



Australian
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Theoretical calculation and machine learning aided design of functional materials for energy conversion

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Declaration

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Statement of Authorship

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Abstract

This thesis investigates the integration of machine learning (ML) and theoretical calculations to design and optimize functional materials for photocatalytic applications. By combining experimental techniques with theoretical calculations, that is, finite-difference time-domain (FDTD) simulations, and density functional theory (DFT) calculations, this work aims to accelerate the discovery of efficient, selective, and scalable photocatalytic systems for CO₂ reduction and seawater splitting. The central focus is on leveraging ML and advanced simulations into experiment to provide new insights into plasmonic photocatalysts and microenvironmental perturbations in photoreaction.

The first study explores the development of Ag-TiO₂ core-shell photocatalysts for the selective reduction of CO₂ to methane (CH₄). A significant contribution of this work is the use of FDTD simulations to model and optimize microenvironmental perturbations, thereby enhancing the catalytic activity of the plasmonic core-shell nanoparticles. Additionally, DFT simulations demonstrate that localized surface plasmon resonance (LSPR)-induced electric field enhancements lower the energy barriers for CO₂ activation and methanation. Experimentally, this system achieves 100% selectivity for CH₄ with a production rate of 75 μmol g⁻¹ h⁻¹. This study emphasizes the advantages of microenvironmental engineering in optimizing photocatalytic activity and selectivity, with FDTD and DFT simulations further elucidating the mechanisms of microenvironmental perturbations.

The second study focuses on the design of Co-NC@Cu core-shell photocatalysts for solar-driven hydrogen production from seawater. By dispersing single Co atoms on a nitrogen-doped carbon (NC) shell surrounding a Cu core, this novel catalyst achieves a hydrogen production rate of 9080 μmol g⁻¹ h⁻¹ and a solar-to-hydrogen (STH) conversion efficiency of 4.78%. A key highlight of this work is the detailed investigation of the local coordination environment of the single Co atoms, as well as the thermodynamic and kinetic effects of electric field perturbations on the catalytic process. DFT calculations reveal that the single Co atoms act as highly active

sites for hydrogen evolution, exhibiting low energy barriers for the reaction. Furthermore, the electric field's role in enhancing the reaction thermodynamics and kinetics was elucidated, providing insights for further optimization of catalytic performance. The integration of single atoms, photothermal effects, and localized surface plasmon resonance (LSPR) demonstrates a robust and efficient design for seawater splitting.

The third study showcases a comprehensive workflow combining ML and DFT calculations to accelerate the discovery and optimization of single-atom-based (SA) 2D photocatalysts. Using a dataset of Janus-TMD materials as a case study, ML models were trained to identify high-activity catalytic sites and screen potential substrates for photocatalytic CO₂ reduction. The ML-driven predictions successfully prioritized optimal single-atom catalysts, with experimental validation confirming the activity and selectivity of two synthesized Janus substrates 1T'-MoOSe and 2H-MoOSe with single-atom Pt. Photocatalytic experiments demonstrated the potential of the ML-guided design in delivering efficient and selective catalysts, underscoring the synergy between computational and experimental approaches. The growing dataset of atomic structures, intermediates, Janus configurations, and adsorption models provides a robust foundation for refining ML models and driving innovations in SA-based 2D materials discovery.

In conclusion, this thesis demonstrates the successful integration of ML, FDTD, and DFT techniques with experimental approaches for the design of advanced functional materials, which contribute to the development of sustainable energy solutions through CO₂ reduction and hydrogen production.

List of Abbreviations

VB	Valence band
CB	Conduction band
UV	Ultraviolet
Vis	Visible
NIR	Near-infrared
AIMD	Ab initio molecular dynamics
CBM	Conduction band maximum
VBM	Valence band maximum
ZnM-LDH	Zn-based layered double hydroxide
ML	Machine learning
ANN	Artificial neural network
NEB	Nudged elastic band
CO2-TPD	CO2-temperature program desorption
MGI	Material Genome Initiative
CCS	Carbon capture and storage
PES	Potential energy surfaces
FF	Fukui function
NN	Neural network
Pc	Phthalocyanine
GBR	Gradient boosting regression
MP	Materials Project
HEA	High-Entropy Alloy
ICSD	Inorganic Crystal Structure Database
KPI	Key performance indicator
XGBR	extreme Gradient Boosting Regression

RFR	Random Forest Regression
KNR	K-Nearest Neighbors
SVR	Support Vector Machines
TOPT	Topology Optimization
TMD	Transition Metal Dichalcogenides
LSPR	Localized surface plasmon resonance
DFT	Density functional theory
CO ₂	Carbon dioxide
CO ₂ RR	CO ₂ reduction reaction
NPs	Nanoparticles
E-field	Electric field
Ovac	Oxygen vacancies
CL	Spatially resolved cathodoluminescence
EELS	Electron energy loss spectroscopy
FDTD	Finite-difference time-domain
FFT	Fast-Fourier-transform
HRTEM	High-resolution transmission electron microscopy
STEM	Scanning transmission electron microscopy
HAADF	High-angle annular dark field
EDS	Energy dispersive spectroscopy
XRD	X-ray diffraction
EPR	Electron paramagnetic resonance
XPS	X-ray photoelectron spectroscopy
EF	Enhancement factor
BET	Brunauer-Emmett-Teller
GC	Gas chromatography
UV-Vis	Ultraviolet-visible

TRPL	Time-resolved photoluminescence
SPVM	Surface photovoltage microscopy
UV-Vis DRS	UV-Vis diffuse reflectance spectroscopy
KPFM	Kelvin probe force microscopy
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
M-NC	Nitrogen-doped carbon materials
STH	Solar-to-hydrogen
NC	Nitrogen-doped carbon
AC-TEM	Aberration-corrected TEM
ICP-OES	Inductively coupled plasma optical emission spectrometry
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near-edge structure
FT-EXAFS	Fourier-transform extended X-ray absorption fine structure
WT-EXAFS	Wavelet transform EXAFS
RDS	Rate-determining steps
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
CVD	Chemical vapor deposition
PLD	Pulsed laser deposition
VASP	Vienna Ab initio Simulation Package

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Chapter 1 Research Context

1. Introduction

Sustainable energy conversion using photocatalysts is a promising approach to simultaneously addressing global environmental challenges and the ongoing energy crisis. Rapid population growth, industrialization, and increased energy consumption have led to severe environmental impacts, particularly the accumulation of carbon dioxide (CO₂) emissions contributing to global warming and climate change.¹⁻² Traditional methods of energy production primarily rely on fossil fuels, exacerbating environmental issues and creating an urgent need for sustainable and renewable energy solutions.

Photocatalysis, which directly utilizes solar energy to drive chemical reactions, has emerged as an ideal solution due to its dual benefits of harnessing inexhaustible solar energy and reducing harmful environmental pollutants. In this thesis, we systematically explore functional photocatalytic materials from three interconnected perspectives: (1) photocatalytic CO₂ reduction into valuable chemical fuels,³ (2) photocatalytic hydrogen production via seawater splitting,⁴ and (3) machine learning (ML)-aided rational design of high-performance photocatalysts.⁵ These research directions are not isolated; rather, they are closely linked by the fundamental principles governing photocatalytic processes, namely the generation, separation, transfer, and utilization of photogenerated electron-hole pairs.

Photocatalytic CO₂ reduction has attracted considerable attention as it offers a direct strategy for converting CO₂, a major greenhouse gas, into value-added products such as methane (CH₄), carbon monoxide (CO), methanol (CH₃OH), and other hydrocarbons.⁶ The conversion of CO₂ through photocatalysis uniquely provides a route to simultaneously mitigate environmental harm and produce chemical fuels. However, achieving efficient and selective CO₂ photoreduction remains challenging due to issues such as rapid electron-hole recombination, limited visible-light absorption, and weak surface catalytic activity.⁷ Thus,

significant efforts are being devoted to engineering novel photocatalysts via strategies including defect engineering, constructing heterojunctions, single-atom catalysis, and surface/interface modulation.⁷

Extending the concept of photocatalysis to renewable hydrogen production, photocatalytic seawater splitting presents an attractive method for clean hydrogen generation. With approximately 97% of Earth's water resources being seawater, developing photocatalysts capable of directly utilizing seawater holds immense practical and economic potential.⁸ Nevertheless, the harsh saline environment poses distinct challenges, such as catalyst corrosion, formation of unwanted by-products, and impaired reaction kinetics. To overcome these barriers, advanced photocatalytic materials are being designed to enhance stability, efficiency, and selectivity, employing techniques like plasmonic enhancements, construction of robust nanostructures, and interface engineering.⁹

Despite significant experimental progress in both CO₂ reduction and seawater splitting, discovering and optimizing photocatalytic materials via traditional experimental methods remains time-consuming and inefficient. Therefore, integrating computational approaches, particularly density functional theory (DFT) calculations and machine learning (ML), into photocatalyst design has become indispensable.¹⁰ Machine learning, supported by abundant computational and experimental data, facilitates rapid screening, prediction, and optimization of photocatalytic performance by identifying key descriptors governing catalyst activity and stability.¹¹ ML-driven methodologies significantly reduce the experimental workload by predicting promising material candidates, thus accelerating the discovery and development of efficient photocatalysts.

In summary, by exploring functional photocatalytic materials through interconnected research on CO₂ photoreduction, seawater splitting, and ML-aided material design, this thesis aims to develop a comprehensive understanding of photocatalytic processes and propose novel

strategies to achieve efficient solar-driven chemical conversions. The goal is to contribute to sustainable energy solutions capable of addressing global environmental and energy challenges through advanced photocatalytic technologies.

1.1 Functional materials for photocatalytic CO₂ reduction

1.1.1 Background

The danger of unchecked global warming is unarguably life-threatening to human civilization and the ecosystem.¹ As CO₂ is a primary culprit for global warming, net CO₂ emissions have been described as a key metric for understanding the effects of global warming due to its direct impact on climate change.² Extensive modeling with energy-economy-environment scenarios or projections to keep the global temperature from rising above 1.5 °C by the year 2100 shows that such a positive outlook is only possible if the global energy system is completely decarbonized (i.e., net-zero global CO₂ emissions) by mid-century, followed by active CO₂ removal (i.e., carbon-negative) in the second half of the century.¹²

The catalytic conversion of CO₂ to valuable energy-related products (e.g., syngas, CH₄, CH₃OH and longer-chain hydrocarbons)¹³ by thermal reforming and hydrogenation,¹⁴⁻²⁰ electrocatalysis,²¹⁻²³ or photocatalysis⁶ could occupy an important position in a future carbon-negative economy by directly replacing non-renewable sources of these molecules, provided that the energy inputs to these processes are themselves derived from renewable sources.²⁴⁻
²⁵ In this regard, photocatalytic strategies stand out by not requiring a secondary medium of energy storage, and being able to realize the CO₂ conversion into high value-added fuels directly via renewable solar energy without external energy input.²⁶ Indeed, photocatalytic CO₂ reduction has been considered to be a 'kill two birds with one stone' approach for sustainable energy production and greenhouse gas reduction.²⁷ In contrast, thermocatalytic approaches to CO₂ conversion (e.g., by hydrogenation to methanol) are energy-intensive and typically require elevated reaction temperatures and pressures as well as a reactant stream with higher Gibbs free energy (e.g., H₂) to drive the reaction, which could adversely affect the process

sustainability and economic viability. Compared with electrocatalysis, photocatalysis can convert sunlight as the inexhaustible primary energy source into chemical energy. Thus, the reduction of CO₂ requiring a hydrogen source and energy can be easily achieved by using water and solar energy.²⁶ Hence, interest in photocatalytic CO₂ reduction as a means to sustainably convert inexhaustible solar energy into compressible chemical energy has rapidly increased in recent years,²⁸⁻²⁹ as evidenced by a Web of Science search showing exponential growth in articles published (Figure 1-1a).

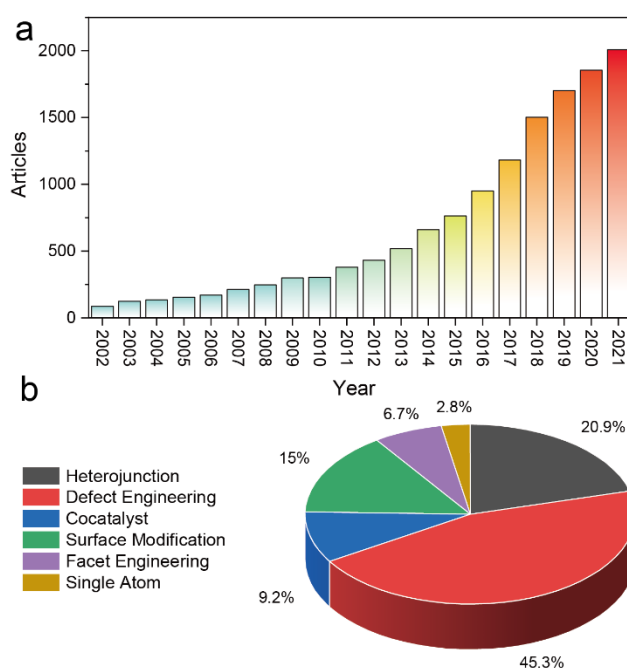


Figure 1-1 Summary of recent photocatalysis literature. a) The yearly number of articles published about photocatalysis (14496 in total for photocatalysis and CO₂ related articles). b) The percentage distribution articles exploring various experimental catalyst engineering strategies for CO₂ photoreduction. (1669 for TS = (photocataly* AND (CO₂ OR Carbon dioxide) AND Heterojunct*), 3626 for TS = (photocataly* AND (CO₂ OR Carbon dioxide) AND (dop* OR defect*)), 736 for TS = (photocataly* AND (CO₂ OR Carbon dioxide) AND (cocata*)), 1202 for TS = (photocataly* AND (CO₂ OR Carbon dioxide) AND (surface AND modi*)), 539 for TS = (photocataly* AND (CO₂ OR Carbon dioxide) AND (facet)), 227 for TS = (photocataly* AND

(CO₂ OR Carbon dioxide) AND (single atom*))). The data was collected from Web of Science searches performed on 28th Jan 2022, covering all articles published to date.

Among all possible CO₂ reduction products, the formation of CH₄ is desirable because of its high energy density, clean combustion characteristics and potential for application as a drop-in replacement for nonrenewable natural gas.³⁰ However, widespread adoption of CO₂-to-CH₄ photoreduction is hampered by the poor activity,³¹ selectivity,³² and stability³³ of presently available photocatalysts, motivating an exhaustive search for active and selective yet stable materials. Experimental catalyst engineering approaches for improving activity and selectivity include heterojunctions,³⁴ defect engineering,³⁵ cocatalysts,³⁶ surface modification,³⁷ facet engineering,³⁸ and single-atom catalysis,³⁹ among which the former two have received the majority of attention in recent years (Figure 1-1b). However, it is also worth noting that single-atom catalysis has very recently emerged as a new frontier in photocatalysis research.⁴⁰ In tandem, first-principles-based and data-driven computational materials design have also stimulated the discovery of new photocatalysts by enabling screening of candidate materials faster than can be readily achieved experimentally.⁴¹

The difficulties of selective and efficient CO₂ photoreduction can be understood by considering how photocatalysts work in general. Solids can be classified as metals, semiconductors, or insulators depending on the distribution of electronic energy levels and hence electron mobility. Of the continuous bands of energy levels representing the electronic wave functions, two principal bands can be characterized: the valence band (VB), which is a set of low-energy bands with filled electronic states, and the conduction band (CB), which corresponds to a high-energy unoccupied electronic state. In metals, the VB and CB overlap to give a continuous energy band, whereas in semiconductors, a small energy gap (known as the band gap) separates the VB and CB. Crucially, electrons can be excited from the VB into unfilled states in the CB by a suitable energy input (e.g., from solar energy), yielding electron-hole pairs that mediate surface redox chemistry. On the other hand, the energy gap in

insulators is much larger and cannot generally be overcome by solar energy. It is this unique ability of semiconductors to generate charge carriers by absorbing light in the solar spectrum that explains their ubiquity in photo-based technologies (i.e., photovoltaic solar cells, photoelectrochemical systems and photocatalysis).⁴²

The main processes in photocatalysis can be explained in three successive steps, 1) the generation of charge carriers (i.e., electron-hole pairs) due to the absorption of light energy corresponding to the energy band gap in a semiconductor (vide supra), 2) separating and transporting charge carriers, 3) chemical reaction between charge carriers and surface species (e.g., adsorbed CO₂).⁴³ The need for simultaneous operation of all three steps poses specific constraints on materials properties. In the first step, a mismatch between the absorption ability of semiconductors and the solar spectrum could result in poor generation of charge carriers necessary for the reduction of CO₂. The sunlight spectrum with a range of 250 to 2500 nm can be divided into ultraviolet (UV), visible (Vis) and near-infrared (NIR) regions, among which the Vis-NIR region accounts for 95% of the total solar photons. Thus, a highly active catalyst should have a narrow band gap for excellent light absorption ability in this region. In the second step, an important design constraint of a photocatalyst is to enable good charge separation for photo-generated electrons and holes, so that these charge carriers would migrate to the surface of catalysts to react with the adsorbed species (e.g., CO₂). In the last step, good chemical adsorption property of CO₂ is essential to realize the interaction between photo-induced charge carriers and reactant CO₂ to form high-value fuels, including CH₄ and CH₃OH. Furthermore, the photoreduction of CO₂ is kinetically and thermodynamically challenging because of the closed-shell electronic configuration and strength of the O=C=O double bonds.⁴⁴ All the relevant reactions for CO₂ conversion to fuel are all endergonic since both CO₂ reduction as well as H₂O oxidation are thermodynamically unfavorable at ambient temperature. The Gibbs free energy ($\Delta G^{\circ}_{\text{redox}}$) values associated with CO₂ reduction by H₂O are:⁴⁵





Moreover, the reduction of CO_2 to CH_4 is an eight-electron process coexisting with other reactions leading to other redox products, including HCOOH , CO , CH_3OH , HCHO , and CH_4 as shown in equation (5) - (11).⁴⁶ At the same time, the involvement of water as a reductant (oxidized into OH^- and H^+ and converted to H_2) leads to the parasitic hydrogen evolution reaction that produces H_2 as another by-product, as shown in equation (7). All of these side reactions pose major selectivity challenges. Furthermore, fundamental differences between the surface kinetics of multi-electron, multi-proton chemical reactions versus sequential single-electron, single-proton steps, not readily apparent from the overall reactions listed below, further complicate the picture.⁴³ Overall, all of these technical challenges have to be overcome by researchers developing highly efficient photocatalysts with high selectivity for CH_4 formation.



1.1.2 Theoretical calculation aided photocatalyst design for reduction of CO_2

Advances in available computational power and computational methods have not only provided a molecular-scale understanding of catalytic action,⁴⁷ but also facilitated the generation of large computational datasets of materials properties, which has in turn allowed the use of data-driven techniques, such as machine learning, for catalyst screening and

design.⁴⁸⁻⁴⁹ The ability to screen candidate materials faster than can be readily achieved experimentally bodes well for the combination of theoretical calculations and experiments, including data-driven strategies assisted by machine learning, as the way forward for photocatalyst development.

Density functional theory (DFT) calculations are based on quantum mechanics and, subject to the approximations made in the simulation, allow the determination of the electronic structure of the system under study. Despite well-known flaws in predicting the electronic properties of strongly correlated materials such as certain transition metal oxides and the availability of more accurate wavefunction-based methods, DFT nevertheless remains the workhorse of computational catalysis owing to its favorable balance between efficiency and accuracy.⁴⁹ DFT studies have proven to be highly successful for proposing and evaluating possible catalytic mechanisms, as well as explaining observed reactivity trends across different materials. Zhao et al.⁵⁰ reviewed the combination of theory and experiments for 2D photocatalyst design in recent years, and Kovačič et al.⁴⁹ reviewed theoretical first-principles description of CO₂ photoreduction and subsequent kinetic or multiscale modeling. These works provide useful guidance for the rational design of new or improved photocatalysts with superior photocatalytic performance, bridging experimental and computational approaches.

In this section, we will restrict ourselves to successful applications of DFT-based and data-driven methods for photocatalyst design and discovery, including the use of electronic descriptors, band engineering and detailed reaction mechanism exploration studies. Notably, we will not discuss 1) the accuracy of presently available DFT exchange-correlation functionals, 2) the adequacy of widely employed computational models for photocatalysts, and 3) the use of ab initio molecular dynamics (AIMD) simulations for the exploration of non-equilibrium phenomena such as single-electron transfer steps,⁵¹⁻⁵² interactions with solvent molecules in liquid-phase reactions⁵³⁻⁵⁴ and dynamic restructuring of the catalyst surface under reaction conditions.⁵⁵

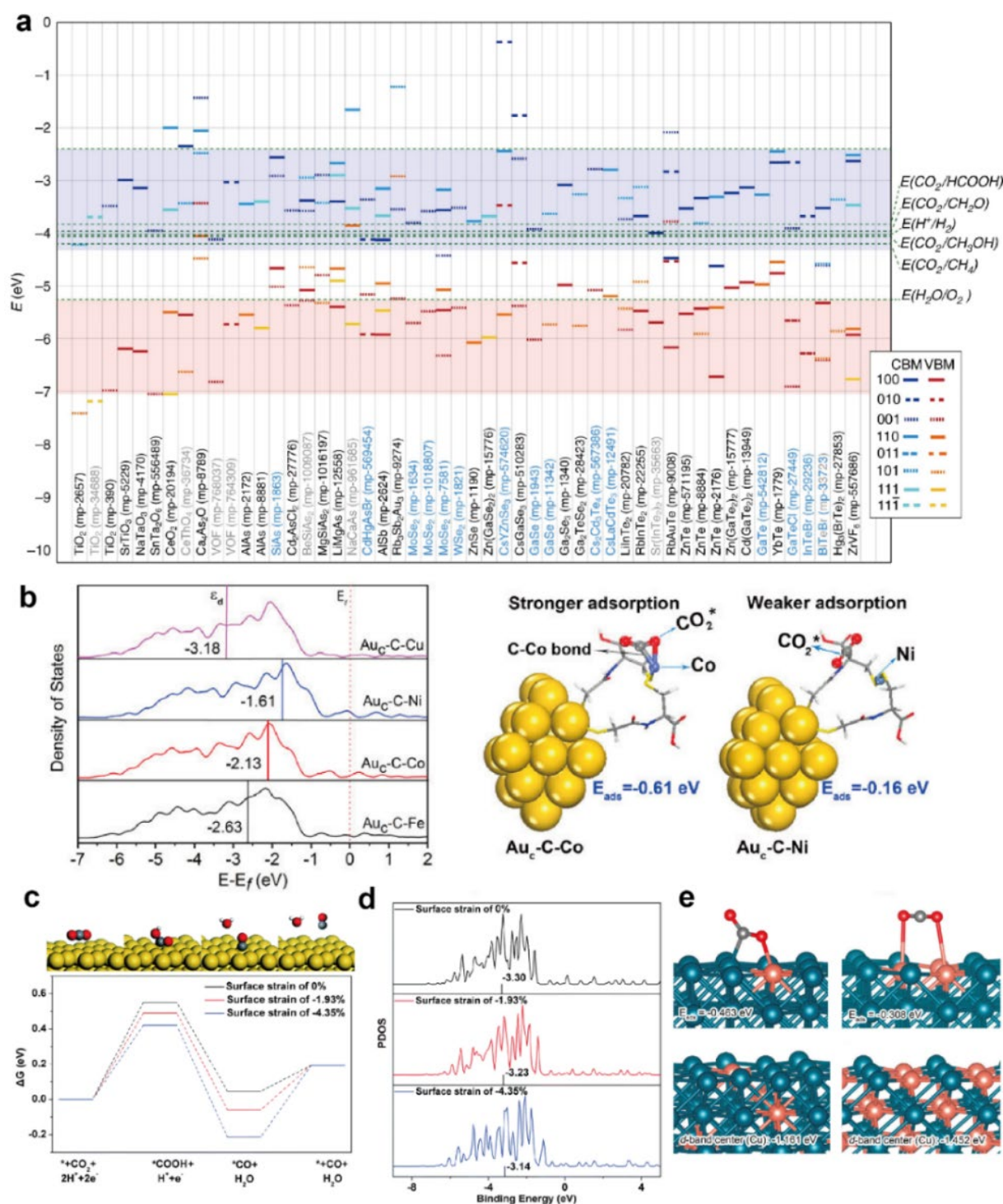


Figure 1-2 (a) The CBM and VBM calculated by DFT for 52 materials.⁵⁷ Copyright 2019, Springer Nature. (b) Tuning the d-band centers to regulate binding energies with CO_2 .⁵⁸ Copyright 2018, ACS Publications. (c) Free energy diagram corresponding to the CO_2 reduction on Au(100) under different surface strains. (d) PDOS of surface atoms on Au(100)

surfaces under different surface strains.⁵⁹ Copyright 2020, RSC Publications. (e) Configurations, adsorption energies of CO₂ and d-band center for Pd₇Cu₁ and Pd₁Cu₁.⁶⁰ Copyright 2017, ACS Publications.

Table 1-1 A summary of descriptors used for photocatalytic CO₂ reductions

Classification	Description	Ref
Constitutional	Atomic number	61-63
Constitutional	Atomic weight	64
Geometric	Atomic radius	41, 65-66
Geometric	Van der Waals radius	64
Geometric	Covalent radius	67
Geometric	Coordination number	62-63
Electronic	Number of d/p electrons	41, 61, 64
Electronic	d /p-band structure	58-59, 65-66, 68-69
Electronic	Electron affinity	41, 61, 65-67
Electronic	Conduction/Valence band	69-71
Electronic	Bandgap	72
Optical	Optical absorption	73
Quantum chemical	Pauling electronegativity	41, 61-63, 65-66
Quantum chemical	First ionization energy	41, 61
Quantum chemical	Ionic potential	65-66
Quantum chemical	Work function	65-66
Thermodynamic	Formation energy	64
Thermodynamic	Adsorption/desorption energy	63, 66, 71, 74-78
Thermodynamic	Binding energy	41, 64, 79-80
Thermodynamic	Gibbs free energy	69, 71, 77, 79, 81-85

		Research Context
Kinetics	Energy barrier in the transition state	79
Kinetics	Reaction species and intermediate	60

Table 1-1 list a summary of descriptors used for photocatalytic CO₂ reductions. As key descriptors for photocatalytic CO₂ reductions, thermodynamic descriptors such as formation energy,⁶⁴ adsorption/desorption energy, binding energy^{41, 64, 79-80} and Gibbs free energy.^{69, 71, 77, 79, 81-85} are widely used to screen and design the photocatalysts. When the product of photocatalytic CO₂RR is CH₄, screening photocatalysts only by thermodynamic descriptors is insufficient. Kinetic descriptors such as adsorption and desorption of reactants/intermediates revealed by transition state analysis from DFT NEB calculations enable to further study the types of intermediates and selectivity of products. Moreover, DFT calculation has limitations for kinetic studies. A more promising approach is to use experimental in situ analytical techniques⁸⁶ combined with DFT thermodynamic and kinetic descriptors to obtain a screen for CO₂ reduction CH₄ activity and selectivity.

As effective descriptors of catalytic properties that are relatively straightforward to calculate by DFT and accessible in materials databases, electronic band descriptors see extensive use in computational catalyst design. For example, the photocatalytic activity mechanism of g-C₃N₄/SnS₂ heterojunction was revealed by DFT calculations.⁸⁷ The excited electrons in the conduction band maximum (CBM) of SnS₂ could easily recombine with the holes in the valence band maximum (VBM) of g-C₃N₄ under the action of an electric field. As a result, photogenerated electrons and holes naturally accumulate in the CBM of g-C₃N₄ and the VBM of SnS₂, respectively. Figure 1-2a also shows the CBM and VBM calculated by DFT for 52 materials as descriptors of catalytic performance, and the blue-shaded regions are considered excellent photocathode candidates for CO₂ reduction and hydrogen production.⁵⁷

The d-band center is the occupied center of gravity of the d-orbital electrons in transition metals and is related to the position of the upper d-band edge.⁸⁸ In 1997, Nørskov et al.⁸⁹ described the relationship between d-band centers and molecular adsorption on metal

surfaces, surface alloys and overlayers. For transition metal-based photocatalysts, the interaction between transition metal d orbitals and CO₂ molecular orbitals is directly reflected in the adsorption energy.⁸⁸ When the d-band center is high, the d-orbital electrons easily interact with the molecular orbitals of CO₂ and intermediates. The photocatalyst has strong adsorption on CO₂ and intermediates, which may lead to difficulty desorption of intermediates and obtaining further reduction products. Electronic descriptors associated with the electronic properties of metals (i.e., d-band centers), enabling the demonstration that the reducibility of redox-active metal oxides is strongly influenced by the electronic structure of the metal, is used to explain the enhancement associated with the noble metal/metal oxide interface catalytic activity.⁹⁰ Subsequently, the d-band center has proven to be an extremely useful electronic descriptor across computational heterogeneous catalysis, including for explaining photocatalytic CO₂ reduction selectivity. Xiong et al.⁶⁹ investigated a homologous series of Zn-based layered double hydroxide (ZnM-LDH) photocatalysts for CO₂ reduction. The d-band centers of ZnGa-LDH and ZnAl-LDH are far from the Fermi level, indicating a reduced electron-donating ability relative to ZnTi-LDH. For ZnFe-LDH and ZnCo-LDH, their d-band center is far away from the Fermi level, making these photocatalysts unable to adsorb and activate CO₂. Therefore, the d-band center positions of M³⁺ and M⁴⁺ cations in ZnM-LDHs can well describe the photocatalytic CO₂ reduction selectivity. For tuning d-band center, Au nanoclusters are used to bridge different metal cations (Fe²⁺, Co²⁺, Ni²⁺, and Cu²⁺) to tune different d-band centers and binding energies with CO₂ shown in Figure 1-2b, which are used to tune electron transfer efficiency and CO₂ activation energy.⁵⁸ Figure 1-2c and d also show that, by adjusting the compressive strain on the Au surface to move the center of the d-band upward, the adsorption of the key intermediate *COOH can be enhanced, while the charge polarization promotes the transfer of interfacial electrons from Pd to Au.⁵⁹ Besides, Long et al.⁶⁰ found that when Cu atoms were exposed on the Pd metal surface, the optimal adsorption configuration of CO₂ occurred on the adjacent Cu-Pd pair. However, the adsorption of CO₂ to the adjacent Cu-Cu pairs was much weaker. The results show that the Cu-Pd atom pairs formed by

separating Cu atoms in the Pd lattice can serve as highly active sites for CO adsorption. Therefore, the adsorption energy of CO₂ can be used as one of the descriptors of activity. In addition, this work also calculated the d-band centers of Cu atoms of Pd₇Cu₁ and Pd₁Cu₁ in two ordered lattices. When one Cu atom is surrounded by more Pd atoms, the electronic structure will be more influenced by the Pd atoms, thus better promoting the d-band center of each Cu site. The elevated Cu d-band center of Pd₇Cu₁ increases the catalytic activity of the Cu site shown in Figure 1-2d and e. All in all, the d-band center serves as an effective descriptor, and different active metals have different d-band centers and adsorption energies for CO₂, thus changing the activity and selectivity for CO₂ reduction.

