

Review

Plasma-Engineered Oxynitride Thin Films for Photoelectrochemical Water Splitting

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Abstract

This critical assessment develops a mechanistic framework for plasma-engineered oxynitride thin films in photoelectrochemical (PEC) water splitting, moving beyond description to predictive understanding. Analyzing 30 peer-reviewed studies (2010–2025) via PRISMA 2020 and a structured reliability framework, we evaluate relationships between plasma conditions, film characteristics, and solar hydrogen generation. Results reveal that plasma power, gas composition, and substrate temperature collectively control nitrogen incorporation, crystallinity, and defect formation. Optimized plasma processing conditions were generally associated with improved photocurrent generation, hydrogen evolution performance, and operational stability relative to thermal synthesis routes across most of the reviewed studies, although the 30-study evidence base is still limited and the proposed power-domain classification should be treated as a preliminary framework requiring validation against additional studies. Mechanistic analysis indicates that moderate plasma energies provide sufficient activation for nitrogen incorporation while minimizing lattice damage and excessive defect formation. A unified conceptual framework is proposed relating plasma parameters, film properties, and PEC performance, providing mechanistic guidance for photoelectrode optimization and future process development. Quality assessment identifies that only 13.3% of studies provide high-confidence evidence (46.7% moderate, 40% low), with most lacking complete plasma diagnostics or long-term stability data, highlighting critical research gaps. The framework establishes that plasma engineering's transformative potential lies in precise control over the composition–structure–property cascade, offering a reproducible route to high-performance oxynitride photoelectrodes for sustainable hydrogen production.



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1. Introduction

The world is moving towards a low-carbon and sustainable energy economy, which requires high-scale and carbon-neutral fuel production technologies. Green hydrogen has become one of the most discussed renewable energy carriers due to its gravimetric energy density, the overall range of application, and the end product, which is water, which does not emit any emissions [1]. Photoelectrochemical (PEC) water splitting to produce hydrogen with sunlight energy represents one of the most direct and sustainable

ways of converting sunlight energy to chemical energy [2,3]. Nevertheless, high solar-to-hydrogen (STH) conversion efficiency is still a permanent scientific and engineering dilemma, mainly constrained by the efficiency of semiconducting photoelectrodes through which water-splitting reactions proceed [4,5].

The incident light is absorbed by a semiconducting material in a PEC cell to create photoexcited electron–hole pairs, which promote the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) at different electrodes [6–8]. The previous dominance of oxide-based semiconductors like TiO_2 , Fe_2O_3 , and BiVO_4 was due to their chemical stability and cheapness [9]. However, TiO_2 has a wide bandgap (generally >3.0 eV) that limits light absorption to the ultraviolet part of the solar spectrum only (about 5% of the full solar spectrum); Fe_2O_3 and BiVO_4 , in fact, have smaller bandgaps (approximately 2.1–2.2 eV and 2.4–2.5 eV, respectively) that permit some visible-light absorption, but their photoelectrochemical performance remains limited by other factors—short hole-diffusion length and rapid surface recombination in Fe_2O_3 , and sluggish oxygen-evolution kinetics with poor electron mobility in BiVO_4 [10]. This drawback substantially limits the overall STH efficiency achievable. The total η_{STH} is given as

$$\eta_{\text{STH}} = \frac{J_{\text{ph}}(1.23 - V_{\text{bias}})}{P_{\text{in}}} \times 100$$

in which J_{ph} represents the photocurrent density, V_{bias} is the bias voltage applied, and P_{in} is the solar power input at AM1.5G. The above relationship highlights the fact that energy conversion efficiency is directly proportional to material properties, including bandgap (E_g), charge-carrier mobility, and surface reactivity. In addition, Figure 1 displays the schematic illustration of the photoelectrochemical (PEC) water-splitting mechanism in oxynitride semiconductors, showing N 2p orbital hybridisation of the valence band and the associated bandgap narrowing (original illustration). When irradiated by visible light (step i), electrons in the valence band (VB) are excited to the conduction band (CB) by photons of energy $E = h\nu$. The photoexcited electrons of the CB catalyze the hydrogen-evolution reaction (step ii), and the photogenerated holes of the VB catalyze the oxygen-evolution reaction (step iii). The redox potentials of H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ against the normal hydrogen electrode (NHE) are also denoted in the diagram, which indicates that the band edges are aligned to perform the overall water splitting.

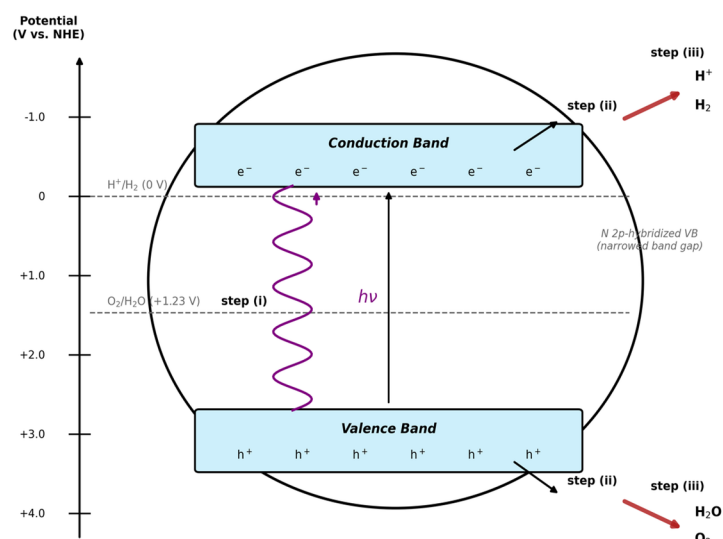


Figure 1. Schematic showing band alignment and charge transfer, illustrating N 2p–orbital hybridization of the valence band (original illustration).

In order to enhance the absorption of light into the visible range, more recent studies have centered on oxynitride-based, mixed-anion semiconductors, with the chemical stability of oxides and the desirable electronic structure of nitrides. The addition of nitrogen to an oxide lattice reduces the bandgap because the 2p orbitals of nitrogen are at a higher energy than the 2p orbitals of oxygen [11]. This changes the position of the valence-band maximum to higher values, allows the absorption of visible light and enhances charge separation. Typical ones include LaTiO_2N , SrTaO_2N , BaNbO_2N , and CaNbO_2N with optical bandgaps in the 1.8–2.5 eV that are ideally placed to utilize solar energy in splitting water [6].

In spite of these benefits, it is still difficult to make quality oxynitride thin films. Traditional synthesis pathways, including ammonolysis and solid-state nitridation, utilize high temperatures ($>900^\circ\text{C}$) and also tend to produce materials with non-uniform distribution of nitrogen, oxygen vacancies, and low crystallinity [12,13]. These structural defects reduce carrier lifetimes and PEC efficiency. Furthermore, these high-temperature processes are energy-demanding, can be scaled with difficulty, and provide poor stoichiometry and microstructure control [14,15].

One method that has emerged in recent years to address these limitations is plasma-assisted synthesis. Low-temperature activation of nitrogen incorporation is facilitated in plasma conditions, which are rich in energetic ions, radicals and excited species, and which enhance defect passivation and surface activation at the same time [16–18]. Other methods, including plasma-enhanced chemical vapor deposition (PECVD), reactive magnetron sputtering, plasma nitridation, and microwave plasma-assisted deposition, offer fine control over plasma power, gas composition, and ion energy [19,20]. Such techniques have been used to fabricate oxynitride films with a customized composition, crystallinity, and surface termination, and have greatly increased photoelectrochemical stability and hydrogen-evolution rates [21,22]. Throughout this review, “plasma-assisted synthesis” is used as the umbrella term for these fabrication routes, while “plasma engineering” refers specifically to the deliberate design and optimization of plasma parameters (power, gas composition, ion energy) to control film properties. “Plasma processing” and “plasma-engineered” (including in the title) are used interchangeably with “plasma-assisted synthesis” elsewhere in this review when referring generally to the fabrication route or its resulting materials, rather than as distinct technical terms.

The recent literature illustrates the transformative nature of plasma-assisted synthesis. Xiao et al. (2023) reported an operation duration of more than 3000 h for a $\text{GaN}:\text{ZnO}/\text{oxynitride}$ heterostructure fabricated through plasma-assisted MOCVD—the longest operation stability reported so far—attributed to consistent nitrogen incorporation and defect elimination [20]. Similarly, Streibel et al. (2024) also obtained plasma-sputtered ZrON thin films with improved band alignment and corrosion resistance, leading to high PEC performance [21]. Both Lawley et al. (2020) and Haydous et al. (2021) later demonstrated that the perovskite-type oxynitrides could have surface termination, crystal orientation, and interfacial chemistry precisely tailored by plasma processing, which had a direct effect on the charge-carrier dynamics and stability under illumination [22,23]. All these results attest to the critical importance of plasma engineering in the development of the structure–property–performance correlation in oxynitride photoelectrodes.

The hydrogen generation efficiency of the PECs using oxides is limited, however, by the electronic and structural constraints of the oxide-based photoelectrodes, which have broad bandgaps (>3.0 eV), limiting the solar absorption to the ultraviolet spectrum (~ 5 percent of the sunlight) [24,25]. To overcome this shortcoming, oxynitride semiconductors, which include LaTiO_2N , SrTaO_2N , BaNbO_2N , and CaNbO_2N , are now viewed as promising substitutes since the introduction of nitrogen also enhances the valence-band

maximum by N 2p-O 2p hybridization, which decreases the optical bandgap down to 1.8–2.5 eV and allows absorption of visible light [26].

Beyond bandgap narrowing, efficient PEC water splitting also requires the conduction-band minimum (CBM) and valence-band maximum (VBM) of the oxynitride to straddle the water redox potentials, i.e., the CBM positioned more negative than the H^+/H_2 potential (0 V vs. NHE) and the VBM positioned more positive than the $\text{O}_2/\text{H}_2\text{O}$ potential (1.23 V vs. NHE) [27]. Because N 2p states lie closer to the Fermi level than O 2p states, N incorporation raises the VBM predominantly through N 2p-O 2p hybridisation while leaving the CBM, which is largely set by the empty d-orbitals of the metal cation, comparatively unchanged; this asymmetric shift is what narrows the bandgap without substantially compromising the material's reducing power [26,27]. Among the oxynitrides considered in this review, TaON ($E_g \approx 2.4\text{--}2.8$ eV) has band edges that comfortably bracket both redox potentials, whereas Ta_3N_5 ($E_g \approx 2.1$ eV) offers stronger visible-light harvesting but a CBM positioned close to the H^+/H_2 level, so its photoanodes typically require an external bias or a co-catalyst to drive the oxygen-evolution reaction efficiently [27]. Plasma-induced defects such as nitrogen vacancies and reduced metal cations (e.g., Ta^{3+}) introduce mid-gap states that can pin the Fermi level and shift the effective band-edge positions measured electrochemically, which is why defect density and nominal band-edge alignment must be considered together when evaluating a plasma-processed oxynitride's suitability for water splitting [28,29].

Despite significant advances, the literature on plasma-engineered oxynitride films lacks four elements: (i) A unified mechanistic framework linking plasma parameters to film properties and PEC performance; current studies typically examine individual variables (plasma power, gas ratio, pressure) in isolation, without modeling their combined effects on structural, optical, and electronic behavior. (ii) An operating-regime classification that explains when and why plasma processing succeeds or fails; the relationships between plasma parameters and film characteristics remain qualitative rather than quantitative, preventing predictive design. (iii) A critical reliability assessment of the evidence base; experimental inconsistencies, non-standardized measurement protocols, and differences in performance metrics across studies make cross-comparison difficult and limit the development of generalized design principles. (iv) Predictive design guidance for rational photoelectrode optimization; the absence of systematic relationships between plasma conditions and performance indicators hinders the translation of laboratory findings to practical device fabrication.

To address these gaps, this study conducts a systematic critical assessment of the peer-reviewed literature (2010–2025) on plasma-engineered oxynitride thin films for solar water splitting. Unlike conventional narrative reviews, this assessment employs a structured analytical framework to extract, synthesize, and critically evaluate evidence, combining qualitative thematic analysis with quantitative synthesis to reveal multi-dimensional correlations between plasma parameters, material properties, and PEC performance indicators. The framework is designed to generate mechanistic insights and predictive capability from existing data, rather than merely cataloging published results.

Unlike previous reviews that primarily summarize reported performance metrics, this study contributes three novel elements: (i) a structured evidence reliability framework tailored to plasma-engineered materials, (ii) a mechanistic process–property–performance framework linking plasma conditions to PEC outcomes, and (iii) a predictive classification of plasma operating conditions for oxynitride photoelectrode optimization.

The objectives of this critical assessment are as follows:

1. Develop a mechanistic process–property–performance framework relating plasma conditions to oxynitride film characteristics and PEC performance, moving beyond descriptive comparison to explanatory understanding.

2. Classify plasma operating conditions according to their dominant plasma–material interaction mechanisms, developing a classification framework for different plasma operating regimes of nitrogen incorporation, defect formation, and crystallinity evolution.
3. Critically evaluate the reliability of current evidence using a structured quality assessment framework tailored to materials science, differentiating high-confidence from lower-confidence findings while retaining all studies with appropriate weighting.
4. Formulate mechanistically informed design guidelines for optimizing oxynitride photoelectrodes, providing evidence-based guidance for plasma parameter selection and process optimization.
5. Identify research gaps and future directions for advancing plasma-engineered solar hydrogen production, highlighting unresolved mechanistic questions and experimental needs.

2. Methodology and Analytical Framework

2.1. Research Design

This study employs a critical synthesis methodology designed to extract mechanistic and predictive insights from the published literature on plasma-engineered oxynitride thin films. Literature identification and screening followed PRISMA 2020 guidelines [30] to ensure transparency and reproducibility. The approach differs from traditional literature reviews in three key respects: (i) a rigorous quality assessment framework weights findings by data reliability; (ii) a multi-variable analysis identifies robust relationships among plasma parameters, material properties, and PEC performance indicators; and (iii) a mechanistic model is developed to explain, not just describe, observed trends.

