liquid interface with cocatalysts designed specifically as hole scavengers, the counter electrode (the oxynitride semiconductor) can be optimized for the oxygen evolution (Equation (2)), which is the main bottleneck of the overall water-splitting process. This bottleneck arises due to the nature of the reactions themselves, when comparing the hydrogen and oxygen evolution reaction, with the latter less favored and more sluggish due to it being a four-electron instead of two-electron transfer process (Equation (1)–(3)).

A figure of merit often used to evaluate and compare PEC performance is the incident photon-to-current conversion efficiency (IPCE), often referred to also as external quantum efficiency (EQE). The IPCE or EQE is the ratio between the photocurrent in the external circuit and the number of photons that strike the photoanode per unit time at a certain wavelength.

2. Materials

In the past several decades, since the now-termed Honda–Fujishima effect was first demonstrated, extensive research in this field has been targeted at trying to find suitable and efficient water-splitting photocatalysts on which the development of cost-effective and state-of-the-art technology could be based. However, despite many efforts, to date, materials fulfilling all the earlier discussed requirements are still not available.

Due to their relatively Earth-abundant, low-cost constituent elements, metal oxides have been investigated thoroughly for this application. For these materials, the position of the VBM depends on the occupancy of the d band of the transition metal. Examples of d0 transition metals with an empty d band would include Ti4+, Zr4+, V5+, Nb5+, Ta5+, and W6+. For d10 element with a filled d band, the list would include Ga3+, In3+, Ge4+, Sn4+, and Sb5+. In both cases, the VB of the transition metal oxide would comprise the O 2p states hybridized with the metal cation states. Instead, the CB states for the materials with d0 electronic structure would primarily consist of the empty 3d/5d orbitals of the constituent cations. For those with a d10 electronic structure, the d band would be filled; therefore, the CB states would consist of the hybridized orbitals of the empty s and p states.

Oxides, however, are typically highly ionic in nature, resulting in a large separation between the CB and VB states. Therefore, many oxides tend to exhibit large bandgaps (Eg > 3 eV), limiting their photoresponse to the UV region of the solar spectrum. Another issue common to many transition metal oxides is the unfavorable alignment of their respective band positions and/or self-reduction/oxidation potentials with respect to the water redox potentials. This limits their ability to generate both H2 and O2 in overall water splitting to just one-half of the reaction, making them usable only in a Z-scheme architecture (two-materials and two-photon excitation mechanism).

Nonoxide semiconductors have also been investigated, Si, CdSe, CdTe, and CdS as examples. Chemical stability is the main drawback for these materials, due to their susceptibility to photocorrosion, and several approaches have successfully looked at ways to prevent/suppress the aforementioned degradation in this class of compounds.

A particularly interesting group of materials showing great potentials for future developments includes several binary and ternary transition metal oxynitrides. This class of materials is the subject of this review.

Compared with transition metal oxides, whose bandgap is typically in the UV energy range, many oxynitrides possess bandgaps in the visible light energy range. This is a consequence of the nitrogen substitution into the oxygen site in the lattice. As discussed previously, the O 2p orbitals determine the energy position of the VBM in the parent oxide. For oxynitrides, the N to O substitution adds N 2p orbitals at energies higher than those of O 2p. Consequently, the VB shifts upward in energy reducing the bandgap, as schematically depicted in Figure 3d. Moreover, as discussed next, the N substitution in same cases affects also the energy position of the CBM, inducing a downward shift in the energy of the band edge that further contributes to the reduction of the bandgap (Figure 3).

An additional important aspect is that, in a number of oxynitride materials, the band edges are almost ideally located in energy to allow, at least theoretically, the use of the photogenerated charge carriers for the so-called overall water splitting. The overall water splitting, described in Equation (3), is defined as the generation of hydrogen and oxygen from water in the optimal 2:1 ratio. This is an important aspect for the efficiency of the system since all of the photogenerated charged species should ideally be

Figure 3. Schematic representation of the effects on the energy positions of the band edges induced by N-to-O substitution in oxides.
consumed in the water-splitting process. In the strongly basic or acidic aqueous electrolytes, typically used for operation, any unused charged species can promote detrimental side reactions leading to photocorrosion of the semiconductor surface under operation conditions.\textsuperscript{[26]}

Among the binary oxynitriles investigated for solar water splitting, a special mention is due to TaO\textsubscript{2}N\textsubscript{y} (TaON). Higashi and colleagues\textsuperscript{[19]} reported in 2012 the first evidence of stable PEC water splitting using a TaON photoanode. The authors demonstrated the possibility to achieve overall water splitting under visible light irradiation, with high PEC efficiency. The TaNO particles were decorated with Co\textsubscript{O} nanoparticles, the active site for hydrogen evolution, by impregnation in aqueous solution. After that, the decorated TaNO particles were deposited by electrophoretic deposition onto a Ti substrate acting as a supporting structure as well as, a current collector. The electrical contact between the TaON grains and, the oxynitride semiconductor and the current collector was provided by a so-called necking procedure, consisting of the dropping of a TaCl\textsubscript{5} methanol solution and drying in air at room temperature, for several cycles. Finally, the photoanode was annealed at 723 K for 30 min under ammonia flow.