The adsorption energy of various molecules on the catalyst surface is another key descriptor for describing the performance of photocatalyst.^{62,63,66} When identifying descriptors describing the photocatalytic performance of catalysts, the types of descriptors chosen at the outset should usually be diverse, broad, and easily accessible. The key is how to choose these descriptors and how to discover/estimate strong correlations with performance photocatalytic CO₂ reduction, especially when dealing with small datasets. Ghiringhelli et al.⁹¹ describe the required characteristics of a set of descriptors that also fits well in photocatalytic CO₂ reduction: a) The calculation of descriptors cannot be as intensive as a key performance indicator. b) It uniquely characterizes materials and basic processes related to properties. c) Different (similar) materials should be characterized by different (similar) descriptors. d) Its size should be as small as possible.

For any chemical reaction, the Gibbs free energy usually determine the activity of catalysts.⁴⁹ Besides thermodynamic factors, kinetic factor (i.e., surface reactivity) is another key factor determining photocatalytic performance. The kinetic process of photocatalysis involves multi-particle kinetic processes such as charge separation and transport, electrons transfer, etc.⁴⁴ Light intensity, surface catalytic active sites, charge separation, adsorption and desorption of reactants/intermediates are considered as the crucial kinetic influence factors in the product selectivity of photocatalytic CO₂RR.⁸⁸ In the DFT calculation, the calculation of the reaction

transition state based on the nudged elastic band (NEB) method is one of the ways to investigate kinetics through observing the adsorption and desorption of reactants/intermediates. The energy barrier of the transition state, which becomes the kinetic criterion of the final reaction product, will show different reaction mechanisms compared with only considering Gibbs free energy. For example, considering the kinetic process, the rate-determining step of M_3C_2 -type MXenes may be the release of H_2O or CH_4 other than the hydrogenation process.⁷⁹ However, the search process of transition states takes much time, especially for CO_2RR , the complexity of the reaction path further increases the cost of the searching transition state. A kinetic model is still needed to understand the photocatalytic CO_2RR process. Hammerschmidt et al.⁹² used kinetic Monte Carlo combined with electromagnetic wave simulations to address the effect of inhomogeneous light absorption on the photocatalytic activity of semiconductor particles, but the model lacks consideration of charge carrier transport and intermediate reaction products. DFT calculations can solve the above problems, but DFT calculation combined with the kinetic model to study the photocatalytic CO_2RR process is hindered by computational cost. Moreover, DFT calculation has limitations for kinetic studies, such as lack of consideration of deactivation happened since the chemisorption of photoreduction intermediate reactions.⁵⁶ A more promising approach to the kinetics of CO_2 photoreduction occurring on photocatalyst surfaces is to use experimental in situ analytical techniques⁸⁶ to gain an intrinsic understanding of the surface activity of CO_2 reduction activity. Researchers use DFT calculations combined with in situ experimental measurements of obtained intermediates to explore reaction mechanisms,⁹³ evaluate potential reaction pathways,⁷² and predict reaction products.⁸²

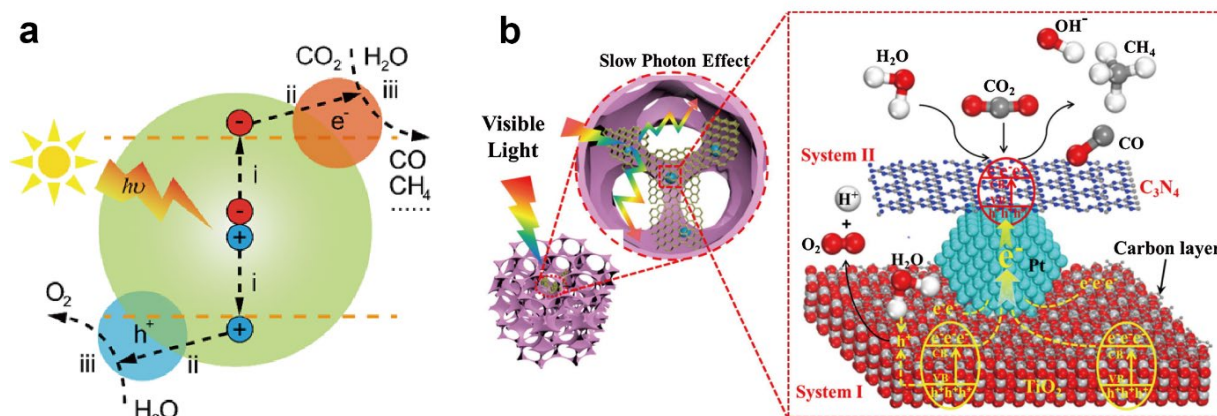


Figure 1-3 (a) Schematic diagram of three steps in photocatalytic CO₂ reduction reactions. (b) The mechanism of 3DOM-CNPTC catalyst for photocatalytic CO₂ reduction with H₂O to CH₄.⁹⁴ Copyright 2020, Elsevier.

In general, as shown in Figure 1-3a, the entire photocatalytic CO₂ reduction reaction includes three main processes: (i) light absorption, (ii) separation and transfer of electron-hole pairs to a solid surface, and (iii) surface reaction for CO₂ reduction.⁹⁵⁻⁹⁶ For the initial absorption step, it is important that the energy of the photons used to generate e^- - h^+ pairs need to be equal or greater than the bandgap of photocatalysts. The proton-assisted electron transfer reaction is one of the indicators of photocatalytic activity. The transfer of excited electrons on the (101) and (001) planes of TiO₂ and the proton-assisted two-electron transfer CO₂ photoreduction were investigated by the DFT method,⁹³ aiming to elucidate the facet-dependent photocatalytic activity of TiO₂ catalysts. The higher CBM generates stronger reducing electrons, and the lower potential barrier leads to a faster reaction rate, which is the reason for the higher activity of the (101) plane. The second step of photocatalytic CO₂ reduction reaction transfers photogenerated electrons from the photocatalyst surface to CO₂. For the sake of enhancing the efficiency of CO₂ photoreduction (demonstrating the ability for charge transfer from solid to the CO₂), inhibiting the recombination of e^- - h^+ pairs or facilitating the charge separation and migration from the catalyst surface to reactants will be necessary. To improve the process, several strategies that have been discussed before aim to make the photocatalyst largely

absorb as much light as possible and prevent charge recombination upon excitation. For example, the efficient separation of holes and electrons in space for Z-type 3DOM-CNPTC catalysts facilitates their participation in catalytic reactions on different surfaces.⁹⁴ As shown in Figure 1-3b, the photoelectrons from the photoexcited $\text{TiO}_2@\text{C}$ are captured by the carbon coating and transferred to the VB of g-CN through the Pt NPs. The photoelectrons react with absorbed CO_2 and H_2O to generate CO and CH_4 , while holes are provided by the valence band of $\text{TiO}_2@\text{C}$. Besides, to understand the process through charge transfer analysis interaction between intermediates and the solid photocatalytic surfaces and the localization, mechanics methods, that is, the first-principles calculation is needed. DFT charge density calculations can also serve as an effective tool for designing heterojunctions. For instance, DFT calculations reveal that Ag atoms at the interface of $\text{Ag}_3\text{PO}_4(111)$ and g- C_3N_4 act as charge recombination centers for charge transfer, facilitating electron-hole separation in the mixed $\text{Ag}_3\text{PO}_4(111)/\text{g-C}_3\text{N}_4$ system through a Z-type mechanism.⁹⁷ The third step of photocatalytic CO_2 reduction reaction is surface reactions. Structural information of photocatalytic solid surfaces such as doping,⁹⁸ defect disorders,⁹⁹ morphologies of solid surface,¹⁰⁰ also affect this process, which can be studied through the DFT calculation as well.

Current DFT research on analyzing reaction mechanisms of photocatalysis is disproportionately focused on thermodynamic descriptors such as adsorption energy,^{63, 66, 71, 74-78} reaction path (Gibbs free energy) analysis,^{69, 71, 77, 79, 81-85}, etc. In photocatalysis, CO_2 can be reduced to several carbonaceous species such as CO, HCOOH, CH_3OH or CH_4 . While the first product in all cases is CO, possible subsequent products include CH_4 , and other hydrocarbon products. The reaction pathway and reaction mechanism can be revealed by the combination of DFT and in situ experiments. For example, detailed studies of possible reaction pathways can explain the significance of the crystal facet regulation strategy. Yan et al.¹⁰⁰ proposed an integrated reaction process for the reduction of CO_2 to CH_4 on TiO_2 materials. It was found that the CO_2 reduction reaction tends to occur on the (101) planes of anatase rather than the (010) planes. In addition, it has been determined that the rate-limiting step for the

(010) plane is the initial reduction of CO_2 , while the (101) plane ends the process with the formation of CH_4 . The rate-determining step ΔG of Z-scheme B-doped $\text{g-C}_3\text{N}_4/\text{SnS}_2$ is much lower than that of $\text{g-C}_3\text{N}_4/\text{SnS}_2$ shown in Figure 1-4a, indicating that the Z-scheme B-doped $\text{g-C}_3\text{N}_4/\text{SnS}_2$ heterostructure is a highly efficient photocatalyst.⁷² It is obvious that the speed rate-determining step of the B-doped $\text{g-C}_3\text{N}_4/\text{SnS}_2$ is different from that of the undoped $\text{g-C}_3\text{N}_4/\text{SnS}_2$, that is, the rate-determining step of CH_4 is shifted from $\text{CO}_2 \rightarrow \text{COOH}^*$ to $\text{CHOH}^* \rightarrow \text{CH}_2\text{OH}^*$. In another study, DFT calculations were employed to clearly understand the reaction sites of Cl^- ions-modified Bi_2WO_6 at the atomic level and found that Cl^- ions bound to the surface of Bi_2WO_6 can hinder the desorption of CO ,⁷⁰ which is favorable for further protonation of $^*\text{CO}$. Notably, Cl^- assisted in protonating $^*\text{CO}$ to $^*\text{CHO}$, where $^*\text{CHO}$ is a critical step in CH_4 formation shown in Figure 1-4b. Importantly, introducing Cl^- provided an alternative pathway for oxidation half-reaction of a lower difficulty (i.e., Cl^- oxidizes with photogenerated holes to form Cl_2 which can later react with H_2O to form HClO and protons) than direct oxidation of H_2O with photogenerated holes to give O_2 and protons. This reaction mechanism was verified experimentally using the spectrophotometry method with N,N' -diethyl-p-phenylenediamine as the chromogenic agent to identify the presence of HClO , a key intermediate species for Cl^- modified Bi_2WO_6 . The modification of Cl^- ions promotes the formation of CH_4 and improves the selectivity of CH_4 . In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is also another experimental technique to reveal reaction intermediates and verify proposed mechanism step calculated in DFT.¹⁰¹ Wang and co-authors developed cobalt dual-atomic-site catalysts with varying Co content from 0.9 to 3.5 wt%.¹⁰¹ In-situ DRIFTS results show an absorption peak corresponding to CHO^* (ca. 1385 cm^{-1}) and CH_3O^* (ca. 1484 and 1190 cm^{-1}) in CoDAC-3.5 (i.e., 3.5 wt% Co), which are key intermediate species for CH_4 formation. Moreover, an absorption peak for CO^* (1917 cm^{-1}) only exists for CoDAC-0.9 catalyst which suggests the ease of CO desorption and hence limited the protonation of CO^* to CHO^* and CH_3O^* . DFT calculations corroborated the observations in in-situ DRIFTS in where the Gibbs free energy for CHO^* formation in CoDAC-3.5 is more negative than that of CO^* formation.

The relative Gibbs free energies, on the other hand, is reversed for the CoDAC-0.9 catalyst. Hence, CoDAC-3.5 which hinders CO desorption, makes it more selective towards CH₄ production. Furthermore, mechanism studies relating to surface reactions (i.e., dissociation of H₂O to give protons and reduction of CO₂) can be understood experimentally from CO₂-temperature program desorption (CO₂-TPD), CO₂ adsorption isotherms to investigate CO₂ desorption step and from DRIFTS to investigate H₂O dissociation step.¹⁰²⁻¹⁰³ Such studies can further validate DFT calculated reaction mechanisms.

All in all, for thermodynamic DFT investigation, adsorption energy,^{63, 66, 71, 74-78} and reaction path (Gibbs free energy) analysis,^{69, 71, 77, 79, 81-85} are the most commonly used to predict the reaction pathway of CO₂ reduction to CH₄ and explain the reason for the selectivity and activity enhancement. Based on the statistics of DFT calculation reaction pathways for CO₂ reduction, there are multiple paths through which the final product is CH₄ shown in Figure 1-4c. The first and second main steps are CO₂ → COOH* and COOH* → CO, respectively. The above two steps have widely been considered as rate-determining steps for CH₄ production.^{71-72, 81, 99} Both steps involve the formation of O-H bonds. Next, the intermediate used to determine whether CO* is reduced to COH* or CHO* by forming O-H or C-H bonds, or forming CO gas, is the first major bifurcation. Then, HCO* is reduced to CHOH* by forming an O-H bond, while HCO* is reduced to CH₂O by forming a C-H bond. In addition, the other major bifurcation where the product is CH₃OH or CH₄ is to generate CH₂OH* or CH₃O*. It is worth noting that CH₃OH* also forms CH₄ under certain catalyst conditions. The main reaction mechanism of photocatalyst reduction of CO₂ is proposed. Most photocatalysts hydrogenate CO₂ to HCOO* or COOH*. In addition, if CO₂ is dissociated and adsorbed, the subsequent CO hydrogenation to CH₃OH or CH₄ through the rapid hydrogenation route of CH₂O could happen.⁴⁹ However, regardless of the mechanism, the reaction process of each intermediate product in the photocatalytic process plays a non-negligible role in the final product and selectivity, as shown in Table 1-2 for the diversity of rate-determining steps for several catalysts.

Table 1-2 DFT-predicted products and rate-determining steps of photocatalytic CO₂ reduction over various photocatalysts.

Photocatalyst	Rate-determining step	Predicted product	Reference
NiO	COOH*→HCOOH*	CH ₄	84
ZnO-110	COOH*→CO*	CH ₄ , CO	71
ZnO-001	CO ₂ *→COOH*	CH ₄ , CO	71
Bi ₂ WO ₆	CO*→CHO*	CH ₄ , CO	70
Vo-CoO	CO ₂ *→COOH*	CH ₄ , CO	99
Vo-Zn-CoO	CO ₂ *→COOH*	CH ₄ , CO	99
anatase (101) TiO ₂	CH ₃ OH*→CH ₄ * ¹	CH ₄	100
anatase (010) TiO ₂	*CO ₂ → COOH*	CH ₄	100
B-doped g-C ₃ N ₄ /SnS ₂	CH ₂ *→CH ₃ *	CH ₄	72
g-C ₃ N ₄ /SnS ₂	CO ₂ → COOH*	CH ₄ , CH ₃ OH	72
Pt/g-C ₃ N ₄	HCOOH*→CHO*	CH ₄	104
Phosphorus-doped g-C ₃ N ₄	HCOOH → H ₂ COOH	CH ₄	98
O/La-CN	CO ₂ *→COOH*	CH ₄ , CO	78
hydroxylated SiC(1 1 1)	CH ₂ O*→CH ₃ O*	CH ₄ , CO	83
Bi ₉ O _{7.5} S ₆	CO ₂ → COOH*	CH ₄ , CH ₃ OH	105
CuSAs/TiO ₂	CH ₂ O*→CH ₂ OH*	CH ₄ , C ₂ H ₄	82
CuSAs+Au-Cu alloy NPs/TiO ₂	CH ₃ *→CH ₄ *	CH ₄ , C ₂ H ₄	82
m-Ni ₃ X-LDH	CO ₂ *→COOH*	CH ₄	77
Cu ₃ SnS ₄	CO*→CHO*	CH ₄	85
Cu-TiO _{2-x}	CO ₂ → COOH*	CH ₄ , CO, H ₂	81
AuCu-TiO _{2-x}	CO ₂ → COOH*	CH ₄ , CO, H ₂	81

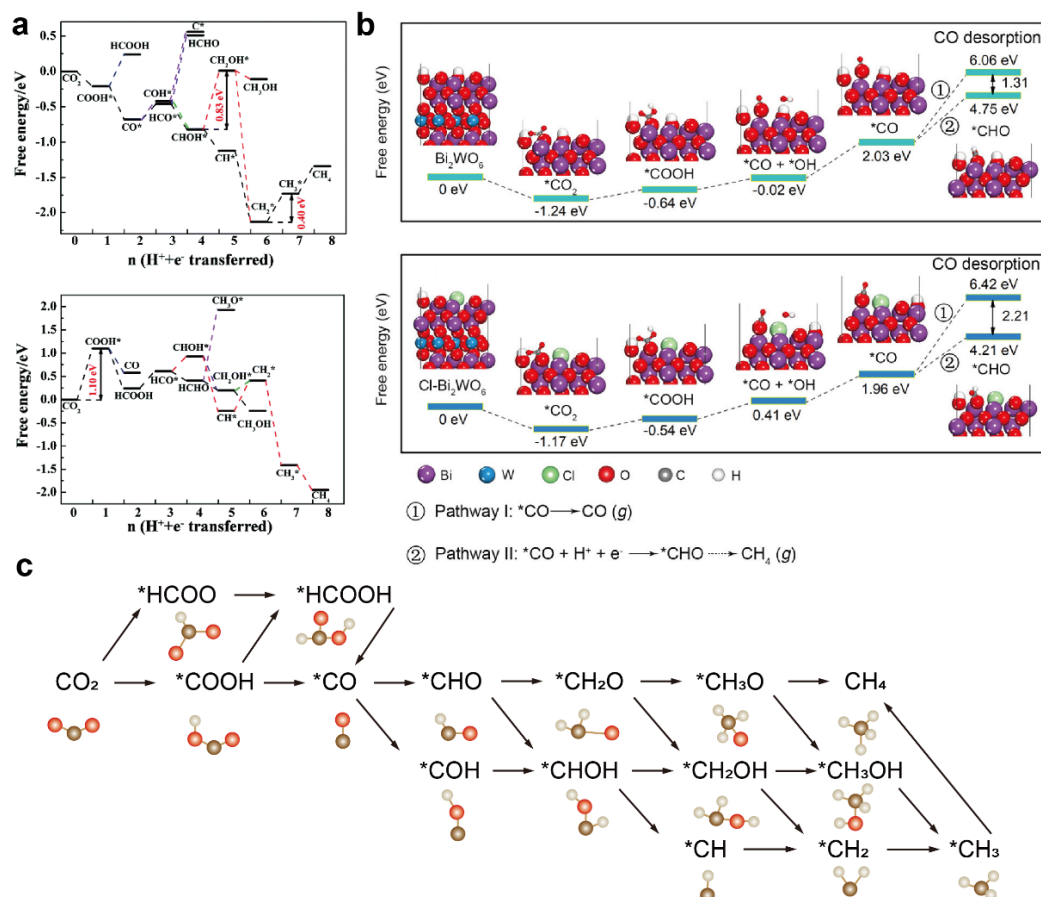


Figure 1-4 (a) Free energy diagram corresponding to the CO₂ reduction reaction path on the Z-scheme B-doped (up) and no doped (down) g-C₃N₄/SnS₂ heterostructure.⁷² Copyright 2018, RSC Publications. (b) Free energy diagrams of CO₂ photoreduction on Bi₂WO₆ (green bars; top) and Cl-modified Bi₂WO₆ (blue bars; bottom).⁷⁰ Copyright 2020, ACS Publications. (c) Theoretical reaction path for CO₂ photoreduction to CH₄. All species refer to surface-adsorbed intermediates where the catalyst surface has been omitted for clarity.

DFT calculations are crucial in electronic description of the photocatalyst. The electronic energy band structure,⁵⁷ d-band center,⁶⁰ adsorption energy,⁶³ coordination number,⁶² etc., showed a high correlation with the CO₂ reduction reaction activity, and these effective features will be helpful for further rapid screening of CO₂ reduction photocatalysts. However, the challenges faced by DFT computation are evident from Table 1-2. The first is that the systems investigated so far tend to have simple and well-defined structures, such as g-C₃N₄,⁷³ metal

oxides,⁸⁴ and other photocatalysts. However, multicomponent systems with complex architectures cannot yet be rigorously investigated by theoretical calculations to the limitations of presently available computational resources. Beyond system size limitations, the large reaction network of all possible steps leading to CH₄ may also be too costly and tedious to fully explore, which can sometimes lead to seemingly conflicting conclusions. It can be seen from Table 1-2 that CO₂* → COOH* is often assumed to be the rate-determining step of the reaction,^{71-72, 81, 99} but not all studies have thoroughly considered all possible CO₂ reduction reaction pathways. Taking the (101) facet of anatase TiO₂ as an example, the rate-determining step of photocatalytic CO₂RR has been reported independently by two different studies to be methanol (CH₃OH) to methane (CH₄)¹⁰⁰ (Table 1-2) and formic acid (HCOOH) to formaldehyde (H₂CO)¹⁰⁶ respectively. The different pathways evaluated in each study likely led to differing conclusions: Yan et al.¹⁰⁰ studied the one-electron pathway CO₂ → COOH* → CO* → CHO* → CH₂O* → CH₂OH* → CH₂OH* → CH₃OH* → CH₄, whereas Ji et al.¹⁰⁶ studied the two-electron pathway CO₂ → HCOOH* → H₂CO* → CH₃OH* → CH₄. However, the optimization of the large number of transition states necessary to fully explore a given reaction network remains too computationally expensive to be routinely performed. Accordingly, we propose several strategies that researchers should consider in order to maximize the utility of their simulations. Firstly, automated reaction network generation tools¹⁰⁷ can be used to systematically enumerate reaction pathways while avoiding human bias. Then, to manage computational cost, the automatically generated network can then be manually pruned according to prior knowledge (e.g., based on surface intermediates identified by in situ experimental studies). Machine learning techniques can also be used to preliminarily screen elementary steps and discard steps predicted to have extremely high barriers. Furthermore, data-driven approaches relying on experimental datasets and computational descriptor libraries may also offer an alternative path forward.

1.2 Functional materials for photocatalytic seawater splitting

By 2050, global energy demand is expected to exceed 810EJ, which is a significant increase compared to 2016 of 28%, and a shift to renewable sources such as solar, wind, geothermal and tidal power is urgently needed to address this growing energy demand because fossil fuels currently used for about 81% of energy consumption.¹⁰⁸ Among them, hydrogen energy has emerged as a candidate because of its zero carbon emissions and the potential for large-scale energy storage and utilization. Proposed as part of the "hydrogen economy" in the 1970s, hydrogen is considered a clean and versatile energy carrier, with water as the only combustion byproduct.¹⁰⁹ By 2050, the demand for hydrogen in the G7 countries is expected to increase by more than 680%, highlighting the important role of hydrogen in the future energy environment.¹¹⁰

At present, hydrogen is mainly produced by steam methane reforming and coal gasification, accounting for more than 95% of global hydrogen production, but it is heavily dependent on fossil fuels and emits considerable greenhouse gases. While water electrolysis faces challenges such as limited scalability, high energy consumption and electrode degradation, it offers a more sustainable alternative.⁹ To overcome these limitations, researchers are increasingly exploring photocatalytic water splitting, which utilizes the photon absorption properties of semiconductor materials to drive the dissociation of water into hydrogen and oxygen using solar energy. This approach, unlike electrocatalysts, benefits from the abundant and cost-effective availability of sunlight, making it a promising strategy for renewable hydrogen production.

Since 97% of the earth's water resources are sea water, the use of this vast and readily available resource for hydrogen production is attracting great attention. Seawater separation not only provides solutions to areas with limited access to fresh water, but also provides pathways to integrate hydrogen production and renewable energy infrastructure.⁸ Excess energy generated during the peak of solar and wind power can be stored as hydrogen, which can address the intermittency of renewable energy sources and improve grid stability. In

addition, the environmental sustainability of seawater separation systems can be assessed through life cycle analysis that assesses the use, manufacture, operation and disposal of resources and minimizes ecological impact.⁹

Despite its potential, photocatalytic seawater splitting faces several technical hurdles. Key challenges include limited light absorption, photocatalytic corrosion, low reactivity, and inefficient charge carrier dynamics. Also, the salinity of seawater, along with the presence of impurities such as trace metals, organic matter and microorganisms, can adversely affect the efficiency and stability of photocatalytic systems. The current solar hydrogen (STH) efficiency for the splitting of seawater remains below the 10% benchmark required for large-scale applications, as specified by the U.S. Department of Energy⁹ Factors such as light scattering, reflection and absorption loss further contribute to these inefficiencies.

Efforts to address these challenges include the development of robust and cost-effective photocatalysts with enhanced light harvesting capabilities, seawater pretreatment techniques, and optimization of reactor designs to improve mass transfer and reaction rates. In addition, the use of sacrificial agents has shown promise in increasing reaction efficiency, but raises concerns about cost, by-product generation, and long-term practicality. Recent innovations in photocatalytic engineering have focused on harnessing the unique properties of nanostructured materials such as plasmonic nanoparticles and monatomic catalysts. These materials provide enhanced catalytic activity through improved charge separation, extended photo response range, and localized surface plasmon resonance (LSPR) effects. For example, integrating an LSPR active material into a photocatalyst can create a strong localized electric field that promotes binding activation and improves the reaction rate.⁸ In addition, hybrid photocatalysts that combine multiple functional components are being developed to enhance stability and efficiency in saline environments.¹¹¹

In the future, advances in photocatalyst design need to be consistent with scalable and sustainable practices. The development of environmentally friendly materials, efficient recycling methods and energy efficient manufacturing processes to ensure the long-term viability of seawater splitting technology, further integrating photocatalyst systems and renewable energy sources, and implementing advanced reactor designs to improve light use and mass transfer are essential to achieving commercial scale deployment.

1.3 Machine learning-aided design of Functional materials

1.3.1 Background

Data-driven innovation is changing the world from every aspect of our lives. Data-driven innovation is commonly used in commercial transactions, such as autonomous vehicles, MuZero and Alphafold (artificial intelligence to master the game and predict protein folding, respectively), by adopting a data-driven approach to the invention of new products and systems based on knowledge extracted from big data by advanced data analysis tools. and the whole technology.¹¹²⁻¹¹⁵ Particularly in material science, the massive amount of data generated by both computations and experiments, in the combination of advancement of ML techniques, have led us to step into the fourth paradigm of scientific research.¹¹⁶

The data-driven paradigm represents the core concept and direction of development of the Material Genome Initiative (MGI), which is driving advances in experimental tools, computational technology and big data analytics.¹¹⁷⁻¹¹⁸ To facilitate the transformation from trial and error to a data-driven paradigm, it is necessary to combine the authority of the three bastions of mathematics and statistics, computer science and materials science with updated knowledge.¹¹⁹ The advancement and proper integration of these domains will benefit the generation and analysis of material data, characterization of uncertainty, and exploration of efficient structure-property relationships, providing new knowledge and accelerating the discovery of innovative materials.

Innovative materials are essential and indispensable to make progress in plenty of applications, from energy conversion and storage to flexible electronics and optoelectronics.^{62, 120-126} For example, new photovoltaic materials that are inexpensive, stable, environmentally friendly, easy to synthesize, and have high power conversion efficiency are being searched by the community.¹²⁷ Another example is the persevering in finding outperformed electrocatalysts with high activity and desired selectivity for carbon dioxide reaction.⁶³ Therefore, the data-driven approach is urgent and necessary to satisfy the growing demand for innovative materials with better and more robust performance.¹²⁸⁻¹²⁹ However, a basic data-driven framework involves three fundamental stages: the employment of data-intensive strategies and ML algorithms,¹³⁰⁻¹³¹ the development of comprehensive database and data generation approaches¹³²⁻¹³³ and the construction of descriptors (bridging data-intensive and experimental strategies).¹³⁴⁻¹³⁵ Therefore, the main goal in this field is to rational design and discover outperformed innovative materials faster and more efficient with the assistance of data-driven approaches. To achieve the goal, it is significant to integrate and utilize the fundamental stages to implement the data-driven process and explore the relationship among composition-structure-process-properties hidden in data.

The data-driven innovative materials discovery has promised some attractive merits because: (1) it has outperformed performance in time efficiency and accuracy compared to conventional trial and error material discovery approaches;¹³⁶⁻¹³⁸ (2) data-driven approaches could quickly learn and extract the complex and implicit inner correlation and knowledge from the massive amount of material data;¹³⁹⁻¹⁴² (3) with the ability to obtain composition-structure-process-property relations, the data-driven material discovery could achieve tailored material design starting from the point of desired functionality;^{136, 143} (4) the advancement of ML models and descriptor construction could directly use complex features such as electron density and molecular graphs for better performance of combinatorial generalization and relational reasoning.^{134, 144} Because of these advantages, many data-driven research articles exhibit potentials of high accuracy and efficiency toward the properties prediction and relation

exploration.¹⁴⁵ Furthermore, some recent examples^{63, 146} show the potential for dynamic and iterative meta-optimization data-driven process, an active learning loop with the synergy of the fundamental stages. Consequently, it is necessary to review the recent advances in data-driven innovative material discovery.

At present, some high-quality reviews on the discussion of data-driven and ML for energy materials,^{120, 139, 147} porous materials,¹⁴¹ high-throughput approaches from density functional theory (DFT) to ML,¹¹⁶ and ML in synthetic chemistry¹⁴⁸ and materials property prediction using ML¹³⁸ have been published. While these discussions have generally focused on a particular type of materials or ML learning techniques, there is a gap in the review of overall synergy among fundamental stages in a framework of data-driven materials innovation, including ML algorithms, materials-related databases, key descriptors and their practical applications. Moreover, with the advancement of each fundamental stage, the local interaction between them, such as ML algorithms for data augmentation and descriptor generation, has demonstrated boosted types of development in very recent years. Accordingly, a timely review of data-driven materials innovation and the emerging broad applications, including energy conversion and storage, environmental decontamination, flexible electronics, optoelectronics, superconductor, metallic glasses, magnet material facilitated by the data-driven process, is expected to promote further research development in the academia and even the industry.

