A review of carbon-based quantum dots for interfacial photocatalysis

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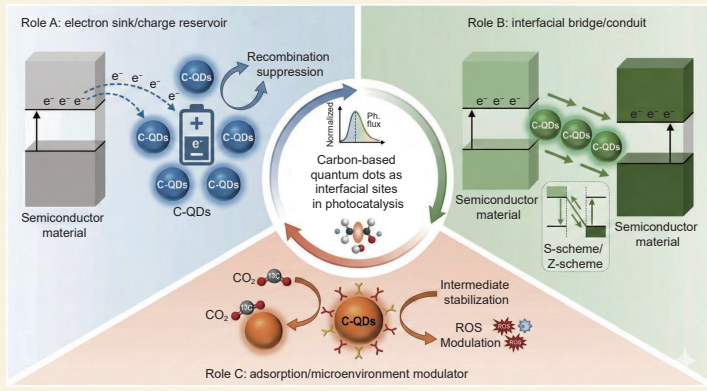
Abstract: Carbon-based quantum dots (C-QDs) have attracted growing attention in photocatalysis because of their tunable surface chemistry, unique electronic structure, and ability to regulate interfacial charge transfer. In recent years, their role has moved beyond that of simple light absorbers or general performance enhancers, and they are increasingly regarded as engineered interfacial components that can control charge separation, reaction-site microenvironments, and product selectivity. However, the broad claim that C-QDs improve photocatalytic performance often lacks clear mechanistic validation, which limits the ability to compare and reproduce reported studies. Recent advances in C-QD-based photocatalysis are reviewed with particular attention to the experimental evidence supporting their proposed roles and mechanisms. Three roles are considered: (a) electron sinks or charge reservoirs, (b) interfacial bridges or charge-transfer conduits, and (c) adsorption or microenvironment modulators. The evidence needed to support these assignments is then discussed, including measurements of band energetics and carrier dynamics, characterization of interfacial coupling, identification of reaction intermediates under working conditions, isotope-labeling experiments, and carbon balance analysis. Representative applications in hydrogen evolution, CO_2 photoreduction, and pollutant degradation/photo-enhanced advanced oxidation processes are also analyzed to clarify how C-QD roles should be matched with reaction-specific metrics. Finally, the review identifies several recurring problems that hinder mechanistic interpretation and comparison between studies: C-QDs are often assigned different functions without sufficient evidence; Z-scheme and S-scheme labels are sometimes used without directly verifying the proposed charge-transfer pathways; reaction intermediates and catalyst behavior are not always examined under actual reaction conditions; and photocatalytic performance is reported using inconsistent metrics and test conditions. This review aims to provide practical guidance for building reliable structure–function relationships and for designing next-generation C-QD-based photocatalysts with clearer mechanisms, stronger reproducibility, and greater application potential.



Key words: Carbon-based quantum dots; Photocatalysis; Interfacial engineering; Charge-transfer pathways; Reaction selectivity

1 Introduction

Over the last three years, carbon-based quantum dots (C-QDs), including carbon quantum dots (CQDs), graphene quantum dots (GQDs), carbon nitride quantum dots (CNQDs), MXene QDs, covalent organic framework (COF)-based QDs, and carbonized polymer dots, have shifted from being seen as "universal performance boosters" to carefully designed components with a key role in photocatalytic interfaces[1–11]. This change is caused by 2 main factors. First, the limits of conventional semiconductor photocatalysts are now recognized as an interfacial issue. Their performance is determined more by the rate of charge separation and transfer, the energetic alignment of the interface, and the local reaction environment, rather than by the light absorption of materials alone[6,12–15]. Recent research in interfacial photoredox chemistry highlights that charge-transfer pathways at interfaces need to be carefully studied us-

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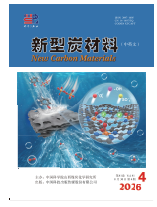

ing advanced spectroscopy and energy measurements, because the efficiency of a catalyst often depends on where charges move and how quickly they reach reactive sites[6]. Second, C-QDs have proven to be versatile both chemically and electronically. Their π-conjugated sp^2 carbon domains, tunable surface dipoles and functional groups, heteroatom or metal coordination, and defects or edge states allow them to serve as electron reservoirs, interfacial bridges, and modulators of the local reaction environment[16–18]. These roles directly address the kinetic limitations in photocatalytic energy conversion and environmental remediation[19–25]. Recent studies highlight C-QDs as important components for solar-to-chemical energy conversion and the design of photocatalytic systems. For example, C-QDs derived from traditional Chinese medicine have been shown to improve charge transfer at interfaces[17]. As indicated by recent publication and citation trends, the growing research activity on this topic is evident, with publication numbers steadily increasing each year, reaching a peak in 2024 with 684 publications, and continuing to receive substantial citations, with 29 050 citations in 2025 (Fig. 1). This trend highlights the rising interest and impact of C-QDs in the field. However, despite this growth, the idea that "C-QDs improve everything" needs to be replaced with clear, evidence-based explanations and practical design rules to make their use in photocatalysis scientifically reliable and reproducible[2].

In the hydrogen evolution reaction (HER), C-QDs were traditionally described mainly as sensitizers that broaden light absorption and inject electrons. This view has gradually been expanded, and in some cases replaced, by an interface-engineering perspective. When properly coupled with semiconductors, C-QDs can help extract electrons, suppress recombination through charge-storage states, and accelerate interfacial electron delivery through Schottky-like or step-scheme (S-scheme) junction behaviors[26–30]. Evidence-based discussions of CQD/semiconductor systems for photocatalytic H_2 production increasingly emphasize the need to evaluate activity improvements using measurable changes in charge lifetime, transfer resistance, and energetic alignment. These improvements should not be judged from light absorption alone[29]. At the same time, studies on broader heterojunction photocatalysis, such as g-C_3N_4-based systems, have developed a more rigorous understanding of charge separation and interfacial phenomena. This has raised the standard for explaining the specific role of C-QDs in composite photocatalysts[31]. This point is important because C-QDs are often added to heterostructures that are already complex. Without careful validation of the interface, it is difficult to determine whether C-QDs truly play a distinct role or simply behave like ordinary conductive mediators or defect-rich additives[32].

Stronger evidence is especially important for

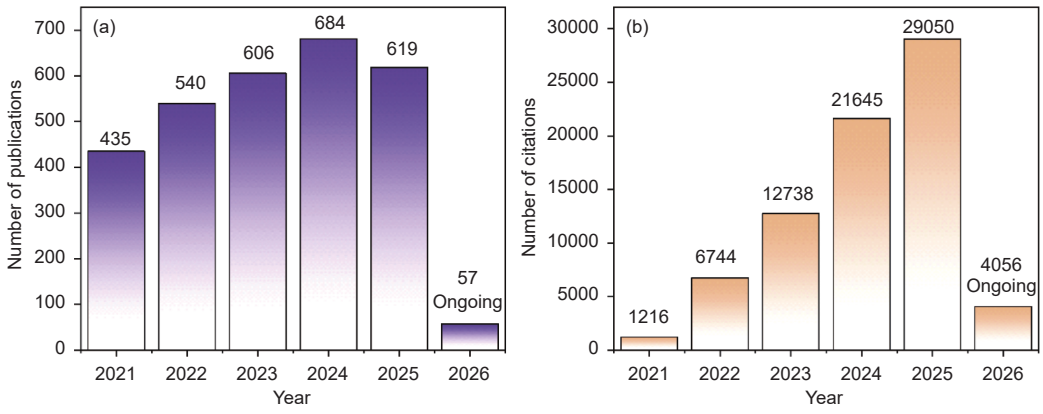

Fig. 1 Publication and citation trends over time for the research topic. (a) Number of publications from 2021 to 2026. (b) Number of citations from 2021 to 2026. The development trend was analyzed based on the Web of Science database, with data collected on February 27, 2026, using the following search terms: "carbon dot*" and "photocata*," "carbon-based dot*" and "photocata*," "graphene quantum dot*" and "photocata*," "carbon nitride quantum dot*" and "photocata*," "MXene quantum dot*" and "photocata*," or "covalent organic framework quantum dot*" and "photocata*." The search was limited to research and review articles published between 2021 and 2026, excluding other types of publications

CO_2 photoreduction (CO_2RR), where product selectivity is strongly affected by how protons and electrons are managed at the interface and how key intermediates, such as *COOH and *CO, are adsorbed[33–37]. Over the past three years, research has increasingly moved toward strongly coupled C-QD/semiconductor heterojunctions with covalent bonding. These structures are designed to better control charge transfer at the interface and stabilize key reaction intermediates, instead of relying only on physical mixing or weak adsorption. A representative example is amide-bonded interface engineering for solar CO_2-to-CO conversion. This connects intentional structural design with the mechanistic identification of the *COOH intermediate, showing that "interfacial sites" can be deliberately constructed rather than simply assumed[38]. At the same time, the development of S-scheme concepts and related verification methods further shows that CO_2RR mechanisms cannot be claimed without solid evidence. Directional charge transfer must be demonstrated, and the carbon source must be carefully verified through methods such as isotopic tracing and carbon balance analysis[39].

Recent studies have shown that emerging C-QDs, such as MXene QDs and COF-embedded QDs, are becoming increasingly important in photocatalysis. Compared with conventional CQDs, GQDs and CNQDs, these new C-QDs offer broader opportunities for interface design and performance improvement. Strategies such as additive-mediated intercalation, surface modification, and lattice-structure tuning have been widely applied to carbon-based materials, MXenes, COFs and their hybrids[40–48]. These approaches can improve both stability and performance. They also provide useful routes for further optimizing the quantum-dot properties of these materials in photocatalytic applications. These emerging carbon-based QDs, especially MXene QDs and CNQDs, show strong potential in photocatalysis because of their favorable optoelectronic properties and adjustable surface functionalities[49]. MXene QDs have high conductivity and abundant surface functional groups, which enable strong coupling with semiconductor photocatalysts. This strong interfacial interaction helps improve charge separation and transport[50]. For instance, nitrogen-doped Ti_3C_2 MXene QDs coupled with 1D CdS nanorods greatly increased photocatalytic hydrogen production to ~ 17 094 μmol g^{-1} h^{-1}. This rate is approximately 14.8 times higher than that of pure CdS, which is about 1155 μmol g^{-1} h^{-1}, mainly because of improved carrier separation and interface contact[51]. Similarly, incorporating QDs into COF matrices can enhance visible-light absorption and improve carrier utilization. For example, confining ZnSe QDs within COF structures broadens the light-harvesting range and leads to better photocatalytic performance under visible light[9–10].

In environmental photocatalysis and photo-enhanced advanced oxidation processes (photo-AOPs), C-QDs have also shifted from being viewed as general activity enhancers to functional interfacial components. They can regulate radicals and reactive oxygen species (ROS), while also tuning the local reaction microenvironment[52–56]. Recent reviews on photo-enhanced deep oxidation for wastewater treatment have discussed CQD-modified catalysts in photocatalysis, photo-Fenton, and photo-persulfate systems[52]. These studies emphasize the importance of interfacial charge separation and radical-generation pathways in improving oxidation performance. Meanwhile, the AOP community has paid increasing attention to how ROS pathways are identified and assigned, especially for singlet oxygen and other non-radical routes. This has shown that unclear mechanistic evidence can easily lead to incorrect building of structure–activity relationships when ROS are inferred only from indirect tests[57–58]. In parallel, reviews focused on C-QD-mediated ROS modulation have shown that C-QDs can regulate ROS generation and ROS suppression. This regulation is closely related to their surface chemistry, precursor-derived features, and interactions with external fields or coupled catalysts. These findings further suggest that interfacial control, rather than bulk optical effects alone, is often the key factor behind their performance[53]. These views are consistent with the broader progress in wastewater photocatalytic AOP research. The field now increasingly requires

evidence of mineralization, total organic carbon (TOC) removal, toxicity changes, and energy-normalized performance, rather than relying only on decolorization kinetics. This higher standard also makes C-QDs-enabled environmental remediation claims more reliable and scientifically meaningful[59].

Fig. 2 provides a timeline of major research developments in C-QDs for photocatalysis from 2021 to 2026. It shows how the role of C-QDs has evolved across different photocatalytic systems, including HER, CO_2RR, and pollutant degradation/photo-AOP. The figure also summarizes representative publications that may have shaped this field, while pointing to both recent progress and remaining challenges.