2.2. Data Sources and Search Strategy

The data collection process drew on several internationally recognized scientific databases to ensure comprehensive coverage and identify the most relevant studies. The major databases used in this review were Scopus, Web of Science, ScienceDirect, Springer-Link, and IEEE Xplore, as they provide extensive coverage of the literature in materials science, thin-film engineering, and renewable-energy technology. Google Scholar was used as a secondary search tool to identify additional cross-referenced or more recently indexed articles not captured by the core database search.

The search strategy was systematically constructed using targeted keywords and Boolean operators. The keywords were combined with the following: plasma-assisted, plasma-enhanced, magnetron sputtering, PECVD, and microwave plasma, oxynitride thin film, perovskite oxynitride, LaTiO_2N , SrTiO_2N , and ZrON . These terms were combined with hydrogen-generation-related keywords, including solar water splitting, photoelectrochemical hydrogen generation, and green hydrogen, to capture the literature relevant to renewable hydrogen production. English-language publications from January 2010 to March 2025 were included to ensure the search captured current, technologically relevant research. Eligible sources included peer-reviewed journal articles, conference papers, and reviews, ensuring high overall quality and reliability.

2.3. Inclusion and Exclusion Criteria

To maintain focus and methodological rigor, predefined inclusion and exclusion criteria were applied during the screening process. These criteria are listed in Table 1:

Table 1. Inclusion and exclusion criteria.

Criterion	Inclusion	Exclusion
Publication Type	Peer-reviewed journal or conference article	Theses, preprints, non-peer-reviewed reports
Language	English	Non-English
Timeframe	2010–2025	Before 2010
Focus	Studies on plasma-assisted synthesis or modification of oxynitride thin films	Studies on bulk oxynitrides, powders, or non-plasma processes
Application	Solar-driven water splitting or hydrogen generation	Photocatalysis not involving hydrogen production
Data Availability	Reports of synthesis parameters, material properties, or photoelectrochemical performance	Conceptual or purely theoretical papers without empirical data

2.4. Screening and Selection Process

The selection of studies was performed based on the PRISMA framework, which consists of four steps, namely identification, screening, eligibility, and inclusion. First, relevant studies were retrieved from the selected academic databases, and reference management tools were used to eliminate duplicates and systematically manage bibliographic data. A relevance screening was conducted on titles and abstracts, followed by a full-text review to evaluate the methodological quality and the relevance to the research objectives. The studies were selected on the basis of high levels of reporting of plasma-assisted synthesis parameters, composition of thin-film, deposition, and photoelectrochemical performance parameters. Only the studies that fulfilled these requirements and demonstrated methodological rigor were carried forward to further qualitative and quantitative synthesis to form the evidence base of the systematic review.

2.5. Data Extraction and Coding

Data were extracted systematically using a purpose-designed, structured Excel spreadsheet. Specific information was recorded on publication metadata, synthesis methodology, material characteristics, and performance results for each included study. The extracted data included the following parameters of the plasma processes: type of source, gas composition, pressure in the chamber, substrate temperature, and deposition time. Material-related information recorded included chemical composition, film thickness, crystallinity, morphology, and optical bandgap. Photoelectrochemical properties, i.e., photocurrent density, hydrogen evolution rate, faradaic efficiency, and stability, were also derived where practicable.

Quantitative values were standardized to common units of measure to allow comparison across studies, such as milliamperes per square centimeter of photocurrent density and nanometers of film thickness. Extracted variables were then organized into conceptual domains using thematic coding that comprised plasma–material interactions, structural modifications, and performance enhancements. In experiments involving several plasma conditions or material sets, the various experimental conditions were coded as distinct records to enable retrieval of the specific contribution of each condition.

2.6. Quality Assessment

A structured evidence reliability framework was developed to evaluate the quality and trustworthiness of the included studies, tailored specifically for materials science and plasma processing research. The five criteria and their weights were adapted from established quality-appraisal approaches used in materials-science systematic reviews, informed by ROBINS-I risk-of-bias domains, with weights assigned by the review team according to each criterion's relative importance for verifying reported PEC performance claims (plasma diagnostics and film characterization weighted most heavily as they underpin the reproducibility of all downstream results), and the resulting rubric was pilot-tested on a subset of studies before being applied to the full corpus. The specific percentages reflect a deliberate two-tier structure: plasma diagnostics and thin-film characterization are weighted most heavily (25% each, 50% combined) because they establish whether a study's reported synthesis conditions and resulting material properties can be independently verified and reproduced at all; without adequate reporting on these two criteria, any downstream PEC performance claim cannot be attributed with confidence to the stated plasma parameters. PEC testing robustness is weighted next (20%), as it governs whether the reported performance values themselves are methodologically sound (standardized conditions, controls, error reporting). Stability and reproducibility are each weighted lowest (15%), not because they are unimportant, but because they were the least consistently reported criteria across the corpus (few studies report multi-sample statistics or extended-duration testing), so weighting them more heavily would have penalized otherwise rigorous studies for a reporting gap common across the field rather than for a genuine methodological weakness. The framework comprises five weighted criteria:

Each study received a weighted score (0–100). Studies scoring >80 were classified as high confidence, 60–79 as moderate confidence, and <60 as low confidence. Low-confidence studies were retained in the analysis but assigned lower evidential weight during interpretation to ensure reliable conclusions. Each study was scored independently by two authors against the criteria in Table 2; disagreements were resolved by discussion with a third author until consensus was reached. The resulting confidence classifications are reported per study in Table 2.

Table 2. Weighted criteria for evidence reliability assessment of included studies.

Criterion	Weight	Assessment Criteria
Plasma Diagnostics	25%	3: Power + pressure + gas + ion energy/density; 2: Power + pressure/gas; 1: Power only
Thin-Film Characterization	25%	3: XRD + XPS + TEM + surface analysis; 2: XRD + SEM + XPS; 1: XRD + SEM only
PEC Testing Robustness	20%	3: Standardized conditions + controls + error analysis; 2: Multiple conditions; 1: Single condition
Stability Assessment	15%	3: >100 h with degradation analysis; 2: 24–100 h; 1: <24 h or none
Reproducibility	15%	3: Multiple samples + statistical analysis; 2: Multiple samples; 1: Single sample

2.7. Risk of Bias Assessment

A modified ROBINS-I framework was adapted for materials science studies. Selection bias was assessed based on synthesis parameter completeness. Detection bias was evaluated based on characterization method appropriateness and calibration. Reporting bias was examined for selective reporting of favorable results only. Studies lacking stability data or using non-standardized PEC conditions were assigned medium risk; those with incomplete plasma diagnostics were assigned high risk. The results are integrated into the confidence scoring presented in Section 3.8.

2.8. Data Synthesis and Analysis

Data synthesis was carried out through qualitative and quantitative approaches. Qualitative thematic synthesis was used to identify recurring patterns in how plasma engineering affects material structure, composition, and performance, focusing on key parameters such as the degree of nitridation achieved during plasma exposure, defect density, and crystal/phase purity as functions of plasma power and gas ratio. Synthesizing these findings yielded a conceptual understanding of how plasma conditions influence charge transport and surface-reaction kinetics during water splitting.

Quantitative synthesis involved the comparative evaluation of reported optical bandgaps, photocurrent densities, hydrogen evolution rates, and stability indicators across the included studies. Rather than calculating pooled performance metrics, the analysis focused on identifying recurring process–property–performance relationships and assessing their consistency across different plasma systems and material compositions. Comparative tables and conceptual frameworks were developed to highlight evidence-supported trends and mechanistic relationships between plasma processing conditions, thin-film characteristics, and photoelectrochemical performance. This approach emphasizes critical interpretation of the literature rather than statistical aggregation of heterogeneous datasets.

2.9. Ethical and Reproducibility Issues

Although this review did not involve human or animal subjects, a high ethical standard was maintained throughout the research. Only publicly available and properly cited studies were used, and all data were referenced according to academic standards. Data collection, coding, and synthesis procedures were reported transparently to ensure reproducibility.

3. Results and Analysis

3.1. Study Selection

The review of the literature was conducted according to the PRISMA 2020 framework to ensure the transparency and reproducibility of the identification and inclusion of the studies [30]. Figure 2 (PRISMA Flow Diagram) presents the information on the total number of records identified by five major academic databases, namely Scopus (310), Web of Science (270), ScienceDirect (220), IEEE Xplore (130), and SpringerLink (57). Following the deletion of 175 duplicates, 812 articles were identified using the titles and abstracts. Out of them, 510 papers were rejected due to being irrelevant to thin films and hydrogen-generation applications based on plasma. Full-text retrieval was sought on the rest ($n = 302$) of the reports, of which 168 were accessed successfully (reports not retrieved: $n = 134$).

While the total number of 138 papers was excluded from the scope of this review owing to the stringent inclusion criteria, only 30 papers ultimately qualified for the review, and this is a reflection of the narrow scope of focused high-quality papers dealing specifically with plasma-engineered oxynitrides applied to PEC water splitting, as opposed to general photocatalysis.

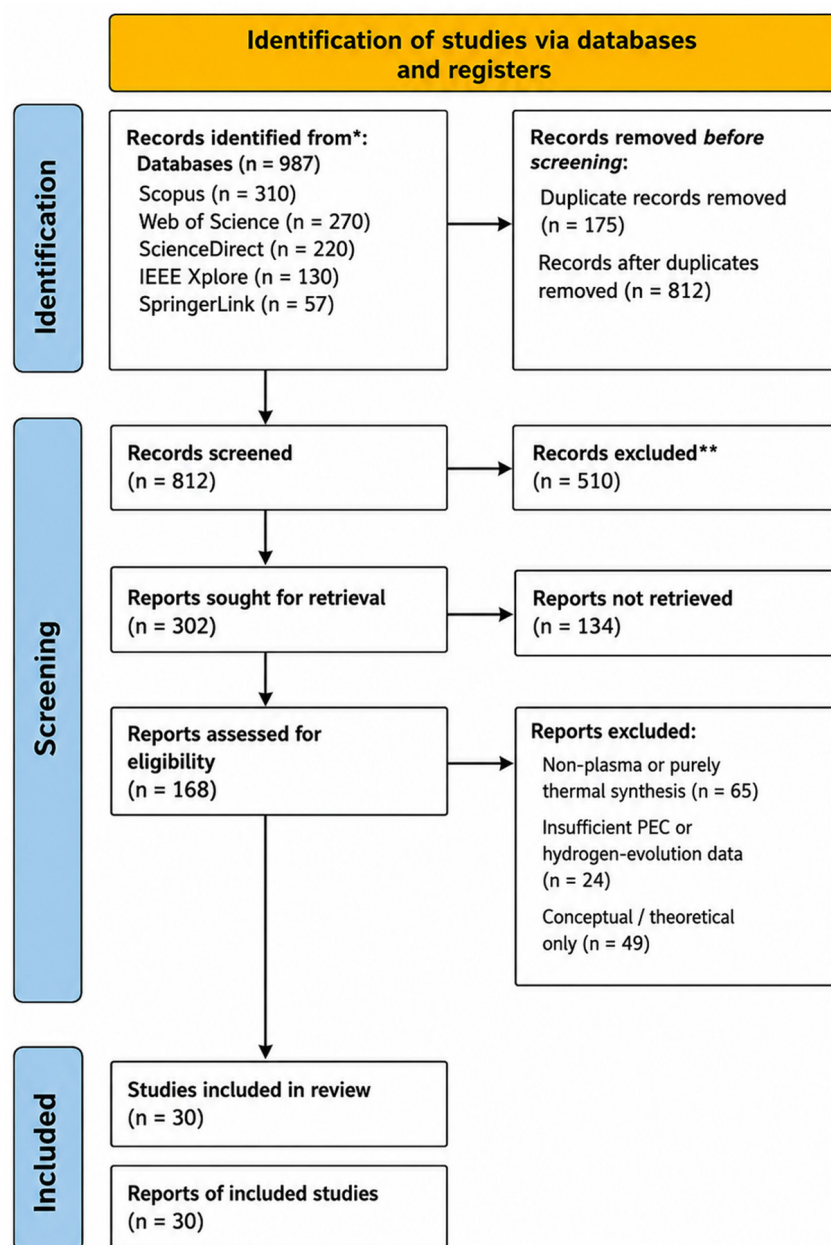


Figure 2. Study selection process: (*) denotes total records identified from databases, and (**) represents papers excluded as irrelevant to plasma-based thin films and hydrogen generation.

3.2. Characteristics of Studies

The 30 studies presented in Table 3 collectively trace the development of plasma-assisted synthesis techniques for oxynitride thin films used in PEC hydrogen generation. Table 3 lists 31 rows corresponding to 30 unique primary studies; one reference (Haydous et al., 2021, ref. [23]) appears twice because that single publication reports two distinct material systems (a perovskite oxynitride and CaNbO_2N) that are treated as separate entries for the purposes of the process–property–performance analysis, consistent with its listing as a single study in Table 7. No other reference is duplicated, and no study is treated as supporting/background literature within Table 3 or Table 7; the same 30 unique primary studies are used consistently throughout the evidence-characteristics table (Table 3), the evidence-reliability table (Table 7), and the corresponding in-text citations. The period following 2018 is associated with a unique increase in research activity, with 80% (24 of 30 dated studies) of the publications reviewed dating from that time. RF plasma sputtering

and PECVD were the most commonly reported methods because they have flexibility in controlling a variety of nitrogen partial pressure, plasma power, and deposition temperature parameters, which have a significant impact on the film stoichiometry and crystallinity. Enhanced ion activation and deeper nitrogen incorporation were accomplished by other methods such as plasma-assisted MOCVD [20], reactive pulsed laser deposition, and microwave plasma nitridation (MPAN).