The same relatively complex procedure was used also for the fabrication of TaON-based photoanodes with the Co\textsubscript{O} nanoparticles postloaded onto the surface of the TaON particulate deposited on Ti substrates. Postloading, instead of preloading, offers the obvious advantage that much less Co\textsubscript{O} nanoparticles are needed to obtain the same surface density of electrochemically active sites. The preloading strategy in fact leads to a large number of Co\textsubscript{O} nanoparticles buried in between TaON grains. These nanoparticles do not contribute to the electrochemical hydrogen generation activity because they are not in contact with the electrolyte. However, the postloading procedure resulted in lowering of the PEC activity due to the significant reduction in the homogeneous-like distribution of the Co\textsubscript{O} nanoparticle decoration when compared with the preloaded samples.

Among the ternary oxynitriles, a number of compounds have been proved to possess suitable characteristics to be used for the fabrication of photoanodes for solar water splitting. These materials typically have in common the perovskite crystal structure AB(O,N)\textsubscript{3}, where the A cation can be La, Ba, Y, Sr, Pr, and Ca, whereas the B site is typically occupied by Ti, Ta, or Nb. Examples are LaTiO\textsubscript{2}N, LaTaON\textsubscript{2}, BaTaO\textsubscript{2}N, CaNbO\textsubscript{2}N, SrTaO\textsubscript{2}N, PrTaON\textsubscript{2}, SrNbO\textsubscript{2}N, and others.

The effects of a different A cation on the structural, electronic, and optical properties of these oxynitride perovskites were characterized using the series ATaO\textsubscript{2}N with the A site occupied by Ba, Sr, and Ca\textsuperscript{[27,28]} In these three materials, the energy position of the VBM, determined by the N substitution in the TaO\textsubscript{6} octahedra, is basically unchanged; therefore, the A cation only affects the properties of the CB. In particular, by reducing the size of the A cation, the crystallographic symmetry is reduced from cubic (Ba), to tetragonal (Sr), and to orthorhombic (Ca). In the Ta–(O,N)–Ta octahedra of the three materials, the bond distances are almost the same, but the bond angle (180° for Ba) is progressively smaller by decreasing the size of the cation. The increased distortion of the crystal structure progressively reduces the width of the CB, whereas the energetic center remains unchanged. The overall result is a widening of the bandgap with reduction in the size of the A cation. This results in bandgaps of about 1.8, 2.1, and 2.4 eV for A = Ba, Sr, and Ca, respectively.

The effect of different B cation was studied comparing Ba and Sr oxynitride tantalates and niobates,\textsuperscript{[28]} where it was noted that the niobates possess smaller bandgaps compared with the tantalates. This property cannot be explained by differences of bond length and/or structural distortion as, in the octahedral coordination, Ta\textsuperscript{5+} and Nb\textsuperscript{5+} ions possess essentially the same ionic radius. The difference between the two ions is electronegativity, which is higher for Nb. In both materials, the t\textsubscript{2g} orbitals of the B cation mainly contribute to the CB. However, for a more electro-negative ion, these orbitals are closer in energy to the 2p orbitals of the anions, which leads to a narrowing of the bandgap.

The literature reports several theoretical and experimental studies on the synthesis and PEC properties of these materials in the form of (cocatalyst-decorated) powders.

The electronic/optical properties for bandgap engineering of hundreds of oxynitride perovskite materials were calculated by Castelli and colleagues\textsuperscript{[29–33]} These computational works provide a vast fundamental playground for the design and discovery of novel materials.

However, to date, none of these oxynitride compounds has achieved efficient overall water splitting (2:1 hydrogen to oxygen ratio). The main reason seems to be related to the high temperature and long thermal treatment in ammonia required for N-to-O substitution into the precursor oxide to form the oxynitride.\textsuperscript{[34]} This ammonolysis process creates crystalline defects, which act as recombination sites for the photogenerated charges. Moreover, self-oxidation is also often observed by detecting also N\textsubscript{2}, not only O\textsubscript{2} and H\textsubscript{2}, among the products of the water-splitting process. This is a clear indication of chemical instability and degradation during operation.

The oxynitride synthesis process has critical importance for the material’s functionality because the details of the preparation procedure determine composition, average grain size, and crystallinity.\textsuperscript{[9,35]} The chemical composition affects the optical absorption properties,\textsuperscript{[18]} the grain size influences the conductive properties and the extent of the solid–liquid interface (surface roughness),\textsuperscript{[16]} and the crystalline quality determines the density of defects, which affect the probability of charge carriers’ recombination.\textsuperscript{[37]} In addition, the surface termination of the particles can significantly influence the water-splitting process by affecting the subsurface to surface charge transfer.\textsuperscript{[38]}

Another very important step, as discussed previously, is the optimization of the surface functionalization process via cocatalyst decoration. This means the selection of the appropriate cocatalyst material and the decoration method.\textsuperscript{[39]} In case of a three-electrode configuration setup, the final fabrication of the photoanode (i.e., electrophoretic deposition of the powder onto a conductive substrate, cocatalyst decoration, and necking procedures) is also a critical step.