The development of the data-driven framework for material innovation is led by extensive studies of ML algorithms, material databases and molecular descriptors. A classical data-driven framework for innovative material discovery processes typically consists of five fundamental stages: goal identification, data processing, feature engineering, ML and analysis, and application (Figure 1-5)¹⁴⁹. This section summarizes commonly used frameworks for data-driven processes, including direct design, inverse design and active learning. Besides, some critical fundamental stages such as data processing, feature engineering, and ML model training, which are necessary in a data-driven process to utilize and process material data, molecular descriptors, and ML algorithms, will be introduced, respectively.¹⁵⁰⁻¹⁵¹

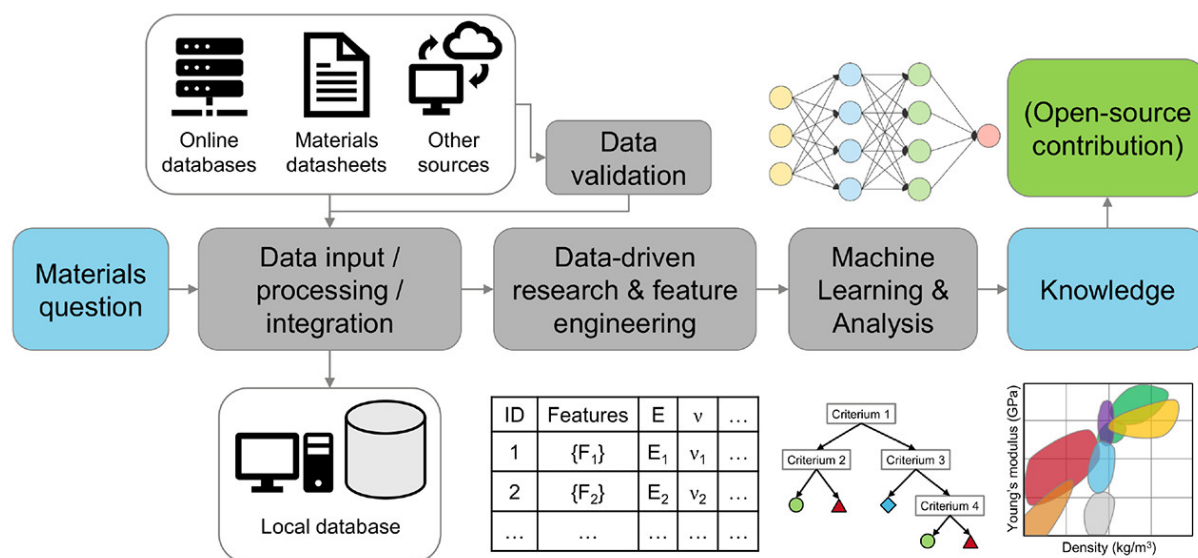


Figure 1-5 The schematic of a ML workflow in the data-driven innovative material discovery process. Reproduced with permission.¹⁴⁹ Copyright 2020, ACS Publications.

The design and selection of the data-driven framework depend on the application and the materials question to be addressed. Though ML is potent and effective in a data-driven process, it is not the panacea to solve all the material questions.¹⁵⁰ ML models cannot find solutions for questions that are ill-posed or not appropriately expressed. An in-depth and comprehensive understanding of the phenomena is necessary to describe the question and convert it to the goal accurately. The goal of a data-driven process should be SMART (specific, measurable, attainable, relevant and timely),¹¹⁶ which is critical and vital for the following fundamental stages. Different ways of goal definition will lead to different outcomes of the data-driven process. For example, for the discovery of outperformed photovoltaic materials, Lu et al.¹⁴⁵ employ ML to predict the bandgap of candidate material, whereas Padula et al.¹⁵² select to predict the power conversion efficiency. Besides, the nature of the material question is also vital for designing the data-driven framework. It is difficult for a classification model to explore the correlation between target properties and input features or for a regression model to distinguish several categories of materials. For instance, Jin et al.¹²⁷ apply a classification ML model to screen out two-dimensional photovoltaic materials with proper power conversion

efficiency. Whereas Sahu et al.¹⁵³ employ a regression ML model to predict the power conversion efficiency of candidate photovoltaic materials. Therefore, to design the data-driven framework, customization in data processing, feature engineering and ML model training is necessary based on the material questions.

With the rapid development of the social economy and improvement of living standards for humans, climate changes caused by excessive emissions of anthropogenic CO₂ and depletion of non-renewable energy sources raise severe challenges to a sustainable future. Currently, electrochemical CO₂ reduction reaction (CO₂RR) presented by researchers can couple carbon-capture storage technology to transform atmospheric CO₂ into fuels or chemicals by various catalysts.¹⁵⁴ CO₂RR is considered a promising, clean, and environmentally friendly strategy to reduce greenhouse gas emissions and resolve the energy crisis. The reduction of CO₂ produces a range of valuable "carbon capture and storage" (CCS) products such as HCHO, HCOOH, CH₃OH, and CH₄.¹⁵⁵⁻¹⁵⁷ Whereas this normal exothermic process is naturally challenging to perform due to the inertness of the CO₂ molecule, thus it depends on the careful selection of highly active electrocatalysts.¹⁵⁸ Therefore, density functional theory (DFT) calculation, widely used to investigate the structure, properties, and reaction mechanisms of electrocatalyst, has become a powerful tool to study catalytic processes and help screen novel electrocatalysts.¹⁵⁹

Although DFT calculations have brought leaps and bounds in the accelerated discovery and design of catalysts,¹¹⁶ high computational costs, constrained space/time systems, and sensitive exchange-correlation functionals still limit DFT calculations are in the footsteps of exploring more complex materials. For example, 1) high-throughput DFT calculations usually require hundreds of thousands or even millions of core hours of supercomputer resources; 2) current DFT calculations cannot describe surface catalytic reactions on amorphous phases, though amorphous structures are common in experimental synthesis; 3) different exchange correlations functional may lead to an error of more than 0.1 eV in the final calculated

adsorption energy, which is already beyond the error predicted by machine learning (ML).⁴¹ Hence, researchers have started to pay attention to taking advantage of ML to solve the above issues.

With the fast development of ML in past decades, ML has received much more attention from researchers in materials science in recent years, and has been used for various applications, such as in photocatalytic⁴⁹ and electrocatalytic¹⁶⁰ CO₂ reduction, water splitting,¹²¹⁻¹²³ fuel cells,¹⁶¹⁻¹⁶² photovoltaics,^{127, 145, 163} nitrogen reduction.¹⁶⁴ Some reviews have discussed the application strategies of ML for energy materials,¹³⁹ ML in DFT,¹¹⁶ ML for the porous material,¹⁴¹ ML in 2D materials¹⁶⁵ and ML in experimental synthesis.¹⁴⁸ However, few reviews discuss ML accelerated calculation and rational design of electrocatalysts for CO₂ reduction with overall synergy in ML workflows.

Different from the previous review on ML in electrocatalytic CO₂ reduction, we mainly divided the application of ML in electrocatalytic reduction of CO₂ into two aspects. For one aspect, researchers constructed a potential function based on artificial intelligence technology to replace the time-consuming quantum chemical calculation process of solving the Schrödinger equation and accelerate the calculation to achieve the purpose of the large-scale and low-cost high-throughput simulation is considered as ML aided in accelerating calculation. For another aspect, the training data originated from high-throughput experimental data or theoretical calculation or model-building data set, which is considered ML aided in the rational design. Therefore, we will offer detailed discussions about the two strategies in the following sections and outline the opportunities and future challenges in ML for electrocatalysts design.

1.3.2 Machine learning-aided in accelerating the calculation

Quantum chemical simulations are usually used to predict the properties of electrocatalysts. However, DFT computations are limited by the accuracy-efficiency trade-off and may become computationally unacceptable depending on the computing system time/space scale. Furthermore, some electrochemical CO₂RR systems, such as multi-metal alloys, are so

complex⁷⁶ that we still have no idea to predict them by performing DFT calculations. To solve the above issue, ML-based force fields,¹⁶⁶ potential functions,⁷⁴ potential energy surfaces (PES)¹⁶⁷ are introduced by researchers to speed up calculation.

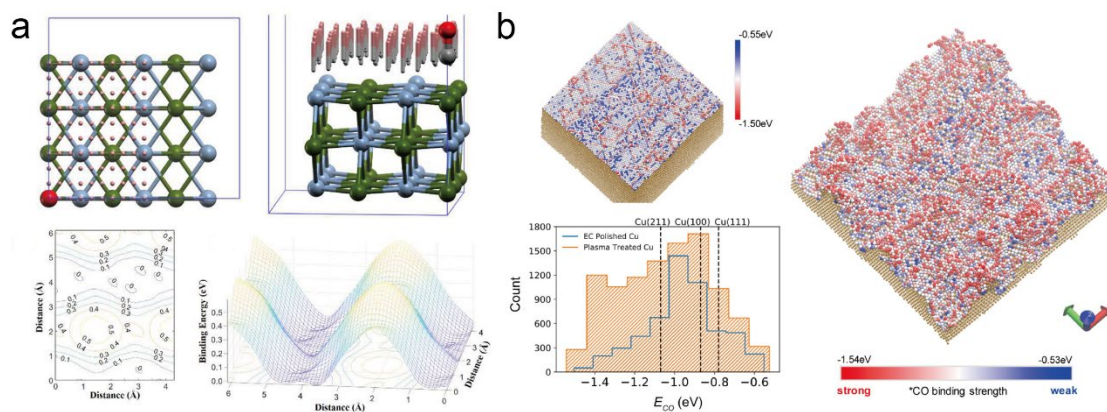


Figure 1-6 (a) Contour plot and 3D view of the positions of chemisorbed CO molecules and CO adsorption energy based on the FF projected onto the Connolly surface.⁷⁴ Copyright 2020, ACS publication. (b) Active site of Cu surfaces roughened by electro-polished and Ar plasma pretreatment visualization by ReaxQM-Machine Learning.¹⁶⁸ Copyright 2020, ACS publication.

Gusarov et al.⁷⁴ developed a novel ML augmented descriptor based on the Fukui function (FF) projected onto a Connolly surface. FFs contain information about the local system's response to perturbations and can be used as descriptors of surface chemistry. By convolving the 2D surface distribution of FFs with specific local modes ($R \sim 3-4$ Å) representing the chemical structure of the reactants, complex reactions with multiple bond formations can be modeled, especially by nonlinear adsorbate and (or) different relative positions of intermediates, as shown in Figure 1-6a, yielding guaranteed reliability. A generic training database of projected FFs was used to select potential active surfaces and their catalytic centers. In the future, it will be possible to replace DFT with new functions based on ML to calculate adsorption energy. Besides, active sites are explored in parallel using an NN-based surrogate model to share information between DFT relaxations, resulting in order of magnitude less explicit DFT computation for activity estimates.¹²⁹ Furthermore, the power-type structural

descriptor developed by Kang et al.¹⁶⁷ together with a feedforward neural network (NN) model with a large dataset of highly complex global accurate potential energy surfaces (PES) and a complex numerical model to predict total energy for large-scale. Recent advances in atomic simulations show great promise to benefit many branches of chemistry with the high speed and high precision to compute large systems. A few reports are using PES to explore the electrocatalytic surface reaction process, which will gradually be utilized in the development process based on ML potential functions.

DFT calculations are severely limited in the ability to handle complex surfaces. To address this conundrum, an ML strategy combined with QM was raised to compute hundreds of 5,000-10,000 surface sites for ReaxFF-grown NPs, which is iteratively trained to achieve an accuracy of 0.05 eV.¹⁶⁶ This ML prediction model is used to predict the performance of all 5,000-10,000 surface sites. Furthermore, the predicted performance of the active site is compared with other properties that can be measured experimentally (XPS, electron density of states, local properties of s, p, d orbitals, work functions) to identify descriptors that may be used to monitor the synthesis of materials with high performance for electrocatalytic CO₂RR. The ReaxQM ML method has been successfully applied to predict the distribution of CO binding energy (ΔE_{CO}) of simulated electrochemically Cu surfaces roughened by plasma pretreatment in Ar (Figure 1-6b),¹⁶⁸ performance of gold nanoparticles (AuNPs) and dealloyed Au₃Fe core-shell NP surfaces in reducing CO₂ to CO,¹⁶⁶ and highly selective for C₂⁺ products in CO reduction on oxide-derived Cu nanoparticles (NPs).¹⁶⁹

1.3.3 ML aided in the rational design

ML-based workflows for materials rational design have been widely used in electrocatalysis. A complete ML-assisted electrocatalytic CO₂ reduction workflow involves four key steps: datasets, descriptors, algorithms, and validation. Besides, building a workflow usually requires an interface to connect each step to achieve high-throughput data interaction. The development and open source sharing of pymatgen,¹⁷⁰ qmpy,¹⁷¹ ASE,¹⁷² and atomate¹⁷³ and

other tools, have stimulated the rapid development of workflow. The sources of data sets are usually generated from existing databases and DFT calculations. Often the data cannot be used directly. Hence, an effective ML model needs to be established through data preprocessing. Descriptors are the key to linking input data and output data. It is necessary to ensure that the correlation between input and output data is highly correlated and lowly correlated between input and output data. In addition, choosing an appropriate ML algorithm is the core step for ML to function. The model performance brought by various ML algorithms is different for different data sets, parameters, etc. Finally, a validated and well-trained ML model will achieve accurate predictions, thereby accelerating materials design and discovery. Wan et al.⁴¹ proposed a rational and innovative framework based on ML accelerated DFT (DFT-ML) shown in Figure 1-7a to study the CO₂RR catalytic activity of hundreds of transition metal phthalocyanine (Pc) DMSCs. The Gradient Boosting Regression (GBR) algorithm was validated as the ideal ML model and used to construct catalytic activity predictions with a root mean square error of only 0.08 eV. The ML prediction results indicate that Ag-MoPc is a promising electrocatalyst for CO₂RR. The DFT-ML hybrid scheme improves the efficiency by a factor of 6.87 compared with DFT. At the same time, the prediction error of DFT-ML is only 0.02 eV, showing the great potential of ML in accelerating the rational design of efficient energy conversion and saving catalysts.

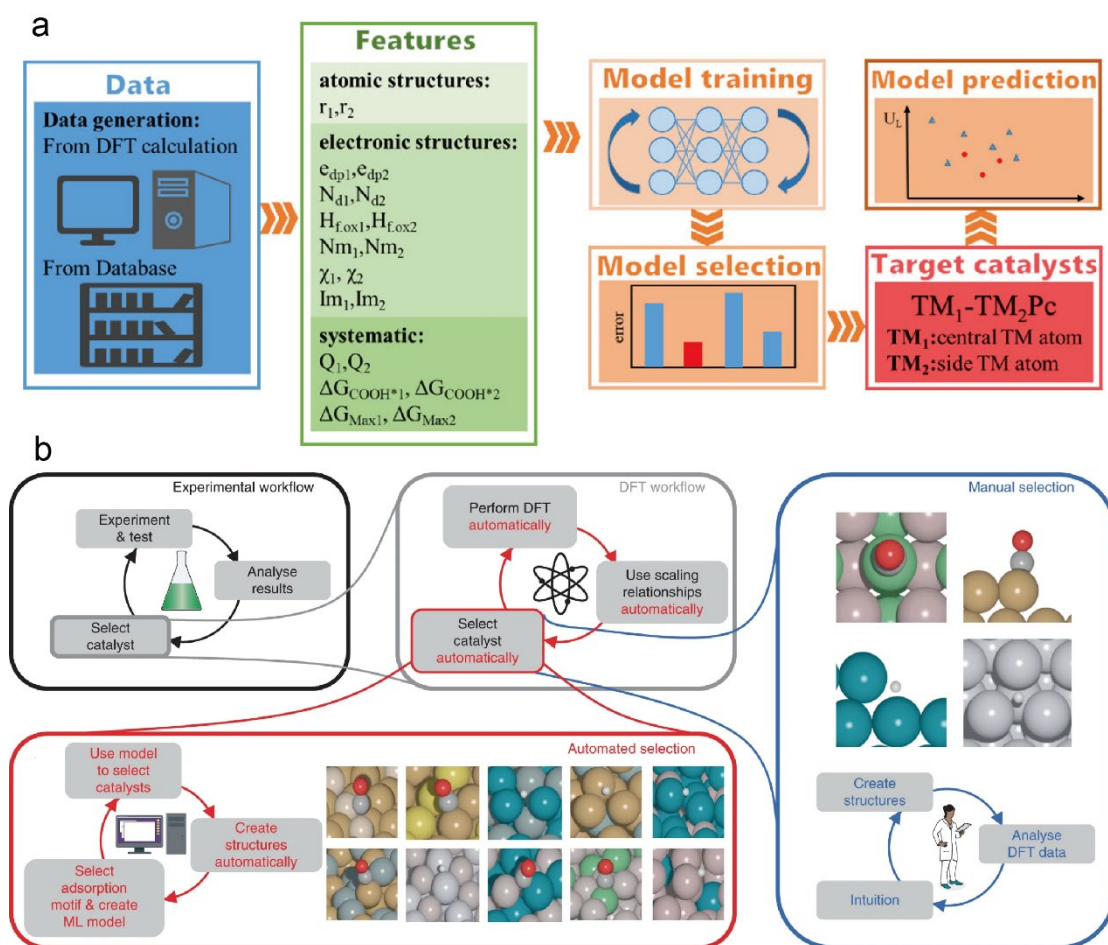


Figure 1-7 (a) Workflow of the ML-accelerated catalytic activity prediction of Pc DMSCs.⁴¹

Copyright 2021, ACS publication. (b) Active learning-based workflow to screen for catalysts⁶²

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Sargent et al.⁶³ collaborated to develop a copper-aluminum electrocatalyst with high Faradaic efficiency using DFT computation and ML. Compared with pure copper, the faradaic efficiency of this copper-aluminum electrocatalyst exceeds 80% at a current density of 400 mA/cm², the highest Faradaic efficiency has been achieved to date. The energy conversion efficiency of the cathode ethylene reaches about 55% (150 mA/cm²). It is worth noting that in this study, they adopted the method of ML, which is employed to construct data sets through DFT calculation, instead of high-throughput experimental screening of trial and error, to achieve the purpose of screening high-performance catalysts. The ML method is used to

quickly search for the optimal bimetallic catalyst components and realize the rational design of catalysts for electrocatalytic CO₂RR.

Furthermore, an advanced active learning workflow was proposed by Ulissi et al.⁶² They designed a fully automated screening method, combining ML and DFT calculations, to automatically search for CO and H adsorption energies on various surface active sites of intermetallic compounds, thereby predicting bimetallic electrocatalysts with high reactivity. Among 31 elements (including 50% of d-block features and 33% of p-block features), they screened out 54 alloys and corresponding 131 surface sites suitable for CO₂ reduction with an automatic ML-based workflow. This workflow uses an ML model to search the space of intermetallic crystals and surfaces for optimal CO₂RR activity. As shown in Figure 1-7b, a closed-loop feedback process, ML screening catalyst, automatic DFT computational validation, and ML model retraining were proposed. It is worth noting that the database generation can be automatically and continuously grown without manual intervention.

In summary, ML-based workflow is roughly achieved through the following four steps:

- 1) Establishment of a dataset/data source.
- 2) Selection and validation of descriptor.
- 3) Selection of ML algorithms.
- 4) Validation and predictions of the model.

Therefore, taking the above-mentioned successful framework for rational design as an example, we will discuss the recent ML in electrocatalytic CO₂ reduction and the challenges in the following sections.

1.3.3.1 Establishment of a dataset/data source

Continued progress in science depends on shared and reproducible data. Building a sizeable open-access database of material properties will help ML accelerate the design of electrocatalysts for CO₂RR.¹⁷⁴ Recent efforts under the Materials Genome Project have led to

extensive reporting of large public databases for computational materials properties. Herein, some popular materials databases could be powerful tools to inspire and design electrocatalysts are presented. An open web-based access database named Materials Project (MP)¹³³ was successfully used to predict the electrocatalyst's adsorption energy.⁶³ For example, 1,499 intermetallic compounds were obtained from a material database named Material Project, and pymatgen¹⁷⁰ was used to enumerate the surfaces of each material, and further triangulate sub-algorithm enumerates the adsorption sites on each surface, thereby obtaining the search space of adsorption sites as a structure file for DFT calculation to establish a data source. As a well-known computational materials database, AFLOW provides a globally available database of 3,312,125 material compounds with over 566,373,375 calculated properties, and the number of data is still growing.¹⁷⁵ The data sources of the above databases are mainly based on theoretical results, whereas ICSD¹⁷⁶ is currently the largest crystal structure data database globally, which contains an almost exhaustive list of inorganic crystal structures, mainly from experimental results. A review by Schleder et al.¹¹⁶ provides a detailed overview of existing high-throughput databases, code, and tools, and brings inspiration to establish a dataset. Although existing databases miss some key descriptors that need to be further processed or calculated by DFT, pre-screening¹⁷⁷ or extracting partially valid descriptors using existing databases⁶³ has already shown its ability to reduce the computational cost to a large extent.

In electrocatalytic CO₂RR, due to the insufficient amount of data obtained from existing databases and missing descriptors, researchers still try to supplement the dataset with the help of DFT. A crystallographic database of 244 different copper-containing intermetallic compounds was established, including 12,229 surfaces and 228,969 adsorption sites.⁶³ DFT simulations were performed on a subset of adsorption sites to calculate their CO adsorption energies. This data was used to train an ML model. The framework then combined ML-predicted CO adsorption energies with 2D selective volcano plots for CO reduction to predict the sites and bimetallic components with the most excellent catalytic activity. Roy et al.¹⁷⁷

considered all possible combinations of 8-atom fcc periodic (111) surface unit cells using 5 metals (Cu, Co, Ni, Zn, and Mg), including pure, bimetallic, trimetallic, tetrametallic, and HEA. The system, of which there are a total of 495 such combinations, involves all possibilities. Afterward, a preliminary stability screening was performed by calculating the atomic-size difference factor, and the ratio taken from Gibbs free energy of mixing for these 495 unit cells. 172 screened stable cells for DFT calculations involving *H, *O, *CO, *HCO, *H₂CO and *H₃CO intermediates for the adsorption of intermediates were built the dataset required for ML training. High throughput electrocatalytic CO₂RR experiments are often difficult to achieve, mainly due to limited catalyst synthesis, testing, and characterization methods. Günay et al.¹⁷⁸ built a database of 471 data points by collecting published results of electrocatalytic CO₂RR experiments. Whereas the equipment and human errors in the experiments from different publications are not negligible. However, the automated robotic experimental platform may reduce the error of the experimental results.¹⁷⁹⁻¹⁸⁰

1.3.3.2 Selection and validation of descriptors

Descriptors are often used to convey relevant information in numerical form to machines through human input. The selected descriptor set will be taken directly as input, or combined into a new simplified but more robust descriptor set through correlation analysis, providing key performance indicator (KPI) fingerprints.¹⁸¹ A good descriptor set offers sufficient resolution for the prediction space.¹³⁹ While this definition obviously depends on the target properties, a typical requirement for target outputs for many materials is that the descriptor set needs to provide a unique correlation, i.e. one-to-one correspondence with crystal/molecular composition and structure. At the same time, the size of the descriptor set should not be too large for efficient training and prediction and to avoid overfitting.

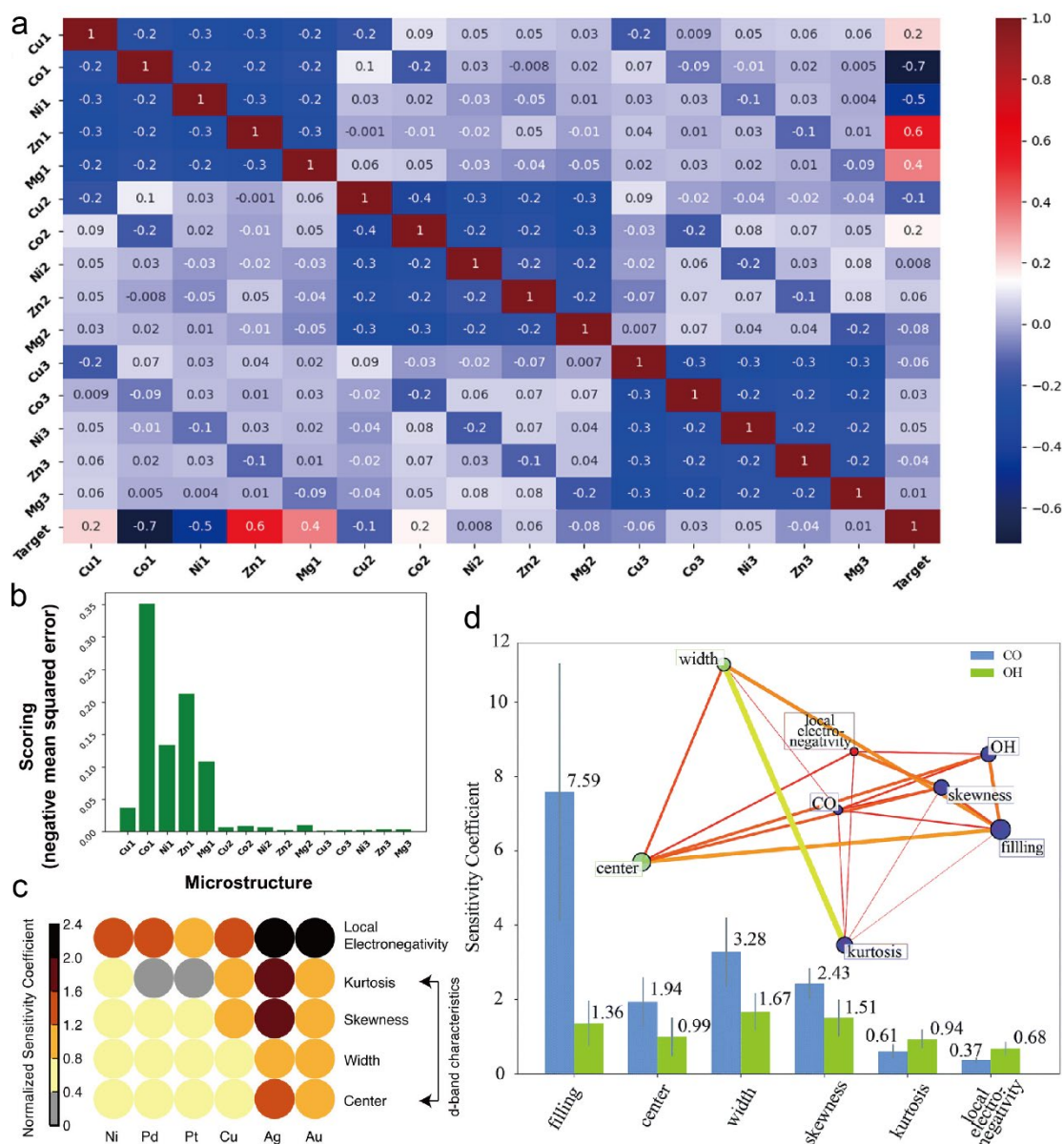


Figure 1-8 (a) Importance ranking for *CO adsorption energy descriptors and (b) correlation matrix of all descriptors and output adsorption energies.¹⁷⁷ 2021, ACS publication. (c) Response coefficients of the trained model for perturbation of the input features.⁶⁸ Copyright 2015, ACS publication. (d) Feature importance scores of *CO and *OH adsorption energies in ANN.⁶⁵ Copyright 2017, RSC publication.

A feedforward artificial neural network (ANN) ML model was used to establish the nonlinear correlation between descriptor vectors and ΔE_{CO} .⁶⁶ The descriptor vector consists of 13 theoretically determined electronic properties, which represent the properties of the clean

adsorption surface, such as the filling (f), center (ϵ_d), width (W_d), skewness (γ_1) and kurtosis (γ_2) of a d-band, and joint with the local Pauling electronegativity (χ_l) determined by delocalized sp-states, were taken as the primary descriptors. Ulissi et al.⁶² used information such as atomic number (Z), electronegativity (c), atomic number (CN), and intermediate adsorption energy (DE) between the element and the adsorbate at the adsorption site to construct a description of the adsorption site. Ma et al.⁶⁶ used ML-assisted rapid and accurate prediction of surface reactivity of metal alloys. The characteristics of the distribution of electronic properties on the catalyst surface and the local Pauling electronegativity, which is mainly determined by the delocalized sp states, are used as the main features. Host metal-related physical constants such as the spatial extent of metal d orbitals, 1 square of adsorbate-metal interatomic d coupling matrix elements, work function, atomic radius, ionization potential, electron affinity, and Pauling electronegativity were employed as secondary features to better characterize the chemical bonding trends on a range of metal surfaces. These properties form a unique fingerprint for each learned sample.

Relatively larger feature spaces may not necessarily lead to more accurate predictions due to the “curse of dimensionality,”¹⁸² a phenomenon in which data becomes sparse in high-dimensional spaces, resulting in model overfitting and increased computation time. Therefore, the researchers employed a rigorous Pearson correlation heatmap process to eliminate low importance or high dependencies. Chen et al.⁶¹ selected the number of d electrons of the metal atom, the electron affinity of the metal atom, the Pauling electronegativity of the metal atom, the first ionization energy of the metal atom, the atomic number of the metal atom, The number of non-metal atoms, the average electron affinity of non-metal atoms, the average Pauling electronegativity of non-metal atoms, the average covalent radius of non-metal atoms, and the average atomic number of non-metal atoms is used as initial features. Figures 1-8a and b show that the 15 input features and the corresponding adsorption energies generated by the surface microstructure are used as outputs.¹⁷⁷ The main content of developing a correlation matrix is

to find the correlation between each input feature to eliminate highly correlated features and reduce the dimensionality of the dataset.¹⁷⁷

The d-band center theory plays a central role in predicting adsorption energy and catalytic activity, and DFT calculations are still needed for large-scale materials screening. Using the d-band width of the muffin-tin orbital theory (to account for the local coordination environment) plus electronegativity (to account for adsorbate renormalization) as a set of simple surrogate descriptors for chemisorption combined with ML methods can achieve low error prediction of CO adsorption energies.⁶⁸ As shown in Figure 1-8c, the d-band center plays a relatively important role in d-band theory for all metal alloys, determining the local Pauli electronegativity of the adsorbate-metal bonding distance and thus the part of interatomic coupling strength in chemical bonding is much more critical than we previously thought.⁶⁶ Figure 1-8d shows the normalized sensitivity coefficients of the *CO and *OH adsorption energies for the 6 main features. The d-band features characterized by lower moments play a more critical role. *CO is more dependent on the d-band features than *OH. The local electronegativity sp-band features indirectly determined by charge transfer are essential for the description phase between *OH and *CO.

Descriptors in the experiments are different from theory, where highest Faradaic efficiency, the highest-rated, and the highest selectivity products have been used as output variables. At the same time, elemental catalyst, support type, cell type, backing layer, membrane type in the cathode, catholyte type and its maximum molarity, anolyte type and its maximum molarity, CO₂ flux, pH, applied potential with Ag/AgCl reference electrode, catalyst loading, catholyte flux and anolyte flux are employed as inputs variables for ML.¹⁷⁸ However, these experimental condition-dependent descriptors cannot be associated with experimental or material databases, leading to a gap between experimental and theoretical data.

