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Electrochemical Design of Semiconductor Photoelectrodes: Morphology, Interfaces, and Kinetic Bottlenecks

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Abstract. Photoelectrochemical conversion offers a conceptually attractive route for storing intermittent solar energy in chemical bonds, yet the practical performance of semiconductor photoelectrodes remains constrained by a well-recognized triad of losses: incomplete light harvesting, inefficient charge separation, and sluggish interfacial reaction kinetics. This invited Review examines electrochemical strategies for improving semiconductor photoelectrochemical performance, with emphasis on three representative systems: metal-assisted chemical etching of n-type silicon, cyclic voltammetry-based electrodeposition of ZnO/TiO_2 heterojunction nanorod photoanodes, and impedance spectroscopy analysis of NiO/AlGaN/n-GaN tandem photoanodes. Rather than treating these examples as isolated case studies, this Review proposes a structure-interface-kinetics framework. In this view, etching controls the optical and geometric boundary conditions of the semiconductor, electrodeposition determines the electronic quality and chemical selectivity of the surface, and impedance spectroscopy identifies the kinetic bottleneck to guide subsequent materials design. The central conclusion is that higher photocurrent density alone is not a sufficient design objective. A credible photoelectrode architecture must simultaneously preserve crystallinity, generate a beneficial interfacial field, expose kinetically competent catalytic sites, and resist corrosion under operating potentials. The Review therefore argues for an analysis-driven design philosophy in which morphology, band alignment, defect chemistry, and charge-transfer resistance are optimized as coupled variables rather than as independent descriptors.

Keywords: photoelectrochemistry, semiconductor photoelectrodes, electrochemical etching, electrodeposition, heterojunctions, impedance spectroscopy

1. Introduction

Semiconductor photoelectrochemistry has long been pursued as a bridge between solar-energy capture and chemical synthesis. In concept, this approach is elegant and straightforward: a semiconductor absorbs photons, separates electron-hole pairs, and directs electrons and holes toward spatially distinct reduction and oxidation reactions. In practice, however, the apparent simplicity conceals a demanding sequence of physical and chemical events. A productive photoelectrode must absorb a sufficient fraction of the solar spectrum, generate carriers that survive transport to the interface, transfer those carriers to solution species at rates competitive with recombination, and

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remain structurally intact in strongly oxidizing or reducing environments. Failure at any one of these steps can dominate the measured photocurrent, and improvement in one descriptor can be offset by deterioration in another. This explains why impressive morphological changes or favorable band-edge diagrams do not automatically translate into durable solar-fuel performance [1, 2].

Electrochemical methods are particularly valuable in this field because they operate precisely at the semiconductor-electrolyte interface, at whichthe decisive losses occur. Electrochemical processing is not only a fabrication tool but also a diagnostic probe. The current transient, impedance response, deposition charge, onset potential, and light-intensity dependence all encode information about the evolving interface [3-5].

This review aims to explore how electrochemical treatment should be applied when the objective is to improve performance in a mechanistically justified manner. To address this question, we consider three systems selected from the literature. The first is metal-assisted chemical etching of n-type Si, where electrodeposited Au nanoparticles define local cathodic sites and enable high-aspect-ratio silicon nanowire arrays. The second is cyclic voltammetry-based electrodeposition of ZnO on rutile TiO_2 nanorods, where a heterojunction and defect-rich oxide overlayer alter charge separation and photoelectrochemical water-splitting activity. The third is a NiO/AlGaN/n-GaN tandem configuration in which AC impedance analysis reveals water oxidation at the photoanode as the dominant resistance. These systems differ in composition, band gap, and operating environment, but together they illustrate a common principle: electrochemical treatments are most powerful when they are used to create measurable improvements in the rate-limiting step rather than merely modifying the surface [6-8].

The thesis advanced here is therefore deliberately conservative but consequential. A semiconductor photoelectrode should not be judged only by the maximum photocurrent density measured under a chosen bias. This distinction is particularly important for nanostructured electrodes. The central task is not to maximize any single structural descriptor, but to balance competing effects through a combination of materials design and electrochemical analysis [9, 10].

