

pH-Responsive Molecular and Interfacial Engineering of Dye-Sensitized Solar Cells: From Protonation Control to Device Stability

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Abstract: Proton activity is often treated as a secondary experimental variable in dye-sensitized solar cells (DSSCs), although it can influence sensitizer protonation, electronic structure, TiO₂ surface chemistry, dye adsorption, interfacial charge transfer, electrolyte behavior, and device stability. This topical review examines the molecular, interfacial, electrochemical, and device-level mechanisms through which proton activity affects DSSC operation, with particular emphasis on the coupling between dye protonation and TiO₂ surface processes. Evidence from primary studies is critically examined to establish how protonation-dependent changes in absorption, redox properties, anchoring geometry, electronic coupling, charge injection, recombination, and photovoltaic parameters contribute to observed device responses. The review further evaluates natural and synthetic pH-responsive sensitizers, anchoring-group chemistry, TiO₂ surface treatment and passivation, electrolyte and solvent effects, and emerging adaptive concepts involving photoacid generators, buffering layers, and dynamic anchors. Rather than proposing a universal optimum pH, the review develops an integrated framework in which sensitizer acidity, semiconductor surface protonation, interfacial coupling, and electrolyte composition are treated as coupled design variables. Particular attention is given to distinguishing reversible proton-responsive switching from irreversible processes such as photobleaching, dye desorption, aggregation, and chemical degradation. An evidence-to-device characterization strategy integrating molecular spectroscopy, surface analysis, electrochemical measurements, photovoltaic testing, and stability assessment is proposed.

The review concludes that systematic control of coupled protonation equilibria, supported by independent experimental controls and multiscale modelling, provides a stronger basis for developing DSSCs with reproducible charge-transfer responses and improved operational stability under chemically dynamic conditions.

Keywords: dye-sensitized solar cells (DSSCs); pH responsiveness; protonation; anchoring groups; charge injection.

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1.0 Introduction

Dye sensitized Solar Cells (DSSCs) constitute an important platform on which to study molecular light harvesting, interfacial electron transfer and low temperature PV fabrication. A typical DSSC consists of a dye-sensitized mesoporous semiconductor photoanode, a redox-active electrolyte, and a catalytic counter electrode. Under illumination, the sensitizer absorbs incident photons and undergoes electronic excitation, followed by electron injection into the conduction band of the semiconductor. The injected electrons are transported through the photoanode and external circuit, while the oxidized dye is regenerated by the electrolyte. The redox mediator is subsequently regenerated at the counter electrode, completing the photovoltaic cycle. The efficiency of these coupled processes is governed by the optical properties of the sensitizer, the energetics of electron injection, the quality of dye

adsorption, interfacial charge-transfer kinetics, and the suppression of charge-recombination pathways. They require a series of coupled processes; dye excitation, injection of electrons into a semiconductor, electron transfer through the photoanode, regeneration of the dye and electron transfer at the counter electrode. The interfacial chemistry between a sensitizer and metal oxide is not limited to an anchoring step, rather it influences the geometry of adsorption, electronic coupling and charge generation (Zhang & Cole, 2015).

The dye-semiconductor interface is particularly important because the anchoring group determines the adsorption geometry, surface binding, electronic communication, and accessibility of the sensitizer to the surrounding electrolyte. Changes in the chemical environment may therefore modify not only dye attachment but also the energetics and kinetics of interfacial electron transfer. These considerations make the molecular and surface chemistry of the photoanode central to understanding variations in DSSC performance.

Proton activity describes the effective chemical activity of hydrogen ions in a system and is related to pH through the thermodynamic definition of proton activity. In aqueous media, pH provides a convenient operational measure, whereas in non-aqueous electrolytes the interpretation of apparent pH requires careful consideration of solvent effects, reference states, and activity coefficients. Proton activity is another chemical variable as many of the DSSC components have ionizable functional groups or surface hydroxyls. The direct evidence of the pH-dependent sensitized photocurrent and changes in TiO₂ surfaces due to protonation was obtained in earlier studies. Meyer (2005) has, for example, reported on large changes in sensitized photocurrent as a function of the pH of the electrolyte and suggested that the protonation of surface states might be the reason. The protonation state of

the sensitizer has been found to affect the photovoltaic response of Ru dyes and, in subsequent combination of theory and experiment, the protonation state of TiO₂ was correlated with both electronic coupling and behaviour of charge-injection at the interface (Nazeeruddin *et al.*, 2003; Anderson *et al.*, 2014).

Collectively, these studies suggest that proton-responsive behavior in DSSCs cannot be interpreted solely in terms of bulk electrolyte acidity. Protonation may alter the electronic structure of the sensitizer, the chemical state of TiO₂ surface hydroxyl groups, the adsorption configuration of the dye, and the interfacial energy landscape governing electron injection. However, the relative contribution of these mechanisms is likely to vary among sensitizers and experimental systems. A systematic comparison of the molecular, surface, and electrolyte factors is therefore necessary to distinguish direct protonation effects from secondary changes in adsorption, surface-state occupancy, recombination, and electrolyte transport.

The key results are relevant because they shift the science/technology question from 'what pH results in the best efficiency?', to a more mechanistic 'how does proton activity flow through molecular and interfacial variables to impact device efficiency?'. This answer will not be simplified into a protonation of a dye. The surface protonation, electrolyte composition, adsorption equilibria, defect states and defect pathways of recombination may change at the same time. The degradation of the DSSC is also controlled by an interplay between physical and chemical processes between dyes, electrolyte, counter electrodes, water, oxygen, temperature and illumination (Sauvage *et al.*, 2014; Kabir *et al.*, 2022), which is further confirmed by the DSSC stability checks. In this context, operational stability should be considered alongside initial



photovoltaic efficiency. A proton-responsive DSSC may exhibit a measurable change in photocurrent or photovoltage while simultaneously undergoing dye desorption, chemical degradation, electrolyte decomposition, or irreversible modification of the semiconductor surface. Consequently, a genuine pH-responsive effect should be evaluated by examining reversibility, repeatability, and retention of photovoltaic performance under controlled operating conditions.