1.3.3.3 Selection of ML algorithms

During the development of ML over the past few decades, different algorithms have been proposed to provide solutions for processing data.¹⁸³ As the basis for data-driven research in materials science, these ML algorithms were introduced and applied to catalyst design. ML algorithms mainly include supervised learning,¹⁸³ unsupervised learning,¹⁸⁴ active learning⁶², deep learning¹⁸⁵, etc. However, limited by the small dataset of electrocatalytic CO₂RR, unsupervised learning and deep learning algorithms for electrocatalyst design were rarely reported.

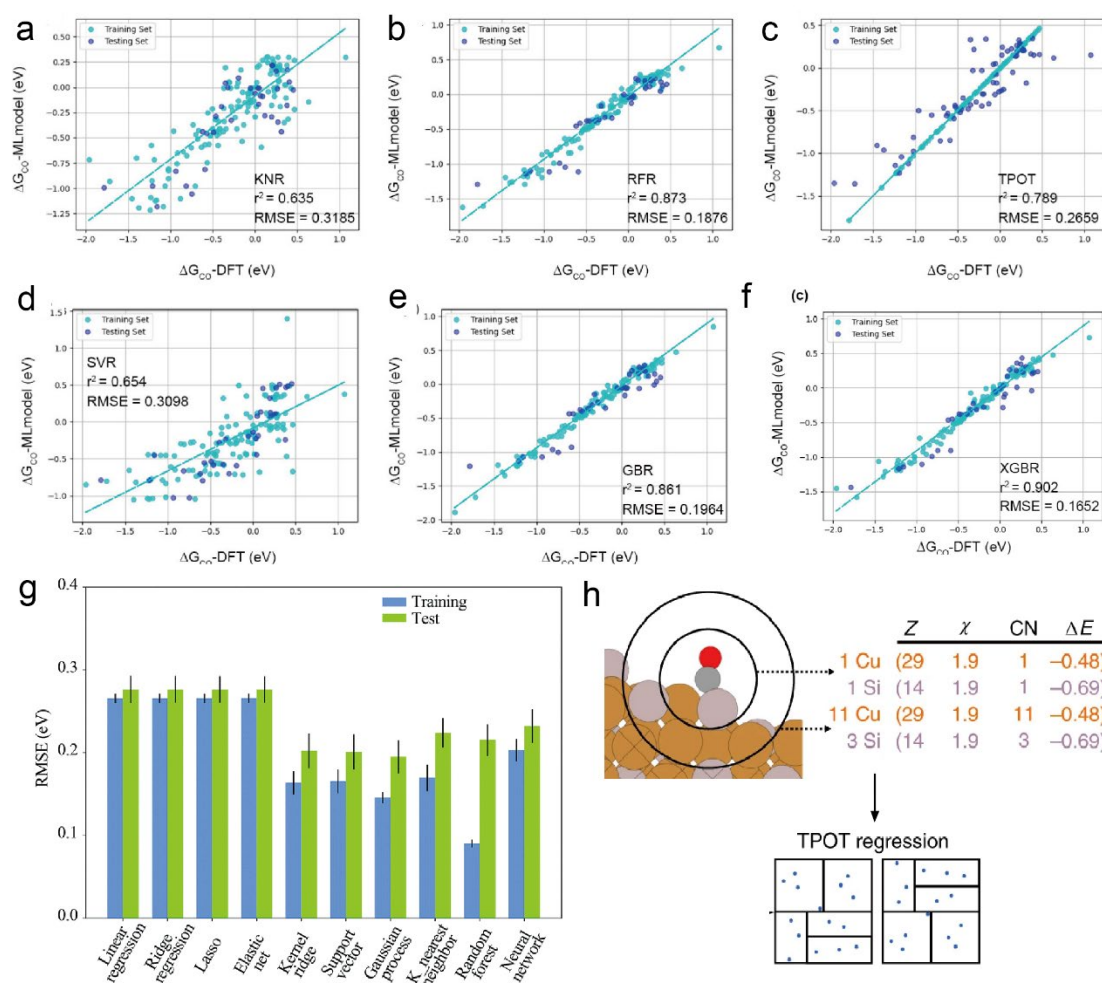


Figure 1-9 Comparison of the predictive performance of models trained by different ML methods: a) KNR, b) RFR, c) TPOT, d) SVR, e) GBR and f) XGBR.⁶⁷ Copyright 2020, ACS publication. g) Comparison of different regression algorithms for training and testing *CO adsorption energies.⁶⁵ Copyright 2017, RSC publication. h) TOPT regression method to predict adsorption energies from the site fingerprints.⁶² Copyright 2018, Springer Nature.

Supervised learning, a learning strategy given both input and output, aims to learn a function that guides the input to the output trained by the provided data.¹⁸³ Chen et al.⁶¹ used the extreme Gradient Boosting Regression (XGBR) model to predict the CO adsorption of atomically dispersed metal-non-metal co-doped graphene systems. Compared with other algorithms, XGBR showed the highest prediction accuracy, followed by Random Forest Regression (RFR) and GBR. K-Nearest Neighbors (KNR) and Support Vector Machines (SVR) models have unsatisfactorily predictive performance with low R^2 scores and high RMSE values. Wu et al.⁶⁷ ML combined with DFT for *CO dimerization and hydrogenation prediction on the catalyst surface. Using multiple ML methods shown in Figure 1-9 a-f, XGBR and GBR show the best performance metrics, with slightly lower error for XGBR. RFR is also a strong predictor comparable to XGBR and GBR. KRR exhibits the most inferior performance, possibly indicating that the linear algorithm oversimplifies the underlying nonlinear problem. KNR, SVR and Light Gradient Boosted Machine (Light GBM) also produce unsatisfactory results. Although ANNs have advanced concepts, they are not suitable for all datasets. Compares the training/testing performance of various ML algorithms. As shown in Figure 1-9g, the linear regression algorithms with varying regularization terms give almost the same results.⁶⁵ The prediction error of CO adsorption energy is 0.28 eV, significantly lower than the other algorithms. With kernel ridge regression, support vector machine, Gaussian process, and K-nearest neighbor, ANN shows similar performance. The random forest algorithm appears to be overfitting, manifesting as minimal training error with limited generalization. Besides, active learning combined with DFT calculations in electrocatalytic CO₂RR has been applied by Ulissi et al.⁶² They used an automated ML tool to select a model, perform DFT calculation and verification on the surface of the optimal binding energy predicted by the model, and complete a total of 42,785 DFT operations. TOPT was considered an ML regression method to predict adsorption energies from the site fingerprints shown in Figure 1-9h.

1.3.3.4 Validation and predictions of the model

A trained ML model needs to make predictions to evaluate model accuracy for validation and further optimization. Before making predictions, we need to verify the evaluation model to ensure the reliability of the prediction results. Usually, 80% of the samples are randomly selected as the training set and the rest of 20% samples as the test set. This random running of the test set from samples is called cross-validation.¹⁸⁶ In addition to failing to make predictions accurately, a failing model will have a high bias (underfitting) if it finds insufficient data for applicable rules, or the algorithm is not flexible enough to reflect the relationship between input and output data. High variance (overfitting) occurs if the model is too complex and has too many parameters.¹⁸⁷

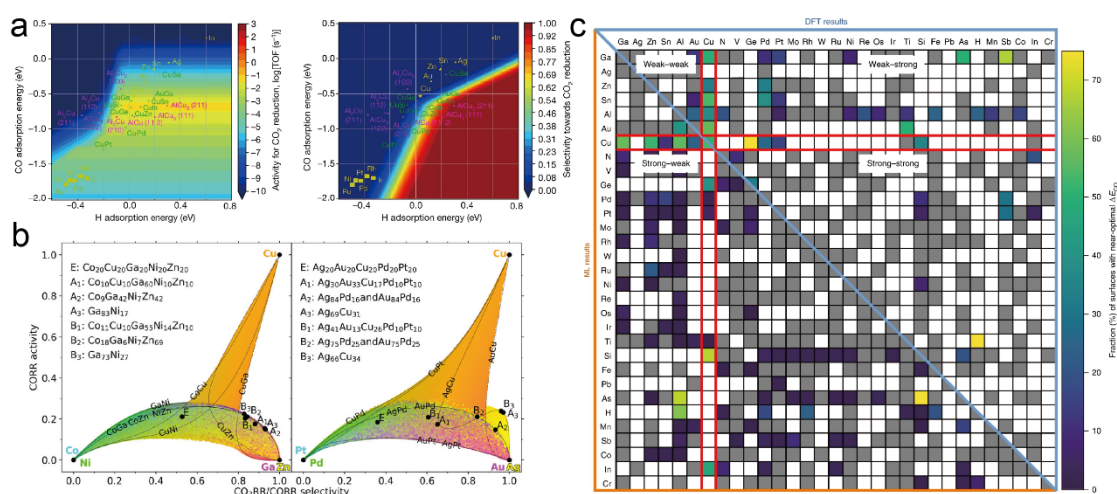


Figure 1-10 (a) Volcano plot for CO₂RR to investigate electrocatalysts performance.⁶³ Copyright 2020, Springer Nature. (b) CO₂RR/CORR selectivity-activity plots to investigate electrocatalysts' performance of multimetallic alloys.⁷⁶ Copyright 2020, ACS publication. CO₂RR activity map of bimetallic electrocatalysts.⁶² Copyright 2018, Springer Nature.

Sargent et al.⁶³ performed DFT calculations on the optimal ML-predicted structures to characterize the changes of reaction energies in the main steps of CO₂ reduction. Benefitting from the introduction of Al, the reaction energy of the C–C bonding rate-determining step is reduced from 1.4 eV to 0.6 eV for Cu (111) and from 0.6 eV to 0.4 eV for Cu (100). Compared with the corresponding pure Cu surface, the reaction energy of the C–C coupling step on the

Cu-Al surface is lower. The DFT results further indicated that the reaction energy for the formation of ethanol intermediate $\text{HO}(\text{CH})\text{CH}$ was higher than that for the formation of C_2H_4 intermediate CCH. Thus, the Cu-Al catalyst inhibited the production of alcohol and promoted the production of C_2H_4 . This work demonstrates the prediction of promising electrocatalysts by combining 2D selective volcano relations (Figure 1-10a) for CO_2RR , DFT, and active ML to optimize catalyst performance. An efficient Cu-Al catalyst was developed for the active and selective electroreduction of CO_2 to C_2H_4 . Roy et al.¹⁷⁷ screened the criteria by the adsorption energy criteria of DFT combined with ML. Finally, seven active catalysts for the selective formation of CH_3OH were obtained, and all active sites for each important intermediate were considered, accelerating the discovery of high-performance multimetallic catalysts and demonstrating the importance of synergy between three or four metals for the activity and selectivity of electrocatalytic reduction of CO_2 to CH_3OH . By combining DFT with supervised ML, Pedersen et al.⁷⁶ predict the CO adsorption energies for all surface sites on the (111) surfaces of disordered CoCuGaNiZn and AgAuCuPdPt HEAs shown in Figure 1-10b, thereby predicting locally optimal disordered alloy compositions. The model can predict effective catalyst candidates without prior knowledge of their catalytic performance. Especially for multi-component alloys, there will be infinite possibilities for the catalytic performance of different compositions. The extreme gradient-enhanced regressor by Wu et al.⁶⁷ identified 81 and 152 unique complementary adsorbate combinations to promote methane and C_2^+ production, respectively, while 80 unique combinations were shown to enhance both methane and C_2^+ production performance. After two years of continuous training, Ulissi et al.⁶² optimized the accuracy of the model prediction, increased the model search space from 20 elements to 31 elements, and predicted the adsorption energies of a series of intermetallic compounds shown in Figure 1-10c for CO and H, including CO adsorption energies of 19,644 sites and the H adsorption energies of 23,414 sites. Although new product-selective catalysts have been successfully found using adsorption energy as the only descriptor, many other factors besides adsorption energy determine the activity and selectivity of catalysts.¹⁷⁷ Thus, this approach

does not always conclusively provide the best catalyst. Still, it can introduce a new approach to discovering new catalysts and generalized analysis of their selectivity for specific products.

1.4 Purpose and scope

- a) The purpose of chapter 2 is to develop a novel Ag-TiO₂ core-shell photocatalyst that leverages plasmon-enabled microenvironment perturbation for efficient and selective photocatalytic CO₂RR. This work addresses key challenges in CO₂RR, including the inertness of the CO₂ molecule and the limitations of traditional photocatalytic designs in achieving both high efficiency and selectivity. By integrating LSPR effects, dynamic reaction microenvironments, and engineered active sites, this study aims to optimize photocatalytic performance for CO₂ conversion into value-added products. The scope of this research encompasses the synthesis of Ag-TiO₂ core-shell nanoparticles, detailed characterization of their structural and electronic properties, and theoretical modeling using DFT and FDTD simulations. The work further evaluates the catalytic performance of the material under solar illumination, focusing on methane production efficiency, selectivity, and stability. This study provides a comprehensive framework for advancing CO₂RR technologies through the synergistic combination of plasmonic enhancement and catalytic microenvironment engineering.

- b) The purpose of Chapter 3 is to develop a novel core-shell photocatalyst, Co-NC@Cu, for efficient and sustainable hydrogen production from seawater using photocatalysis. The project addresses critical challenges in seawater splitting, including the high cost and limited availability of noble metals and the need for sacrificial agents, by designing a low-cost, noble-metal-free catalyst. By leveraging the integration of LSPR effects, single-atom active sites, and a favourable reaction microenvironment, this study seeks to achieve high photocatalytic efficiency and long-term stability. The scope

encompasses material synthesis, characterization, theoretical modelling using DFT, and practical evaluation of the catalyst's performance in seawater hydrogen production.

- c) The purpose of chapter 4 is to establish a comprehensive database for single-atom-based 2D TMD materials using high-throughput DFT calculations and to leverage ML for efficient material design and performance prediction. This chapter addresses the critical need for scalable, cost-effective, and high-performance catalysts by integrating computational and data-driven approaches to accelerate the discovery and optimization of single-atom catalysts. This research aims to uncover fundamental relationships between atomic-scale structures and catalytic properties, driving innovation in material design for energy conversion applications.

1.5 Significance and aims

In Chapter 2, the experimental investigation of Ag-TiO₂ core-shell photocatalytic materials, combined with DFT and FDTD calculations, explores interface interaction dynamics, reaction pathways, and product analysis. The chapter holds significance in three key areas:

- a) **Broad Scope of Research and Advanced Knowledge:** The design spans a wide range of chemical and materials science disciplines, encompassing advanced knowledge in theoretical calculations, photochemistry, redox reactions, and novel redox systems.
- b) **Emerging Possibilities in Catalyst Design through Microenvironment Engineering:** Advances in nanomaterial synthesis have made it increasingly feasible to fabricate multifunctional and complex catalytic structures with precise synthesis capabilities in laboratory settings. Beyond traditional reaction mechanisms, microenvironment engineering has gained significant attention in electrocatalysis. Supported by DFT and FDTD simulations, this chapter demonstrates the fabrication of multifunctional photocatalysts capable of designing reaction-specific electric fields. This approach

establishes a new framework for improving CO₂RR performance by combining localized plasmonic electric fields with tunable microenvironment perturbations, enabling simultaneous optimization of efficiency, selectivity, and stability in CO₂RR.

- c) Insights into Plasmonic Effects and Their Role in CO₂RR: With a comprehensive understanding of plasmonic effects, the chapter explores their impact on the behavior of intermediate species near plasmonic nano-hybrid interfaces and their influence on the formation of CO₂ reduction products. Predictive computational studies further reveal how illumination conditions modulate electric fields, determining the contribution of excited charge carriers to the reaction.

This work will make some impact to be summarized below:

- a) The study provides mechanistic and quantitative guidance on the influence of localized electric fields on photocatalytic activity and the selectivity of ambient redox reactions, paving the way for emerging energy conversion applications.
- b) The chapter explores multifunctional photocatalysts with adjustable nanostructures and localized electric fields, aiming to maximize the synergy between catalyst structures and plasmonic effects as informed by simulation results.
- c) The combined effect of electric fields and surface vacancies alters catalytic activity and selectivity, allowing the fine-tuning of CO₂RR pathways. This integration opens new possibilities for designing microenvironments for CO₂RR, particularly in enhancing product selectivity.

In Chapter 3, we aim to develop a novel Co-NC@Cu core-shell photocatalyst for highly efficient and sustainable hydrogen production from seawater via photocatalysis. This work

combined advanced material design, experimental validation, and theoretical insights to plasmonic photocatalysts for seawater splitting.

- a) Photocatalyst Design and Synthesis: The Co-NC@Cu core-shell photocatalyst will be synthesized with Cu nanoparticles as the plasmonic core, surrounded by a nitrogen-doped carbon (NC) shell decorated with atomically dispersed Co active sites. This structure leverages the localized surface plasmon resonance (LSPR) effect of Cu to enhance solar absorption, improve charge separation, and promote the redox reaction efficiency.
- b) Theoretical Insights into Plasmonic Effects: Through DFT and FDTD simulations, we will investigate the catalytic mechanism at the atomic level. This includes understanding how Co active sites modulate the reduction reaction energy barriers, and how the local electric field (E-field) induced by the LSPR effect perturbs the reaction environment to optimize redox pathways. These simulations will provide quantitative guidance for enhancing efficiency and selectivity.
- c) The catalytic activity, solar-to-hydrogen (STH) conversion efficiency, and stability of the Co-NC@Cu photocatalyst will be systematically evaluated. Key performance metrics include a hydrogen production rate exceeding $9080 \mu\text{mol g}^{-1} \text{h}^{-1}$, an STH efficiency of 4.78%, and long-term stability (>340 hours) under solar illumination. The catalyst's performance will also be benchmarked against state-of-the-art seawater photocatalysts.

This work will make some impact to be summarized below:

- a) This project addresses the dual challenges of energy shortages and environmental pollution by enabling seawater splitting for hydrogen production. Using an earth-abundant and sustainable resource, this work provides a cost-effective pathway for clean energy generation without reliance on noble metals or sacrificial agents.

- b) By combining LSPR effects, tunable reaction microenvironments, and single-atom active sites, this project establishes a new framework for photocatalyst design. This approach not only optimizes the efficiency and selectivity of seawater hydrogen production but also opens opportunities for innovative material engineering strategies.
- c) The integration of experimental and theoretical approaches will advance the understanding of how localized electric fields, surface vacancies, and reaction microenvironments influence catalytic activity. These insights will drive the development of next-generation photocatalysts for broader applications in energy conversion and environmental remediation.

In Chapter 4, we aim to establish a properly single atom based 2D materials database through high-throughput DFT calculations, and efficiently guide material design and performance prediction with the aid of machine learning.

- a) Database construction: Through data generated from high-throughput DFT calculations and the open-source database, with the help of high-throughput data tools pymatgen¹⁷⁰, and ASE¹⁷², the single atom catalyst database will be created to realize classification, management, storage, search, and analysis of data. Based on a newly constructed database, a well-trained ML model is able to easily describe the available physical properties and limiting potentials and use these models to predict the catalytic performance of other dual single atom active sites.
- b) Material discovery: high-throughput DFT computing will combine machine learning, code for high-throughput structure construction, interface between structure and high-throughput DFT calculation, and existing algorithm to screen and discover new multi-element coordinated single atom catalyst and substrate effects for redox reactions based on established databases and other available databases.

- c) Catalytic activity: high-throughput DFT screening of all possible coordination environment, different substrates and composition of single atoms, and then catalytic activity based on the target catalysts under the external perturbation of electric field, light, heat, or the combined effects.

This work will make some impact to be summarized below:

- a) Due to challenges of energy shortage and environmental pollution, means of utilizing $\text{H}_2\text{O}/\text{CO}_2/\text{N}_2/\text{O}_2$ by converting them to higher value products is attracting widespread attention; particularly as these products have potential as industrial fuels/chemicals. An important strategy for $\text{H}_2\text{O}/\text{CO}_2/\text{N}_2/\text{O}_2$ utilisation is the use of electro-/photo-chemical energy conversion to produce the value-added chemicals/fuels. This project will spearhead the materials design of a new generation of catalysts based on cost-effective single atoms anchored on the catalysts. This includes innovative catalyst fabrication based on sustainable methods, tailoring of reaction environments, and application development for efficient conversion to high-value products with improved selectivity. The project will drive significant advancements in how we understand the correlations between the underpinning nano-atomic architectures and the functionalities of the resulting single atom catalysts.
- b) This project aims to construct a larger dataset of single-atom based 2D material catalysts using high-throughput DFT calculations. This dataset will not only accelerate the discovery of new catalysts but also enable the classification, screening, and performance prediction of single-atom based catalysts. By designing a new generation of cost-effective catalysts with single atoms anchored on various supports, the project will establish a database of over 100,000 configurations of single-atom based 2D materials. This expansive resource will drive sustainable methods for innovative catalyst manufacturing, tailored reaction environments, and application development to efficiently transform inputs into higher-

value products with greater selectivity. The project will make substantial progress in understanding the correlation between fundamental atomic-scale structures and the functional properties of single-atom based catalysts, advancing the field of nano-structured catalysis.

- c) High-throughput screening of single-atoms based catalysts for energy conversion requires the support of computational resource in the search space, and the cost of developing the high-performance catalyst is significantly reduced by identifying and removing ineffective catalysts from the screening step. The research not only accelerate the discovery of new catalysts, but also achieve the classification, screening and performance prediction of single atom catalysts. In addition, if this workflow could be further developed for practice, it will also be applicable to other single atoms catalyst with other different substrates.

Chapter 2 Microenvironment Engineering of Photocatalysts for CO₂ Reduction: A Theoretical and Experimental Approach

2. Introduction

The utilization of solar energy enabled by photocatalysts to convert CO₂ into chemical fuels holds immense potential for fostering sustainable human development.¹⁸⁸ However, existing photocatalysts used for CO₂ reduction reaction (CO₂RR) encounter significant obstacles in both efficiency and selectivity.^{7, 189} Improving efficiency without compromising selectivity in CO₂RR, and ensuring long-term operability of these enhancements, are key research priorities globally.¹⁹⁰⁻¹⁹¹ In terms of sacrificial agent-free CO₂ methanation, numerous photocatalysts have emerged over the past five years. Various strategies to improve performance, such as heterostructures, element doping, defect engineering, single-atom methods, and surface functionalization. In these studies, catalysts that achieve near-perfect selectivity (~100%) often exhibit only a mediocre methane production efficiency, even when subjected to elevated pressure and/or temperature.^{6, 32, 192-193} Undoubtedly, a paradigm shift in catalyst design is necessary to achieve an excellent balance between efficiency, selectivity and stability in CO₂RR.

Metallic plasmonic nanoparticles (NPs) with localized surface plasmon resonance (LSPR) have gained attention for photocatalysis. When integrated with photoactive semiconductors, they offer multiple benefits in plasmonic photocatalysis. Specifically, they expand the semiconductor's photo-response range,¹⁹⁴⁻¹⁹⁵ promote charge separation and transfer,¹⁹⁶ harness LSPR to convert light into a strong electric field (E-field) for chemical bond activation,¹⁹⁷⁻¹⁹⁸ and facilitate non-radiative LSPR decay into hot carriers, influencing reactivities.¹⁹⁹⁻²⁰⁰ In traditional plasmonic catalysts, plasmonic NPs are normally deposited onto other functional semiconductors.²⁰¹⁻²⁰³ This configuration presents an inherent limitation wherein only the regions adjacent to the metal-semiconductor junction experience plasmonic

enhancement/modulations from the plasmonic particle. Consequently, the remaining metallic particle's surface area remains largely ineffective, resulting in low plasmon utilization efficiency. The metal-semiconductor core-shell structure with perfect/smooth semiconductor shell coverage enhances the metal-semiconductor contacting areas, but the plasmon meets with an undesirable quenching effect. For example, the hot carrier injection rate decreases significantly with the increase of shell thickness for Al@TiO₂ core-shells.²⁰⁴ Designing high-performance LSPR photocatalysts that maximize metal-semiconductor contact areas while consistently preserving metal's plasmon enhancement at the semiconductor active sites presents a formidable challenge.²⁰⁵⁻²⁰⁶ As a result, most plasmonic photocatalysts still suffer from low conversion efficiency and poor selectivity control.¹⁹⁴

In this work, we have developed Ag-TiO₂ core-shell NPs comprised of an Ag NP core enveloped by a particulate shell layer. This outer shell layer is constructed from densely interconnected, ultrafine TiO₂ NPs. These individual particulate NPs naturally interlink on a glass substrate, where the inner Ag core's nanoplasmonic effect can be propagated outward, giving rise to enhanced nanoplasmonic effect among the interlinked NPs. The strong E-fields generated by these Ag NPs core emerge on the active nanosurface of TiO₂ NPs, serving as dynamic modulators for photocatalytic reactions occurring in close proximity. This results in the effective tailoring of the reaction pathways while retaining high activity in our integrated system. Additionally, the hydrogen treatment applied in this work exposed more oxygen vacancies (O_{vac}), thereby generating more active sites on the nanosurface of the TiO₂. The spatially resolved cathodoluminescence (CL) indicates that individual NPs have a limited distribution of resonance energy, while interconnected NPs achieve effective broadband absorption in the visible and near-infrared regions. Electron energy loss spectroscopy (EELS) provides insights into the plasmonic effect of Ag-TiO₂ core-shell structures, demonstrating that the plasmon effectively transfers to the shell outer layer rather than being quenched. Enhancement of the electric field at the interconnecting points of plasmonic NPs is monitored

by finite-difference time-domain (FDTD) simulations. The synergistic effect of plasmonic networks, active O_{vac}, and complementary light harvesting enhanced the selectivity and activity of pure-water mediated CO₂ methanation, enabling a high 75 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH₄ production rate with a near 100% CH₄ selectivity under solar illumination. These values are superior to those reported based on the pure-water mediated photocatalysis. Density functional theory (DFT) calculations indicated that TiO₂ with vacancies would help suppress CO desorption and generate 6- and 8-electron products, and the stronger E-field modulation from plasmonic networks will further decrease the energy barrier of rate-determining steps while simultaneously increasing the energy barrier of generating other undesirable C1 products. The Ag-TiO₂ NPs developed in this work incorporate plasmonic enhancement, coupling the local plasmonic E-field and active O_{vac} directly onto the TiO₂ nanosurface without any distance separation. The unique integration fulfils the net enhancement of catalytic efficiency and simultaneous control of product selectivity in TiO₂. This work provides guidance for designing ultra-efficient, direct coupling between universal plasmonic E-field and active sites on the same metal oxide semiconductors, enabling optimal CO₂ methanation via reaction microenvironment tunable redox reactions.

2.1 Methods

Chemicals preparation. CTAC (cetyltrimethylammonium chloride) 0.1 M; Na₂S (sodium sulfide) 10 mM; CTAC 30 mM; Ascorbic acid 0.5 M; AgNO₃ (silver nitrate) 0.1 M; NaBH₄ (sodium borohydride) 20 mM; DI water.

Preparation of solution A (Ag Seeds). Ag seeds were prepared in a 25 mL round-bottom flask by mixing 9.5 mL of DI water with 25 μL of 0.1 M AgNO₃, 50 μL of 0.1 M CTAC, and 425 μL of 20 mM NaBH₄. The mixture was stirred at room temperature at 600 rpm for 1 hour. The resulting golden-yellow colloidal solution, named Solution A, contains Ag nanoparticles and has a total volume of 10 mL.

Preparation of solution B. In a 250 mL round bottom flask, add 80 mL 30 mM Hexadecyltrimethylammonium chloride (CTAC), 1 mL 10 mM Na_2S , and 20 mL 0.1 M AgNO_3 . Stir the solution at 600 rpm for 10 minutes. The resulting solution is named solution B.

Preparation of solution C. Add 10 mL solution A into solution B to form solution C.

Preparation of solution D (Ag NPs). Solution C was stirred at 800 rpm and heated in an oil bath to 70 °C. After maintaining this temperature for 20 minutes, 20 mL of 0.5 M ascorbic acid was added. The solution gradually turned from translucent to grey and then to blackish grey after 1 hour of heating at 70 °C. The flask was removed from the oil bath and cooled to room temperature naturally. The solution was centrifuged at 7800 rpm for 10 mins to collect the Ag nanoparticles, which were washed twice with DI water. The final pellet was re-dispersed in 30 mL of DI water to obtain a stable colloidal solution of silver nanoparticles, named Solution D.

Synthesis of Ag-TiO₂ core-shell. A 100 mL round-bottom flask was used to prepare the Ag-TiO₂ core-shell nanoparticles. First, 60 mL of ethanol was added to the flask, followed by 1000 μL of titanium (IV) butoxide (TBT). The mixture was stirred at 600 rpm for 10 minutes to ensure homogeneity. Then, 5 mL of Solution D (Ag nanoparticles) was added, and the mixture was stirred at 600 rpm for 30 minutes. The mixture was centrifuged at 7800 rpm for 5 minutes, washed three times with ethanol, and re-dispersed in 50 mL of DI water. The dispersion was stirred at 600 rpm and maintained at 100 °C for 2 hours. After cooling to room temperature, the solution was centrifuged at 7800 rpm for 5 minutes and washed once with ethanol.

The final sample was dispersed in 10 mL of ethanol and transferred to a quartz boat. It was annealed in a muffle furnace at 450 °C for 2 hours with a heating rate of 5 °C/min to obtain the Ag-TiO₂ core-shell nanoparticles without hydrogen treatment. For hydrogen reduction, the sample was dispersed in a quartz boat and annealed in a tube furnace at 300 °C for 2 hours under a gas mixture of 90% Ar and 10% H₂ (heating rate: 5 °C/min).

Synthesis of TiO₂ (Control): The same method was employed for TiO₂ synthesis, but the 5 mL of Solution D was omitted.

Sample characterization

TEM images, HAADF-STEM imaging and EDS mapping were recorded by JEOL 2100F FEGTEM. The surface analysis of X-ray photoelectron spectroscopy (XPS) was collected by an Al K α X-ray source, 1486.6 eV (Kratos AXIS Ultra DLD). SEM images were recorded by Zeiss UltraPlus Field emission scanning electron microscope. XRD patterns were acquired by Bruker X-ray diffractometer (Cu K α). EPR spectra were acquired by a Bruker E500 spectrometer equipped with a Bruker ER 4122 SHQE resonator. UV-Vis absorption spectra and band gap calculation were according to the data obtained by a Shimadzu UV-3600 UV-Vis spectrophotometer. FT-IR spectrum was collected from the Fourier transform infrared spectroscopy (Bruker FT-IR Vertex 70 spectrometer). The Brunauer-Emmett-Teller (BET) surface area was measured by using micromeritics ASAP-2020. Light source is 300 W Xenon lamp from PerfectLight. Gas products were analyzed by Nexis GC-2030 (Shimadzu Scientific instruments) which is equipped with a thermal conductivity detector (TCD), and a flame ionization detector (FID) with the ShinCarbon column. More characterization details are described in the Supplementary Methods section. CO-TPD was conducted using Thermo Scientific TPDRO-1100 series equipment fitted with a TCD detector. 50 mg sample was first flushed with He for 5 min before H₂ reduction treatment with 5 vol% H₂/N₂ from 50 °C to 300 °C (5 °C ramping rate) and held at 300 °C for 2 hours. After reduction, the reactor was allowed to cool down to 50 °C for CO saturation with 10 vol% CO/He for 30 mins. Subsequently, He was flown to remove any physically adsorbed CO. CO₂-TPD profile was recorded with temperature ramping at 10 °C/min in 30 mL/min He flow. Samples without undergoing H₂ reduction treatment were instead subjected to dehydration at 120 °C for 30 min (10 °C ramping rate) before CO saturation.