As shown, the preparation of functional PEC materials and devices for solar hydrogen generation is not trivial. Probably, the oxynitride semiconductor most investigated is LaTiO\textsubscript{2}N (LTON) both, experimentally\textsuperscript{[34,35,40–44]} and computationally.\textsuperscript{[45,46]} LTON powders decorated with various cocatalysts (Ir, W, and Ni oxides, Pt, Co phosphate) show very encouraging water-splitting performance in alkaline solution when illuminated with visible light.
Matsukawas and colleagues have shown for instance that as-prepared LTON particles are surrounded by a La–O–rich skin layer whose atomic arrangement does not match the crystal lattice of the bulk of the particle. This leads to a large surface defect density resulting in enhanced charge carrier recombination, a highly detrimental effect. Post-treatment involving chemical etching and annealing not only removes the outer displaced layer, but also leads to a Ti-rich surface where the Ti ions are partially reduced. The Ti ions at the surface act as electrochemically active sites for the oxygen evolution reaction, significantly increasing the PEC performance with respect to the as-prepared LTON particles.

The fundamental importance of surface functionalization has been recently further highlighted by Wang and co-authors on BaTaO2N. Single-crystal powders of this material were decorated with Pt nanoparticles through sequential steps of impregnation–reduction and photodeposition with the assistance of RbCl flux. The resulting functionalized powders were tested with respect to H2 generation showing two orders of magnitude improvement in performance compared with powders decorated with conventional methods.

Greatly encouraging results were obtained with the development of the solid solution of GaN and ZnO with general formula (Ga1-xZnx)(N1-xOx) (GZNO). After loading the GZNO particles with cocatalysts, excellent performance for hydrogen generation in an overall water-splitting process was achieved in aqueous solution with pH 4.5. For this material, Rh2-xCrO3 turned out to be the best co-catalyst. In addition, no noticeable chemical degradation was observed after a three-day PEC test. Further improvements were achieved by coating the decorated nanoparticles with amorphous layers of Si and Ti oxides, which turn into an oxyhydroxide layer during operation.

The role of additional oxyhydroxide coating onto the metal or metal–oxide cocatalyst nanoparticles was clarified by Takata and co-workers. The authors studied the photocatalyst system made of LaTaON2 powder, decorated with Rh nanoparticles as H2 evolution cocatalyst, coated with a thin layer of CrO3. This layer is an electronic insulator and prevents O2 molecules, generated elsewhere during the water-splitting process, to reach the surface of the Rh nanoparticles. At the same time, protons from the electrolyte can cross the Cr oxyhydroxide layer, to reach the Rh nanoparticle where H2 evolution takes place. The authors suggest that the main advantage of such an engineered cocatalyst design is the separation of the O2 and H2 molecules; therefore, the reverse reaction for water formation is suppressed.

In a later study of the LaTaON2 system, Pan and colleagues highlighted the fundamental importance of bandgap engineering to improve the PEC performance of the photocatalyst. Using LaTaON2 as photoabsorber, it is not possible to efficiently evolve hydrogen since the VBM is too high in energy and thus too close to the water reduction potential. The partial substitution of Mg in the Ta site leads to the formation of LaMg1.1Ta3.3O11.3N2.3x. Due to the lower N content, the VBM shifts downward in energy, leaving the CBM almost unaffected. The bandgap is wider but, as the authors demonstrated, there is still sufficient overlap with the visible light energy range to achieve very interesting performance in terms of overall water splitting. To fabricate the complete Mg-doped LaTaON2 photocatalyst, the authors used Rh2-xCrO3 as a cocatalyst plus an additional functional coating of TiO2. The TiO2 layer, that becomes Ti oxyhydroxide during operation, was applied to hinder the back-reaction of water formation from the evolved O2 and H2. To further increase the hydrogen production and the chemical stability of this photocatalyst, a SiO2 layer was used before the photodeposition of TiO2 to improve the quality and adhesion of this electrochemically active top layer.

3. Thin Films Versus Particulate Oxynitride Photoanodes

We introduce here the comparison between thin films and powder samples for PEC applications starting with an important pre-amble. As discussed above, the fabrication of particulate-based photocatalysts can be very complex. A thin film-based approach does not make things easier. The device fabrication by thin-film deposition technology can also be very challenging. Moreover, it is incomparably more expensive and difficult to apply for large areas. Considering that affordability and mass production of a large active area are among the most important prerequisites for realistic technological applications, thin films are very much at disadvantage compared with powders. In addition, the surface of thin films in contact with the aqueous electrolyte is atomically flat, which implies that the area illuminated by the light corresponds to the area that can be potentially electrochemically active for water splitting. On the contrary, the surface of a powder-based device is very rough. Considering the typical average grain size and density of active sites for different oxynitride materials, it was estimated that, for the same illuminated area, the solid–liquid interface is between 50 and 80 times larger for powder-based samples than for thin films. This makes the photocurrent density that can be measured with thin films much lower than that of the same material in the form of powder.

