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Is It Real Type-II or S-Scheme? A Three-Phase Diagnostic Protocol for Identifying Potentially Mislabeled Heterojunction Photocatalysts

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ABSTRACT

The absence of standardized diagnostic protocols has fostered widespread mechanistic uncertainty in heterojunction photocatalysis, with numerous Type-II claims lacking conclusive interfacial and kinetic evidence. In response, I propose a three-phase, seven-step diagnostic framework structured as an evidence hierarchy: Phase I (Steps 1–3) establishes foundational band alignment, Phase II (Steps 4–5) probes the interfacial electronic structure, and Phase III (Steps 6–7) validates dynamic charge-transfer pathways. An evaluation of 30 purported Type-II systems reveals a critical validation gap: only 3.3% (1/30) achieves full validation, leaving 10.0% (3/30) characterized as thermodynamic paradoxes (electrical sign-reversals) and 86.7% (26/30) in a pervasive evidence vacuum (stalling at foundational alignment). This protocol is offered as a diagnostic tool to help the field move from heuristic assignment toward more evidence-based rational design of photocatalysts.

1 | Introduction

Type-II heterojunctions represent a cornerstone of photocatalyst design, promising efficient charge separation through staggered band alignment for applications critical to global decarbonization, including solar fuel production and the mineralization of persistent organic pollutants [1–30]. However, the recent emergence of competing models, particularly the S-scheme and Z-scheme, has exposed fundamental ambiguities in mechanistic assignment [31–40]. These models share identical physical configurations while proposing fundamentally different charge-transfer pathways, creating a validation crisis where the same system can be interpreted through contradictory frameworks (Figure 1) [41–44].

To establish the physical foundation for the diagnostic framework, a brief review of heterojunction physics is necessary. When two semiconductors with different work functions are brought

into contact, Fermi level equilibration occurs: electrons flow from the higher Fermi level (lower work function) to the lower Fermi level until alignment is achieved [31–40]. This charge transfer creates a space-charge region, inducing band bending and an internal electric field (IEF) following Anderson's rule. The resulting band diagram, whether straddling (Type-I), staggered (Type-II), or broken-gap (Type-III), governs charge carrier dynamics. In a Type-II staggered alignment, both the conduction and valence bands of one component are lower than those of the other, enabling spatial charge separation. Carrier transport across the interface is governed by drift (driven by the IEF) and diffusion (driven by concentration gradients). Interface dipoles, defect states, or Fermi level pinning can modify idealized band alignment, adding complexity to experimental interpretation. The combination of these concepts (e.g., band alignment, Fermi equilibration, vacuum referencing, band bending, space-charge region, IEF generation, and drift-diffusion dynamics) collectively provides the theoretical basis for the thermodynamic Sign Rule

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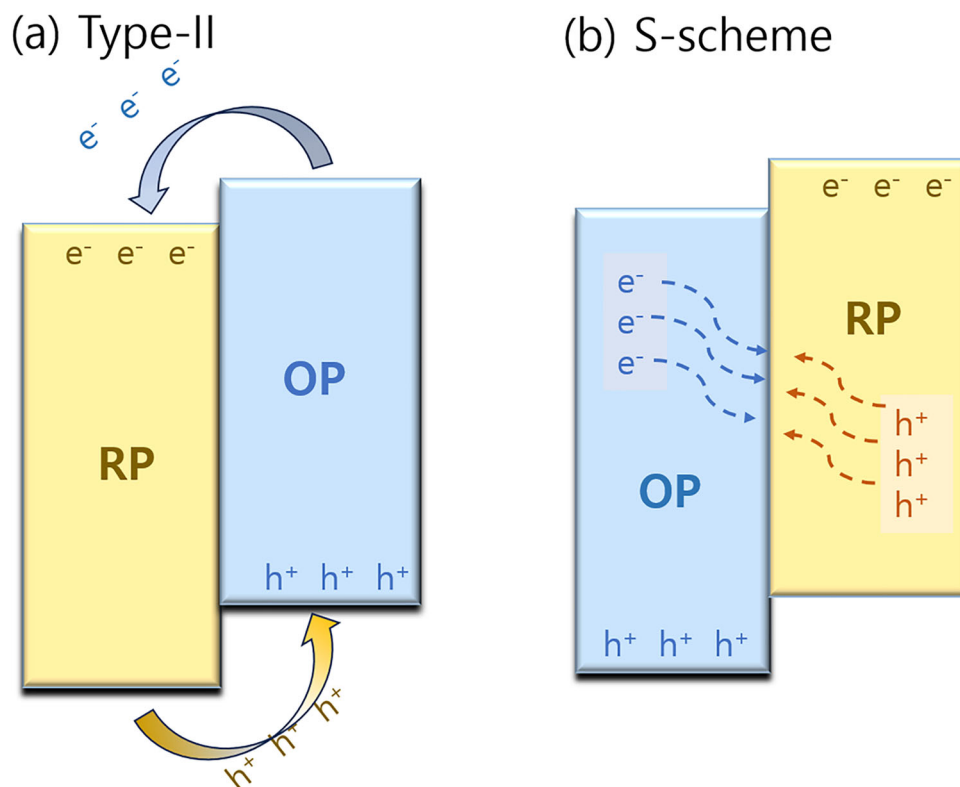


FIGURE 1 | Same structure but opposite flows: Charge-transfer dichotomy in Type-II vs. S-scheme heterojunctions: (a) Type-II heterojunction: Electrons and holes migrate toward lower-energy bands, spatially separating carriers but reducing redox power. (b) S-scheme heterojunction: The same physical interface facilitates recombination of weaker carriers while retaining high-energy electrons and holes in their respective higher-energy bands, thereby preserving strong redox potentials. [Correction added on August 3, 2026, after first online publication: Figure 1b has been updated in this version.]

(ΔCBM , ΔVBM , ΔE_F , and ΔWF). A thorough understanding of these principles is essential for the correct application of the diagnostic protocol.