TRPL Measurements

TRPL curves are captured at room temperature using an Horiba iHR 320 mm spectrophotometer equipped with a compact single-photon silicon detector (PPD-900, detection range between 350-920nm). A 375-nm picosecond pulse laser (Horiba DeltaDiode) is used as an excitation source with a pulse width of 45 ps. The laser light is focused on the samples through an Olympus BX53 microscope equipped with a 50x objective lens and an X-Y micropositioner. All measurements are done with a 16.6 MHz repetition rate. The lifetimes are calculated by fitting the decay curves with a biexponential decay function.

The finite difference time domain (FDTD) simulations

The theoretical finite difference time domain (FDTD) simulations were all performed by performing Lumerical (FDTD solutions, Lumerical Solutions, Inc., Vancouver, Canada) software. The optical parameters of Ag and TiO₂ used in FDTD simulation were calculated from the results of DFT calculations. We assumed that the background medium was air with an index of refraction of 1.0. A total field-scattered field (TFSF) source of light consisting of plane waves was used as the incident light source. A uniform grid size of 1 nm (x, y, and z) was accepted to ensure the accuracy of E-field calculations. A frequency-domain field distribution monitor was used to evaluate the E-field distribution. The perfectly matched layer (PML) absorbing boundary conditions was considered. The E-field magnitude from the incident light was received by following steps ²⁰⁷:

$$I_{\text{ave}} = c\epsilon_0 E_0^2/2$$

$$E_0 = (2I_{\text{ave}}/c\epsilon_0)^{1/2}$$

where I_{ave} is the intensity of incident solar simulator (100 mW/cm²), c is the speed of light, ϵ_0 is the permittivity of free space, and E_0 is the maximum E-field strength.

Density functional theory (DFT) calculations

The DFT calculations were studied by using the Vienna ab initio Simulation Package (VASP) code²⁰⁸⁻²⁰⁹. Projector Augmented Wave (PAW) pseudopotentials²¹⁰ was used to deal with the core electrons and the Perdew-Burke-Ernzerhof (PBE) function of the generalized gradient approximation (GGA)²¹¹ was used to describe electron exchange and related interactions. The cutoff energy of the plane wave basis was set to 420 eV. The convergence criteria for energy and force are set to less than 10⁻⁴ eV and 10⁻² eV/Å, respectively. In addition, the van der Waals (vdW) correction was considered for the dispersion correction using Grimme's DFT-D3 method²¹². For calculating optical properties of Ag and TiO₂, the Brillouin zone was sampled with 30 × 30 × 30 and 20 × 20 × 10 Monkhorst-Pack grids for Ag and TiO₂, respectively. The 2 × 2 × 1 supercells are used to construct slab model for calculating free energy to avoid the interactions caused by periodicity. The vacuum of 10 Å was set to avoid interlayer interactions. For calculating free energy, the Brillouin zone was sampled with a 3 × 3 × 1 Monkhorst-Pack grids.

Calculation of selectivity

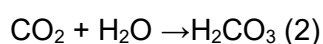
The selectivity for CH₄ was calculated by the amount of electron transfer during the reaction:

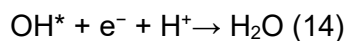
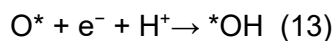
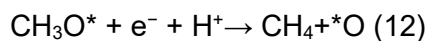
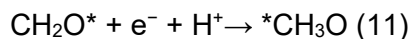
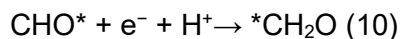
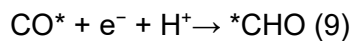
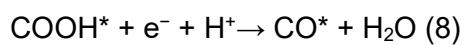
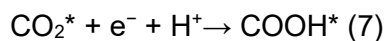
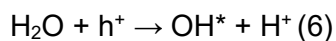
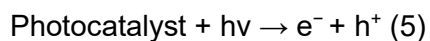
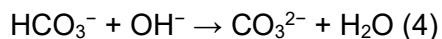
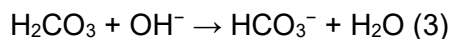
$$SCH_4\% = [8 \cdot R(CH_4)] / [2 \cdot R(CO) + 8 \cdot R(CH_4)] \cdot 100\%$$

Where the R(CO) represents the yield of CO while the R(CH₄) represents the yield of CH₄.

Reaction pathway

Specific reaction processes during CO₂ photoreduction to CH₄ process:





Photocatalytic experiments

The photocatalytic CO₂ reduction reaction was carried out in a gas-solid phase reaction in a quartz reactor tightly sealed by a septum and parafilm. The reaction was conducted under light irradiation of a 300 W Xe lamp (PLS-SXE300D, Perfect Light) with AM 1.5G filter without the use of any sacrificial agents. Typically, 5 mg of the sample was dispersed in 2 ml deionized water and was sonicated (B2500R-DTH, Branson) for 15 min. Then, the suspension was dropped onto a glass substrate, and dried at room temperature naturally to form a thin film.

Subsequently, the glass substrate with the sample was placed into the reactor for the gas-solid phase reaction. Then, the reactor was sealed and purged with pure CO₂ for 20 mins to remove the air. At last, the Xe lamp was turned on to conduct the photoreaction. All experiments were repeatedly performed three times. The photocatalysts were collected and dried after photocatalytic reaction done. Afterwards, the dried photocatalysts were tested for the subsequent cycle of CO₂ photoreduction. The recyclability of photocatalysts was examined in five consecutive cycles.

2.2 Results and Discussion

2.2.1 Understanding the Structure of Ag-TiO₂ Core-shell

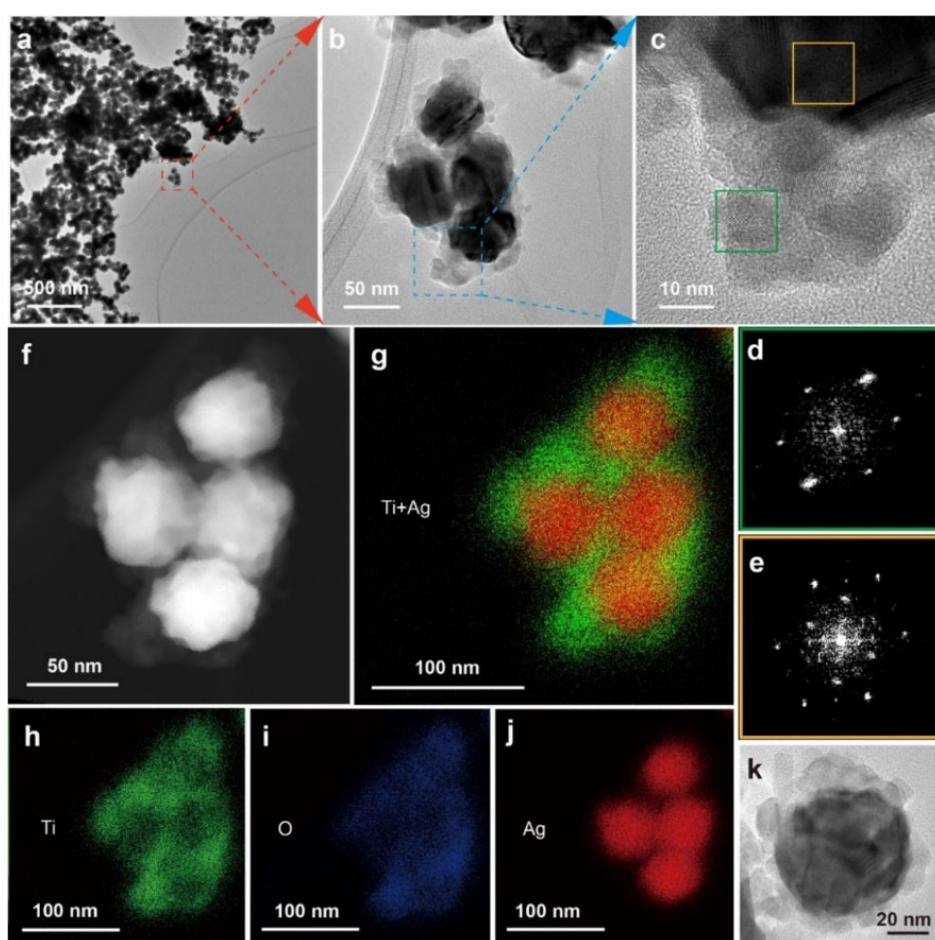


Figure 2-1 HRTEM and EDS element mapping. (a)-(c), HRTEM image of the Ag-TiO₂ NPs as the photocatalyst. Fast-Fourier-transform (FFT) images of the (d) TiO₂ (green rectangle) and

(e) Ag (orange rectangle) from (c). (f) HAADF-STEM image of 4 units of Ag-TiO₂ NPs and (g) the corresponding element mapping for (h) Ti, (i) O and (j) Ag. (k) HRTEM image of a single unit composed of an asymmetric Ag-TiO₂ NP.

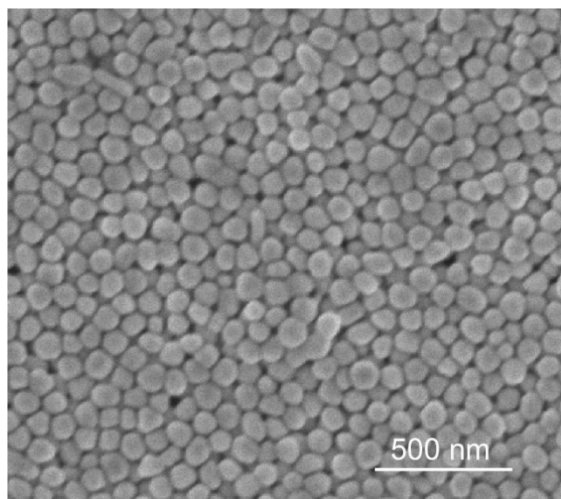


Figure 2-2 SEM image of the Ag NPs used for Ag- TiO₂ photocatalyst. The size of Ag NPs is around 55-60 nm.

The high-resolution transmission electron microscopy (HRTEM) measurements in Figure 2-1a-c show the sample composed of core-shell NPs with uniform 55-60 nm Ag NP cores encapsulated by a particulate shell layer, constructed from densely interconnected TiO₂ NPs. The uniformly sized Ag NPs used in the synthesis were also observed in the SEM of Figure 2-2. As shown in Figure 2-1c, obvious crystalline structures were observed in the HRTEM image, and the FFT pattern of Figures 2-1d and e indicated the formation of highly crystalline TiO₂ and Ag after the calcination and hydrogen reduction treatment.

The measured spacing is 0.24 nm and 0.35 nm (Figure 2-3) after inverse FFT, which can be attributed to the (111) planes of Ag and the (110) planes of TiO₂, respectively. The HRTEM (Figure 2-1b), which corresponds to a larger area scan, confirm that the surface of Ag NPs sample after calcination is enveloped by TiO₂ NPs, forming an interlinked system, composed of asymmetric Ag-TiO₂ NPs (Figure 2-4). While an appropriately quantified precursor can

synthesize a thin layer of the shell, excessive or inadequate precursor will result in the failure of the synthesis of the desirable particulate shells (Figure 2-5 and 2-6). The Ag-TiO₂ NPs are also visualized by scanning transmission electron microscopy (STEM) with high-angle annular dark field (HAADF) imaging (Figure 2-1f). In addition, energy dispersive spectroscopy (EDS) mapping and corresponding spectra (Figures 2-1g-j and Figure 2-7) show that Ti and O elements are consistently distributed around the surface of Ag NPs, further validating the formation of the Ag-TiO₂ NPs. Figure 2-1k shows the HRTEM image of a single Ag NP wrapped by the particulate TiO₂ shell.

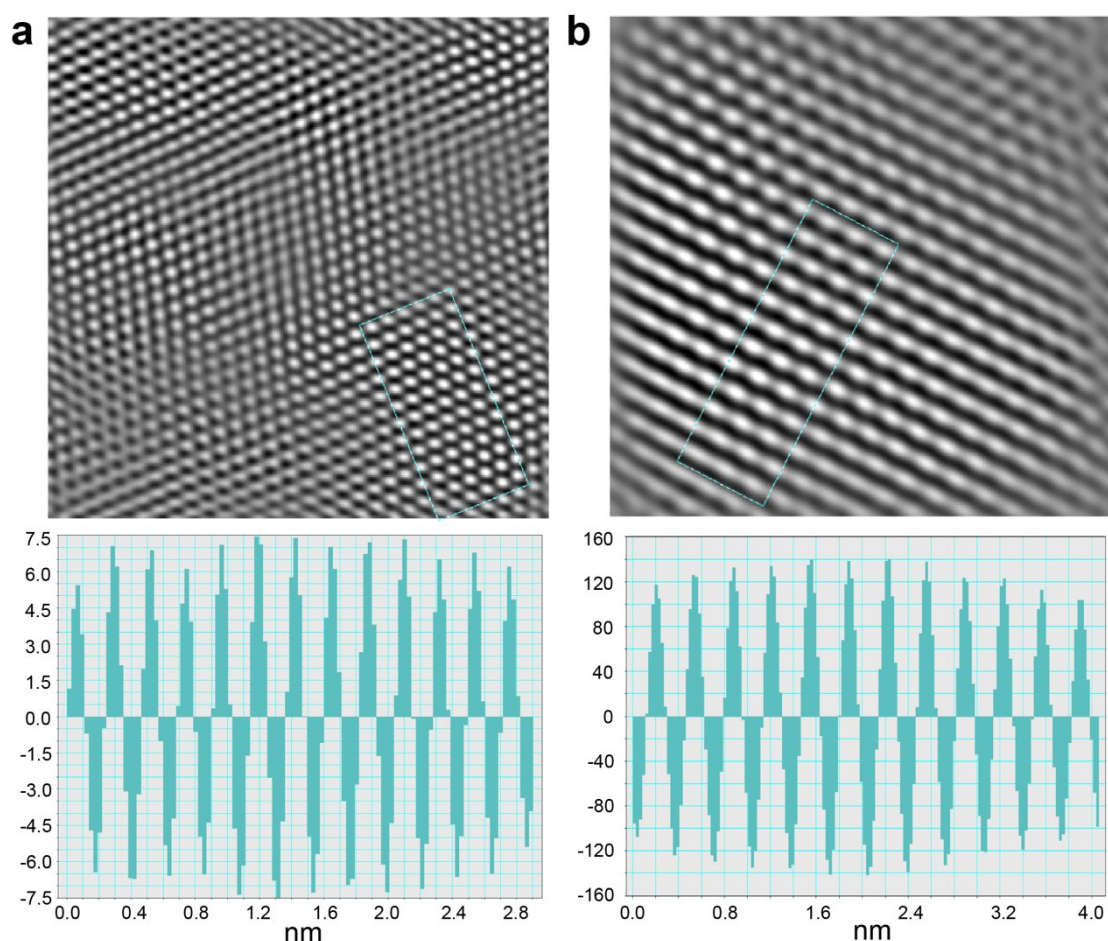


Figure 2-3 The Fourier filter image (FFI) and lattice distance measurement via image software of (a) Ag and (b) TiO₂. The measured spacing is 0.35 nm for a, and 0.24 nm for b, which can be attributed to the (110) planes of TiO₂ and the (111) planes of Ag, respectively.

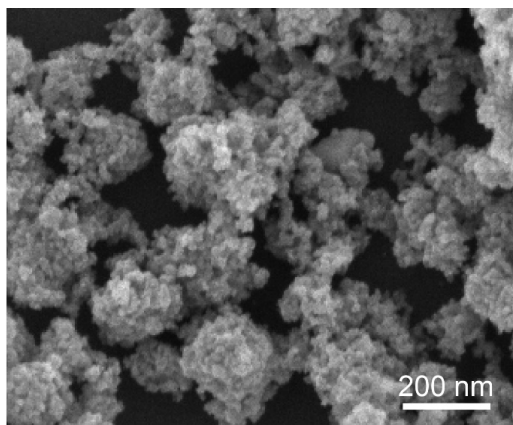


Figure 2-4 SEM The SEM image of Ag-TiO₂ core-shell photocatalyst synthesized using 1000 μ L TTB precursors.

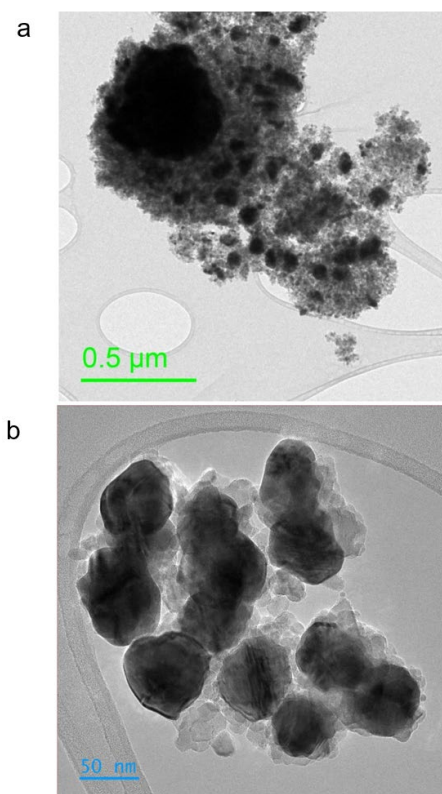


Figure 2-5 The HRTEM image of Ag-TiO₂ synthesis by insufficient volume of precursors (500 μ L TTB). (a) Insufficient TiO₂ precursor promotes the aggregation of Ag NPs due to incomplete encapsulation. (b) Insufficient TiO₂ precursor causes partial coverage of Ag NPs by TiO₂, resulting in a lack of uniform core-shell structures, as demonstrated.

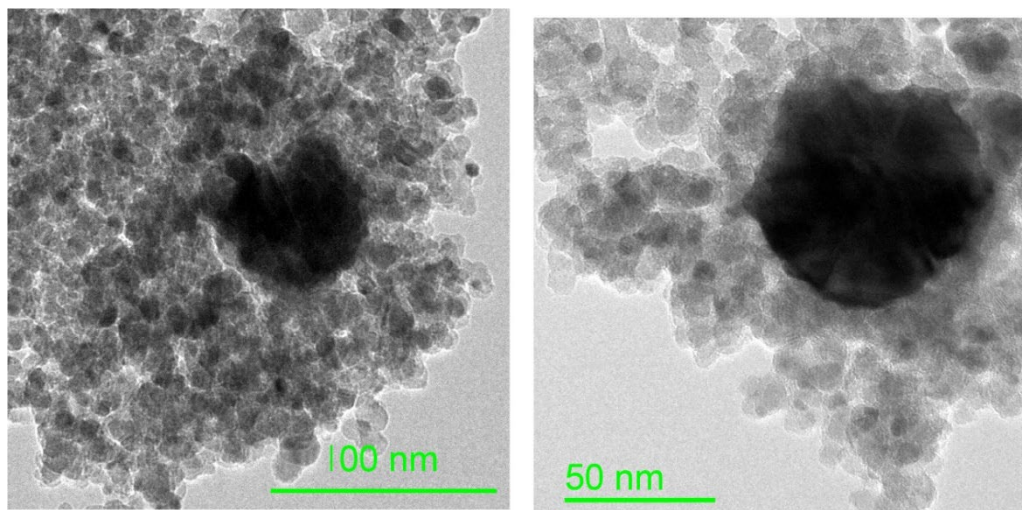
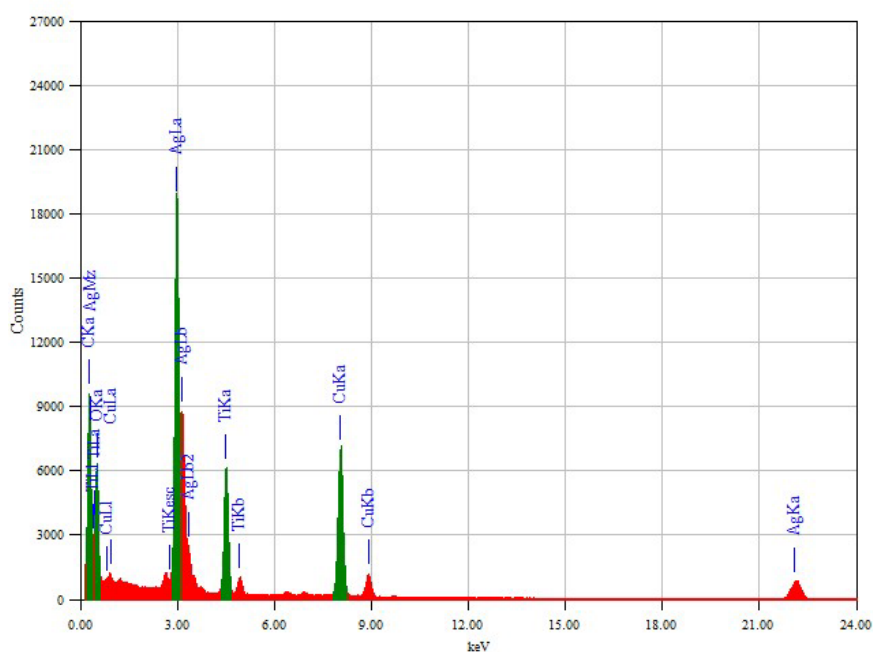


Figure 2-6 The HRTEM image of Ag-TiO₂ synthesis by excess of precursors (1500 uL TTb).

Ag NPs are covered by a large amount of TiO₂.



48.0°, 53.9°, 55.1°, 62.7° and Ag at 44.3° and 77.5° (orange area) in the Ag-TiO₂. The hydrogen-treated sample shows a reduced peak of surface adsorbed O²⁻ and an increased peak of paramagnetic Ti³⁺ through electron paramagnetic resonance (EPR) characterization shown in Figure 2-8b.

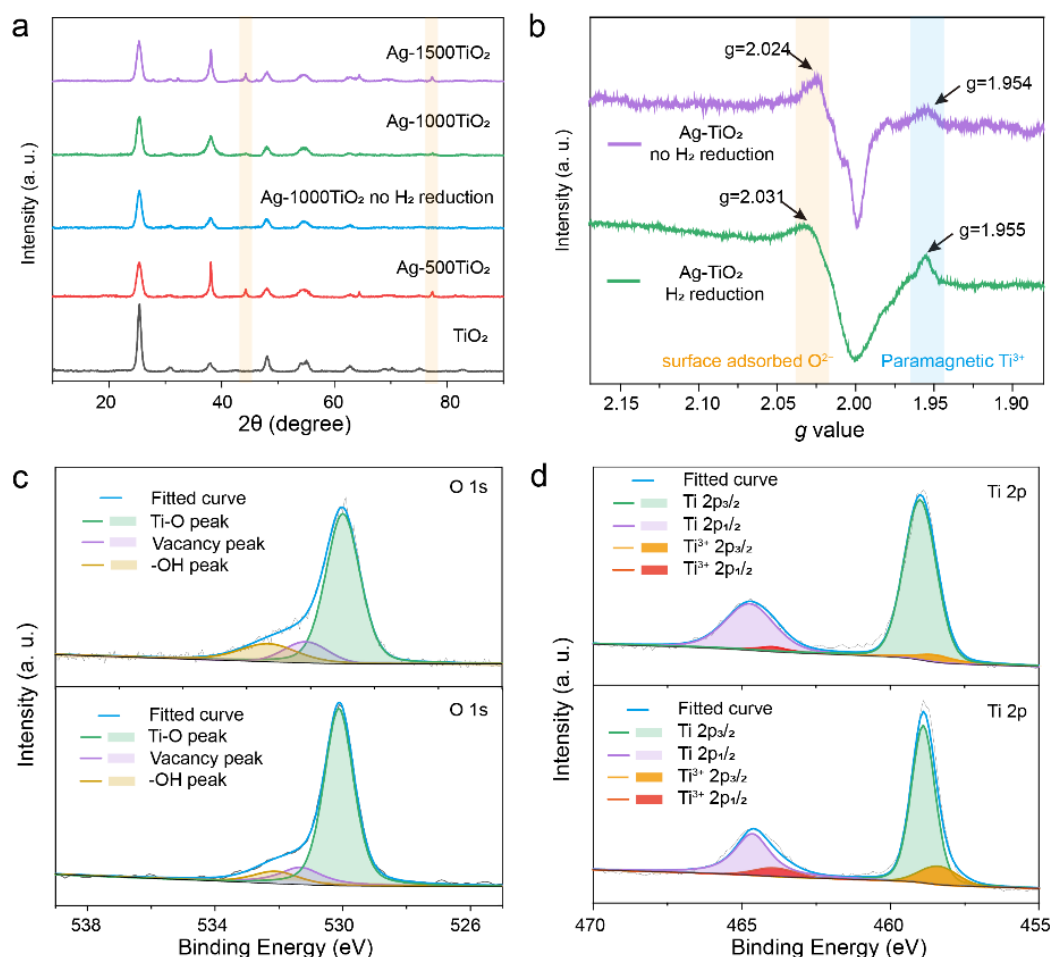


Figure 2-8 XRD, EPR and XPS characterization. (a) XRD profiles of Ag-TiO₂ NPs under optimization with different precursors. (b) EPR spectra of Ag-TiO₂-1000 samples with and without hydrogen reduction treatment. XPS spectra for (c) O 1s, and (d) Ti 2p peak of Ag-TiO₂-1000 sample without (top) and with (bottom) hydrogen reduction. Ag-TiO₂-1000 is named by the amounts of precursor.

Hydrogen can partially reduce the TiO₂ NPs driven by hydrogen reduction,²¹³ forming OH groups, and injecting electrons into TiO₂ to create Ti³⁺ sites.²¹⁴ To reveal the chemical

composition and electronic properties of the Ag-TiO₂ photocatalysts, X-ray photoelectron spectroscopy (XPS) was performed with the results shown in Figures 2-8c, 2d and Figure 2-9-2-12. The Ti 2p XPS spectrum reveals two peaks at 458.8 and 464.6 eV that are assigned to Ti 2p_{3/2} and Ti 2p_{1/2}, indicating the Ti⁴⁺ oxidation state in TiO₂. In addition, secondary peaks at 458.4 eV and 463.9 eV can be discerned, which are indexed to Ti³⁺ Ti 2p_{3/2} and Ti 2p_{1/2}. The O 1s XPS core-level spectrum can be divided into three spin-orbit peaks at 530.2, 531.4, and 532.3 eV, corresponding to metal-oxygen bonds (Ti-O), vacancies with low oxygen coordination, and adsorbed hydroxyl groups or H₂O, respectively.²¹⁵

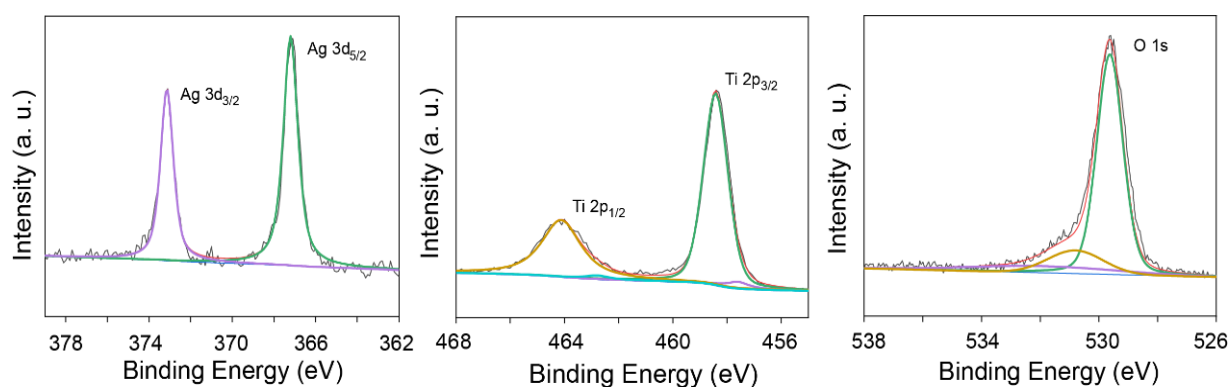


Figure 2-9 XPS spectra for Ag 3d, Ti 2p and O 1s peak for 2D TiO₂ Ag photocatalyst without hydrogen reduction treatment.

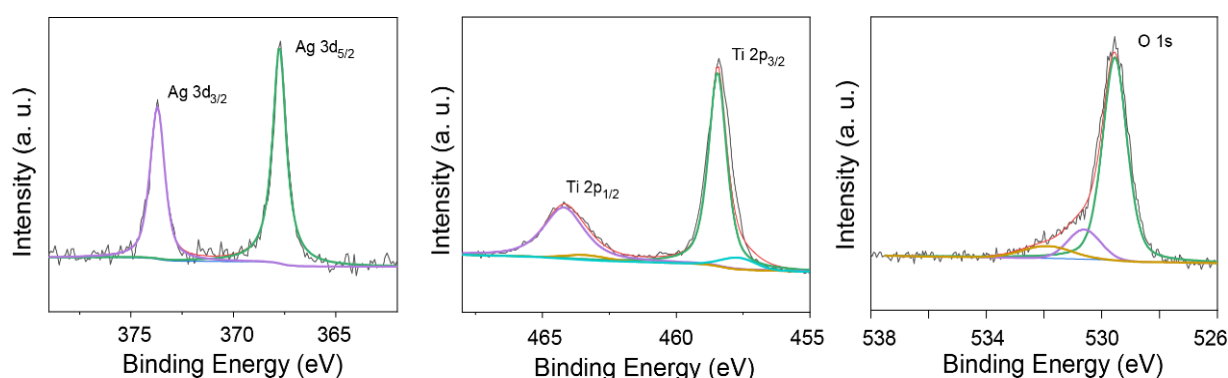


Figure 2-10 XPS spectra for Ag 3d, Ti 2p and O 1s peak for 2D TiO₂ Ag photocatalyst with hydrogen reduction treatment.

