

Review paper

Understanding photoelectrocatalysis across scales: Computational studies towards enlightenment and innovation[☆]

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ABSTRACT

Photoelectrochemical (PEC) catalysis has attracted considerable attention in the context of sustainability, enabling opportunities for solar powered processes such as water splitting to hydrogen, CO₂ reduction to hydrocarbons (fuels), or conversion of nitrogen-based species (e.g. nitrates) to ammonia. The PEC catalytic systems considered here entail light absorption, charge generation, bulk charge-carrier transport, recombination, interfacial charge transfer and surface reactions, inherently spanning multiple length and time scales. Such processes have traditionally been developed through chemical intuition and trial-and-error experimentation, but computational methods are increasingly proving useful in guiding innovation in this field. Yet, while electronic-structure methods provide indispensable microscopic descriptors, and continuum models address device-level transport, a persistent gap remains in the handoffs through the mesoscopic regime, where spatial heterogeneity, stochasticity, and non-equilibrium driving forces collectively determine catalytic performance.

In this Review, we examine modelling approaches for PEC catalysis across multiple scales. We first discuss recent advances in electronic-structure methods for describing excited states, band alignment, charge localisation, polarons and excitons. We then proceed to explore the atomistic modelling approaches for treating nonadiabatic dynamics, thermally assisted charge transfer, polaron hopping and elementary reaction mechanisms. Finally, we consider mesoscale kinetic and multiscale transport-reaction models, including kinetic Monte Carlo (kMC) and related stochastic approaches, emphasising how different choices of mesoscale state variables enable descriptions of charge transport, reaction kinetics, material evolution and reactor-scale coupling. Building on this multiscale perspective, we discuss emerging challenges specific to PEC catalysis and conclude by outlining future directions towards integrated multiscale modelling frameworks that connect parameter transfer and atomistic reaction energetics with stochastic reaction dynamics and macroscopic PEC performance.

1. Introduction

Light-driven catalysis offers a compelling route for converting solar energy into chemical fuels and feedstocks, enabling reactions that are difficult or inefficient under purely thermal or electrochemical conditions [1–3]. By coupling light absorption and charge separation to catalytic redox chemistry, semiconductor photocatalysts and PEC systems provide complementary routes for driving redox chemistry using renewable energy [1,4]. For PEC systems in particular, the tight coupling of photophysics and electrochemistry with interfacial reactivity introduces substantial complexity: performance depends sensitively

on light–matter interactions, charge transport, interfacial energetics and operating conditions far from equilibrium [5,6].

Representative light-driven transformations include CO₂ reduction to fuels and chemicals [7,8], nitrogen fixation to ammonia [3], selective oxygen reduction to hydrogen peroxide [9], water splitting [1], and light-assisted C–H and C–N bond formation [10]. Despite this chemical diversity, these transformations share recurring kinetic challenges, including multi-charge accumulation, competing reaction pathways, coverage-dependent activity and poisoning, coupled mass and charge transport, and dynamic feedback between charge-carrier populations

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Abbreviations

ΔSCF	delta self-consistent-field method
G_0W_0	single-shot GW approximation
NV⁻	negatively charged nitrogen-vacancy
scQPGW1	self-consistent quasiparticle GW approach
AP	approximate projection
BEP	Brønsted–Evans–Polanyi
BSE	Bethe–Salpeter equation
CASPT2	complete active space second-order perturbation theory
CASSCF	complete active space self-consistent field
CBM	conduction-band minimum
CFD	computational fluid dynamics
CI	configuration interaction
CI-NEB	climbing-image nudged elastic band
CIS	configuration-interaction singles
CPA	classical path approximation
DFT	density functional theory
DFT-MD	density-functional-theory-based molecular dynamics
DFTB	density-functional tight binding
DISH	decoherence-induced surface hopping
DO	direct optimisation
DO-MOM	direct-optimisation maximum-overlap method
DOS	density of states
EHAM	Emin–Holstein–Austin–Mott
FE	Faradaic efficiency
FNV	Freysoldt–Neugebauer–Van de Walle correction
FSSH	fewest-switches surface hopping
GGA	generalised-gradient approximation
GMF	generalised mode-following
GW	quasiparticle approximation based on the one-particle Green function and screened Coulomb interaction
HF	Hartree–Fock
HOMO	highest occupied molecular orbital
HSE	Heyd–Scuseria–Ernzerhof screened hybrid functional
HSE06	2006 parametrisation of the Heyd–Scuseria–Ernzerhof screened hybrid functional
HTST	harmonic transition-state theory
IDPP	image-dependent pair potential
IMOM	initial maximum-overlap method
IPCE	incident photon-to-current efficiency
kMC	kinetic Monte Carlo
KS	Kohn–Sham
LDA	local-density approximation
LR-TDDFT	linear-response time-dependent density functional theory
LUMO	lowest unoccupied molecular orbital
MCTDH	multiconfiguration time-dependent Hartree
MEP	minimum-energy path
MFE	mean-field Ehrenfest
MK	microkinetic
ML	machine learning
MOM	maximum-overlap method
MP2	second-order Møller–Plesset perturbation theory
MS	multiple spawning
NAC	nonadiabatic coupling

NAMD	nonadiabatic molecular dynamics
NBRA	neglect of back-reaction approximation
NEB	nudged elastic band
NIR	near-infrared
NOCM	nonoxidative methane coupling
OER	oxygen evolution reaction
OLED	organic light-emitting diode
PBE	Perdew–Burke–Ernzerhof functional
PCET	proton-coupled electron transfer
PEC	photoelectrochemical
PES	potential-energy surface
PV	photovoltaic
QSGW	quasiparticle self-consistent GW with vertex-corrected screening
ROKS	restricted open-shell Kohn–Sham
RT-TDDFT	real-time time-dependent density functional theory
SCF	self-consistent field
SGM	square-gradient minimisation
SIC	self-interaction correction
SRH	Shockley–Read–Hall
STEP	state-targeted energy projection
TDA	Tamm–Dancoff approximation
TDDFT	time-dependent density functional theory
TOF	turnover frequency
TSH	trajectory surface hopping
TST	transition-state theory
UV	ultraviolet
VBM	valence-band maximum

and surface chemistry under illumination [11,12]. When applied to a PEC system, external bias can provide an additional driving force for carrier separation after excitation [5,6].

Predictive materials design therefore requires processes operating across multiple length and time scales to be connected. Electronic structure and band alignment establish thermodynamic driving forces, whereas defects, interfaces and morphology govern carrier localisation, mobility and recombination [4,5,13]. The spatial organisation and chemical state of catalytic sites then determine whether the available charge is converted selectively into products [11,12]. Materials with the same nominal composition can consequently exhibit markedly different activity, selectivity and stability depending on their nanoscale structure and operating environment [14,15]. Experimentally separating these contributions remains difficult because their characteristic scales overlap and their observables are often coupled [16–18].

The development of light-driven catalytic materials and devices has traditionally relied heavily on chemical intuition and trial-and-error screening [5,19]. Although this approach has produced important advances, progress towards predictive design remains constrained by limited experimental throughput, imperfect control of interfacial structures and defect populations, and the difficulty of operando characterisation under realistic illumination and reaction conditions. Mechanistically grounded modelling can help separate coupled contributions, explore materials and operating regimes systematically, and identify measurements that most effectively discriminate between competing mechanisms [20].

The available modelling approaches provide complementary but incomplete descriptions of these processes. Electronic-structure and excited-state calculations determine excitation energies, charge localisation, interfacial energetics and elementary reaction barriers, while atomistic simulations resolve structural fluctuations and molecular

reaction mechanisms [19,21]. Mesoscopic models, including kMC, capture stochastic transport, recombination and reaction events over longer length and time scales [22,23]. Continuum and device-scale models connect effective kinetics to macroscopic charge and species transport, reactor geometry and operating conditions [6,24]. The central challenge is therefore not the absence of modelling methods, but the reliable transfer of physical states, parameters and uncertainties between them.

In this Review, we examine how electronic-structure, atomistic, mesoscopic and continuum modelling frameworks can elucidate phenomena and processes from excitation and carrier dynamics to interfacial chemistry, and predict catalytic turnover and measurable performance. Rather than organising the discussion primarily by application label, we ask which processes and state variables each framework resolves, what information can be transferred between scales and which experimental observables can provide validation. We centre the discussion on PEC systems and use semiconductor photocatalysis as an exemplar application domain; studies on photovoltaic (PV) systems, optoelectronics, batteries and thermocatalysts are included only where they provide transferable modelling concepts.

In our discussions, PEC devices refer broadly to systems in which a light absorber is integrated into a photoelectrode assembly and supplies photogenerated charge to an electrolyte-facing reaction interface. The absorber may be an inorganic or organic semiconductor or a molecular sensitiser, and it may contact the electrolyte directly or transfer charge through protective, charge-selective or catalytic layers. We include externally wired and internally connected monolithic architectures, while treating a separate photovoltaic module driving an independently constructed electrolyser as PV–electrolysis [5,6,24,25].

By contrast, suspended semiconductor photocatalysts couple reduction and oxidation chemistry without an external circuit or terminal electrode potential. External bias may be applied to a PEC device, but it is not a defining requirement of the PEC class. Throughout this Review, *photo(electro)catalysis* is used only as an umbrella term for semiconductor photocatalysis and PEC catalysis and does not imply that their boundary conditions or observables are interchangeable. More detailed terminology and architectural distinctions are introduced in Section 2.

The intended scope is methods-focused rather than an exhaustive materials survey. Among the studies considered, the most continuous cross-scale coverage concerns TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$ and BiVO_4 . Targeted examples involving chromia [26], layered double hydroxides [27], organic semiconductor–electrolyte interfaces [28], carbon nitride coupled to molecular catalysts [29], dye/cocatalyst assemblies [30,31], mixed-halide perovskites [32] and upconversion particles [33] provide a broader test of method transferability. Materials such as WO_3 , Cu_2O and III–V photoelectrodes, while of interest to the PEC field, are not surveyed comprehensively; conclusions concerning those families should therefore be interpreted at the process level rather than as material-specific validation.

This Review is structured as follows. Section 2 establishes the shared photon-to-product process sequence and the additional electrochemical boundary conditions introduced by PEC architectures. Sections 3 and 4 examine electronic-structure and atomistic approaches, respectively, before Section 5 considers mesoscopic kinetic modelling and its connection to continuum and device descriptions. Before concluding, Section 6 outlines near-term theoretical research priorities for predictive multiscale modelling of photo(electro)catalytic systems. These priorities include community benchmark systems linked to operando measurements, automated and interoperable parameter transfer between scales, and machine-learned excited-state and reactive potentials.

2. Coupled photophysical, electrochemical and catalytic processes

To establish the process framework used throughout this Review, we divide the pathway from incident photon to catalytic turnover into processes related to the charge carriers’ “lifecycle” and processes related to

chemistry. The former include photon absorption and photoexcitation, generation of separated carriers, carrier localisation, trapping/detrapping, transport and recombination, and productive interfacial charge transfer at a reaction interface. The latter include surface reaction steps, and product release with active-site regeneration. This sequence is shared by semiconductor photocatalysts and PEC photoelectrodes, including sensitised and hybrid assemblies. Both classes are subject to optical, interfacial and reactor-transport boundary conditions; PEC operation additionally imposes photoelectrode architecture, electrode-potential and circuit constraints, considered separately below. Fig. 1 summarises the shared sequence and the recombination pathways that compete with productive chemistry.

2.1. Shared photon-to-product sequence

The shared sequence can be illustrated by band-to-band photoexcitation of a semiconductor absorber. In this case, absorption of photons with energy $h\nu \geq E_g$ can create electron–hole excitations that may subsequently separate and supply carriers for interfacial redox reactions. The pioneering water-splitting experiments at an illuminated TiO_2 electrode by Fujishima and Honda provide an early PEC example [109]. We use the six labels in Fig. 1 and Table 1 to record which parts of this pathway a model resolves. They are process-coverage categories rather than dynamically independent stages of a strictly sequential mechanism; the processes may overlap, compete and feed back on one another.

A covers **photon absorption and photoexcitation**, including formation and early relaxation of the initially excited state. Depending on dielectric screening and exciton binding energy, photoexcitation may produce an effectively unbound electron–hole pair or a bound exciton; the latter may relax, migrate, recombine or dissociate [110–112]. **G** covers the **generation of separated carriers**, whether they are generated directly by photoexcitation, by exciton dissociation or by intercomponent charge transfer. In sensitised molecular–semiconductor assemblies, chromophore excitation can be followed by electron injection into the semiconductor [113,114]. At heterojunctions, intercomponent charge transfer can likewise generate spatially separated carriers [115].

Defect-derived states within the band-gap (in-gap states) may enable sub-band-gap absorption or alter initial carrier separation, depending on their type, depth, concentration and location [66,116]. Competing early-time recombination, classified under **T**, reduces the carrier population available for subsequent surface chemistry [66,114,116]. The electronic-structure and excited-state approaches reviewed in Section 3 provide the principal microscopic description of **A**, **G** and the earliest recombination processes within **T**.

T covers **carrier localisation, trapping, detrapping, transport and recombination** in the bulk and at interfaces. Photogenerated carriers can couple to the surrounding lattice [117]. With sufficiently strong local coupling, an electron or hole can become localised together with the induced lattice distortion, forming a small polaron [118]. Small-polaron transport may then proceed through thermally activated hopping at sufficiently high temperatures [119]. Electron–hole recombination may be radiative, emitting a photon, or non-radiative. In phonon-mediated non-radiative pathways, the released energy is transferred to lattice vibrations. An important non-radiative route is defect-mediated Shockley–Read–Hall (SRH) recombination, in which electrons and holes are captured sequentially by a defect state in the band gap [120,121]; defects can also participate in radiative transitions [34]. The characteristic times of localisation, transport and recombination span broad, overlapping ranges that depend on the material, carrier state and local environment [34,35]. Within **T**, defects, dopants, heterojunctions and surface motifs can alter trap populations, carrier motion and recombination kinetics [116]. The competition between transport and recombination determines whether carriers reach a collecting contact [122,123] or a surface reaction site [13] before

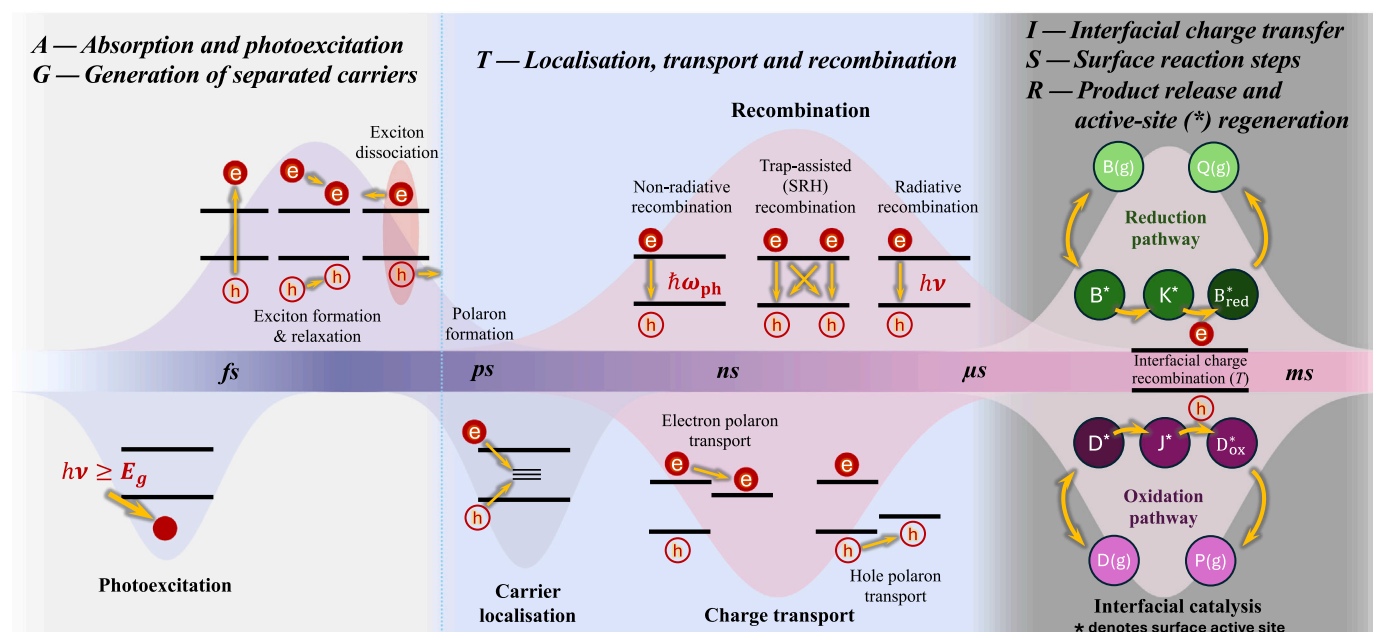


Fig. 1. Representative local photon-to-product processes and the *A–G–T–I–S–R* classification for semiconductor photocatalysis and PEC catalysis. *A* denotes photon absorption and photoexcitation; *G*, generation of separated carriers; *T*, carrier localisation, trapping, detrapping, transport and recombination; *I*, productive interfacial charge transfer at a reaction interface; *S*, surface reaction steps; and *R*, product release with active-site regeneration. Exciton formation and relaxation belong to *A*, whereas dissociation into separated carriers belongs to *G*. The first recombination icon represents a phonon-mediated non-radiative pathway; the pathways and timescales are illustrative, overlapping and system-dependent; for a detailed discussion of photoinduced processes and their timescales in TiO₂, see Schneider et al. [34]. A bare * denotes an available site and *X** a surface-bound species. *B* and *D* are generic reactants and *Q* and *P* their products. The gas labels (g) are illustrative; analogous dissolved or ionic species may occupy these roles. PEC-specific device boundary conditions are not shown.

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recombining. At a nonequilibrium steady state under continuous illumination, the continuity equations describing the motion of charge carriers relate photogeneration to bulk and interfacial recombination and to net fluxes across reaction interfaces and, where present, collecting contacts [123,124]. Transport, trapping, recombination and the interfacial boundary conditions together establish the steady-state spatial distributions of electrons and holes. Modelling *T* therefore links electronic descriptions of localisation and defect states to mesoscale descriptions of spatially distributed carrier dynamics.

I denotes **productive interfacial charge transfer at a reaction interface**, but charge transfer alone does not establish catalytic turnover. Photogenerated electrons or holes may then transfer to solution redox species at semiconductor–electrolyte boundaries [124], or to adsorbed intermediates or cocatalysts [13,17]. When electron transfer is coupled to proton motion, the process may proceed through proton-coupled electron transfer (PCET) [125]. A chemically resolved PCET step may therefore contribute to both *I*, through its charge-transfer component, and *S*, which stands for **surface reaction steps**, through its accompanying proton or bond rearrangement. *S* includes reactant adsorption and chemical transformations among surface-bound intermediates [13, 17], whereas *R* covers **product release and active-site regeneration**, thereby completing catalytic turnover [12]. Interfacial charge recombination, including back charge transfer, belongs to *T* and competes with productive *I* pathways [95,126]. Activity and selectivity consequently depend on surface electronic structure, elementary barriers, intermediate coverages, branching among competing pathways and the chemical state of active sites [11–13]. Embedding this local sequence within a PEC architecture introduces architectural, electrostatic, circuit and electrolyte-transport boundary conditions, considered next.

2.2. PEC architectures, boundary conditions and observables

PEC architectures differ in how the photoabsorber, electrolyte-facing reaction interface and complementary half-reaction are coupled. In a directly exposed photoelectrode, the absorber contacts the

electrolyte and forms part of the reaction interface. Protected, buried-junction and sensitised architectures instead distribute light harvesting, charge transport, protection of the semiconductor from degradation and catalysis among separate components [7]. Sustained operation requires complementary half-reactions and overall electron-equivalent and material balances [5,13]. In PEC assemblies, this entails closed electronic and ionic current paths, whether the components are externally wired or internally connected and whether or not external bias is applied [1,24]. In suspended photocatalysts, carrier transport within particles and, where relevant, between particles is coupled to reactant and product transport through the surrounding phase; these systems normally have no external circuit from which a terminal current can be measured [5,13].