The problem is particularly apparent in natural dyes, because some of the classes of natural dyes contain pH or protonation-dependent chromophores and other natural dyes can be unstable from a photochemical and/or chemical perspective. This literature has been reviewed from a variety of points of view including potential, stability deficiencies, dye source, and efficiency; however, the general topic of proton-activity mechanisms has not been emphasized (Prabavathy *et al.*, 2017; Alim *et al.*, 2022). This provides a chance to relate pigments' chemistry to a wider literature of interface engineering.

Natural pigments such as anthocyanins and other oxygen-containing chromophores are particularly relevant to proton-responsive studies because their absorption characteristics may change with protonation, deprotonation, tautomerization, or structural transformation. Nevertheless, a reversible color change does not necessarily demonstrate reversible photovoltaic switching. The distinction between reversible protonation, dye desorption, photobleaching, and chemical decomposition is therefore essential when evaluating the suitability of natural dyes for pH-responsive DSSC applications.

Although previous studies and reviews have examined sensitizer chemistry, dye anchoring, TiO₂ surface engineering, natural dye stability, and protonation-dependent photo-electrochemical behavior, these aspects have largely been investigated as separate components of DSSC operation. An integrated

framework linking dye protonation equilibria, TiO₂ surface protonation, anchoring geometry, interfacial electronic coupling, charge injection, recombination, and device stability remains insufficiently developed. In particular, the absence of standardized experimental strategies for distinguishing dye protonation effects from surface modification, electrolyte changes, and irreversible degradation limits the mechanistic interpretation of pH-dependent photovoltaic responses. Addressing this gap requires a coordinated analysis that connects molecular protonation measurements with surface characterization, electrochemical testing, photovoltaic evaluation, and long-term stability assessment.

The significance of this review lies in its integration of molecular protonation chemistry with semiconductor surface engineering and device-level photovoltaic analysis. By distinguishing dye protonation effects from TiO₂ surface modification, electrolyte-mediated changes, and degradation processes, the proposed framework may support more reliable interpretation of pH-dependent DSSC behavior. It also identifies experimental controls and characterization strategies needed to evaluate reversible proton-responsive operation and guide the development of DSSCs with improved charge-transfer control and operational stability.

Against this background, this topical review aims to critically examine the molecular, interfacial, and device-level mechanisms through which proton activity influences DSSC operation and stability. Particular attention is given to sensitizer protonation, TiO₂ surface chemistry, dye anchoring, electrolyte composition, charge injection, recombination, and degradation. The review further seeks to distinguish experimentally established strategies from emerging design hypotheses



and to propose an evidence-to-device framework for evaluating pH-responsive DSSC architectures.

. Proposed questions in this review are: The review is guided by the following questions:

- (i) Which molecular and interfacial processes in DSSCs are sensitive to proton activity?
- (ii) How do these processes influence dye–TiO₂ electronic coupling, charge injection, recombination, and photovoltaic performance?
- (iii) Which pH-responsive molecular and interfacial engineering strategies are supported by experimental evidence, and which remain emerging hypotheses?
- (iv) What experimental and characterization procedures are required to validate reversible pH-responsive behavior and assess its implications for DSSC stability?

2.0 Scope and Review Approach

This topical/technical review examines the molecular, interfacial, and device-level factors governing pH-responsive behavior in TiO₂-based dye-sensitized solar cells (DSSCs). The scope includes sensitizer protonation, dye anchoring and adsorption, TiO₂ surface protonation, electrolyte and solvent effects, charge injection, recombination, photovoltaic performance, and operational stability. Broader photoelectrochemical systems are considered only where their findings provide mechanistic insight relevant to DSSC operation. Particular emphasis is placed on the relationship between proton activity, molecular electronic structure, dye–TiO₂ interfacial coupling, and device-level charge-transfer processes. The literature was examined thematically, with emphasis on primary experimental studies, theoretical investigations, and established reviews addressing protonation, pH-dependent sensitized photocurrent, TiO₂ surface chemistry, dye anchoring, charge injection, recombination, and DSSC stability. The literature was organized into five interconnected themes: (i) molecular sensitizer

protonation and electronic structure; (ii) dye anchoring and adsorption at TiO₂; (iii) TiO₂ surface protonation and interfacial charge-transfer processes; (iv) electrolyte composition, solvent effects, and proton activity; and (v) photovoltaic performance, degradation, and operational stability. Findings were compared according to sensitizer structure, anchoring group, semiconductor surface treatment, electrolyte environment, and measurement conditions. Particular attention was given to distinguishing direct experimental evidence from mechanistic interpretations and proposed engineering hypotheses. Because the available studies do not provide a sufficiently standardized data set for quantitative meta-analysis, reported photovoltaic efficiencies were not pooled. Instead, the review emphasizes mechanistic comparison, experimental controls, and evidence-based design principles.