Perovskite-type oxynitrides, including LaTiO_2N , SrTaO_2N , and CaNbO_2N , were found to be the dominant material systems due to their favorable band structures for visible-light capture and their stability in aqueous conditions [31–35]. Ta_3N_5 -based photoanodes fabricated via RF/DC magnetron sputtering and plasma-enhanced CVD, together with NH_3 nitridation, similarly emerged as a well-represented material system in this corpus, with several studies reporting photocurrent densities in the $5.9\text{--}8.1\text{ mA cm}^{-2}$ range at 1.23 V [36–40]. Recent developments have seen the change to heterostructured and hybrid systems (e.g., $\text{GaN: ZnO/oxynitride}$, $\text{LaTiO}_2\text{N/TiN}$) with better charge separation and conductivity [31,32,41,42]. Material characterization was done comprehensively in all the studies, with the most widely used methods being XRD, XPS, SEM/TEM, UV-Vis spectroscopy, and EIS, and some of the recent studies have utilized in situ and synchrotron analyses to study the mechanism of plasma–surface interactions [35,43–47]. Most of the plasma-engineered films attained photocurrent densities between 2.5 and 4.0 mA cm^{-2} with stability retention well above 90% under standard illumination, compared with their thermally nitrided counterparts. Taken together, these results indicate that plasma-assisted routes provide better compositional control, increased crystallinity, and better PEC performance, which represents a solid basis for the quantitative synthesis and comparative analysis in the following sections.

Table 3. Characteristics of included studies ($n = 30$).

Reference	Material System	Plasma Technique	Characterization Methods	Key Findings	PEC Performance/Stability
[20]	GaN: ZnO/Oxynitride heterostructure	Plasma-assisted MOCVD	XRD, XPS, Chronoamperometry	Achieved $>3000\text{ h}$ operation, superior nitrogen incorporation	3.8 mA cm^{-2} ; $>95\%$ stability (10 h)
[21]	ZrON thin film	RF Plasma Sputtering	UV-Vis, SEM, XPS	Bandgap tuning ($\sim 2.3\text{ eV}$), corrosion-resistant surface	2.9 mA cm^{-2} ; 93% retention
[41]	LaTiO_xN_y	Reactive PLD (N_2/H_2 plasma)	Synchrotron XRD, Neutron reflectometry	Surface vs. bulk N-incorporation mapped	Enhanced charge separation; $E_g = 2.4\text{ eV}$
[22]	LaTiO_xN_y	N_2 Plasma Reactive Sputtering	AFM, in situ XPS	Controlled surface evolution under illumination	2.6 mA cm^{-2} ; minor N-loss over 300 h
[23]	Perovskite oxynitride	Plasma-Assisted PRCLA	SIMS, LEIS, XPS	O-plasma passivation reduced recombination	Improved charge transfer efficiency
[31]	LaTiO_xN_y	Pulsed Laser Deposition	TEM, XRD, PEC	(001)-oriented films show the best PEC activity	2.4 mA cm^{-2} ; stable 6 h operation

Table 3. Cont.

Reference	Material System	Plasma Technique	Characterization Methods	Key Findings	PEC Performance/Stability
[32]	LaTiO ₂ N	Soft X-ray ARPES	ARPES, XRD	Identified hybridized valence bands	Enhanced visible-light absorption
[32]	SrTiON + CoPi nanoparticles	RF Sputtering + Plasma	UV-Vis, PEC, XRD	CoPi improved OER kinetics	4.1 mA cm ⁻² ; +40% H ₂ evolution
[29]	LaTiO ₂ N/Co ₃ O ₄ /NiO _x photoanode (plus literature review)	Electrophoretic Deposition (EPD)	Chronoamperometry (AM1.5G and ~130 suns), gas evolution	Self-oxidation (N ₃ ⁻ → N ₂) competes with OER; capacitive charging contributes to initial photocurrent decay	Photocurrent retention (PR10 min@60 min): 60% at 1 sun (AM1.5G), 29% at ~130 suns; Faradaic efficiency typically >90% for (oxy)nitrides broadly; cocatalyst loading (CoPi, NiO _x) mitigates photocorrosion
[34]	LaTiO ₂ N + TiN	Plasma-assisted Deposition	XPS, UV-Vis, TEM	TiN inclusion boosted conductivity	3.5 mA cm ⁻² ; stable neutral pH
[33]	Oxide/oxy-nitride systems	Reactive Plasma Chemistry	Time-resolved Spectroscopy	Tracked nitrogen–oxygen reaction pathways	Key plasma chemistry insight
[43]	Multiple oxide systems	Review (comparative)	Comparative analysis	Highlighted stability–efficiency trade-offs	Theoretical benchmark
[48]	N-doped TiO ₂ nanotubes	Plasma Nitridation	SEM, PEC, UV-Vis	Expanded absorption to the visible range	+40% photocurrent vs. undoped
[49]	Ta ₃ NyO _x nanoparticles (core–shell nanostructure)	DC Reactive Magnetron Sputtering (Ar/N ₂)	Electron microscopy, XPS, optical spectroscopy	Crystalline core with amorphous, N-depleted periphery; plasmonic and photoluminescent	Bandgap and composition tunable via N ₂ flow (core-region Eg < 2.0 eV)
[50]	ZrTiON	Reactive Magnetron Sputtering (Zr target, Ti ribbons)	XPS, AFM	Ti incorporation tuned oxide/nitride/oxy-nitride phase content	58–96% photodegradation efficiency (methylene blue); improved corrosion resistance after 8 h exposure
[46]	TaON thin films	PECVD	XPS, AFM, PEC	Reduced trap density, improved OER	3.7 mA cm ⁻² ; 90% stability

Table 3. Cont.

Reference	Material System	Plasma Technique	Characterization Methods	Key Findings	PEC Performance/Stability
[23]	CaNbO ₂ N	Plasma-Assisted PRCLA	XRD, SEM, LEIS	Enhanced visible absorption (E _g = 2.2 eV)	Higher charge lifetime
[47]	SrTaO ₂ N	RF Magnetron Sputtering	XRD, UV-Vis, PEC	Dense grains, uniform nitridation	0.019 mA cm ⁻² (Ta substrate, 600 nm film); stability not reported
[36]	Ta ₃ N ₅ (semi-transparent)	High-power RF Magnetron Sputtering + NH ₃ Nitridation	XRD, STEM/TEM, IPCE, TAS	PEC-PV tandem w/CuInSe ₂	7.4 mA cm ⁻² @1.23 V; STH 9% → 4% (2 h)
[51]	Ta ₃ N ₅	RF Magnetron Sputtering + NH ₃ Treatment	XRD, SEM, XPS, PEC	IrO ₂ suppresses self-oxidation	~10× photocurrent gain; stability half-life 1.2 → 2.3 min
[37]	Ta ₃ N ₅ /SiO ₂ (self-conductive)	RF Sputtering + NH ₃ Nitridation (725–850 °C)	XRD, SEM, Hall effect, XPS, PEC	Hall mobility 1.72 cm ² V ⁻¹ s ⁻¹	5.9 mA cm ⁻² @1.23 V; HC-STH 1.0% @0.95 V
[38]	GaN/Ta ₃ N ₅	Sputtering–Nitridation + GaN EB Evaporation	XRD, TEM/STEM-EDS, XPS, EIS, GC	Onset improved 0.8 → 0.65 V	8 mA cm ⁻² stable 10 h @1.2 V; Faradaic ~100%/12 h
[52]	Mg:GaN/Ta ₃ N ₅	Ta ₃ N ₅ (RF Sputtering + NH ₃) + Mg:GaN via PCVD	XRD, SEM, XPS depth profile, PEC/IPCE	N ₂ vs. NH ₃ post-anneal comparison	Combined optimum: onset ~0.3 V, 1.4 mA cm ⁻²
[53]	Ta-Ti oxynitride (TaTiON)	DC Reactive Magnetron Co-Sputtering	RBS, GIXRD, nanoindentation, 4-point probe	Single oxynitrides crystalline; co-sputtered amorphous	Hardness TaON 14.8/TiON 8.8 GPa; sheet resistance 247 → 3.26 × 10 ⁶ Ω/sq
[54]	Tantalum oxynitride (TaON)	DC Magnetron Sputtering (fixed N ₂ , variable O ₂) + RTA	XRD, Raman, SEM, EDS, 4-point/Hall	Dual optical bandgaps	Bandgaps 2.6–3.2 & 0.8–1.1 eV; 29.5% methyl orange degradation (6 h)
[39]	Ta ₃ N ₅ (thin-film transfer)	RF Sputtering + Oxidation/Nitridation + Back-Contact Transfer	XRD, SEM/STEM/TEM-EDS, PEC, GC	NbNx back contact improves performance	3.5 mA cm ⁻² @1.23 V; Faradaic ~unity
[40]	Ta ₃ N ₅ (PCVD route)	Plasma-Enhanced CVD + NH ₃ Nitridation (900 °C)	XRD, SEM, HRTEM, XPS, PEC/IPCE, GC	Multilayer TaO _x /Ta ₃ N ₅ /Ta ₃ N ₅ + Ta ₂ N/Ta	8.1 mA cm ⁻² @1.23 V; IPCE 67% @540 nm; stable 60 min

Table 3. Cont.

Reference	Material System	Plasma Technique	Characterization Methods	Key Findings	PEC Performance/Stability
[55]	ZrO _{2-x} N _x	Reactive HiPIMS (pulsing 800–1200 Hz)	TR-OES, XPS, XRD, UV-Vis-NIR/Tauc	Eg narrows with pulsing frequency	Eg 3.43 → 2.20 eV; MB degradation 4.0% → 32.7% (4 h)
[56]	Tantalum oxynitride (TaO _x N _y)	DC Reactive Magnetron Sputtering (85%N ₂ + 15%O ₂)	XPS, UV-Vis-NIR, TEM/HRTEM, AFM	Eg tunable via partial pressure	Eg 1.43–2.67 eV; UV + H ₂ O ₂ ~82%, VIS + H ₂ O ₂ ~34% photodegradation
[57]	TiN/TiO _x N _y bilayer	DC Reactive Magnetron Sputtering (sequential layers)	EDAX, XRD, FESEM, UV-Vis-NIR, PEC J-V	Eg tunable via TiN thickness	Eg 3.29 → 2.82 eV; PEC photocurrent peaks at 9 nm TiN
[58]	Heavily N-doped TiO ₂ (TiON)	Reactive DC Magnetron Sputtering + Excimer Laser Annealing	XRD, HRTEM, XPS, UV-Vis	Laser annealing suppresses N loss vs. thermal	N/Ti ~9.52% retained (laser) vs. >50% loss (thermal); degradation rate 2× higher

3.3. Mechanistic Plasma–Process–Property Relationships

Table 3 shows 30 representative studies that constitute the basis of the analysis of this review. They all illustrate the scientific path of plasma-engineered oxynitride thin films—the basics of the interaction between plasma and the surface of the material, up to the enhancement of the electronic structure and PEC performance. Through this segment, their results are combined, cross-cutting mechanisms are determined, and the improvements of the crystallinity, optical absorption, charge transfer, and hydrogen evolution performance are quantified.

Rather than treating plasma power as an isolated variable, the framework interprets plasma processing as a cascade in which operating conditions influence species dissociation, ion bombardment, and surface activation, which subsequently govern nitrogen incorporation, defect evolution, crystallinity, electronic structure, and PEC performance. This process–property–performance perspective provides a mechanistic basis for comparing studies that employ different plasma systems and deposition conditions. Figure 3 presents this unified framework, which serves as the organizing principle for the quantitative analysis that follows.

Figure 3: Unified plasma–process–property–performance framework for oxynitride thin film synthesis and photoelectrochemical water splitting. The framework illustrates the cascade from plasma operating parameters through plasma–material interactions to film properties, electronic properties, and PEC performance. Arrows indicate mechanistic relationships inferred from the published literature and synthesized through comparative analysis of 30 studies.

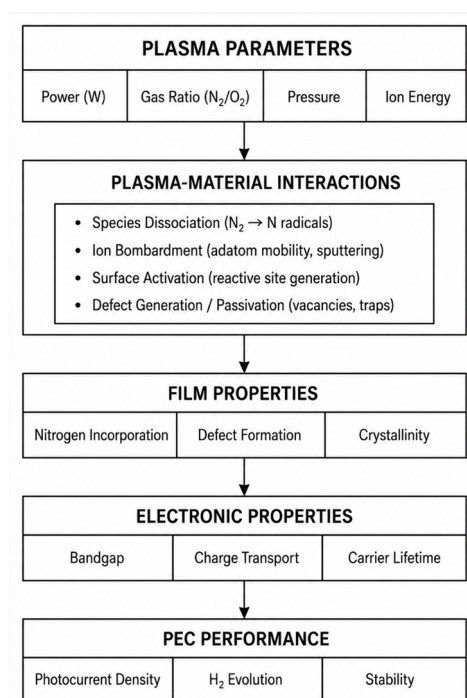


Figure 3. Unified plasma–process–property–performance framework for oxynitride thin film synthesis and photoelectrochemical water splitting.

3.3.1. Emerging Plasma Operating Domains and Mechanistic Pathways

Comparative analysis of the 30 studies reveals that plasma processing conditions can be grouped into three broad operating domains based on their dominant plasma–material interaction mechanisms. This classification emerges from systematic evaluation of reported relationships between plasma parameters (power, gas composition, pressure) and resulting film properties (nitrogen incorporation, crystallinity, and defect density). Rather than imposing rigid thresholds, the domains are defined qualitatively according to the predominant physical and chemical processes governing film growth. Where individual studies did report plasma diagnostics, approximate ranges can be associated with each domain: the lower-power domain generally corresponds to RF/DC powers below roughly 100 W (or equivalent low ion-flux microwave/PECVD conditions), the intermediate domain to roughly 100–250 W, and the higher-power domain to plasma source powers above approximately 250–350 W, at which excessive ion bombardment (inferred qualitatively from the reported power settings, since matched measurements of ion energy, electron density, or radical flux were not available across the reviewed corpus) favors metallic-nitride formation and carrier-trapping defects rather than substitutional nitrogen incorporation. Because comparable ion-energy or electron-density data were not reported for most of the reviewed studies, these power ranges should be understood as empirical, indicative associations derived from the available literature rather than as direct ion-energy thresholds or universal plasma-physics boundaries. These figures should be read as indicative rather than universal, since reactor geometry, plasma source design, and precursor chemistry were not standardized across the reviewed studies and comparable ion-energy or electron-density measurements were not reported for every study.

Lower-Power Domain

At lower plasma powers, electron density and ion energy are generally expected to be lower (inferred from plasma-physics principles rather than measured directly in most reviewed studies), resulting in incomplete dissociation of nitrogen-containing precursor

gases. The dominant nitrogen-containing species are molecular ions and vibrationally excited molecules, which have lower reactivity compared to atomic nitrogen radicals. This regime is characterized by:

- Limited dissociation and reduced reactive species generation.
- Incomplete nitridation with lower nitrogen incorporation.
- Amorphous or mixed-phase film structures with reduced crystallinity.
- Wider optical bandgaps limiting visible-light absorption.