Despite clear progress, the transferability and reproducibility of C-QD photocatalysis are still limited by three common problems. First, the role of C-QDs is often unclear because they can affect light absorption, interfacial energetics, and surface chemistry at the same time, while the observed performance improvement is sometimes attributed to only one factor without proper control experiments. Second, heterojunction labels are often overused, especially for Z-scheme and S-scheme systems, where assignments are sometimes based only on band positions rather than verified directional charge transfer. Third, interface and operando evidence remains insufficient, as photoluminescence (PL) quenching or scavenger tests are often used in place of direct energetic mapping and in situ spectroscopy. Recent reviews on S-scheme photocatalysts have increasingly pointed out these problems and reached a similar conclusion. Mechanistic

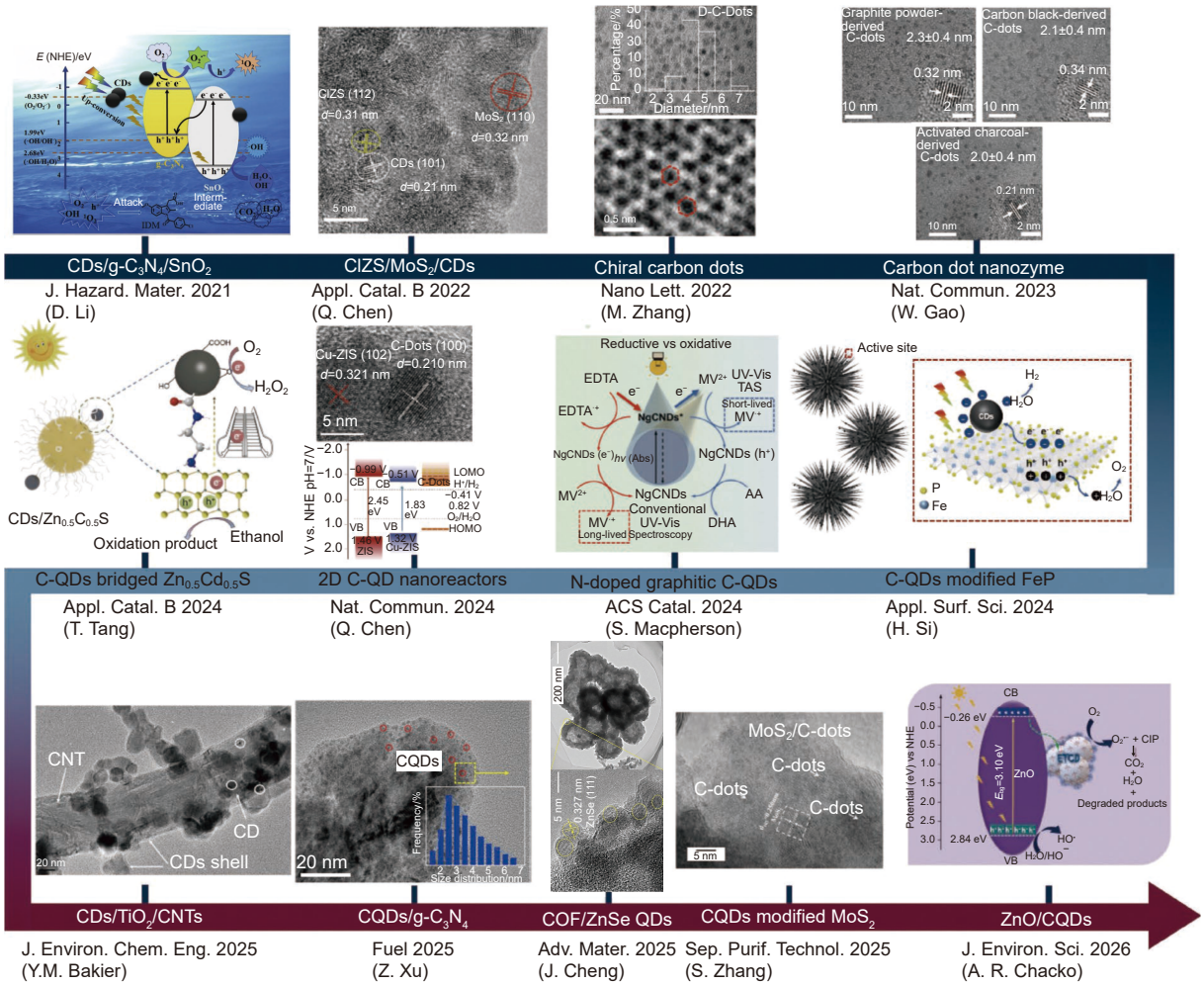

Fig. 2 Timeline of key academic research developments in the field of C-QDs for photocatalysis from 2021 to 2026. The timeline highlights the evolving role of C-QDs across various photocatalytic systems, including hydrogen evolution, CO_2 reduction, and pollutant degradation. Representative figures were adapted from Refs.[3–5,10,23–24,60–65] with permission from Elsevier, ACS, Nature Publishing Group, and Wiley, copyright 2021-2026

claims should be supported by a clear evidence chain that connects structure, energetics, ultrafast charge dynamics, and the formation of intermediates or final products[66].

Unlike previous reviews, this work addresses these gaps by focusing on rigorous evidence standards for assigning and validating the roles of C-QDs. Specifically, we call for the standardized reporting metrics that make results from different studies easier to compare. This would improve the reliability and reproducibility of C-QD photocatalysis research. To support this goal, we summarize a minimal checklist of "reaction-specific must-report metrics" in Table 1. This checklist defines the essential performance metrics and validation controls required for HER, CO_2RR and pollutant degradation/photo-AOPs. By defining what must be reported, Table 1 helps reduce the tendency to select only the most favorable metrics. For HER, this includes apparent quantum yield (AQY) normalized to photon flux. For CO_2RR, it includes $^{13}CO_2$ validation and carbon balance. For AOPs, it includes TOC removal, toxicity changes, and energy-normalized figures of merit. Together, these standardized metrics support more transferable and evidence-based design rules.

To make this framework easier to apply, Fig. 3 summarizes it as a role, evidence, and metrics roadmap. The figure links the three main roles of C-QDs, namely electron sink/reservoir, interfacial bridge/conduit, and adsorption/microenvironment modulator, with the corresponding minimum evidence sets. These evidence sets include energetics, dynamics and charge flux, interfacial coupling strength, and operando identification of intermediates and reaction pathways. The roadmap also connects these roles and evidence requirements with reaction-specific benchmarking metrics for HER, CO_2RR and photo-AOPs. By linking common problems (e.g., unclear role assignment, overuse of Z-scheme or S-scheme labels, and mechanistic claims based only on indirect evidence) to the specific measurements needed for validation, Fig. 3 serves as a concise practical checklist. It helps improve both the credibility of mechanistic interpretations and the comparability of results across different studies. Against this background, this short review focuses on the recent shift of C-QDs from sensitizers to functional interfacial sites. It aims to summarize the minimum evidence needed to assign the roles of C-QDs in photocatalytic systems with

Table 1 Minimum recommended reporting checklist for C-QD photocatalysis in typical reaction scenarios

Reaction types	Minimum required performance metrics	Minimum required validation and controls	Key method notes & references
HER	AQY at specified wavelength(s); Incident photon flux (or calibrated irradiance + spectrum); Rate normalized to active mass/area; Stability (time-on-stream)	Optical setup details (light source spectrum, power, reactor geometry); Sacrificial agent identity/concentration; Gas quantification method; Catalyst reuse/post-mortem characterization	[a] AQY definition & calculation: ref.[67][b] Photon flux measurement & reporting best practice: ref.[68][c] H_2 gas quantification (GC-TCD/GC-BID method): refs.[69–71]
CO_2RR	Product rates + selectivity (μmol g^{-1} h^{-1}, specify all detected products); Carbon balance; Stability (≥5 h cycling); (If claimed) energy efficiency proxy	$^{13}CO_2$ isotope labeling (GC-MS analysis, m/z verification); Dark/blank controls (no light; no CO_2; no catalyst); Exclusion of adventitious carbon (catalyst washing + control); Quantified CO_2 uptake/availability	[d] $^{13}CO_2$ isotope tracing protocol & pitfalls: ref.[72][e] False-positive sources & rigorous reporting protocol: ref.[73][f] In situ DRIFTS for reaction intermediate tracking: ref.[74][g] CO_2 photoreduction kinetics & product quantification: ref.[75]
Pollutant Degradation/ Photo-AOPs	TOC removal (mineralization), not only decolorization; Toxicity/biodegradability trajectory (≥1 assay); Energy-normalized metric, electrical energy per order (EEO or kWh·m^{-3}·$order^{-1}$); Stability/leaching data	ROS/pathway evidence (EPR/operando preferred over scavenger tests alone); Matrix effects test (real water or secondary effluent); Byproduct identification (LC-MS/GC-MS) where feasible	[h] TOC Detection — Instrument Types, Methods & Standards: (1) High-temperature catalytic combustion/NDIR; (2) UV/persulfate oxidation/NDIR; (3) Heated persulfate/NDIR: refs.[76–82][i] EEO definition, calculation & standard reporting (IUPAC): ref.[83]; updated IUPAC report: ref.[84][j] EPR/ESR spin-trapping (DMPO) for ROS detection: ref.[85] (DMPO for ·OH/O_2·$^-$; BMPO preferred for superoxide; EPR instrument: Bruker EMXplus or equivalent; in situ cell recommended)[k] In situ EPR for AOP radical identification: ref.[86]

Notes: EEO is widely used in UV-AOP communities to compare energy demand across systems; importing energy-normalized reporting into photo-AOP/ C-QD studies is an efficient way to prevent "rate constant theater."[87]
EPR/ESR, electron paramagnetic/spin resonance;
DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy;
GC-TCD, gas chromatography with thermal conductivity detector;
GC-BID, gas chromatography with barrier ionization discharge detector;
BMPO, 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide;
DMPO, 5,5-dimethyl-1-pyrroline N-oxide;
IUPAC, International Union of Pure and Applied Chemistry

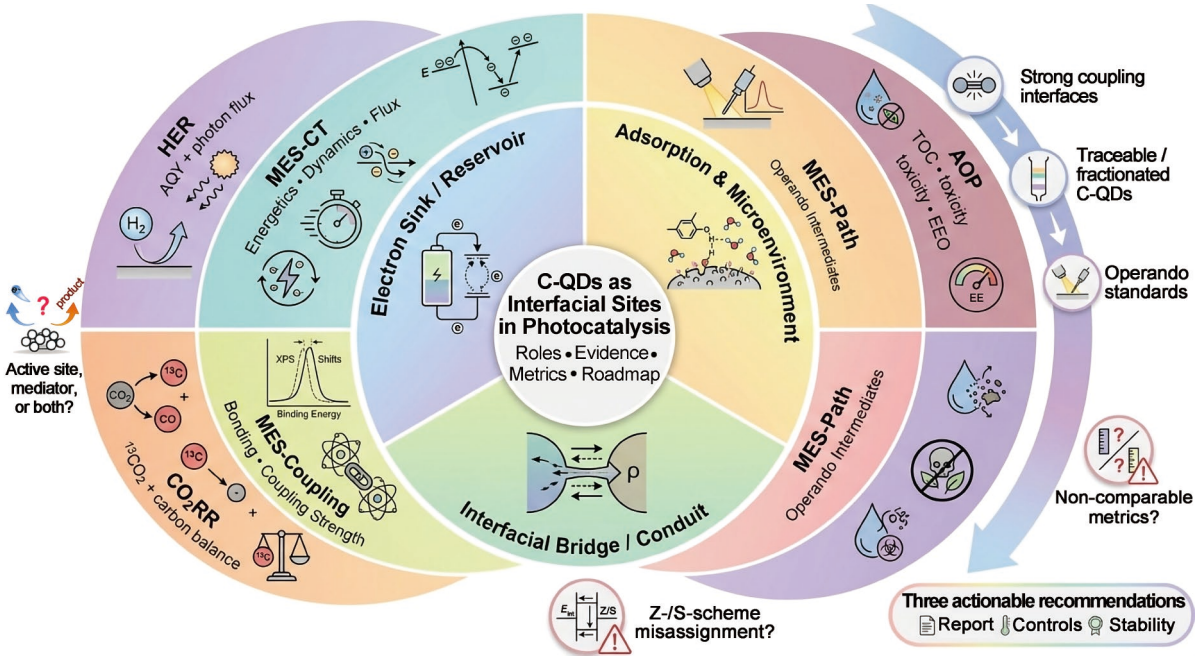

Fig. 3 Carbon dots as engineered interfacial sites in photocatalysis: a role, evidence, and metrics roadmap. The schematic summarizes the transition of C-QDs from general sensitizers to functional interfacial units. The inner ring defines three core roles: electron sink/reservoir, interfacial bridge/conduit, and adsorption/microenvironment modulator. The middle ring links these roles to the corresponding minimum evidence sets (MESs), including the MES for charge transfer (MES-CT), which covers energetics, dynamics, and charge flux. MES-Coupling, which evaluates interfacial bonding and coupling strength. And MES-Path, which focuses on operando or near-operando pathway validation. The outer ring aligns these evidence standards with representative applications, including HER, CO_2RR, and photo-enhanced AOPs, together with reaction-specific metrics such as photon-flux-normalized AQY, $^{13}CO_2$ validation and carbon balance, TOC removal, toxicity evolution, and energy-normalized efficiency. Peripheral callouts highlight key controversies and future priorities, including active-site assignment, Z-scheme and S-scheme verification, metric comparability, strong interfacial coupling, C-QD traceability, operando standardization, and stability validation

confidence, identify common pitfalls that may lead to overinterpretation, and extract design rules that can be applied in HER, CO_2RR, and environmental/AOP systems. These discussions are centered on interfacial energetics, charge-transfer kinetics, and the control of reactive-site microenvironments[2].

2 Three core roles of carbon dots

Fig. 4 summarizes the functional landscape of C-QDs in photocatalysis using a simple three-role model. Instead of classifying C-QDs by synthesis methods or surface groups, the figure organizes their reported behaviors into 3 mechanistically useful roles: Role A as an electron sink/reservoir, Role B as an interfacial bridge/conduit, and Role C as an adsorption/microenvironment modulator. Importantly, each role is linked to the type of evidence needed to support it. This evidence-matching framework is designed to avoid over-attributing the role of C-QDs based on single indirect signal, such as PL quenching. It also helps make role assignment more consistent across different materials and reaction systems. As shown in Fig. 4, Role A describes cases where C-QDs primarily trap or store electrons. This process delays back recombination and extends carrier lifetime. Therefore, the strongest evidence for Role A usually comes from time-resolved charge dynamics, such as time-resolved PL (TRPL) and transient absorption (TA), together with charge-transport or charge-flux measurements, such as electrochemical impedance spectroscopy (EIS) and transient photocurrent tests. This evidence is especially convincing when these signals change consistently with photocatalytic activity. Role B describes C-QDs as electronically coupled interlayers that promote charge extraction across interfaces. In multi-component systems, they may also help guide the direction of charge flow. To support this role, dynamic evidence alone is not enough. Energetic alignment and built-in electric field measurements are also required to support the proposed charge-flow pathway. Suitable techniques include ultraviolet photo-