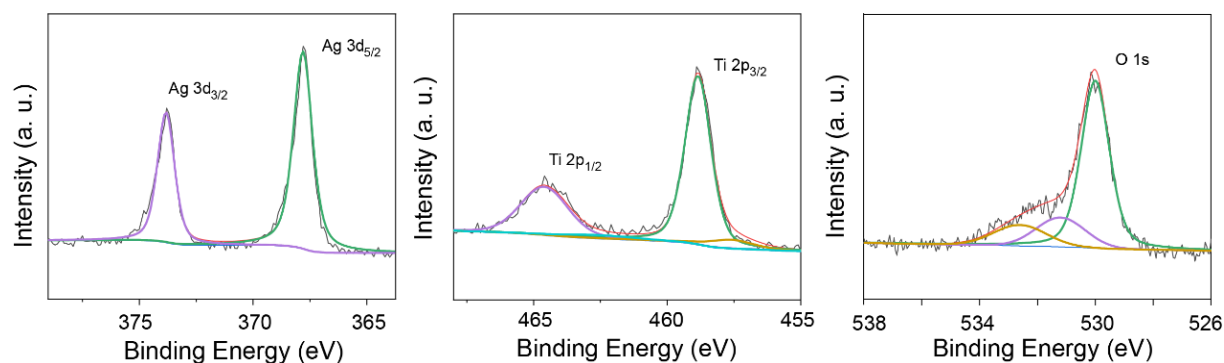


Figure 2-11 XPS spectra for Ag 3d, Ti 2p and O 1s peak for Ag-TiO₂ photocatalyst synthesized by using 500TTB precursors.

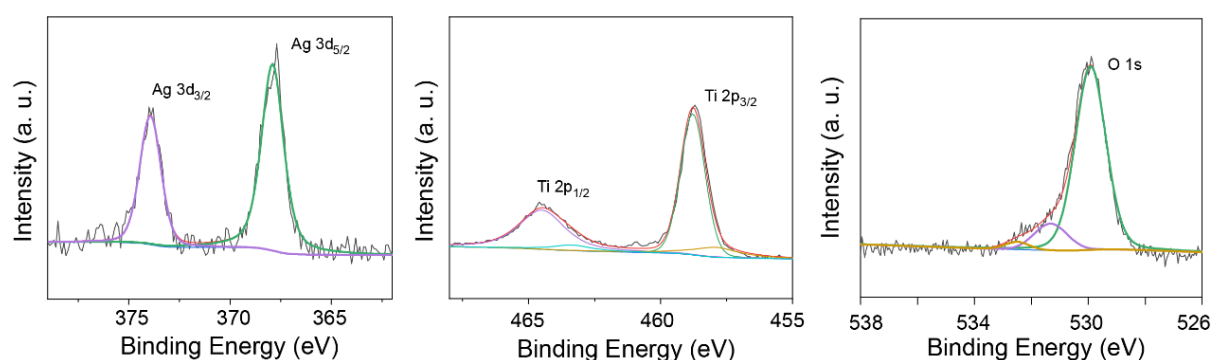


Figure 2-12 XPS spectra for Ag 3d, Ti 2p and O 1s peak for Ag-TiO₂ photocatalyst synthesized by using 1500TTB precursors.

Figure 2-13 shows the Ti K-edge XANES spectra for TiO₂ samples before and after H₂ treatment. The slight shift to a lower energy for the H₂-treated TiO₂ sample suggests partial reduction of Ti⁴⁺ to Ti³⁺. This reduction is indicative of a decrease in the average oxidation state of Ti. The reduction of Ti⁴⁺ to Ti³⁺ under H₂ treatment is typically accompanied by the generation of oxygen vacancies. These vacancies play a crucial role in enhancing catalytic activity by acting as electron donors or trapping sites, thus modifying the electronic structure of TiO₂. In addition, compared with TiO₂, O 1s and Ti³⁺ 2p XPS observations of hydrogen-treated TiO₂ combined with EPR results indicate the metal oxide support is peppered with more O_{Vac} defects. Introducing O_{Vac} leads to the appearance of new surface defects, which enhances

photoabsorption range of the system and promotes carrier separation.²¹⁶ Therefore, all samples underwent H₂ reduction treatment unless otherwise labelled 'no H₂ reduction'.

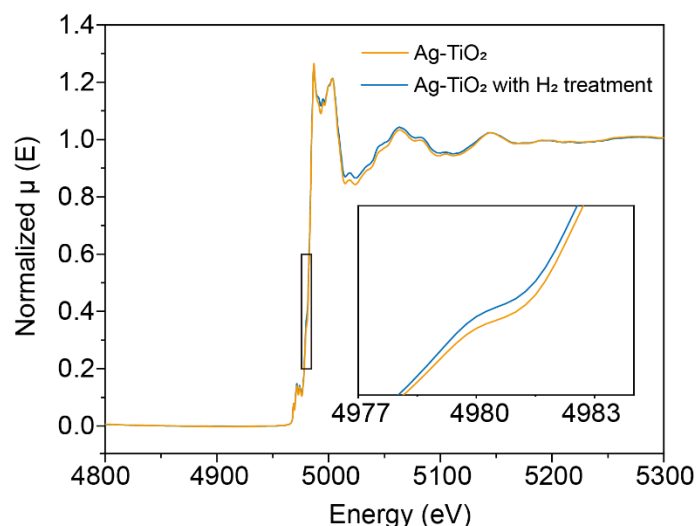


Figure 2-13 The Ti K-edge XANES spectra for Ag-TiO₂ without and with H₂ treatment

2.2.2 Surface Local Microenvironment Modulations

Spatially resolved CL spectroscopy was performed to investigate the spatial and energy distribution of the emissions of photons in the core-shell structure.²¹⁷ Integration over different wavelength ranges from 300 to 850 nm was considered to analyze the CL signal. Figure 2-14a presents the SEM image of the region scanned for CL. Figure 2-14b clearly depicts the CL emission signal reflected from the brightened areas, indicating that the regions with strong CL signals cover all the NPs. Figure 2-14c shows the CL signal of a single core-shell scanned in the green rectangular region in Figure 2-14a, displaying a main peak at 500 nm. Meanwhile, Figure 2-14d illustrates the CL signal of multiple connected core-shells scanned in the orange rectangular region in Figure 2-14a, exhibiting a broad peak from 500 to 700 nm.

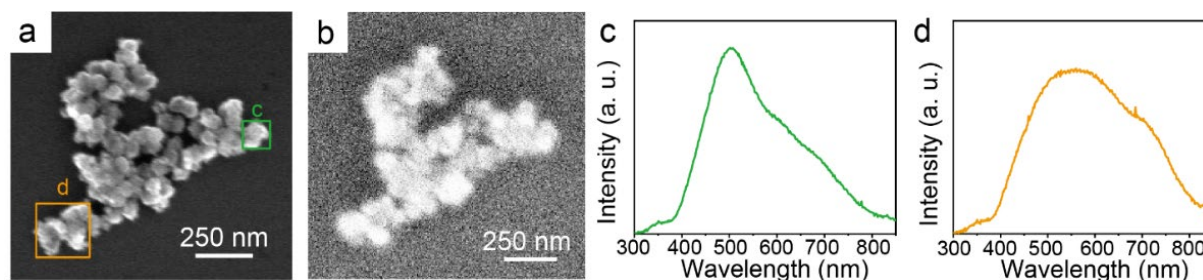


Figure 2-14 Characterization of surface local microenvironment. (a) SEM image of the CL scanning region. (b) CL emission signal. The CL emission signal in the (c) green and (d) orange rectangular region.

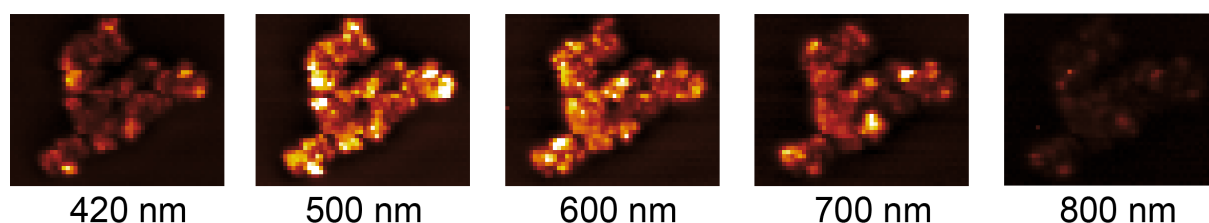


Figure 2-15 CL intensity maps under different wavelengths.

Figure 2-15 displays intensity maps of CL emission obtained at different wavelengths, showing strong CL signals distributed at various positions within the range of 420-700 nm. These results further emphasize the multiple emissions produced at different wavelengths are due to the interconnected core-shell NPs, contributing to the overall broadband absorption of visible light.²¹⁸

To further study the enhanced light absorption of the core-shell system by plasmonic Ag NPs, EELS was combined with STEM-HAADF imaging to measure the local optical response of Ag NPs.²¹⁹ One core-shell NP was selected as an example to reveal the influence of the TiO₂ shell on the plasmonic properties. Figure 2-16a displays the STEM-HAADF image (top) and elemental mappings of the core-shell NPs (bottom). Three example positions are indicated in the top image of Figure 2-16a, and their corresponding EELS spectra are shown in Figure 2-16b.

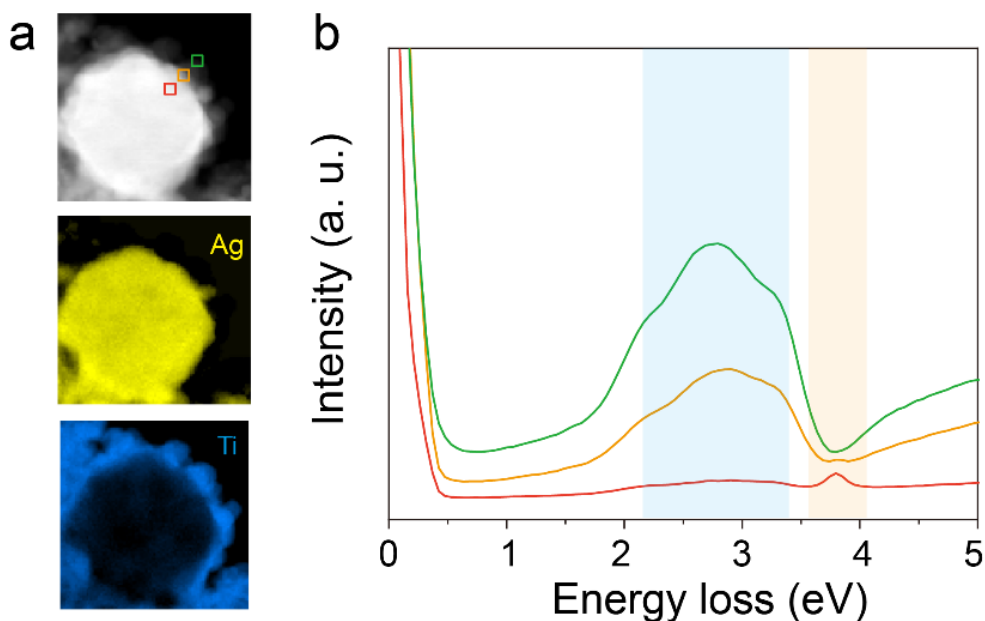


Figure 2-16 (a) The STEM-HAADF images and elemental mappings of a single core-shell NP. (b) EELS spectra from 3 different positions shown in the top Figure of (a).

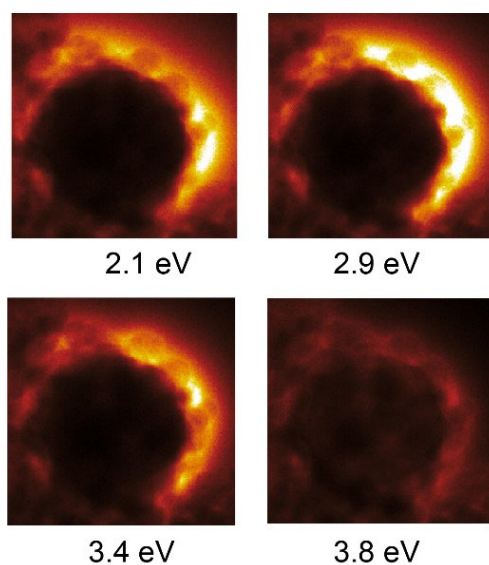


Figure 2-17 EELS mappings of the core-shell NP with selected energies from 2.1-3.8 eVs.

In Figure 2-16, the EELS spectra exhibit two main absorption peaks at 2.95 (light blue region) and 3.80 eV (light orange region), attributed to the edge and bulk signals of Ag NPs, respectively,²²⁰ correspondingly to photon absorption at wavelengths of 420 nm and 326 nm.

The EELS mapping results in Figure 2-17 further demonstrate that the core-shell NPs exhibit LSPR in the range of 2.1-3.4 eV, well matched to the light blue region in Figure 2-16, showing that the plasmon effectively transfers to the outer layer of the shell rather than being quenched. To gain further insights into local E-field distribution associated with the plasmonic properties of Ag NPs, the FDTD simulations were conducted based on STEM-HAADF results for structure modeling and the optical properties calculated by DFT (Figures 2-18 and 2-19).

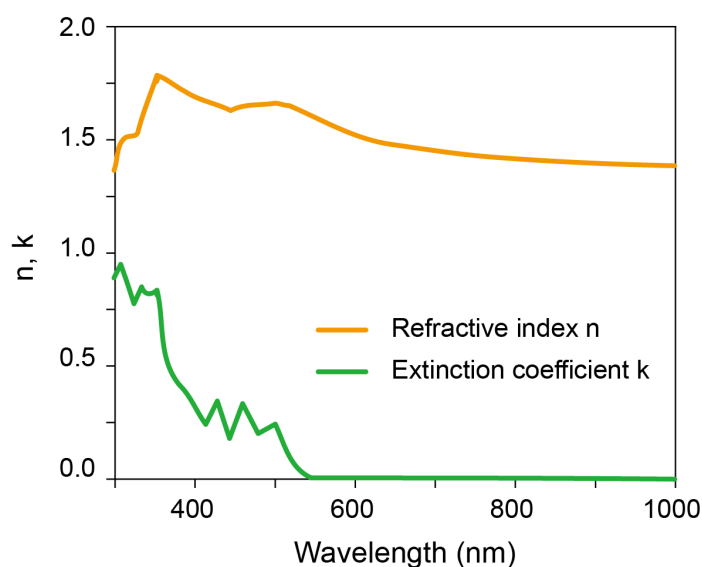


Figure 2-18 Refractive index (n) and extinction co-efficient (k) versus wavelength of TiO₂.

Through this approach, we can thoroughly examine the local E-field enhancement, induced by LSPR, across the entire Ag-TiO₂ plasmonic systems in response to incident light. Researchers are accustomed to utilizing LSPR to enhance reaction activity, employing a straightforward synthesis process to deposit plasmonic NPs onto functional substrates.²⁰² However, metal NPs positioned on the catalyst surface can reduce the catalyst's accessible active area and experience decreased overall plasmon utilization efficiency as a result of the limited metal-semiconductor junction aforementioned. Recently, the localized core-shell structures were proposed, achieved through the use of more complicated synthesis strategies.^{204, 206, 221} In these structures, the catalytic active surfaces (i.e., semiconductor metal

oxides) are fully exposed as an outer shell, encapsulating the core metal NPs within the active layers, thus addressing the drawback of metal NPs occupying valuable active sites on the catalytic active surfaces. However, for the incomplete core shells (i.e., cores with partially covered shells), the active plasmonic areas with decent E-field enhancement are very limited. While ideal complete core-shells seem to be the logical catalyst design, the E-field of the LSPR intrinsic to the metal particle core inevitably gets attenuated, leading to a ‘quenching’ phenomenon or a limited enhancement in the hexagonal Ag particle, as illustrated in Figure 2-20.

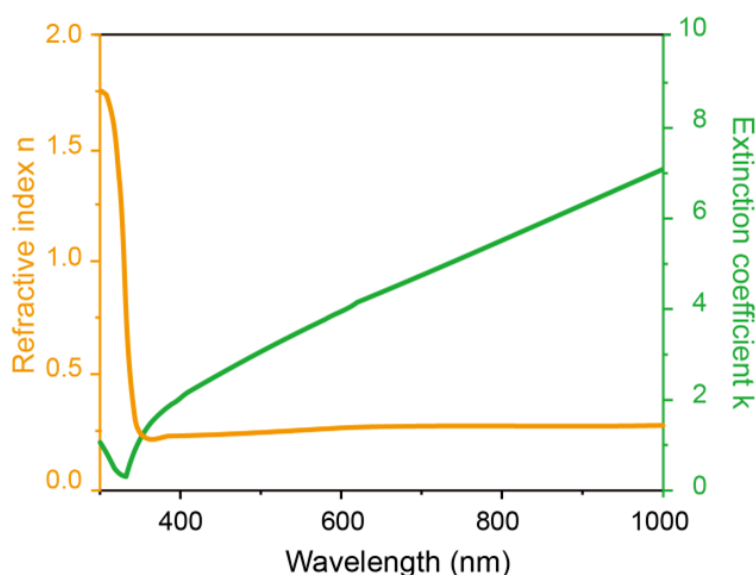


Figure 2-19 Refractive index (n) and extinction co-efficient (k) versus wavelength of Ag.

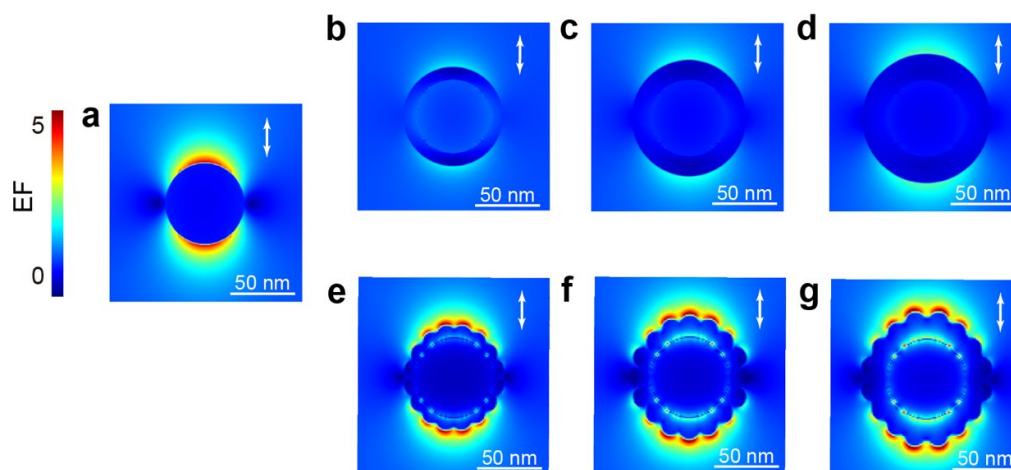


Figure 2-20 The effect of thickness on the electric field enhancement of CSNA units. (a) pure Ag NPs; (b) 10 nm perfect shell; (c) 15 nm perfect shell; (d) 20 nm perfect shell; (e) 10 nm particulate shell; (f) 15 nm particulate shell; (g) 20 nm particulate shell. The wavelength of incident light is from 300 to 1000 nm.

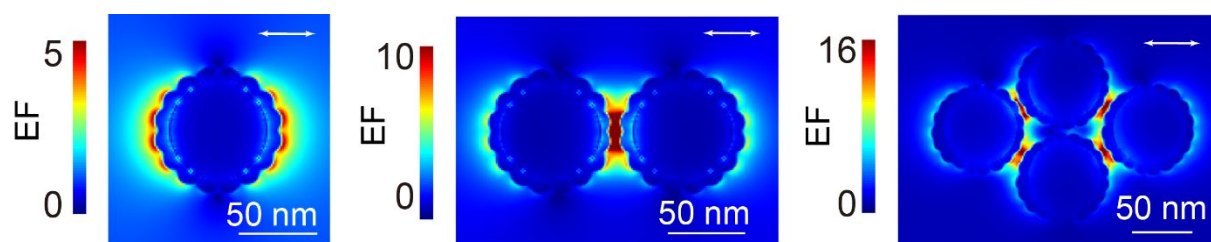


Figure 2-21 Calculated distribution of the E-field for single, double and quadruple Ag-TiO₂ core-shell based units, modeled with a particulate TiO₂ shell.

Herein, the rugged, asymmetric shell of TiO₂ particles with Ag NPs exhibits a surprisingly better enhancement of local E-field compared with a perfectly smooth shell. Besides, Figure 2-21 shows that a single imperfect Ag-TiO₂ unit can increase the E-field enhancement factor (EF) by a factor of 5. The coupling of two and four units can cumulatively increase the EF by factors of 10 and 16, respectively, surrounding the outer nanosurface of particulate TiO₂. Therefore, the interlinked interface contributes to a further superior cumulative enhancement

of LSPR. This observed phenomenon resembles a second generation of plasmons on the TiO₂ nanosurface, propelled by the initial, central plasmons originating from the Ag cores.

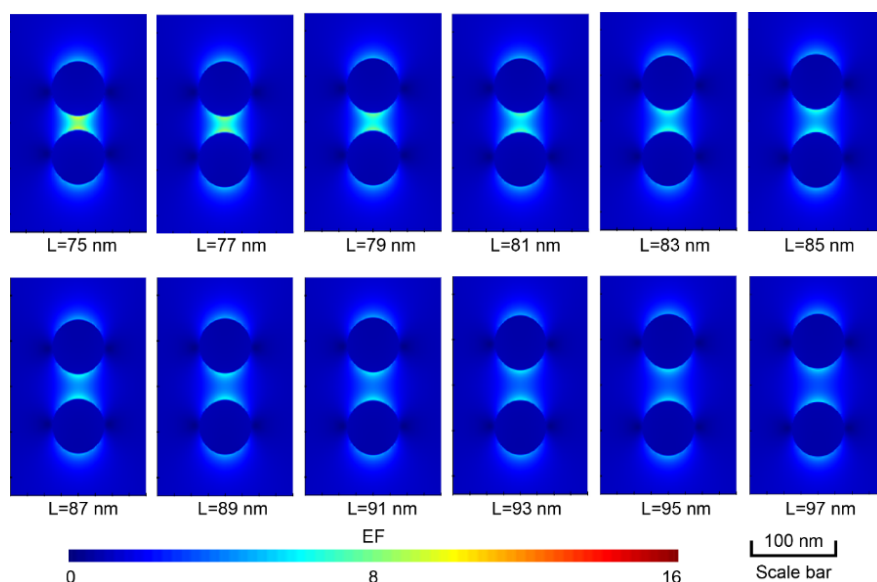


Figure 2-22 The effect of interunit distance on the electric field enhancement of Ag-Ag units. The wavelength of incident light is from 300 to 1000 nm.

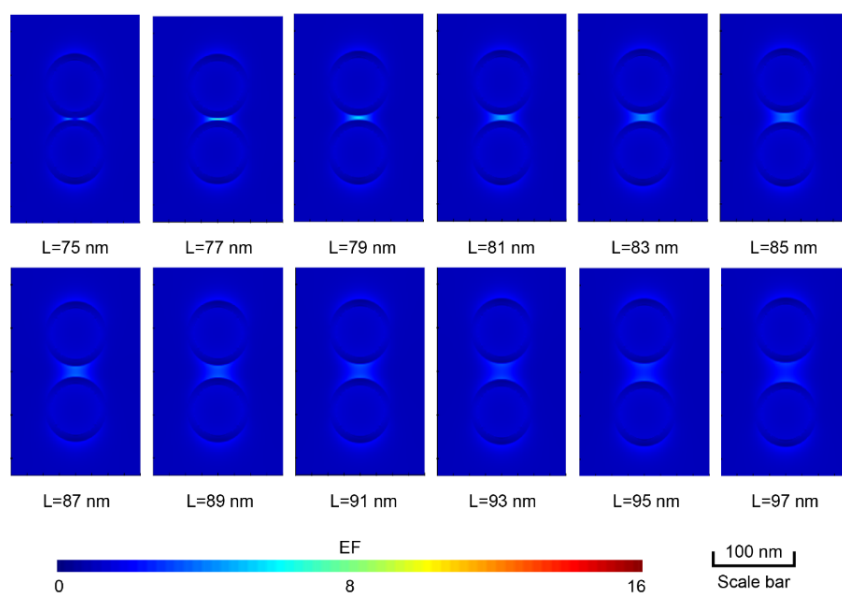


Figure 2-23 The effect of interunit distance on the electric field enhancement of Ag-TiO₂ core-shell double units for perfect shell. The wavelength of incident light is from 300 to 1000 nm.

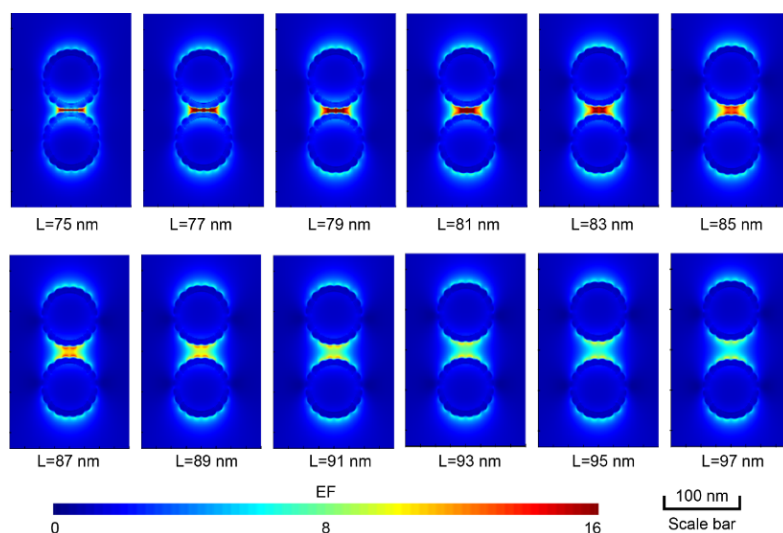


Figure 2-24 The effect of interunit distance on the electric field enhancement of Ag-TiO₂ core-shell double units for imperfect shell. The wavelength of incident light is from 300 to 1000 nm.

Moreover, Figures 2-22-2-24 shows the influence of inter-unit gap distance on the enhancement of the E-field, which suggests that the inter-unit distance within the range of 0-4 nm can maintain the strong E-field enhancement. Beyond 4 nm, the inter-unit E-field gradually attenuates, underscoring the necessity of a densely populated NPs design.

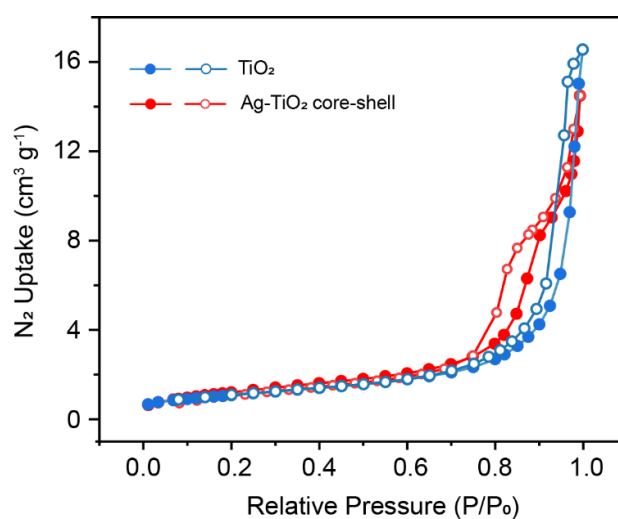


Figure 2-25 BET analysis showing the CO₂ adsorption-desorption isotherms.

Table 2-1 BET analysis showing the surface area and pore size of samples.

	BET Surface Area	Pore Size
TiO ₂	87.00 m ² /g	26.38 nm
Ag-TiO ₂ CSNA	102.08 m ² /g	19.68 nm

BET results in Figure 2-25 and Table 2-1 provide evidence of higher porosity and gas adsorption capacity in the photocatalyst, indirectly validating the successful creation of a dense porous structure. Therefore, these results indicate that the enhanced light absorption and strengthened E-field in the interconnected Ag-TiO₂ NPs create conducive surface local reaction microenvironments that tune the reaction pathways, significantly contributing to the selective CO₂RR, as discussed below.

2.2.3 Photocatalytic Performance of Ag-TiO₂

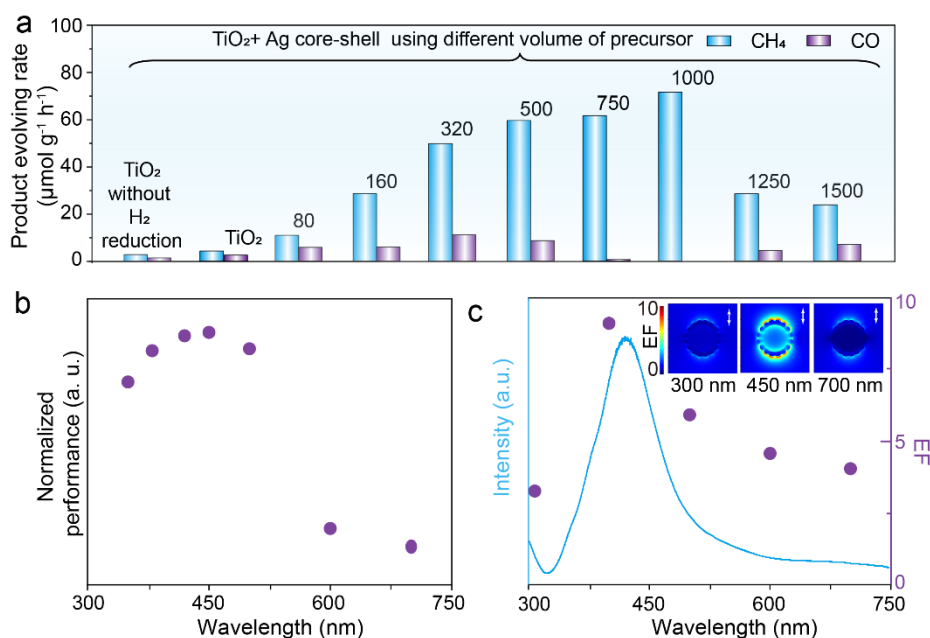


Figure 2-26 (a) Comparison of products for CO₂RR on Ag-TiO₂ photocatalysts. (b) Wavelength-dependent performance measured for CO₂RR on Ag-TiO₂ photocatalysts. (c) The UV-Vis for 55-60 nm Ag NPs and the wavelength dependent EF.

We conducted a comparative investigation of the photocatalytic CO₂RR of various materials under the simulated AM1.5G illumination, without any sacrificial reagents in Figure 2-26a. Note that in this study, a gas-phase reaction for CO₂RR was employed to circumvent the challenge of CO₂'s low solubility in water.¹⁹⁰ We studied the photocatalytic performance of the core-shell based structures synthesized using different TiO₂ precursors (80-1500 μ L). Among these samples, the highest CH₄ yield of 75 μ mol g⁻¹ h⁻¹ was observed in the sample using 1000 μ L TiO₂ precursor, exhibiting state-of-the-art benchmark performance among reported photocatalysts, with no other C1 gas detected by gas chromatography (GC) shown in Figures 2-27 and 2-28.