Studies operating in this domain include low-power PECVD conditions [46] and early-stage RF sputtering conditions [21,43], where photocurrent densities remain below the levels achieved in the intermediate domain.

Intermediate-Power Domain

In the intermediate domain, increased plasma activation enhances dissociation of nitrogen-containing species and promotes nitrogen incorporation into the growing film. Enhanced plasma activation is expected to increase the availability of reactive nitrogen species, facilitating nitrogen incorporation into the growing film. This domain is characterized by:

- Enhanced nitridation with improved nitrogen incorporation.
- Higher crystallinity with dense columnar morphology.
- Improved charge carrier transport and reduced recombination.
- Bandgap tuning to the visible-light range.

Several of the highest-performing studies were associated with this domain [21,42,43], suggesting that balanced plasma activation may favor the simultaneous optimization of nitridation, crystallinity, and charge transport. Optimized conditions were generally associated with higher photocurrent densities and improved stability, outperforming both lower-power and higher-power conditions.

Higher-Power Domain

At excessive plasma powers, ion energies exceed thresholds for controlled nitridation. The dominant processes shift from substitutional incorporation to detrimental effects, including:

- Resputtering of deposited material, introducing surface roughness.
- Formation of metallic nitride phases rather than oxynitrides.
- Defect generation through energetic ion bombardment and lattice damage.
- Surface heating promoting nitrogen desorption, counteracting incorporation.

Studies in this domain [20] (with exceptional stability via in situ passivation) demonstrate that while higher power can achieve narrow bandgaps, performance gains are often offset by defect-induced recombination. The domain represents a trade-off where performance outcomes become increasingly dependent on defect management and surface passivation strategies beyond the intermediate domain. Table 4 summarizes the characteristics of each operating domain.

Importantly, these domains should not be interpreted as fixed processing windows applicable to all plasma systems. Rather, they represent generalized mechanistic tendencies emerging from the reviewed literature. The exact transition between domains depends on reactor configuration, plasma chemistry, substrate temperature, pressure, and deposition methodology.

The framework in Figure 4 illustrates the cascade from application requirements through plasma regime selection, qualitative process guidance, and expected outcomes based on the synthesized evidence from 30 studies. The intermediate-power domain was associated with balanced performance across multiple metrics in most of the studies

reviewed here. This framework is intended as a conceptual guide rather than a universal prescription, as plasma chemistry, reactor geometry, and material composition influence the precise boundaries between domains and the optimal processing conditions. Because the three-domain classification is derived from only 30 studies, it should be regarded as a preliminary, testable hypothesis rather than an established result; the addition of further studies, particularly at the low- and high-power extremes that are currently under-represented in the corpus, could shift the proposed domain boundaries.

Table 4. Emerging plasma operating domains for oxynitride thin film synthesis: dominant mechanisms, film characteristics, and PEC performance.

Domain	Dominant Mechanism	Film Characteristics	Typical PEC Performance	Representative Studies
Lower-Power	Limited dissociation; incomplete nitridation	Lower nitrogen incorporation; reduced crystallinity; wider bandgap	Lower photocurrent density; moderate stability	[21,23,43]
Intermediate-Power	Enhanced dissociation; substitutional nitridation	Improved nitrogen incorporation; higher crystallinity; tunable bandgap (visible range)	Higher photocurrent density (2.5–4.0 mA cm ^{−2}); >90% stability	[20,31,32,35,41,42]
Higher-Power	Resputtering; defect generation; phase transitions	Metallic nitride formation; surface roughness; excess defects	Reduced or saturated photocurrent; stability compromised	[20,28,59]

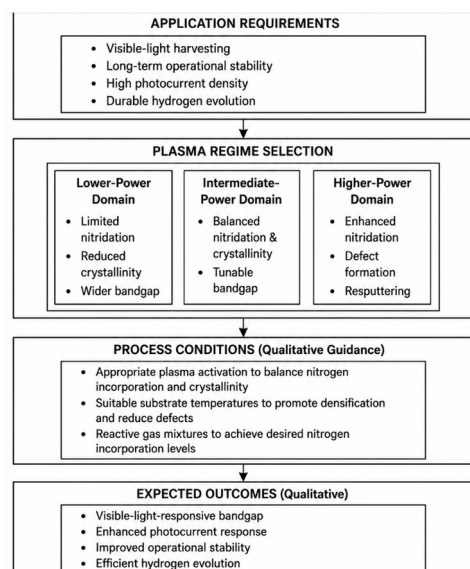


Figure 4. Conceptual framework for plasma-assisted oxynitride optimization.

To assess the robustness of this classification, a sensitivity check was performed by restricting the corpus to the 4 studies rated high confidence in Table 7 (out of 30 scored studies, alongside 14 moderate- and 12 low-confidence sources). Under this restriction, the qualitative ordering of the three domains is preserved: the available evidence suggests that the transition from insufficient to substitutional nitrogen incorporation, and the further transition toward defect-dominated, metallic-nitride-favoring conditions at higher power, both remain directionally consistent. However, the specific numerical boundaries

separating the domains are considerably less well constrained under this restriction, since several of the observations supporting the higher-power domain in particular come from moderate- or low-confidence sources; excluding these leaves the higher-power boundary anchored by very few studies. This indicates that the lower- and intermediate-domain boundaries are comparatively stable to the inclusion or exclusion of lower-confidence evidence, while the higher-power boundary is the most sensitive and should be interpreted with corresponding caution. Because the reviewed literature is unevenly distributed across the power range, with limited representation at the low- and high-power extremes, the addition of further studies is expected to refine the precise numerical boundaries rather than overturn the qualitative three-domain structure. On this basis, the observed trend across the available evidence is treated as a preliminary framework rather than a definitive, universally applicable model.

3.3.2. Evolution of Plasma Synthesis Strategies

The examined publications indicate a shift to the use of plasma-assisted synthesis (as compared to thermally driven nitridation) after 2018. Techniques based on plasma have taken over due to the ability to control more finely the amount of nitrogen insertion and growth of the films at lower temperatures, like RF sputtering, PECVD, and microwave plasma nitridation.

Xiao et al. (2023) used plasma-assisted MOCVD to achieve record-breaking stability of over 3000 h of operation in a GaN:ZnO/oxynitride heterostructure (Figure 5), while Streibel et al. (2024) used RF sputtering to tune the bandgap of ZrON to 2.3 eV [20,21]. Both experiments demonstrate that the rate of precursor dissociation using plasma activation is faster, leading to increased reactivity and nitrogen-rich films with increased density despite moderate substrate temperatures (approximately 400 °C). A similar plasma-driven densification strategy is evident in the Ta₃N₅ photoanode literature: Higashi et al. used high-power RF sputtering with NH₃ nitridation to achieve semitransparent, self-conductive Ta₃N₅ films, while Zhong et al. combined sputtering–nitridation with a GaN stabilizing layer, and Wang et al. demonstrated a thin-film transfer route with an NbN_x back contact—together illustrating the range of sputtering-based strategies used to control Ta₃N₅ film density, conductivity, and interfacial quality [36,38,39].

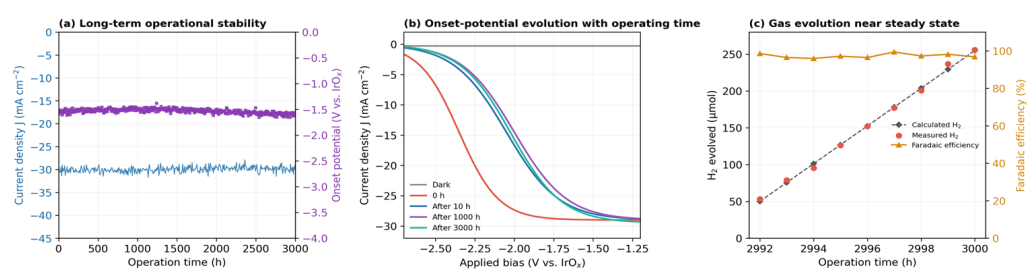


Figure 5. (a) Long-term photocurrent stability, (b) onset-potential evolution, and (c) gas-evolution characteristics of an oxynitride photoanode under continuous operation, redrawn from the reported findings to illustrate the observed trends (original illustration).

Throughout the corpus, plasma power density was identified as a factor that determined stoichiometric balance. At excessive plasma power (e.g., above roughly 350 W in this corpus), metallic nitrides (e.g., TiN, TaN) and carrier-trapping defects form instead of substitutional nitrogen incorporation (i.e., N replacing O sites), whereas at insufficiently low power, nitrogen sites remain incompletely filled and carrier generation is reduced. The literature on reactive PLD and PECVD [41,46] also demonstrates that the partial pressure of nitrogen in the plasma has a direct impact on the valence-band edge by creating N 2p–O 2p hybrid states, which are responsible for the absorption of light in the visible range.

The most commonly used method was RF magnetron sputtering, which provided good control of film density and stoichiometry by varying the RF power (100–400 W) and N_2/O_2 ratio. The pulsed DC sputtering technique (e.g., Streibel et al.), however, allowed for achieving higher deposition rates without significant arcing, resulting in ZrON films with more uniform nitrogen distribution [21]. PECVD and microwave plasma methods preferred higher N incorporation at lower substrate temperatures; sometimes, higher defect densities were obtained.

Plasma parameters show a clear correlation with film stoichiometry, as obtained by XPS, being higher from ~0.3 to ~0.8 when the RF power is increased from 100 to 300 W, thus obtaining a narrower bandgap (~0.3 to ~0.5 eV), but still crystallinity > 80%. Very high powers (>350 W) can result in the formation of metallic nitride phases or in an increase in oxygen vacancies.

3.3.3. Structure–Activity Correlations Across the Broader Oxynitride Photoelectrode Literature

The evidence assembled in this review supports a single connected mechanistic chain rather than a set of independent observations: plasma parameters (power, gas composition, pressure) determine the population of reactive species at the plasma–surface interface (ions, radicals, energetic neutrals), which in turn governs the extent and mode of nitrogen incorporation and the resulting point-defect density in the growing film. This defect and nitrogen-incorporation state directly sets the film’s structural and electronic properties—crystallinity, valence-band hybridization, and optical bandgap—which govern the efficiency of charge-carrier generation and transport, and ultimately determine the film’s PEC activity and long-term operational stability. Each subsequent argument in this review, including the broader-literature correlations discussed below, is interpreted against this same causal sequence rather than as a standalone finding.

Situating the present plasma-focused corpus within the wider oxynitride photoelectrode literature strengthens the mechanistic case for the process–property–performance framework proposed in Sections 3.3 and 3.4. Studies on non-plasma-processed oxynitride photoanodes converge on the same two structure–activity levers identified here for plasma-engineered films: (i) point-defect and dopant control within the semiconductor bulk, and (ii) interfacial/cocatalyst engineering at the semiconductor–electrolyte junction. Gradient Mg-doping of Ta_3N_5 , for example, reshapes the internal band-edge energetics to accelerate charge separation rather than simply passivating surface states [27], and heterogeneous doping strategies have been shown to decouple light absorption from carrier transport in Ta_3N_5 thin-film photoanodes, allowing each property to be optimized semi-independently [60]. These findings parallel the defect-density and nitrogen-incorporation trends identified for the plasma-processed films reviewed here (Section 3.3.1), reinforcing that the intermediate-defect-density regime favored by moderate plasma energies is not an artifact specific to plasma processing but reflects a more general structure–activity principle across oxynitride photoelectrodes.

At the interface, cocatalyst and surface-modification strategies developed for other oxynitride photoanodes offer a complementary, post-synthesis route to the performance gains this review attributes to bulk plasma engineering. A $BaTaO_2N$ photoanode decorated with CoO microflowers achieved near-unity Faradaic efficiency for oxygen evolution by kinetically protecting the oxynitride surface against photocorrosion, extending operational stability without altering the underlying film synthesis [61]. Interfacial modification of Ta_3N_5 photoanodes with hole-storage layers and mixed-metal-oxide cocatalysts has similarly been shown to suppress interfacial recombination and improve charge-transfer efficiency largely independently of how the underlying film was deposited [62]. More broadly, interfacial d-band-center modulation, demonstrated for Si–Ir coupled systems, has

been shown to markedly improve both activity and durability under the more demanding acidic conditions relevant to some water-splitting configurations, underscoring that judicious interface engineering can extend a photoelectrode's operating window without modifying the underlying light-absorbing film [63]. Considered alongside the plasma-parameter thresholds discussed in Section 3.3.1, this suggests that the highest-performing oxynitride photoelectrodes are likely to combine plasma-optimized bulk defect density with dedicated interfacial engineering, rather than relying on either strategy alone; this combined approach is currently under-represented within the plasma-specific literature reviewed here and is highlighted as a priority direction in Section 5.

3.4. Quantitative Analysis of Process–Property Relationships

Oxynitride thin-film synthesis via plasma-based methods exhibits several quantitative and qualitative patterns across the reviewed literature. The relationship among plasma parameters, structural evolution in the material, and resulting performance indicators is presented in Figure 6 and comprises the thematic framework of the current analysis.

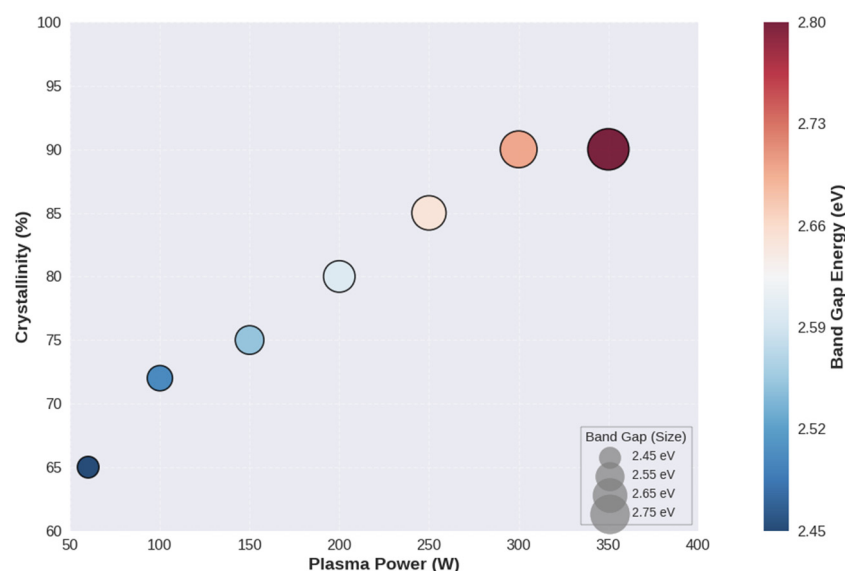


Figure 6. Relationship between plasma parameters, material structural evolution, and the resultant performance indicators.