3.0 Mechanistic Basis of pH Effects in DSSCs

Fig. 1 presents a schematic framework linking proton activity to the molecular, interfacial, and device-level behavior of dye-sensitized solar cells (DSSCs). Changes in proton activity can alter the protonation state of the sensitizer, thereby modifying its electronic structure, optical absorption, redox properties, and excited-state characteristics. These molecular changes may subsequently influence electron injection into TiO₂, while simultaneous changes in TiO₂ surface protonation can modify surface charge, defect-state occupancy, energy alignment, and interfacial electronic coupling. Proton activity may also affect dye adsorption and anchoring geometry, interfacial recombination, electrolyte-mediated charge transport, and dye regeneration. The combined effects of these molecular and interfacial processes are ultimately reflected in device-level photovoltaic parameters, including short-circuit current density (JSC), open-circuit voltage (VOC), fill factor (FF), power



conversion efficiency (PCE), and operational stability.

3.1 Protonation of the sensitizer

Protonation of an ionizable dye site can be written as $HA \rightleftharpoons H^+ + A^-$ and in systems where a conventional pH concept applies, the protonated/deprotonated populations can be related to the pH of the system by the Henderson–Hasselbalch equation, which relates pH to the ratio of protonated and deprotonated species as follows,

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

For a pH-responsive dye, it helps predict the protonation-state population at a given pH and therefore the expected optical, electronic, and interfacial response.

Changes in protonation can redistribute electron density within the sensitizer and alter its absorption spectrum, redox properties, molecular dipole moment, hydrogen-bonding interactions, and electronic communication with the semiconductor surface.

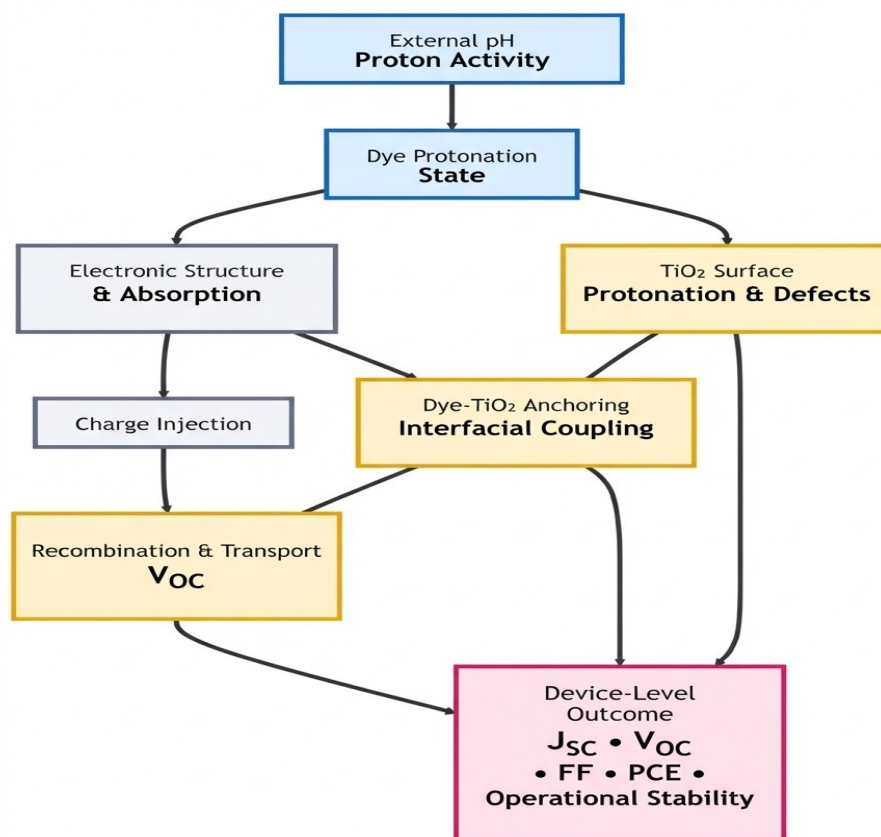


Fig. 1: Schematic diagram of mechanistic procedure linking proton activity to DSSC performance

These effects are strongly dependent on molecular structure, the position of the ionizable group, the nature of the anchoring functionality, and the surrounding solvent and electrolyte environment. Consequently, no

universal relationship can be assumed between pH and photovoltaic performance across different sensitizers.

For ruthenium-based sensitizers, changes in protonation state have been associated with



variations in photovoltaic characteristics, including short-circuit photocurrent density and open-circuit photovoltage (Nazeeruddin *et al.*, 2003). The mechanistic implication is that proton responsiveness cannot be considered solely as a bulk-electrolyte property. Instead, the local chemical environment of the sensitizer, particularly the protonation state and chemical form of its anchoring groups, can influence dye adsorption, interfacial electronic coupling, and subsequent charge-transfer processes.

3.2 Protonation of TiO_2 and surface-state chemistry

TiO_2 is an amphoteric oxide whose surface hydroxyl groups can undergo protonation and deprotonation depending on the surrounding chemical environment. Consequently, changes in proton activity can modify surface charge, electrostatic interactions, defect-state occupancy, and the energetic alignment between the semiconductor and adsorbed sensitizer (Ni *et al.*, 2026). These surface processes are particularly relevant to DSSCs because electron injection, interfacial charge separation, and recombination are strongly influenced by the electronic and chemical characteristics of the dye– TiO_2 interface.

Sensitized photocurrent in TiO_2 -based systems has been reported to exhibit pronounced pH dependence. Meyer (2003) discussed the possible role of surface-state protonation in charge compensation and photocurrent generation, highlighting the importance of semiconductor surface chemistry in proton-dependent photoelectrochemical behavior. Subsequent theoretical and experimental investigations have further indicated that protonation of TiO_2 surfaces can influence interfacial electronic coupling and electron-injection kinetics in dye-sensitized systems (Anderson *et al.*, 2014).