The target chemistry introduces additional constraints. For CO₂ reduction, gas–liquid transfer [127] and electrolyte transport [128] determine CO₂ availability at the reaction interface. At CO₂-reducing cathodes in bicarbonate electrolytes, cathodic consumption of proton donors and/or generation of OH[−] can raise the interfacial pH; coupled transport and reactions among CO₂(aq), HCO₃[−] and CO₃^{2−} can then make the near-surface CO₂ concentration differ from its bulk value [128]. These effects influence competition with hydrogen evolution and branching among products with different carbon and electron stoichiometries [128]. System-level device and reactor models should therefore connect CO₂ delivery, product-specific reaction rates and the complementary oxidation reaction [127]. More generally, the electrolyte introduces a reactive boundary condition rather than merely functioning as an ionic conductor: composition, pH, reactant activities and double-layer structure influence interfacial electron-transfer kinetics [129], including PCET [125]. Diffusion, migration and convection can also limit reactant supply or product removal [24,128] and permit species crossover [24], so device- or reactor-scale observables need not reflect intrinsic surface kinetics alone.

Architecture also determines how charge is distributed and where electrostatic potential differences arise. At a directly exposed

Table 1

Application class and physical-process coverage of all system-specific computational application studies whose physical results are substantively discussed in this Review, together with selected cross-cutting methodological examples. General background references, reviews and sources used only for definitions or figure adaptation are not classified. The columns distinguish photon absorption and photoexcitation (A), generation of separated carriers (G), carrier localisation, trapping, detrapping, transport and recombination (T), productive interfacial charge transfer at a reaction interface (I), surface reaction steps (S), and product release with active-site regeneration (R). “E” denotes an explicitly represented process, “P” a partial, imposed, phenomenological or descriptor-level treatment, and “–” a process absent from the particular modelling study cited. Application classes are photocatalytic (PC), photoelectrocatalytic (PEC), photovoltaic (PV), and methodologically analogous (MA). The class denotes the stated application context and does not imply end-to-end completeness; the six process columns provide that separate assessment.

Study	Class	A	G	T	I	S	R	Primary output and principal scope limit
<i>Cross-cutting photovoltaic example</i>								
Schankler et al. [36]	PV	E	P	E	–	–	–	Calculated excitation- and radiative-recombination shift currents with quasi-equilibrium photocarrier populations; no spatial transport or chemistry.
<i>Electronic-level applications and benchmarks</i>								
Araujo-López et al. [37]	PC	P	–	–	–	P	–	Anatase structural and electronic-property calibration with a static CO ₂ -adsorption descriptor; no explicit photoexcitation, carrier dynamics or reaction pathway.
Chen et al. [38]	MA	–	–	P	–	–	–	Static hematite defect localisation and thermodynamic alignment; no carrier dynamics or interface.
Crespo-Otero & Walsh [39]	PEC	–	–	–	P	–	–	Hydrated BiVO ₄ surface ionisation potentials and band-edge shifts; no excitation or kinetics.
Daga & Maschio [40]	MA	P	–	P	–	–	–	Imposed crystalline excited states with excitation-density-dependent localisation descriptors; no carrier dynamics or interface.
Gavnholt et al. [41]	MA	–	P	P	P	–	P	Imposed metal-to-adsorbate resonance and static back-transfer/desorption descriptors; no photon excitation or explicit reaction dynamics.
Gudmundsdóttir et al. [42]	MA	–	–	P	–	–	–	Self-interaction corrected calculation of electron hole localisation in periodic solid.
Hellman et al. [43]	MA	P	P	P	P	P	–	Imposed gas-surface charge-transfer configurations and static excited-state potential-energy surfaces; transfer and dissociation dynamics are not resolved.
Ivanov et al. [44]	MA	P	–	P	–	–	–	Imposed, defect-localised NV [–] -centre excitation and excited-state relaxation; no carrier dynamics or interface.
Kang & Hybertsen [45]	MA	E	–	–	–	–	–	GW/BSE optical spectra and bound-exciton energies; no exciton dissociation, carrier transport or reaction.
Kowalczyk et al. [46]	MA	E	–	–	–	–	–	Organic-dye vertical-excitation benchmark.
Landmann et al. [47]	MA	E	–	–	–	–	–	TiO ₂ optical response; no mobile carriers or chemistry.
Mackrodt et al. [48]	MA	P	–	E	–	–	–	Imposed NiO excitations with explicitly resolved local excitonic and diffuse charge-transfer states; no dynamics, interface or chemistry.
Morgan & Watson [49]	PC	–	–	P	–	–	–	Static defect and self-trapped-polaron energetics in anatase TiO ₂ ; no carrier dynamics or surface chemistry.
Möslinger et al. [50]	PEC	P	–	E	–	–	–	Imposed self-trapped-exciton configurations, binding energies and TDDFT emission pathways in BiVO ₄ ; no carrier separation, transport, interface or chemistry.
Mowbray & Migani [51]	PV	E	P	–	E	–	–	Dye-TiO ₂ optical spectrum and charge-transfer excitons; no chemistry.
Patrick & Giustino [52]	MA	P	–	–	–	–	–	Quasiparticle gap as an absorption-threshold descriptor.
Schmerwitz et al. [53]	MA	E	P	–	–	–	–	Excited-state stationary points, potential-energy curves and charge-transfer benchmarks; no dynamics, interface or chemistry.
Selenius et al. [54]	MA	E	P	–	–	–	–	Intramolecular charge-transfer excitation benchmark.
Sun et al. [55]	PC	E	–	P	P	P	–	Bulk optical spectra and ground-state H ₂ O/TiO ₂ level alignment, adsorption energetics and hole-trapping/transfer descriptors; no photoinduced dynamics or pathway kinetics.
Suzuki et al. [56]	PC	E	P	–	E	–	–	Adsorbate-to-TiO ₂ excitation and initial phenol oxidation; downstream products proposed.
Wang et al. [57]	PC	E	P	–	E	E	E	Ground- and excited-state H ₂ O ₂ /O ₂ formation and desorption pathways; no illumination-dependent carrier populations or turnover kinetics.
Wiktor et al. [58]	PEC	E	–	–	–	–	–	BiVO ₄ quasiparticle and optical gaps and BSE absorption including spin-orbit and vibrational renormalisation; no carrier separation, transport, interface or chemistry.
<i>Atomistic applications</i>								
Agrawal et al. [59]	PC	P	P	E	–	–	–	Dopant-dependent charge separation and non-radiative carrier dynamics in g-C ₃ N ₄ ; no reaction interface or product chemistry.
Chen et al. [60]	PEC	P	P	E	–	–	–	Oxygen-vacancy-mediated trapping and non-radiative electron-hole recombination in BiVO ₄ ; no productive interfacial transfer or chemistry.
Cheng et al. [61]	PEC	P	P	E	–	–	–	Oxygen-vacancy-dependent carrier trapping and non-radiative recombination in BiVO ₄ ; excitation and initial carrier population imposed, with no reaction interface or chemistry.
del Olmo et al. [62]	PC	E	P	–	P	E	–	Quantum-sized BiVO ₄ -cluster optical states, ionisation and water-deprotonation barriers; no carrier transport or complete OER cycle.
Deskins & Dupuis [63]	MA	–	–	E	–	–	–	TiO ₂ polaron barriers, couplings and hopping rates; carriers imposed.
Ghosh et al. [64]	MA	–	–	E	P	–	–	Hematite polaron migration and adsorbate-induced electron transfer to NO ₂ ; gas-sensing context without photoexcitation or catalytic turnover.
Gu et al. [65]	PC	P	E	E	–	–	–	Imposed excitation followed by explicit interface-specific carrier transfer and recombination dynamics across mixed-phase TiO ₂ ; no reaction interface.
Gumber et al. [66]	PC	P	P	E	–	–	–	Defect-dependent charge separation, trapping and non-radiative recombination in g-C ₃ N ₄ ; no interfacial reaction or product formation.
Iordanova et al. [67]	MA	–	–	E	–	–	–	Marcus-theory electron and hole hopping mobilities and crystallographic anisotropy in bulk hematite; no photoexcitation, interface or chemistry.
Iordanova et al. [26]	MA	–	–	E	–	–	–	Bulk chromia polaron mobility; transferable hopping workflow.

(continued on next page)

Table 1 (continued).

Migani & Blancafort [68]	PC	P	P	P	E	E	–	Excitation-dependent O–H dissociation, charge-localised excitons and hydroxyl formation on rutile TiO ₂ (110) under UHV; no carrier transport or complete OER cycle.
Rosso & Dupuis [69]	MA	–	–	E	–	–	–	Hematite small-polaron localisation and distance-dependent internal reorganisation energetics; no carrier population dynamics, interface or chemistry.
Tritsaridis et al. [70]	PC	P	P	P	E	E	–	Imposed vertical excitation followed by nonadiabatic hole localisation, interfacial transfer and water dissociation; no optical generation, bulk transport or turnover.
Wei et al. [71]	PC	P	E	E	–	–	–	Imposed excitation followed by explicit anatase–rutile charge separation and recombination dynamics; solid–solid interface only.
Yang et al. [72]	PC	P	P	E	E	E	–	Photoinduced charge dynamics in pristine and B/O-codoped g-C ₃ N ₄ slabs, and water photodissociation and proton hopping in heptazine–water clusters; H ₂ formation and catalytic turnover are not resolved.
You et al. [73]	PC	E	E	E	E	E	P	Nonadiabatic carrier transfer, water dissociation and H ₂ formation at a g-C ₃ N ₄ /water interface; complementary oxidation and sustained catalytic turnover are not closed.
Zhang et al. [74]	PEC	P	P	E	–	P	–	Carrier trapping and recombination on pre-hydroxylated BiVO ₄ (010); hydroxylation is represented through imposed surface structures rather than a reaction pathway.
Zhao et al. [27]	PC	P	–	–	P	E	P	Layered-double-hydroxide band-edge screening and CO ₂ free-energy pathways with product-state descriptors; no carrier kinetics or closed turnover.
<i>Mesoscopic, interfacial and reactor applications</i>								
Ansari-Rad [75]	PV	–	–	E	E	–	–	Dye-regeneration transients with electrolyte diffusion; no product chemistry.
Bedoya-Lora et al. [76]	PEC	P	P	P	P	P	E	Three-dimensional PEC reactor model resolving gas generation, desorption, transport, membrane crossover and collection; local photophysics and catalytic chemistry are represented through reduced relations.
Berger & Newman [77]	PEC	E	E	E	P	P	P	One-dimensional optical, semiconductor, electrolyte and membrane transport with closed electronic and ionic currents; interfacial chemistry is reduced, while gas fluxes, crossover and collection are modelled.
Canavan & Dauenhauer [78]	PC	P	–	–	–	E	E	Generic photon-promoted catalytic turnover; no semiconductor or electrode.
Cattray et al. [79]	PEC	P	P	P	P	P	P	PEC plant performance, degradation, cost and uncertainty; underlying kinetics aggregated.
Fatahillah et al. [80]	PC	P	–	–	–	E	E	Three-dimensional flow, UV-radiation and species transport coupled to fitted ZnO surface and near-wall gas-phase chemistry; carrier generation, transport and interfacial transfer are lumped.
Govindarajan et al. [81]	MA	–	–	–	E	E	E	Iterative microkinetic–continuum coupling for electrocatalytic CO ₂ reduction to CO; transferable local-state–response–flux scheme without photophysics.
Hammerschmidt et al. [82]	PC	E	P	P	P	E	E	Spatial CO ₂ -reduction turnover with local recombination and bulk–surface hopping; long-range carrier transport omitted.
Hankin et al. [83]	PEC	P	P	P	P	P	–	Experimentally parameterised hematite photocurrent relations embedded in two- and three-dimensional reactor models; carrier dynamics and molecular surface chemistry are aggregated.
Haussener et al. [24]	PEC	P	P	P	P	P	P	Validated PEC device transport and design; molecular surface kinetics aggregated.
Klumpers et al. (Bumblebee code) [84]	MA	E	E	E	–	–	–	Organic–electronic photoabsorption, exciton/polaron generation, hopping, recombination and electrode injection; no catalytic or electrolyte chemistry.
Liu [85]	PC	P	P	E	E	P	–	Stochastic photogeneration, carrier transport and interfacial-transfer activity proxy; no product-release cycle modelled.
Liu et al. [86]	PC	–	–	E	E	P	–	TiO ₂ trap relaxation and one-electron O ₂ transfer; no products.
Liu, Wu & Li [87]	PC	–	–	E	E	P	–	TiO ₂ –O ₂ electron-transfer transients; no product-forming network.
Liu et al. [88]	PC	–	–	E	E	P	–	Multiple-trapping transport and O ₂ transfer; no chemical cycle.
Liu et al. [89]	PEC	–	–	E	–	–	–	Bulk BiVO ₄ polaron mobility; photoanode component model.
Liu & Zhao [90]	PC	P	P	E	E	P	–	Phenomenological photogeneration and porous-TiO ₂ transport linked to effective activity; molecular surface chemistry lumped.
Maestri & Cuoci [91]	MA	–	–	–	–	E	E	Reactor flow, heat and mass transport coupled to thermocatalytic turnover.
Pahlevanpour & Bashiri [92]	PC	P	P	P	P	E	E	Au/TiO ₂ H ₂ evolution with phenomenological photogeneration and fitted, spatially lumped photophysics.
Pahlevanpour & Bashiri [93]	PC	P	P	P	P	E	E	Ni/TiO ₂ H ₂ evolution with phenomenological photogeneration and fitted, spatially lumped photophysics.
Pasumarthi et al. [94]	PEC	–	P	E	–	–	–	Doped-BiVO ₄ electron mobility with imposed photo- and dopant-derived carrier populations; no optical transport, interface or OER.
Peter [95]	PEC	P	P	P	E	P	–	Optical generation, surface-hole transfer, recombination and Fermi-level pinning; molecular OER steps and product release absent.
Roy et al. [96]	PC	P	P	P	P	E	E	Photo/thermal NOCM turnover; carrier generation and transport omitted.
Ruth et al. [32]	PV	P	P	P	–	–	–	Mixed-halide photosegregation kinetics; no catalytic interface.
Ruth & Kuno [97]	PV	P	P	P	–	–	–	Carrier–composition feedback during perovskite photosegregation; no catalysis.
Sinha et al. [98]	PEC	–	–	–	P	E	E	Imposed-potential hematite OER turnover with potential-dependent PCET steps; illumination and carrier supply omitted.
Sun et al. [99]	PC	E	E	E	E	E	E	Optical absorption, carrier drift–diffusion, microkinetics and near-surface species transport for CO ₂ reduction; steady-state operation, reduced complementary oxidation and no complete reactor environment.
Tkaczibson & Ardo [30]	PEC	P	P	E	E	P	P	Multi-charge electrocatalyst turnover with lumped chemistry, product release and site regeneration; optical absorption and bulk-carrier motion assumed.
Tkaczibson & Ardo [31]	PEC	P	P	E	E	P	P	Interparticle charge accumulation and thresholded catalyst turnover; molecular chemistry, product release and bulk-carrier motion lumped.
van den Boorn et al. [100]	PEC	P	E	E	E	E	E	Self-consistent semiconductor drift–diffusion–Poisson and OER microkinetics; electrolyte transport, counter-electrode chemistry and complete-cell closure are absent.
Wang et al. [28]	PEC	E	E	E	E	P	–	P3HT–electrolyte photocurrent and O ₂ transfer; no active-site catalytic cycle.
Wang, Bu & Wang [33]	PC	E	P	E	–	–	–	Upconversion, optical transport and carrier collection; no interfacial chemistry.

(continued on next page)

Table 1 (continued).

Wang, Furube & Gao [101]	PC	P	P	E	–	–	–	Plasmon-driven Au-to-TiO ₂ injection, electron diffusion and back-recombination; no reaction-interface transfer or chemistry.
Wu & Ping [102]	PEC	–	–	E	–	–	–	Landau–Zener BiVO ₄ polaron mobility; photoanode component model.
Yang et al. [103]	PEC	P	P	P	P	P	E	Multiphysics PEC CO ₂ -to-CO reactor model with a semi-empirical photoelectrode response, carbonate speciation and two-phase transport; semiconductor dynamics and molecular surface chemistry are aggregated.
Yu et al. [104]	MA	–	–	E	–	–	–	Battery Li-ion/electron-polaron diffusion; transferable transport method.
Zhu et al. [29]	PC	E	E	E	P	E	E	Integrated particulate-PC CO ₂ reduction with phenomenological carrier-to-surface electron-transfer coupling; complementary oxidation chemistry and complete reactor/electron-equivalent closure not resolved.
<i>Kinetic-acceleration applications</i>								
Chatterjee & Voter [105]	MA	–	–	–	–	–	–	General superbasin acceleration algorithm; no light-driven application.
Dybeck et al. [106]	MA	–	–	–	–	E	E	Stiffness scaling validated for thermal Fischer–Tropsch catalysis.
Prats et al. [107]	MA	–	–	–	–	E	E	Graph-based stiffness scaling on thermal catalytic benchmarks.
Puchala et al. [108]	MA	–	–	–	–	–	–	Absorbing-Markov-chain acceleration for defect-cluster evolution.

semiconductor–electrolyte contact, equilibration may create semiconductor-side space charge and associated band bending whose magnitude and spatial extent depend on doping and solution conditions [126,129]; interfacial states can further modify this behaviour [17]. When the depletion width predicted by a planar model becomes comparable to the particle dimensions, however, a distinct depletion layer adjoining a neutral bulk is no longer a valid approximation; the charge and potential profiles must instead be determined for the finite geometry [123]. In multilayer assemblies, the electrostatic potential profile can include changes across the absorber space-charge region and electrolyte-facing double layer [129], as well as across buried junctions, functional-layer interfaces and contacts [1]. Where net current flows through a photoelectrode assembly, finite electronic and ionic conductivities produce additional ohmic potential drops in the solid components and electrolyte [24]. Under illumination, photogenerated carriers, ionised defects and charged interfacial species, together with any applied electrical boundary conditions, determine this potential distribution self-consistently [17]; slow interfacial transfer can therefore cause charge accumulation and shift the potential partition [95]. Where the carrier populations admit a local quasi-equilibrium description, their electrochemical potentials can be represented by electron and hole quasi-Fermi levels, whose gradients drive carrier transport [95,123]. Consequently, for a contacted photoelectrode, a potential imposed relative to a reference electrode is an external boundary condition, whereas a measured potential is an observable. Neither is generally identical to the local interfacial potential drop [123,129]; the driving force for a particular charge-transfer step depends on the difference between the local carrier and redox electrochemical potentials [95]. Reported electrode potentials should therefore specify the reference scale, electrolyte composition and pH [128], and the illumination conditions [130]; any correction for uncompensated solution resistance should also be reported because this resistance can distort measured current–potential behaviour [1]. For suspended photocatalysts, no external electrode potential is generally imposed [17]; carrier populations and local interfacial driving forces instead emerge from illumination, recombination, charge balance and the coupled kinetics of the oxidation and reduction half-reactions [13].

Validation should match the processes represented. Where terminal current is accessible, photocurrent measures terminal charge flow [126], but does not identify the chemical product [5] or, by itself, demonstrate catalytic turnover [13]. Product-specific Faradaic efficiency (FE) then provides a charge-accounting metric for electrocatalytic [128] and PEC operation [131]. For product p at steady state,

$$FE_p = \frac{n_p Fr_p}{|j_{ss}|}, \quad (1)$$

where r_p is its net molar formation flux per electrode area, n_p is the number of electron equivalents transferred per molecule of p formed, F is the Faraday constant and j_{ss} is the measured steady-state current

density. Thus, FE_p is the fraction of the measured charge assigned to product p , rather than a molar or carbon selectivity.