Having that said, the use of thin films can bring highly rewarding achievements, especially for surface and interface science. Experiments reported in literature point at physicochemical surface modifications as one of the main drawbacks of oxynitride materials used for solar water splitting. Thin films of oxynitride materials grown on conductive substrates are excellent model systems to study (in the three-electrode configuration) surface and interface effects driven by the PEC process.

The main feature of thin films is the atomically flat surface that allows strictly surface-sensitive studies, a condition very difficult to achieve with powder samples. Such a flat surface can be decorated with cocatalyst nanoparticles in a well-controlled manner and/or coated with oxide layers to prevent self-oxidation and hinder the back reaction between O2 and H2, as previously discussed.

Another very important advantage of thin films over powders is that the synthesis temperature for powder samples (≈1300 °C) is typically about 500 °C higher than the temperature needed to grow oxynitride films with high crystalline quality. This can be of great importance for fundamental studies because it reduces the formation of crystalline defects, which introduce spurious effects (not related to the intrinsic properties of the material under investigation) acting as recombination sites for the photogenerated charges.
The literature also shows that the morphological features of the grains and the details of the necking procedure in particulate samples, necessary to establish good electrical contact among grains and between grains and current collector, can introduce spurious effects that significantly affect the PEC capabilities, even for the very same material.[56] This of course makes it more problematic for the comparison between experiments. For thin films instead, the necking procedure is not required, as the films are typically fully dense and grow directly on conductive substrates with very good adhesion.[56] The two very different sample designs, thin film and powder, are schematically illustrated in Figure 4.

Finally, oxynitrides films can grow epitaxially oriented on single-crystal substrates[57] or seed conducting layers.[58] Different out-of-plane surface orientations of the substrate drive the growth of the oxynitride film along different crystallographic orientations.[59,60] This allows probing the charge carrier migration and bulk-to-surface extraction across different families of lattice planes. Theoretical simulations and preliminary experiments suggest that these properties can be significantly anisotropic with respect to the crystal lattice directions. The selection of specific grain facets during the oxynitride particles formation may allow achieving considerably enhanced PEC properties.[61–64]

4. Oxynitride Thin Films for Solar Water Splitting

The literature reports very few examples of fabrication of thin films of materials of interest for PEC water splitting. Le Paven-Thivet and colleagues[60] demonstrated for the first time, to the best of our knowledge, the successful use of oxynitride thin films for this purpose. LTON films were fabricated by radio frequency magnetron sputtering on Nb-doped SrTiO₃ substrates, an electronically conductive material. Depending on deposition parameters, the films were either polycrystalline, textured, or (100) epitaxially oriented with the single-crystal substrate. The water oxidation reaction was characterized with and without surface functionalization using a colloidal solution of IrO₂. For the IrO₂-decorated films, the epitaxially oriented films exhibited an increase in the PEC performance compared with the textured and polycrystalline counterparts. This was ascribed to the highest crystalline quality of the epitaxial films, which reduces the probability of charge carrier recombination.

Unfortunately, this research line on sputter-deposited oxynitride thin films for PEC hydrogen generation has not been developed further.

Our group at the Paul Scherrer Institute developed an alternative fabrication method and sample design for oxynitride thin film-based photoanodes to be used as model systems for fundamental studies. Our selected deposition method is pulsed reactive crossed-beam laser ablation (PRCLA).[57,65] Our sample design relies on epitaxial TiN seed layers[58] (the current collector of the photoanode) growth in situ on different single-crystal substrates to drive the oxynitride film growth along different crystallographic orientations. In the following section, we briefly summarize the working principle of the deposition method and the advantages of the sample design selected.

4.1. Pulsed-Reactive Crossed-Beam Laser Ablation

This is a modification of conventional pulsed laser deposition (PLD).[66] The difference is that a nozzle valve, with a piezoelectric actuator, is placed near the laser spot at the target material.[65] The target material for oxynitride film deposition is made of suitable precursor oxides. For instance, for the deposition of LTON films, we use a target of La₂Ti₂O₇.[59] For BaTaOₓNx films, we use a target of Ba₅Ta₄O₁₅.[52] For CaNbO₂N films, we use a target of Ca₂Nb₂O₇.[9]

The nozzle valve, triggered by the laser pulses, injects pulsed gas jets in the vacuum chamber, in the region just in front of the laser spot at the target material. In our experimental setup, shown in Figure 5, the nozzle valve opens 50 μs before the laser hits the target and injects a gas pulse of ammonia near the laser spot. The nozzle valve remains open for 450 μs and then closes and waits for the next laser pulse. This establishes a relatively

![Figure 4. Schematics of thin films and particle-based photoanodes. Reproduced with permission.[52] Copyright 2022, American Chemical Society.](image-url)
high partial pressure of ammonia confined, in space and time, just in front of the laser spot at the target. The kinetic energy of the ablated species is high enough to break the ammonia molecules, making atomic N and various NH species available for chemical interactions. This is the main mechanism for N incorporation during the ablation process, while at the relatively high deposition temperature required for the growth of the film, the absorption of H does not occur and the film is fully dehydrated.