A physics-based diagnostic for mechanism discrimination can be derived from band positions and Fermi levels. All energetic differences can be defined as $\Delta X = X(\text{RP}) - X(\text{OP})$, where RP is the Reduction Photocatalyst, and OP is the Oxidation Photocatalyst. Accordingly, a validated Type-II heterojunction requires a fully positive signature: (+, +, +, +) ($\Delta\text{CBM} > 0$, $\Delta\text{VBM} > 0$, $\Delta E_F > 0$, $\Delta\text{WF} > 0$). In contrast, an S-scheme requires a fully negative signature: (−, −, −, −). Here it is important to note that ΔE_F and ΔWF use different reference scales: ΔE_F is typically reported in volts vs. NHE (from Mott-Schottky measurements), while ΔWF is reported in electronvolts vs. vacuum (from UPS or KPFM). This “Sign Rule” provides an unambiguous thermodynamic criterion; however, the literature reveals profound confusion. Systems claimed as Type-II often report $\Delta E_F < 0$ [28, 29], while others show (−, −) band alignments characteristic of the S-scheme [15].

The Sign Rule is derived from fundamental thermodynamic principles. For a Type-II heterojunction, electrons and holes migrate toward lower-energy bands, requiring $\Delta\text{CBM} > 0$ and $\Delta\text{VBM} > 0$. Fermi level equilibration upon contact drives spontaneous charge transfer from the higher Fermi level component to the lower, requiring $\Delta E_F > 0$ and $\Delta\text{WF} > 0$ (with consistent convention). An S-scheme requires the opposite pattern ($\Delta\text{CBM} < 0$, $\Delta\text{VBM} < 0$, $\Delta E_F < 0$, $\Delta\text{WF} < 0$). Thus, the Sign Rule is a logical consequence of

thermodynamic constraints. The framework is therefore intended as a consistency check based on reported data, not as an absolute predictor of complex real-world behavior. The Sign Rule is a diagnostic heuristic, not an established physical law. The protocol is offered as a proposal for community discussion and refinement, acknowledging that more sophisticated criteria may emerge in the future.

To elaborate on the reference conventions introduced above: ΔCBM and ΔVBM are derived from band edge potentials measured via Mott-Schottky or UV-vis DRS, typically referenced to NHE or vacuum depending on the measurement method. ΔE_F is referenced to NHE (from Mott-Schottky), while ΔWF is referenced to vacuum ($E_{\text{vac}} = 0$ eV) from UPS or KPFM. Because ΔE_F and ΔWF use different reference scales, they are not linked by a simple conversion equation such as $\Delta\text{WF} = -\Delta E_F$. That equation would only hold if both quantities were referenced to the same scale. Instead, each quantity independently reflects the direction of charge transfer upon contact based on its own reference convention. A positive ΔE_F (vs. NHE) indicates that the reduction photocatalyst (RP) has a higher (more negative) Fermi level and thus acts as an electron donor upon contact (Figure 1). A positive ΔWF (vs. vacuum) independently indicates that the RP has a higher work function, which, under vacuum referencing, also corresponds to electron donation upon contact. The Sign Rule therefore requires both $\Delta E_F > 0$ and $\Delta\text{WF} > 0$ for Type-II assignment, but this is an empirical heuristic derived from the physical interpretation of each measurement separately, not a mathematical consequence of a unified equation.

TABLE 1 | Three-phase, seven-step diagnostic framework for heterojunction validation.

Phase	Step	Diagnostic objective	Primary experimental methods	Evidence level ^a	Points
Phase I	S1	Functional Role	Sacrificial tests, photodeposition	Assumed	1
	S2	Phase Purity	XRD, SEM, XPS (Survey/Core)	Synthesized	—
	S3	Band Edge Potential	UV-Vis DRS, Mott-Schottky (M-S)	Obligatory	1
Phase II	S4	Fermi Alignment	UPS, XPS-VB, KPFM	Obligatory	1
	S5	Charge Separation	Surface Photovoltage (SPV), Steady-state PL	Qualitative	1
Phase III	S6	Interfacial Dynamics	In-situ XPS, TRPL, TAS	Qualitative	1
	S7	Final Classification ^b	Thermodynamic Sign Rule Analysis	Synthesized	—
Total					5^c

^aEvidence Level: **Obligatory** = Required for classification. **Qualitative** = Important supporting evidence. **Assumed** = Basic prerequisite.

^bThe final classification (e.g., Type-II and S-scheme) is based on the accumulated evidence and the synthesized thermodynamic analysis.

^cThe point system is based on the number of validated steps completed. A score of 5/5 indicates that all essential experimental and analytical criteria have been met for reliable heterojunction classification.

It is further acknowledged that the Sign Rule derivation assumes ideal interfaces such as no defects, no interfacial dipoles, no Fermi-level pinning, no surface states, and no strain-induced band shifts. Real photocatalytic heterojunctions often deviate from these ideal conditions. Key non-ideal effects include: (i) interface dipoles arising from chemical bonding or charge transfer at the contact, which can shift band positions by up to 1 eV; (ii) Fermi-level pinning by surface states, which can fix the Fermi level irrespective of bulk band positions; (iii) strain-induced band shifts due to lattice mismatch; (iv) surface reconstruction and adsorbates that modify work functions; and (v) non-equilibrium carrier dynamics under illumination that alter band bending. These effects can modify or even reverse the idealized sign predictions. The Sign Rule is therefore proposed as a necessary consistency check (if the signs contradict the claimed mechanism, the assignment is almost certainly incorrect) rather than a sufficient condition (sign alignment alone does not guarantee the claimed mechanism, due to possible non-ideal interface effects). The framework is offered as a diagnostic heuristic for community discussion and refinement, not as an established physical law. A full mathematical derivation from equilibrium electrostatics, including explicit treatment of the separate reference conventions for ΔE_F and ΔW_F , is provided in Section S13.

To systematically diagnose and resolve this crisis, I introduce a novel three-phase, seven-step diagnostic framework that quantifies validation completeness through a transparent scoring system (0–5 points) (Table 1). A representative cohort of 30 heterojunction systems explicitly claiming a Type-II mechanism, reported from 2021–2025, was analyzed. The complete dataset for all 30 systems is provided in Table S1. The systems span a wide range of materials (oxides, chalcogenides, carbon nitrides, and 2D materials) and journals of varying impact, ensuring that the diagnostic conclusions reflect broad trends rather than niche subsets. The distribution of material classes within the cohort is shown in Table S2. Although limited in number, this dataset captures the methodological diversity and reporting practices across the field during a period when mechanistic discrimination became critical following the formal introduction of the S-scheme concept in 2019 [32].