2. Electrochemical processing as a materials-design language

Electrochemical synthesis precisely controls the nucleation, growth, dissolution selectivity, and photo-oxidation location in electrodeposition and etching by continuously regulating the reaction driving force and extent through potential, current, and charge. This control method is naturally compatible with the interfacial reactivity of semiconductor materials that is governed by band bending, carrier concentration, surface states, and light. As a result, electrochemical processing is particularly suitable for semiconductor materials. In this Review, the three case studies are therefore interpreted as examples of electrochemical control over different dominant variables. Metal-assisted chemical etching of Si primarily demonstrates structural control through metal-catalyzed localized dissolution. ZnO/TiO_2 electrodeposition illustrates interfacial and defect-chemical control through heterojunction formation and oxygen-vacancy-related charge separation. GaN tandem-cell analysis demonstrates kinetic diagnosis through the quantitative deconvolution of series resistance and photoanode charge-transfer resistance. The value of placing these examples side by side is that they reveal the incomplete nature of any one-dimensional optimization strategy.

3. Metal-assisted chemical etching of silicon

Silicon remains a benchmark semiconductor because of its abundance, mature processing infrastructure, and favorable visible-light absorption. Its use as a photoelectrode, however, is

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complicated by surface recombination, corrosion, and the long-standing difficulty of reconciling efficient light harvesting with stable interfacial chemistry. Nanostructuring offers one attractive solution. Silicon nanowire arrays can reduce optical reflection, increase the optical path length, provide large interfacial area, and relax constraints on minority-carrier diffusion length. Yet the fabrication of nanowires must be sufficiently mild and scalable to preserve the economic advantages of Si. Metal-assisted chemical etchingis therefore a particularly instructive route [6, 11, 12].

In the MACE mechanism considered here, Au nanoparticles deposited on n-Si act as local cathodic sites in an HF/H_2O_2 solution. H_2O_2 reduction at the Au surface generates holes, and these holes are injected across the Au/Si contact into the underlying Si. Local oxidation of Si weakens the Si-Si network, and the oxidized silicon is dissolved by HF. The Au layer not only acts as a catalyst but also defines the spatial locations where the semiconductor will be chemically removed [6].

The data summarized in the original manuscript show that Au(I) and Au(III) baths lead to distinct nanoparticle distributions and etched morphologies. Au(I) deposition at pH 4 produces a more uniform nanoparticle layer and, after etching, a more vertically aligned nanowire array with narrower diameter distribution. Au(III), although able to generate deep etching under sufficiently negative potentials, produces a less uniform morphology. This difference demonstrates why deposition chemistry must be considered part of the photoelectrode design, not merely a preparatory step.

These observations indicate that longer deposition or more negative potential increases etch depth. More negative potentials and longer times increase Au loading and coverage, thereby increasing the number of local cathodic sites for H_2O_2 reduction. However, excessive or nonuniform metal coverage can promote lateral etching, particle coalescence, and mechanical fragility. A high-aspect-ratio morphology must be evaluated alongside carrier collection and surface passivation. A nanowire array that maximizes surface area but lacks passivation may behave more like a recombination amplifier than a photocurrent amplifier.

The broader implication is that MACE should be understood as an electrochemical patterning strategy governed by coupled nucleation and dissolution. Unlike lithographic nanowire fabrication, it can be conducted at low temperature and over large areas. Unlike purely chemical roughening, it can be tuned by metal deposition potential, charge, and bath composition. MACE establishes optical and geometric advantages, after which conformal passivation, catalyst deposition, or junction formation must be introduced to control the enlarged interface. Without this second step, the increased area can intensify the very interfacial losses that originally prompted nanostructuring [1, 6, 13].

4. Electrodeposited ZnO/TiO_2 heterojunctions

TiO_2 is the canonical oxide photoanode: chemically robust, inexpensive, and synthetically versatile. Its principal limitations are also well known: a wide band gap restricts absorption mainly to the ultraviolet region, and charge recombination at surface and grain-boundary sites can be severe. Rutile TiO_2 nanorods partially address these problems by providing oriented transport pathways from the semiconductor-electrolyte interface to the FTO substrate. The remaining challenge is to engineer the interface so that photogenerated carriers are separated and transferred before recombination occurs. Electrodeposition of ZnO onto TiO_2 nanorods provides a useful model for this problem [7, 9, 10]. Figure 1 supports the discussion of band alignment, carrier migration, and the interpretation of type-II heterojunction behavior.