Importantly, these observations demonstrate that a change in DSSC performance with

proton activity cannot automatically be assigned to sensitizer protonation alone. Dye protonation and semiconductor surface protonation may occur simultaneously, and their individual contributions may either reinforce or oppose one another. Appropriate experimental controls are therefore required to distinguish molecular protonation effects from changes in TiO_2 surface chemistry.

3.3 Dye anchoring and interfacial coupling

Anchoring groups are functional groups within sensitizer molecules that facilitate adsorption and electronic communication between the dye and the semiconductor surface. Carboxylic acid and cyanoacrylic acid functionalities have historically been widely investigated, while phosphonic acids, catechols, hydroxamates, and related donor groups have also been explored as alternative anchoring motifs (Zhang & Cole, 2015). Their influence on DSSC performance depends on several interrelated factors, including adsorption geometry, binding strength, surface coverage, molecular orientation, electronic conjugation, and the extent to which the anchoring group forms part of the electron-transfer pathway.

Protonation can modify this balance by changing the charge distribution, binding affinity, hydrogen-bonding interactions, and adsorption geometry of the anchoring group. The protonated and deprotonated forms of a sensitizer may therefore exhibit different affinities for TiO_2 and different pathways for electronic coupling across the dye–semiconductor interface. Consequently, proton activity should be considered together with anchoring chemistry rather than treated as an independent optimization variable. Computational and experimental investigations that simultaneously examine protonation, adsorption geometry, and interfacial electronic coupling can provide a more mechanistic basis for designing pH-responsive DSSCs.



4.0 pH-Responsive Dye Design

4.1 Natural dyes and intrinsic pH responsiveness

Natural pigments provide useful model systems for investigating proton-dependent sensitization because many of their chromophores contain ionizable functional groups that respond to changes in proton activity. Anthocyanins are a notable example, exhibiting pronounced pH-dependent changes in molecular structure and optical absorption. Natural-dye-based DSSCs have attracted interest because of the availability and renewable origin of many pigment sources; however, their practical application is frequently constrained by limited photochemical stability, susceptibility to oxidation, and degradation under prolonged illumination and electrolyte exposure (Prabavathy *et al.*, 2017; Alim *et al.*, 2022).

The principal design lesson is therefore not that natural dyes provide an immediately practical route to adaptive pH-responsive DSSCs, but that their molecular chemistry offers valuable model systems for establishing relationships between protonation equilibria, chromophore structure, and optical response. Future studies should explicitly distinguish reversible protonation-induced spectral switching from irreversible processes such as photobleaching, oxidation, aggregation, desorption, and chemical decomposition. These processes should be quantified through repeated pH cycling and controlled illumination experiments under electrolyte and interfacial conditions representative of actual DSSC operation.

4.2 Synthetic dyes with ionizable functional groups

Incorporating titratable functional groups into donor- π -acceptor sensitizers provides a more controllable strategy for introducing proton-responsive behavior. The electronic properties of substituents can be tailored to regulate the acidity or basicity of selected molecular sites

while simultaneously influencing charge distribution and optical transitions. Nevertheless, an appropriate pKa alone is insufficient to establish a useful pH-responsive sensitizer. A viable dye must also exhibit strong and suitably positioned light absorption, favorable ground- and excited-state energetics, efficient electron injection into TiO₂, stable adsorption, rapid regeneration by the redox mediator, and adequate photochemical and chemical stability.

Computational prediction of pKa values can therefore serve as a useful molecular-screening tool, particularly when combined with calculations of electronic structure, absorption characteristics, redox potentials, and dye-TiO₂ interactions. However, predicted pKa values should be experimentally validated because protonation equilibria can differ substantially with solvent composition, ionic strength, ion pairing, electrolyte composition, temperature, and the presence of the semiconductor surface. Surface-bound dyes may also exhibit protonation behavior that differs from that of the corresponding free molecules in solution.

4.3 What should constitute a pH-responsive DSSC dye?

Table 1 defines the criteria and evidence needed to validate a pH-responsive DSSC system, covering reversible protonation, optical and electronic response, TiO₂ compatibility, photovoltaic relevance, and operational stability.

5.0 Interface Engineering for pH-Dependent DSSCs

pH-dependent DSSCs can be understood as an interface-engineering problem because the chemical environment of the TiO₂ surface can influence dye adsorption, electronic coupling, charge injection, recombination, and ultimately photovoltaic performance. Importantly, modification of the semiconductor surface by acid treatment or other chemical processes may occur simultaneously with protonation of the



sensitizer. Surface treatments should therefore be designed and controlled so that changes originating from semiconductor modification

can be distinguished from those arising directly from dye protonation.

Table 1: Validation criteria and recommended evidence for pH-responsive DSSC architectures

Criterion	What should be demonstrated	Recommended evidence
Reversible protonation	Repeated pH cycling without irreversible spectral loss	UV–Vis titration + cycling
Optical response	Systematic, reversible spectral change	Absorption spectra and isosbestic analysis
Electronic response	Protonation changes relevant excited/redox properties	CV, spectroelectrochemistry, calculations
TiO₂ compatibility	Stable adsorption across intended pH window	Desorption/adsorption measurements, FTIR/XPS
Photovoltaic relevance	Change in JSC/VOC/FF linked to protonation rather than degradation	Replicated J–V + controls
Operational stability	Response retained during prolonged illumination	Long-term ageing with periodic characterization

This section considers TiO₂ surface treatment, protonation, passivation, defect control, and emerging adaptive-interface concepts. Particular attention is given to distinguishing relatively established interface-engineering approaches from proposed adaptive strategies, including reversible proton-control elements and dynamic anchoring concepts, for which DSSC-specific experimental validation remains limited.