The framework progresses sequentially through Phase I: Structural & Band Alignment (Steps 1–3), Phase II: Interfacial Electronic Structure (Steps 4–5), and Phase III: Pathway & Mechanism (Steps 6–7) (Figure 2). Critically, the scoring incorporates an “X” flag in Step 7 to identify systems where high-quality experimental evidence is undermined by internal electrical contradictions (e.g., $\Delta E_F/\Delta W_F$ signs that oppose the claimed mechanism) (Table 2). This approach moves beyond binary “valid/invalid” judgments to a graded, evidence-based assessment that distinguishes between incomplete data and fundamentally inconsistent interpretations.

This study addresses the critical validation gap through a systematic re-evaluation of the 30 purported Type-II systems using this diagnostic framework. By converting scattered case studies into a quantitative field-level assessment, I expose not only categorical mislabeling but also a universal evidence vacuum where even high experimental scores can mask fundamental electrical contradictions. The proposed protocol aims to offer a concrete, actionable standard to eliminate heuristic assignment, restore mechanistic rigor, and unlock the latent potential of misclassified systems for rational photocatalyst design. Beyond diagnostics, this framework elevates reproducibility, fosters credible structure-activity relationships, and offers journal editors and reviewers a scalable tool to appraise mechanistic claims, collectively shifting the field from a narrative-driven to an evidence-anchored discipline, where design is guided by validated charge-transfer pathways rather than assumed alignments.

2 | Results

2.1 | The Three-Phase, Seven-Step Diagnostic Framework

To systematically diagnose and resolve the validation crisis, a mandatory three-phase, seven-step diagnostic framework has been built to progress sequentially through Phase I: Structural & Band Alignment (Steps 1–3), Phase II: Interfacial Electronic Structure (Steps 4–5), and Phase III: Pathway & Mechanism,

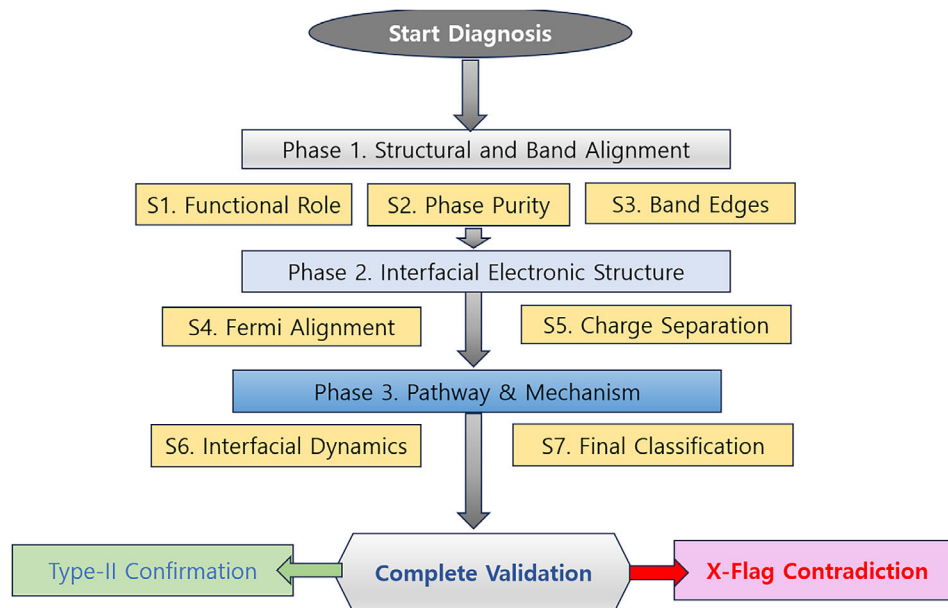


FIGURE 2 | A stepwise three-phase, seven-step diagnostic protocol for heterojunction mechanism validation: The protocol progresses sequentially through Phase I: Structural & Band Alignment (Steps 1–3), Phase II: Interfacial Electronic Structure (Steps 4–5), and Phase III: Pathway & Mechanism (Steps 6–7). Each step corresponds to specific experimental benchmarks, culminating in a diagnostic score (0–5) and an X-flag for thermodynamic contradictions. See Table 2 for detailed scoring criteria. The X flag is triggered only when experimentally measured $\Delta E_F/\Delta WF$ (UPS/XPS-VB/KPFM) show a clear sign contradiction (e.g., negative ΔE_F or ΔWF for a Type-II claim) with $|\Delta| \geq 0.05$ eV; near-zero or ambiguous values do not trigger the flag without corroborating evidence.

TABLE 2 | Diagnostic scoring guide and flag system for heterojunction validation.

Final score	Phases completed	Evidence quality	X-Flag criteria
0	None	DFT/model only	Not applicable
1–2	Phase I only	Band alignment only	None
3–4	Phases I+II	Electronic structure verified	None
5	All three phases	Full dynamic proof	None
X-Flag	<i>Any score</i>	High-quality data	$\Delta E_F/\Delta WF$ contradicts band alignment

X-Flag: Applied when electrical data contradicts Type-II assignment despite good diagnostics

which concludes with Step 7 (Final Classification). Unlike previous steps, Step 7 acts as a synthetic gatekeeper. It does not merely aggregate points but reconciles the experimental evidence from Steps 1–6 against the Sign Rule. If high-quality data from Phase II (S4–S5) or Phase III (S6) contradicts the foundational alignment, Step 7 triggers an “X” flag. This flag identifies a “Mechanistic Paradox”: studies that possess sophisticated characterization but fail the fundamental requirement of thermodynamic consistency (Figure 2).

A transparent scoring system (0–5 points) is developed to quantify validation completeness, where scores correspond directly to phase completion: 0 indicates insufficient experimental data (e.g., DFT-only studies), 1–2 indicate completion of Phase I (band alignment), 3–4 indicate completion of Phases I–II (interfacial electronic structure), and 5 indicates full validation through all three phases (Table 2). Crucially, an “X” flag is applied in Step 7

when high-quality experimental evidence is undermined by internal electrical contradictions (e.g., $\Delta E_F/\Delta WF$ signs that oppose the claimed mechanism). This approach moves beyond binary “valid/invalid” judgments to a graded assessment that distinguishes between incomplete data and fundamentally inconsistent interpretations. (See Methods 5.1 for scoring application details.)