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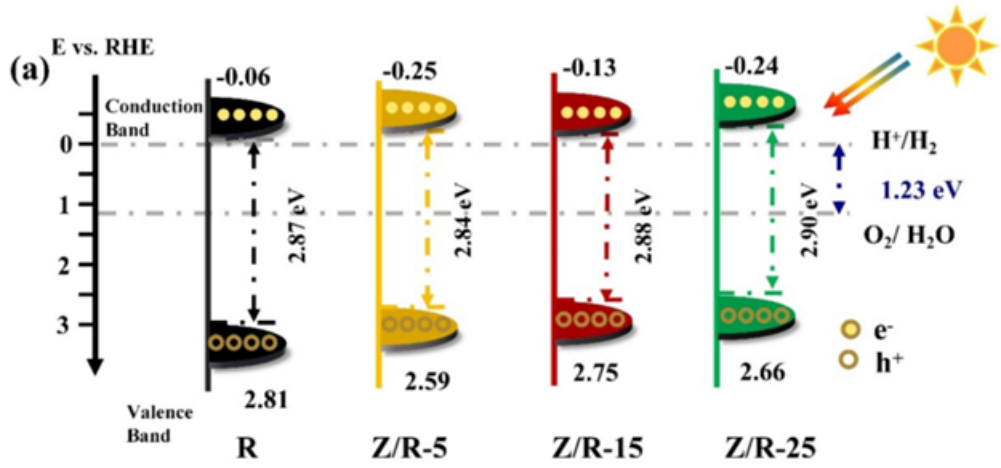

Figure 1. Type-II heterojunction behavior

The original study employs cyclic voltammetry-based electrodeposition to introduce controlled amounts of ZnO onto annealed rutile TiO_2 nanorod arrays. Samples are denoted Z/R-5, Z/R-15, and Z/R-25 according to deposition charge. The central observation is that an intermediate ZnO loading gives the best performance. Z/R-15 reaches a photocurrent density of 2.7 mA cm-2 at 1.23 V versus RHE, approximately 3.5 times that of bare TiO_2, and 1.87 mA cm^{-2} at 0.5 V versus RHE, approximately 18.7 times that of bare TiO_2. The IPCE value reaches 46% at 390 nm and rises to about 90% at 357 nm under an applied negative bias. Hydrogen evolution reaches 53.2 micromol cm^{-2} h^{-1}, roughly 3.3 times the value of the TiO_2 reference. These numbers are important, but the more instructive result is the dependence of the photoelectrochemical performance on deposition amount.

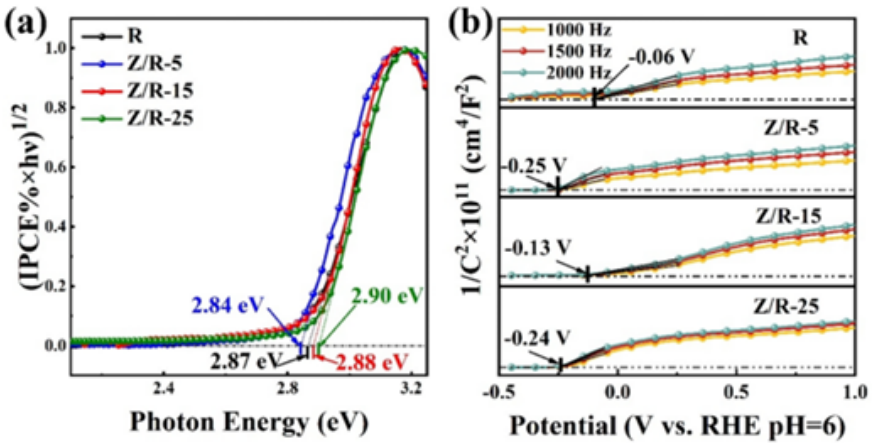

Figure 2. Band-edge shifts and carrier-density changes

The comparison between deposition before and after TiO_2 annealing is also significant. Depositing ZnO on already crystallized TiO_2 avoids subjecting the interface to a second high-temperature treatment that can alter defect density, crystallographic quality, and ZnO morphology. This observation is a reminder that thermal history is part of interface design. A heterojunction is not defined only by its two nominal semiconductors; it is defined by the atomic and defect structure created during synthesis. Cyclic voltammetry-based electrodeposition is valuable because the

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deposition charge and potential window allow systematic exploration of that structure. Figure 2 is used to connect band-edge shifts and carrier-density changes with the enhanced photoelectrochemical response.

A mature interpretation of the ZnO/TiO_2 system must therefore go beyond the terminologyof type-II, Z-scheme, or S-scheme labels. These labels are convenient, but they can obscure the fact that experimentally measured performance depends on competing kinetic rates. If an interfacial field separates carriers but the surface reaction remains slow, holes can accumulate and accelerate photocorrosion. If defect states increase carrier density but also increase nonradiative recombination, the net photocurrent may decline. If ZnO forms a thick layer, the heterojunction may become optically and electronically parasitic. Thus, the appropriate question is not which schematic band model is most favorable, but which interfacial configuration lowers the dominant recombination and charge-transfer losses under working conditions.