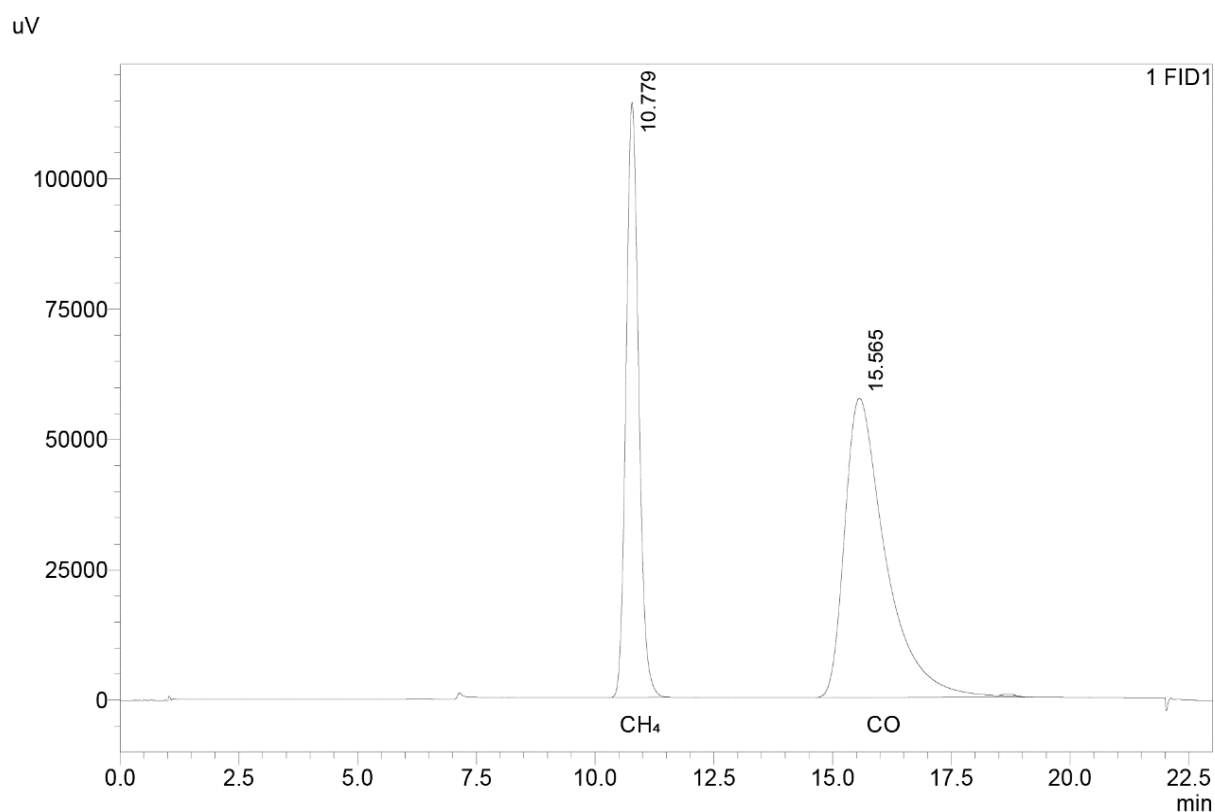
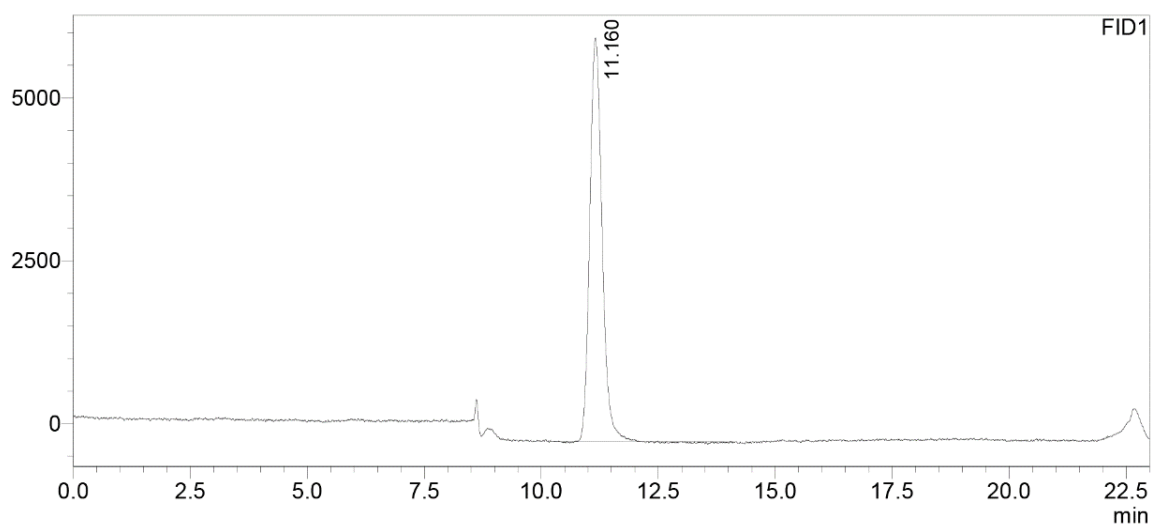


Figure 2-27 Analysis of gas chromatography measurement for standard C1 gas by a flame ionization detector (FID) with the ShinCarbon column.

<Chromatogram>

uV



<Peak Table>

FID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.160	112994	6199	100.000		M	
Total		112994	6199				

Figure 2-28 Verification of no CO emission from the gas chromatography detection by a flame ionization detector (FID) with the ShinCarbon column. Analysis of gas chromatography measurement for gas after photocatalytic reduction of CO₂ using the Ag-TiO₂ core-shell dense network sample with the best performance.

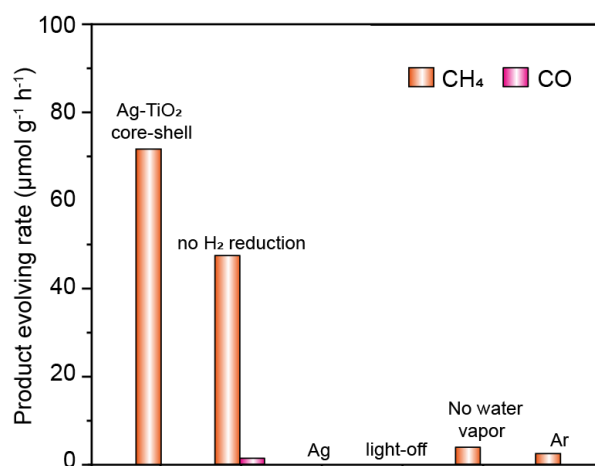


Figure 2-29 The controlled experiments of photocatalytic CO₂ reduction to CH₄ over Ag-TiO₂ core-shell.

To elucidate the essential role of light in the photocatalytic CO₂ conversion process, we conducted a series of controlled experiments (Figure 2-29) that demonstrated no products were detected in the dark. Furthermore, the hydrogen reduction effect induced by hydrogen treatment, which creates O_{vac} on TiO₂, evidenced the further improvement in the photocatalyst performance. The optimized Ag-TiO₂ sample also showcased notable photochemical stability and consistent photoactivity over five test cycles, demonstrating its long-term durability (Figure 2-30).

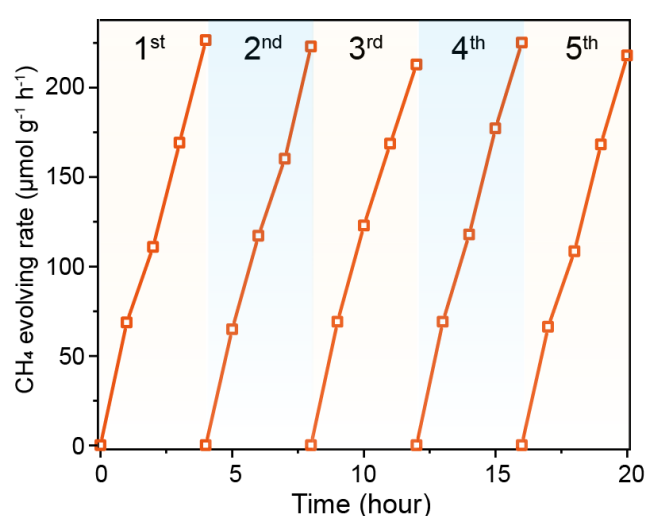


Figure 2-30 Representative efficiency profile of CO₂ reduction to CH₄ over Ag-TiO₂ core-shell for five consecutive tests.

Given the superior photocatalytic performance in CO₂RR granted with Ag-TiO₂ photocatalysts, we endeavored to investigate and understand its photophysical properties that underpin the remarkable performance in CO₂RR. While the Ag-TiO₂ NPs have been confirmed to exhibit broad-spectrum visible light absorption, further investigation is warranted regarding their performance under different wavelengths of light. Figure 2-26b indicates that the wavelength range with the remarkable performance primarily lies within the ultraviolet and visible light range below 600 nm, with a noticeable decrease in performance above 600 nm. Figure 2-26c shows that the intensity of the E-field is highly correlated with the Ultraviolet-

visible (UV-Vis) region of Ag NPs, with the most ideal local E-field enhancement near the peak around 420 nm.²²² UV-Vis diffuse reflectance spectroscopy in Figure 2-31 confirmed that the optimized plasmonic core-shell based photocatalyst exhibits a broader absorption range, thus greatly enhancing light absorption and facilitating the conversion of incident photons into more electrons/holes for redox reactions.²⁰⁰

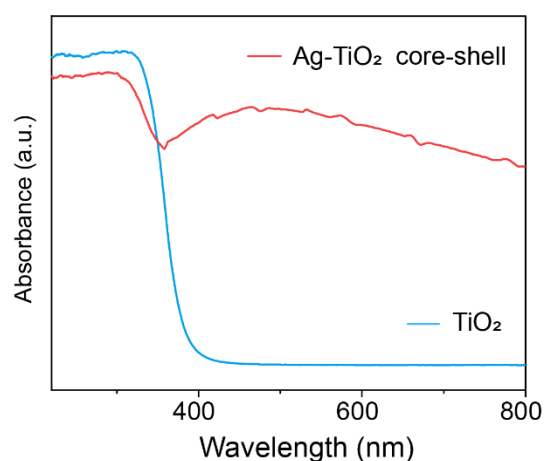


Figure 2-31 UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) spectra of TiO₂ and Ag-TiO₂ core-shell.

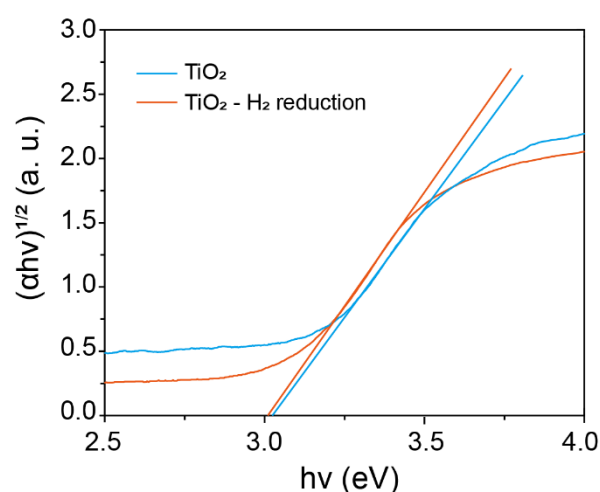


Figure 2-32 The band gap energies of TiO₂ with and without H₂ reduction transformed by UV-vis diffuse reflectance spectra. The band gap of TiO₂ is 3.03 eV and that of TiO₂ with H₂ reduction is 3.01 eV.

Besides, H_2 reduction at a low temperature (300 °C) primarily results in the formation of oxygen vacancies on the TiO_2 surface, exerting minimal influence on its light absorption and band gap (Figure 2-32). Thus, the broad light absorption range is attributed to TiO_2 for wavelengths < 400 nm and to the Ag- TiO_2 hybrid structure for wavelengths between 400-800 nm. Moreover, the Ag- TiO_2 exhibits faster carrier lifetimes, determined by time-resolved photoluminescence (TRPL) in Figure 2-33 and 2-34, resulting in efficient charge carrier transfer at the interface.²²³

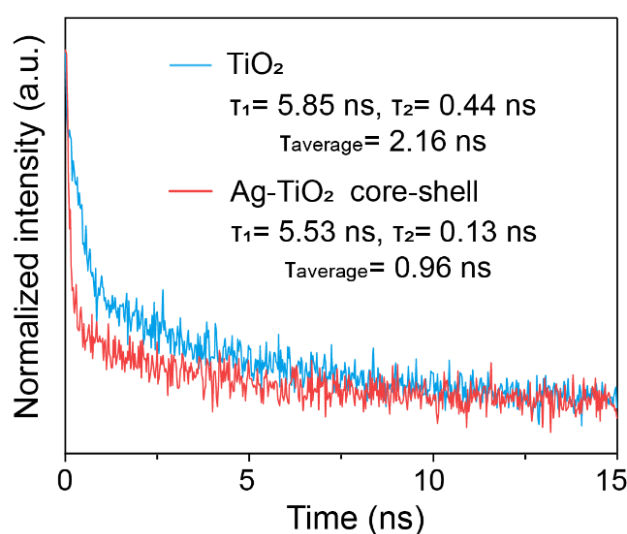


Figure 2-33 The time-resolve photoluminescence (TRPL) spectra of TiO_2 and Ag- TiO_2 core-shell. All unlabeled samples underwent H_2 reduction treatment.

Driven by smaller ϵ_i values of Ag throughout the visible spectrum (Figures 2-35 and 2-36), suggesting that Ag NPs exhibit LSPR. The analysis of the plasmonic local microenvironment for Ag- TiO_2 NPs has shown that LSPR can effectively propagate to the surface of the TiO_2 shell. Therefore, the excited carriers have the opportunity to participate in reduction reactions near the surrounding regions, specifically on the TiO_2 particulate shells, facilitating chemical transformation on TiO_2 surfaces and enhancing the photoactivity of CO_2 methanation.^{198, 224}

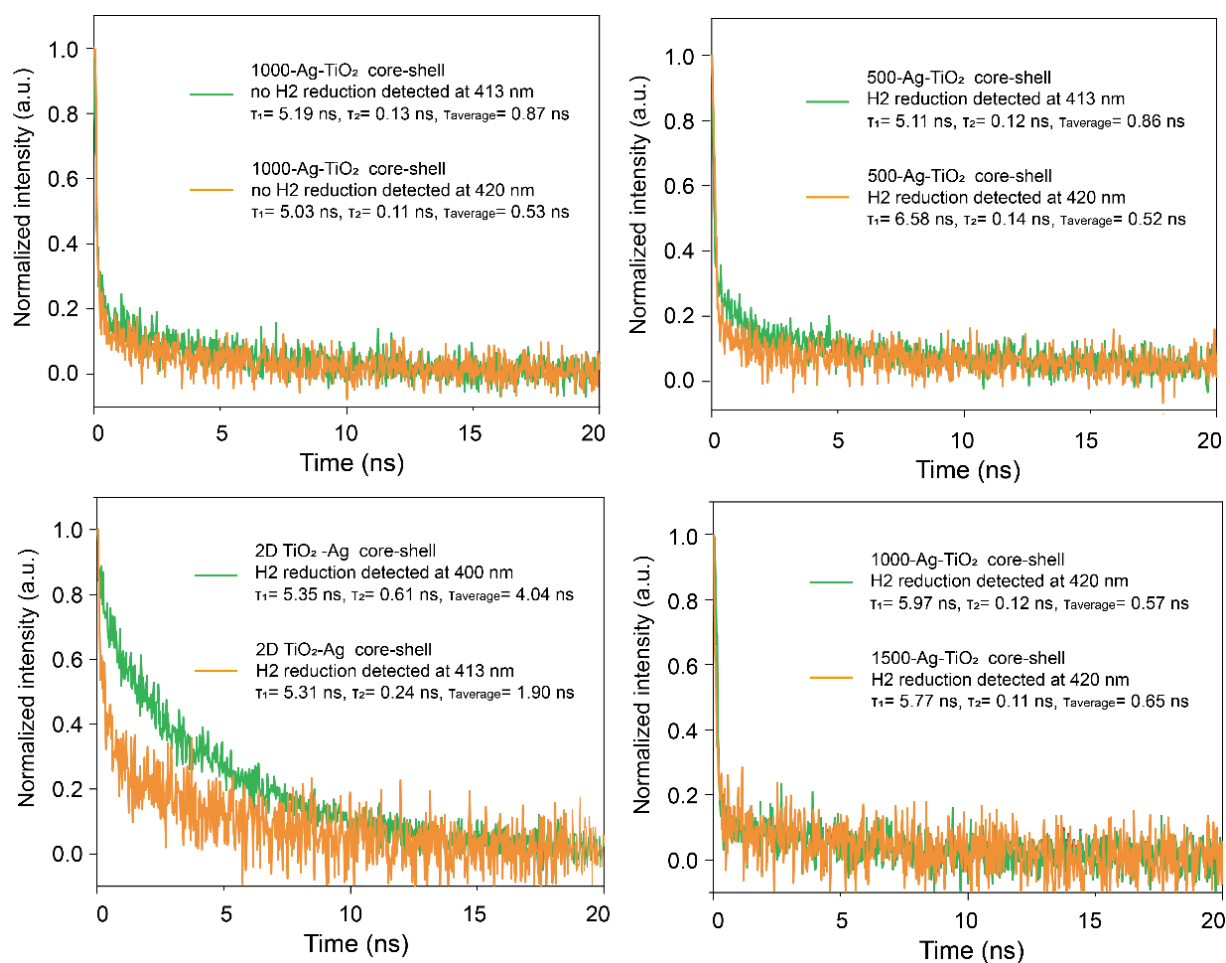


Figure 2-34 The comparison of time-resolve photoluminescence (TRPL) decay curves.

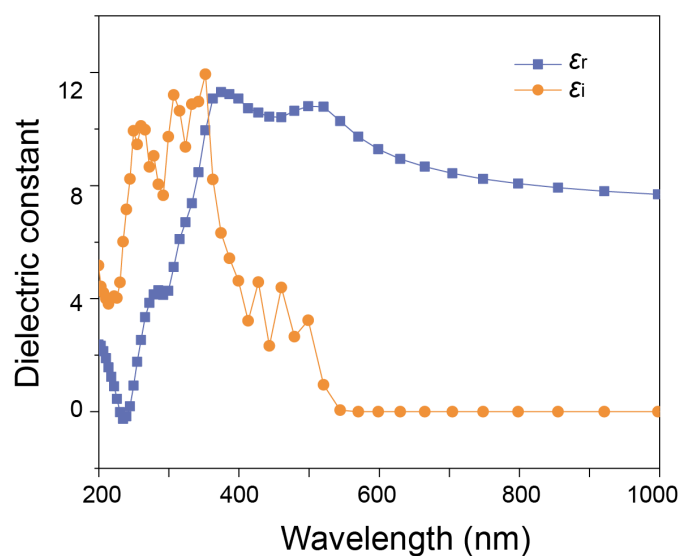


Figure 2-35 The real (ε_r) and imaginary (ε_i) parts of the dielectric properties for TiO₂.

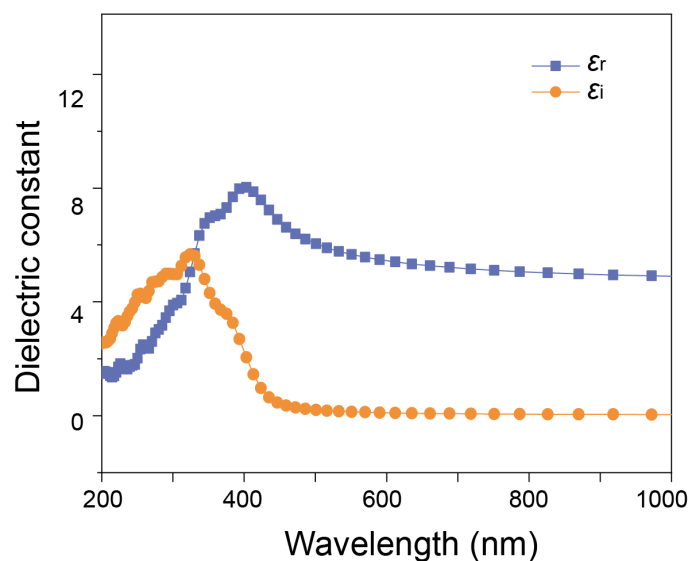


Figure 2-36 The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric properties for Ag.

To further understand the surface charge distribution of these core-shell nanoparticles, nanometer-resolution surface photovoltage microscopy (SPVM) using kelvin probe force microscopy (KPFM) is an effective tool for studying the spatial correlation between the photo-generated charge distribution and the structural morphology, as well as the relationship between light absorption and carrier migration/transfer mechanisms.²²⁵⁻²²⁶ As shown in Figures 2-37, the negative SPV indicates the surface imaging of photo-generated electrons.²²⁷ The changes in SPV intensity before and after illumination at wavelengths of 400 and 450 nm are significant, which aligns with the behavior of the light absorption spectrum, demonstrating that charge generation is light-driven. Additionally, we observed that the widespread electron distribution on the surface, combined with the rapid electron transfer dynamics indicated by TRPL, suggests that photo-generated electrons can quickly transfer to the TiO_2 shell surface to participate in the reaction. This, in turn, enables the sustained reduction of CO_2 into multi-electron products.

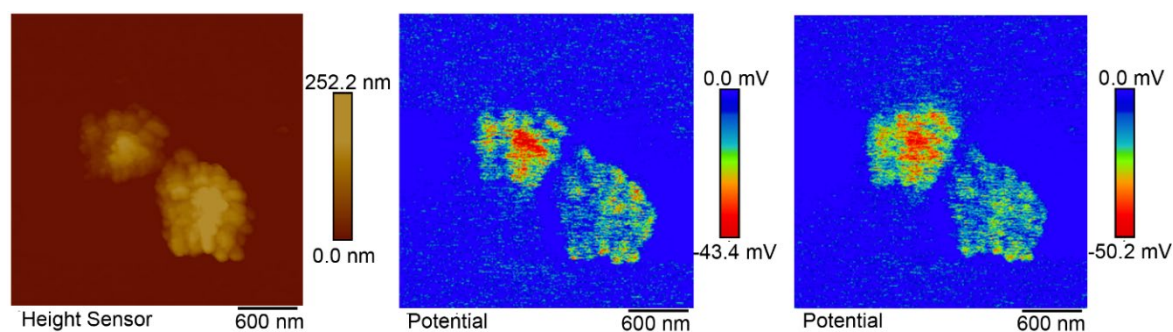


Figure 2-37 AFM image of Ag-TiO₂ core-shell. The SPVM images showing the $\Delta\text{SPV} = \text{SPV}_{\text{without light}} - \text{SPV}_{\text{with light}}$ at different wavelengths of 400 nm and 500 nm.

2.2.4 Insights into the mechanism of E-field modulation

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was subsequently performed to identify surface intermediates and investigate CO₂ activation and conversion. As depicted in Figure 2-38a-d, the observed spectra reveal the presence of several surface species, including *CO (2,076 cm⁻¹), *COOH (1,610, 1,380, and 1,312 cm⁻¹), *COO (1,535 cm⁻¹), and m-CO₃²⁻ (1,445 cm⁻¹). In addition, intermediates such as *CH₃O (1,136 cm⁻¹) and *CHO (1,055 cm⁻¹) were also observed, which are crucial indicators of a reaction pathway leading to CH₄ formation. In Figure 2-38b and d, after H₂ treatment, the *CO peak at 2,076 cm⁻¹ becomes more pronounced. This observation suggests that the catalyst treated with H₂ converts more CO₂ into *CO intermediates, which likely contributes to improved catalytic performance by facilitating the subsequent hydrogenation steps necessary for CH₄ formation. Notably, while the *CHO peak weakens over prolonged light exposure for the catalysts shown in Figures 2-38a-c, it remains stable for the H₂-treated Ag-TiO₂ catalyst in Figure 2-38d. This observation highlights the sustained generation of CO₂ reduction intermediates, particularly *CHO, which is recognized as a crucial intermediate for CH₄ formation. These findings align well with the reaction pathway analysis, highlighting the critical role of H₂ treatment to generate oxygen vacancy for Ag-TiO₂ in enhancing intermediate stability and promoting CH₄ production.

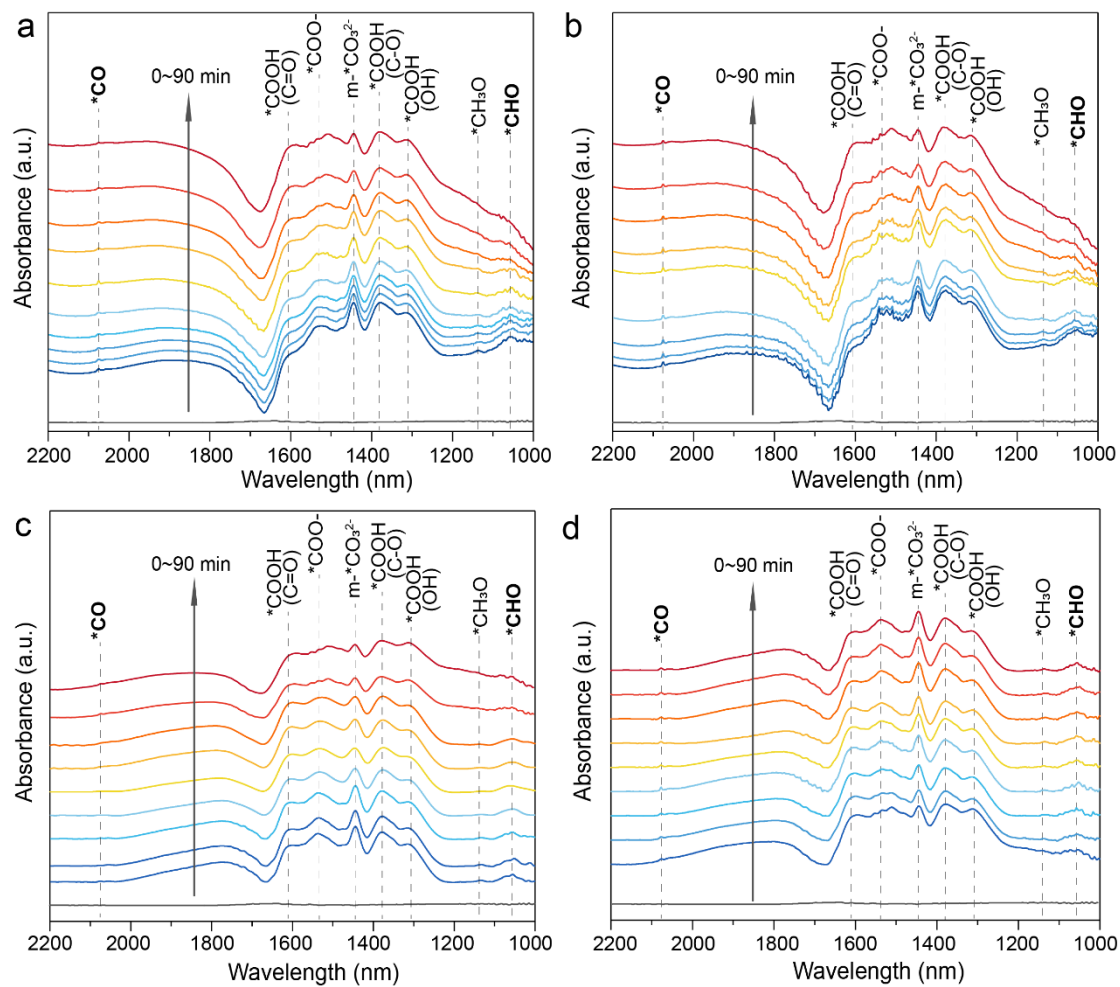


Figure 2-38 In situ DRIFTS spectra recorded for intermediates under 0 (dark) to 90 (light) minutes irradiation for (a) TiO_2 , (b) TiO_2 with H_2 treatment, (c) Ag-TiO_2 and (d) Ag-TiO_2 with H_2 treatment.

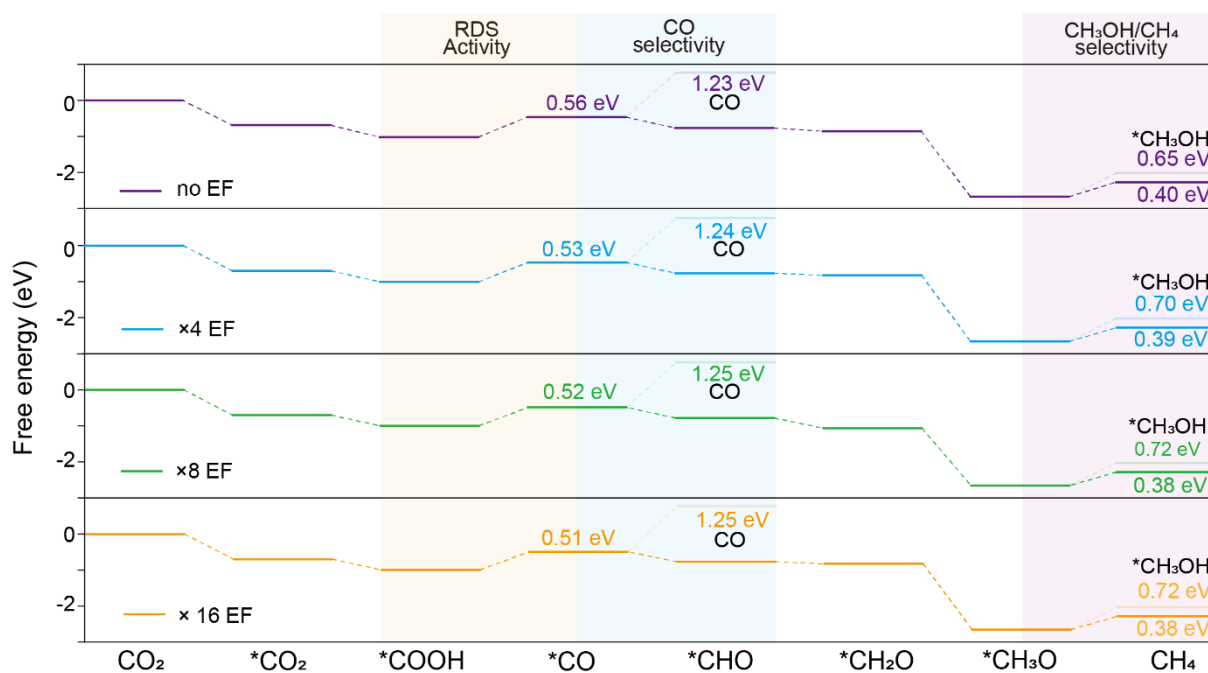


Figure 2-39 Potential energy diagram for the CO₂(g) photoreduction to CH₄(g) on TiO₂ with O_{vac} under no and different enhancement factors (EF) from E-field by DFT calculations. EF means the enhancement factor of E-field.