The relationship between plasma power, crystallinity, and bandgap reflects the interplay of competing mechanisms. At lower plasma powers, ion energy is generally expected to be limited (inferred from reported power settings rather than measured directly across the corpus), likely insufficient to overcome surface diffusion barriers. Adatoms occupy metastable positions, resulting in amorphous or nanocrystalline structures with higher defect densities and wider bandgaps. As power increases, ion bombardment provides the activation energy required for adatom migration to thermodynamically favorable lattice sites. The resulting densification and grain growth reduce grain boundary scattering, enhance carrier mobility, and facilitate substitutional nitrogen incorporation. This substitutional incorporation raises the valence band maximum through N 2p–O 2p hybridization, narrowing the bandgap to the visible-light range. Studies operating in the moderate power range generally report enhanced crystallinity, reduced defect densities, and optimized bandgap values compared to lower or higher power conditions, although the magnitude of these gains varies across the reviewed studies.

However, the simultaneous improvement in crystallinity and bandgap narrowing does not continue indefinitely. At excessive plasma powers, energetic ion bombardment induces collision cascades that generate lattice disorder and oxygen vacancies. The accumulation of

point defects introduces mid-gap states, which manifest as band tailing. This degradation mechanism explains the saturation and subsequent decline in optical quality observed at the highest power conditions, where performance becomes dominated by defect-induced recombination rather than structural ordering.

Plasma power, gas composition, and substrate temperature were found to be closely interrelated, jointly influencing nitrogen incorporation efficiency and film crystallinity. Studies employing RF plasma sputtering and PECVD generally reported optimized nitrogen replacement of between 250 and 350 W on N_2/O_2 or NH_3/Ar gases. Multiple studies reported that increased plasma activation enhanced nitridation depth and visible-light absorption through greater nitrogen incorporation. These effects were generally associated with narrower optical bandgaps and improved photoelectrochemical performance, although the magnitude of the response varied according to plasma configuration, material composition, and processing conditions.

Process–property relationships identified across the reviewed literature show that plasma acts as an active chemical mediator: partial reduction of the metal cation (e.g., $Ti^{4+} \rightarrow Ti^{3+}$) and controlled replacement of oxygen by nitrogen are both directly associated with changes in electronic band alignment. The following (Figure 7) is a complement of this and demonstrates a parameter–performance correlation, where moderate plasma power yields higher crystallinity and photocurrent density, whereas excessive power causes surface damage and over-incorporation of nitrogen.

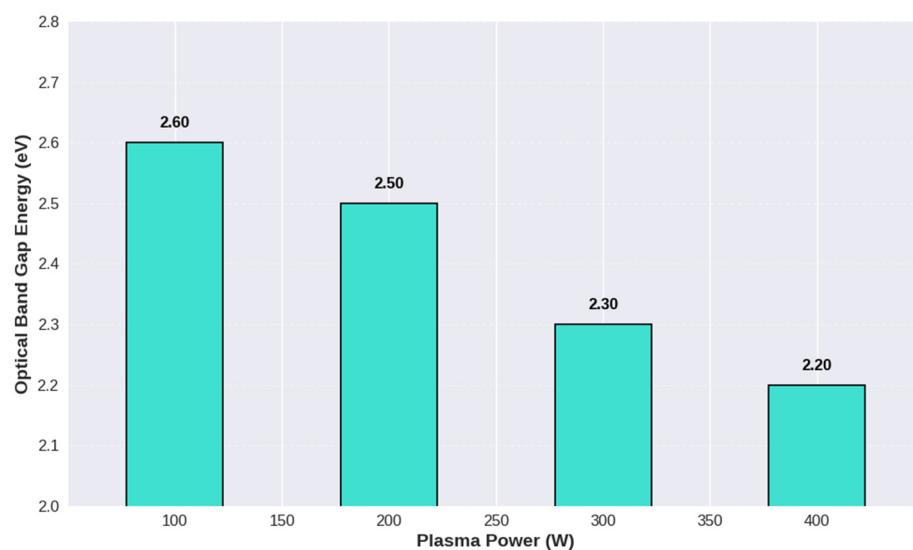


Figure 7. Effect of plasma power on optimal bandgap energy.

Moreover, most RF sputtering and PECVD research findings indicated that the best crystalline deposition was attained at a substrate temperature of 400–500 °C with fewer oxygen vacancies and stable perovskites like $LaTiO_2N$ and $SrTaO_2N$ [29,32,41,42]. Conversely, low temperatures (below 350 °C) gave amorphous or mixed-phase oxynitrides that had low conductivity and low photocatalytic activity.

The most commonly used method was RF magnetron sputtering, which enabled good control of film density and stoichiometry through variation in RF power (100–400 W) and N_2/O_2 ratio. Pulsed DC sputtering (e.g., Streibel et al.) allowed for higher deposition rates and reduced arcing, resulting in more even nitrogen distribution in ZrON [21]. PECVD and microwave plasma methods favored higher nitrogen incorporation at lower substrate temperatures, though sometimes at the cost of higher defect density.

Plasma processing parameters were generally found to influence film stoichiometry and nitrogen incorporation across most of the reviewed studies. Studies employing higher

plasma activation generally reported increased nitrogen incorporation, narrower optical bandgaps, and improved crystallinity. However, the exact magnitude of these effects varied substantially among plasma systems and material compositions, emphasizing the importance of considering reactor-specific conditions rather than relying on universal scaling relationships. Metallic nitride phases or higher oxygen vacancies are often formed when the power is too high (>350 W).

Reported STH values varied considerably across studies depending on experimental conditions (such as 1-sun versus concentrated sunlight, electrolyte pH of 7–13, and the use or absence of sacrificial agents). Most studies reported photocurrent density at 1.23 V rather than full STH. The only way to compare these studies directly was to normalize reported values to AM 1.5G illumination and consistent bias conditions. All plasma-engineered film samples generally performed better than their thermal counterparts under similar testing conditions, and standardized testing procedures are urgently needed to enable reliable meta-analyses.

3.5. Influence of Plasma Parameters on Structural and Optical Properties

Figure 7 and Table 5 reveal an inverse correlation between plasma power and optical bandgap, reflecting the dominant role of nitrogen incorporation in modifying the electronic structure. At lower powers, reactive nitrogen species are primarily molecular ions with limited reactivity, resulting in lower nitrogen incorporation. The valence band maximum remains predominantly O 2p character, preserving wider bandgaps. As power increases, electron impact dissociation of nitrogen-containing precursor gases generates atomic nitrogen radicals that substitute into oxygen lattice sites. Each substitutional nitrogen contributes N 2p states at energies higher than O 2p, progressively raising the valence band maximum and narrowing the bandgap. Concurrently, the increased ion flux enhances adatom mobility, promoting densification and the transition from porous to columnar morphologies. However, at excessive powers, the formation of metallic nitride phases and the introduction of oxygen vacancies create band tailing effects that can broaden the apparent bandgap despite continued nitrogen incorporation. Several studies suggest that intermediate plasma activation conditions frequently provide a favorable balance between bandgap reduction and structural quality [20,21,34,35,46,47].

Table 5. The representative influence of plasma parameters on key material properties across several studies.

Plasma Process	Power (W)	Deposition Temp (°C)	Crystallite Size (nm)	Bandgap (eV)	Surface Morphology
PECVD (Low Power)	100	350	25	2.65	Porous, irregular grains
PECVD (Medium)	200	400	45	2.50	Compact, uniform grains
RF Sputtering (High Power)	400	450	75	2.30	Dense columnar texture
MPAN (Optimized)	300	400	60	2.25	Smooth, oriented grains

Directly analogous power-bandgap tuning has been reported for other plasma-processed oxynitride and nitrogen-doped oxide systems: reactive HiPIMS synthesis of $\text{ZrO}_{2-x}\text{N}_x$ showed the bandgap narrowing from 3.43 to 2.20 eV as pulsing frequency increased, while reactive sputtering of heavily nitrogen-doped TiO_2 showed a comparable narrowing effect with nitrogen incorporation, together supporting the generality

of the nitrogen-incorporation mechanism described above across multiple host oxide lattices [55,58].

3.6. Impact on Photoelectrochemical Hydrogen Generation

Figure 8 demonstrates that photocurrent density increases with plasma power, reaching saturation at higher power conditions. This behavior reflects the coupling of several factors. First, bandgap reduction expands the absorption range from primarily ultraviolet to visible wavelengths, increasing the fraction of solar photons available for carrier generation. Second, improvement in crystallinity reduces grain boundary recombination, extending minority carrier lifetimes. Third, enhanced nitrogen incorporation introduces shallow acceptor states that improve hole conductivity and reduce surface recombination velocity. The combination of these effects explains the observed increase in photocurrent with increasing plasma power, which is consistent with findings reported across multiple studies [20,21,35,43].

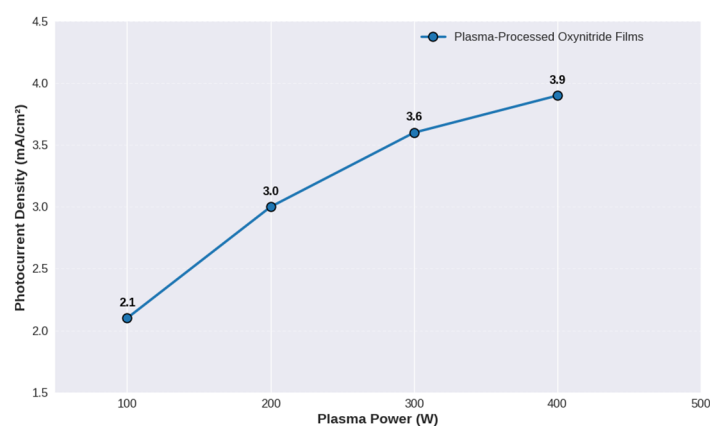


Figure 8. Effect of plasma power on photocurrent density.

Quantitatively, Ta₃N₅ photoanode studies in this corpus report photocurrent densities spanning approximately 3.5 to 8.1 mA cm^{−2} at 1.23 V, depending on the specific sputtering or PECVD conditions and post-deposition treatment used [53,56,60,61], consistent with the power-dependent trend described above. A related PECVD-based study combining Mg:GaN modification with Ta₃N₅ similarly found that the post-deposition annealing atmosphere (N₂ versus NH₃) strongly affected the trade-off between onset-potential improvement and retained photocurrent, underscoring that post-synthesis treatment, not only in situ plasma power, shapes final device performance [52].

However, the saturation and potential decline beyond certain power levels arise from the accumulation of recombination centers. While nitrogen incorporation continues, the simultaneous generation of oxygen vacancies and interstitials introduces mid-gap states that serve as recombination centers. The balance between beneficial nitrogen doping and detrimental defect generation shifts at higher power conditions. This trade-off is reflected in the photocurrent density reaching a plateau, with further power increases producing diminished returns or performance degradation. Studies indicate that intermediate power conditions, typically associated with moderate plasma activation, provide the optimal balance for maximizing photocurrent density while minimizing defect-induced losses [20,47].

3.7. Comparative Analysis: Plasma vs. Non-Plasma Routes

Figure 9 and Table 6 indicate that plasma-assisted synthesis frequently produces oxynitride thin films with superior structural, optical, and photoelectrochemical characteristics compared with conventional thermal processing routes. Across the reviewed studies,

plasma processing was commonly associated with enhanced crystallinity, narrower visible-light-responsive bandgaps, improved photocurrent generation, higher hydrogen evolution activity, and greater operational stability.

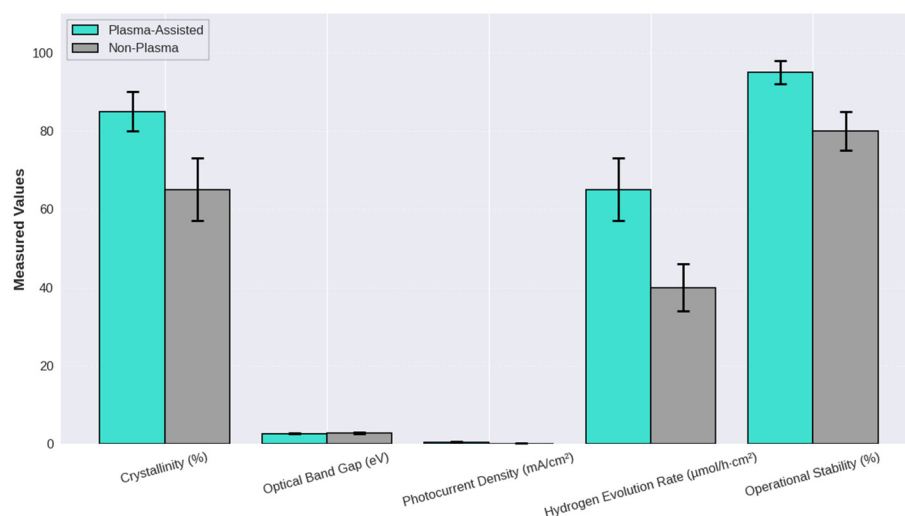


Figure 9. Comparative performance trends of plasma-assisted versus thermally synthesized oxynitride thin films.

Table 6. Qualitative comparison of typical performance characteristics reported for plasma-assisted versus thermally synthesized oxynitride thin films.