For an electrically addressable photoelectrode, incident photon-to-current efficiency (IPCE) measures the number of electrons collected per incident photon at wavelength λ [130]. If $IPCE(\lambda)$ and FE_p are reported as fractions and obtained from the same monochromatic steady-state experiment on the same photoelectrode, using the same current basis and consistent background treatment for current and product formation, then their product is $n_p N_p / N_\gamma$ [131], where N_p and N_γ are the numbers of product molecules and incident photons, respectively. Thus, the product gives electron equivalents associated with product species p per incident photon, while division by n_p gives molecular yield per incident photon. For charge closure in a multi-product reaction such as CO₂ reduction, product-specific FE values should be determined for all significant products at the electrode, including H₂ [128]. Product flux and current density should be evaluated on the same electrode-area basis and over the same steady-state interval [128], because transient charging currents need not correspond to interfacial product formation [95].

Where terminal current is inaccessible, as in many suspended-photocatalyst systems [126], the charge denominator required for conventional FE is unavailable [131]. Matched reduction- and oxidation-side product amounts and stoichiometry provide material and electron-equivalent closure, while photon-to-product quantum yield characterises photon utilisation [5,13]; where sacrificial electron donors or acceptors are used, their consumption and stoichiometric role should also be included in the reaction balance [5,13]. For contacted PEC cells, product-resolved metrics should be combined with steady-state current–potential behaviour [5] and, where relevant, current transients or impedance responses [95]. For particulate photocatalysts, validation should instead combine reduction- and oxidation-side product rates with photon-to-product quantum yields [5,13] and, where relevant to the model, time-resolved spectroscopic observables [5,17]. Where external bias is applied, its electrical-energy input should be reported separately and explicitly accounted for in the chosen overall energy-efficiency calculation [1,5]. Together, these considerations define architecture-dependent system-closure requirements.

2.3. Coupling physical processes across scales

Meeting these architecture-dependent closure requirements across scales requires more than placing modelling methods along length- and time-scale axes [133,134]. The local state of a catalytic interface is closely coupled to its device- or reactor-scale reaction environment [133,135]. A multiscale handoff occurs when the output of one model supplies a state variable or field, a constitutive parameter, or a boundary flux or source term required by another. The transfer is one-way when, for example, calculated energetics parameterise a kinetic model without feedback. It is bidirectional when, for example, a larger-scale model supplies the local operating state to an interface model and

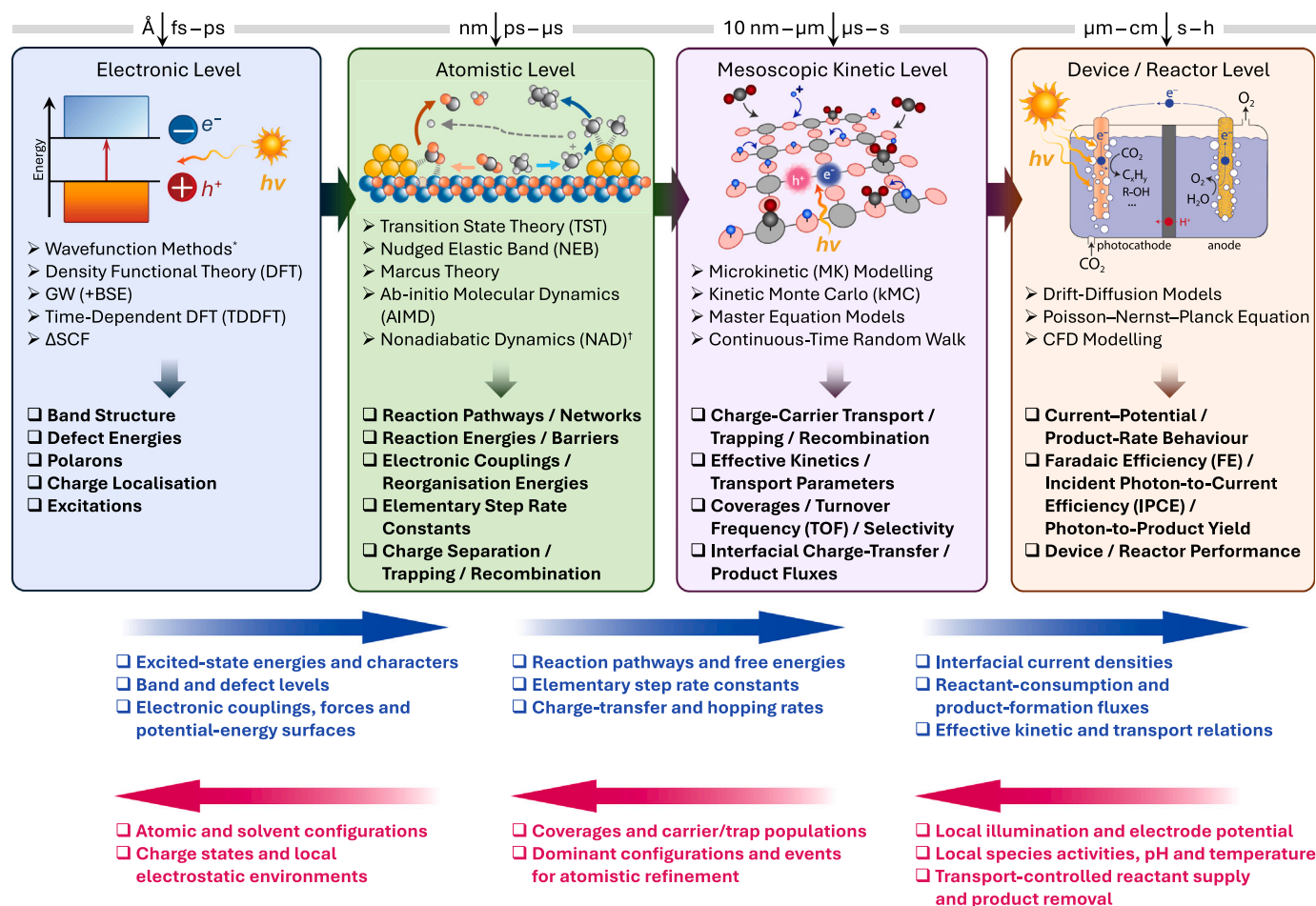


Fig. 2. Hierarchy of computational approaches commonly used to model photocatalytic and PEC systems across length and time scales, showing representative methods and outputs at the electronic, atomistic, mesoscopic-kinetic and device/reactor levels. The lower solid blue arrows indicate representative forward parameter or response transfers to the next modelling level; the left-pointing magenta arrows indicate feedback quantities returned only where adjacent models are explicitly coupled. The listed exchanges are representative rather than universal and need not all appear in a given model.

* Wavefunction-based methods are not considered in detail in this Review.

† Nonadiabatic dynamics are typically performed only over fs-ps timescales.

Source: The reaction illustration in the atomistic panel is adapted with permission from Scheme 1 of Ref. [132]. Copyright © 2024 Wiley-VCH GmbH.

the resulting interfacial response is returned to the larger-scale balance equations; the coupled models must then be solved self-consistently. Fig. 2 locates representative methods and outputs within this hierarchy; the discussion below identifies how those outputs can become inputs to adjacent descriptions.

A well-established one-way handoff is the transfer of electronic-structure and atomistic predictions into elementary-event models. For example, Sinha et al. used density functional theory (DFT)+*U* reaction free energies and a constrained-density-functional-theory-based molecular dynamics (DFT-MD) proton-transfer barrier to parameterise potential-dependent elementary rate constants for a lattice-kMC OER network [98]. Zhu et al. subsequently passed the surface-to-total electron-density ratio obtained from a transient random-walk/multiple-trapping carrier model into the rate constants of a surface-kMC CO₂-reduction module [29]. This handoff is also one-way: the reaction module does not return a carrier-consumption flux, complementary oxidation is assumed ideal, and reactor transport is not resolved. Feedback towards lower-scale models is less common; in an iterative workflow, predicted coverages, carrier or trap populations and local operating states can be used to select the atomistic configurations and elementary events requiring refinement.

Broader partial integrations have also been attempted. For photocatalytic CO₂ reduction, Sun et al. used calculated electronic and optical

properties, carrier mobilities, and adsorption and reaction energetics to parameterise optical-absorption, carrier drift-diffusion, microkinetic (MK) and near-surface continuum species-transport models [99]. Surface electron and hole concentrations and their reaction rates are exchanged between the carrier and MK modules, while surface concentrations and species reaction rates are iterated between the continuum and MK modules. The coupled calculation returns product-formation rates and selectivities, with the predicted H₂, CO and CH₄ formation rates compared with experiment. The framework spans much of the photon-to-product sequence, but adopts a steady-state representation, treats complementary oxidation in reduced form, and does not resolve a complete reactor environment. At a photoanode interface, van den Boorn et al. bidirectionally coupled illumination-driven carrier drift-diffusion and Poisson electrostatics to an MK model of the OER [100]. The semiconductor drift-diffusion-Poisson model supplies the interfacial electron and hole densities entering the MK rate expressions; the MK coverage balances determine the surface coverages of the OER intermediates, and the associated valence- and conduction-band charge-transfer current densities are returned as boundary fluxes in the semiconductor electron and hole continuity equations. This provides self-consistent coupling between semiconductor carrier dynamics and interfacial chemistry and yields steady-state interfacial current-density-potential curves, an experimentally accessible photoelectrode

observable; however, electrolyte transport, the counter-electrode reaction and the complete cell or reactor environment are not included. Together, these studies provide complementary near-end-to-end integrations rather than a single complete PEC case: Sun et al. [99] include electronic-structure and atomistic parameter generation but model a suspended photocatalyst, whereas van den Boorn et al. [100] reach an experimentally accessible PEC current–potential observable but do not generate the kinetic parameters from electronic-structure or atomistic calculations within the same workflow and do not include the complete cell or reactor environment.

At device and reactor scales, models differ in how explicitly the local photoelectrode response is represented. Some solve carrier transport, electrostatics and interfacial charge transfer together with electrolyte transport, whereas others replace part or all of this local physics with measured, fitted or reduced relations that map local illumination, potential and composition onto current and product fluxes. Berger and Newman coupled optical generation, electron and hole transport, semiconductor electrostatics and interfacial charge transfer to electrolyte and membrane transport within a one-dimensional PEC cell model [77]. This closes the electronic and ionic current paths, although catalytic chemistry is represented through reduced interfacial rate relations and hydrodynamic flow is not spatially resolved. Hankin et al. instead transferred parameters measured on smaller hematite electrodes into an experimentally parameterised local photocurrent relation used in two- and three-dimensional reactor models and tested against measurements on $0.1 \times 0.1 \text{ m}^2$ electrodes [83]. In a related three-dimensional framework, Bedoya-Lora et al. additionally treated H_2/O_2 generation and desorption, dissolved-gas transport, membrane crossover and gas collection, with current and gas-flux predictions tested in a 2 dm^3 reactor [76]. A more explicit local-state–response-flux exchange was implemented by Govindarajan et al. for electrocatalytic CO_2 reduction to CO: surface CO_2 concentration, pH and electrolyte potential from the continuum model are supplied to a steady-state MK model at each cathode-boundary node, while the resulting CO partial current density is returned and converted stoichiometrically into CO_2 -consumption and OH^- -production boundary fluxes until convergence [81]. Although not light-driven, this provides a transferable coupling pattern for PEC modelling. For reactor-scale photo(electro)catalysis, Fatahillah et al. coupled three-dimensional turbulent flow, discrete-ordinate UV-radiation transport and species transport to experimentally fitted surface and near-wall gas-phase reaction kinetics [80], while Yang et al. combined a semi-empirical Gärtner–Butler photoelectrode relation with bicarbonate/carbonate speciation, gas-product–liquid two-phase flow, heat transfer and species transport for PEC CO_2 reduction to CO [103]. Collectively, these studies resolve different portions of the device or reactor environment, while the local interfacial response ranges from explicit carrier transport or self-consistent microkinetic coupling to experimentally parameterised or semi-empirical constitutive relations.

Cross-scale coupling also requires assumptions that may be innocuous within an isolated model to be reconciled at each interface. Energies and electrochemical potentials must use consistent reference scales and operating conditions, as discussed in Section 2.2; atomistic rates must refer to the same species, site types, standard states and site densities represented by the kinetic model; and transferred currents, species fluxes and product rates must share consistent sign, area and stoichiometric conventions. When a steady-state kinetic closure is coupled to transient carrier or transport equations, the assumed separation of timescales must also be stated explicitly. Charge and species conservation, thermodynamic consistency where applicable, and uncertainty propagation then provide checks at each handoff [133,134]. The representative forward handoffs and conditional feedbacks to which these checks apply are summarised in Fig. 2, while Table 1 identifies whether the *A–G–T–I–S–R* process blocks are represented explicitly, treated partially or phenomenologically, or omitted, together with each study's principal output and scope limitation.

In summary, the principal gap is not the absence of models at any individual scale, but incomplete and insufficiently validated handoffs through the mesoscopic regime: from local carrier and electrostatic states to molecular turnover, and from local charge-transfer and reaction fluxes back to device or reactor balances. No reviewed model combines atomistically parameterised elementary-step kinetics, spatially resolved photogeneration and carrier dynamics, reactor-scale radiation, flow and species transport, and architecture-appropriate system closure within a single experimentally validated workflow. For contacted PEC assemblies, this requires closed electronic and ionic current paths; for suspended photocatalysts, it requires complementary half-reaction, material and electron-equivalent closure.

Reliable coupling additionally requires validation of both individual handoffs and system-level predictions. The workflow, ontology and data requirements for automating these exchanges are considered in Section 6.2. The objective is not necessarily to solve every scale simultaneously, but to make each transfer, feedback and approximation explicit and auditable.

3. Electronic-level modelling studies

Electronic structure calculations play a fundamental role in understanding photocatalytic processes, providing insight into charge localisation, defect states, and reaction energetics at catalytic surfaces. A key question in modelling photocatalytic materials is whether excess electrons and holes remain delocalised or become trapped at specific lattice sites. In many semiconductor photocatalysts charge carriers can localise and couple to lattice distortions, forming polarons [136]. Polaron formation can strongly influence charge transport, recombination behaviour, and surface reactivity, and therefore plays an important role in determining photocatalytic performance [49].

This section focuses on DFT and related methods used to study photocatalysis. DFT provides a favourable balance between computational cost and accuracy for large or extended systems compared with wavefunction-based methods such as configuration interaction (CI), second-order Møller–Plesset perturbation theory (MP2), or coupled-cluster approaches [137]. For properties involving electronic excitations in solids, the *GW* approximation alongside the Bethe–Salpeter equation (BSE), TDDFT, and ΔSCF will be discussed.

3.1. Methods

3.1.1. Density functionals

A major challenge when using DFT for modelling is choosing the optimal approximation of the energy functional. A common issue encountered is the fact that the widely used local-density approximation (LDA) and generalised-gradient approximation (GGA) functionals tend to overly delocalise electrons. This is a consequence of the self-interaction error [138,139]. It stems from the fact that Kohn–Sham (KS) functionals estimate the classical Coulomb interaction between the electrons from the total electron density, while the exchange energy is estimated using local or semi-local approximations. As a result, even a system containing a single electron is predicted to have repulsive Coulomb interaction and this error is larger the more localised the electron is. Some refer to this as the delocalisation error [140]. This issue is particularly important in photocatalytic materials because the degree of charge localisation strongly affects the description of defect states, trapped carriers, and polaron formation.

Fock exchange contains the same self-interaction but with an opposite sign, so the Hartree–Fock (HF) approximation is self-interaction free, and hybrid density functionals which mix a GGA form with some fraction of Fock exchange, can to some extent cancel out the error. But, the optimal scaling factor for Fock exchange is strongly system dependent and different approaches are taken when simulating solids than molecules. Some hybrid functionals have been developed specifically for use in solid state systems [141,142]. The use of hybrid

functionals has, however, been limited by the large computational cost of Fock exchange calculations as well as difficulties with their use for metals (poor description of bands around the Fermi level, convergence issues etc.) [143].

A popular approximate method for mitigating the self-interaction error that requires less computational effort is the Hubbard U model, taken from Hubbard's model for the transition between conducting and insulating systems [144]. The U term represents an on-site interaction that can overcome the spurious electron self-repulsion. The strength of this term can be optimised either by fitting to experimental data for e.g. the bandgap, or using theoretical methods such as a linear response theory [139]. It is important to note that it is generally impossible to optimise this parameter to give accurate values for all properties of interest, and in some cases no value of U can give a match to experimental values [37].

While the addition of the Hubbard U term or some fraction of Fock exchange can help get proper localisation, a more fundamental approach is to explicitly remove the self-interaction error with a self-interaction correction (SIC). Perdew and Zunger [138] proposed to do this orbital by orbital, i.e. within an independent electron approximation. However, this represents an overcorrection and, analogous to hybrid density functionals, a scaling factor has been introduced [145–148]. A simple factor of 1/2 works well in many applications, giving for example good estimates of the band gap for a wide range of insulators [149]. Defects corresponding to energy levels in the gap can also be well reproduced, including proper localisation of the spin density, as exemplified by calculations of Al dopant in α -quartz [42]. Since the corrected functional is not unitary invariant, the orbitals need to be complex valued functions [150].

Ongoing work on SIC includes the development of a local scaling factor that takes into account the extent to which orbitals overlap. Full SIC is needed when there is no overlap, while no SIC should be applied when the orbitals are highly delocalised as in metals. In molecules with delocalised orbitals, such as benzene, SIC with a scaling factor of 1/2 has been shown to lead to symmetry breaking [151], while recently developed local scaling retains the symmetry [152].

3.1.2. Polarons and excitons

As mentioned in Section 2, photocatalysis is initiated by photo-excitation of an electron, creating an electron–hole pair. Depending on the dielectric screening or electron–hole interactions, the pair may remain bound as an exciton or separate into free or localised charge carriers. Electrons or holes may subsequently localise at different lattice sites, defects or surfaces, accompanied by local structural changes, forming polarons. Polarons are typically studied by introducing excess electrons or holes into a simulation cell and performing a ground state calculation. Such calculations can reveal whether the electron/hole localises at specific lattice sites and provide insight into the structural distortions associated with polaron formation [63]. For photocatalysis, the interactions between localised carriers and adsorbed species are also of interest.

Including an isolated electron or hole polaron will introduce net charge to the simulation cell, which is problematic for periodic boundary conditions. A compensating background charge, commonly a homogeneous background (by getting rid of $G = 0$ component in plane-wave codes), is therefore typically added in electronic-structure codes to maintain overall charge neutrality. However, the calculated energies can contain finite-size errors due to artificial electrostatic interactions between periodically repeated charged defects, interactions with the compensating background charge, and shifts in the electrostatic reference that require potential alignment [153–156]. Several correction schemes have been developed to mitigate these artefacts, including the Makov–Payne correction [154] and the Freysoldt–Neugebauer–Van de Walle correction (FNV) [155,156].

For surface calculations using slab models, additional complications arise due to the anisotropic dielectric environment and the presence

of vacuum regions. In such cases, modified electrostatic correction schemes or slab-specific implementations of the FNV method [157,158] are required to obtain reliable energies for charged defects and polarons. Careful treatment of these effects is therefore essential when modelling charge localisation and photo-induced charge carriers in photocatalytic materials, where surface processes often play a central role.

Compared with the extensive literature on charge localisation and polarons, less work has addressed excitons in photocatalytic solids, even though excitonic effects can influence light absorption, charge separation, and recombination. Methods for calculating excited states in solids can broadly be grouped into many-body perturbation theory approaches such as the GW approximation and the BSE, TDDFT, and Δ SCF approaches.

3.1.3. GW approximation and the Bethe–Salpeter equation

As mentioned previously, DFT calculations using semilocal functionals typically do not give particularly accurate results when used for semiconductors and insulators, typically underestimating the band gap and incorrectly describing localised states [140]. While Section 3.1.1 mentions different choices of density functional that can improve this, an alternative option is to use the GW approximation, which can often be used for a better description of properties such as fundamental band gaps, band-edge positions, and defect ionisation energies [159,160].