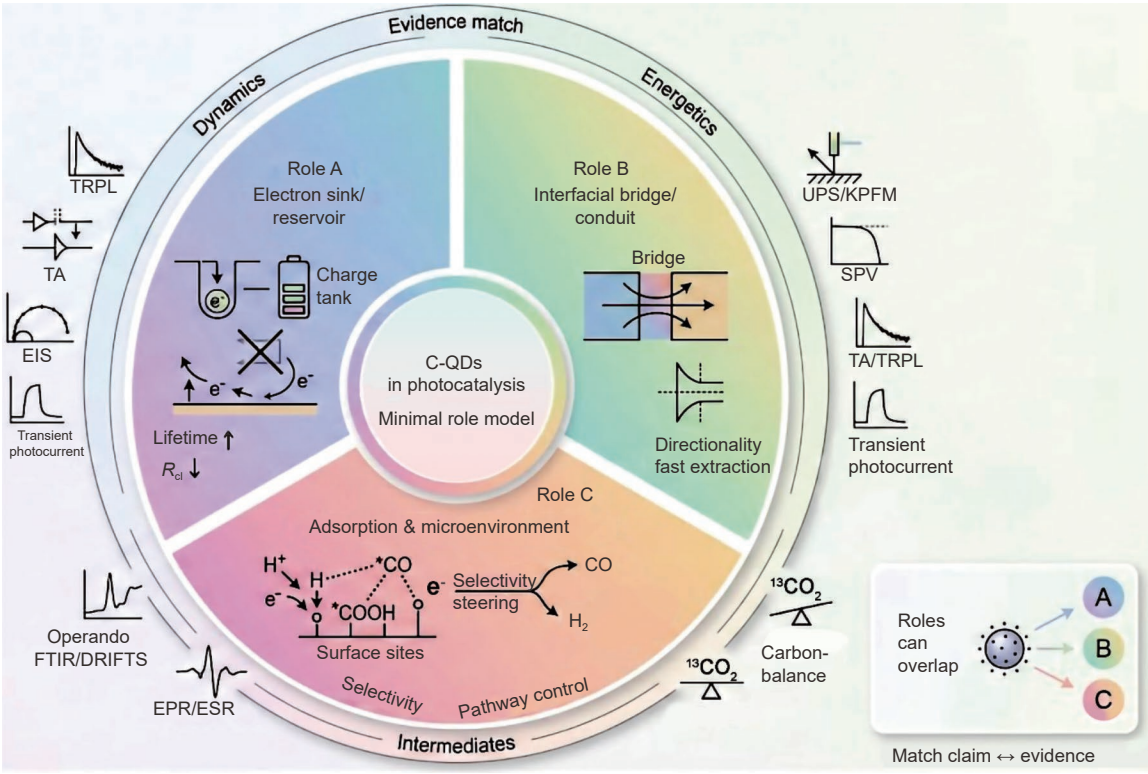

Fig. 4 Minimal three-role model of C-QDs in photocatalysis with corresponding evidence requirements. The schematic classifies C-QD functions into three roles: Role A, electron sink/charge reservoir for recombination suppression and lifetime extension; Role B, interfacial bridge/conduit for charge extraction and directional charge flow; and Role C, adsorption/microenvironment modulator for intermediate stabilization and selectivity control. Each role is matched with the minimum evidence needed for credible mechanistic assignment, including carrier dynamics, interfacial energetics, and intermediate or pathway probes. Because these roles can coexist in one C-QD–catalyst system, each claimed function should be supported by the appropriate evidence set

electron spectroscopy (UPS), Kelvin probe force microscopy (KPFM), and surface photovoltage (SPV) measurements. Role C is the most directly related to catalysis. It describes how C-QDs regulate adsorption and local microenvironment, thereby stabilizing key intermediates and controlling product selectivity. This role is especially important in CO_2RR and oxidation/photo-AOP systems. Therefore, stronger evidence is needed, including intermediate and pathway probes, such as operando Fourier-transform infrared spectroscopy (FTIR)/DRIFTS and EPR/ESR. When relevant, isotope validation and carbon balance (e.g., $^{13}CO_2$ tracing) should also be included. Importantly, Fig. 4 also shows that these roles may coexist in the same C-QD catalyst system. Therefore, a rigorous interpretation should not force C-QDs into a single role. Instead, each mechanistic claim should be matched with the appropriate evidence set.

2.1 Role A: Electron sink/charge reservoir for recombination suppression and lifetime extension

Recent studies on C-QD-based photocatalysts suggest a consistent view: when improved activity cannot be explained by light-harvesting alone, electron trapping and storage are often the main functions of C-QDs[62,88]. In C-QD/semiconductor hybrids used for HER and related reduction reactions, C-QDs can accept photogenerated electrons from the host semiconductor or an excited sensitizer. In this way, they act as a temporary electron reservoir, delaying back recombination and supplying electrons for subsequent surface reactions. This role is often supported when the composite shows quenched steady-state PL, but stronger evidence comes from changes in charge dynamics and transport. These include prolonged charge-carrier lifetimes from TRPL analysis, reduced interfacial transfer resistance from EIS, and enhanced transient photocurrent. Importantly, these changes should correlate with increased H_2 evolution rather than simply with stronger light absorption.

To make the MES for charge transfer (MES-CT) easier to apply, claims of TRPL lifetime extension

should be supported by clear multi-component analysis rather than by a single apparent lifetime. For example, authors should report the fitting model (e.g., bi-exponential or tri-exponential reconvolution fitting with the instrument response included). They should also provide amplitude-weighted and intensity-weighted average lifetimes (namely, $\langle\tau\rangle$A and $\langle\tau\rangle$I) and explain the physical meaning of each component (e.g., fast interfacial transfer or trapping and slower radiative or non-radiative recombination). Similarly, EIS-based claims of reduced interfacial charge-transfer resistance (R_{ct}) should clearly state the electrolyte as well as the bias and illumination conditions. The selected equivalent circuit should also be justified. A typical model is R_s–(R_{ct}//Cdl/CPE), with additional transport elements (e.g., Warburg diffusion) included when low-frequency tails are observed. Circuit selection should be based on the features of the Nyquist and Bode plots, the goodness of fit, and whether the fitted parameters are physically reasonable and stable across repeated measurements. This helps ensure that the reported R_{ct} is comparable and not simply an artifact caused by overfitting with an overly complex circuit.

Reviews on C-QD-assisted photocatalytic hydrogen production now clearly identify this electron-reservoir behavior as one of the 2 main functions of CQDs in semiconductor hybrids[29]. The C-QDs/FeP system in Fig. 5 provides a clear example. Microscopy and elemental mapping confirm close contact between C-QDs and FeP, while the proposed charge-flow pathway suggests that photogenerated electrons are transferred to C-QDs and temporarily stored there before participating in H_2 evolution. This example treats C-QDs as interfacial electron reservoirs rather than simple light-harvesting additives. It therefore supports our Role A interpretation and highlights the need to report the related MES-CT dynamics and flux evidence, such as TRPL/TA, EIS, transient photocurrent measurements, when HER enhancement is attributed to charge storage[62].

Role A is simple but useful because it can explain performance improvements across many different architectures. These include weakly adsorbed C-QDs on oxide surfaces, strongly coupled junctions, and even systems where C-QDs serve as the main photoactive component[63,89–90]. For a short review, the key point is to distinguish real charge-storage behavior from general optical responses. PL quenching is widely observed, but only some studies provide evidence that truly supports charge storage and delayed re-

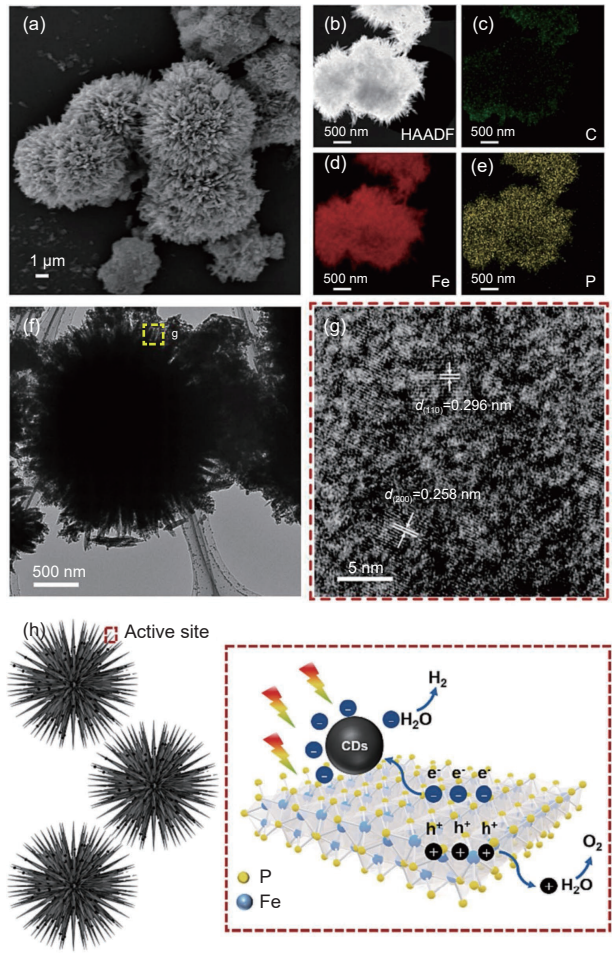

Fig. 5 C-QD–FeP interfacial architecture and the proposed charge-flow mechanism for photocatalytic overall water splitting. (a-g) Scanning electron microscopy (SEM), high-angle annular dark-field scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (HAADF-STEM/EDS) maps of C, Fe, and P, transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) images of 4% C-QDs/FeP show an urchin-like FeP morphology with uniformly distributed carbon and resolved FeP lattice fringes, supporting intimate C-QD–FeP contact required for interfacial charge storage and transfer in Roles A and B. (h) Proposed mechanism: electrons generated in FeP are transferred to C-QDs and stored there, enabling H_2 evolution through Role A, while holes retained on FeP oxidize water to O_2. This mechanism is consistent with the MES-CT framework, which links interfacial function to charge-transfer dynamics and flux evidence rather than relying on optical proxies. Reproduced from ref.[62] with permission from Elsevier, copyright 2024

combination. Recent mechanistic studies in photocatalysis have shown that carrier dynamics must be resolved from the ultrafast to microsecond timescale to support claims of charge storage or mediation. This is important because different quenching pathways can produce similar steady-state optical signals[14]. As summarized in Fig. 6a, complementary time-resolved spectroscopies, including TRPL, TA, and time-resolved infrared spectroscopy (TRIR), can distinguish trapping and detrapping, interfacial electron transfer, and radiative or non-radiative recombination. These techniques provide a direct way to determine whether quenched PL reflects productive charge management or simply parasitic charge loss. Fig. 6b further highlights the design relevance of Role A by summarizing studies in which longer excited-state lifetime is often associated with higher H_2 evolution activity. This trend supports recombination suppression as a transferable strategy for C-QD-containing photocatalysts. At the same time, it also highlights the need for comparisons that are normalized by experimental conditions and photon flux when conclusions are drawn across different studies.

One particularly useful direction is to engineer the electronic states of C-QDs to strengthen their electron-sink behavior. This can be achieved, for example, through controlled ionization or surface-functional tuning. In this way, C-QDs are treated as deliberately designed electron sinks that extend charge separation and improve catalytic turnover[89]. When Role A is truly active, it often produces transferable system-level signatures. These include a higher steady-state electron population at reduction sites, better tolerance to fluctuating light intensity, and improved AQYs when photon flux is properly normalized. In this sense, Role A helps explain why a small amount of C-QDs can enhance photocatalytic activity. However, it becomes a defensible design rule only when supported by lifetime and charge-transfer diagnostics, rather than by light-harvesting arguments alone[29].

2.2 Role B: Interfacial bridge/charge-transfer conduit for cross-interface transfer and directional charge flow

Role B extends beyond the electron-sink function by treating C-QDs as interfacial conductors or bridges. In this role, C-QDs accelerate charge extraction across junctions and may also guide the direction of charge flow in multi-component systems[27,91–93]. This role is increasingly used to explain all-solid Z-scheme and S-scheme heterostructures[94]. In these systems, the photocatalytic performance strongly depends on which component retains the strong redox carriers after interfacial recombination. Recent studies have reported C-QD-containing architectures where C-QDs are deliberately integrated as carrier-transfer bridges in Z-scheme systems. Their purpose is

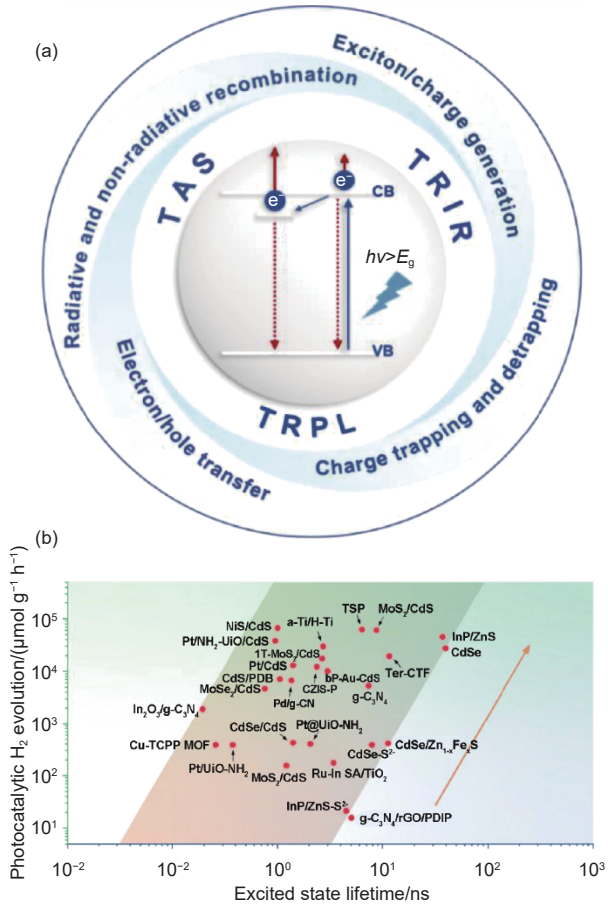

Fig. 6 (a) Complementary time-resolved spectroscopies supporting the dynamics component of the proposed evidence chain. The schematic shows how TRPL, TA, and TRIR can track exciton or carrier generation, trapping and detrapping, interfacial electron and hole transfer, and radiative or non-radiative recombination over relevant timescales. These measurements provide key readouts for validating Roles A and B within MES-CT. (b) Literature-level correlation between excited-state lifetime and photocatalytic H_2 evolution. Longer excited-state lifetimes are generally associated with higher H_2 production, supporting lifetime extension and charge management as major factors in C-QD-enabled HER. The observed scatter, however, highlights the need for photon-flux–normalized benchmarking. Reproduced from ref.[14] with permission from Elsevier, copyright 2025

to provide a low-barrier pathway for the recombination of less useful carriers, while preserving the desired redox carriers on the appropriate reaction partners[27]. As shown in Fig. 7, CQDs are intentionally placed between $ZnIn_2S_4$ and CeO_2 to act as carrier-transfer bridges in an all-solid Z-scheme system for visible-light HER. This bridge helps lower the kinetic barriers at the interface and promotes directional charge flow. By promoting the recombination of the less useful carriers while preserving strongly reducing electrons for H_2 evolution, this architecture shows that C-QDs can act as true interfacial conduits rather than passive additives.