2.2 | Systematic Re-Evaluation Reveals a Three-Tier Validation Crisis

Applying the diagnostic framework to a representative cohort of 30 claimed Type-II systems reveals a stratified validation landscape (Figure 3). The scoring distribution exposes three critical tiers:

Tier I: Complete Validation (3.3%)

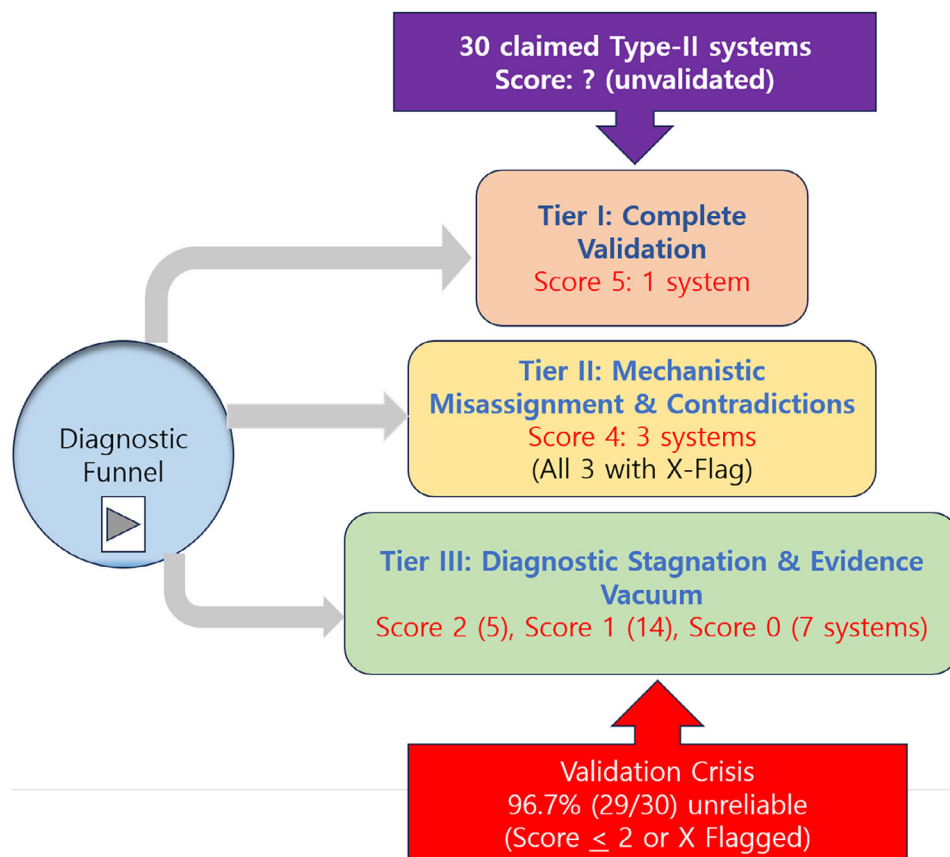


FIGURE 3 | Diagnostic analysis via the heterojunction validation funnel. This funnel illustrates the hierarchical stratification of 30 reported Type-II systems and exposes a 96.7% gap in comprehensive mechanistic validation.

Only one system (1/30) achieves a complete diagnostic score through all three phases. This demonstrates that full mechanistic validation, incorporating foundational alignment, interfacial electronic structure, and dynamic pathway evidence, remains exceptionally rare.

Tier II: The Thermodynamic Paradox (10.0%)

This tier encompasses three unique systems whose reported data fundamentally contradict their claimed mechanisms [15, 28, 29]. All three receive an “X” flag due to electrical data ($\Delta E_F/\Delta WF$) that directly oppose Type-II requirements. Notably, [15] also exhibits a $(-, -)$ band alignment signature, representing a dual failure of both thermodynamic alignment and electrical consistency.

Tier III: Diagnostic Stagnation and Evidence Vacuum (86.7%)

The vast majority of studies fail to progress beyond the foundational validation stage. Fully 26 out of 30 systems (86.7%) score no higher than 2, meaning they stall at Phase I (Structural & Band Alignment). The detailed score distribution and phase completion breakdown are presented in Tables S3 and S4, respectively. These studies either provide only basic band data without essential Fermi-level or work-function measurements (Score 1–2) or rely exclusively on computational models without experimental role verification (Score 0). This widespread stagnation indicates that current reporting standards are insufficient to

advance research into the interfacial and kinetic regimes required for true mechanistic validation.

It is acknowledged that Phase II and Phase III measurements (e.g., UPS, TRPL, in situ XPS) are technically demanding and resource-intensive. Their absence in many studies may reflect practical constraints rather than oversight or neglect. Therefore, the term ‘evidence vacuum’ is not intended as a criticism of individual studies but rather as a field-level observation that the current standard of evidence is insufficient to discriminate between competing mechanistic models. A more nuanced interpretation is that the field operates under a ‘tiered reporting’ norm, where most studies appropriately focus on foundational band alignment, while full mechanistic validation remains a higher-tier goal for systems with exceptional performance or unresolved mechanistic ambiguity.

2.2.1 | Composition of the Dataset: Experimental versus Computational Studies

It is noted that among the 30 analyzed systems, 7 (23.3%) are DFT-only computational studies (Score 0), while the remaining 23 (76.7%) are experimental or combined experimental-theoretical studies. The inclusion of DFT-only studies is important to provide a complete picture of the Type-II heterojunction literature, revealing the proportion of theory-based versus experiment-based research in this field. These computational studies are

not criticized for lacking experimental data; rather, they are included to demonstrate the uniform application of the diagnostic framework across all study types and to show that purely theoretical predictions constitute a substantial fraction (nearly one-quarter) of claimed Type-II systems. Excluding these 7 DFT-only studies from the analysis yields similar proportions for the remaining 23 experimental studies: Complete Validation (4.3%), Thermodynamic Paradox (13.0%), and Evidence Vacuum (82.6%). The main conclusions of the study are therefore robust to the inclusion or exclusion of computational papers.