After leaving the ammonia high-pressure region of the vacuum chamber, all resulting chemical species expand within the plasma plume in environmental conditions very similar to vacuum. This avoids further interactions with the surrounding gaseous environment, which typically lead to N losses favoring reoxidation of the ablated species. Conventional PLD, using a steady N\(_2\) and/or NH\(_3\) flow to set a uniform gas background, turned out to be not efficient enough for promoting N incorporation into the film. Moreover, in our experience, to promote N incorporation, PRCLA should be performed at high deposition temperatures (above 700 °C) and high laser energy densities at the target (above 3 J cm\(^{-2}\)). This technique can be applied for the growth of any oxynitride materials.

### 4.2. Sample Design

Even using PRCLA with ammonia gas pulses at optimized experimental parameters, achieving the desired N content in the film using conventional oxide substrates can be a major issue. Examples are LTON\(^{[59]}\) and SrTaO\(_2\)N (STON)\(^{[67]}\) while for instance in our experience for BaTaO\(_2\)N the N incorporation seems more facile. In general, the use of oxide substrates (such as SrTiO\(_3\), LaAlO\(_3\), Al\(_2\)O\(_3\), MgO, and others) leads to films with relatively low N content. In addition, the need for electronically conductive substrates for the PEC characterizations dramatically limits the exploitable substrate materials. The use of TiN-buffered oxide substrates turned out to be a highly rewarding strategy.

TiN is an electronic conductive (metal-like) material with suitable mechanical properties and very good chemical stability especially in the reducing environment created with the NH\(_3\) gas pulse during deposition. It grows (100) and (111) epitaxially oriented on (100) MgO and (0001) Al\(_2\)O\(_3\) substrates, respectively.\(^{[58,69]}\) In the case, for example, of LTON thin films, the TiN layer allows the growth of (001) epitaxially oriented films on TiN-coated MgO and (011) oriented films on TiN-coated Al\(_2\)O\(_3\) substrates.\(^{[59]}\)

Moreover, the TiN seed layer acts as a sort of N reservoir for the growing oxynitride film. The O content of the plasma plume generated from the oxide target and, in some cases, the oxygen exchange between substrate and film favor the oxidation of the film, with consequent N loss. The TiN layer can exchange relatively large amount of O and N with the growing oxynitride film, becoming Ti\(_n\)N\(_x\)O\(_y\), with small changes of crystal structure and conducting properties, thus providing an additional source of N for the growing film.

Figure 6 shows the cross section of one of our samples as seen by scanning transmission electron microscopy. This is the STON.
film epitaxially grown on the TiN-coated sapphire substrate. The epitaxial relation is (0001) Al2O3 // (111) TiN // (010) SrTaO3N. The STON film is coated with a thin layer of NiOx acting as protective layer and O evolution catalyst.

4.3. Photoelectrochemical Characterization of Thin Films

Figure 7 shows an example of the measurements of oxynitride thin-film photocurrent densities as a function of the applied potential under chopped illumination.[61] The films were fabricated following the procedure described earlier. The figure shows the comparison of two LTON epitaxial films, grown along different crystallographic orientations. The films are coated in situ with a thin layer of NiOx acting as protective coating and cocatalyst. On average, the (011)-oriented films show a remarkable increase of photocurrent density in comparison with the (001) oriented films.

Comparing the measured photocurrent values with those measured with particulate-based samples is difficult and somehow debatable. This is due to the very different surface roughness that results in different extent of the solid–liquid interface and, as a consequence, potentially very different average surface density of electrochemically active sites.

Most of the figure of merits used for the evaluation of the PEC performance, such as the IPCE defined previously, are physicochemical properties normalized with respect to the illuminated area of the sample, without considering the different roughness and Brunauer–Emmett–Teller (BET) surface area. Under this perspective, the ideal model system is actually a thin film, which has negligible roughness (for this type of application). However, using this criterion, thin-film and powder samples are not comparable unless taking into consideration the 50–80% larger solid–liquid interface achievable with powder-based samples. Under this oversimplified approximation, the PEC activity of thin films reported in literature is comparable or in some cases, higher, than that measured with bulk samples of the same material and with similar cocatalyst functionalization. However, it is worth underlining that the available bibliographic contributions on thin films are very limited in number.