Importantly, recent studies on heterojunction photocatalysts, especially S-scheme systems, increasingly emphasize the need to verify the direction of charge transfer. This requires evidence from energetic alignment, built-in electric fields, and charge dynamics, rather than relying only on band positions[39,66,95–96]. Authoritative reviews on S-scheme photocatalysts emphasize that such claims should be supported by both energy-band alignment measurements and carrier-dynamics evidence[66]. This is where C-QDs become especially valuable. Their surface dipoles, functional groups, and coupling strength can be adjusted, allowing them to act as programmable interlayers. Through this tunability, C-QDs can regulate interfacial band bending and charge-transfer kinetics, which are both central to the directionality required in S-scheme systems[66].

Recent studies on covalently bonded interfaces, although not always based on C-QDs, offer useful conceptual guidance. They show that bond-mediated electronic coupling can promote ultrafast and directional charge transfer by lowering interfacial resistance and stabilizing built-in electric fields. Under these conditions, an interfacial bridge has a clear physical function rather than serving only as a structural decoration[97]. For C-QD-enabled composites, this leads to a clear guideline. If C-QDs are claimed to act as interfacial bridges, the study should provide evidence of stronger coupling (e.g., chemical bonding or clearly enhanced interfacial interactions). It should also show faster interfacial charge transfer through methods such as transient spectroscopy, photovoltage, or photocurrent kinetics. PL quenching alone is not sufficient to support this claim[14].

2.3 Role C: Adsorption and microenvironment modulation for intermediate binding, selectivity control, and reaction competition

Role C is the most directly catalytic among the three roles. In this role, C-QDs influence photocatalysis by modulating adsorption, stabilizing key intermediates, and tuning the local reaction microenvironment, including polarity, hydrogen bonding, and proton availability. These effects can shift product selectivity and suppress competing reaction pathways. This role is most evident in CO_2 photoreduction and selective oxidations/AOP systems, where surface chemistry and intermediate binding strongly influence product distribution[38,52–53,98]. Therefore, the evidence for Role C should be sensitive to reaction intermediates and be closely matched to the specific reaction. In situ or operando spectroscopy is most useful when peak assignments are supported by proper control experiments and cross-validation, rather than being inferred only from product ratios.

In CO_2RR, credible mechanistic studies increasingly combine interfacial design with evidence at the intermediate level. For example, covalent interface engineering has been used to promote solar-driven CO_2-to-CO conversion while identifying *COOH as a key intermediate. This shows that well-designed interface chemistry can stabilize important adsorbates and facilitate the subsequent conversion steps[38,99]. Beyond C-QD-specific studies, influential CO_2RR photocatalysis papers and reviews have placed strong emphasis on $^{13}CO_2$ isotopic labeling and in situ or operando spectroscopy. These methods are essential for confirming the carbon source and tracking intermediates or products, which is exactly the level of evidence required to support Role C[100]. For the minimal role model, the message is clear. If C-QDs are claimed to tune product selectivity, this claim should be supported by evidence that directly probes intermediates and reaction pathways, such as in situ FTIR/EPR, isotopic

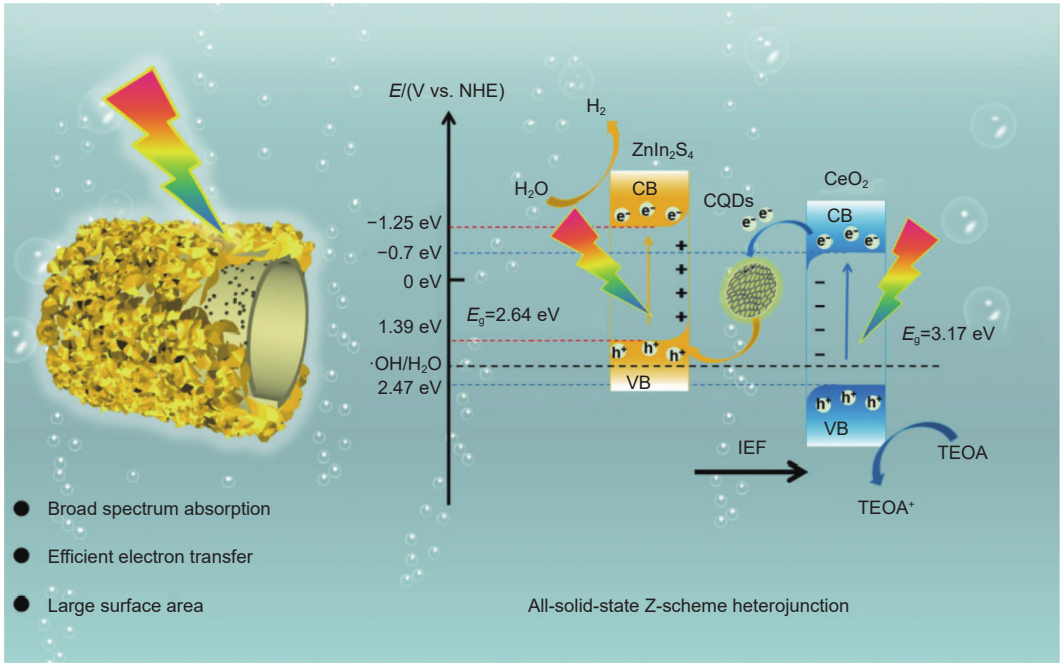

Fig. 7 CQDs as a photogenerated carrier-transfer bridge in an all-solid-state Z-scheme heterostructure for visible-light HER. The schematic illustrates a $ZnIn_2S_4$/CQDs/CeO_2 architecture in which CQDs function as an interfacial charge-transfer conduit in Role B. This conduit facilitates the directional recombination of less-reactive carriers, retains high-energy electrons and holes for redox reactions, and suppresses undesired back recombination. This example illustrates the transition from treating CQDs as a simple sensitizer to recognizing them as engineered interfacial sites, as emphasized in the MES-CT and MES-Coupling evidence-chain framework. Reproduced from ref.[27] with permission from Springer, copyright 2025

labeling, and carbon balance analysis. It should not be inferred from product ratios alone[100].

In environmental photocatalysis and photo-enhanced AOPs, Role C is mainly reflected in the regulation of ROS pathways and adsorption-driven pollutant activation. This includes controlling the balance between superoxide and singlet oxygen, as well as between radical and non-radical reaction routes[21,101]. Recent reviews on carbon-dot-mediated ROS modulation suggest that C-QDs can regulate both ROS generation and ROS suppression through their surface chemistry, precursor-derived features, and coupling with physical fields. This perspective presents C-QDs as controllable modifiers of the local reaction microenvironment, rather than as general activity enhancers[53]. As summarized in Fig. 8, carbon-dot-derived ROS modulators can work through several distinct control modes. They can promote ROS generation through stimulus-activated pro-oxidant pathways, as shown in Fig. 8a, or suppress ROS through antioxidant and ROS-scavenging activity, as shown in Fig. 8b. They can also enable bidirectional and photoswitchable ROS regulation, allowing ROS outputs to be adjusted for improved selectivity, as shown in Fig. 8c. The application examples in Fig. 8d further indicate the broader principle that carbon dots can be used to program the local reaction microenvironment[53]. This point is important because AOP studies are particularly vulnerable to mechanistic overinterpretation, such as assigning ROS types based only on scavenger tests. Recent efforts to improve ROS identification and pathway assignment in oxidation photocatalysis further show why Role C should be evaluated using clear evidence standards[53]. In this context, in situ FTIR peak assignments should be linked to reaction-specific fingerprints and validated with proper controls. These controls may include dark/light switching tests and feed or blank experiments, such as pollutant-free, catalyst-free, and C-QD-free baselines. This is necessary because many FTIR bands may originate from the solvent, adsorbed water, surface hydroxyl groups, or carbonate contamination rather than from true reaction intermediates. Therefore, practical reporting should include three key elements. First, the exact background-subtraction protocol should be clearly described. Second, the time-re-

solved evolution of diagnostic bands should be reported. Third, at least one independent confirmation method should be provided (e.g., EPR spin trapping to identify ROS or LC/GC-MS) to correlate intermediates with products. These steps help avoid overinterpreting changes in a single spectral band.

A recent and particularly informative example of Role C is the development of site-specific electron-transfer cascades in carbon-dot-based photocatalysis. Inspired by enzymatic microenvironments, these systems treat C-QDs not simply as electron sources, but as structured platforms that coordinate electron-transfer steps and guide product selectivity, such as H_2O_2 formation[7]. Such studies support the view that "interfacial sites" are not just a conceptual label. With proper structural control, C-QDs can be designed to carry specific microenvironmental functions that are mechanistically interpretable and potentially transferable across different photocatalytic systems. More broadly, these examples suggest a simple and transferable practice for MES-Path. Peak assignments from FTIR, DRIFTS, or ATR should be reported as both a hypothesis and a validation process. The hypothesis should be based on band positions that are consistent with the literature, while the validation should come from control experiments. Ideally, isotopic labeling or perturbation tests should also be used to confirm the expected peak shifts or on/off responses under reaction-relevant conditions.

2.4 Application of the three-role model

Role A accounts for longer carrier lifetimes through recombination suppression. Role B explains the rewiring of directional charge flow through interfacial conduction. Role C describes selectivity changes driven by intermediate stabilization and microenvironment control[2,32]. Importantly, a single C-QD can contribute to more than one role. The purpose of this minimal model is not to impose a rigid classification, but to ensure that each mechanistic claim is supported by the appropriate type of evidence. For Roles A and B, this mainly requires charge-dynamics evidence. For Role C, intermediate and

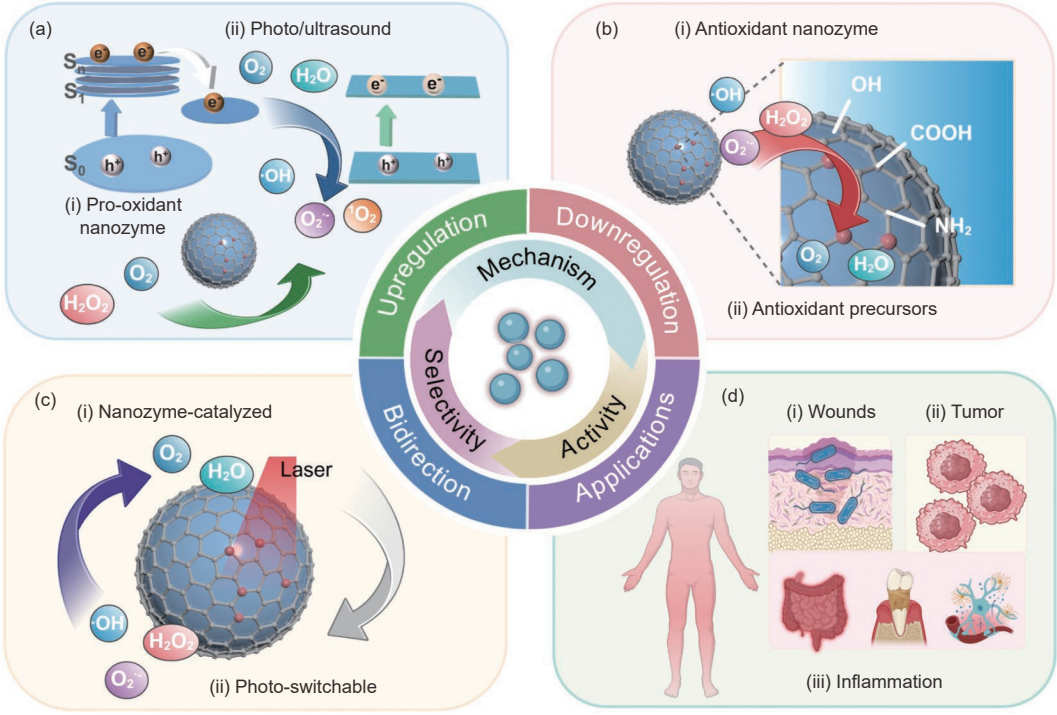

Fig. 8 Overview of carbon-dot-derived ROS modulators (CDRMs) and their regulation modes. (a) CDRMs enhance ROS generation through stimulus-activated pro-oxidant pathways. (b) CDRMs suppress ROS levels through antioxidant/ROS-scavenging activity. (c) Bidirectional ROS regulation enables switchable ROS generation or suppression, thereby improving reaction selectivity. (d) Representative biomedical applications enabled by these control strategies. In this framework, panels a–c serve as mechanistic analogues for Role C in environmental photocatalysis and photo-AOPs, highlighting the need for pathway-resolved evidence (e.g., EPR/ESR measurements and operando probes) when linking activity improvements to ROS steering. Reproduced from ref.[53] with permission from Elsevier, copyright 2025

ROS validation are more important. This approach helps to keep the resulting design rules transferable across HER, CO_2RR, and environmental/photo-AOP systems[89]. This role overlap is reasonable because C-QDs are structurally heterogeneous by nature. During carbonization, molecular precursors can first form carbonized polymer dots and then further evolve into carbon nanodots with diverse internal motifs and surface groups (Fig. 9a). Moreover, several optical and chemical functional units can coexist within the same C-QD, including aromatic domains, heteroatom doping, and molecular chromophores (Fig. 9b). As a result, the same material may serve multiple functions at once. It can act as a charge reservoir in Role A, an interfacial conduit under strong coupling conditions in Role B, and a microenvironment or adsorption modulator in Role C.