2.2.2 | Confidence Intervals for the Observed Proportions

To assess the robustness of these proportions against sampling uncertainty, 95% confidence intervals (CIs) were calculated using the Wilson score interval method ($n = 30$). The results are as follows: Complete Validation (Score 5): 3.3% [95% CI: 0.2–18.4%]; Thermodynamic Paradox (X-Flag): 10.0% [95% CI: 2.8–27.2%]; Evidence Vacuum (Score ≤ 2): 86.7% [95% CI: 69.2–95.6%]. While the confidence intervals for the smaller two tiers overlap considerably due to the limited sample size, the lower bound of the Evidence Vacuum interval (69.2%) remains substantially above 50%. This indicates that insufficient validation is not merely a sampling artifact but rather a prevailing condition within the analyzed cohort. Notably, only 20% of studies report both ΔE_F and ΔWF (Table S5), highlighting a major reporting gap in interfacial electronic structure validation. Validation trends from 2021 to 2025 are summarized in Table S6.

It is acknowledged that lower-scoring systems (Scores 0–2) could also harbor thermodynamic contradictions, but they cannot be assessed for the X flag because the required ΔE_F and ΔWF data are not reported. Consequently, the reported proportion of thermodynamic paradoxes (10.0%) represents a lower bound; the true prevalence may be higher. It is hence important to address a potential concern about methodological circularity. The diagnostic framework presented here is a proposed heuristic; it has not been independently validated against an external standard. The conclusions about misclassification or inconsistency are therefore conditional on the acceptance of the Sign Rule as a reasonable consistency check. When the manuscript states that a system exhibits a “thermodynamic contradiction” or is “inconsistent with Type-II assignment,” this means: under the proposed Sign Rule, the reported ΔCBM , ΔVBM , ΔE_F , and ΔWF signs do not match the pattern required for Type-II. This is an observation of internal inconsistency within the reported data relative to the heuristic, not an external proof that the Sign Rule is correct in all aspects. The framework is offered for community discussion and testing; its utility will be determined by whether it helps researchers identify genuinely problematic assignments or instead produces false positives. Future work involving independently validated reference systems will be necessary to improve the framework’s predictive accuracy.

Before interpreting these results, it is important to consider two competing explanations for the low validation rate. One

possibility is that many reported Type-II systems are indeed misclassified or insufficiently validated, reflecting a field-wide gap in mechanistic rigor. A second possibility is that the Sign Rule itself is overly restrictive, oversimplified, or physically incomplete. For example, the sign requirements may not hold under non-ideal interface conditions (dipoles, pinning, and strain), or the 0.05 eV threshold may be too stringent. The manuscript does not assume the first interpretation over the second. Instead, it presents the empirical observation that under the proposed Sign Rule, only 1 out of 30 systems shows full internal consistency. Whether this reflects a genuine validation crisis or a limitation of the heuristic is a question for the community to decide through further testing and refinement. The framework is offered as a diagnostic tool to stimulate discussion, not as complete proof of widespread error.

2.2.3 | Limitation Statement Regarding Dataset Size and Representativeness

It is acknowledged that the dataset, while intentionally selected to span diverse material classes, journal tiers, and publication years (2021–2025), is limited to 30 systems. The selection followed a transparent, PRISMA-inspired workflow documented in Figure S1 and Table S13, detailing each stage from the initial 4,409 records to the final curated cohort. This criterion-based sampling approach is designed for diagnostic illustration—to demonstrate that even in a curated cohort of papers explicitly reporting the minimum required data (band positions), the depth of mechanistic validation is systematically shallow—not for population prevalence estimation. The reported proportions (with 95% confidence intervals) should therefore be interpreted as illustrative of prevailing trends within this representative cohort rather than as statistically definitive estimates for the entire field. Broader surveys involving larger, randomized samples would be required to establish population-level prevalence rates, and such studies are encouraged as future work.

2.3 | Critical Diagnostic Insights

The “Score 4X” Paradox: Among the analyzed cohort, a striking anomaly emerged (Table 3): three systems [15, 28, 29] achieved high experimental scores (≥ 4) but were assigned an “X” flag. Detailed characterization data for these top-scoring systems are provided in Tables S7–S9. The specific electrical contradictions in X-flagged systems are detailed in Table S10. Despite executing advanced techniques like UPS and TRPL, these studies reported ΔE_F or ΔWF signs that diametrically oppose Type-II requirements. This suggests that, under the proposed Sign Rule, experimental completeness does not guarantee internal consistency with the claimed mechanism. Without the Step 7 sign-check, these contradictions remain “hidden” behind the narrative of high-impact characterization. Consequently, I propose that electrical sign-alignment ($\Delta E_F/\Delta WF$) must be treated as a recommendable prerequisite for any Type-II or S-scheme claim.

The S-Scheme Misclassification: The diagnostic framework identified four systems [6, 7, 9, 15] with band alignments incompatible with Type-II operation. These mislabeled systems exhibiting (–,–) band alignments are listed in Table S11. Among these, three systems [6, 9, 15] exhibited the (–,–) thermodynamic

TABLE 3 | Application of the diagnostic framework to 30 reported Type-II systems.

Score	Count	%	Systems (Ref #)	Diagnostic interpretation	Flag (X)
5	1	3.3%	[25]	Complete validation through all phases	None
4X	3	10.0%	[15, 28, 29]	High-quality experiments, but $\Delta E_{\text{F}}/\Delta\text{WFF}$ contradicts Type II	Flagged
4	0	0.0%	—	—	—
3	0	0.0%	—	—	—
2	5	16.7%	[12, 16, 21, 22, 26]	Phase I complete (Band + Fermi alignment)	None
1	14	46.7%	[2, 5, 10, 11, 13, 14, 17–20, 27, 30]	Phase I partial (Band data only)	None
0	7	23.3%	[1, 6–9, 23, 24]	Insufficient experimental data (DFT only/Model)	N/A
Total	30	100%		Unreliable claims (Score ≤ 2 or X flagged): 96.7%	

signature of an S-scheme. These misclassifications stem from two distinct origins: First, three systems [6, 7, 9] are model-based (DFT-only) studies (Score 0) within the Tier III vacuum, where computational predictions incorrectly label (–,–) or (–,+) alignments as Type-II from the outset. Second, [15](Bi₂O₃/Bi₄O₅Br₂) appears as a critical experimental case of mislabeling; despite a high experimental score (4), its thermodynamic signature aligns more closely with S-scheme operation. If the Sign Rule is accepted, re-evaluating such systems could potentially identify high-performance S-scheme photocatalysts that were previously misclassified.