In the GW framework, the exchange–correlation potential is replaced by a non-local, energy-dependent electron self-energy, Σ , constructed from the one-particle Green function G and the screened Coulomb interaction W . This formulation explicitly accounts for electron–electron interactions beyond the mean-field description of standard DFT [159,160]. In practice, GW is most often applied perturbatively on top of a DFT starting point (for example, single-shot GW approximation (G_0W_0)), although partially or fully self-consistent variants can reduce the dependence on the initial electronic structure at increased computational cost [161].

The improved description of band gaps and band-edge positions is important when investigating photocatalytic materials. These properties can affect predictions of light absorption thresholds, redox driving forces, band alignment, and charge-trapping levels. For oxide photocatalysts such as TiO_2 , GW calculations have significantly improved the description of band gaps and band-edge energetics compared with semilocal functionals [47,52].

Beyond providing a better description of ground state and quasi-particle properties, the BSE can be used with the GW approximation to describe electronic excitations (excitons) [159]. The BSE describes neutral excitations by explicitly accounting for the Coulomb interaction between the excited electron and the hole it leaves behind [162]. Solving the BSE enables the calculation of exciton binding energies and optical absorption spectra, providing a direct connection between electronic structure and experimentally observable optical properties. For example, GW +BSE calculations have been used to investigate quasi-particle band structures and optical excitations in oxide photocatalysts such as TiO_2 [45].

GW and GW +BSE calculations can lead to greater accuracy, but they are computationally demanding and require careful convergence with respect to basis size, number of empty states, dielectric screening, and Brillouin-zone sampling [160]. As a result, these approaches are typically applied to benchmark electronic and optical properties of selected materials and structures rather than for routine large-scale screening.

3.1.4. Time-dependent density functional theory

Electronic excitations are more commonly described within the DFT framework using TDDFT. This approach, based on the Runge–Gross theorem [163], calculates the density in a changing external potential field [164]. Linear-response time-dependent density functional theory (LR-TDDFT) uses the linear-response function of the density when

affected by a change in the external potential to derive the Casida equation, which is used to calculate excitation energies [165]. This method has been widely adopted, as it is computationally cheap compared to wave-function based methods or the *GW* approximation, and provides reasonable accuracy [164,166]. However, LR-TDDFT is known to have problems when dealing with higher energy excitations and excitations involving a large charge transfer [54,164]. Additionally, in the usual adiabatic approximation, it has difficulties describing doubly excited states, near-degenerate electronic configurations, and conical intersections involving the ground state [21,167].

Improvements to LR-TDDFT implementations have focused particularly on the choice of functionals. The use of range-separated functionals has been shown to increase the accuracy of some charge transfer excitations, but many functionals do not universally describe excitations well for a wide range of charge transfer distances [54]. Another alternative that goes beyond the linear-response formalism is real-time time-dependent density functional theory (RT-TDDFT), by which the density is propagated in real time as a response to an external potential that can represent an applied field or a laser pulse. By going beyond the linear-response formalism, it is possible to explore a wider range of excitations, including higher energy excitations resulting from strong fields [168,169]. Problems in describing double excitations and dependence on the choice of functional still remain however.

3.1.5. Δ SCF methods

Δ SCF is another family of methods that has attracted increasing interest in recent years. Of particular interest are methods that calculate excited states as stationary points of an energy functional [46,53,170]. This can be clarified using Fig. 3 where a contour graph showing the energy of an electronic configuration of an H_2 molecule is shown with respect to electronic degrees of freedom. Here a minimal basis set is used comprised of bonding and anti-bonding molecular orbitals σ_g and σ_u^* . The two occupied electronic orbitals are described as a linear combination of the two molecular orbitals: $\Psi_{\alpha/\beta} = \cos(\phi_{\alpha/\beta})\sigma_g + \sin(\phi_{\alpha/\beta})\sigma_u^*$. The ground state is the global minimum, whereas the first and second excited states in the Δ SCF formulation correspond to the first and second order saddle points on the energy surface respectively.

These methods have been shown to give reasonably accurate estimates of the excitation energy, with some added advantages such as the ability to calculate analytical excited state Hessians [46]. Despite this, Δ SCF has historically seen less use compared to TDDFT methods due to challenges such as variational collapse, where the calculation converges on a different state than the one desired. Additionally, there are difficulties in dealing with states with a multi-reference character as is the case for density functional calculations in general [21].

To avoid variational collapse and improve the convergence to excited states a number of different strategies have been used. A popular method is the maximum-overlap method (MOM), where the orbitals chosen to be occupied in each step of the self-consistent field (SCF) cycle are the ones with the greatest overlap with a set of reference orbitals [171]. These can be the occupied orbitals in the previous step or constructed from the initial guess using the initial maximum-overlap method (IMOM) [172]. Direct optimisation (DO) formulates the variational problem as an optimisation of the orbitals through the use of a unitary transformation of a set of reference orbitals. This method can be combined with MOM in the direct-optimisation maximum-overlap method (DO-MOM) for excited-state calculations [170].

Other schemes have been developed that convert the saddle point search into a minimisation problem. These include the σ -SCF method [173], where an excited state with an energy close to a value ω is found by minimising the expectation value of the operator $(H - \omega)^2$, and the square-gradient minimisation (SGM), where the problem of converging onto extrema is instead converted into a minimisation problem by minimising the square of the gradient of the energy with respect to the electronic degrees of freedom [174]. The state-targeted energy projection (STEP) approach uses a level shift to increase the

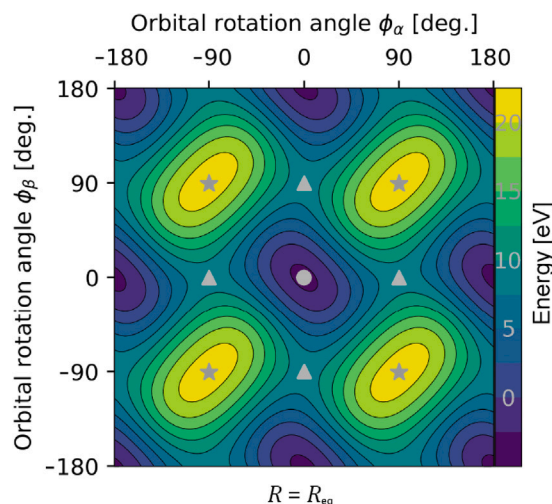


Fig. 3. Energy of an H_2 molecule with respect to electronic degrees of freedom using a minimal basis set consisting of bonding σ_g and anti-bonding σ_u^* molecular orbitals. The axes show the orbital rotation angle ϕ for the α and β orbitals, describing the mixing between the bonding and anti-bonding orbitals. The circle represents the energy minimum corresponding to the ground state, whereas the triangles and stars represent 1st and 2nd order saddle points respectively on the energy surface. These saddle points correspond to the first and second excited states in the Δ SCF formulation.

Source: Adapted with permission from the upper-left panel of Fig. 1 of Ref. [53]. Copyright © 2023 American Chemical Society.

energy of virtual unoccupied orbitals so that they are higher than the highest occupied orbital in the excited state and thus also converts the convergence to a minimisation problem [175].

A different approach underlies the generalised mode-following (GMF) method, which uses an appropriate search algorithm to directly converge onto a saddle point of a given order, by inverting the gradient components along the eigenvectors corresponding to the lowest n eigenvalues of the electronic Hessian [53]. This method has been shown to avoid variational collapse in the vicinity of conical intersections, allowing for a calculation of a potential-energy surface (PES) for excited states by converging onto the same order saddle point. This method does, however, require the correct saddle point order of the excited state, which can often be difficult to estimate *a priori*.

Open-shell singlet states can pose a problem when using Δ SCF methods, as they cannot be described using a single Slater determinant; this can in some cases result in significant spin contamination. Ziegler's formula [176] and the approximate projection (AP) method [177,178] use a converged triplet determinant to correct the energetics of the calculated spin-contaminated determinant, often leading to improved energetics [21,54,175,179,180]. The restricted open-shell Kohn–Sham (ROKS) approach uses a determinant where the orbitals can either be singly or doubly occupied, instead of using two different spin channels [181].

These improved methods have increased interest in the use of Δ SCF in recent years, as these methods are cheap and yield reasonably accurate energetics. In some cases, such as excitations with a large charge-transfer, Δ SCF performs better than TDDFT or configuration-interaction singles (CIS) [21,54,180]. Excitation energetics are also typically less dependent on the choice of functional compared to TDDFT [21]. Some of these methods have been adapted for use with plane-wave basis sets and with orbital dependent functionals [179].

3.2. Applications

A selection of electronic structure studies on photocatalysis can be found in Table 2. In the following subsections we will discuss

Table 2

Representative studies using excited-state electronic-structure methods for extended systems.

Study	System	Property or process modelled	Methodology
<i>GW and BSE studies</i>			
Sun et al. [55]	Anatase TiO ₂ (101) and Rutile TiO ₂ (110)	Water photooxidation and interfacial level alignment	LDA, PBE, HSE06, G_0W_0 , scQPGW1 and BSE
Mowbray & Migani [51]	Rutile TiO ₂ (110)	Catechol–TiO ₂ optical absorption and charge-transfer excitons	HSE06, G_0W_0 and BSE
Wiktor et al. [58]	Monoclinic BiVO ₄	Fundamental and optical gaps and absorption spectrum	PBE, PBE0, HSE, G_0W_0 , QSGW and BSE
<i>TDDFT studies</i>			
Wang et al. [57]	H ₂ O on rutile TiO ₂ (110)	Competing O ₂ /H ₂ O ₂ formation pathways	PBE- and HSE06-based LR-TDDFT
Suzuki et al. [56]	Anatase TiO ₂ (001)	Phenol oxidation	Long-range corrected TDDFT, hybrid functionals
Möslinger et al. [50]	BiVO ₄	Self-trapped excitons	TDDFT, hybrid functionals
<i>ΔSCF studies</i>			
Mackrodt et al. [48]	Bulk NiO	Low-energy local and charge-transfer excitations and Stokes shifts	Direct ΔSCF with orbital-level shifting and relaxed excited-state structures
Daga and Maschio [40]	LiF, Si, diamond, NiO and CuI (piperazine)	Excitation energies	MOM, energy gradients
Ivanov et al. [44]	NV [−] centre in diamond	Optical excitation of defect states	Direct orbital optimisation with analytical forces
Hellman et al. [43]	Cl and Cl ₂ on Na(100)	Electron-transfer-induced chemiluminescence	DFT-adapted ΔSCF with prescribed electron-hole occupations
Gavnholt et al. [41]	N ₂ on Ru(0001); N ₂ , CO and NO on Ni(001); CO and NO on Ni(111); and CO on Pd(111) and a Pd step	Excited-state PESs	Linear-expansion ΔSCF with explicit potential-energy-surface mapping

Selected abbreviations: quasiparticle approximation based on the one-particle Green function and screened Coulomb interaction (*GW*); Bethe–Salpeter equation (BSE); single-shot *GW* approximation (G_0W_0); quasiparticle self-consistent *GW* with vertex-corrected screening (QSGW); self-consistent quasiparticle *GW* approach (scQPGW1); Heyd–Scuseria–Ernzerhof screened hybrid functional (HSE); 2006 parametrisation of the Heyd–Scuseria–Ernzerhof screened hybrid functional (HSE06); time-dependent density functional theory (TDDFT); linear-response time-dependent density functional theory (LR-TDDFT); delta self-consistent-field method (ΔSCF); maximum-overlap method (MOM); negatively charged nitrogen-vacancy (NV[−]) centre.

some recent studies of particular interest that demonstrate some of the methods discussed in Section 3.1.

3.2.1. Electronic level alignment in TiO₂

The level alignment of the molecular orbitals of adsorbed species and the electron bands of the substrate is often a useful predictor of the activity of a photocatalyst. In particular, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can align with the valence-band maximum (VBM) and conduction-band minimum (CBM) of the substrate. Accurate knowledge of this alignment can provide a description of the propensity of electrons or holes to migrate from the substrate to the adsorbate [55].

In this context, Sun et al. [55] investigated the photocatalytic activity of H₂O photo-oxidation on TiO₂ anatase and rutile surfaces. Anatase has been shown experimentally to be more active than rutile, but in this work the authors aimed at explaining this difference in activity. They specifically looked into the level alignments between adsorbed water on the anatase (101) and rutile (110) TiO₂ surfaces, both with and without oxygen vacancies and with varying coverages of adsorbed water molecules. From a methodological standpoint, the LDA, Perdew–Burke–Ernzerhof functional (PBE), and HSE06 were used in this study, alongside G_0W_0 calculations to describe the electronic structure of the materials. BSE calculations were also done to calculate the dielectric constants and optical band gaps of the two different TiO₂ structures. The *GW* calculations were found to be necessary for an accurate enough description of the electronic structure.

The results showed that the HOMO of water on anatase is more closely aligned with the VBM compared to rutile. These levels are even more closely aligned for dissociated water (OH). This showed that adsorbed water on anatase has a higher propensity to attract holes from the substrate and that dissociated water has a higher propensity than intact water. The effect of oxygen vacancies was also investigated, showing that *GW* calculations are necessary to get an accurate description of the position of the Ti³⁺ 3d electrons relative to the Fermi

level. This work shows that trends in photocatalytic activity can be established through knowledge of an interface's electronic structure and level alignment.

3.2.2. Absorption spectrum in BiVO₄

In order to gain a better understanding of the electronic structure of BiVO₄, Wiktor et al. performed a comprehensive analysis of different methods to model the band structure of BiVO₄ [58]. They considered the semilocal PBE functional alongside the hybrid PBE0 and HSE functionals along with G_0W_0 calculations using wave functions from calculations using each of the three functionals as a starting point, as well as quasiparticle self-consistent *GW* with vertex-corrected screening (QSGW). Of these methods, the PBE results for the band gap were the closest to experiment, with all of the other methods overestimating the band gap. This is surprising as semilocal functionals tend to underestimate the band gap in semiconductors.

This surprising result was shown, however, to be a result of a cancellation of errors. As bismuth is a heavy element, spin–orbit coupling effects can shift orbital energies considerably. Additionally, the thermal vibrations of the material can have an effect. When including corrections for spin–orbit coupling effects, thermal vibrations and nuclear quantum effects, Wiktor et al. [58] found that this decreased the calculated band gap significantly. This brought the values from hybrid functional and *GW* calculations closer to experiment, while PBE underestimated the band gap, in line with results on other semiconductors. Additionally, by solving the BSE to include excitonic effects, the optical band gap from the QSGW calculation was in excellent agreement with experimental values. This highlighted the difficulty in modelling BiVO₄ accurately using DFT methods and the need to include corrections for various effects.

3.2.3. Exciton modelling in BiVO₄

Self-trapped excitons have been shown experimentally to appear after photoabsorption in BiVO₄; however, it is difficult to understand

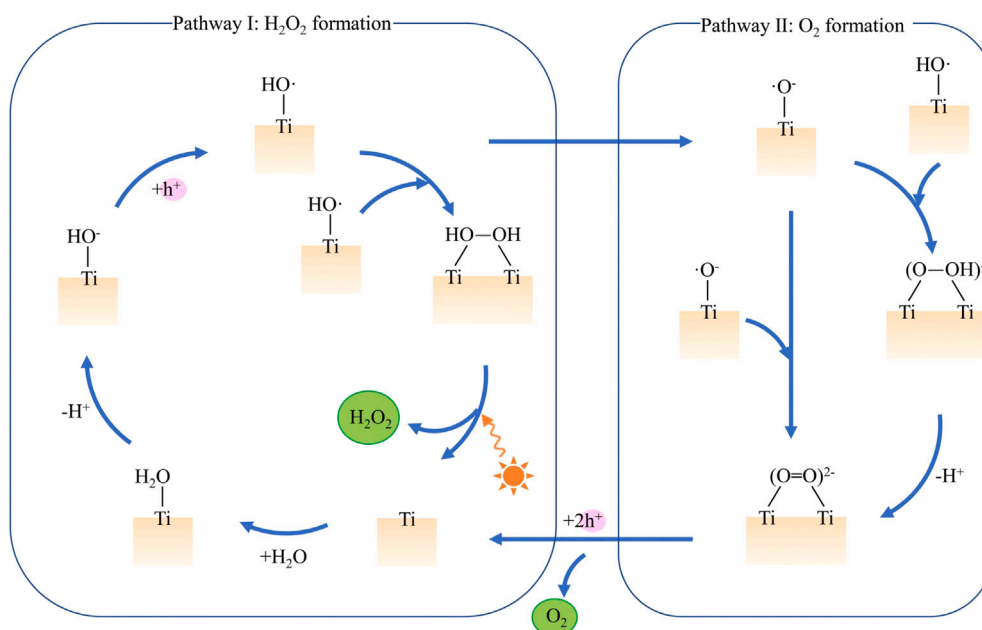


Fig. 4. Schematic diagram of two photocatalytic pathways for two water molecules adsorbed on rutile TiO_2 (110) surface. Pathway I shows the gradual conversion of surface hydroxyl groups to produce H_2O_2 , and Pathway II illustrates the stepwise transformation of adsorbed oxygen species into O_2 .
 Source: Reproduced from Fig. 1 of Ref. [57] under the CC BY 3.0 licence (<https://creativecommons.org/licenses/by/3.0/>). Copyright © 2025 The Author(s). Published by the Royal Society of Chemistry.

the nature of these states through experiment alone. Motivated by this, Möslinger et al. performed a computational investigation of self-trapped excitons in BiVO_4 and compared their energies with those of separated electron and hole polarons [50]. They used the $\text{PBE0}(\alpha)$ functional, tuning the fraction of exact exchange to reproduce selected electronic properties. Ground-state triplet calculations identified two self-trapped-exciton configurations with similar energies, suggesting that both could be populated under experimental conditions. Comparison with the corresponding separated-polaron configurations showed that the predicted exciton binding is sensitive to the fraction of exact exchange, ranging from 10–40 meV with $\text{PBE0}(14\%)$ to 150–310 meV with $\text{PBE0}(22\%)$.

The authors then used TDDFT to calculate optical transitions from the two self-trapped-exciton configurations. The resulting spectra contained multiple peaks arising from transitions between localised electron and hole states and from mixed transitions involving delocalised states near the valence-band maximum. They therefore proposed that multiple emission peaks can arise from different transitions within a single self-trapped-exciton configuration, rather than necessarily indicating several distinct localised states.

3.2.4. Photo-excitation driven processes on a TiO_2 surface

TDDFT has been used in modelling photocatalysis in extended systems, particularly TiO_2 . For instance, Wang et al. [57] investigated photocatalytic water dissociation on a rutile TiO_2 (110) surface. The dissociation can proceed through two pathways involving the oxidation of two water molecules: a two electron pathway that produces H_2O_2 ($2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$) and a four electron pathway that produces O_2 ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$). These pathways are shown in Fig. 4; however, the details of the oxidation processes and the selectivity of the different pathways are poorly understood.

Thus motivated, this study investigated a large set of competing elementary steps leading to the formation of either H_2O_2 or O_2 [57]. Gibbs free-energy changes and ground-state activation barriers were calculated for the proposed pathways. The resulting barriers indicated that O_2 formation can proceed thermally at room temperature without photoexcitation.

Elementary steps that had high activation energy values were then recalculated in the presence of light-induced excitation via the TDDFT approach, to investigate the effect of photo-excitation on the selectivity. The results showed that the formation of a $\text{HO}\cdot\text{-OH}$ bond had a higher activation energy in the excited state compared to the ground state, while the $\text{O}\cdot\text{-H}$ bond dehydrogenation processes showed similar barriers in the excited and ground states. These reactions were thus presumed to proceed via ground-state thermal catalysis. The desorption of H_2O_2 from the surface was found to have a significantly reduced activation energy in the excited state, so that process was assumed to proceed due to photocatalysis.