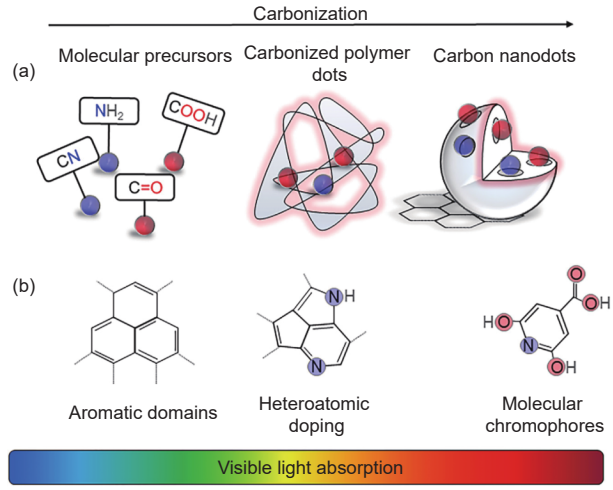

Fig. 9 Structural diversity of carbon dots and its implications for role assignment in the minimal model. (a) Carbonization of molecular precursors produces structurally heterogeneous C-QDs, ranging from carbonized polymer dots to carbon nanodots, with progressively evolving embedded functional motifs and surface groups. (b) Aromatic domains, heteroatom doping, and molecular chromophores are highlighted as key contributors to visible-light absorption. This emphasizes that structure-resolved design and characterization are essential for mechanistically assigning Roles A–C and for ensuring that functional claims are properly supported by evidence within our framework. Reproduced from ref.[89] with permission from Cell Press, copyright 2024

3 Evidence standards for assigning C-QD roles

3.1 Charge-transfer evidence based on energetics, dynamics, and charge flux (MES-CT)

To credibly assign Role A (namely, electron sink or charge reservoir), or Role B (namely, interfacial bridge), the evidence should connect three key aspects: energetic driving forces, time-resolved carrier dynamics, and measurable charge-transport or charge-flux outcomes[66,95–96,102–103]. This type of evidence triangulation is increasingly emphasized in advanced discussions of heterojunction photocatalysts. Because these systems often involve complex interfaces and ambiguous mechanisms, single-proxy interpretations (e.g., PL quenching alone) are no longer reliable[104].

The following MES for charge transfer (MES-CT) is recommended as a baseline for C-QD-containing systems.

(1) Energetics and built-in electric field: these measurements are required to justify the proposed direction of charge flow. Authors should combine UPS, which provides information on the valence-band edge and work function, or Kelvin probe/KPFM, which maps the work function, with at least one complementary method that directly reflects interfacial energetics. Suitable methods include surface photovoltage or photovoltage spectroscopy, and Mott–Schottky analysis where it is appropriate. This evidence package is particularly important when a study claims Z-scheme or S-scheme behavior, or any directional restructuring of charge flow. Recent reviews on S-scheme photocatalysts emphasize that such interpretations should be supported by work-function alignment and band-bending evidence, namely built-in electric field, rather than being inferred from band positions alone[39,91].

(2) Charge dynamics: dynamic measurements are needed to determine whether charge transfer or charge storage actually occur. TRPL should include multi-component lifetime analysis rather than relying only on an average lifetime. TA, including fs-TA or ns-TA depending on the expected transfer timescale, should be used as a complementary method. Together, TRPL and TA can distinguish true interfacial electron transfer or charge storage from non-radiative loss pathways that may also cause PL quenching. The need for dynamic verification is consistent with the broader trend in heterojunction photocatalysis, where ultrafast-

to-microsecond carrier processes are increasingly resolved to support mechanistic assignments[104].

(3) Charge flux and electrical response: these measurements show whether the observed charge-transfer kinetics can be converted into usable charge flow. Transient photocurrent and EIS should be reported together, with light/dark comparison, R_{ct} trends and fitting assumptions clearly stated. Increasingly, high-quality heterojunction studies combine photocurrent and EIS results with spectroscopic evidence. This shows that claims of improved charge separation are more convincing when they are supported by both reduced interfacial resistance and increased charge flux[105].

Mapping MES-CT onto Roles A and B: A Role A claim is most convincing when lifetime extension, measured by TRPL or TA, is accompanied by reduced charge-transfer resistance and increased photocurrent, measured by EIS and transient photocurrent. These signals should also change consistently with the observed photocatalytic activity[29,61–62,103,106]. This evidence logic is illustrated in Fig. 10a-f. After C-QDs are introduced into the Cu-In-Zn-S quantum dots (CIZS)/MoS_2 system, the composite shows quenched PL and faster TRPL decay, indicating suppressed recombination. It also shows increased transient photocurrent and a smaller EIS semicircle, suggesting higher charge flux and lower interfacial charge-transfer resistance. These changes occur together with improved HER polarization and performance. This supports a charge-reservoir or electron-sink interpretation for Role A, because the activity enhancement is consistent with the co-variation of charge dynamics and charge flux[61]. A Role B claim requires all of the above evidence, together with an energetic explanation for why charge flow should be directional. This explanation should be supported by methods such as UPS, KPFM, or SPV. The reason is that an interfacial bridge implies not only faster charge transfer, but also a reorganized charge-flow pathway. This view is consistent with recent S-scheme reviews, including those focused on CO_2RR, where charge-flow directionality is treated as the key feature that must be verified[39].

3.2 Interfacial coupling strength: distinguishing chemical coupling (covalent/coordination) from physical adsorption (MES-Coupling)

The transition from sensitizers to interfacial sites is essentially a shift from weakly interacting additives to chemically coupled interlayers. These interlayers can reshape interfacial energetics and charge-transfer kinetics[38,103,107–108]. High-level studies on heterojunction photocatalysts have shown that poorly defined interfaces are a common source of unreliable mechanistic interpretations and overclaimed charge-transfer pathways. These problems often arise from unclear interfacial contact, lattice mismatch, or uncontrolled surface chemistry[104]. In C-QD-based composites, this problem is further complicated by the intrinsic heterogeneity of C-QDs, including differences in size, surface states, and functional groups. Without evidence of coupling strength, the claim that C-QDs act as interfacial bridges can easily become difficult to distinguish from a more general electron-trapping role (namely, Role A) or even from a simple dispersant effect.

The following MES for interfacial coupling (MES-Coupling) is recommended when claiming Role B or interfacial-site functions.

(1) XPS core-level shifts and supported electronic-structure changes: a convincing case should combine interface-sensitive XPS core-level shifts, such as C 1s, N 1s, O 1s, and relevant metal signals, with evidence of electronic-structure changes from UPS or KPFM. The XPS shifts can indicate charge redistribution and possible bond or coordination formation, while changes in work function or valence-band position help explain the modified carrier-transfer pathway[102].

(2) Vibrational and structural confirmation of bonding: FTIR, DRIFTS, and solid-state nuclear magnetic resonance (NMR), when feasible, can provide important evidence for interfacial bonding. These methods are especially useful when XPS alone cannot rule out spectral overlap from physical mixtures. This issue is particularly relevant in polymeric carbon nitride, MOF/COF, and organic-inorganic hybrid sys-

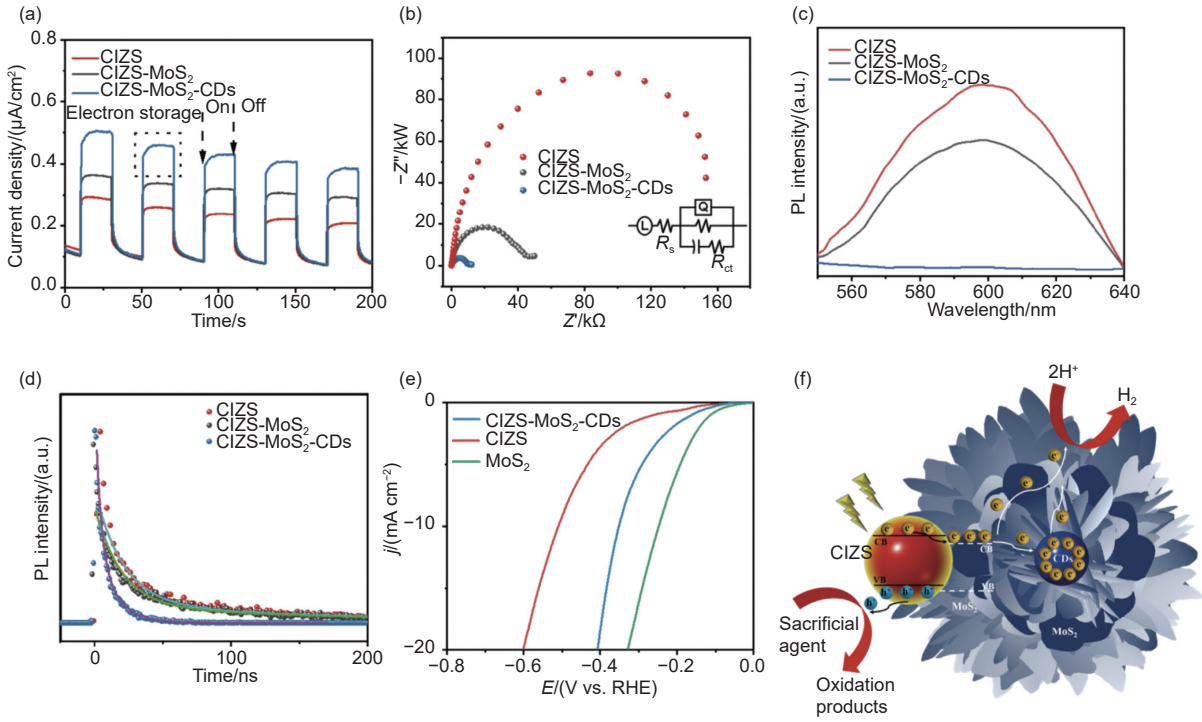

Fig. 10 MES-CT dynamics and flux evidence supporting Roles A and B in C-QD-enabled HER. (a-d) Transient photocurrent, EIS with equivalent-circuit fitting, steady-state PL, and TRPL collectively reveal improved charge extraction and transport, together with suppressed recombination, after C-QDs are introduced into a CIZS/MoS_2 heterostructure. (e,f) Light-assisted HER polarization and the proposed charge-transfer schematic further connect these spectroscopic and electrochemical signatures to faster interfacial charge delivery and improved H_2 evolution performance. Reproduced from ref.[61] with permission from Elsevier, copyright 2022

tems, where multiple binding motifs may coexist[109].

(3) Coupling and dynamics linkage: evidence of strong interfacial coupling should be supported by kinetic signatures that show faster charge transfer, such as TA, TRPL, or time-resolved photovoltage. Otherwise, the observed bonding may only represent structural contact rather than a functional bridge for charge transport[104].

3.3 Operando and near-operando evidence for intermediates and pathways in Role C (MES-Path)

Role C, which involves adsorption and microenvironment modulation, has the strongest impact on selectivity, especially in CO_2RR, selective oxidation, and AOP systems. For this reason, it is also the role most prone to over-interpretation[110–116]. Recent methodological discussions in photocatalytic and photochemical research emphasize that mechanistic assignments based only on scavenger tests or product distributions are often not unique. More convincing pathway attribution increasingly requires operando or near-operando evidence at the intermediate level[110]. Accordingly, we define the MES for intermediates and pathways (MES-Path) as the baseline evidence package for supporting Role C claims.

EPR/ESR (preferably in situ under illumination): for ROS-driven environmental photocatalysis and photo-AOPs, EPR provides stronger evidence than scavenger tests alone. Scavenger tests can introduce secondary reactions, interact with the catalyst, or produce misleading decreases in reaction rates. Recent studies have therefore emphasized that scavengers must be tested for non-interference, and that mechanisms based only on scavenger results remain fragile[117].

In situ FTIR/DRIFTS: for CO_2RR and selective transformation reactions, tracking surface-bound intermediates by vibrational spectroscopy is increasingly regarded as a key part of mechanism-based catalyst design. Typical examples include *COOH and *CO-related intermediates in CO_2RR, as well as adsorbed oxygen-containing species in oxidation reactions. This evidence is especially important when claiming that C-QDs serve as interfacial active sites[118].

$^{13}CO_2$ isotope tracing and carbon balance as essential requirements for CO_2RR: renewed attention to false positives in photochemical and photoelectrochemical CO_2 reduction has shown that carbon-containing catalysts, binders, and adventitious organic residues may generate products that are incorrectly assigned to CO_2RR. Therefore, isotope tracing, carbon balance analysis, and strict control experiments should be treated as minimum requirements for any claim that C-QDs tune CO_2RR selectivity[119].

3.4 Common pitfalls in role assignment

(1) Inferring Z-scheme or S-scheme behavior from band positions alone: recent reviews on S-scheme photocatalysts, including those focused on CO_2RR, emphasize that charge-flow directionality must be supported by work-function alignment, built-in electric field evidence, and dynamic signatures. Without this evidence, the same results could often be explained by Type-II charge transfer, trap-mediated recombination, or dye-sensitization effects[39].

(2) Treating PL quenching as direct evidence of productive charge transfer: PL quenching can also result from non-radiative loss pathways. Without supporting evidence from TRPL/TA and charge-flux measurements, such as photocurrent and EIS, improved charge separation remains unproven. This issue has been repeatedly emphasized in high-level discussion of heterojunction interpretation[104].

(3) Relying only on scavenger tests for ROS or pathway assignment and omitting $^{13}CO_2$ validation in CO_2RR: recent studies and perspective articles emphasize that scavengers can interact with catalysts or participate in photochemical side reactions, so their non-interference must be validated. For CO_2RR, isotope tracing and carbon balance analysis are also necessary to avoid false-positive product assignments[117].

4 In situ characterization and first-principles insights into C-QD photocatalysts

Understanding how C-QDs affect photocatalytic performance requires more than post-synthesis analysis. It also requires in situ and real-time probing of charge dynamics, surface states, and structural evolution during photoactivation. At the same time, first-principles calculations, such as density functional theory (DFT) and time-dependent DFT (TD-DFT), have become important tools for understanding electronic structures, carrier-transfer pathways, and reaction energetics. Fig. 11 provides an integrated overview of in situ characterization and first-principles calculations used to study C-QDs in photocatalysis. It highlights key methods for probing charge dynamics, surface chemistry, and interfacial electron transfer.

4.1 In-situ spectroscopic characterization

Ultrafast transient spectroscopy is essential for capturing carrier dynamics in CQDs and C-QD-based composites from the femtosecond to nanosecond timescale. Techniques such as TRPL and TA spectroscopy allow direct observation of charge separation, charge transfer, and recombination processes. For example, ultrafast TA spectroscopy was used to examine electron and hole dynamics in CQDs and their interactions with electron acceptors. These studies revealed how surface states and core states regulate charge-transfer pathways after photoexcitation[120]. In addition, advanced TA methods could enable in situ monitoring of photoinduced changes in carrier populations. This makes it possible to connect excited-state kinetics with photocatalytic efficiency[14].