The Universal Evidence Vacuum: The finding that 86.7% of studies (26/30) score ≤ 2 underscores that the vast majority of reported Type-II systems exist in an evidence vacuum. They establish basic band alignment but lack the interfacial electronic characterization (Phase II) and dynamic pathway proof (Phase III) required to validate the proposed charge-transfer pathway. This prevalence indicates that current reporting standards are insufficient to discriminate between plausible alignment and validated mechanism, perpetuating the reproducibility crisis in heterojunction photocatalysis.

3 | Discussion

3.1 | The Diagnostic Framework as a Corrective Tool: Resolving Inconsistency and Incompleteness

The diagnostic framework does not merely quantify a problem; it provides a structured pathway to its resolution. The “X” flag represents the framework’s most critical corrective innovation. It specifically identifies patterns that, under the Sign Rule, constitute a “thermodynamic contradiction”, a state where elegant data, obtained by advanced characterization tools (e.g., UPS, PL, and sacrificial/scavenger tests), are used to support an impossible conclusion. By mandating Step 7 as a discrete, reportable milestone, the protocol forces researchers to reconcile their interfacial electronic data with their mechanistic labels. For systems like ref. 15, which exhibit a (–, –) alignment, the framework provides a “redemptive” pathway: by acknowledging the S-scheme signature, the authors could have claimed a system with preserved redox potentials, a far more valuable scientific finding than a mislabeled Type-II assignment.

Similarly, the framework transforms the “**evidence vacuum**” from an ambiguous shortcoming into a defined gap in a diagnostic sequence. A score of ≤ 2 is not just “low evidence”; it explicitly indicates arrest at Phase I (Structural & Band Alignment), pinpointing exactly which validation milestones, interfacial electronic characterization (Phase II) and dynamic proof (Phase III) are missing (Figure 3). This shifts the narrative from vague criticism to a clear prescription: studies must progress through these phases sequentially to make a credible mechanistic claim.

It is further noted that the X flag is necessarily applied only to systems with sufficient experimental data (Scores ≥ 4). Lower-scoring systems lack the interfacial electronic characterization required to detect electrical contradictions. Therefore, the 10.0%

proportion of thermodynamic paradoxes identified in this cohort should be interpreted as a conservative estimate. The field-wide prevalence of such contradictions may be substantially higher, as many studies simply do not report the data needed to detect them. However, it is also important to recognize that a more balanced interpretation is warranted. Phase II and Phase III characterization techniques are not universally accessible, and their application requires significant expertise and instrumentation. Many studies reasonably prioritize Phase I validation as a cost-effective first step. The diagnostic framework does not mandate that every study must achieve full validation (Score 5). Rather, it provides a transparent scale for assessing the depth of evidence provided. Studies that report only Phase I data are not ‘deficient’ per se; they simply make a lower-tier evidence claim. The crisis arises only when such limited evidence is used to support strong mechanistic conclusions (e.g., unambiguous Type-II assignment). The framework therefore encourages authors to match the strength of their mechanistic claims to the depth of their evidence, rather than to treat all studies without Phase II/III data as inherently flawed.

A note of caution is warranted. The finding that only one system achieves full validation under the Sign Rule could be interpreted in two ways. It may indicate that the field has systematically overclaimed Type-II mechanisms without sufficient evidence. Alternatively, it may indicate that the Sign Rule itself is too restrictive. For instance, the requirement that all four signs be positive may not account for real-world complexities such as interfacial dipoles or Fermi-level pinning. The framework does not adjudicate between these interpretations. Rather, it provides a transparent, reproducible method for assessing internal consistency. The community is invited to test the Sign Rule against well-characterized reference systems and to refine the criteria based on accumulated evidence. If future work demonstrates that many genuinely correct Type-II systems fail the sign test, the criteria should be adjusted accordingly.

3.2 | Systemic Misclassification: A Case for Mechanistic Re-Evaluation

The erroneous classification of four systems exhibiting non-Type-II band alignments as Type-II reflects a systemic, rather than isolated, misclassification tendency in the literature. The framework traces this error to its root: the “theory-first” assignment of RP/OP roles based on computed or assumed band positions, bypassing the experimental role justification mandated in Step 1. This is most consequential for experimental studies like [15], where high-quality data support an S-scheme interpretation, yet the initial heuristic label persists.

This misclassification has tangible scientific costs. It obscures structure-activity relationships (e.g., why a certain co-catalyst placement fails), misdirects synthetic optimization (e.g., tuning the wrong interface), and leaves high-redox-potential S-scheme candidates hidden within the Type-II literature. The framework provides the tool for correction: re-evaluating these systems by starting with experimental role proof (Step 1) and following the diagnostic sequence can correct their mechanistic identity, potentially unlocking new understanding and performance.

3.3 | Implementing a New Standard: From Diagnosis to Community Practice

For the framework to contribute to resolving the crisis, it could transition from an analytical tool to a community-discussed guideline. This requires adoption at multiple levels:

1. **For Authors: A Mandatory Diagnostic Appendix.** Future submissions should include a completed diagnostic scorecard (as provided in the SI) as a transparency and self-assessment tool, clearly indicating phase completion and any “X” flags.
2. **For Journals and Reviewers: An Editorial Checklist.** Journals may consider integrating the three-phase, seven-step protocol into their submission guidelines. Reviewers should be empowered to request missing evidence corresponding to the claimed mechanism’s required phase, moving peer review toward validated evidence chains.
3. **For the Field: Prioritized Re-evaluation.** The community should prioritize the re-investigation of foundational or high-impact systems using this protocol. This would correct the mechanistic baseline and rebuild a reliable knowledge foundation for rational design.

The framework’s logic (**foundational validation** → **interfacial analysis** → **operational proof**) is generalizable beyond photocatalysis to any field where interfacial charge transfer is paramount (e.g., electrocatalysis and photovoltaics). Its adoption represents a shift from a **narrative-driven model**, where mechanism is a label applied to a structure, to an **evidence-anchored model**, where mechanism is a conclusion proven through a diagnostic sequence.