Property	Plasma-Assisted Films	Thermally Synthesized Films
Crystallinity	Generally higher	Generally lower
Optical Bandgap	Typically narrower	Typically wider
Photocurrent Density	Typically higher	Typically lower
Hydrogen Evolution Rate	Typically higher	Typically lower
Operational Stability	Typically higher	Typically lower

Note: The qualitative trends shown are based on the reviewed studies. Actual performance varies with material composition, plasma conditions, and testing protocols.

These advantages are attributed primarily to the unique capabilities of plasma environments, including the generation of highly reactive nitrogen species, enhanced surface activation, controlled ion bombardment, and the ability to promote crystallization at reduced processing temperatures. Such effects facilitate nitrogen incorporation, improve film densification, reduce undesirable defect formation, and enhance charge-carrier transport properties.

Studies by Xiao et al., Streibel et al., Lawley et al., and Pichler et al. [20,21,31,32], and other plasma-assisted investigations generally reported improvements in one or more performance metrics relative to comparable non-plasma approaches. However, the magnitude of improvement varied substantially among studies because of differences in material composition, reactor configuration, plasma source design, substrate temperature, and testing methodology.

Consequently, plasma-assisted synthesis should not be viewed as a universally superior processing route under all conditions. Rather, the available evidence suggests that its effectiveness depends on achieving an appropriate balance between nitrogen incorporation, crystallinity development, and defect control. This balance ultimately governs the photoelectrochemical performance and long-term stability of oxynitride photoelectrodes.

The figure illustrates consistent trends observed across the reviewed studies, with plasma-assisted films generally exhibiting higher crystallinity, narrower bandgaps, higher photocurrent densities, and improved stability. Error bars indicate variability across the reviewed studies.

Long-Term Stability and Degradation Mechanisms

One of the main challenges for oxynitride thin films is long-term operational stability in aqueous electrolyte. The results of the different studies reviewed indicated that the thermal stability of plasma-engineered films was generally higher than that of their thermally prepared counterparts. The record of >3000 h operation of the plasma-assisted MOCVD GaN: ZnO/oxynitride heterostructure was reported by Xiao et al. (2023), due to defect passivation and nitrogen uniformity [20].

The following are common mechanisms of degradation reported:
Nitrogen loss (photocorrosion) during extended exposure to light, particularly when exposed in alkaline conditions.

- Creation of surface oxygen vacancies or amorphous layers.
- Poor adhesion at high plasma powers (delamination).

A representative illustration of the nitrogen-loss degradation mechanism is provided by a sputtered Ta₃N₅ photoanode, which exhibited an approximately 10-fold photocurrent decay with a stability half-life of only 1.2–2.3 min under continuous illumination; loading the surface with an IrO₂ co-catalyst suppressed this self-oxidation and substantially extended the operational half-life, consistent with the passivation-based mitigation strategies discussed below [51].

These are addressed by plasma-assisted methods by reducing the processing temperature and performing in situ surface passivation. However, most of the studies performed stability testing for less than 100 h. Further research should be directed toward the development of standard accelerated stability testing procedures and towards realistic operating conditions (such as intermittent illumination and neutral pH).

3.8. Evidence Reliability Assessment

The evidence reliability framework introduced in Section 2.6 was applied to all 30 included studies. Table 7 presents the assessment results for each study.

Table 7. Evidence reliability assessment of included studies across five weighted criteria (plasma diagnostics 25%, thin-film characterization 25%, PEC testing robustness 20%, stability assessment 15%, reproducibility 15%).

Ref	Author	Year	Plasma Diag	Charac	PEC Test	Stability	Repro	Confidence
[20]	Xiao	2023	2	3	3	3	2	High
[21]	Streibel	2024	2	2	3	2	2	Moderate
[41]	Pergolesi	2022	1	3	2	1	2	Moderate
[31]	Pichler	2017	1	3	2	1	2	Moderate
[32]	Lawley	2023	1	2	2	1	2	Low
[42]	Amer	2023	1	2	3	1	2	Moderate
[29]	Werner	2024	1	2	2	2	1	Low
[34]	Hojamberdiev	2022	1	3	3	1	2	Moderate

Table 7. *Cont.*

Ref	Author	Year	Plasma Diag	Charac	PEC Test	Stability	Repro	Confidence
[33]	Chen	2015	3	1	1	1	2	Low
[43]	Dong	2021	1	2	2	1	1	Low
[46]	Haydous	2020	1	2	2	1	2	Low
[47]	Le Paven	2020	2	2	3	1	2	Moderate
[22]	Lawley	2020	3	3	3	1	3	High
[48]	Pisarek	2023	2	2	2	1	1	Low
[23]	Haydous	2021	3	3	3	1	2	High
[50]	Cristea	2023	2	1	1	2	1	Low
[49]	Pleskunov	2021	1	2	1	1	1	Low
[36]	Higashi	2022	2	3	3	2	1	Moderate
[51]	Yokoyama	2011	2	2	2	1	1	Low
[37]	Higashi	2023	2	3	3	1	1	Moderate
[38]	Zhong	2017	2	3	3	3	1	High
[52]	Nurlaela	2018	2	3	3	1	1	Moderate
[53]	Cristea	2022	3	3	1	1	1	Moderate
[54]	Li	2021	2	3	1	1	1	Low
[39]	Wang	2016	2	3	3	1	2	Moderate
[40]	Nurlaela	2020	2	3	3	1	1	Moderate
[55]	Matei	2023	3	3	1	1	1	Moderate
[56]	Cristea	2019	3	3	1	1	1	Moderate
[57]	Mohamed	2020	2	2	2	1	1	Low
[58]	Li & Shang	2010	2	2	1	1	2	Low

3.8.1. Confidence Classification

Based on the weighted scoring framework, studies were classified as high, moderate, or low confidence. Moderate-confidence studies form the largest group (46.7%, 14 of 30 scored studies), followed by low-confidence studies (40%, 12 of 30); together, these account for the large majority of the corpus. Moderate-confidence studies typically show adequate characterization and PEC testing but incomplete plasma diagnostics or limited stability data, while low-confidence studies exhibit more substantial reporting limitations. Only a smaller subset (13.3%, 4 of 30) demonstrate exceptionally comprehensive reporting sufficient for High confidence.

3.8.2. High-Confidence Studies

Studies in this category provide comprehensive characterization (XRD, XPS, TEM, AFM, UV-Vis, EIS), standardized PEC testing (AM 1.5G with controls), and extended stability data (>100 h with degradation analysis). These studies are prioritized in quantitative synthesis.

3.8.3. Moderate-Confidence Studies

Studies in this category generally provide adequate characterization and PEC testing but may lack comprehensive plasma diagnostics (reporting power and pressure but not ion

energy or density), stability testing of limited duration (24–100 h), or detailed error analysis. Moderate-confidence studies are retained in the quantitative synthesis but assigned lower evidential weight during interpretation.

3.8.4. Low-Confidence Studies

Studies in this category include review articles (which are not experimental and therefore score low on plasma diagnostics criteria), mechanistic studies lacking PEC data, supporting studies using non-plasma processes, and studies with incomplete reporting. For example, several plasma-sputtered oxynitride/nitride studies in this corpus provide strong compositional and structural characterization (RBS, GIXRD, XPS) but report mechanical, optical, or photocatalytic dye-degradation performance rather than PEC-specific electrochemical testing, and are scored low confidence on that basis despite the rigor of their materials characterization [53,54,56,57]. Low-confidence studies are retained in the analysis but assigned the lowest evidential weight. Their findings are used only to support qualitative trends that are independently confirmed by higher-confidence studies.

3.8.5. Implications for Interpretation

Unlike conventional literature aggregation approaches, the present framework explicitly differentiates evidence quality and reporting completeness, ensuring that conclusions are informed primarily by the most reliable studies rather than treating all studies as equivalent sources of evidence. This directly addresses the need for critical evaluation of individual plasma publications, as emphasized in recent editorial assessments of the field.

Consequently, findings from high-confidence studies were prioritized when interpreting process–property–performance relationships, while moderate- and low-confidence studies were used primarily to support broader qualitative trends.

3.9. Research Contradictions and Evidence Gaps

The synthesis of 30 studies reveals several unresolved contradictions that highlight critical gaps in current understanding. These contradictions represent opportunities for future research and underscore the need for standardized methodologies.

3.9.1. Contradiction 1: Plasma Power vs. Performance Trade-Off

Multiple studies identify an optimum power range for PEC performance [20,21,47], but the exact position of this optimum varies significantly. Xiao et al. report optimal performance at relatively higher power with exceptional stability [20], while Streibel et al. [21] observe degradation above lower thresholds. This discrepancy likely arises from differences in reactor geometry, plasma source design, and substrate temperature, which influence ion energy distributions independently of applied power. The absence of systematic ion energy measurements across studies prevents the determination of whether power or ion energy is the fundamental control parameter.

3.9.2. Contradiction 2: Nitrogen Incorporation vs. Defect Formation

Several studies employing PECVD and microwave plasma approaches report enhanced nitrogen incorporation at relatively lower substrate temperatures [35,44,46], whereas sputtering-based studies often require different processing conditions to achieve comparable compositions. However, these methods are also associated with higher defect densities and reduced crystallinity in some reports [43,45]. The underlying mechanism, whether the apparent advantage of one technique outweighs the disadvantages of another, remains unclear without systematic comparative studies conducted under identical plasma diagnostics and characterization protocols.

3.9.3. Contradiction 3: Plasma Technique vs. Film Quality

Different plasma techniques (PECVD, sputtering, microwave plasma, and plasma-assisted laser routes) frequently produce different balances between nitrogen incorporation, crystallinity, and defect density. However, direct comparisons remain difficult because plasma diagnostics and characterization protocols vary substantially among studies, making it unclear whether observed differences arise from the technique itself or from variations in processing conditions and reporting practices.

3.9.4. Contradiction 4: Stability Reporting Inconsistency

Stability testing duration ranges from 10 h to 3000 h [20], with no standardized protocol for illumination cycling, electrolyte composition, or failure criteria. This variation prevents meaningful comparison across studies and makes it difficult to identify degradation mechanisms. While exceptional 3000 h stability has been reported [20], most studies report only 10–100 h, raising questions about the representativeness of short-term tests for practical applications.

Collectively, these contradictions and evidence gaps indicate that plasma power alone cannot be considered a universal predictor of oxynitride photoelectrode performance. Instead, performance emerges from the interaction of plasma conditions, reactor configuration, film composition, defect chemistry, and testing methodology. Future studies should therefore prioritize standardized plasma diagnostics, harmonized PEC testing protocols, and comprehensive reporting of plasma–material interaction parameters. Such efforts will facilitate more reliable cross-study comparisons and support the future development of robust predictive process–property–performance models for plasma-engineered oxynitride photoelectrodes.

3.10. Limitations of the Current Evidence Base

The evidence base is constrained by several significant limitations that affect the interpretation and generalizability of findings:

Inconsistent Plasma Diagnostics: While all studies report power, fewer than half report ion energy, radical flux, or electron density. This limits the development of quantitative process–structure relationships and prevents direct comparison across different plasma systems.

Different PEC Testing Protocols: Variations in illumination conditions (AM 1.5G vs. other sources), electrolyte composition (pH 7–13), and electrode configurations hinder cross-study comparison of photocurrent densities and stability metrics.

Limited Long-Term Stability Testing: The majority of studies report stability testing of less than 100 h, with only one study [20] exceeding 1000 h. This is insufficient for assessing practical applicability where operational lifetimes of thousands of hours are required.

Ex Situ Characterization: Most studies characterize films after deposition rather than during growth, missing transient phenomena that may control film properties. In situ diagnostics could reveal the evolution of nitrogen incorporation and defect formation during plasma processing.

Limited Realistic Operating Conditions: Only one study [20] reports performance under conditions approaching practical operation (neutral pH, intermittent illumination, two-electrode configuration). Laboratory testing under idealized conditions may not translate to real-world performance.

4. Discussion

This systematic review of oxynitride thin films synthesized via plasma-assisted methods for photoelectrochemical hydrogen generation shows substantial improvement over

traditional thermal or chemical synthesis routes in terms of structural organization and functional performance. The reviewed literature shows that plasma-based methods, such as RF sputtering, PECVD, microwave plasma nitridation, and plasma-assisted MOCVD, offer good control over nitrogen incorporation, crystallinity, and defect concentration, which directly translate into high photocurrent densities, low bandgap, and high operational stability. This tendency is especially prominent in the works carried out since 2018, which implies an increased interest in research on the use of plasma activation to generate hydrogen in a sustainable way. Studies employing intermediate plasma activation conditions, typically associated with appropriate substrate temperatures reported in the reviewed studies, were generally associated with high crystallinity, narrow optical bandgaps, and dense, oriented microstructures, which promote efficient absorption of visible light and reduce charge recombination [20,21,29,31–35,41,43–48,50]. The presented enhancements in photoelectrochemical activity underscore the importance of plasma-based partial reduction of metal cations and substitutional incorporation of nitrogen in regulating the electronic band structure and charge-carrier generation and transport.

A key contribution of the present work is that it moves beyond simple performance comparison by integrating evidence from multiple studies into a mechanistic process–property–performance framework and a structured evidence reliability assessment. This approach enables interpretation of why specific plasma conditions influence PEC performance rather than merely documenting that such relationships exist.

Comparison with the earlier literature shows that plasma-assisted methods have transformative potential. Earlier studies were mostly based on thermally assisted nitridation or chemical doping, which led to lower crystallinity, wider bandgaps, and lower photocurrent densities; plasma-based films generally outperform non-plasma-based films across a range of indicators [28,59]. Specifically, the improved crystallinity, optical absorption, and photocurrent density indicate that plasma activation not only enhances precursor dissociation and nitrogen incorporation but also suppresses defect formation, producing more photocorrosion-resistant surfaces. These results build on earlier reviews, which emphasized qualitative correlations between film structure and PEC efficiency, by providing quantitative data on the optimal plasma processing windows to balance the crystallinity, nitrogen substitution, and bandgap tuning. Additionally, the development of heterostructured and hybrid oxynitride materials, including GaN: ZnO/LaTiO₂N and LaTiO₂N/TiN, illustrates how interfacial engineering can be combined with plasma-mediated strategies to simultaneously boost charge separation, electrical conductivity, and stability, offering a significant advance in materials design for solar water splitting [5,20,21,32,33,35,44,47,50]. All 30 core studies in Table 3 are plasma-processed by inclusion criteria, so no non-plasma subset exists within that corpus itself. The general drawbacks of traditional non-plasma synthesis routes (thermal ammonolysis, solid-state nitridation) are discussed qualitatively in the Introduction with reference to the broader materials-synthesis literature (e.g., refs. [12,13]); these sources support the general claim that such routes tend to require high temperatures and yield lower crystallinity, but they report different material systems and testing protocols than the plasma-processed corpus and are not the source of matched, study-by-study performance data. No directly matched quantitative comparison under identical testing conditions was possible between plasma- and non-plasma-synthesized oxynitride films; accordingly, Figure 9 and Table 6 present a schematic, illustrative comparison reflecting generally reported directional trends in the wider literature (consistent with the qualitative “typically higher/lower” framing in Table 6), rather than a quantitative meta-analysis of specific matched studies.