The details of the H_2O_2 desorption step were further investigated, specifically in the presence of photo-excitations in TiO_2 , with electrons and holes distributed across the lattice [57]. As H_2O_2 desorbs, the holes are captured by the H_2O_2 molecule, lowering the barrier of desorption. These calculations were done using both PBE and the hybrid HSE06 functionals. A small difference was shown between the PBE and HSE06 calculations that led to the transition state being located at different points along the reaction pathway for that elementary step in the excited state. This was attributed to the PBE functional delocalising the holes and electrons more, and failing to describe the band gap accurately enough.

The explicit consideration of excited states by Wang et al. [57] provided valuable insight into how photo-excitation affects the selectivity of the two pathways. The study is limited however in that the excited states were only calculated on points along the reaction pathway found in the ground state. This makes the assumption that the reaction pathway remains the same in the excited state, which might not be the case. This could be remedied by using a method to calculate excited states that can also provide forces, in order to find transition pathways independently of the ground state.

3.2.5. Concentration of excited electrons

When modelling excited states in extended periodic systems using ΔSCF methods that converge onto excited states, a number of issues may arise. Accessible excitations with this method are typically limited, being within the Γ -point due to symmetry constraints. Yet, due to band structure folding when using supercells, some excitations that are away

from the Γ -point in the primitive cell become centred on the Γ -point and can therefore be accessed [40,48]. A second issue is controlling the concentration of excited electrons in the system. An extreme scenario is when a primitive unit cell is calculated using a single Γ -point, in which case an entire occupied band is excited to a conduction band leading to an extremely high concentration of excited electrons corresponding to one electron per primitive cell.

Mackrodt et al. [48] tackled both of these problems in their investigation of low energy excitations in NiO by using appropriate supercells and carefully checking the convergence of the properties of interest with respect to the supercell size. Using this approach, excitation energy values in agreement with experimentally observed values were obtained. Of particular note is that LDA and GGA functionals that typically underestimate the band gap of NiO by an order of magnitude, and HF which overestimates the band gap, both give excitation energies close to experimental values when used with the Δ SCF approach.

Another advantage of this approach was that changes in charge and spin densities as well as the density of states could be examined for each of the excited states considered, delivering greater insight than what is accessible from a ground state calculation alone. With this method, forces can also be obtained, and were used to calculate Stokes shifts for one of the excitations.

Daga and Maschio [40] used a different approach to tackle the problem of exciton concentration. In particular, the exciton concentration was adjusted by changing the number of k -points that were sampled in the reciprocal space. They also introduced a method by which a sphere around the Γ -point with a radius r_s is defined, and the k -points within that sphere also undergo an excitation from the selected valence band to a conduction band. This corresponds to the physical case of a non-monochromatic light source triggering the excitation. These methods were tested on bulk silicon, diamond and LiF systems [40]. Additionally, they were used to investigate Stokes shifts in NiO and $[\text{Cu}(\text{piperazine})_{0.5}]_{\infty}$, a luminescent copper(I) halide. The advantage in this approach is that excitation concentration can be calculated using a primitive unit cell without considering expensive supercells. Supercells are still needed however to access excitations through band structure folding.

4. Atomistic level modelling studies

4.1. Methods

4.1.1. Excited state dynamics

Excited-state dynamics provide key insights into the initial steps of photocatalysis, enabling an understanding of how charge carriers are generated and how critical nonradiative processes, such as recombination, energy transfer, and spin transport, evolve to ultimately determine catalytic efficiency. Rapid injection of photogenerated electrons and holes from a light absorbing unit into a material can produce high photocurrents [182]. Additionally, energy transfer into specific vibrational modes can promote selective chemical transformations in photocatalytic systems. These processes can be effectively modelled using excited state approaches, particularly NAMD techniques, which capture the interplay between electronic and nuclear motion [183].

NAMD methods provide a framework for describing interactions between electronic states mediated by the nuclear vibrations, thus extending the modelling capabilities beyond the Born–Oppenheimer approximation [183,184]. Nonadiabatic effects are especially significant in regions of the PES characterised by a high density of states (DOS) and small energy gaps, such as conical intersections. In addition to energies and forces, NAMD simulations often require calculating nonadiabatic couplings (NACs), which further increases their complexity. NACs are inversely proportional to the energy gaps between electronic states and therefore become infinite at conical intersections. Because many photocatalytically relevant systems exhibit a high DOS, evaluating these couplings becomes particularly challenging [182].

While methods that treat both electrons and nuclei fully quantum mechanically, such as multiconfiguration time-dependent Hartree (MCTDH) [185], can be applied to molecules with many vibrational degrees of freedom, their computational cost becomes prohibitive for systems relevant to photoelectrocatalysis. As a result, semiclassical and mixed quantum–classical approaches based on trajectories are commonly employed. Other methods that incorporate nuclear quantum effects and have been applied to condensed-phase systems, such as ring-polymer molecular dynamics representing each atom as a ring polymer in an extended phase space [186,187], have not yet been exploited for materials relevant for photoelectrocatalysis.

Within mixed quantum–classical frameworks, the most widely used methods for practical applications are mean-field Ehrenfest (MFE), trajectory surface hopping (TSH), and multiple spawning (MS) (Fig. 5). MFE dynamics propagate nuclei classically under forces derived from the quantum-mechanical expectation value of the electronic wavefunction, enabling a coherent superposition of states at relatively low computational cost [183,184]. However, because the nuclei evolve on an averaged PES, MFE fails to capture wavepacket branching, can produce unphysical dynamics outside regions of strong NAC, and does not satisfy detailed balance [183,184]. TSH, particularly its most popular variant, the fewest-switches surface hopping (FSSH) algorithm, propagates nuclei on a single PES while allowing stochastic transitions between states [183,184]. To recover the quantum behaviour, a swarm of trajectories is propagated. Owing to its favourable balance between accuracy and computational cost, TSH has become the most widely used approach for NAMD simulations in both gas-phase and condensed-phase systems, and can even be computationally cheaper than MFE when multiple electronic states are involved, as it requires forces from only one PES at a time [184]. Despite its widespread use and computational efficiency, FSSH is fundamentally an *ad hoc* method and lacks a rigorous treatment of decoherence, leading to artificially persistent electronic coherences. As a result, empirical decoherence corrections are routinely employed in molecular simulations [188]. Alternative approaches, such as decoherence-induced surface hopping (DISH), have been developed to account for decoherence more explicitly within the surface-hopping framework and have found widespread application in condensed-phase simulations [189]. In contrast to TSH, MS methods provide a more rigorous semiclassical treatment by expanding the nuclear wavefunction in a time-dependent Gaussian basis that can split in regions of strong NAC, enabling improved treatment of decoherence and, in principle, convergence to the exact solution, albeit at higher computational cost [190].

As highlighted in the cyclobutanone photochemistry prediction challenge [191], the reliability of NAMD simulations depends critically on the quality of the underlying excited-state electronic structure description [183,192]. Including both dynamical and static correlation is typically required to accurately describe excited-state processes. Although single-reference approaches such as TDDFT struggle to accurately describe the topology of crossings between the ground (S_0) and the first excited state (S_1) and cannot account for double excitations [167,193], they remain widely used due to their favourable computational cost, and are often the only feasible option for large systems or condensed-phase applications. In contrast, multiconfigurational methods such as complete active space self-consistent field (CASSCF) [194] and complete active space second-order perturbation theory (CASPT2) [195] are required to properly describe multiconfigurational wavefunctions, but they introduce additional challenges, including the need to carefully define problem-specific active spaces and to maintain their stability along the main reaction coordinate that can affect the stability of the active space in the simulations [183].

Moving from molecular systems to the condensed phase introduces additional challenges, particularly for photocatalytic reactions occurring at solid–liquid interfaces. In these cases, it is not sufficient to model only the bulk material; the structure and dynamics of the interface with the solvent must also be considered. This requires careful construction

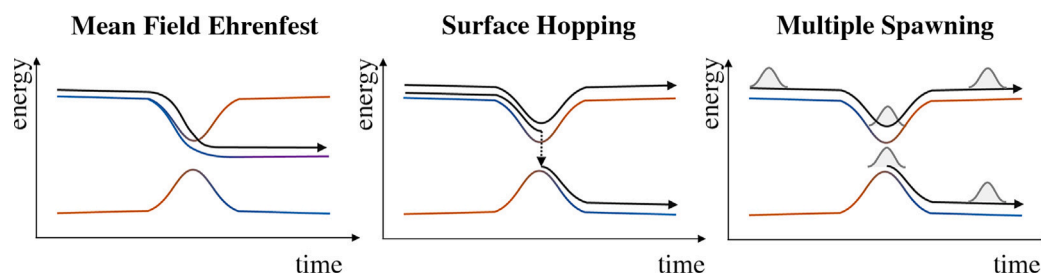


Fig. 5. Most popular trajectory-based methods for NAMD.

Source: Adapted with permission from Figs. 2–4 of Ref. [183]. Copyright © 2018 American Chemical Society.

of interfacial models, often supported by molecular dynamics simulations to adequately sample the solvent configuration in contact with the surface. For aqueous systems, quantum effects such as proton tunnelling may play an important role, and these are not always well captured by standard semiclassical approaches [196]. A further key consideration is the choice between cluster and periodic models for extended systems: while cluster models can be effective when excitations are localised (e.g., at defects), their validity should be assessed against periodic representations.

For NAMD in condensed-phase systems, a set of approximations is required to reduce the computational cost of these simulations. It is important to note that many trajectories are typically propagated, making cost reduction essential for obtaining good statistics for the ensemble. The necessary approximations arise both from the treatment of nuclear motion and from the choice of electronic structure method, including how NACs are computed. Many applications in the condensed-phase systems are based on the classical path approximation (CPA) and the neglect of back-reaction approximation (NBRA), where nuclei are propagated with state-independent forces [114]. Nuclear trajectories, typically obtained from ground-state molecular dynamics, are used to construct the time-dependent vibronic Hamiltonian, making CPA efficient by avoiding excited-state forces and velocity rescaling. While this approximation is suitable for structurally rigid systems, it breaks down for molecular cases involving bond breaking or isomerisation, where forces in simulations must be evaluated for the instantaneous electronic state. Some of the methodological challenges and practical solutions associated with modelling photoelectrochemical materials have been thoroughly reviewed by Smith and Akimov who provide an insightful discussion of current limitations, emerging strategies, and best practices in the field [182].

In terms of electronic structure modelling, several of the methods outlined in Section 3.1 have been widely applied to the study of materials relevant for photoelectrochemical applications. DFT, TDDFT, and the Tamm–Dancoff approximation (TDA) have been employed extensively to investigate both cluster models and periodic systems, as well as solid–liquid interfaces [57,70]. Approaches based on constrained or Δ SCF formalisms have also been proposed to capture excited-state properties with reduced computational overhead [197]. In addition, semiempirical techniques offer a valuable alternative for large-scale simulations, significantly lowering computational cost. Among these, density-functional tight binding (DFTB) and its extensions have emerged as affordable yet sufficiently accurate options for modelling extended systems and complex interfacial environments [198]. With the rapid development of machine learning (ML) and its growing application to NAMD, the coming years are expected to see a significant increase in studies exploring NAMD for photoelectrocatalysis [199,200].

Different implementations of NAMD are available, including codes that interface with electronic structure methods, such as Newton-X [201], SHARC [202], JADE [203], PyRAI2MD [204], NEXMD [205], and PYXAID [206] among others. In addition, several electronic structure packages have incorporated their own implementations of NAMD

methods, such as TSH in Turbomole [207] and OpenQP [208], and Ehrenfest dynamics in GPAW [209]. While Newton-X and SHARC have traditionally been applied to molecular systems, they have recently been generalised to simulate extended materials by interfacing with electronic structure codes that employ periodic boundary conditions. Recent developments, such as the CP2K–Newton-X interface [210,211], enable simulations to be carried out within the TDA. Similarly, SHARC has implemented an interface with VASP based on the NBRA approach [212]. Frameworks such as the Libra library [213] and PYXAID [206] have also been developed to support NAMD simulations in materials, providing a range of tools and interfaces that facilitate these types of calculations.

4.1.2. Thermally assisted transitions

While the main driving force for photochemical reactions is the energy from the absorbed photon, thermally induced transitions also play an important role. This includes migration of the electron and hole polarons and the reaction of a polaron with a molecule at the surface of the solid. Since excited electronic states are involved in the overall process, the rate of such transitions is often estimated using Marcus theory, which is based on a diabatic model. If, however, the coupling between the electronic energy surfaces is strong, leading to significant energy separation, an adiabatic approach within transition state theory can suffice. Here, a brief overview of these methods is given and examples taken from studies of polarons.

Marcus theory. For electron hopping between two different species without bond breaking/formation, Marcus formulated a landmark theoretical approach for rate calculations in the mid 50s [214,215]. The core idea of Marcus theory is that electron transfer occurs near the crossing of diabatic surfaces, that is when the two electronic states (“before” and “after” electron transfer) become equal in energy. The two PESs correspond to the electron being centred on two different sites, a donor and an acceptor site. This requires thermally induced reorganisation of the atoms in order to bring the donor and acceptor electronic states into energetic degeneracy. The rate constant for the electron hopping process is formulated as:

$$k^{\text{Marcus}} = \frac{2\pi}{\hbar} |V_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp \left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right]. \quad (2)$$

The main parameters determining the rate of electron transfer are the reaction free energy (driving force) ΔG^0 , the electronic coupling V_{AB} and the reorganisation energy λ . If the electronic coupling is large, the energy difference between the PESs can be sufficiently large that the system is confined to the lower one and the transition can be described as being adiabatic. Then transition state theory (see below) can be applied.

The Emin–Holstein–Austin–Mott (EHAM) theory [119] was developed through several distinct works to describe charge transport in solids where charge carriers move as localised polarons instead of travelling as Bloch waves. Whereas Marcus theory describes a single electron transfer between two sites, EHAM theory describes charge

transport in an extended system of localised sites and gives a framework for calculating several macroscopic properties, such as electronic conductivity, mobility and diffusion.

Deskins & Dupuis [63] point out that both Marcus and EHAM theories apply the harmonic approximation and use equivalent quantities (activation energy, electronic coupling, reorganisation energy) to derive mathematically equivalent rate formulas. In this work, Marcus theory is used to get kinetic rates for electron transfer between neighbouring lattice sites. These rates are then incorporated into the EHAM framework to calculate macroscopic properties that can be compared to experiment.

Transition state theory. If the transition takes place on a single PES, i.e. an adiabatic process, then transition-state theory (TST) can be applied. It was developed concurrently in the Chemistry community by Eyring and co-workers (referred to as “activated complex theory”) [216] and in the Physics community by Wigner [217]. Here, the latter formulation will be followed. The key concept is the dividing surface, $\ddagger$, which separates the set of atom positions corresponding to the initial state from the rest of the configuration space. The dividing surface necessarily surrounds the initial state and should correspond to a region with low probability. The transition state is the dividing surface with a small thickness so as to include the full number of degrees of freedom in the system. The rate constant is estimated from the following key assumptions: (1) the system remains on the same electronic energy surface, (2) the transition is slow enough for a Boltzmann distribution to be established in all degrees of freedom in the initial state, (3) the displacements of the atoms are described with classical dynamics, and (4) the transition state is only crossed once by a reactive trajectory that starts in the initial state and ends in some final state long enough to reach thermal equilibrium there. If the dividing surface is approximated locally as a hyperplane, the TST expression for the rate constant becomes:

$$k^{\text{TST}} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R} \quad (3)$$

where $\mu_{\perp}$ is the reduced mass corresponding to a displacement of the atoms normal to the hyperplane and Z_S is a configuration integral for a subregion S , $Z_S = \int_S \exp[-E(R)/(k_B T)] dR$. Here S is chosen to be the reactant basin in Z_R or the transition state dividing surface in $Z_{\ddagger}$, and the integrals are carried out over the corresponding hypervolume or hyperplane. TST takes into account the effect of entropy as well as a possible energy barrier for the transition. In fact, it gives an exact estimate for the rate of effusion of an ideal gas through a hole of a container, where the transition state only involves an entropic barrier.

Most often, TST is used within the harmonic approximation where the energy surface of the initial state is approximated by a second order Taylor expansion around the energy minimum of the initial state, and that of the transition state is similarly approximated by an expansion around first order saddle points on the energy rim surrounding the initial state [218]. The harmonic transition-state theory (HTST) expression for the rate constant for transitions through the region near one of the saddle points becomes:

$$k^{\text{HTST}} = \frac{\prod_{i=1}^D \nu_{R,i}}{\prod_{i=1}^{D-1} \nu_{\ddagger,i}} e^{-(E_{\text{SP}} - E_{\text{min}})/(k_B T)} \quad (4)$$

where D is the number of vibrational degrees of freedom, ν denotes vibrational frequency, and E_{SP} and E_{min} denote the energy at the saddle point and initial state minimum. The harmonic approximation can only give a good estimate of the rate if the energy surface is smooth enough for a single energy minimum to characterise well the initial state and a single first order saddle point to represent a hyperplanar transition state. This typically applies to solids and surfaces of solids at not too high temperature.

The key challenge when applying HTST is the identification of the relevant saddle points on the energy surface. When a final state

is specified, the minimum-energy path (MEP) for the transition can be calculated using the nudged elastic band (NEB) method [219]. It starts with some trial path represented by discretisation points, that are referred to as “images” of the system. An optimisation algorithm is then used to bring the images down to the nearest MEP. The distribution of the images along the path is controlled by spring forces acting only between adjacent images. An important aspect of the method is to estimate the tangent to the path at each image and allow only the perpendicular atomic force obtained from the energy surface to act on each image, as well as the parallel component of the spring force. The highest energy image can be driven up to the maximum along the MEP in the climbing-image nudged elastic band (CI-NEB) method [220]. An important aspect of the method is to generate a good trial path and this can be done in several ways, for example using the image-dependent pair potential (IDPP) method and its more recent sequential implementation [221].

A more general method where the final state of the transition is not specified involves climbing up the energy surface starting from the vicinity of the initial state minimum and homing in on a nearby saddle point [222,223]. In this way, unexpected final states and the transition mechanism associated with each one can be discovered. Such calculations are, however, more computationally demanding than CI-NEB calculations and need to be repeated several times in order to sample the various low lying saddle points on the energy rim surrounding the initial state. Since the final state of the transition is not specified, this approach can be used to simulate long timescale thermally induced evolution of the system in the so-called adaptive kinetic Monte Carlo algorithm [224].

4.2. Applications

A selection of atomic scale studies of electron transport and dynamics can be found in Table 3. In the following subsections we will discuss some representative studies of particular interest that demonstrate some of the methods discussed in Section 4.1.

4.2.1. Electron mobility in TiO₂

For some photocatalytic reactions, a mixture of rutile and anatase TiO₂ has been shown to have greater reactivity than either of the two phases on their own. This has been theorised to be due to photo-excited electrons migrating from the anatase to the rutile phase, leading to an excess of holes on the anatase surface thereby increasing its activity. Electron mobility has been shown to be greater in anatase compared with rutile. To better understand this, Deskins & Dupuis [63] investigated electron transport in TiO₂ in the two phases using the DFT+ U approach with a Hubbard U value of 10 eV. The high value of U was chosen in order to match experimental band gap values for both rutile (~3.0 eV) and anatase (~3.2 eV), while also ensuring full localisation of the excess electron. Excess electrons appeared as localised polarons centred on Ti-atoms in the DFT models, resulting in reduced Ti³⁺ (compared with normal Ti⁴⁺).