5. Analysis of Electronic Structure by Resonant Inelastic X-Ray Scattering

Thin films were used for a detailed characterization of the effect on the electronic structure of N substitution into the O lattice site in LTON.[70] It is well known that the main modification induced by the N substitution in the electronic structure is the creation of additional energy levels (N 2p orbitals) above the VBM, which consists of the O 2p orbitals in the parent oxide.[71] However, a direct comparison of the electronic structure of the precursor oxide and oxynitride is not so straightforward because the two materials possess different crystalline structures and oxidation states of the cations.[72,73]

As an example, LaTiO3N exists in a wide range of N content. Depending on the N content, the valence state of Ti is a mix of 3+ and 4+ and solely 4+ in the case of LaTiO2N. The precursor oxide is La2Ti2O7, which is an insulator with a monoclinic crystal structure where the valence state of Ti is 4+.

By PRCLA and PLD thin films of LaTiO3N and LaTiO3.5–2 were fabricated, tuning the O-to-N ratio in LTON and the O content in the La–Ti oxide sample in a way that the two samples were isostructural (orthorhombic perovskite) with the same valence state of the Ti ions, as revealed by XPS analysis.

These two samples were used to compare the electronic structure and the electronic density of states in the two materials. We used resonant inelastic X-ray scattering (RIXS), a combination of X-ray absorption and emission spectroscopy, whose working principle is schematically described in Figure 8, to probe the first unoccupied energy levels in the conduction band and the...
upper occupied energy levels in the valence band, respectively. These characterizations allow the measurement of the relative shifts in energy of the band edges between the two materials, as shown in Figure 8II. The bandgaps of the two materials were instead measured by near-IR–UV–vis spectroscopy.

The comparative analysis confirmed the expected upward shift in the energy of the VBM of the oxynitride with respect to the isostructural oxide but showed also something unexpected. About 30% of the total bandgap reduction of the oxynitride with respect to the oxide arises from a downward shift in the energy of the CBM of the oxynitride due to N substitution.

Two mechanisms can justify this effect: the different structural distortions of Ti(N,O) and TiO octahedra and the lower electronegativity of N with respect to O that leads to different electron density distributions between the cations and anions in the two materials.

More experiments are currently ongoing to compare other oxynitride materials with isostructural parent oxides with the same valence state of the B cation. This research activity aims at characterizing in depth the effect of N for O substitution to provide more precise tools for bandgap engineering and the rational design and development of novel photocatalysts.

6. Oxynitride Thin Films for Neutron Reflectometry and Surface-Sensitive (Operando) X-Ray Absorption Spectroscopy

Oxynitride thin films were recently used to characterize the surface layers (ex situ) and the oxynitride–water interface under operando conditions. Lawley and colleagues combined neutron reflectometry (NR) and grazing-incidence X-Ray absorption spectroscopy (GIXAS) to explore how the PEC reactions modify the surface of LTON oxynitride thin films. The authors were able to detail the short-range structural, electronic, and compositional properties of the thin films and how these properties evolved due to the PEC reactions.

Differences in the NR curves when comparing before and after the PEC measurements qualitatively signify that physicochemical (compositional) changes occurred. The scattering length density profiles obtained from the fitting of the reflectometry curves reflect changes of the density profile of the samples and suggest that these changes are due to the slight loss of N at and near the surface, predominantly within the first 3 nm from the surface.

Exploring the LTON thin films with GIXAS (ex situ) and varying the incident angle between 0° and 1°, the authors were able to distinguish between the surface layers (3 nm resolution) and the bulk of the samples. Here, element-specific data showed that the titanium B cations of the perovskite oxynitride LTON undergo a slight disorder, lowering its local octahedral symmetry. Disorder could be expected; however, the surprise for the authors came when they observed that the Ti spectra did not shift in energy, suggesting that there was no oxidation, as would typically be assumed and previously hypothesized, neither reduction, as would be expected upon the generation of vacancies. The second surprise came when they observed changes, albeit small, in the energy position of the La GIXAS spectra, signifying partial changes in the oxidation state and/or charge transfer. These
observations suggest that La retains partial $d^1$ electron density\textsuperscript{[73--77]} and does not solely exist as $3+$, as typically assumed. The authors could minimize/prevent these detrimental changes observed by NR and GIXAS by decorating the surface of the oxynitride photocatalysts with an iridium oxide cocatalyst while increasing the PEC performance.

These findings, although interesting in themselves, provide new possibilities for the optimization of solar water-splitting photocatalyst–cocatalyst systems. NR and GIXAS also provide a number of advantages. In particular, both of the techniques can be employed in situ (in water), therefore, offering a route for operando characterizations.

Lawley and colleagues brought their ex situ study one step further with the aim to monitor the oxynitride–water interface under operando conditions (in electrolyte, with applied bias and light source).\textsuperscript{[67]} However, this in itself brings a number of complications and limitations. First, it requires a cell for the aqueous electrolyte and three-electrode cell setup which is compatible for NR and GIXAS measurements. Second, the presence of water significantly attenuates the incident X-Ray beam and, in the case of NR, deuterated electrolyte would be required to remove attenuation due to the hydrogen present in water.