The ZnO/TiO_2 example also shows why electrodeposition is more than a low-cost synthesis method. Since the deposition amount can be quantified by charge, and since CV can repeatedly control nucleation and growth, electrodeposition provides an experimental route to map performance as a function of interfacial coverage. This mapping is essential for identifying optima. In a syntematic design strategy, one would combine deposition-charge series, transient photocurrent, IPCE, Mott-Schottky analysis, and impedance spectroscopy to decouple optical absorption, carrier density, interfacial transfer, and lifetime. Only then can one determine whether the observed enhancement arises from genuine junction improvement or from a geometric increase in active area.

5. GaN-based tandem photoanodes

III-nitride semiconductors occupy a distinctive place in photoelectrochemical research. Their band gaps, polarization fields, and chemical robustness make them attractive for water splitting, particularly in heterostructures such as AlGaN/GaN. In the system, NiO serves as a water-oxidation cocatalyst and as a partial protection layer that redirects holes toward productive oxygen evolution rather than semiconductor corrosion [8, 14, 15].

Impedance analysis reveals why. In the two-electrode system, the total internal resistance is about 208 ohms, of which the charge-transfer resistance accounts for approximately 178 ohms, or 86%. In the three-electrode analysis, the photoanode-cell resistance is about 193 ohms, which accounts for 93% of the total resistance, while the photoanode charge-transfer resistance is about 175 ohms, representing 91% of the photoanode-cell resistance. These values identify the water-oxidation reaction at the NiO/AlGaN/electrolyte interface as the dominant kinetic bottleneck. Improving bulk conductivity or reducing solution resistance will not produce a proportional performance increase if the interfacial oxidation step remains rate limiting [8, 16].

The light-intensity dependence further strengthens this interpretation. As the light intensity increases from 0.5 to 2 sun equivalents, the photoanode charge-transfer resistance decreases substantially, whereas the ohmic resistance changes little. This behavior suggests that the active reaction area or density of available photogenerated holes increases with light intensity. The result is consistent with a surface reaction limited by the supply and transfer of photogenerated holes rather than by ionic conduction through solution. It also indicates that a higher density of active interfacial sites, improved hole-selective transport to NiO, or a more active oxygen-evolution catalyst could reduce the dominant resistance.

The degradation observed after prolonged operation is equally informative. SEM and EDS indicate roughened regions and partial exposure of the sapphire substrate, which suggests photo-corrosion or etching of AlGaN, likely initiated at defect sites such as dislocations. NiO improves

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selectivity but does not fully eliminate degradation. In this sense, stability is not a separate property that can be tested after activity optimization; it is an expression of interfacial kinetics. Slow oxygen-evolution charge transfer increases the residence time of oxidizing holes at vulnerable semiconductor sites.

The GaN example therefore provides the strongest argument for an analysis-led design philosophy. Impedance spectroscopy reveals a more precise target: reducing the water-oxidation charge-transfer resistance at the photoanode. Possible routes include increasing the NiO coverage without blocking light, using mixed NiFe oxyhydroxides or other oxygen-evolution catalysts, engineering tunnel-thin protective layers, reducing dislocation density in AlGaN, and constructing graded or polarization-enhanced junctions that deliver holes to catalytic sites more efficiently.

Many photoelectrode studies report improved photocurrent after surface modification without specifying whether the enhancement originates from reduced charge-transfer resistance, suppressed recombination, enhanced absorption, or mitigated corrosion. As a result, design rules remain empirical. The GaN work demonstrates the value of decomposing the full-cell resistance into physically meaningful components. To move toward practical devices, the field cannot rely solely on materials discovery; it must develop an engineering framework that identifies the rate-determining step under operating conditions.

6. Cross-comparison

The three examples can be placed on a common map. Si MACE modifies the structural boundary conditions for absorption and surface area. ZnO/TiO_2 electrodeposition modifies the interfacial electronic landscape and defect distribution. GaN impedance analysis identifies the kinetic resistance that dominates a complete device. Their comparison shows that electrochemical methods are not interchangeable; each is best matched to a particular bottleneck. A concise summary is given in Table 1.