Electron hopping between two different Ti-atoms in different directions in the bulk was further modelled. The reorganisation energy λ and the electronic coupling V_{AB} were calculated for all of the transport directions considered in order to use them for Marcus theory calculations of electron transport rates. The results of this work [63] showed no significant difference between the two phases in the diabatic activation barriers for electron transport. The electronic coupling was, however, much greater in rutile along the [001] direction than for other transport directions considered, thereby lowering the effective activation energy and giving a higher rate of electron transport in rutile than in anatase. This was attributed to an incomplete description of the system, where structural defects and applied voltages are known to play a significant role in electron transport. The electron transport rate calculated for the [001] direction in rutile was found to be in reasonable agreement with experimental values.

Table 3

Representative atomistic studies of reaction pathways, thermally assisted charge transport, and excited-state carrier and reaction dynamics.

Study	System	Process modelled	Methodology
<i>Reaction pathways</i>			
Migani & Blancafort [68]	Rutile TiO ₂ (110)	Water Oxidation	CI-NEB
<i>Thermally assisted transport</i>			
Rosso & Dupuis [69]	Hematite (α -Fe ₂ O ₃)	Small-polaron reorganisation energetics	Cluster calculations using direct and four-point reorganisation-energy methods
Iordanova et al. [26]	Chromia (α -Cr ₂ O ₃)	Charge transport	Marcus theory
Deskins & Dupuis [63]	Anatase and rutile TiO ₂	Electron transport	Marcus theory, EHAM
<i>Excited state dynamics</i>			
Wei et al. [71]	Mixed phase anatase and rutile TiO ₂	Charge carrier lifetimes	Global-flux surface hopping/FSSH; DISH
Gu et al. [65]	Three anatase/rutile TiO ₂ interfaces	Intraband relaxation and charge separation; electron-hole recombination	FSSH; DISH
Tritsaris et al. [70]	Rutile TiO ₂ (110)/Water Interface	Hole-mediated water splitting	Ehrenfest
Zhang et al. [74]	Hydroxylated BiVO ₄ (010) surface	Charge carrier dynamics	DISH
Cheng et al. [61]	BiVO ₄ with oxygen vacancy	Charge carrier trapping and recombination	DISH
Chen et al. [60]	BiVO ₄ with oxygen vacancy	Charge carrier trapping and recombination	DISH
You et al. [73]	g-C ₃ N ₄ /water interface	Photoexcitation, charge transfer and water dissociation; H diffusion and H ₂ -formation pathways	RT-TDDFT Ehrenfest NAMD; CI-NEB
Agrawal et al. [59]	Pristine g-C ₃ N ₄ and O-at-N, B-at-N and B-at-C substitutional models	Dopant-dependent charge trapping and non-radiative recombination	Time-domain DFT + DISH-NAMD; FSSH comparison
Yang et al. [72]	Pristine and B/O-codoped GCN slabs; heptazine–water clusters	Electron–hole recombination; H-atom photodissociation and proton hopping	DISH-NAMD for slabs; TDDFT-based TSH for clusters
Gumber et al. [66]	Defect-modified and O-doped g-C ₃ N ₄	Charge carrier trapping and recombination	DISH

Abbreviations: climbing-image nudged elastic band (CI-NEB); decoherence-induced surface hopping (DISH); Emin–Holstein–Austin–Mott (EHAM); trajectory surface hopping (TSH).

4.2.2. Polaron mobility in α -Fe₂O₃

Thermally activated charge transport in hematite, α -Fe₂O₃, is commonly described as hopping of small polarons localised on Fe sites. Rosso and Dupuis quantified the internal reorganisation energy associated with such hops [69], and Iordanova et al. subsequently combined reorganisation energies and electronic couplings within Marcus theory to analyse electron and hole mobilities and their crystallographic anisotropy [67].

More recently, Ghosh et al. [64] calculated the MEP for small-polaron migration using the NEB method with electronic structure obtained from DFT+*U*. The activation energy for hops between sites is estimated to be 0.12 eV in close agreement with experimental measurements [225]. The polaron is found to remain localised along the migration path. The migration from bulk to the Fe-terminated hematite (0001) surface was furthermore calculated and its quenching by adsorbed NO₂. Migration towards the surface stabilises the polaron and charge is transferred from the oxide to the admolecule. This eliminates the localised Fe²⁺ polaron so adsorption of NO₂ alters polaron populations and thereby modulates charge transport in hematite, providing a mechanism for chemical sensing.

The DFT+*U* approach does not, however, give a satisfactory description of the various properties that are needed for simulations of photocatalytic activity of metal oxides. The choice of the magnitude of the *U* parameter is quite arbitrary, and a single value can typically not reproduce all the relevant properties. Note that an estimate of the formation energy of metal oxides cannot be obtained since the *U* correction is not appropriate for the pure metal and GGA functionals give a poor estimate of the O₂ binding energy. The formation energy of defects is similarly hard to obtain from DFT+*U* calculations. These issues have, for example, recently been discussed by Chen et al. [38] who make use of experimental estimates in combination with DFT+*U* calculations to establish consistent alignment of chemical potentials.

4.2.3. Charge separation in TiO₂

As mentioned above, mixed anatase/rutile systems have often been shown to have increased photocatalytic activity compared to pure systems of either of the two phases. This is commonly thought to be due to the migration of electrons from anatase to rutile. Experiments, however, have given inconsistent results on the increase in activity and the reported charge carrier lifetimes, differing by orders of magnitude. Gu et al. [65] investigate how the interface between the two phases affects the lifetime of charge carriers.

This work investigated a range of different interfaces between anatase and rutile TiO₂. The interfaces were first screened using DFT to see which ones were thermodynamically stable and three interfaces were identified: (114)_A/(211)_R, (110)_A/(011)_R and (110)_A/(100)_R. NAMD simulations were then performed on these three structures using FSSH to investigate the ease of transport of electrons across the interface. For all three structures the electron transfer from rutile to anatase happened very rapidly, with a relaxation lifetime of < 40 fs for all interfaces.

The electron–hole recombination across the interface was also studied, this time with the DISH method. This was used to calculate the carrier recombination lifetime of the three interfaces studied. This showed that the (114)_A/(211)_R interface had the longest carrier recombination lifetime of 26.2 ns, compared with 6.9 ns for (110)_A/(011)_R and 1.9 ns for (110)_A/(100)_R. This extended lifetime can be explained by the combination of weak NAC and short decoherence times for that interface. This theoretical study provided an explanation for the differing values reported in experiment, highlighting that the type of interface between the two phases plays a key role in the increase in photocatalytic activity.

4.2.4. Hole-mediated water splitting on TiO₂ surfaces

Tritsaris et al. investigated the dynamics of photogenerated holes at the rutile TiO₂(110)/water interface using Ehrenfest dynamics employing the GPAW implementation [209] with real-time propagation

and the PBE+*U* density functional [70]. These simulations provide key insights into the water-splitting mechanism. At the beginning of the process, the hole was found to be almost entirely localised on the water molecule, followed by its dissociation into a surface-bound –OH group at a Ti site. Subsequently, the hole transfers to a subsurface oxygen atom, where its charge distribution resembles a p_z orbital.

The authors also found that water photooxidation strongly depends on the local atomic environment and experimental conditions, and that oxidation to hydroxyl species can occur through a synergy of photoinduced and thermal effects. For the stoichiometric surface, oxidation by a photogenerated hole was not observed for excitation energies near the TiO_2 band gap, because no water-associated electronic states are present close to the valence band maximum of the surface. In contrast, titanium interstitials located beneath the surface enhance water adsorption, lower the activation energy for thermal dissociation, and act as hole-trapping centres until charge transfer to water occurs, thereby promoting its oxidation.

4.2.5. Oxygen vacancies in BiVO_4

BiVO_4 has attracted considerable attention as a photoanode for photoelectrochemical water oxidation because of its favourable optoelectronic properties, including a suitable band gap and strong visible-light absorption [226,227]. Despite these advantages, its performance remains limited by poor charge transport and rapid nonradiative recombination of photogenerated electrons and holes, resulting in efficiencies well below the theoretical limit. To understand the microscopic origins of these losses, Cheng et al. [61] and Chen et al. [60] employed NAMD simulations within the DISH framework, combined with DFT+*U* and RT-TDDFT approaches, to investigate charge-carrier dynamics in pristine BiVO_4 and oxygen-vacancy-containing systems. Both studies showed that neutral oxygen vacancies create localised V^{4+} polaronic states within the band gap that act as efficient charge-carrier traps and recombination centres. These defect states increase nonadiabatic coupling, reduce the effective band gap, and introduce trap-assisted recombination pathways, leading to substantially faster electron–hole recombination than in pristine BiVO_4 . As a result, photogenerated charge carriers are rapidly lost, identifying oxygen-vacancy-induced polarons as a major factor limiting the photoelectrochemical performance of BiVO_4 . Importantly, Cheng et al. further demonstrated that ionisation of the oxygen vacancy eliminates the polaronic trap states and restores carrier lifetimes close to those of the pristine material [61]. Together, these studies establish that the oxidation state of oxygen vacancies critically influences charge-carrier dynamics and highlight defect and polaron engineering as key strategies for improving the efficiency of BiVO_4 photoanodes.

Beyond bulk defect chemistry, the electronic structure and energy-level alignment of BiVO_4 are also highly sensitive to the surface environment, particularly to the degree of hydration and hydroxylation [39, 74]. Building on these insights into the role of oxygen-vacancy-induced polarons, Zhang et al. examined how surface hydroxylation, which develops under water-splitting conditions, modifies the charge-carrier dynamics of the $\text{BiVO}_4(010)$ surface [74]. Using the same combination of DFT+*U*, TDDFT and NAMD simulations within the DISH framework, they demonstrated that hydroxyl groups formed through water dissociation can significantly mitigate the adverse effects of electron polarons. Surface hydroxylation stabilises polarons at the surface, shifts the associated defect states closer to the valence band maximum, and suppresses high-frequency V–O stretching vibrations that strongly contribute to electron–phonon coupling. These changes reduce the NAC responsible for electron–hole recombination and extend charge-carrier lifetimes by up to several orders of magnitude. The study therefore revealed that hydroxyl species generated as reaction intermediates are not merely passive spectators but actively modify the electronic structure and polaron dynamics of BiVO_4 , thereby enhancing photocatalytic performance. More broadly, these findings demonstrate that the impact of polarons on charge-carrier recombination can be controlled through the local chemical environment, providing valuable design principles for improving metal-oxide photoelectrodes.

4.2.6. Doping and defects in C_3N_4

Fully organic photocatalytic systems have also attracted considerable attention for photocatalytic applications, particularly graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [228]. As a π -conjugated semiconductor, $\text{g-C}_3\text{N}_4$ has emerged as a promising visible-light photocatalyst owing to its low cost, chemical stability, low toxicity, and suitable electronic band structure. NAMD simulations based on RT-TDDFT revealed the transport pathway of photogenerated charge carriers at the $\text{g-C}_3\text{N}_4/\text{H}_2\text{O}$ interface for water splitting [73]. The mechanism proceeds through sequential photoexcited electron–hole generation, photocarrier transport, hole-driven hydrogen transfer from interfacial water, and finally hydrogen gas evolution through H–H recombination.

To enhance $\text{g-C}_3\text{N}_4$ photocatalytic performance, a range of modification strategies have been investigated, including morphology engineering, molecular incorporation, doping, and defect engineering. Doping with non-metallic elements, including O, N, C, P, and B, seems to be effective in improving the catalytic activity of these materials [59,66,72,229]. NAMD simulations have also provided valuable molecular-level insight into the influence of these modifications on the excited-state behaviour of $\text{g-C}_3\text{N}_4$ [59,66,72]. RT-TDDFT simulations using the PBE functional showed that $\text{g-C}_3\text{N}_4$ containing N-vacancy and CN-group defects, as well as the corresponding O-doped system, exhibits three defect-induced midgap states [66]. These states are localised on the defect-containing tri-s-triazine unit and play a dual role in the excited-state dynamics. While they promote photoinduced charge separation, which is beneficial for photocatalytic activity, they also act as carrier traps and recombination centres that accelerate nonradiative relaxation. Consequently, the defects reduce charge-carrier lifetimes to the tens-of-picoseconds timescale. However, recombination is significantly suppressed in the O-doped system, leading to carrier lifetimes that are approximately five times longer than in the N-vacancy/CN-defective material. This behaviour provides a mechanistic explanation for the enhanced photocatalytic degradation of pollutants observed experimentally. Similar NAMD simulations have shown that boron doping in $\text{g-C}_3\text{N}_4$ enhances photocatalytic activity by promoting efficient charge separation and extending charge-carrier lifetimes through slower recombination [59].

Yang et al. investigated ultrafast hydrogen evolution in B/O-codoped $\text{g-C}_3\text{N}_4$ using both periodic slab and molecular cluster models. Their slab simulations showed that the codoped material promotes more efficient charge separation and exhibits a longer electron–hole recombination lifetime than pristine $\text{g-C}_3\text{N}_4$, with recombination occurring on a 29.43 ns timescale compared to 17.97 ns in the undoped material. Their cluster simulations also showed a higher probability of PCET within the first 100 fs, together with faster radiationless relaxation in the B/O-codoped system, helping to explain its enhanced photocatalytic hydrogen-evolution activity [72].

5. Mesoscopic kinetic-level studies

5.1. Methods

5.1.1. Kinetic Monte Carlo and stochastic kinetic modelling

Stochastic kinetic models such as kMC methods capture the intermediate scale (meso-scale) between electronic-/atomistic-level calculations and macroscopic device or reactor observables [230–233]. Their defining feature is the simulation of large numbers of discrete events in space and time. These events can be photon absorption, electron–hole pair generation and recombination, polaron trapping/de-trapping and diffusion, as well as chemical species adsorption, desorption, diffusion and reaction [230,231,233]. The state space of the system is a discrete set with each state representing the configuration of adsorbates on a lattice of active sites and the location/identity of carriers (electrons, holes and trapped charges). The state evolves based on the computed rate for each possible event. Under the Markovian assumption, the trajectories are therefore coarse-grained representations of the long-time

electronic/atomistic dynamics of the system [230,231,233], enabling the connection of micro-scale phenomena with experimentally measured rates, activities, selectivities, and transients. Unlike mean-field rate equations, stochastic kinetic approaches are able to resolve spatial inhomogeneity, transport limitations, finite particle size, multi-site adsorbates, lateral interactions and statistical fluctuations that often control apparent kinetics [232,233].

Several methodological choices determine the fidelity and cost of a kMC simulation. The surface or material morphology must first be mapped onto a lattice, graph or particle network [232,233]. The elementary events and associated rate expressions must then be defined, together with how the event rates depend on the local chemical environment [233]. In realistic catalytic systems, adsorbate–adsorbate interactions can strongly affect reaction energies and, through detailed balance, the corresponding activation barriers. These effects are often represented by combining an energetic model for the local environment, such as a cluster-expansion Hamiltonian, with Brønsted–Evans–Polanyi (BEP) relations that map changes in reaction energy onto changes in activation energy [233–235].

While the kMC approach is quite mature for thermocatalytic reaction simulation, as evidenced by the wide adoption of well maintained simulation codes [236–239], photocatalytic reactions entail additional processes and sources of complexity that require further methodological development. Existing frameworks that incorporate descriptions of light–matter interactions exist, e.g. the Bumblebee code [84] for simulating organic light-emitting diode (OLED) devices, and such frameworks can be further developed or integrated into chemistry-driven kMC for comprehensive simulations of photocatalysts.

5.1.2. Computational challenges: stiffness and acceleration

A particularly important methodological issue for photocatalytic kMC is temporal stiffness. In thermal heterogeneous catalysis, stiffness commonly arises when fast diffusion events occur several orders of magnitude more frequently than slow surface reactions that control the turnover frequency [233]. An analogous, and arguably more fundamental, problem arises in photocatalysis because electronic or polaronic processes and surface chemical reactions naturally occur on very different time scales. Polaron hopping, charge migration, trapping and de-trapping may be rapid and locally quasi-equilibrated, whereas interfacial electron transfer, PCET, bond scission or bond formation, product desorption or multi-electron catalytic turnover can be much slower. A direct kMC simulation that treats all these processes on the same footing may therefore spend most of its computational effort sampling fast charge-transport events, while the rare surface reaction or recombination events that determine the quantum yield, selectivity or photocurrent are sampled only infrequently. A useful mesoscale simulation approach must therefore preserve the kinetic competition between transport, recombination and reaction, without becoming overburdened by repeated sampling of quasi-equilibrated charge-transport events.

Channel-based stiffness-scaling schemes provide one possible route for alleviating temporal stiffness in kMC simulations [106,107]. In these approaches, quasi-equilibrated fast and reversible event channels are identified from their event statistics, and their rate constants are dynamically rescaled so that they remain faster than the slower non-quasi equilibrated event channels but no longer dominate the simulation. By reducing the computational effort spent sampling kinetically uninformative events, these methods can substantially accelerate simulations while preserving the essential competition between charge-carrier generation and recombination, transport and reaction. Recent developments have generalised this concept to complex graph-theoretical kMC models involving multiple site types, large reaction networks and strong lateral interactions [107].

The underpinning approximation is based on the concept of a superbasin: a cluster of kMC states connected through fast transitions, while transitions between states belonging to different superbasins are slow.

Accelerated-superbasin kMC modifies the rates of frequently occurring intrabasin processes in such a way that the frequency of these processes is lowered (hence the computational savings) but the rate of escaping the superbasin is practically unaffected by this approximation [105]. Alternative approaches based on the theory of absorbing Markov chains and basin-finding approaches classify states as transient (those within a superbasin of interest) and absorbing (states in any other superbasin), and use this information to estimate escape probabilities and residence times more efficiently than direct simulation [108]. These methods are particularly useful when the kinetics are dominated by long sequences of reversible transitions separated by relatively rare escape events.

Stiffness-scaling approaches are computationally efficient and readily applicable to evolving reaction networks, but introduce a controlled approximation and therefore require validation against unscaled (or at least, less aggressively scaled) calculations where possible. Superbasin-based and absorbing-Markov-chain approaches can provide higher fidelity descriptions of metastable dynamics, but generally require identification and analysis of the underlying basin structure. Both classes of methods are likely to be important for realistic photocatalytic kMC models that combine fast polaron transport, trapping and recombination processes with slower multi-step surface reaction networks.

5.1.3. Photo(electro)catalysis-specific considerations

A second methodological challenge is the fidelity of the spatial representation. The surface or material morphology can be represented at different levels of complexity, ranging from idealised lattices to explicit nanoparticle geometries and mesoporous particle networks. Recent random-walk Monte Carlo models have moved beyond simplified lattice descriptions towards physically realistic three-dimensional representations in which charges or molecular redox states migrate over the surface of spherical nanoparticles, across interconnected particle assemblies, or through mesoporous films [30,31]. In such models, neighbour lists, surface curvature, film depth, optical attenuation and interparticle neck regions become part of the kinetic description rather than post-processing corrections. This spatial realism is particularly important for PEC systems. Light absorption is depth-dependent, so the initial distribution of photogenerated carriers may vary along the illumination direction. Recombination and catalytic turnover depend on how far photogenerated charges must travel before reaching a reactive interfacial site or catalytic centre. The spatial distribution of catalytic sites can also be highly nonuniform. The same overall catalyst loading can lead to different kinetic outcomes depending on whether catalytic centres are isolated, clustered, located near the illuminated surface, or buried within a porous network. Three-dimensional random-walk and kMC implementations can therefore capture effects that would be averaged out in mean-field or highly simplified lattice models, including local charge accumulation, spatially heterogeneous recombination, interparticle transport bottlenecks and the probability of accumulating multiple redox equivalents at a catalytic centre [30,31]. The cost is more elaborate bookkeeping, larger state spaces and more demanding convergence requirements, which further connects the challenge of implementing high-fidelity 3D representations of the simulation domain to the stiffness problem discussed above.