Attenuation also means that the Ti K absorption edge ($\approx$5 keV) is too low in energy to measure in the presence of water for GIXAS. Therefore, for operando GIXAS measurements a different oxynitride material was used. SrTa$_2$O$_5$ (STON) was selected, another promising oxynitride\textsuperscript{[56,78--82]} but, more importantly, the A and B cations, Sr and Ta, respectively, are of a suitable energy range for operando GIXAS measurements in water. With the custom-made cell schematically shown in Figure 9, the authors looked at the evolution of the STON surface due to the PEC tests for hydrogen and oxygen generation from water and characterized the effects of light and applied voltage stimuli.

Due to the relatively high energy range (several keV) needed to probe the geometric and chemical environments of the cations, especially in the presence of water, these measurements do not provide information regarding the anions (O and N). To address this problem, complimentary ex situ XPS was also performed.

The measurements show that, as the potential was increased above 1.3 V versus RHE, the oxynitride photocatalyst suffers from a physicochemical change at the surface. Dissolution of SrO$_x$ into the alkaline electrolyte was observed, accompanied by an increase in electron density on Sr. Moreover, lattice Sr and Ta enrichment at the surface due to SrO$_x$ loss was also observed, as well as changes in hybridization of the N 2p and O 2p states due to changes in surface hydrophilicity. The latter effect was evidenced by the increased adsorbed OH/O(OH)$_2$/H$_2$O content and the slight loss of N from the structure, where N remains chemisorbed as N$_2$/NO$_x$ species.

The work\textsuperscript{[67]} to date presents the first operando surface-sensitive characterization of the oxynitride–liquid interface during the visible light-driven oxygen evolution reaction. It is worth noticing that only the development of thin film-based photodevices makes these measurements possible.

### 7. Oxynitride Thin Films for Surface Functionalization to Distinguish Surface and Bulk Effects

LTOn-based thin-film photoanodes were fabricated adding in situ, a continuous layer of NiO$_x$ onto the LTON surface to promote the extraction of the photogenerated holes.\textsuperscript{[61]} This can be considered as an ideal model photoanode, since all spurious effects arising from powder deposition, decoration, and necking are avoided. As expected, after NiO$_x$ deposition, a dramatic increase of photocurrent density was observed. For example, at the applied potential of 1.35 V versus RHE, the NiO$_x$-coated samples showed a photocurrent density about 50 times higher than the value measured with the bare LTON films. Moreover, photogenerated charges with significantly lower energy could be effectively extracted after applying the NiO$_x$ coating, indicating again a more facile charge extraction efficiency.

In this experiment, epitaxial films with two different crystallographic orientations, (001) and (011), were used. The results confirmed previous measurements showing noticeable dependence of the photocurrent density on the crystalline orientation, but the NiO$_x$ coating revealed an additional remarkable effect. The IPCE (or EQE) measurements shown in Figure 10 revealed a 30% improvement in the performance for the (011)-oriented sample, compared with the (001) in the visible light energy range between 2.4 and 3 eV. Such an effect was not detectable with the bare LTON films where the inefficient surface charge extraction dominates the PEC performance.

Assuming comparable photocurrent generation in the two samples, this observation points at a significantly higher mobility of photogenerated charge carriers across the (011) crystalline planes compared with (001).

The peculiar aspect of this experiment is that the surface functionalization of epitaxially oriented thin films, by boosting surface charge extraction, unveiled previously unknown bulk effects.

Figure 9. Operando reactor cell for surface-sensitive GIXAS measurements. a) Trimetric view of the cell and GIXAS geometry used during measurements, where the grazing-incidence X-rays enter through a Mylar foil covered side window (PIPS denotes a passivated implanted planar silicon detector). b) Cross-sectional internal view. Reproduced with permission.\textsuperscript{[67]} Copyright 2022, Royal Society of Chemistry.
design and discovery of novel materials. This review discusses alternative research approaches and investigation tools that the use of thin films can offer to the scientific community. A few examples are listed below.

Thin-film samples allow the characterization and comparison of materials while, avoiding, or at least limiting, spurious side effects arising from the different synthesis routes, electrophoretic deposition parameters, cocatalyst decoration methods, and necking procedures.

Thin-film deposition technology makes it possible to fabricate the complete photoanode (current collector, oxynitride semiconductor, and cocatalyst layer) in situ, which means in the clean and very well-controlled environment of a vacuum chamber.

Highly ordered epitaxial films can be deposited on conductive substrates driving the growth along different crystallographic orientations. Compared with conventional powder-based samples, these films possess a much lower density of crystalline defects, which are among the main causes of photocharge recombination. Moreover, using epitaxial thin films, several fundamental mechanistic steps of the PEC water-splitting process can be investigated along and across selected families of lattice planes, as well as facing the electrolyte with different surfaces and surface terminations. These mechanistic steps include, for example, the potentially anisotropic charge carrier migration, the bulk-to-surface transfer, the charge extraction, and consumption at the co-catalyst sites.