Another aspect that has been brought to the fore by the review is the ability of plasma-assisted methods to deliver long-term operational stability. Exemplary stability has been

reported in some studies, including more than 3000 h in GaN:ZnO heterostructures, indicating that plasma techniques enable levels of surface passivation and defect control not readily achievable with traditional thermal techniques [20].

The performance improvement, in conjunction with the studies, all indicate that plasma is an effective chemical mediator that affects the bulk and surface characteristics via controlled cation reduction, nitrogen incorporation, and defect passivation [28,59,64]. These mechanistic perspectives contribute to the understanding of plasma–surface interactions and their immediate effects on the photoelectrochemical response, and this is an area of the literature that has frequently left the link between plasma-generated species (ions, radicals, and energetic neutrals) and the resulting surface chemistry as an insufficiently resolved mechanistic pathway, rather than characterizing this plasma–surface interaction step explicitly.

The synthesized evidence suggests several considerations for optimizing plasma-engineered oxynitride photoelectrodes. The reviewed literature indicates that intermediate plasma activation conditions are frequently associated with improved balances between nitrogen incorporation, crystallinity, and PEC performance. The evidence also suggests that appropriate substrate temperature selection is important for balancing crystallinity, nitrogen incorporation, and defect formation, though the optimal processing window remains dependent on plasma configuration, material composition, and reactor design. Similarly, reactive gas mixtures can be tuned to influence nitrogen incorporation levels, though the optimal ratio depends on the specific plasma system and material system. These observations are intended as qualitative guidance rather than universal prescriptions, as the exact processing windows depend on reactor configuration, plasma source design, and deposition methodology.

Although these are good results, the contemporary literature has some limitations. Numerous studies rely on short-term laboratory testing, often under idealized illumination and pH conditions, which prevents direct extrapolation to real-world, large-scale solar hydrogen applications. Inconsistency in reporting plasma parameters, e.g., ion energy, gas composition, and deposition time, limits reproducibility and cross-comparison across studies. Moreover, high-performance systems are capable of demonstrating impressive photocurrent and stability; however, they frequently use complicated or expensive methods of deposition, which can be barriers to scalability. These limitations emphasize the need to improve experimental reporting and test scalable plasma deposition plans and to test operational stability under realistic environmental conditions in the future.

Looking ahead, combining plasma-assisted synthesis with heterostructured designs and co-catalyst incorporation holds even greater potential to improve the efficiency of charge separation, the kinetics of oxygen evolution, and the overall efficiency of hydrogen generation. Computational modeling and machine learning could be paired with in situ characterization to offer predictive control of the plasma parameters, allowing the rational design of oxynitride films with optimal structural and electronic characteristics. This emerging application of plasma-based methods to control defect chemistry, surface passivation, and electronic structure heralds a paradigm shift in photoelectrode fabrication, positioning plasma-synthesized oxynitride thin films as one of the enabling technologies for next-generation, sun-driven hydrogen production.

The findings suggest that plasma-engineered oxynitrides are good materials for practical solar hydrogen systems, particularly when paired with co-catalysts and protective layers. However, scalable, cost-effective, large-area deposition and standardization remain open challenges.

5. Conclusions

This critical assessment demonstrates that plasma-assisted synthesis of oxynitride thin films offers significant advantages over conventional thermal routes for photoelectrochemical water splitting. The key contributions of this study are threefold. First, a structured evidence reliability framework was developed and applied to 30 studies. The evidence reliability assessment revealed substantial variation in plasma diagnostics reporting, characterization completeness, and stability evaluation across the reviewed studies, while the majority of studies exhibit reporting limitations that constrain the development of quantitative process–structure–property relationships. Second, the analysis identifies three distinct plasma operating domains, lower-power, intermediate-power, and higher-power, each characterized by different dominant mechanisms: surface activation, substitutional nitridation, and resputtering/defect generation, respectively. The intermediate-power domain was generally associated with the most favorable balance between nitrogen incorporation, crystallinity, and PEC performance among the studies reviewed. Third, the study highlights unresolved contradictions in the literature, including discrepancies in optimal power ranges, trade-offs between nitrogen incorporation and defect formation, and inconsistencies in stability reporting. These contradictions indicate that plasma power alone cannot serve as a universal predictor of performance; instead, performance emerges from the complex interplay of plasma conditions, reactor configuration, film composition, defect chemistry, and testing methodology. Collectively, these findings provide a conceptual framework for guiding future plasma engineering efforts toward the rational design of high-performance oxynitride photoelectrodes for sustainable hydrogen production.

Beyond evaluating the existing literature, the present study provides a structured framework for interpreting how plasma–material interactions govern nitrogen incorporation, crystallinity evolution, defect formation, and ultimately hydrogen production performance. By integrating mechanistic understanding with evidence reliability assessment, this work establishes a foundation for more reproducible and scientifically rigorous development of plasma-engineered oxynitride photoelectrodes. Future advances will depend on standardized diagnostics, long-term stability assessment, and the generation of datasets capable of supporting quantitative predictive models.

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Abbreviations

The following abbreviations are used in this manuscript:

AFM	Atomic Force Microscopy
AM1.5G	Air Mass 1.5 Global (solar spectrum standard)
ARPES	Angle-Resolved Photoemission Spectroscopy
CB	Conduction Band
CVD	Chemical Vapor Deposition

DFT	Density Functional Theory
E _g	Bandgap Energy
EIS	Electrochemical Impedance Spectroscopy
HER	Hydrogen Evolution Reaction
IEEE	Institute of Electrical and Electronics Engineers
MOCVD	Metal–Organic Chemical Vapor Deposition
MPAN	Microwave Plasma-Assisted Nitridation
NHE	Normal Hydrogen Electrode
OER	Oxygen Evolution Reaction
PEC	Photoelectrochemical
PECVD	Plasma-Enhanced Chemical Vapor Deposition
PLD	Pulsed Laser Deposition
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-Analyses
RF	Radio Frequency
ROBINS-I	Risk Of Bias In Non-Randomized Studies of Interventions
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
STH	Solar-to-Hydrogen
TEM	Transmission Electron Microscopy
UV-Vis	Ultraviolet–Visible Spectroscopy
VB	Valence Band

References

1. Elazab, M.; Elgohr, A.T.; Bassyouni, M.; Kabeel, A.E.; Attia, M.E.H.; Elshaarawy, M.K.; Hamed, A.K.; Alzahrani, H.A. Green hydrogen: Unleashing the potential for sustainable energy generation. *Results Eng.* **2025**, *27*, 106031. [\[CrossRef\]](#)
2. Zhao, Y.; Niu, Z.; Zhao, J.; Xue, L.; Fu, X.; Long, J. Recent advancements in photoelectrochemical water splitting for hydrogen production. *Electrochem. Energy Rev.* **2023**, *6*, 14. [\[CrossRef\]](#)
3. Cheng, W.-H.; De La Calle, A.; Atwater, H.A.; Stechel, E.B.; Xiang, C. Hydrogen from sunlight and water: A side-by-side comparison between photoelectrochemical and solar thermochemical water-splitting. *ACS Energy Lett.* **2021**, *6*, 3096–3113. [\[CrossRef\]](#)
4. Song, H.; Luo, S.; Huang, H.; Deng, B.; Ye, J. Solar-driven hydrogen production: Recent advances, challenges, and future perspectives. *ACS Energy Lett.* **2022**, *7*, 1043–1065. [\[CrossRef\]](#)
5. Vilanova, A.; Dias, P.; Lopes, T.; Mendes, A. The route for commercial photoelectrochemical water splitting: A review of large-area devices and key upscaling challenges. *Chem. Soc. Rev.* **2024**, *53*, 2388–2434. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Zhang, H.; Liu, J.; Xu, T.; Ji, W.; Zong, X. Recent advances on small band gap semiconductor materials (≤ 2.1 eV) for solar water splitting. *Catalysts* **2023**, *13*, 728. [\[CrossRef\]](#)
7. Yang, L.; Li, F.; Xiang, Q. Advances and challenges in the modification of photoelectrode materials for photoelectrocatalytic water splitting. *Mater. Horiz.* **2024**, *11*, 1638–1657. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Marwat, M.A.; Humayun, M.; Afridi, M.W.; Zhang, H.; Abdul Karim, M.R.; Ashtar, M.; Usman, M.; Waqar, S.; Ullah, H.; Wang, C. Advanced catalysts for photoelectrochemical water splitting. *ACS Appl. Energy Mater.* **2021**, *4*, 12007–12031. [\[CrossRef\]](#)
9. Reenamole, G. Metal oxide nanomaterials for visible light photocatalysis. In *Emerging Nanomaterials for Catalysis and Sensor Applications*; CRC Press: Boca Raton, FL, USA, 2023; pp. 103–130.
10. Rizzi, G.A.; Girardi, L. Metal oxides for photoelectrochemical fuel production. In *Tailored Functional Oxide Nanomaterials: From Design to Multi-Purpose Applications*; Wiley: Weinheim, Germany, 2022; pp. 339–377.
11. Witjaksono, G.; Junaaid, M.; Khir, M.H.; Ullah, Z.; Tansu, N.; Saheed, M.S.B.M.; Siddiqui, M.A.; Ba-Hashwan, S.S.; Algarni, A.S.; Magsi, S.A. Effect of nitrogen doping on the optical bandgap and electrical conductivity of nitrogen-doped reduced graphene oxide. *Molecules* **2021**, *26*, 6424. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Paredes, P.; Rauwel, E.; Rauwel, P. Surveying the synthesis, optical properties and photocatalytic activity of Cu₃N nanomaterials. *Nanomaterials* **2022**, *12*, 2218. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Ban, J.; Xu, H.; Cao, G.; Fan, Y.; Pang, W.K.; Shao, G.; Hu, J. Synergistic effects of phase transition and electron-spin regulation on the electrocatalysis performance of ternary nitride. *Adv. Funct. Mater.* **2023**, *33*, 2300623. [\[CrossRef\]](#)
14. Gupta, P.; Toksha, B.; Rahaman, M. A critical review on hydrogen based fuel cell technology and applications. *Chem. Rec.* **2024**, *24*, e202300295. [\[CrossRef\]](#) [\[PubMed\]](#)
15. ul Haq, T.; Haik, Y. *Electrochemical Water Splitting: Fundamentals, Challenges and Advances*; Springer Nature: Singapore, 2024.