A further complication is the treatment of non-local electrostatic interactions. Photocatalytic and photoelectrochemical systems involve charged species, including polarons, trapped carriers, ionised defects, charged adsorbates and electrolyte ions, whose Coulomb interactions may extend well beyond the immediate coordination environment. On the timescale of the process considered, the bound-charge dielectric response of the solid and electrolyte – including electronic, lattice and solvent polarisation – renormalises these interactions but does not by itself make them short-ranged. Redistribution of sufficiently mobile electronic carriers in the solid and ions in the electrolyte can provide additional free-charge screening through space-charge and double-layer

formation [129]. Although modern kMC methods can incorporate interactions beyond nearest neighbours, the computational cost increases substantially as the effective interaction range grows, particularly when dynamic many-body electrostatic interactions are considered. These interactions may influence carrier transport, trapping, recombination and interfacial charge transfer, and therefore represent additional numerical challenges for predictive mesoscale modelling. Explicit Coulomb treatments have been demonstrated in kMC models of charge transport in organic semiconductors and electrochemical interfaces, where hopping rates depend on the many-body electrostatic energy landscape [28]. In polaronic oxide photoelectrodes, by contrast, dopant-polaron interactions have more often been incorporated through DFT-derived local energetics and hopping barriers rather than as fully dynamic many-body electrostatic treatments [102].

The methodological considerations discussed above are reflected in the diverse mesoscale and multiscale models developed for photocatalytic and photoelectrochemical systems. Although these models differ in physical scope, numerical implementation and degree of coarse-graining, they can all be viewed as upscaled representations of selected elementary processes outlined in Section 2. A useful way to compare them is to identify which quantities are propagated explicitly and which processes are described by effective rates, boundary conditions or fitted parameters. The explicit variables may range from optical excitation profiles and carrier or trap populations to surface coverages, molecular redox states, ion/defect concentrations, and reactor-scale quantities such as local composition, temperature and flow. This modelling choice determines whether the emphasis falls on excitation, charge carrier transport, surface charge accumulation, surface chemistry, material evolution or reactor-scale transport. Table 4 summarises representative studies from this perspective.

5.2. Applications

5.2.1. Surface reaction kinetics with simplified photo-physics

At the surface-reaction end of mesoscale modelling, the aim is often not to resolve the full sequence of photo-induced and thermally activated physicochemical events, but to understand how illumination, photogenerated charges or photon-triggered events modify the stochastic evolution of a catalytic reaction network. In such models, the propagated state variables are usually adsorbate configurations, surface intermediate populations, surface charge or hole states, or lumped chemical-species populations. Photon absorption, carrier generation, migration, trapping, recombination and interfacial charge transfer are treated implicitly, phenomenologically, or through effective photoactivation steps rather than being resolved as separate charge generation and transport processes. This level of coarse-graining is useful for identifying surface-kinetic bottlenecks, coverage effects, reaction-network branching, non-equilibrium steady states, and the kinetic consequences of stochastic photon arrival.

Following this approach, Sinha et al. developed a multiscale model for the OER at the hematite–water interface by coupling DFT+*U*, DFT-MD and lattice kMC simulations [98]. The study did not explicitly describe photon absorption, electron–hole generation or hole transport and supply through the semiconductor. Instead, the imposed electrode potential enters the electrochemical free energies and potential-dependent rate constants of the PCET steps. The mesoscale state variable was therefore the surface configuration of OER intermediates (*H₂O, *OH, *O and *OOH), which is propagated using kMC with DFT+*U*-derived reaction energetics and a constrained-DFT-MD proton-transfer barrier, assumed for the remaining proton-transfer steps. The simulations showed that *OH accumulates on the hematite surface, identifying the *OH → *O conversion as both the potential-limiting and kinetically rate-limiting step. Although the model does not resolve the preceding photophysical processes, it demonstrates how stochastic surface-intermediate populations govern potential-dependent interfacial OER turnover under the imposed electrode-potential boundary condition.

Still within the framework of phenomenological stochastic reaction-network modelling, Pahlevanpour and Bashiri developed a Gillespie stochastic reaction-network model for photocatalytic hydrogen production from water–methanol mixtures over Au/TiO₂ [92] and Ni/TiO₂ [93] photocatalysts. The models include photogeneration of electron–hole pairs, explicit electron–hole recombination, adsorption of H₂O and CH₃OH, hole-driven oxidation of adsorbed water or methanol, proton adsorption/reduction, H₂ formation, and methanol-derived oxidation pathways to CO₂. Recombination was treated as a lumped stochastic reaction event, $h^+ + e^- \rightarrow \text{light/heat}$, rather than as spatial carrier encounter or trap-mediated loss. The system state was therefore described by time-dependent populations of chemical species and active sites, while photon absorption, carrier transport, trapping, interfacial charge separation and spatial heterogeneity were not resolved. These studies are useful as fitted stochastic reaction-network descriptions for analysing how photogeneration, recombination, sacrificial-agent chemistry and surface-site availability influence apparent H₂ evolution rates, but their predictive scope is limited by phenomenological rate constants adjusted to experimental concentration–time data.

Aiming at assessing the potential benefits of dynamic photo/thermal surface catalysis, Roy et al. combined DFT+*U* calculations with lattice kMC simulations to investigate photocatalytic nonoxidative methane coupling (NOCM) on rutile TiO₂(110) under sequential photo- and thermo-catalytic operation [96]. Unlike phenomenological photocatalytic reaction-network models, the photochemical activation step was treated explicitly by introducing photogenerated hole polarons on surface O_{2c} sites. DFT+*U* calculations showed that these hole polarons fundamentally alter the reaction mechanism, promoting homolytic CH₄ activation and lowering the activation barrier by about 70% relative to the thermocatalytic pathway, while also dramatically reducing the barrier for subsequent C–C coupling. The rates estimated from the DFT energetics were then incorporated into a kMC model based on a Ti_{5c}/O_{2c} surface lattice, with elementary events including light irradiation, CH₄ photoactivation, C–C coupling, hydrogen diffusion and H₂ formation. The simulations showed that under ultraviolet (UV) irradiation at 315.15 K, CH₄ activation and ethane formation proceed readily, but the catalyst surface becomes poisoned by accumulated H* species because hydrogen diffusion and H₂ formation remain kinetically inaccessible at room temperature. Switching off the light and subsequently increasing the temperature to approximately 690 K activates hydrogen evolution and regenerates the O_{2c} active sites, completing the catalytic cycle. Rather than treating photo- and thermocatalysis as competing processes, this work demonstrates how they can be combined within a single lattice kMC framework to identify sequential operating conditions that overcome kinetic bottlenecks.

From a more generic kinetic perspective, Canavan and Dauenhauer recently formulated kMC and MK models of photon-promoted surface catalysis, using a minimal A(g) → B(g) reaction through A* and B* intermediates [78]. Illumination was represented by a site-normalised photon arrival frequency, f_{arrival} , which opens an additional photodesorption channel, $B^* + h\nu \rightarrow B(g) + *$, in competition with thermal adsorption, surface reaction and desorption. The model shows that photon-promoted desorption can move a desorption-limited catalyst above its dark Sabatier behaviour, but only until $A^* \rightarrow B^*$ becomes the limiting step. As f_{arrival} increases, the system passes from a thermal-desorption-controlled regime, through a photon-arrival-controlled regime, to a surface-reaction-controlled regime. The maximum effective rate occurs when the photon arrival frequency matches the relevant surface kinetic rate constant, providing a simple mesoscale interpretation of catalytic resonance, near-zero apparent activation barriers under photon-controlled conditions, and light-driven non-equilibrium conversion.

Table 4
Representative mesoscale and multiscale models discussed in Section 5.2.

Study	System	Main state variables and fields	Processes and couplings represented	Methodology
<i>Surface reaction kinetics with simplified photophysics</i>				
Sinha et al. [98]	Hematite photoanode (OER)	Surface intermediate occupation configuration (*H ₂ O, *OH, *O, *OOH)	Potential-dependent PCET reaction network and surface intermediate population dynamics	DFT+ <i>U</i> thermodynamics + DFT-MD proton-transfer barrier + lattice kMC
Pahlevanpour and Bashiri [92,93]	Au/TiO ₂ and Ni/TiO ₂ photocatalysis	Time-dependent populations of surface and solution species	Photogeneration, lumped recombination, adsorption, surface reactions and H ₂ evolution	Gillespie stochastic reaction-network simulation with fitted rate constants
Roy et al. [96]	Nonoxidative methane coupling on rutile TiO ₂ (110)	Surface adsorbate configuration and surface hole-polaron states	CH ₄ photoactivation, C–C coupling, H diffusion, H ₂ formation and sequential photo-thermal operation	DFT+ <i>U</i> energetics + lattice kMC
Canavan and Dauenhauer [78]	Generic photon-promoted surface catalysis	Single-site occupation state (*, A*, B*) and site-normalised photon arrival frequency f_{arrival}	Reversible adsorption, surface reaction and desorption; selective photon-promoted desorption $B^* + h\nu \rightarrow B(g) + *$; photon-arrival statistics and non-equilibrium conversion	Variable-time-step kMC and MK modelling; fixed-time-step kMC for Poisson, perfectly spaced and coordinated photon streams
<i>Charge generation, transport and accumulation</i>				
Hammerschmidt et al. [82]	Faceted anatase TiO ₂ nanoparticles for CO ₂ reduction	Spatial photon absorption field, surface electron density and adsorbate coverages	Optical-field heterogeneity, spatially varying carrier supply and surface reaction kinetics	Electromagnetic simulation + reduced electron-density model + lattice kMC
Wang et al. [33]	NaYF ₄ @semiconductor core-shell nanoparticles	Photon packet statistics and carrier collection probabilities	NIR photon propagation, scattering, upconversion emission, photon absorption and carrier diffusion	Monte Carlo radiative transport + carrier diffusion model
Liu et al. [89]; Wu and Ping [102]; Pasumarthi et al. [94]	Pristine and W/Mo-doped BiVO ₄	Polaron occupations on crystallographic hopping networks	Small-polaron hopping, dopant-modified site energies and network-controlled carrier mobility	DFT+ <i>U</i> hopping energetics + Marcus/Landau-Zener rate theory + lattice kMC
Liu et al. [85–88,90]; Wang et al. [101]	Nanoparticulate TiO ₂ assemblies	Individual electron transport/trapping states, trap populations and quasi-Fermi level	Multiple trapping/detrapping, diffusion, interfacial transfer, recombination and trap-filling dynamics	Random-walk Monte Carlo + quasi-equilibrium/trap-DOS transport models
Tkaczibson and Ardo [30,31]	Dye- and cocatalyst-modified semiconductor nanoparticles	Redox-state configuration of surface-bound dyes and electrocatalysts	Photoexcitation, lateral self-exchange charge hopping, recombination, catalyst charging and catalytic turnover	Discrete-time random-walk Monte Carlo
<i>Integrated transport-reaction coupling</i>				
Ansari-Rad [75]	Dye-sensitised mesoporous TiO ₂ photoelectrodes	Oxidised dye population and spatial distribution of reducing redox species in electrolyte-filled pores	Redox-species diffusion, long-range dye regeneration and electron-dye recombination	Spatial kMC with Marcus-type distance-dependent electron transfer
Zhu et al. [29]	Semiconductor photocatalysts for CO ₂ conversion	Carrier populations and surface reaction intermediates/products	Photon absorption, carrier transport, trapping/detrapping and recombination; phenomenological carrier-to-cocatalyst transfer followed by CO ₂ -reduction and competing H ₂ -evolution kinetics	Multiple-trapping random walk + one-way handoff to surface-reaction kMC
Maestri and Cuoci [91]	Heterogeneous catalytic reactors	Gas-phase fields and mean surface coverages	Flow, heat and mass transport coupled to surface reaction kinetics	CFD + mean-field surface MK modelling
<i>Photoinduced material evolution</i>				
Ruth et al. [32]; Ruth and Kuno [97]	Mixed-halide perovskites under illumination	Halide composition, vacancy distribution and photocarrier occupation statistics	Vacancy-mediated ion migration, photosegregation, carrier localisation and composition-carrier feedback	Lattice kMC with composition-dependent optical/electronic feedback

Abbreviations: computational fluid dynamics (CFD); density functional theory (DFT); density-functional-theory-based molecular dynamics (DFT-MD); density of states (DOS); kinetic Monte Carlo (kMC); microkinetic (MK); near-infrared (NIR); oxygen evolution reaction (OER); proton-coupled electron transfer (PCET).

5.2.2. Charge generation, transport and accumulation

Unlike the reaction kinetics models discussed above, the following studies explicitly treat photogenerated charge carriers as the primary mesoscale state variables. Depending on the material system, these state variables may represent spatially resolved photogenerated carrier densities, localised polarons, trap-state populations, or discrete surface charges. Collectively, these models describe the evolution of photogenerated carriers from their creation, through transport within the semiconductor, to their accumulation at reactive sites, thereby revealing how charge dynamics rather than surface chemistry alone can become the dominant kinetic bottleneck controlling photocatalytic activity.

Focusing first on charge creation via optical excitation, a common assumption in many photocatalytic kinetic models is spatially uniform excitation, i.e., that all surface sites experience the same photon

absorption rate and therefore the same carrier supply. However, Hammerschmidt et al. [82] showed computationally that even for a single semiconductor nanoparticle this assumption can fail. By coupling electromagnetic wave simulations with kMC modelling of CO₂ reduction on faceted anatase TiO₂ nanoparticles, it was demonstrated that nanoscale field heterogeneities generate strongly non-uniform photon absorption profiles, which propagate into laterally varying electron densities, surface coverages and local turnover frequencies, as illustrated in Fig. 6(A). The resulting spatial heterogeneity in the activity was sufficiently strong that different regions of the same facet could operate in different kinetic regimes and exhibit different rate-controlling steps. At the particle level, a trade-off between activity and efficiency was observed: resonant particle sizes displayed higher average turnover frequencies but lower efficiencies because a larger fraction of absorbed photons generated carriers in the bulk rather than near reactive surface sites.

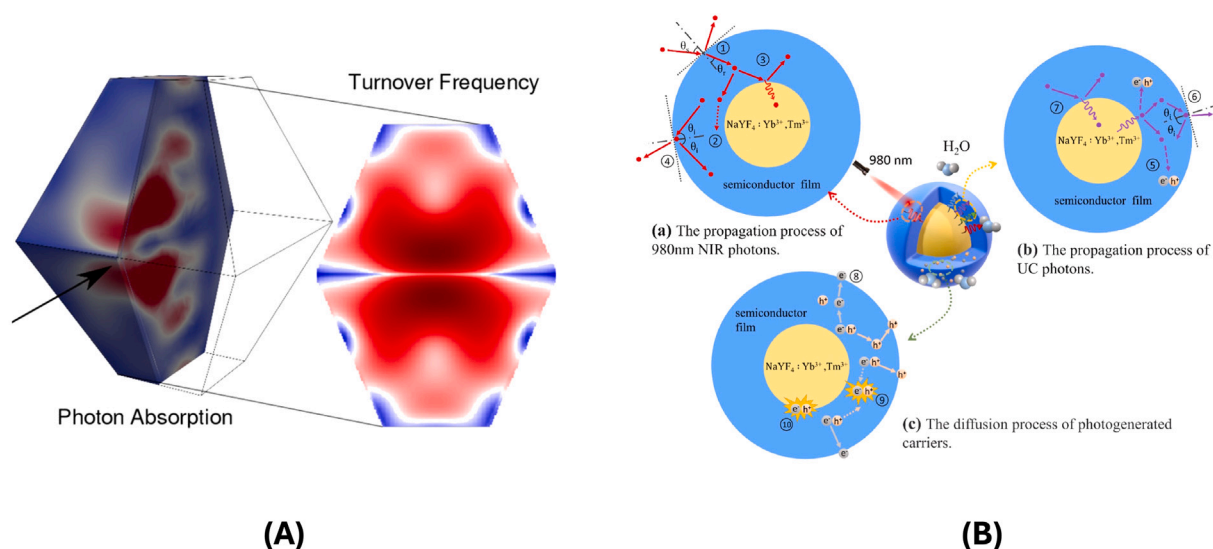


Fig. 6. Representative mesoscale approaches for incorporating spatially heterogeneous optical excitation in photocatalytic materials. (A) Coupling of electromagnetic wave simulations with kMC surface chemistry reveals how non-uniform photon absorption within a semiconductor nanoparticle produces spatial variations in surface electron density, local turnover frequency and reaction mechanism. (B) Monte Carlo radiative-transfer modelling of upconversion core-shell photocatalysts explicitly tracks NIR photon propagation, upconversion emission, photon absorption and photogenerated-carrier diffusion to quantify photoelectric conversion efficiency.

Source: (A) Reproduced with permission from the graphical abstract of Ref. [82]. Copyright © 2020 American Chemical Society. Permission conveyed through Copyright Clearance Center, Inc. (B) Reproduced with permission from Fig. 1 of Ref. [33]. Copyright © 2023 Elsevier B.V.

The study highlighted that experimentally observed rates represent spatial averages over highly heterogeneous local kinetics, implying that mechanistic conclusions derived from averaged observables should be interpreted with care [82].

As an alternative approach to describing light through a continuum electromagnetic field, Wang et al. [33] developed a stochastic framework by explicitly treating photon packets as particles. Using the Monte Carlo method, the light transmission and absorption were coupled with the carrier diffusion, allowing simulation of NIR photon propagation, upconversion emission, and subsequent photoelectric conversion in NaYF₄@semiconductor core-shell nanoparticles, as illustrated in Fig. 6(B). Photon free paths were sampled from exponential Beer-Lambert attenuation statistics, and scattering events were described using the Henyey-Greenstein phase function to account for anisotropic angular redistribution. Each photon packet carries a statistical weight that is reduced upon absorption events. NIR photons absorbed in the NaYF₄ core generate upconversion emission, and the emitted photons are subsequently tracked through the semiconductor shell using the same stochastic radiative-transport formalism. The simulations quantitatively demonstrated how shell thickness, refractive-index contrast, scattering strength, and carrier diffusion length jointly determine optimal structural parameters for maximising conversion efficiency.

Once photogenerated carriers are created, their migration through the semiconductor frequently becomes the dominant kinetic bottleneck preceding interfacial charge transfer. Existing mesoscale models describe this transport using different state variables depending on the underlying transport mechanism. In materials such as BiVO₄, where carriers localise as small polarons, transport is naturally represented as stochastic hopping between discrete lattice sites. In contrast, transport in nanoparticulate TiO₂ has traditionally been described using trap-mediated transport, in which the evolving occupation of sub-bandgap trap states governs carrier mobility and lifetime.

To describe hole-polaron transport in monoclinic BiVO₄, Liu et al. [89] constructed a crystallographic hopping network from DFT+*U* calculations. Symmetry-inequivalent hopping pathways were identified, activation barriers were computed from PESs, and temperature-dependent hopping rates were evaluated using Marcus charge-transfer

theory before being propagated by lattice kMC. This enabled macroscopic diffusion coefficients and mobilities to be extracted from rate theory with energetics obtained with DFT without fitted transport parameters. The simulations demonstrated that although rapid intra-tetrahedral hopping occurs within individual VO₄ units, macroscopic mobility is controlled by much slower inter-tetrahedral hopping across Bi-O bridges, so the effective activation energy reflects the slowest percolating transport pathways rather than the lowest individual hopping barrier. Wu and Ping [102] subsequently refined the hopping-rate description by replacing Marcus theory with Landau-Zener charge-transfer theory, thereby explicitly incorporating electronic coupling between diabatic polaron states to account for intermediate adiabaticity. Pasumarthi et al. [94] further extended the Marcus/Holstein model to W- and Mo-doped BiVO₄, finding little change in hopping barriers or mobility and a conductivity increase driven mainly by additional electron carriers.