An additional very important application of thin films is that this sample design allows the use of investigation methods not applicable to powder samples that can potentially provide innovative and/or complementary information.

The in-depth density profile of the sample can be inferred by neutron and X-Ray reflectometry. By comparing these measurements before and after PEC tests, it is possible to identify local changes of density (chemical composition) in the sample as a result of oxygen or hydrogen generation.\[74\]

In particular, the use of neutrons instead of X-Ray photons allows probing the sample also in situ, that is, in the presence of the aqueous electrolyte under realistic operation conditions, provided deuterated water is used. This is not possible with X-Ray reflectometry due to the photon absorption in water. Neutrons also have the added advantage in that, they are sensitive to the lighter elements (H, N, O) compared with X-rays.\[84\–86\]

X-Ray absorption spectroscopy (XAS) is an invaluable tool in Materials Science to probe the local geometric and chemical environment at the atomic level of selected atoms in the lattice. During the PEC process, no major changes are expected in the bulk of the involved materials. It is instead at the surface, in contact with water, where the electrochemical reactions take place, that one expects to see the results of the physicochemical activity. Surface-sensitive XAS at grazing-incidence angle of the X-Ray beam is possible, providing the availability of well-defined and flat surfaces. The availability of thin films enables this experimental approach. Moreover, the way has been recently paved for operando characterizations, that is, monitoring real time the physicochemical evolution of the surface during solar water splitting operation.

Thin films of oxynitride materials allowed clear distinction between bulk and surface effects after suitable surface functionalization with thin cocatalyst coating. Furthermore, such a

**Figure 10.** a) Normalized external quantum efficiency of bare oriented LTON films. b) Normalized external quantum efficiency of NiOx-decorated oriented thin films. The dashed line represents the bare LTON (011) film for facilitated comparison. Reproduced with permission.\[61\] Copyright 2020, the Royal Society of Chemistry.

Computational and experimental efforts are currently ongoing to identify the thermodynamically favorable low-Miller-index surfaces (characterized by the lowest Gibbs free energy) and develop methods to favor the oxynitride particulate grain growth with selected crystal facets (those with the best charge extraction properties).

**8. Conclusions and Outlook**

Thin-film deposition technologies have had so far a very marginal role for the research and development of materials for photoelectrochemical applications, such as hydrogen generation by solar water splitting, but also sustainable and renewable production of other chemicals.

This contribution aims at highlighting the importance thin films may have for fundamental studies and for the rational

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**Figure 10.** a) Normalized external quantum efficiency of bare oriented LTON films. b) Normalized external quantum efficiency of NiOx-decorated oriented thin films. The dashed line represents the bare LTON (011) film for facilitated comparison. Reproduced with permission.\[61\] Copyright 2020, the Royal Society of Chemistry.
sample design allowed unveiling materials’ properties never observed before.

Future work would look at the effect of applied potential and the synergistic effects’ first row transition metal-based cocatalysts have on the performance and stability of the oxynitride photocatalyst templates. It has already been shown that passivation layers and cocatalysts can prevent/minimise the noted degradation and improve long-term performance.

To drive this advancement for the discovery of novel materials and the improvement of existing materials, able to fulfil all the requirements for efficient solar-to-hydrogen conversion, requires the comprehensive understanding of the photocatalyst surfaces’ electronic structure and how it evolves.

The most direct experimental method to probe the electronic structure with k-space resolution is angle-resolved photoemission spectroscopy (ARPES). In a typical ARPES experiment, the ARPES experiment, by elemental and even chemical-state requirements for efficient solar-to-hydrogen conversion, requires a comprehensive understanding of the direct electronic structure of the oxynitride and their evolution across the PEC reaction.

With the advantage of the enhanced probing depth, SX-ARPES provides a unique opportunity to explore both materials and the interface properties in the case of photocatalyst–cocatalyst/ passivation layers, as well as their reactivity and evolution.

We hope that these considerations on oxynitride films for solar water splitting will help colleagues, stimulate further discussion, and suggest alternative research approaches to achieve deeper understanding of this class of materials. In particular, we would like to point out the fundamental role that oxynitride thin films can play for characterization methods, employing the use of large-scale research facilities such as synchrotron light source and neutron spallation source. The presence of flat surfaces and interfaces allows the use of neutron reflectometry to compare, for example, the density profile of the sample before and after PEC tests. Grazing-angle XAS is a powerful method to probe the photoexcitation of the solid/liquid interface also in operation conditions.

We wish the scientific community would find in the near future new ways to overcome current limitations for efficient, sustainable, and renewable photoelectrochemical solar fuel and chemical production.

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Conflict of Interest

The authors declare no conflict of interest.

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operando spectroscopy, oxynitride photocatalysts, photoelectrochemical hydrogen generation, solar water splitting, thin films

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