Other steady-state and time-resolved optical techniques, such as UV-vis absorption, PL, and time-correlated single photon counting, are also widely used to evaluate the optical responses of CQDs. These methods help reveal how CQDs behave and how their emission is quenched when they interact with substrates or co-catalysts[121].

Structural and chemical in situ probes, such as XPS and FTIR, are essential for tracking changes in surface functional groups, chemical states, and bonding during synthesis and catalytic operation. These methods are often combined with microscopic techniques, such as TEM, to monitor morphological evolution and active-site formation in real time[121].

4.2 First-principles calculations for mechanistic

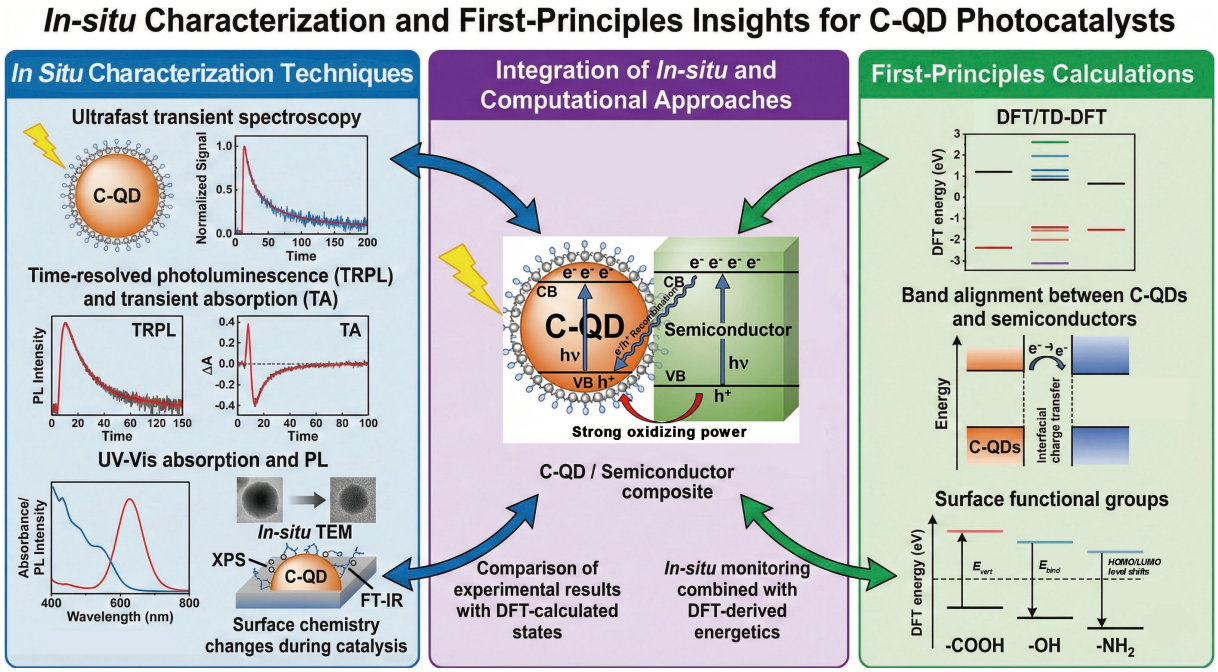

Fig. 11 Schematic illustration of the integrated framework combining in-situ characterization and first-principles calculations for elucidating C-QD photocatalytic mechanisms. The approach synergizes experimental insights into real-time charge carrier dynamics and surface chemistry evolution (left panel) with theoretical predictions of electronic structures, band alignments, and functional group energetics (right panel). The central panel highlights how integrating these spectroscopic and computational techniques enables the comprehensive decoding of complex interfacial charge transfer pathways, such as Z-scheme mechanisms, within C-QD/semiconductor composite systems under irradiation

understanding

First-principle computational methods provide atomic-level and electronic-level insights that are difficult to obtain from experiments alone. DFT is especially useful for understanding how surface functional groups, dopants, and defects in C-QDs affect band structure, density of states, and charge distribution. For example, DFT and TD-DFT have been used to connect specific surface groups and structural motifs with absorption and emission properties, and to explain how oxygen-containing functional groups, such as carbonyl and hydroxyl groups, influence spectroscopic signatures[122].

By calculating the band alignment between C-QDs and connected semiconductors or molecular acceptors/donors, first-principle models can predict favorable pathways for interfacial electron transfer. They can also help explain experimental TA and PL results. Such combined theoretical and experimental approaches have clarified how dopants (e.g., N, B, and P) and heterojunction structures affect charge-transfer rates and photocatalytic activity. These insights can guide the design of more efficient C-QD-based photocatalytic systems[123].

4.3 Integration of in-situ characterization with computational modeling

The most convincing mechanistic studies in CQD photocatalysis combine in situ characterization with theoretical calculations. For example, carrier lifetimes observed by TA can be compared with calculated electronic states to identify the structural features that promote charge separation or suppress recombination, such as midgap states introduced by heteroatom doping[120]. Similarly, in situ FTIR monitoring of adsorbed intermediates can be combined with DFT-derived reaction energetics to clarify key steps such as CO_2 activation or ROS formation. This integrated approach provides stronger mechanistic evidence and helps support claims that C-QDs act as active sites rather than merely as electron sinks.

5 Reaction case studies linking roles, evidence and metrics

Fig. 12 visually summarizes the alignment of C-QD roles, supporting evidence, and performance met-

rics across 3 major reaction scenarios: HER, CO_2RR, and pollutant degradation/photo-AOPs. In HER, C-QDs mainly modulate charge management by serving as electron sinks and interfacial bridges, corresponding to Roles A and B. These functions promote charge separation and extraction. For fair performance comparison, AQY should be normalized to the incident photon flux. For CO_2RR, C-QDs mainly regulate adsorption and the local reaction microenvironment, corresponding to Role C. By stabilizing key intermediates such as *COOH and *CO, they can facilitate product formation and influence product selectivity. This role is supported by intermediate-level evidence, including in situ FTIR/DRIFTS signals and $^{13}CO_2$ labeling to verify the carbon origin of the products. In pollutant degradation/photo-AOP systems, C-QDs regulate ROS pathways that drive pollutant removal. Performance evaluation should therefore focus on TOC removal, mineralization, and energy-normalized efficiency to ensure consistent and meaningful comparisons. Fig. 12 highlights the need to match each proposed role with suitable evidence and to report standardized, normalized metrics. This alignment is essential for accurate evaluation and meaningful comparison of photocatalytic performance.

5.1 HER dominated by Roles A and B with photon-flux-normalized AQY reporting

(1) Key conclusion 1: performance gains in most C-QD-enabled HER systems mainly arise from improved charge management rather than enhanced light harvesting.

Over the past three years, studies on C-QD/semiconductor systems for HER have shown that the most reproducible improvements are mainly related to Role A and Role B. In Role A, C-QDs act as electron sinks or charge reservoirs by providing storage or trap states that extend the lifetime of reductive carriers and suppress back recombination. In Role B, C-QDs serve as electronically coupled interlayers that accelerate charge transfer across interfaces by lowering the kinetic barriers for charge extraction and delivery[26–27,29,88,92]. This interpretation is consistent with current S-scheme and Z-scheme views of HER as an interface-limited process. Effective architectures are those that preserve strong redox carriers while promoting fast recombination of less useful carriers at the interface. When C-QDs are intentionally introduced as junction mediators, this behavior closely matches the function of Role B[124].

(2) Key conclusion 2: bridge claims for Role B in HER require evidence of directional charge transfer. Without such evidence, Role A is usually the more defensible assignment.

HER studies often use S-scheme terminology to argue that C-QDs optimize charge migration. However, the S-scheme in HER literature now makes it clear that directional charge transfer must be validated by work-function alignment, band-bending evidence, and carrier-dynamics measurements. Without such evidence, similar activity trends may also be explained by Type-II charge transfer, trap-mediated separation, or surface passivation[66,95–96,125–126]. In simple terms, weakly coupled C-QDs are more likely to act as electron sinks, corresponding to Role A. Only when strong coupling and favorable energetics are clearly demonstrated can C-QDs be credibly described as conduits that rewire charge flow, corresponding to Role B[124].

(3) Key conclusion 3: for HER, reporting practices can strongly influence perceived performance, so AQY should be normalized to incident photon flux under clearly stated conditions.

For HER, comparisons based only on μmol g^{-1} h^{-1} are rarely meaningful across different experimental setups. Recent discussions emphasize that normalizing activity to the incident photon flux and clearly defining AQY can reduce much of the apparent performance variation that might otherwise be mistaken for material superiority[127]. At the same time, the broader photocatalysis community increasingly emphasizes transparent AQY reporting under clearly stated conditions, including wavelength, light intensity, and temperature. This highlights why photon-flux normalization and complete optical parameters should be treated as basic reporting requirements rather than optional details[128].

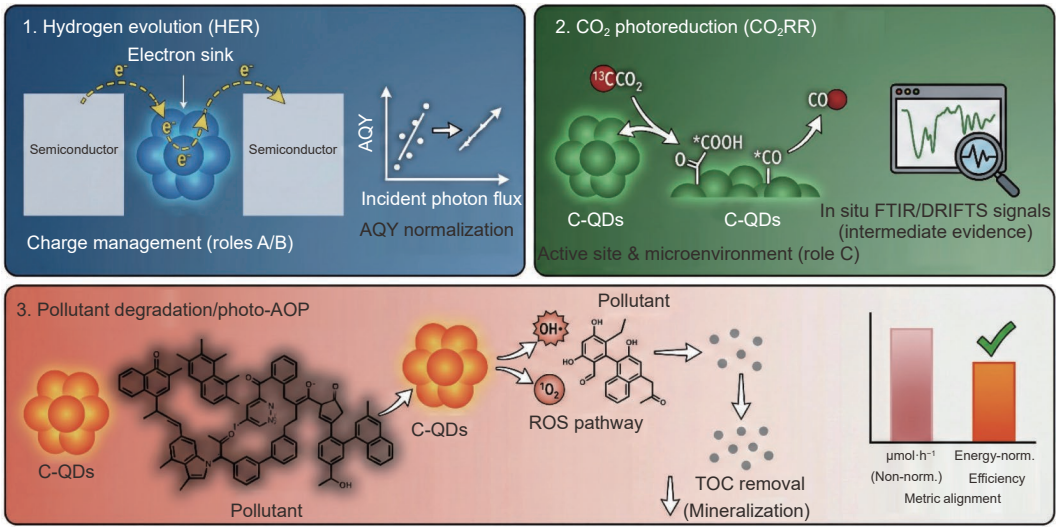

Fig. 12 Role, evidence, and metric alignment for C-QD-based photocatalysis. (1) In HER, C-QDs mainly act as electron sinks and interfacial bridges, corresponding to Roles A and B, with performance evaluated using photon-flux-normalized AQY. (2) In CO_2RR, C-QDs regulate adsorption and the local microenvironment, corresponding to Role C, where intermediate evidence from in situ FTIR/DRIFTS and $^{13}CO_2$ labeling is required for product validation. (3) In pollutant degradation and photo-AOPs, C-QDs modulate ROS pathways, with evaluation focused on TOC removal, mineralization, toxicity evolution, and energy-normalized efficiency

5.2 CO_2RR selectivity controlled by Role C with intermediate evidence, carbon balance, and $^{13}CO_2$ validation

(1) Key conclusion 1: in CO_2RR, C-QDs have the clearest impact when they regulate adsorption and the local reaction microenvironment, because product selectivity is largely governed by reaction intermediates.

Unlike HER, where charge delivery often plays the dominant role, CO_2RR is highly sensitive to the stabilization of key intermediates, such as *COOH and *CO, local proton availability, and the suppression of competing HER[111]. Therefore, the most meaningful effect of C-QDs in CO_2RR often lies in Role C. By tuning intermediate binding and the local reaction microenvironment, C-QDs can influence reaction pathways and product distributions, rather than simply improving charge separation. This is why high-quality CO_2RR studies increasingly connect interface design with intermediate-level evidence instead of relying only on product ratios[129].

(2) Key conclusion 2: CO_2-derived products must be verified rather than assumed, making $^{13}CO_2$ labeling and carbon accounting essential baseline requirements.

False positives and carbon-source ambiguity remain persistent challenges in CO_2 photoreduction. Method-focused studies have therefore emphasized robust approaches for confirming product carbon origin and reporting reliable reaction kinetics[130]. Recent high-level CO_2RR papers commonly use $^{13}CO_2$ labeling to verify the carbon source of products, together with strict control experiments. This practice has become an expected standard, especially when C-QDs are claimed to improve selectivity through Role C[131].

(3) Key conclusion 3: role, evidence, and metric alignment in CO_2RR require in situ intermediate tracking, isotope-based validation, and robust selectivity metrics.

If Role C is claimed, the study should provide evidence of intermediates or reaction pathways, such as in situ FTIR/DRIFTS or operando signals, and verify the carbon source through $^{13}CO_2$ labeling and carbon balance analysis[33,72–73,132]. Without this evidence, the mechanistic assignment remains uncertain, regardless of how high the reported CO production rate is[130].

5.3 Pollutant degradation and photo-AOPs with emphasis on TOC, toxicity, and energy-normalized metrics

(1) Key conclusion 1: evaluation should move beyond dye decolorization toward mineralization, tox-

icity, and energy-normalized performance.

The environmental photocatalysis and AOP literature increasingly make it clear that dye decolorization kinetics alone are not sufficient to evaluate treatment performance. More meaningful assessment requires TOC removal, which reflects mineralization, together with toxicity changes and energy-normalized cost metrics[133–135]. This view fits well with the interfacial-site framework. C-QDs may regulate ROS pathways and adsorption microenvironments through Role C, but their real impact should be evaluated using practical endpoints that are relevant to wastewater treatment applications[136].

(2) Key conclusion 2: ROS pathway assignment remains a major source of mechanistic uncertainty, and scavenger tests alone are insufficient for Role C claims.

AOP studies are particularly prone to overinterpretation because different ROS and non-radical pathways can produce similar apparent kinetics[137–140]. Consistent with current guidance in photocatalysis, mechanistic claims, such as the dominance of $^1O_2$, should be supported by direct or diagnostic evidence and linked to measurable outcomes beyond the apparent rate constant, k_{app}. This is also why studies on singlet-oxygen-driven systems increasingly report practical metrics, including energy consumption, rather than relying only on mechanistic narratives[141].