Table 1. Comparative interpretation of the three electrochemical strategies discussed in this Review

System	Electrochemical lever	Main gain	Principal risk	Design implication
n-Si nanowires	Au electrodeposition followed by MACE	High surface area and light trapping	Surface recombination, lateral etching, corrosion	Use MACE as optical scaffold, then passivate and catalyze
ZnO/TiO_2 nanorods	CV electrodeposition of ZnO	Improved charge separation and carrier lifetime	Excess defects or thick ZnO layers	Optimize deposition charge, not simply loading
NiO/AlGaN/n-GaN	Impedance-resolved tandem operation	Identification of charge-transfer bottleneck	Photo-corrosion at defect-rich sites	Design catalysts and protection to reduce Rct

In photoelectrochemical design, although morphology amplification is an effective way to enhance light absorption, high surface area is beneficial only when the interfacial properties are favorable and catalytically competent; otherwise, it becomes a source of recombination and corrosion. Furthermore, the band alignment of heterojunctions is often simplified to a band-alignment type, but the actual performance is greatly influenced by defect chemistry and preparation conditions; transient or impedance measurements are necessary to reveal the true working mechanism. However, even if the structure is reasonable, the interface charge transfer kinetics often becomes the rate-limiting step, and each performance enhancement may simultaneously give rise to new vulnerabilities.Stability, in turn, reflects the competition between target reactions and material

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degradation. Therefore, future optimization must shift from single-factor turning to multi-dimensional parameter space, using kinetic parameters such as charge transfer resistance, carrier lifetime, Faraday efficiency, and degradation rate as targets, and coupling with machine learning to achieve causality-oriented design, rather than merely pursuing photocurrent density [17].

7. Design principles for next-generation semiconductor photoelectrodes

Several design principles emerge from the analysis. Semiconductor design needs to match the carrier transport scale and control surface recombination. By using chemically selective interfaces and catalysts, one can direct the photovoltage towards the target reaction. Defects are engineered to regulate transport. Multi-level characterization is employed to diagnose the specific loss mechanisms, and the optimization of half-cell should be considered as early as possible within the constraints of voltage, resistance, and crosstalk in the full cell.

8. Conclusion

The next stage of semiconductor photoelectrochemistry will be defined less by discovering isolated high-performing materials and more by integrating operando diagnosis with controllable electrochemical synthesis. Electrochemical routes are uniquely suited for this because the same setup that deposits a catalyst can measure its nucleation transient, the same illuminated cell driving water splitting can perform impedance analysis, and the same potential program etching a semiconductor can reveal corrosion onset—creating a powerful continuity between fabrication and measurement.

Operando spectroscopy is crucial because in situ Raman monitoring can observe surface intermediates and catalyst phase transitions, while ambient pressure X-ray photoelectron spectroscopy can clearly determine the oxidation state and band bending. Meanwhile, transient absorption or time-resolved photoluminescence can distinguish bulk recombination from interfacial charge extraction. When these techniques are combined with electrochemical impedance spectroscopy and product analysis, provided that the measurement results reflect the actual working conditions, empirical optimization can be transformed into causal design.

Data-guided optimization using machine learning must evolve beyond models trained solely on photocurrent density, as such models may rely on artifacts or unstable morphologies. Instead, synthesis variables should be treated as inputs and multiple mechanistic targets—absorption, onset potential, charge-transfer resistance, carrier lifetime, Faradaic efficiency, and degradation rate—as outputs, enabling robust Pareto-front optimization. Environmental and manufacturing considerations, including low-toxicity etchants, recyclable electrolytes, reduced noble-metal loading, and scalable deposition, must be embedded from the start rather than appended after proof-of-concept.

Conceptually, this field should shift from maximizing photocurrent to directing photovoltage and photogenerated carriers to the target reaction, while minimizing entropy generation and material damage. This requires precise resistance distribution, controllable interfaces, stable catalysts, and structural designs that can decouple optical absorption from catalytic functions without introducing recombination effects.

The discussed examples—metal-assisted chemical etching of Si for high-surface-area light-trapping, electrodeposition of ZnO on TiO_2 nanorods to control heterojunctions and defect chemistry, and impedance analysis of NiO/AlGaN/n-GaN tandem photoanodes pinpointing interfacial water-oxidation kinetics as the limiting factor—illustrate the toolbox's power. The most

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valuable interventions reduce an identified loss mechanism while preserving optical absorption, carrier transport, chemical selectivity, and stability. The unifying conclusion is that electrochemical processing should be viewed as a coupled design and diagnostic methodology, simultaneously optimizing morphology, interfacial energetics, defect chemistry, and reaction kinetics to progress from impressive component demonstrations to durable solar-fuel devices.

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