5.1 TiO₂ surface treatment and protonation

The chemical state of TiO₂ can be modified before sensitization through acid treatment and other surface-conditioning procedures. Such treatments may alter surface hydroxylation, protonation equilibria, defect populations, surface charge, and the electronic properties of the photoanode. In some studies, improvements in photovoltaic performance have been observed following acid-related modification of TiO₂; however, the underlying mechanism is system-dependent. Anderson *et*

al. (2014) demonstrated that surface protonation can influence electronic coupling and charge-injection processes at dye–TiO₂ interfaces, while earlier investigations by Arakawa and co-workers examined changes in DSSC performance following acid treatment of TiO₂ films (Wang *et al.*, 2005; Arakawa & Hara, 2003).

These findings emphasize the need for appropriate experimental controls. Changes in proton activity or acid treatment applied directly to the photoanode should be distinguished from changes in the protonation state of the sensitizer. Without such controls, an observed improvement or deterioration in photovoltaic performance could be incorrectly attributed to the pH responsiveness of the dye when it actually results from modification of the TiO₂ surface, defect states, adsorption characteristics, or interfacial energetics.

5.2 Passivation and defect control

Electron trapping and interfacial recombination can be influenced by intrinsic defects, surface



states, and structural imperfections within TiO_2 . Surface passivation, controlled doping, morphological optimization, and appropriate selection of anchoring chemistries therefore represent important approaches to interface engineering. These modifications can affect conduction-band energetics, trap-state density, electron transport, surface charge, and recombination kinetics, illustrating the multidimensional nature of TiO_2 optimization in DSSCs (Roose *et al.*, 2015).

For pH-responsive systems, however, passivation must be designed so that unwanted surface reactions are suppressed without eliminating the intended proton-responsive behavior. A passivation layer that blocks surface sites may reduce recombination while simultaneously restricting dye adsorption, proton accessibility, or interfacial charge transfer. Consequently, the effect of passivation should be evaluated using complementary surface, electrochemical, and photovoltaic measurements rather than inferred from a single performance parameter.

5.3 Dynamic and adaptive interfaces: evidence versus hypothesis

An emerging design concept is to introduce components capable of dynamically regulating proton activity near the dye- TiO_2 interface. Potential approaches include reversible photoacid generators, proton-buffering or proton-transport components, and dynamic anchoring chemistries. Photoacid systems have been investigated in other light-responsive chemical environments and can provide externally triggered changes in proton concentration under appropriate conditions (Liao, 2022). However, the integration of such components into a fully functional pH-adaptive DSSC should be regarded as an emerging design hypothesis rather than an established DSSC technology unless supported by direct device-level evidence. The principal experimental challenge is to establish whether a local proton-control element can

reproducibly modify sensitizer protonation without introducing unacceptable optical losses, parasitic absorption, mass-transport resistance, chemical instability, dye desorption, or additional recombination pathways. Demonstration of such a system would require evidence of reversible proton modulation, preservation of dye loading and interfacial integrity, reproducible photovoltaic response, and stability during repeated light/dark and pH cycles.

6.0 Electrolyte, Solvent and Proton Activity

Electrolytes influence DSSC performance through several interconnected processes, including redox kinetics, viscosity, mass transport, dye regeneration, interfacial recombination, and chemical stability. Electrolyte composition and degradation are consequently important determinants of the performance and long-term stability of liquid-electrolyte DSSCs (Sauvage *et al.*, 2014). In pH-responsive DSSCs, however, proton activity requires particular attention because conventional pH is not a universally transferable quantity across different non-aqueous electrolyte systems.

Aqueous systems permit the conventional operational use of pH measurements, whereas non-aqueous and mixed-solvent systems may require careful definition of proton activity, reference states, solvent effects, and measurement procedures. Apparent pH values obtained in different solvents or electrolyte compositions should therefore not automatically be treated as thermodynamically equivalent. Comparisons between studies should specify the solvent, electrolyte composition, proton source, measurement method, temperature, and reference-electrode conditions whenever proton activity is used as a mechanistic variable.

Buffering may be desirable because it can help maintain a more stable proton activity near the dye/ TiO_2 interface. However, buffer species



can also modify ionic strength, viscosity, mass transport, redox kinetics, and surface adsorption, and may compete with the sensitizer for available surface sites. Buffering strategies should therefore be evaluated against appropriate unbuffered and chemically matched controls. Such controls are necessary to determine whether an observed photovoltaic change results specifically from stabilization of proton activity or from secondary changes in electrolyte properties.

7.0 Characterization Strategy: From Molecular Response to Device Performance

A comprehensive characterization strategy is required to establish pH responsiveness in DSSCs across molecular, interfacial, electrochemical, and device levels. Changes in bulk proton activity may influence sensitizer protonation, electronic structure, optical absorption, TiO₂ surface chemistry, interfacial coupling, charge injection, recombination, and ultimately photovoltaic performance, as summarized in Fig. 2. Because these processes can occur simultaneously, complementary measurements are necessary to distinguish genuine and reversible proton-responsive behavior from semiconductor surface modification, dye desorption, electrolyte effects, photochemical degradation, and other confounding processes.

The evidence-to-device framework therefore integrates molecular and optical measurements with surface characterization, electrochemical analysis, time-resolved measurements, photovoltaic testing, and long-term stability assessment. UV-Vis spectroscopy and controlled protonation titrations can establish molecular optical responses; FTIR and surface-sensitive techniques can investigate adsorption and interfacial chemical changes; electrochemical and time-resolved methods can probe charge-transfer and recombination processes; and photovoltaic measurements can determine whether molecular or interfacial

changes translate into reproducible changes in JSC, VOC, FF, and PCE.