(3) Key conclusion 3: energy-normalized performance should be reported when discussing efficiency.

Energy consumption reporting, including EEO and treatment cost proxies, has become an important focus in reviews of oxidation and degradation processes. This trend is also evident in TiO_2-based photocatalysis, where standardized scale-up metrics have been analyzed and compared[84,142]. For C-QD-enabled AOPs, these metrics provide a practical framework for moving beyond laboratory kinetic constants toward comparable and decision-relevant performance evaluation[143].

Table 2 summarizes the key conclusions from reaction case studies in photocatalysis, with a focus on HER, CO_2RR, and pollutant degradation/photo-AOPs. In HER, C-QDs improve charge management by acting as electron sinks or interfacial bridges, corresponding to Roles A and B, while directionality evidence is required to support Role B claims. In CO_2RR, C-QDs mainly affect adsorption and the local reaction microenvironment, corresponding to Role C, and $^{13}CO_2$ labeling together with carbon balance is needed to verify CO_2-derived products. In pollutant degradation and photo-AOPs, the evaluation focus has shifted from decolorization to mineralization, toxicity reduction, diagnostic ROS evidence, and energy-normalized metrics. Overall, Table 2 emphasizes the importance of standardized reporting, clear role assignment, and robust validation for advancing C-QD-based photocatalysis.

6 Key controversies and practical solutions

Fig. 13 summarizes the key controversies in C-QD photocatalysis. These include whether C-QDs function as true catalytic sites or mainly as charge or energy carriers, the overuse of Z-scheme and S-scheme terminology, and the poor comparability of photocatalytic performance metrics. The first controversy can be addressed through a tiered interpretation. C-QDs should be assigned as electron sinks or interfacial bridges, corresponding to Roles A and B, unless intermediate-level evidence, such as substrate adsorption or activation, supports their function as active sites, corresponding to Role C. The second controversy concerns the misuse of Z-scheme and S-scheme labels. Such claims should be supported by charge-flow directionality and energetic-alignment evidence, rather than by band positions alone. The third controversy involves non-comparable performance metrics. This issue can be addressed by using energy-normalized metrics and standardized reporting practices, which allow more meaningful comparisons across studies. These practical solutions are important for making C-QD photocatalysis more reproducible and reliable.

Table 2 Summary of key conclusions, role/evidence/metric alignment, and corresponding references for reaction case studies in photocatalysis

Reaction types/Study focus	Key conclusion	Role/evidence/metric alignment	Refs.
HER	In most C-QD-enabled HER systems, performance gains are primarily "charge-management gains," not light-harvesting gains.	Roles A/B dominate; CQDs often act as electron reservoirs or interfacial mediators to improve charge separation and extraction.	[89]
HER	"Bridge" claims (Role B) in HER must be backed by directionality evidence, otherwise the most defensible assignment is Role A.	Strong coupling, work-function/band alignment, and carrier dynamics evidence are required to support interfacial bridge claims.	[88]
HER	AQY must be normalized to incident photon flux and conditions.	Photon-flux normalization and full reporting reduce performance variance between systems.	[29]
CO_2RR	In CO_2RR, C-QDs most credibly matter when they alter adsorption/microenvironment (Role C).	Carbon dots can broaden light absorption, boost charge transport, and alter surface adsorption for CO_2 reduction.	[144]
CO_2RR	Claims of CO_2-derived products must be proven with isotopic/carbon balance validation.	Control experiments and mechanistic validation (e.g., $^{13}CO_2$) are essential for product attribution.	[145]
CO_2RR	Role–evidence–metric alignment: in situ intermediates + isotope validation + selectivity metrics.	CO_2RR assignments require direct studies of intermediates (in situ spectroscopy) and carbon verification.	[64]
Pollutant degradation / Photo-AOPs	Focus on mineralization (TOC/toxicity) and energy-normalized metrics.	Advanced photocatalysis evaluation must include TOC and toxicity outcomes, not just decolorization.	[146]
Pollutant degradation / Photo-AOPs	ROS pathway assignment should be based on direct evidence, not just scavengers.	Mechanistic claims (e.g., singlet oxygen) require diagnostic ROS detection techniques.	[147]
Pollutant degradation / Photo-AOPs	Report energy-normalized performance metrics when discussing 'efficiency'.	Standardized energy metrics (electrical energy per order etc.) are needed for comparability.	[148]

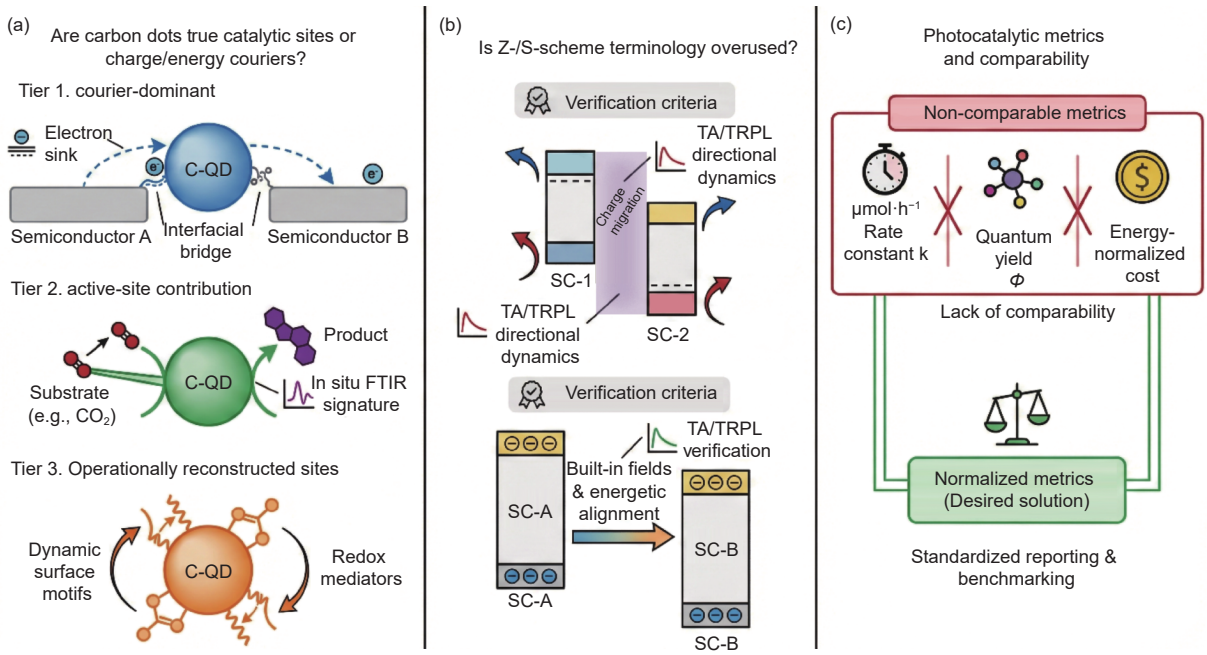

Fig. 13 Key controversies in C-QD photocatalysis and practical validation criteria. (a) Distinguishing C-QDs as electron sinks, interfacial bridges, active sites, or dynamically reconstructed species. (b) Verification of Z-scheme and S-scheme assignments through directional charge-transfer evidence, energetic alignment, and built-in field validation. (c) Standardization of photocatalytic metrics to improve comparability across studies, including photon-flux-normalized AQY, carbon balance, TOC removal, toxicity evolution, and energy-normalized performance

6.1 Controversy 1: catalytic sites or charge and energy carriers

A recurring debate in C-QD-enabled photocatalysis is whether C-QDs should be considered intrinsic active sites or functional auxiliaries. In the first scenario, they directly participate in substrate activation and bond formation or cleavage. In the second, they mainly shuttle charges or energy to other catalytic centers. For this review, the answer is not simply either-or. A more reliable approach is to assign roles based on the type and strength of supporting evidence.

Tier 1, functions dominated by charge storage and charge transfer involving Roles A and B: the most conservative and often most defensible interpretation

is that C-QDs act as electron sinks or charge reservoirs, corresponding to Role A, and/or as interfacial bridges, corresponding to Role B. This assignment is appropriate when the mechanistic evidence mainly comes from energetics, charge dynamics, and charge flux measurements, such as UPS/KPFM, TRPL/TA, photocurrent, and EIS, but lacks direct evidence of substrate-derived intermediates bound to C-QDs. This interpretation is consistent with recent reviews on C-QD photocatalysis, which emphasize that improved HER-type activity is often associated with enhanced charge separation and transfer, rather than with clearly demonstrated new catalytic sites on C-QDs[88].

Tier 2, active-site contribution with the emergence of Role C: C-QDs can be credibly described as active sites only when intermediate-level evidence supports adsorption or activation on C-QD-derived surface motifs. Such evidence may include in situ FTIR/DRIFTS signals that change with C-QD incorporation, or operando spectroscopy showing the involvement of C-QD-bound species. Proper control experiments are also needed to rule out interpretations in which C-QDs only serve as supports or auxiliary components. This level of evidence is increasingly expected in selective transformations and CO_2RR, where pathway control depends strongly on intermediate binding and local microenvironment effects[149].

Tier 3, operationally reconstructed sites: a third and often overlooked possibility is dynamic reconstruction during photocatalytic operation. In this case, the species that act as active sites under reaction conditions may differ from the original as-synthesized C-QDs. Examples include newly formed redox mediators or reconstructed surface motifs. Recent operando-focused studies on active-site circulators and redox-mediator reconstruction show why post-mortem and operando validation are essential. These methods help distinguish intrinsic C-QD active sites from mediators that are generated in situ during the reaction[150].

6.2 Controversy 2: overuse of Z-scheme and S-scheme terminology with minimum validation criteria

The rapid adoption of Z-scheme and especially S-scheme terminology has created a credibility problem. Many studies label a junction as Z-scheme or S-scheme based only on band positions or qualitative PL quenching, while lacking direct evidence of directional charge flow and built-in electric fields. These two features are essential because they distinguish Z-scheme and S-scheme mechanisms from Type-II charge transfer or trap-mediated separation. Comprehensive reviews on S-scheme photocatalysts now emphasize verification toolkits and common misassignments, making it clear that charge-flow directionality must be demonstrated rather than assumed[66].

Minimum validation criteria, namely the MES for Z-scheme and S-scheme assignment (MES-ZS): a C-QD-containing system should not be described as a Z-scheme or S-scheme photocatalyst unless it satisfies all three of the following requirements:

(1) Energetic alignment and built-in field evidence: UPS and/or KPFM should be used to demonstrate work-function changes, Fermi-level alignment, and plausible band bending or internal electric fields at the interface[66].

(2) Directional charge dynamics: time-resolved signatures from TA, TRPL, time-resolved photovoltage, or SPV should be consistent with the proposed carrier-transfer pathway. Ideally, these measurements should show accelerated interfacial charge separation that matches the expected S-scheme charge-flow topology[96].

(3) Consistency with redox outcomes: the observed redox performance should match the claimed retention of strong redox carriers. Examples include simultaneous improvement in reduction and oxidation half-reaction proxies, or selectivity shifts that cannot be explained by light absorption changes alone[39].

6.3 Controversy 3: non-comparable photocatalytic metrics and minimum reporting requirements

A major barrier to transferability is that studies often report the metrics that make performance appear most favorable, such as μmol h^{-1} or pseudo-first-order rate constants. However, these metrics are frequently presented without photon-flux normalization, carbon balance, or energy-normalized cost analysis. Recent perspective articles on photocatalysis emphas-

ize that the field needs clearer and more comparable reporting standards as it moves from proof-of-concept studies toward deployable technologies[149].

7 Conclusions and outlook: from additive sensitizers to engineered interfacial sites

Over the past three years, carbon-dot-enabled photocatalysis has rapidly moved from treating C-QDs as broadband additive sensitizers to designing them as programmable interfacial sites. These sites can measurably regulate interfacial energetics, charge-flow pathways, and surface microenvironments, as summarized in Fig. 14. This Review argues that the next major advance will come not simply from higher apparent reaction rates, but from role-specific and falsifiable evidence that connects function with mechanism. These roles include Role A as an electron sink or charge reservoir, Role B as an interfacial bridge that enables directional charge transfer, and Role C as an adsorption and microenvironment modulator that controls selectivity. Looking ahead, transferable design rules are most likely to emerge from the combination of strong interfacial coupling, fractionated and traceable C-QDs, and standardized operando workflows. These workflows should connect interfacial energetics, charge dynamics, intermediates, and final products, as illustrated in Fig. 14.

Table 3 summarizes recent studies on the use of C-QDs in advanced photocatalysts for environmental and energy-related applications. It covers several major reaction scenarios, including HER, CO_2RR, photo-AOPs, and photocatalytic pollutant degradation. Across these systems, C-QDs can improve electron transfer, light absorption, and charge separation. However, challenges remain, particularly in clarifying their mechanisms, optimizing C-QD loading, and ensuring long-term stability. Common preparation methods include hydrothermal synthesis, microwave-assisted processes, and carbonization, which are widely used to integrate C-QDs with different semiconductor platforms. Overall, C-QDs can significantly enhance photocatalytic performance, but further studies are needed to define their roles more clearly and improve their durability in practical applications.