3.4 | Limitations: Non-Ideal Interfaces and Experimental Uncertainties

3.4.1 | Interface Dipoles and Fermi-Level Pinning

When two semiconductors are brought into contact, charge transfer can create an interfacial dipole layer that shifts the vacuum level across the interface. This dipole can alter the effective band alignment by 0.5–1.0 eV, potentially changing the sign of ΔCBM or ΔVBM from that predicted by isolated band positions. Similarly, surface states can pin the Fermi level at the interface, preventing the equilibration assumed in the idealized derivation. In such cases, the Sign Rule may produce false positives (signs align but the mechanism is not Type-II) or false negatives (signs contradict, but the mechanism is actually Type-II). The framework does not resolve these complexities; it merely provides a consistency check based on the reported data. When interface dipoles or pinning are known or suspected, the Sign Rule should be applied with caution.

3.4.2 | Depletion-Layer Formation and Non-Equilibrium Dynamics

The Sign Rule is derived from equilibrium electrostatics (Fermi level equilibration in the dark). Under illumination, photo-generated carriers modify the charge distribution across the

interface, altering band bending and the internal electric field. Non-equilibrium effects, such as carrier accumulation, charge screening, and photovoltage, can transiently change the effective band alignment. Equilibrium measurements (e.g., UPS and KPFM) therefore may not fully capture operando behavior. The framework does not address these dynamic effects; it is limited to equilibrium characterization. Future refinements incorporating operando measurements (e.g., in situ XPS, transient KPFM) are encouraged.

3.4.3 | Experimental Uncertainties in UPS/KPFM

Work function measurements by UPS or KPFM have typical uncertainties of ± 0.05 – 0.1 eV due to sample charging, surface contamination, tip calibration, and spectral fitting. Reported ΔW_F values within ± 0.1 eV of zero should therefore be treated as ambiguous rather than definitive. The X-flag threshold of $|\Delta I| < 0.05$ eV is a pragmatic choice based on typical instrumental resolution; measurements with $|\Delta I| < 0.1$ eV without corroborating evidence should not trigger an X-flag. This threshold is a rough guideline, not a sharp physical boundary. Researchers are encouraged to report measurement uncertainties explicitly. When reported ΔE_F or ΔW_F values fall between 0.05 eV and 0.1 eV, sign assignments should be treated as tentative. The X-flag should only be applied when the contradiction is clear and unambiguous (e.g., $\Delta E_F = -0.3$ eV for a Type-II claim). Marginal deviations that may be within experimental error should not trigger the X-flag without corroborating evidence.

3.4.4 | Summary of Limitations

The Sign Rule and X-flag framework are diagnostic heuristics rather than absolute physical laws. They are most reliable for idealized systems with clean interfaces, no dipoles, no pinning, and well-resolved measurements. For complex systems with known non-ideal effects, the framework should be applied with caution, and sign contradictions with small magnitude ($|\Delta I| < 0.1$ eV) should be considered inconclusive. The framework is offered as a starting point for community discussion and refinement, not as a definitive adjudicator of mechanistic truth.

4 | Conclusions

This study exposes and codifies a profound validation crisis in heterojunction photocatalysis. Through the development and application of a three-phase, seven-step diagnostic framework, we move from observing scattered problems to defining their systemic causes: thermodynamic inconsistency despite experimental effort and arrested validation at the band-alignment stage.

The framework provides a potential corrective. It introduces the “X” flag as a specific diagnostic for electrical contradiction, and it defines sequential phase completion as the rigorous path to a credible mechanistic claim. Applied to 30 reported Type-II systems, it reveals that complete validation is exceptionally rare (3.3%), while thermodynamic contradictions in otherwise well-characterized systems (10%), categorical mislabeling (13.3%), and

a pervasive evidence vacuum (86.7%) are the norm. It is acknowledged that this low validation rate (only 3.3% of systems achieving Score 5) could reflect either widespread misclassification or limitations of the Sign Rule itself (e.g., overly restrictive criteria, failure to account for non-ideal interface effects). Distinguishing between these possibilities requires independent validation using well-characterized reference systems, which is strongly encouraged as future work.

The proposed solution is a change in practice, not just perception. By adopting the framework as a reporting standard, through author checklists, reviewer guidelines, and community-led re-evaluation, the field can eliminate heuristic assignment, correct the mechanistic record, and establish a new, rigorous foundation for the rational design of advanced photocatalysts and related energy materials. The framework is offered as a proposal for community discussion and refinement, not as a final or universally binding rule. It is hoped that the protocol will evolve through collective input from the photocatalysis research community to adapt to new discoveries and emerging characterization techniques. While the present study focuses on retrospective diagnostic validation, prospective application of the framework to guide the design of new heterojunctions is a logical and necessary next step. Such prospective validation, where the framework is used to predict the expected charge-transfer mechanism of a deliberately designed system prior to experimental characterization, would further establish its practical utility and is strongly encouraged in future studies.

5 | Methods

5.1 | Dataset Construction and Analysis

A PRISMA-inspired workflow was implemented to ensure transparent and reproducible study selection (Figure S1 and Table S13). A Web of Science search was conducted using the query: (“type-II heterojunction” OR “type II heterojunction”) AND (photocataly*) for publications from January 2021 to December 2025. The search returned 4,409 records. Title and abstract screening was done to identify records explicitly mentioning Type-II heterojunction mechanism and photocatalytic activity. Exclusion criteria at this stage were review articles, conference abstracts, editorials, and studies not mentioning photocatalytic activity. After screening, 250 records remained. Full-text eligibility assessment was then applied to the following inclusion criteria: (i) explicit claim of Type-II heterojunction mechanism; (ii) reported conduction band minimum (CBM) and valence band maximum (VBM) values (experimental or computational); (iii) sufficient characterization data for diagnostic evaluation; (iv) primary research article (not review or perspective). Exclusion criteria were: (i) mechanism unclear or not explicitly Type-II; (ii) no experimental or computational demonstration of band alignment; (iii) insufficient photocatalytic data; (iv) non-primary research. After full-text assessment, 70 records met the eligibility criteria.

Final cohort curation involved additional qualitative considerations to ensure diversity and non-redundancy: (i) exclusion of highly redundant studies (e.g., multiple papers on nearly identical material systems from the same research group); (ii)

preferential inclusion of studies spanning diverse material classes (oxides, chalcogenides, carbon nitrides, and 2D materials); (iii) exclusion of studies with overlapping material systems already well-represented; (iv) consideration of citation impact as a proxy for field visibility, although no paper was excluded solely on low citation count. After curation, 30 studies were selected for the final diagnostic cohort. The median citation count for the final cohort was 12 (range: 1–60), compared to a median of 5 (range: 0–120) for the initial 250 screened records, indicating that the final cohort is enriched for studies with measurable field impact. A detailed citation comparison between the final cohort and the initial screening pool is provided in Table S14.