A complementary description was developed for TiO₂, where photogenerated electrons undergo multiple trapping and detrapping events rather than discrete polaron hopping. Liu et al. developed stochastic random-walk Monte Carlo models based on the multiple-trapping description of electron transport to investigate carrier transport, interfacial electron transfer and recombination in TiO₂ nanoparticle assemblies [85–87]. In these models, the system state is defined by the instantaneous transport and trapping states of individual electrons, which evolve through diffusion, trapping, detrapping, recombination and interfacial transfer events. Ensemble averages of the resulting stochastic trajectories yield the evolving trap-state population, while under rapid trapping–detrapping conditions the carrier distribution can be represented by a quasi-equilibrium trap population characterised by a quasi-Fermi level, enabling reduced analytical transport models. These studies showed that dispersive transport, relaxation kinetics and carrier mobility emerge from the combined effects of trap energetics, nanoparticle connectivity and geometry, with recent work reporting approximately $\tau \propto R^2$ scaling consistent with diffusion-controlled transport to interfacial recombination sites [101]. Here τ is the electron recombination time and R is the particle radius. While continuum multiple-trapping models have long dominated descriptions of charge transport in TiO₂, DFT+*U* studies [63] also support a small-polaron

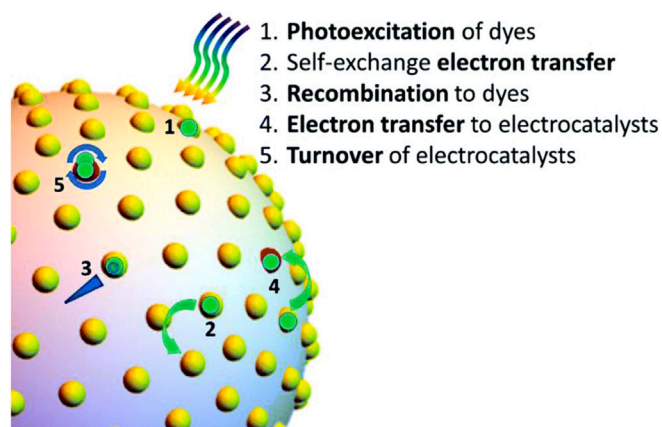


Fig. 7. Monte Carlo framework for modelling surface charge accumulation on dye-sensitised semiconductor nanoparticles through photoexcitation, charge hopping, recombination, catalyst charging and catalytic turnover.

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picture in which electrons localise on Ti sites and migrate by thermally activated hopping, a description that has been coupled to lattice kMC in rutile TiO_2 battery models [104].

Finally, many photocatalytic transformations require multiple photogenerated charges to accumulate at the same catalytic centre before turnover can occur. To study this problem, Tkaczibson and Ardo developed discrete-time random-walk Monte Carlo models that they applied to dye-sensitised semiconductor nanoparticles bearing surface-bound redox-active electrocatalysts [30,31]. In these models, the mesoscale state variable is the redox-state configuration of surface-bound dyes and electrocatalysts, together with the corresponding charge population in each TiO_2 nanoparticle, as illustrated in Fig. 7. The transport of injected electrons and holes within the TiO_2 nanoparticle was not explicitly simulated; instead, photoexcitation was assumed to produce oxidised/reduced dye molecules with unit quantum yield, after which the stochastic evolution of surface-bound molecular charges was propagated through self-exchange electron transfer, recombination with the semiconductor support, and electron transfer to electrocatalysts. The 2019 study [30] showed that multi-electron turnover is governed by the competition between lateral surface hopping and recombination, captured largely by the ratio $\tau_{\text{recomb}}/\tau_{\text{hop}}$, and that pulsed excitation can generate charge-population statistics that differ from those under continuous illumination when multiple redox equivalents are required. The 2020 follow-up work [31] introduced touching, necked, rod-like and clustered particle assemblies to allow interparticle charge transport, showing that unoccupied molecular sites and local molecular connectivity can strongly affect charge accumulation, while the full three-dimensional geometry is often less important than the number and continuity of adjacent molecular sites. Together, these studies identify surface charge accumulation as a distinct mesoscale bottleneck: photocatalytic turnover is determined not only by intrinsic charge-transfer rates, but by the probability that multiple charges reach the same catalytic site before recombination.

5.2.3. Integrated transport–reaction frameworks

The studies discussed above isolate different parts of the photocatalytic sequence. In operating photocatalytic and photoelectrochemical systems, however, these processes are coupled. Charge carriers that survive transport determine the probability of interfacial electron transfer, while surface reactions and electrolyte-side mass transport determine whether these charges are productively consumed, recombine, or remain kinetically inaccessible. Integrated stochastic frameworks

therefore aim to connect carrier dynamics, interfacial transfer, electrolyte transport and surface chemistry within a single probabilistic description.

In this context, Ansari-Rad developed a spatial kMC model to investigate dye regeneration kinetics in dye-sensitised solar cells by explicitly coupling long-range interfacial electron transfer with diffusion of reducing redox species in the electrolyte [75]. The mesoscale state variables comprise the population of oxidised dyes on the TiO_2 surface and the spatial distribution of mobile reducing species in the electrolyte-filled pore space. Dye regeneration is described by a Marcus-type distance-dependent electron-transfer rate, while the reducing species undergo stochastic diffusion before regenerating oxidised dyes. The simulations showed that regeneration is initially governed by the intrinsic long-range electron-transfer rate, whereas at later times depletion of nearby reducing species makes electrolyte diffusion increasingly important, giving rise to stretched decay kinetics. Consequently, apparent regeneration rate constants extracted from transient absorption measurements depend not only on intrinsic electron-transfer kinetics but also on electrolyte transport and donor depletion, illustrating how interfacial transport and reaction become inseparable at the mesoscale.

Aiming at an integrated description of carrier transport and surface reactivity, Zhu et al. developed a probabilistic framework for photocatalytic CO_2 conversion by coupling charge-carrier dynamics with surface reaction kinetics [29]. In this model, photon absorption generates electron–hole pairs, carriers undergo random transport with trapping, detrapping and recombination, and the ratio of surface to total electron density provides a phenomenological electron-transfer probability that multiplies the elementary rates in the kMC reduction module, as illustrated in Fig. 8. This is a one-way handoff: the surface-reaction module does not return a carrier-consumption flux to the carrier model. The framework therefore links light absorption, carrier survival, active-site capture and multi-electron CO_2 reduction within a single stochastic description. A central implication is that, although the stoichiometric electron number in $\Delta G = -nFE$ remains fixed by the target CO_2 reduction product, the probability of completing the corresponding multi-electron transfer event is governed by stochastic carrier generation, transport, recombination, interfacial transfer and reactant supply. Using $\text{g-C}_3\text{N}_4/[\text{Co}(\text{bpy})_3]^{2+}$ as a validation system, the model reproduced activity trends associated with defect density, band-potential alignment and solvent-dependent CO_2 availability, highlighting the need to balance carrier-transfer probability with intrinsic surface reaction kinetics.

At the outer scale, local kinetic models must be embedded in continuum descriptions of the operating environment. In the methodologically analogous thermocatalytic CatalyticFOAM framework, Maestri and Cuoci coupled mean-field surface MK kinetics to CFD, allowing local composition, temperature and flow and the resulting surface rates to be solved self-consistently [91]. This architecture illustrates the local-state–response-flux exchange defined in Section 2.3, but extension to photo(electro)catalysis would additionally require radiative and carrier-state inputs to the surface kinetics and the return of interfacial charge-transfer and reaction fluxes to the device or reactor balances.

5.2.4. Light-induced material evolution and degradation

The frameworks discussed above generally assume that the photoactive material remains structurally fixed while carrier populations and surface reactions evolve. In many photoactive semiconductors, however, illumination can also drive defect migration, ion redistribution and phase segregation. Such changes are important because they continuously modify the electronic landscape experienced by photogenerated carriers, thereby altering carrier transport, recombination and ultimately photocatalytic performance.

Mixed-halide perovskites provide a clear example. Ruth et al. combined kMC simulations with optical measurements to investigate light-induced halide segregation in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ [32]. Halide ions migrate through vacancy-mediated hopping, while photogenerated carriers preferentially occupy lower-band-gap I-rich regions, creating a feedback between carrier localisation and ion migration. The simulations

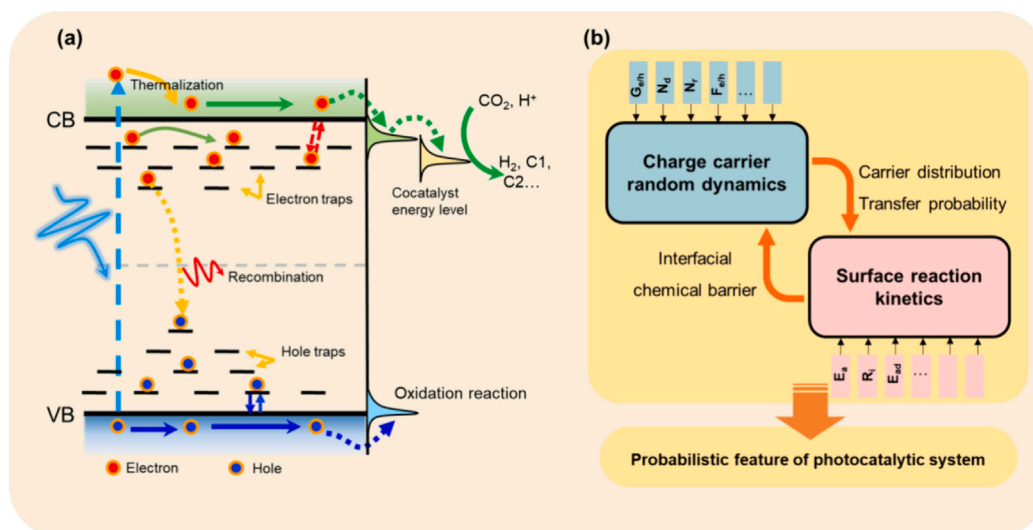


Fig. 8. Integrated probabilistic framework for photocatalytic CO₂ conversion, coupling charge-carrier random dynamics with kMC surface reaction kinetics. Source: Reproduced with permission from Fig. 2 of Ref. [29]. Copyright © 2025 American Chemical Society. Permission conveyed through Copyright Clearance Center, Inc.

reproduced experimentally observed segregation kinetics and showed that vacancy concentration controls the rate of photosegregation. Subsequent work further demonstrated that carrier statistics influence the evolution of the segregated domains and the resulting electronic structure during illumination [97]. Although demonstrated for perovskites, these studies highlight a broader challenge for photocatalysis: under prolonged illumination, the material itself may evolve, requiring mesoscale models to couple carrier dynamics with the evolution of the material state.

6. Theoretical priorities for photo(electro)catalysis

Photo(electro)catalytic technologies are now timelier than ever, in the context of solar powered production of fuels and chemicals from sustainable resources such as water and atmospheric gases, as well as CO₂ as a waste product to be recycled. Towards this end, intense experimental research efforts are already underway and roadmaps outlining the research needs and steps towards adoption in broad-scale applications have been proposed [240–242]. Theoretical and computational research is advancing rapidly, as demonstrated in the preceding discussions, paving the road for coordinated synergistic efforts to deliver impact. We therefore outline three near-term research priorities that could substantially advance the theoretical understanding and rational design of photo(electro)catalytic systems over approximately the next five years.

6.1. Benchmarking and validation

Benchmarking in photo(electro)catalytic research is crucial as it establishes common practices and standards against which the research community can assess the performance of photo(electro)catalytic materials and devices. As in (thermo)catalysis science [243], benchmarking in photo(electro)catalysis science is a multifaceted challenge, that must involve concerted efforts between theoreticians and experimentalists. Fundamental aspects that need to be agreed upon revolve around the choice of materials and processes that can serve as standards against which assessments are made, the material properties or process key performance indicators that can be measured and computed accurately, and the establishment of standard measuring/computing practices. BiVO₄ and TiO₂ could for instance serve as benchmark materials, whose properties, such as band gaps, defect states, and

charge carrier dynamics, can be probed with spectroscopy and predicted with theory. Standardised synthesis methods and well-informed computational models that faithfully reproduce the structures of these materials would be vital. Comparisons of experimental results with computational predictions would enable the benchmarking and further development of theoretical approaches at the electronic and atomistic levels. At the mesoscopic and macroscopic (process) levels, water splitting, as a representative process common to photocatalytic and PEC systems, could be chosen for benchmarking, and the challenge would be to define standard photocatalytic reactors and PEC devices, together with protocols for operando measurements of material properties and system performance. Comparisons of performance under different operating modes, e.g. thermal catalysis versus photocatalysis [96] or photoelectrocatalysis versus electrocatalysis [244], together with combinations of complementary techniques (such as optical-absorption and current-density measurements, as in [244]), would be indispensable for cross-validating results and offering deeper insights into the mechanisms that drive performance. Going beyond electronic-structure calculations and comparing experimental results with kinetic-model predictions is a practice that is gaining ground in thermal catalysis and, crucially, electrocatalysis [245]. A multiscale kinetic framework would complement, rather than replace, measurements of intrinsic catalytic activity by connecting those measurements to coupled chemistry and transport models under operating conditions [245]. Building and coupling such models nevertheless remains challenging for materials that restructure dynamically.

Within such benchmark programmes, matched computational and experimental targets should be defined at each handoff: absorption spectra and band-edge positions; carrier densities, lifetimes and mobilities; intermediate coverages and elementary rate constants; product-specific rates and selectivities; FE, IPCE and steady-state current-potential behaviour for contacted PEC cells; and photon-to-product yields with matched oxidation- and reduction-side product balances for suspended photocatalysts. These quantities should be computed and, where experimentally accessible, measured or otherwise constrained for the same material state, illumination, electrolyte, temperature and geometry and, for time-integrated observables, the same sampling interval; uncertainty should be reported at each level, consistent with the architecture-specific validation requirements in Section 2.2.

6.2. Automated parameter-transfer and interoperable workflow standards

The development of such complex models necessitates reliable handling of large datasets, including calculated material properties, elementary-step and reaction energetics, and transport parameters, as well as seamless coupling of models at the various relevant levels from electrons to reactors and devices. At individual modelling levels, sophisticated workflow infrastructure already supports reproducibility and interoperability, particularly for electronic-structure calculations; examples include AiiDA-based common workflows [246] and Atomic Simulation Recipes [247]. Extending this infrastructure towards covering the multiple scales and levels of modelling relevant to photo(electro)catalytic systems is non-trivial, first and foremost because a semantic framework capturing the relevant information passed across scales is currently lacking. This information includes models and relevant parameters capturing excitation, carrier dynamics, surface chemistry, solid–liquid and solid–gas interfacial dynamics, and macroscopic transport phenomena. Thus, a prerequisite of orchestrating a workflow is agreeing on an appropriate ontology that would include standardised definitions of model variants (e.g. different levels of theory adopted in electronic structure calculations), as well as the intermediate physical quantities passed between the models adopted at different scales. A second challenge relates to the development of data repositories appropriate for the needs of multiscale modelling. Established repositories for electronic-structure results include NOMAD [248] and the Materials Project [249]. However, comparable repositories that link standardised carrier-kinetic and reaction data across scales for photo(electro)catalytic systems are not yet established. Such repositories should be developed in tandem with workflow infrastructure once standardised definitions of the information exchanged across scales have been encoded in an ontology.

6.3. Machine-learned excited-state and reactive potentials

The simulation of photoexcitation-driven processes in photo(electro)catalytic systems relies on excited-state calculations, which are computationally expensive, accentuating the need for fast and accurate approaches. Ground-state machine-learning potentials have developed rapidly and are increasingly used in chemistry and materials science [250,251]. Recent work has focused on developing machine-learned potentials for excited states; a recent perspective is provided in [199]. Representative molecular examples include OMNI-P2x [252], reported as the first universal excited-state neural-network potential but currently limited to neutral molecules in singlet electronic states; SpaiNN, an open-source Python package for machine-learning-driven surface-hopping NAMD [253]; and X-MACE, which introduces a smooth representation of non-smooth excited-state PESs [254]. Challenges in the context of modelling photo(electro)catalytic systems pertain to the need to model complex systems involving extended structures, i.e., bulk and surfaces as opposed to merely isolated molecules, surface-solvent interfaces, as well as dopant atoms and their interplay with polarons and adsorbates [255]. Developing machine-learned potentials for reactions, charged species, and excited states presents particular challenges because the models must describe bond rearrangement, long-range charge redistribution, and electronic-state dependence. Depending on the system and target property, these effects may be represented using global descriptors, local descriptors augmented with non-local information, or combinations of both [199,256]. Overcoming these challenges and designing accurate and transferable potentials for reactive chemistries that include photoexcitation would be truly enabling for in-depth fundamental investigations of the electronic and atomistic processes underpinning photo(electro)catalytic systems.

7. Conclusions and perspective

Photocatalytic and photoelectrochemical systems operate through a complex sequence of coupled photophysical and chemical processes spanning a wide range of temporal and spatial scales. As discussed throughout this review, understanding and predicting their behaviour therefore requires modelling approaches capable of capturing phenomena ranging from electronic excitations and charge localisation at the electronic scale to charge transport, recombination, chemical events at the atomistic scale, and catalytic turnover under non-equilibrium operating conditions at the mesoscopic and macroscopic scales.

Electronic-structure methods provide essential insight into the fundamental energetics governing photo(electro)catalytic processes, including excited-state properties, band alignment, defect physics, charge localisation, and elementary reaction barriers. These approaches have significantly advanced our understanding of charge-generation mechanisms and the role of material composition and electronic structure in determining system performance. Atomistic modelling further enables the investigation of surface reaction mechanisms, adsorption energetics, and the influence of local structural environments on catalytic activity and selectivity.

However, many key aspects of photo(electro)catalysis arise from collective phenomena that extend beyond the scope of purely atomistic descriptions. Charge-carrier transport, recombination dynamics, multi-charge accumulation, and stochastic surface reaction events occur over mesoscopic length and time scales and are strongly influenced by spatial heterogeneity and dynamic operating conditions. Mesoscopic kinetic frameworks, particularly kMC approaches, therefore provide a natural bridge between atomistic energetics and experimentally observable catalytic behaviour.

Beyond the three enabling priorities discussed in Section 6, three broader scientific challenges remain for predictive modelling of photo(electro)catalytic systems:

- **Charge transport and recombination under operating conditions.** Accurately describing charge-carrier dynamics in realistic materials requires models capable of capturing defect distributions, carrier trapping, polaron transport, and recombination pathways under illumination and, for photoelectrodes, applied bias.
- **Dynamic material evolution and degradation.** Photocatalyst and photoelectrode surfaces often undergo structural evolution under reaction conditions, including defect formation, surface reconstruction, and degradation. Capturing these dynamic structural changes within predictive modelling frameworks remains difficult.
- **Interfaces, transport and reactor environment.** Photo(electro)catalytic performance is shaped not only by semiconductor-side carrier dynamics and surface chemistry, but also by the composition of the surrounding liquid or gas phase, pH where relevant, reactant availability, mass transport, electric fields and reactor geometry. Coupling local kinetic models to continuum descriptions of mass, charge, heat and fluid transport remains essential for connecting microscopic mechanisms to device- or reactor-level observables.

Looking forward, predictive multiscale modelling of photo(electro)catalysis will depend on the three near-term priorities identified in Section 6: community benchmark systems connecting theory with operando measurements; automated, interoperable workflows for transferring parameters across scales; and accurate machine-learned potentials for excited-state and reactive processes. Progress in these areas must be accompanied by improved descriptions of charge transport and recombination, dynamic material evolution, and interfacial and reactor-scale environments under operating conditions. Combining electronic-structure calculations, atomistic reaction models, mesoscale kinetics and continuum transport with experimental validation offers a route towards predictive modelling and rational design of next-generation photo(electro)catalytic systems.

CRediT authorship contribution statement

Yilun Gong: Writing – review & editing, Writing – original draft. **Alec Elías Sigurðarson:** Writing – review & editing, Writing – original draft. **Rachel Crespo-Otero:** Writing – review & editing, Writing – original draft. **Hannes Jónsson:** Writing – review & editing, Writing – original draft, Supervision. **Michail Stamatakis:** Writing – review & editing, Supervision.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work ChatGPT-5 was used for literature searches as well as editing and streamlining the wording of the manuscript. The content was thoroughly reviewed and edited by the authors, who take full responsibility for the content of the published article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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