7.1 UV-Vis and pH titration

UV-Vis titration provides a convenient first-line method for evaluating pH-dependent optical responses of sensitizers. A rigorous experiment should determine whether spectral changes are reversible and reproducible over repeated protonation-deprotonation cycles. Measurements should include appropriate replication, controlled increments of proton activity around the transition region, and controls for dilution, ionic strength, solvent composition, and temperature. The appearance of an isosbestic point may provide evidence for an interconversion between dominant spectroscopic species, although its presence alone does not establish a simple two-state equilibrium or exclude parallel degradation pathways. Repeated cycling and complementary chemical characterization are therefore required to distinguish reversible protonation from irreversible decomposition, aggregation, or photobleaching.

Fourier-transform infrared spectroscopy (FTIR) can provide information on changes in carboxyl, carbonyl, hydroxyl, and other functional groups associated with protonation, deprotonation, and adsorption. In sensitized TiO₂ systems, comparison of the vibrational spectra of the free dye, protonated/deprotonated dye, and dye adsorbed on TiO₂ can help identify changes in anchoring interactions and the chemical environment of the sensitizer. Attenuated total reflectance FTIR (ATR-FTIR) can provide additional information on surface-associated vibrational features of adsorbed sensitizers.

FTIR observations should be complemented by surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), Kelvin-probe measurements, and microscopy. These techniques can provide complementary information on surface composition, chemical states, surface potential, morphology, and



changes occurring at the dye–TiO₂ interface. Because individual spectroscopic features may have multiple possible assignments, interpretation should be supported by

appropriate reference spectra and, where possible, independent characterization methods.

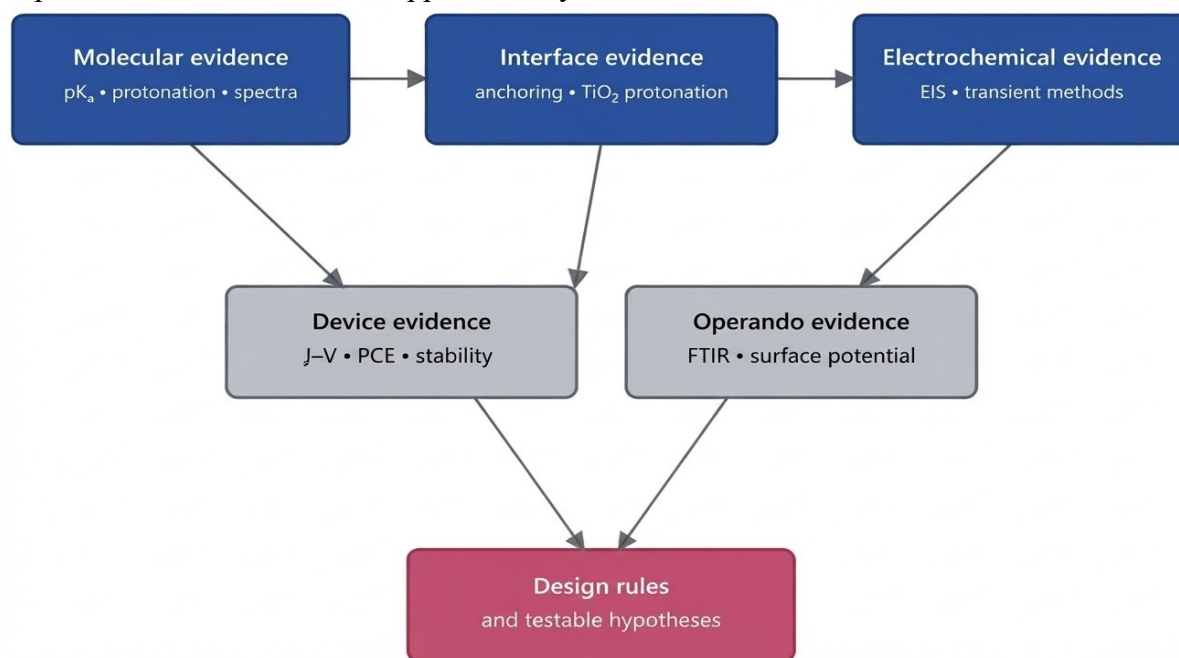


Fig. 2. Evidence-to-device framework for evaluating pH-responsive DSSCs.

7.2 FTIR and surface-sensitive measurements

7.3 Electrochemical and time-resolved methods

Electrochemical impedance spectroscopy (EIS) can assist in distinguishing changes in charge-transfer resistance, transport processes, interfacial recombination, and other impedance-related characteristics associated with pH-dependent operation. Time-resolved spectroscopic methods, including transient absorption or related excited-state measurements, can provide information on excited-state lifetimes and electron-injection kinetics. These measurements are particularly important because an increase in steady-state photocurrent does not, by itself, demonstrate faster electron injection.

Photocurrent can increase because of changes in light absorption, dye loading, surface coverage, electrolyte conductivity, regeneration kinetics, or recombination losses.

A mechanistic interpretation therefore requires correlation of photovoltaic measurements with independent measurements of dye protonation, optical absorption, adsorption, charge injection, and recombination. Where EIS is used, equivalent-circuit parameters should likewise be interpreted cautiously and supported by complementary measurements because similar impedance features can arise from different physical processes.

7.4 Photovoltaic measurements and stability

J–V characterization should be performed under well-defined and reproducible illumination conditions, with multiple independently prepared devices used to assess experimental variability. The principal photovoltaic parameters should include short-circuit current density (JSC), open-circuit voltage (VOC), fill factor (FF), and power conversion efficiency (PCE), together with appropriate measures of uncertainty. For pH-



responsive DSSCs, the electrolyte composition, dye-loading procedure, photoanode conditioning, measurement sequence, and proton-activity control should be standardized across experimental groups.