5.1.1 | Data Extraction and Sign Convention

Each of the 30 selected systems was re-analyzed using the authors' original data to calculate ΔCBM , ΔVBM , ΔE_F , and ΔWF following the $\Delta X = X(\text{RP}) - X(\text{OP})$ convention, where RP is the Reduction Photocatalyst, and OP is the Oxidation Photocatalyst. All work function values have been converted to the consistent convention $\text{WF} = E_{\text{vac}} - E_F$, with E_{vac} referenced to 0 eV, ensuring that ΔE_F and ΔWF share the same sign requirement for a given mechanism (i.e., $\Delta E_F > 0$ and $\Delta\text{WF} > 0$ for Type-II; $\Delta E_F < 0$ and $\Delta\text{WF} < 0$ for S-scheme).

5.1.2 | Scoring Application and Data Categorization

The diagnostic framework was applied uniformly to all 30 systems (Table 2). Mode-based studies [1, 8, 23] relying exclusively on density functional theory (DFT) without experimental validation were assigned a **score of 0**, as the framework requires experimental evidence for mechanistic claims. Experimental studies were scored based on phase completion: **Scores 1–2** for Phase I (band alignment), **Scores 3–4** for Phases I+II (interfacial electronic structure), and **Score 5** for completion of all three phases. The “X” flag was applied only when the following two conditions were met simultaneously: (1) high experimental data quality, defined as experimentally measured values (not DFT or literature-derived) for both ΔE_F (or equivalent Fermi level offset) and ΔWF (or equivalent work function difference) obtained via UPS, XPS-VB, or KPFM; and (2) clear sign contradiction, where the reported sign of ΔE_F or ΔWF unequivocally opposed the sign pattern required for the claimed mechanism (i.e., any negative ΔE_F or ΔWF for a Type-II claim, or any positive ΔE_F or ΔWF for an S-scheme claim). A single ambiguous or near-zero measurement ($|\Delta| < 0.05$ eV) did not trigger the X flag unless corroborated by additional contradictory evidence. The 0.05 eV threshold is a pragmatic choice based on typical UPS and KPFM resolution limits (± 0.05 – 0.1 eV); it is not a physically derived boundary. Measurements with $|\Delta|$ between 0.05 and 0.1 eV should be treated as ambiguous, and researchers are encouraged to report experimental uncertainties explicitly. The X-flag is intended to flag clear contradictions, not marginal or statistically insignificant deviations. Regarding variability between measurement techniques, UPS, KPFM, and XPS-VB measure different quantities (work function, contact potential difference, and valence band offset, respectively) and are subject to different sources of error. Direct quantitative comparison of ΔWF values obtained from different

techniques is not recommended without cross-calibration. The framework therefore treats each reported value on its own terms; if a study reports ΔWF from UPS and also from KPFM, both must satisfy the sign requirement, but small numerical differences between them are expected and do not trigger the X-flag unless both clearly contradict the claimed mechanism. This scoring logic ensured consistent, transparent evaluation across diverse study types (Table 2).

All proportions were calculated from the sample of 30 systems. Confidence intervals for proportions were computed using the Wilson score interval method, which is recommended for binomial proportions with small sample sizes. No inferential statistical tests (e.g., hypothesis tests) were performed, as the analysis is descriptive and diagnostic rather than confirmatory. The calculated intervals are presented in Section 2.2.

To avoid circular reasoning, RP and OP roles are assigned based on experimental evidence from Step 1 of the diagnostic framework (selective photodeposition or scavenger tests), not on the assumed band alignment or mechanism. If no such experimental evidence is available, the roles are assigned provisionally based on reported band positions, but such cases are noted as having lower validation confidence (Scores ≤ 2). This approach ensures that the sign pattern analysis serves as an independent consistency check rather than a self-confirming exercise.

5.2 | Diagnostic Framework Development

The three-phase framework was developed iteratively through application to the dataset. Phase boundaries were defined based on **evidence hierarchy**: foundational (Phase I), interfacial (Phase II), and dynamic (Phase III). Scoring criteria were calibrated to differentiate between evidence quality levels, with the “X” flag introduced specifically to capture electrical contradictions observed in high-scoring systems.

5.2.1 | Definition of Minimum Standard for Step 1 (Functional Role Assignment)

For Step 1 of the diagnostic framework (Functional Role Assignment), acceptable experimental evidence must unambiguously identify which component acts as the RP and which as the OP. The minimum standard is satisfied by at least one of the following:

- Selective photodeposition of noble metals (e.g., Pt, Au, and Ag) visualized by TEM/EDS, where metal nanoparticles preferentially deposit on the RP;
- Selective scavenger tests demonstrating that the reduction half-reaction (e.g., Cr(VI) reduction and H_2 evolution) is primarily mediated by one component and the oxidation half-reaction (e.g., Rhodamine B degradation and $\bullet\text{OH}$ generation) by the other;
- Operando or in situ spectroscopy (e.g., XPS or Raman) showing reversible electron density changes consistent with directional charge transfer from OP to RP under illumination.

Photodeposition alone is considered sufficient when clear spatial localization is shown. Transient absorption spectroscopy (TAS) alone is not considered sufficient for Step 1 assignment unless combined with selective quenching controls. In cases where no experimental role assignment is provided, Step 1 is marked “X” and the maximum achievable score is capped at 3 (even if Phases II and III are completed), because the foundational assignment of RP/OP remains unvalidated.

5.3 | Statistical and Pattern Analysis

Descriptive statistics characterized score distributions. Pattern-recognition identified clusters of similar validation failures. Confidence intervals (95%) were calculated for key proportions. All analysis was conducted with transparency and reproducibility as primary objectives.

5.4 | Protocol Implementation Tools

The complete framework is provided as an executable scoring template in Supporting Information, including decision algorithms, evidence weighting schemes, flag application criteria, and a fillable diagnostic worksheet (Table S12). This transforms the protocol from theoretical critique to practical community standard.

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Conflicts of Interest

The authors declare no conflicts of interest.

Teaser

A three-phase diagnostic protocol suggests that 96.7% of Type-II claims in a curated cohort lack full mechanistic evidence.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: adfm76570-sup-0001-SuppMat.docx.