16. Chen, H.; Yuan, D.; Wu, A.; Lin, X.; Li, X. Review of low-temperature plasma nitrogen fixation technology. *Waste Dispos. Sustain. Energy* **2021**, *3*, 201–217. [[CrossRef](#)] [[PubMed](#)]
17. Di, L.; Zhang, J.; Zhang, X.; Wang, H.; Li, H.; Li, Y.; Bu, D. Cold plasma treatment of catalytic materials: A review. *J. Phys. D Appl. Phys.* **2021**, *54*, 333001. [[CrossRef](#)]
18. Sun, X.; Bao, J.; Li, K.; Argyle, M.D.; Tan, G.; Adidharma, H.; Zhang, K.; Fan, M.; Ning, P. Advance in using plasma technology for modification or fabrication of carbon-based materials and their applications in environmental, material, and energy fields. *Adv. Funct. Mater.* **2021**, *31*, 2006287. [[CrossRef](#)]
19. Liu, Y.; He, J.; Zhang, N.; Zhang, W.; Zhou, Y.; Huang, K. Advances of microwave plasma-enhanced chemical vapor deposition in fabrication of carbon nanotubes: A review. *J. Mater. Sci.* **2021**, *56*, 12559–12583. [[CrossRef](#)]
20. Xiao, Y.; Kong, X.; Vanka, S.; Dong, W.J.; Zeng, G.; Ye, Z.; Sun, K.; Navid, I.A.; Zhou, B.; Toma, F.M. Oxynitrides enabled photoelectrochemical water splitting with over 3,000 hrs stable operation in practical two-electrode configuration. *Nat. Commun.* **2023**, *14*, 2047. [[CrossRef](#)] [[PubMed](#)]
21. Streibel, V.; Schönecker, J.L.; Wagner, L.I.; Sirotti, E.; Munnik, F.; Kuhl, M.; Jiang, C.-M.; Eichhorn, J.; Santra, S.; Sharp, I.D. Zirconium oxynitride thin films for photoelectrochemical water splitting. *ACS Appl. Energy Mater.* **2024**, *7*, 4004–4015. [[CrossRef](#)] [[PubMed](#)]
22. Lawley, C.; Nachtegaal, M.; Stahn, J.; Roddatis, V.; Döbeli, M.; Schmidt, T.J.; Pergolesi, D.; Lippert, T. Examining the surface evolution of LaTiOxNy oxynitride solar water splitting photocatalyst. *Nat. Commun.* **2020**, *11*, 1728. [[CrossRef](#)] [[PubMed](#)]
23. Haydous, F.; Luo, S.; Wu, K.-T.; Lawley, C.; Döbeli, M.; Ishihara, T.; Lippert, T. Surface analysis of perovskite oxynitride thin films as photoelectrodes for solar water splitting. *ACS Appl. Mater. Interfaces* **2021**, *13*, 37785–37796. [[CrossRef](#)] [[PubMed](#)]
24. Xia, C.; Wang, H.; Kim, J.K.; Wang, J. Rational design of metal oxide-based heterostructure for efficient photocatalytic and photoelectrochemical systems. *Adv. Funct. Mater.* **2021**, *31*, 2008247. [[CrossRef](#)]
25. Raub, A.A.M.; Bahru, R.; Nashruddin, S.N.A.M.; Yunus, J. Advances of nanostructured metal oxide as photoanode in photoelectrochemical (PEC) water splitting application. *Heliyon* **2024**, *10*, e39079. [[CrossRef](#)] [[PubMed](#)]
26. Maeda, K. (Oxy) nitrides with d 0-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. [[CrossRef](#)] [[PubMed](#)]
27. Xiao, Y.; Feng, C.; Fu, J.; Wang, F.; Li, C.; Kunzelmann, V.F.; Jiang, C.-M.; Nakabayashi, M.; Shibata, N.; Sharp, I.D.; et al. Band structure engineering and defect control of Ta₃N₅ for efficient photoelectrochemical water oxidation. *Nat. Catal.* **2020**, *3*, 932–940. [[CrossRef](#)]
28. Huang, Y.; Meng, L.; Xu, W.; Li, L. The positive versus negative effects of defect engineering for solar water splitting: A review. *Adv. Funct. Mater.* **2023**, *33*, 2305940. [[CrossRef](#)]
29. Werner, V.; Lora, F.B.; Chai, Z.; Hörndel, J.; Praxmair, J.; Lubert, S.; Haussener, S.; Pokrant, S. Stability and degradation of (oxy) nitride photocatalysts for solar water splitting. *RSC Sustain.* **2024**, *2*, 1738–1752. [[CrossRef](#)] [[PubMed](#)]
30. Sarkis-Onofre, R.; Catalá-López, F.; Aromataris, E.; Lockwood, C. How to properly use the PRISMA Statement. *Syst. Rev.* **2021**, *10*, 117. [[CrossRef](#)] [[PubMed](#)]
31. Pichler, M.; Si, W.; Haydous, F.; Téllez, H.; Druce, J.; Fabbri, E.; Kazzi, M.E.; Döbeli, M.; Ninova, S.; Aschauer, U. LaTiOxNy thin film model systems for photocatalytic water splitting: Physicochemical evolution of the solid–liquid interface and the role of the crystallographic orientation. *Adv. Funct. Mater.* **2017**, *27*, 1605690. [[CrossRef](#)]
32. Lawley, C.; Arab, A.; Hartl, A.; Staykov, A.; Döbeli, M.; Schmitt, T.; Pergolesi, D.; Lippert, T.; Strocov, V.N. Momentum-resolved electronic structure of LaTiO₂N photocatalysts by resonant Soft-X-ray ARPES. *Commun. Mater.* **2023**, *4*, 15. [[CrossRef](#)]
33. Chen, J.; Stender, D.; Pichler, M.; Döbeli, M.; Pergolesi, D.; Schneider, C.W.; Wokaun, A.; Lippert, T. Tracing the plasma interactions for pulsed reactive crossed-beam laser ablation. *J. Appl. Phys.* **2015**, *118*, 165306. [[CrossRef](#)]
34. Hojamberdiev, M.; Mora-Hernandez, J.M.; Vargas, R.; Heppke, E.M.; Yubuta, K.; Yamakata, A.; Kadirova, Z.; Torres-Martínez, L.; Teshima, K.; Lerch, M. Eliciting the contribution of TiN to photoelectrochemical performance enhancement of Imma-LaTiO₂N at neutral pH. *Mater. Today Energy* **2022**, *27*, 101053. [[CrossRef](#)]
35. Rafique, S.; Han, L.; Mou, S.; Zhao, H. Temperature and doping concentration dependence of the energy band gap in β-Ga₂O₃ thin films grown on sapphire. *Opt. Mater. Express* **2017**, *7*, 3561–3570. [[CrossRef](#)]
36. Higashi, T.; Nishiyama, H.; Nandal, V.; Pihosh, Y.; Kawase, Y.; Shoji, R.; Nakabayashi, M.; Sasaki, Y.; Shibata, N.; Matsuzaki, H.; et al. Design of semitransparent tantalum nitride photoanode for efficient and durable solar water splitting. *Energy Environ. Sci.* **2022**, *15*, 4761–4775. [[CrossRef](#)]
37. Higashi, T.; Nishiyama, H.; Pihosh, Y.; Wakishima, K.; Kawase, Y.; Sasaki, Y.; Nagaoka, A.; Yoshino, K.; Takanabe, K.; Domen, K. Physicochemical insights into semiconductor properties of a semitransparent tantalum nitride photoanode for solar water splitting. *Phys. Chem. Chem. Phys.* **2023**, *25*, 20737–20748. [[CrossRef](#)] [[PubMed](#)]
38. Zhong, M.; Hisatomi, T.; Sasaki, Y.; Suzuki, S.; Teshima, K.; Nakabayashi, M.; Shibata, N.; Nishiyama, H.; Katayama, M.; Yamada, T.; et al. Highly active GaN-stabilized Ta₃N₅ thin-film photoanode for solar water oxidation. *Angew. Chem. Int. Ed.* **2017**, *56*, 4739–4743. [[CrossRef](#)] [[PubMed](#)]

39. Wang, C.; Hisatomi, T.; Minegishi, T.; Nakabayashi, M.; Shibata, N.; Katayama, M.; Domen, K. Thin film transfer for the fabrication of tantalum nitride photoelectrodes with controllable layered structures for water splitting. *Chem. Sci.* **2016**, *7*, 5821–5826. [[CrossRef](#)] [[PubMed](#)]
40. Nurlaela, E.; Nakabayashi, M.; Kobayashi, Y.; Shibata, N.; Yamada, T.; Domen, K. Plasma-enhanced chemical vapor deposition Ta₃N₅ synthesis leading to high current density during PEC oxygen evolution. *Sustain. Energy Fuels* **2020**, *4*, 2293–2300. [[CrossRef](#)]
41. Pergolesi, D.; Lawley, C.; Lippert, T. Thin-Film Oxynitride Photocatalysts for Solar Hydrogen Generation: Separating Surface and Bulk Effects Using Synchrotron X-Ray and Neutron-Based Techniques. *Sol. RRL* **2022**, *6*, 2200286. [[CrossRef](#)]
42. Amer, M.S.; Arunachalam, P.; Ghanem, M.A.; Al-Mayouf, A.M.; Weller, M.T. Photoelectrochemical performance of strontium titanium oxynitride photo-activated with cobalt phosphate nanoparticles for oxidation of alkaline water. *Nanomaterials* **2023**, *13*, 920. [[CrossRef](#)] [[PubMed](#)]
43. Dong, B.; Cui, J.; Qi, Y.; Zhang, F. Nanostructure engineering and modulation of (Oxy) Nitrides for application in visible-light-driven water splitting. *Adv. Mater.* **2021**, *33*, 2004697. [[CrossRef](#)] [[PubMed](#)]
44. Lin, L.; Xu, H.; Gao, H.; Zhu, X.; Hessel, V. Plasma-assisted nitrogen fixation in nanomaterials: Fabrication, characterization, and application. *J. Phys. D Appl. Phys.* **2020**, *53*, 133001. [[CrossRef](#)]
45. Saroni, A.; Alizadeh, M.; Goh, B.T.; Wan, C.W.N.A.C.; Asari, S.A.M.; Chia, M.Y.; Chiu, W.S. In-depth investigation on the self-catalyzed growth of W₂N/In₂O₃ composite nanowires synthesized via nitrogen plasma assisted in-situ thermal annealing for boosting photoelectrochemical performance. *J. Phys. Chem. Solids* **2023**, *182*, 111574. [[CrossRef](#)]
46. Haydous, F.; Waag, F.; Si, W.; Li, F.; Barcikowski, S.; Gökce, B.; Lippert, T. The effect of downstream laser fragmentation on the specific surface area and photoelectrochemical performance of barium tantalum oxynitride. *Appl. Surf. Sci.* **2020**, *510*, 145429. [[CrossRef](#)]
47. Le Paven, C.; Ziani, A.; Marlec, F.; Le Gendre, L.; Tessier, F.; Haydoura, M.; Benzerger, R.; Cheviré, F.; Takanabe, K.; Sharaiha, A. Structural and photoelectrochemical properties of SrTaO₂N oxynitride thin films deposited by reactive magnetron sputtering. *J. Eur. Ceram. Soc.* **2020**, *40*, 6301–6308. [[CrossRef](#)]
48. Pisarek, M.; Krawczyk, M.; Gurgul, M.; Zaraska, L.; Bienkowski, K.; Hołdyński, M.; Solarz, R. Plasma-assisted N-doped TiO₂ nanotube array as an active UV-vis photoanode. *ACS Appl. Nano Mater.* **2023**, *6*, 10351–10364. [[CrossRef](#)]
49. Pleskunov, P.; Košutová, T.; Vaidulych, M.; Nikitin, D.; Krtouš, Z.; Ali-Ogly, S.; Kishenina, K.; Tafiichuk, R.; Biederman, H.; Gordeev, I.; et al. The sputter-based synthesis of tantalum oxynitride nanoparticles with architecture and bandgap controlled by design. *Appl. Surf. Sci.* **2021**, *559*, 149974. [[CrossRef](#)]
50. Jiang, C.; Moniz, S.J.; Wang, A.; Zhang, T.; Tang, J. Photoelectrochemical devices for solar water splitting—materials and challenges. *Chem. Soc. Rev.* **2017**, *46*, 4645–4660. [[CrossRef](#)] [[PubMed](#)]
51. Yokoyama, D.; Hashiguchi, H.; Maeda, K.; Minegishi, T.; Takata, T.; Abe, R.; Kubota, J.; Domen, K. Ta₃N₅ photoanodes for water splitting prepared by sputtering. *Thin Solid Film.* **2011**, *519*, 2087–2092. [[CrossRef](#)]
52. Nurlaela, E.; Sasaki, Y.; Nakabayashi, M.; Shibata, N.; Yamada, T.; Domen, K. Towards zero bias photoelectrochemical water splitting: Onset potential improvement on a Mg:GaN modified-Ta₃N₅ photoanode. *J. Mater. Chem. A* **2018**, *6*, 15265–15273. [[CrossRef](#)]
53. Cristea, D.; Velicu, I.-L.; Cunha, L.; Barradas, N.; Alves, E.; Craciun, V. Tantalum-titanium oxynitride thin films deposited by DC reactive magnetron co-sputtering: Mechanical, optical, and electrical characterization. *Coatings* **2022**, *12*, 36. [[CrossRef](#)]
54. Li, C.; Hsieh, J.-H.; Chuang, Y.R. Experimental investigation on the sputtering process for tantalum oxynitride thin films. *Photonics* **2021**, *8*, 53. [[CrossRef](#)]
55. Matei, T.; Tiron, V.; Jijie, R.; Bulai, G.; Velicu, I.-L.; Cristea, D.; Crăciun, V. Band-gap engineering of zirconia by nitrogen doping in reactive HiPIMS: A step forward in developing innovative technologies for photocatalysts synthesis. *Front. Chem.* **2023**, *11*, 1239964. [[CrossRef](#)] [[PubMed](#)]
56. Cristea, D.; Cunha, L.; Gabor, C.; Ghiuta, I.; Croitoru, C.; Marin, A.; Velicu, L.; Besleaga, A.; Vasile, B. Tantalum oxynitride thin films: Assessment of the photocatalytic efficiency and antimicrobial capacity. *Nanomaterials* **2019**, *9*, 476. [[CrossRef](#)] [[PubMed](#)]
57. Mohamed, S.H.; Zhao, H.; Romanus, H.; El-Hossary, F.M.; Abo EL-Kassem, M.; Awad, M.A.; Rabia, M.; Lei, Y. Optical, water splitting and wettability of titanium nitride/titanium oxynitride bilayer films for hydrogen generation and solar cells applications. *Mater. Sci. Semicond. Process.* **2020**, *105*, 104704. [[CrossRef](#)]
58. Li, Q.; Shang, J.K. Heavily nitrogen-doped titanium oxide thin films by reactive sputtering and excimer laser annealing. *J. Am. Ceram. Soc.* **2010**, *93*, 3039–3042. [[CrossRef](#)]
59. Li, P.; Fan, Y.; Chen, Q.; Chen, W.; Zhang, S.; Wang, X.; Guo, W.; Sun, J.; Li, X.; Cao, Y. Epitaxy and Electronic Properties of Ultrawide Bandgap Aluminum Oxynitride Films. *ACS Appl. Electron. Mater.* **2025**, *7*, 5364–5370. [[CrossRef](#)]
60. Xiao, Y.; Fan, Z.; Nakabayashi, M.; Li, Q.; Zhou, L.; Wang, Q.; Li, C.; Shibata, N.; Domen, K.; Li, Y. Decoupling light absorption and carrier transport via heterogeneous doping in Ta₃N₅ thin film photoanode. *Nat. Commun.* **2022**, *13*, 7769. [[CrossRef](#)] [[PubMed](#)]

61. Wei, S.; Chang, S.; Yang, F.; Fu, Z.; Liu, G.; Xu, X. Stable and efficient solar-driven photoelectrochemical water splitting into H₂ and O₂ based on a BaTaO₂N photoanode decorated with CoO microflowers. *Chem. Commun.* **2021**, *57*, 4412–4415. [[CrossRef](#)] [[PubMed](#)]
62. Wang, P.; Than Oo, A.M.; Chen, L.; Zhang, D. Recent advances of interfacial modification over tantalum nitride photoanodes for solar water oxidation: A mini review. *Front. Chem.* **2025**, *13*, 1600959. [[CrossRef](#)] [[PubMed](#)]
63. Li, C.-Q.; Yang, N.; Song, K.; Yin, Z.-H.; Chen, L.; Tan, H.; Tian, F.-X.; Chen, Z.; Liu, H.; Wang, J.-J. Interfacial d-Band Center Modulation via Si–Ir Coupling Enables Efficient and Durable Acidic Solar Water Splitting. *Angew. Chem. Int. Ed.* **2026**, *65*, e24928. [[CrossRef](#)] [[PubMed](#)]
64. Hashizume, T.; Hasegawa, H. Effects of nitrogen deficiency on electronic properties of AlGaN surfaces subjected to thermal and plasma processes. *Appl. Surf. Sci.* **2004**, *234*, 387–394. [[CrossRef](#)]

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