Stability studies should also specify illumination intensity, spectral conditions, temperature, atmospheric environment, sealing procedure, electrolyte composition, and the criterion used to define degradation. Measurements performed during ageing should ideally include periodic characterization of optical, electrochemical, and photovoltaic properties so that a loss of performance can be distinguished from reversible proton-responsive switching. Such a combined approach is necessary to determine whether an apparent improvement in charge-transfer behavior is sustained during operation or is accompanied by dye degradation, desorption, electrolyte deterioration, or increased recombination.

8.0 Integrated Design Rules

Table 2. Integrated design variables, trade-offs, and evidence requirements for pH-responsive DSSCs

Design variable	Potential effect	Main trade-off	Evidence needed
Dye pKa	Controls protonation population	Wrong pKa may give little response or excessive protonation	pH titration + electronic characterization
Anchoring group	Controls adsorption and electronic coupling	Strong binding may not maximize injection	FTIR/XPS + device testing
TiO ₂ protonation	Changes surface electrostatics and states	Can alter recombination and VOC	Surface characterization + EIS
Electrolyte proton activity	Changes multiple interfacial equilibria	May alter redox kinetics and stability	Controlled electrolyte matrix
Buffering layer	May stabilize local proton activity	Adds transport/interface complexity	Matched controls + impedance
Photoacid/rPAG	Potential dynamic proton control	Photo-fatigue and parasitic chemistry	Repeated light/dark cycling
Passivation	Can suppress traps/recombination	May block adsorption or proton access	Surface and photovoltaic controls

Table 2 summarizes proposed integrated design principles for pH-responsive DSSCs by relating each design variable to its anticipated function, principal trade-offs, and experimental evidence required for validation. The framework emphasizes that dye acidity, anchoring chemistry, TiO₂ surface protonation, electrolyte composition, buffering components, photoacid systems, and surface passivation should be considered as coupled variables rather than independent optimization parameters.

Each intervention may influence proton control, charge injection, recombination, or transport, but the same intervention can also introduce competing effects. Consequently, claims of improved pH responsiveness should be supported by coordinated molecular, interfacial, electrochemical, photovoltaic, and stability measurements. The design principles in Table 2 should therefore be interpreted as evidence-based working guidelines rather than universal performance rules.



9.0 Research Gaps and Future Directions

Despite increasing evidence that proton activity can influence sensitized TiO₂ systems, an integrated framework quantitatively or mechanistically relating dye acidity, sensitizer protonation, TiO₂ surface protonation, anchoring geometry, interfacial electronic coupling, and device-level photovoltaic parameters remains insufficiently developed. Existing studies frequently vary several of these parameters simultaneously, making it difficult to isolate the contribution of individual proton-responsive processes. Standardized experimental matrices that independently control sensitizer protonation and semiconductor surface protonation are therefore needed.

A second major gap concerns the distinction between reversible proton-responsive switching and irreversible degradation. A change in absorption intensity or color with proton activity does not necessarily demonstrate a useful or reversible photovoltaic response. Repeated pH cycling under dark and illuminated conditions should therefore be combined with measurements of spectral recovery, dye retention, chemical integrity, photovoltaic performance, and interfacial properties. Such experiments would help distinguish reversible protonation-deprotonation from photobleaching, oxidation, aggregation, desorption, and electrolyte-induced degradation.

A third research gap concerns the integration of multiscale computational modelling with experimental characterization. Quantum-chemical calculations can be used to evaluate protonation energetics, electronic structure, absorption properties, and redox characteristics, while explicit dye-TiO₂ models can provide insight into adsorption geometry and interfacial electronic coupling. These calculations should be integrated with spectroscopic, electrochemical, and

photovoltaic measurements rather than treated as substitutes for experimental validation.

Finally, the proposed concept of adaptive proton control requires direct experimental testing. A systematic validation pathway could involve: (1) selecting a sensitizer with experimentally demonstrable and reversible protonation; (2) characterizing its optical and electronic response as a function of proton activity; (3) measuring its adsorption and interfacial behavior on TiO₂; (4) independently characterizing TiO₂ surface protonation in the absence of the dye; (5) quantifying charge-injection and recombination kinetics; (6) fabricating matched DSSCs with controlled electrolyte and surface conditions; and (7) evaluating photovoltaic response and long-term stability during repeated proton-activity and illumination cycles. Such a sequence would improve the ability to distinguish causal relationships from correlations and provide a stronger basis for evaluating adaptive pH-responsive DSSC architectures.

10.0 Conclusions

Proton activity represents an important but insufficiently integrated variable in the molecular and interfacial operation of dye-sensitized solar cells (DSSCs). This review demonstrates that changes in proton activity can influence sensitizer protonation, molecular electronic structure, optical absorption, redox characteristics, TiO₂ surface protonation, dye adsorption, anchoring geometry, interfacial electronic coupling, charge injection, recombination, and electrolyte-mediated charge transport. These interconnected processes can ultimately affect short-circuit current density, open-circuit photovoltage, fill factor, power conversion efficiency, and operational stability. The overall response, however, is system-dependent and cannot be generalized to a single optimum pH applicable to all DSSC architectures.



A central outcome of the review is that pH-dependent photovoltaic behavior should be interpreted through coupled molecular, semiconductor, interfacial, and electrolyte processes rather than through bulk proton activity alone. Sensitizer structure and pK_a, anchoring-group chemistry, TiO₂ surface protonation, adsorption geometry, and electrolyte composition can interact in ways that either enhance or counteract one another. Consequently, observed changes in photovoltaic performance should not automatically be assigned to dye protonation without independently evaluating changes in TiO₂ surface chemistry, dye loading, adsorption, charge injection, recombination, and electrolyte properties.