(1) Strongly coupled interfaces will become a central design principle rather than an optional feature. S-scheme and related heterojunction concepts have encouraged the field to treat charge-flow directionality as a measurable property, involving work function, band bending, and built-in electric fields,

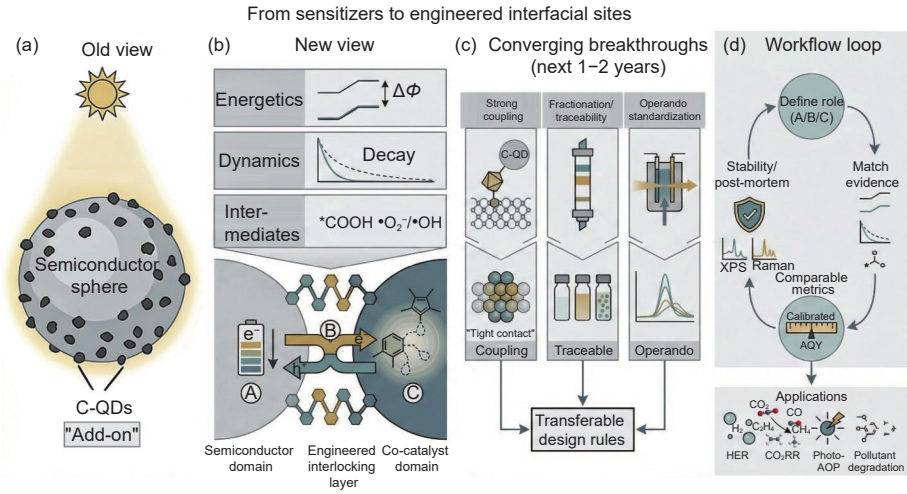

Fig. 14 From sensitizers to engineered interfacial sites in carbon-dot-enabled photocatalysis. (a) Conventional view of C-QDs as broadband sensitizers on semiconductor surfaces. (b) Updated framework in which C-QDs serve as programmable interfacial units that regulate energetics, charge-transfer dynamics, and reaction microenvironments through three roles: electron sink/charge reservoir, interfacial bridge for directional charge flow, and adsorption/microenvironment modulator for selectivity control. (c) Emerging directions toward transferable design rules, including strong interfacial coupling, C-QD fractionation and traceability, and operando standardization. (d) Role-linked workflow for converting mechanistic claims into reproducible structure–function relationships through role definition, matched evidence, comparable metrics, and stability/post-mortem validation across HER, CO_2RR, photo-AOPs, and pollutant degradation

Table 3 Summary of critical information on the use of C-QDs in the development of advanced photocatalysts for environmental and energy-related applications, including HER, CO_2RR, photo-AOPs and pollutant degradation

Reaction types/Study focus	Key findings/methods	Advantages	Disadvantages	Preparation methods	Critical statements	Refs.
HER	C-QDs enhance electrocatalytic HER activity by facilitating charge transfer and providing active sites.	CQDs improve electron transfer and conductivity; tunable surface chemistry.	Still limited mechanistic understanding and activity often below precious metals.	Various CD synthesis methods including hydrothermal, pyrolysis, surface doping.	CQDs offer flexible design for HER catalysts but need deeper mechanistic quantification and long-term stability studies.	[151]
HER	C-QDs/TiO_2 hybrids improve visible light absorption and charge separation, boosting H_2 production.	Broad optical absorption; enhanced charge separation; cost-effective.	Catalyst performance still highly dependent on semiconductor support and light intensity.	Microwave/hydrothermal, bottom-up carbonization.	CQD incorporation enhances visible-light response, but scalability & stability require improvement.	[152]
HER	Hydrothermal synthesis is popular for C-QDs, providing control over morphology and doping.	Clean, cost-effective, scalable.	Doping and heterostructure integration remains complex.	Hydrothermal carbonization of organic precursors.	Hydrothermal methods allow facile C-QD preparation, but control of size & surface states is vital.	[153]
HER	C-QDs were used in combination with $CoMoO_4$ and g-C_3N_4 to enhance photocatalytic H_2 evolution under visible light; Maximum hydrogen evolution rate of 4916.63 mmol g^{-1} h^{-1} was achieved.	High hydrogen evolution rate; C-QDs derived from low-cost coal, providing an environmentally friendly, sustainable alternative for H_2 production.	Excess C-QDs beyond the optimal amount reduces hydrogen evolution due to aggregation.	C-QDs were synthesized from coal using H_2O_2-assisted ultrasonic treatment;Composite catalysts were prepared by combining $CoMoO_4$, g-C_3N_4, and C-QDs.	The addition of C-QDs significantly improved the H_2 evolution performance; The optimal catalyst had the highest efficiency and stability in H_2 evolution; SCQDs act as both electron acceptors and donors, enhancing electron transfer and separation.	[154]
CO_2RR	C-QD-modified heterojunction catalysts (e.g., CQDs-TiO_2/$SrTiO_3$) show improved CO and CH_4 production.	Up-conversion light harvesting; enriched active sites; enhanced CO_2 adsorption.	Absolute production rates still modest; selectivity control remains challenging.	Hydrothermal integration; compositing with metal oxides.	CQDs improve light harvesting & charge separation, but reaction pathways and intermediate stabilization remain under-explored.	[98]
CO_2RR	Reviews summarize strategies where C-QDs participate in CO_2 photoreduction, highlighting redox and light absorption roles.	Offers comprehensive insight into CQD roles in CO_2RR; discusses synthetic procedures.	Many mechanistic hypotheses lack direct operando evidence.	Bottom-up and top-down CQD syntheses with functionalization.	Reviews emphasize the need for operando and isotopic studies to prove mechanistic claims.	[145]
CO_2RR	Quantum dot photocatalysts including C-QDs are reviewed for water splitting and environmental applications.	Offers context for light harvesting and carrier separation mechanisms.	C-QDs are part of a larger class with varied behavior.	Broad QD synthesis techniques.	Understanding QDs' interaction with host photocatalysts is crucial.	[155]
CO_2RR	General review of QDs including carbon types for CO_2 photoreduction.	Historical perspective and broad QD context.	Less focused specifically on CQDs.	N/A (topic overview).	Lays foundational context but not CQD-specific.	[156]
HER, CO_2RR	C-QDs enhance electrocatalytic reactions including HER and CO_2RR via high surface area and active sites.	Rich functional groups; high conductivity; low toxicity.	Practical performance still inferior to noble metal catalysts.	C-QD composites via doping, surface engineering.	Electrocatalytic C-QD applications show promise but require optimization of composite structures.	[157]
CO_2RR, HER	Classic review on synthesis and optical properties of C-QDs, including redox processes relevant to catalysis.	Highly cited foundational overview.	Broad and not exclusively catalysis-focused.	Multiple synthetic routes.	Provides baseline understanding of CQD properties for catalysis design.	[158]
CO_2RR, HER, and dye and pollutant degradation	Reviews discuss heterojunction, doping, and surface engineering of C-QDs for broad photocatalysis applications.	Summarizes strategies for enhancing photocatalytic performance.	Emphasizes challenges like stability and charge recombination suppression.	Various nanocomposite formation strategies.	Surface modification and heterojunction formation are critical for real improvements.	[159]
Pollutant Degradation	CQDs were embedded in Bacillus subtilis cell walls, enhancing extracellular respiration and promoting ·OH generation. The C-QDs facilitated electron transfer, improving pollutant degradation.	Enhances microbial advanced oxidation via electron transfer; significantly accelerates pollutant degradation.	The full mechanistic pathway of C-QD-induced electron transfer needs further validation.	Citric acid and NaOH hydrothermal synthesis of C-QDs.	C-QDs help overcome extracellular electron transport limitations in B. subtilis, aiding pollutant removal, but more research is needed on long-term applications.	[160]

Table 3 (Continued).

Reaction types/Study focus	Key findings/methods	Advantages	Disadvantages	Preparation methods	Critical statements	Refs.
Photo-AOPs	C-QDs enhance pollutant degradation through AOPs by activating ROS.	C-QDs improve degradation of recalcitrant organic pollutants through effective ROS activation.	Poor reproducibility across different pollutants and conditions.	Synthesized by hydrothermal or pyrolysis methods; surface functionalization to enhance reactivity.	The C-QDs in AOPs show strong potential, but standardized performance metrics are required for comparability across systems.	[161]
Photo-AOPs	C-QDs-functionalized polymer carbon nitride (PCN) were synthesized for photocatalytic activation of peroxymonosulfate (PMS) for BPA degradation under visible light.	Enhanced light absorption and improved charge separation; Enlarged surface area, which is beneficial for pollutant adsorption.	Limited performance with high catalyst dosages due to light shielding.	C-QDs synthesized via hydrothermal method; PCNC (PCN and C-QDs) obtained by thermal polymerization and calcination at 550 °C.	C-QDs in PCN offer high photocatalytic activity, but the excess C-QDs can limit performance due to light shielding.	[162]
Pollutant degradation based on Z-scheme photocatalysis	CQDs enhance the generation of $^{\cdot}OH$ in dark reactions and improve the photo-elimination capacity of Fe^0 and TiO_2; DFT calculations and LC-MS were used to propose MNZ degradation pathways and identify degradation products.	High degradation efficiency (99.36%) of MNZ compared to other catalysts; Excellent resistance to environmental factors such as different water matrices; Minimal toxicity of degradation products.	Performance drops with excess CQDs, which can block active sites.	CQDs-TiO_2(b) was synthesized via solvothermal method, followed by embedding nZVI through liquid reduction in an anaerobic box.	The Z-scheme heterojunction optimizes the performance, especially in visible-light-driven processes; The role of CQDs is crucial in improving the degradation efficiency of MNZ, both in the dark and under light.	[163]
Photo-AOPs	CQDs with amine (A-CQDs) and carboxyl (C-CQDs) groups were synthesized; A-CQDs exhibited superior photocatalytic activity for H_2O_2 photolysis, producing $^{\cdot}OH$; The degradation of petroleum pollutants and real textile wastewater was enhanced under visible light.	High photocatalytic efficiency for degrading aromatic hydrocarbons and textile wastewater; Enhanced visible light absorption and reduced electron-hole recombination.	Higher catalyst concentration leads to saturation and reduced photocatalytic efficiency.	CQDs were derived from plant-based biomass using a cost-effective, sustainable carbonization process at 300 °C.	A-CQDs showed better performance due to nitrogen functionality, which improved charge separation and visible light harvesting; A-CQDs were more effective for wastewater remediation and reduced toxicity of treated water.	[164]
Pollutant degradation	CQDs modified g-C_3N_4 and $BiVO_4$ for enhanced visible light photocatalysis of benzyl paraben (BzP); The composite showed improved charge separation and redox ability, enhancing degradation efficiency.	Efficient degradation of BzP under visible light; Good stability and reusability of the GCN-CQDs/BVO composite.	Incomplete degradation under high concentrations of BzP;The presence of certain coexisting ions (e.g., NO_3^-, SO_4^{2-}) can negatively impact degradation.	CQDs were synthesized using a hydrothermal method with citric acid and ethylenediamine; The composite was prepared via a hydrothermal method.	CQDs enhanced the photocatalytic activity by improving charge separation; The degradation rate of BzP was significantly higher with the CQDs-mediated Z-scheme composite.	[165]

rather than as a label inferred only from band positions. Recent authoritative reviews on S-scheme photocatalysts emphasize the need for verification tools and in situ or ex situ evidence to support directional charge-transfer claims[66,94,166]. The same logic applies to C-QD-containing systems. The most impactful advances are likely to come from interface chemistry, including the design of interfacial bonds, surface dipoles, and coupling strengths that can accelerate charge transfer and stabilize desired charge distributions in a controlled way. In this context, interfacial sites will become a predictive design concept rather than a post hoc explanation.

(2) Fractionation and traceability of C-QDs will be essential for building credible design rules. Recent reviews on C-QDs have emphasized that bottom-up synthesis often produces heterogeneous dots with broad size distributions and unpredictable defects. This heterogeneity directly weakens reproducibility and makes mechanistic assignment more difficult[167]. At the same time, biomass-derived or compositionally variable precursors can further affect batch-to-batch reproducibility. This issue will become increasingly important as C-QD-based photocatalysts move toward practical evaluation[168]. Near-term progress will therefore depend strongly on methodology. Routine fractionation by size or surface state, standardized reporting of purification processes and yields, and traceable C-QD descriptors are needed to enable meaningful comparison across laboratories. Reviews

on chromatographic purification and scalable synthesis also show that purity and manufacturability are now part of the core scientific discussion, rather than separate engineering concerns[169].

(3) Operando standardization will help distinguish durable mechanisms from one-off explanations. As the field moves from simply reporting enhanced activity to defining engineered interfacial functions, operando and near-operando evidence will play an increasingly important role in determining whether a mechanism is convincing. The broad catalysis and photocatalysis communities have already accelerated the development and standardization of operando tools. These include spatially resolved probe microscopies and operando methods that directly link local activity with charge-transfer behavior, providing a useful model for C-QD-enabled systems[170]. For C-QDs, the implication is clear. Mechanistic claims, especially those involving Role C and pathway or selectivity control, will be persuasive only when intermediate and pathway probes, together with post-mortem reconstruction checks, become routine rather than exceptional.

(4) Three actionable recommendations can turn design rules from general statements into reproducible practice. First, a minimum reporting checklist should be explicitly linked to the claimed role. For Roles A and B, this means routinely reporting an energetics, dynamics, and charge-flux evidence package, such as UPS/KPFM, TRPL/TA, photocurrent, and EIS, together with calibrated photon flux and spectral conditions. For Role C, the baseline evidence should include pathway-resolved probes, such as in situ FTIR/DRIFTS or EPR/ESR, as well as isotope labeling validation and carbon balance when relevant. This role-linked reporting approach follows the verification logic emphasized in recent S-scheme discussions and helps prevent mechanistic claims from relying on a single indirect signal[66]. Second, coupling-strength controls should become a standard part of experimental design. At least one control that weakens interfacial coupling without changing the bulk composition should be included. Examples include blocking functional groups, comparing a physical mixture with a covalently or coordination-coupled assembly, or using an inert carbon analogue. Such controls can help distinguish true bridge or conduit behavior from general electron trapping, surface passivation, or dispersant effects. This simple control directly addresses a common source of Role B overclaiming in heterojunction studies[95]. Third, any proposed design rule should be supported by stability testing together with post-mortem characterization and, ideally, operando validation. In HER, CO_2RR, and photo-AOP systems, time-on-stream tests should be paired with post-reaction analysis of C-QD integrity and interface chemistry, using methods such as XPS, Raman, FTIR, leaching analysis, and structural-evolution monitoring. This is important because reconstructed states can dominate apparent performance in heterogeneous and defect-rich C-QD systems. Closing this validation loop turns mechanistic narratives into defensible structure-function relationships, in line with the broader move toward operando-informed catalysis and reproducibility-aware materials processing[170].

Taken together, these steps turn the transition from sensitizers to interfacial sites into a testable workflow: define the role, require matching evidence, report comparable metrics, and validate stability and structural persistence. This workflow provides a direct route toward the next stage of progress and toward conclusions that remain valid as the field continues to evolve.

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