The review further establishes the importance of distinguishing reversible proton-responsive behavior from irreversible degradation. A pH-dependent spectral change does not, by itself, demonstrate a useful or stable photovoltaic switching mechanism. Reliable identification of genuine proton-responsive DSSCs therefore requires repeated protonation–deprotonation cycles, controlled illumination experiments, molecular spectroscopy, surface characterization, electrochemical measurements, replicated photovoltaic testing, and long-term stability assessment. Such measurements provide the evidence necessary to establish causal relationships between proton activity, interfacial chemistry, and device performance.

From a design perspective, dye acidity, anchoring chemistry, TiO₂ surface treatment, electrolyte proton activity, buffering, and passivation should be considered coupled variables rather than independent optimization parameters. Photoacid generators, buffering layers, and dynamic anchors offer potentially interesting routes toward adaptive proton control, but these concepts remain emerging strategies requiring direct DSSC-level validation. Their evaluation should include not

only proton-control capability but also optical losses, mass-transport resistance, parasitic reactions, dye retention, recombination, photochemical stability, and cycling durability. Overall, the development of pH-responsive DSSCs requires a transition from empirical pH optimization toward mechanism-based molecular and interfacial engineering. Future research should combine experimentally validated protonation equilibria with explicit characterization of dye–TiO₂ interactions, multiscale computational modelling, controlled electrolyte environments, and device-level validation. Such an integrated evidence-to-device framework can provide quantitative design principles for engineering DSSCs with reproducible charge-transfer behavior and improved stability under chemically dynamic operating conditions.

11.0 References

- Alim, M. A., Repon, M. R., Islam, T., Mishfa, K. F., *et al.* (2022). Mapping the progress in natural dye-sensitized solar cells: Materials, parameters and durability. *ChemistrySelect*, 7, e202201557. <https://doi.org/10.1002/slct.202201557>
- Anderson, N. A., *et al.* (2014). Effect of sensitizer structure and TiO₂ protonation on charge generation in dye-sensitized solar cells. *The Journal of Physical Chemistry C*, 118, pp. 16927–16940. <https://doi.org/10.1021/jp5004853>
- Arakawa, H., & Hara, K. (2003). Current status of dye-sensitized solar cells. *Semiconductor Photochemistry and Photophysics/Volume Ten*, 10, 118. <http://dx.doi.org/10.1002/0470014008.ch15>
- Kabir, F., Manir, S., Bhuiyan, M. M. H., *et al.* (2022). Instability of dye-sensitized solar cells using natural dyes and approaches to improving stability—An overview. *Sustainable Energy Technologies and Assessments*, 52, 102196. <https://doi.org/10.1016/j.seta.2022.102196>



- Liao, Y. (2022). Reversible photo control of proton chemistry. *Physical Chemistry Chemical Physics*, 24. <https://doi.org/10.1039/D1CP05627A>
- Meyer, G. J. (2005). Molecular approaches to solar energy conversion with coordination compounds anchored to semiconductor surfaces. *Inorganic chemistry*, 44(20), 6852-6864. <https://doi.org/10.1021/ic0505908>
- Nazeeruddin, M. K., *et al.* (2003). Investigation of sensitizer adsorption and the influence of protons on current and voltage of a dye-sensitized nanocrystalline TiO₂ solar cell. *The Journal of Physical Chemistry B*. <https://doi.org/10.1021/jp022656f>
- Ni, Q., Qi, Y., Johnson, S., Mahajan, D., Upreti, S., Vaezsis, S., Pradhan, N.R., Ray, P.C., Gu, X., Patton, D. a & Li, D., Dai, Q. (2026). Protonation as a Simple Strategy to Activate Interfacial Modifiers for High-Performanc Perovskite Solar Cells. *Organic Electronics*, 107475.
- Prabavathy, N., Shalini, S., Balasundaraprabhu, R., Velauthapillai, D., Prasanna, S., & Muthukumarasamy, N. (2017). Enhancement in the photostability of natural dyes for dye-sensitized solar cell (DSSC) applications: A review. *International Journal of Energy Research*, 41, pp. 1372–1396. <https://doi.org/10.1002/er.3703>
- Roose, B., Pathak, S., & Steiner, U. (2015). Doping of TiO₂ for sensitized solar cells. *Chemical Society Reviews*, 44, 8326–8349. <https://doi.org/10.1039/C5CS00352K>
- Wang, Z. S., Yamaguchi, T., Sugihara, H., & Arakawa, H. (2005). Significant efficiency improvement of the black dye-sensitized solar cell through protonation of TiO₂ films. *Langmuir*, 21, 10, pp. 4272-4276. <https://doi.org/10.1021/la050134w>
- Sauvage, F., *et al.* (2014). A review on current status of stability and knowledge on liquid electrolyte-based dye-sensitized solar cells. *Advances in Chemistry*, 2014, 939525. <https://doi.org/10.1155/2014/939525>
- Zhang, L., & Cole, J. M. (2015). Anchoring groups for dye-sensitized solar cells. *ACS Applied Materials & Interfaces*, 7, 3427–3455. <https://doi.org/10.1021/am507334m>

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Conflict of interest

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Ethical Consideration

Not applicable

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Ibrahim O. Abdulsalami: Conceptualization, Methodology, Investigation, Formal analysis, Software, Data curation, Visualization, Writing – original draft, Writing – review and editing, Supervision. Stella A. Emmanuel: Investigation, Methodology, Data curation, Formal analysis, Validation, Review and editing