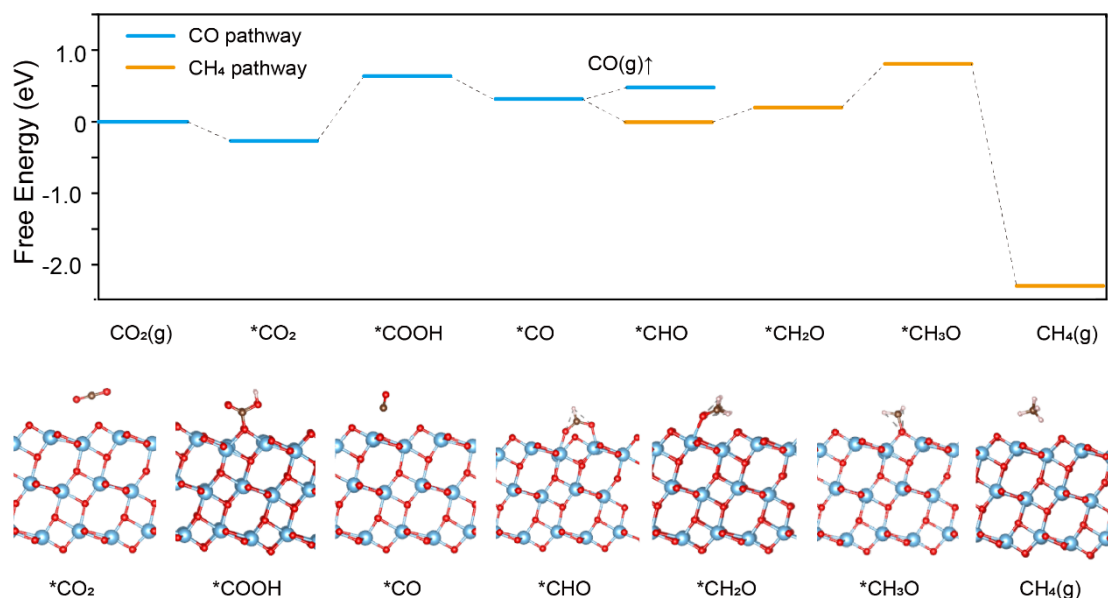


Figure 2-40 Potential energy diagram and absorption model of intermediates for the CO₂(g) photoreduction to CH₄(g) on TiO₂.

These observations are consistent with the computationally predicted results shown in Figure 2-39 Optimizing the desorption-adsorption and hydrogenation reactions of the reaction intermediates in the reaction steps can adjust their Gibbs free energy, thereby regulating the final products.⁶ DFT calculations (Figure 2-40) have shown that TiO₂ (101) is a potential candidate for reducing CO₂ to CH₄ or CH₃OH.²²⁸⁻²³⁰

Importantly, our previous work has demonstrated that the plasmonic electric near-field can thermodynamically regulate the reaction paths of photoreforming of CH₃OH.²⁰² The high selectivity towards CH₄ was then studied by comparing the free energy barriers of different intermediates. In Figure 2-39, we investigated the influence of the E-field on the Gibbs free energy of each reaction steps in CO₂RR and found that TiO₂ with oxygen vacancies is more thermodynamically feasible to produce CH₄. This provides a basis for designing catalysts that prioritize high selectivity for CO₂ conversion to CH₄. Reaction barriers and rate-determining step (RDS) are key descriptors for evaluating CO₂RR performance, and intermediate adsorption structures were modeled for all potential sites.⁴⁹ The calculated results showed that TiO₂ vacancies can suppress the production of CO, and the energy barriers for the RDS (*COOH→*CO) are reduced from 0.56 eV in the absence of E-field to 0.51 eV under a ×16 E-field modulation. The reduced energy barrier enhances the overall reduction process assisted by the photoexcited electrons from TiO₂ and the hot electrons injected from Ag. Besides, the application of ×4 to ×16 E-field modulation elevates the thermodynamic barrier for CH₃OH formation by 50 meV to 70 meV. This elevation becomes more pronounced under larger E-field modulation, making CH₄ generation more favorable.

A schematic diagram of the CO₂ reduction mechanism involving 8 cooperative proton-electron transfer steps is analyzed in Figure 2-41, demonstrating the synergistic effect of vacancies and E-fields. Vacancies make C atoms of *CO and O atoms of *CH₃O difficult to desorb from the active sites, while the E-field makes hydrogenation reactions more favorable to occur on C instead of O of *CH₃O, increasing the possibility of CH₄ formation. These results

highlight the importance of the synergistic effect of defective TiO₂ and E-field for achieving high selectivity in high-efficient CO₂ methanation. As shown in Figure 2-41, both vacancies and modulation E-fields are indispensable for achieving high selectivity to generate CH₄ on the rugged nanosurface of defective TiO₂. Therefore, the stellar performance stems from the synergy between enhanced nanoplasmonic effect and the supply of light-driven redox charge carriers and that leads to nearly 100% selectivity with exceptional efficiency of 75 $\mu\text{mol g}^{-1} \text{h}^{-1}$. Both experimental observations and DFT analysis provide substantial evidence for this performance.

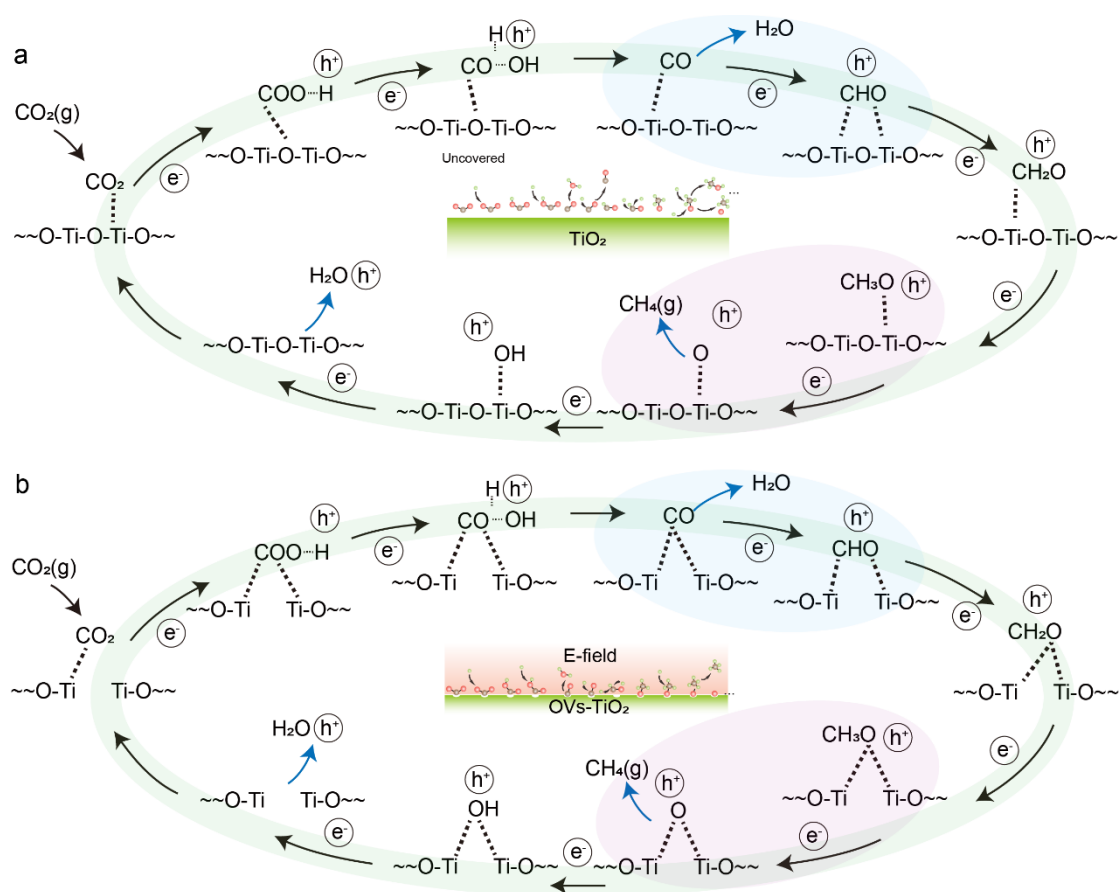


Figure 2-41 Schematic diagram of TiO₂ surface reaction (a) without, and (b) with vacancies and E-field. The E-field and vacancies can prevent the detachment of the adsorption intermediate CO and promote the hydrogenation reaction occurring on C atoms. EF means the enhancement factor.

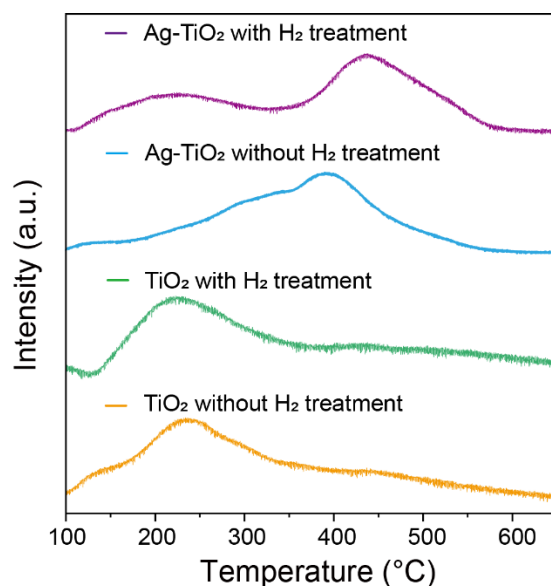


Figure 2-42 Temperature Programmed Desorption (TPD) profiles of CO on TiO₂ and Ag-TiO₂, with and without H₂ treatment.

The CO-Temperature Programmed Desorption (CO-TPD) tests were conducted to compare the CO desorption capacities of photocatalysts in the temperature range of 100 to 650 °C. The desorption temperature of CO reflects the binding strength between CO and the catalyst-the higher the desorption temperature, the more stable the CO binding, which facilitates the involvement of CO intermediates in subsequent hydrogenation reactions. TPD curves in Figure 2-42 indicate that desorption at lower temperatures tends to correspond to weakly bound monodentate structures of CO adsorption. In contrast, higher desorption temperature ranges reflect medium to strongly bound sites. These strongly bound sites may hinder CO desorption, favoring its hydrogenation into other products due to the extended surface residence time. It can be observed that the introduction of oxygen vacancies through H₂ treatment results in minimal changes to the CO desorption peak for TiO₂. This is because pure TiO₂, when calcined under 10% hydrogen at 300 °C for 2 hours, is unable to generate sufficient oxygen vacancies. Moreover, without Ag NPs as a substrate, the synthesis of TiO₂ tends to result in particle agglomeration rather than maintaining discrete nanoparticles, leading to a smaller BET surface area compared to Ag-TiO₂. Consequently, the possibility of surface oxygen reduction during

H₂ treatment is further diminished. However, the higher CO desorption peak for Ag-TiO₂ significantly shifts to higher temperatures. As shown in the TPD curves in Figure 2-42, the desorption peak for Ag-TiO₂ moves from 396°C to 474°C after H₂ treatment. This shift indicates that H₂ treatment, by introducing more oxygen vacancies for Ag-TiO₂, enhances CO binding and prevents its early desorption, thereby improving CO retention on the catalyst surface for subsequent hydrogenation, ultimately leading to CH₄ formation.

2.3 Conclusion

A plasmonic-metal oxide NP with LSPR characteristics and outstanding photocatalytic activity are constructed by modulating the surface local microenvironment. This is achieved through a cleverly designed asymmetric imperfect core-shell structure formed from densely interconnected, ultrafine TiO₂ NPs encapsulating Ag cores, maximizing exposed catalytic surface areas. The design leverages maximized utilization of plasmon, nanoplasmon-enhanced local E-field, and surface activation through oxygen vacancies. The successful development of the Ag-TiO₂ NPs can spontaneously improve reaction selectivity and activity, favoring thermodynamics and delivering exceptional performance in sustained CO₂RR with 100% CH₄ selectivity and a conversion rate yield of 75 $\mu\text{mol g}^{-1} \text{h}^{-1}$. The results represent the current state-of-the-art benchmark performance for fully selective photocatalysts. Moreover, this work offers novel insights into how maximum-utilized plasmonic, cumulatively-enhanced microenvironments influence selectivity and activity in a photocatalytic system. The findings from this work are applicable to other nanoplasmon-driven photocatalytic processes and can be generalized to a broader spectrum of light-mediated chemical reactions, including photothermal catalysis and photoelectrocatalysis. These reactions are crucial for advancing renewable energy applications. This work demonstrates the feasibility of engineering advanced photocatalytic materials through rational manipulation of plasmonic microenvironments, significantly contributing to the broader goal of designing functional photocatalysts for sustainable energy conversion applications.

Chapter 3 Designing Plasmonic Photocatalysts for Hydrogen Production in Seawater: A Theoretical and Experimental Study

3. Introduction

Amidst an escalating global demand for clean energy in response to climate change, the imperative for advancing hydrogen energy production technologies is increasingly apparent.²³¹ Within the contemporary landscape of energy conversion technologies, photocatalysis stands out as an energy-saving and environmental friendliness with capability of utilizing abundant resources, such as sunlight and water, to generate hydrogen.²³²⁻²³³ Additionally, attention is progressively shifting towards the utilization of seawater for photocatalytic hydrogen production. Seawater is an earth-abundant and virtually limitless resource, covering approximately 71% of the Earth's surface, and providing 96.5% of the planet's water resource for sustainable energy generation.²³⁴ Leveraging the immense expanse of seawater as a feedstock for hydrogen production via photocatalysis has far-reaching potential applications.²³⁵ Developing photocatalysts with high hydrogen production performance and stability under saline environments is essential for the development of scalable photocatalytic systems. The utilization of untreated water sources, notably seawater, to drive photocatalytic reactions is on the rise. However, achieving higher reaction efficiency and long-term stability demands elevated criteria for photocatalysts. This necessitates the integration of co-catalysts,²³⁶ heterojunctions,²³⁷ and other engineering strategies,²³⁸ although their practicality remains subject to scrutiny.

Despite yielding promising research outcomes, the efficient production of hydrogen through seawater splitting largely relies on noble metals and/or sacrificial agents.^{8, 232, 239-240} The scarcity of noble metals and the additional costs associated with sacrificial agents have limited their widespread application due to high expenses. Hence, there is an urgent need to develop low-cost, high-performance catalysts without noble metals as co-catalysts or sacrificial agents.

Atomically dispersed non-noble metal atoms immobilized on nitrogen-doped carbon materials (M-NC) are widely recognized for their efficiency as catalysts in photocatalytic reactions, including carbon dioxide (CO₂) reduction,²⁴¹ H₂O₂ production,²⁴² CH₄ oxidation,²⁴³ and water splitting²⁴⁴ etc. Their high performance stems from the abundance of highly exposed active sites and efficient transport of photogenerated charge carriers. By modulating the coordination environment to modify the electronic structure of atomic metal sites, M-NC can enhance activity, selectivity, and reaction kinetics for specific catalytic reactions. Besides, metal plasmonic nanoparticles (NPs) with localized surface plasmon resonance (LSPR) effects have shown great potential in energy conversion due to their ability to expand the photo-response range,¹⁹⁴⁻¹⁹⁵ and activate chemical bonds through the LSPR-induced electric-field (E-field).¹⁹⁷⁻¹⁹⁸ In typical plasmonic photocatalytic systems, plasmonic NPs are usually deposited onto functional semiconductors.²⁰¹⁻²⁰³ However, this configuration limits plasmonic enhancement to the interface region between the metal and semiconductor, and also causes the plasmonic NPs to potentially block reaction sites on the semiconductors. A core-shell structure with the plasmonic material at the core and the semiconductor material at the shell could overcome these challenges by uniformly distributing plasmonic enhancement around the NPs without blocking reaction sites of the semiconductor.²⁰⁴ However, to our best knowledge, few studies have reported on the design of core-shell photocatalysts that combine M-NCs with the LSPR effect specifically for seawater splitting.

In this work, we developed a photocatalyst with the core-shell structure named Co-NC@Cu, comprising Cu NPs as cores covered with N-doped carbon (NC) as a shell, anchored/distributed with Co atoms, for photocatalytic seawater splitting. This catalyst demonstrates superior hydrogen production efficiency of 9080 $\mu\text{mol g}^{-1}\text{h}^{-1}$, i.e., 4.78% solar-to-hydrogen (STH) conversion efficiency, and exceptional long-term stability (over 340 hours) without adding any noble metals or sacrificial agents. We show that the high performance results from the unique integration of the reaction environment, broad solar absorption, LSPR

effect, and single atoms, synergistically enhancing the catalytic efficiency. The favorable reaction environment generated by physicochemical properties of seawater, including the focus-light induced thermal effect and salt-ions (Na^+ , Cl^-) enabled local charge polarization, leads to increased reaction temperature and prolonged carrier lifetimes, thus significantly enhancing the redox capability of the charges. Broad solar absorption occurs on Co-NC@Cu which promotes the generation of photoexcited charges. The LSPR effect of the illuminated Cu NPs concentrates light energy, generating and providing hot plasmonic charge carriers to the Co-NC catalyst, thereby facilitating the redox reactions on its surface. DFT calculations show that the atomic Co anchored on the NC shell, serving as the active site, exhibits low reduction reaction energy barriers. Furthermore, under the perturbation of the local E-field, the reduction and oxidation reaction energy barriers were further reduced, thereby enhancing the overall redox reaction activity. This work provides guidance for highly efficient coupling between the reaction environment, broad light absorption, plasmonic E-field, and active atomic sites, thereby achieving optimal seawater hydrogen production through redox reactions.

3.1 Methods

Experimental synthesis

Chemicals preparation. CuO (Sigma-Aldrich-Copper (II) oxide); $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich-Cobalt (II) chloride hexahydrate); Nitric acid (Sigma-Aldrich-ACS reagent, 70%); Formamide (Sigma-Aldrich-ACS reagent, $\geq 99.5\%$); DI water. All the chemical reagents were of analytical grade and used without any further purification.

Preparation of Co-NC@Cu. Synthesis of Co-NC@Cu involves several steps. Initially, 1g of CuO is dispersed in 30 mL of formamide (HCONH_2) and stirred for 30 min until the solution is uniformly colored. Subsequently, 100 mg of CoCl_2 (corresponding to 183.3 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) is added to the solution, and the mixture is transferred into a 100 mL autoclave for hydrothermal

treatment at 180°C for 12 hours. Under these reaction conditions, formamide converts into amorphous nitrogen-doped carbon (NC) material. After the hydrothermal reaction, the material is washed 4 times with 1:1 ethanol and water, with centrifugation at 7800 revolutions per minute (rpm). The washed material is then treated with 0.1 mM dilute nitric acid 3 times, followed by water rinsing to remove the nitric acid. Subsequently, the material is dried in a vacuum oven at 60°C for 12 hours. The dried powder sample is ground and placed into a quartz boat, followed by annealing in an Ar environment in a tube furnace. The reaction temperature is set at 400°C for 4 hours with a heating rate of 10°C per min. Finally, the resulting sample is ground again to complete the synthesis process.

Preparation of NC@Cu. The synthesis steps for NC@Cu are same as Co-NC@Cu, except for adding CoCl₂.

Sample characterization

X-ray absorption spectroscopy (XAS) experiments were performed on the Medium Energy X-ray Absorption Spectroscopy (MEX-1) beamline stationed at the Australian Synchrotron (AS). The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data for Co K-edge were acquired under ambient conditions. The subsequent interpretation of XAS data was facilitated using the ATHENA software suite.²⁴⁵ The surface analysis of X-ray photoelectron spectroscopy (XPS) was collected by an Al K α X-ray source, 1486.6 eV (Kratos AXIS Ultra DLD). A FEI Verios scanning electron microscope (SEM) and equipped with Everhart-Thornley and immersion in-lens detectors for secondary electrons detection, was used to image the morphology of the samples. The same system was used to acquire cathodoluminescence signals by using a Gatan MonoCL4 Elite system. Full spectrum CL maps were acquired using a charge-coupled device (CCD). XRD patterns were acquired by Bruker X-ray diffractometer (Cu K α). EPR spectra were acquired by a Bruker E500 spectrometer equipped with a Bruker ER 4122 SHQE resonator. Light source is 300 W Xenon

lamp from PerfectLight. Gas products were analyzed by Nexis GC-2030 (Shimadzu Scientific instruments) which is equipped with a thermal conductivity detector (TCD), and a flame ionization detector (FID) with the ShinCarbon column. TRPL curves are captured at room temperature using an Horiba iHR 320 mm spectrophotometer equipped with a compact single-photon silicon detector (PPD-900, detection range between 350-920nm). A 485-nm picosecond pulse laser (Horiba DeltaDiode) is used as an excitation source. The laser light is focused on the samples through an Olympus BX53 microscope equipped with a 50x objective lens and an X-Y micropositioner. Micro-Raman spectroscopy measurements are conducted using a Horiba Labram system, which is equipped with confocal optics, a 532 nm diode-pumped solid-state (DPSS) laser, and a charge-coupled device (CCD) Si detector with detection range of 540-1000 nm. The laser light is focused onto the samples through a PL FLUOTAR microscope objective (50x magnification and a 0.55 numerical aperture). The excitation power directed onto the sample remains consistent across all measurements unless specified otherwise in the manuscript. The Co content in all samples was measured by an ICP-OES 5110 by Agilent. For obtaining accurate metal compositions, specimens, which were diluted by dissolving powder samples in 10% HNO₃, were collected with the ion concentration below 200 ppm.

The finite difference time domain (FDTD) simulations

The theoretical finite difference time domain (FDTD) simulations were all performed by performing Lumerical (FDTD solutions, Lumerical Solutions, Inc., Vancouver, Canada) software. The optical parameters of Cu and Co-NC used in FDTD simulation were calculated from the results of DFT calculations. We assumed that the background medium was seawater with an index of refraction of 1.34. A total field-scattered field (TFSF) source of light consisting of plane waves was used as the incident light source. A uniform grid size of 1 nm (x, y, and z) was accepted to ensure the accuracy of E-field calculations. A frequency-domain field distribution monitor was used to evaluate the E-field distribution. The perfectly matched layer

(PML) absorbing boundary conditions was considered. The E-field magnitude from the incident light was received by following steps ²⁰⁷:

$$I_{\text{ave}} = c\epsilon_0 E_0^2/2$$

$$E_0 = (2I_{\text{ave}}/c\epsilon_0)^{1/2}$$

where I_{ave} is the intensity of incident solar simulator (600 mW/cm²), c is the speed of light, ϵ_0 is the permittivity of free space, and E_0 is the maximum E-field strength.

Density functional theory (DFT) calculations

The DFT calculations were studied by using the Vienna ab initio Simulation Package (VASP) code ²⁰⁸⁻²⁰⁹. Projector Augmented Wave (PAW) pseudopotentials ²¹⁰ was used to deal with the core electrons and the Perdew-Burke-Ernzerhof (PBE) function of the generalized gradient approximation (GGA) ²¹¹ was used to describe electron exchange and related interactions. The cutoff energy of the plane wave basis was set to 420 eV. The convergence criteria for energy and force are set to less than 10⁻⁴ eV and 10⁻² eV/Å, respectively. In addition, the van der Waals (vdW) correction was considered for the dispersion correction using Grimme's DFT-D3 method.²¹² For calculating optical properties of Cu and Co-NC, the Brillouin zone was sampled with 30 × 30 × 30 and 10 × 10 × 1 Monkhorst-Pack grids, respectively. The supercells are used to construct slab model for calculating free energy to avoid the interactions caused by periodicity. If mentioned, the E-field is included into the Gibbs energy calculations of reaction steps. This information could not be found anywhere The vacuum of 15 Å was set to avoid interlayer interactions. For calculating free energy, the Brillouin zone was sampled with a 3 × 3 × 1 Monkhorst-Pack grids.

Photocatalytic experiments

The photocatalytic seawater splitting reaction was carried out in a liquid-solid phase reaction in a quartz reactor tightly sealed by a septum. The reaction was conducted under light irradiation of a 300 W Xe lamp (PLS-SXE300D, Perfect Light) with AM 1.5G filter without the use of any noble metal and sacrificial agents. Typically, 2 mg of the sample was dispersed in 10 ml artificial seawater and was sonicated (B2500R-DTH, Branson) for 10 min. The solution was then transferred into a reaction vessel and stirred. Subsequently, the reactor was sealed and purged with pure Ar for 15 minutes to remove air. Finally, the Xenon lamp was turned on to initiate the photocatalytic reaction. Following completion of the photocatalytic reaction, the reactor was allowed to cool, and GC measurements were conducted at room temperature.

For long-term stability testing, after each cycle of 23 hours of reaction, the light source was turned off. The reactor was then degassed again by purging with pure Ar for 15 minutes to remove gases from the previous reaction cycle, and the light source was reactivated to initiate the next reaction cycle.

Solar-to-Hydrogen (STH) conversion efficiency

To calculate Solar-to-Hydrogen (STH) conversion efficiency, we attempted to calculate STH considering the efficiency of the AM 1.5G solar spectrum. Based on previous work in solar-driven photocatalytic overall water splitting systems, the STH efficiency can be calculated as follows:²³²

$$\eta_{STH} = \frac{n_{H_2} \times \Delta A}{P_{solar} \times S \times t} \times 100\%$$

where n_{H_2} molar amount of the produced H_2 , ΔA is the Helmholtz free energy at the given temperature and volume, P_{solar} is the irradiance of 6 Sun (600 mW cm⁻²) of the AM 1.5G standard solar spectrum, S is the illuminating area (2 cm²), t is the reaction time.

STEM-EDS & STEM-EELS methods and analysis

Samples for aberration corrected scanning transmission electron microscopy (AC-STEM) were prepared by drop casting 5 μL of the sample dispersed in ethanol onto a Au TEM grid with lacey carbon support film.

AC-STEM imaging, energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were performed on a JEOL GrandARM300F2 operated at 300 kV and with a 24 mrad convergence angle. The collection semi-angles for the high angle annular dark field (HAADF) detector were 79-180 mrad and the bright field (BF) STEM detector had an outer collection semi-angle of 10 mrad. The instrument is equipped with dual 158 mm^2 silicon drift X-ray detectors for EDS acquisition.

EELS mapping was collected using a Gatan Continuum (model 1069) spectrometer with a Gatan K3 direct electron camera. EELS mapping was performed with the high energy resolution entrance aperture which has a collection semi-angle of 72 mrad and spectra were recorded at a dispersion of 9 meV/channel. ADF images recorded alongside the EELS data were collected on the Gatan ADF detector (model 807) with collection semi-angles of approximately 50-150 mrad. The energy resolution is given by the FWHM of the zero-loss peak (ZLP) and was measured to be 0.405 eV.

For all spectra the zero loss and core loss regions of the spectrum were acquired simultaneously using the DualEELS mode and the ZLP was subsequently used to correct for any energy drift during the map due to scan or environmental instabilities during the acquisition.

The background zero loss was fitted and extracted using a non-linear least square fitting with a power law ($Ae^{-b\Delta E}$; where A, b are fitting constants and ΔE is the energy loss). The maps shown are extracted from the map using 0.2 eV wide windows located on the observed plasmon peaks in the EELS spectrum centered at 2.0 eV, 2.3 eV and 2.6 eV.

3.2 Results and Discussion

3.2.1 Characterization of Co-NC@Cu Catalysts

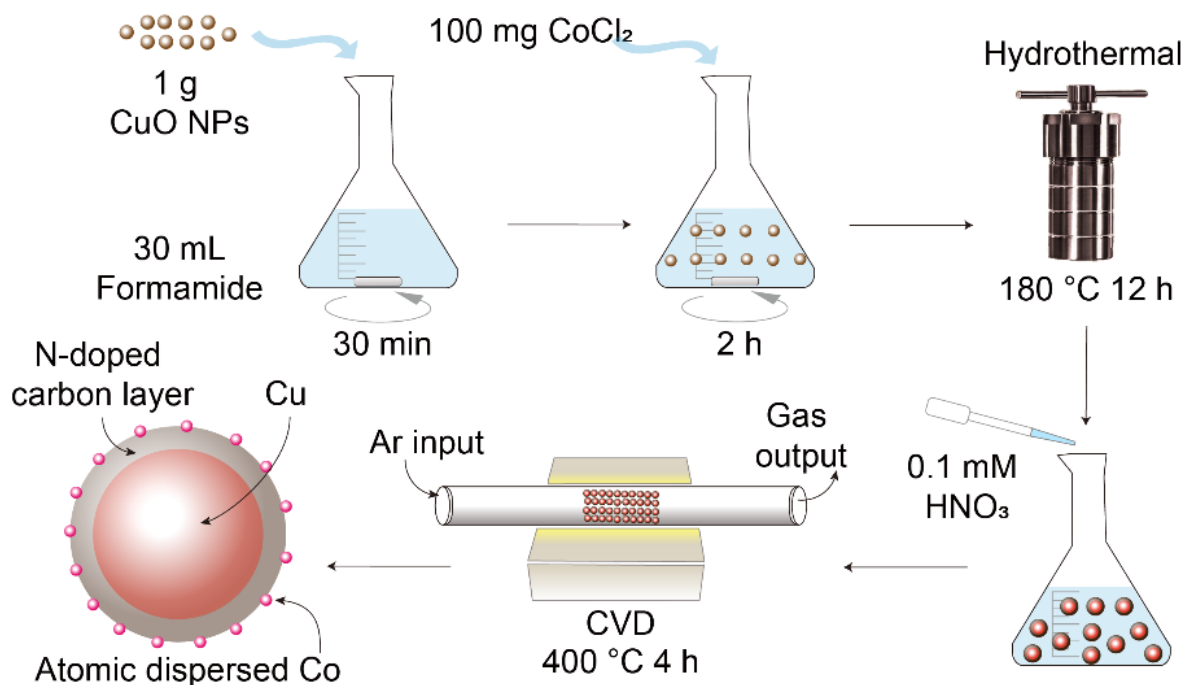


Figure 3-1 Schematic diagram of the synthesis process of Co-NC@Cu.

The synthesis method²⁴³ for the Co-NC@Cu catalyst is illustrated in Figure 3-1, where CuO and CoCl₂ are dispersed in formamide (HCONH₂) and subjected to hydrothermal treatment at 180 °C for 12 hours. Under these reaction conditions, formamide underwent conversion to the amorphous nitrogen-doped carbon (NC) material. After dilute acid treatment and Ar annealing, the Co precursor formed a Co-N bond with the NC layer. The Cu NPs are reduced from the initial CuO NPs during this process to form a core.

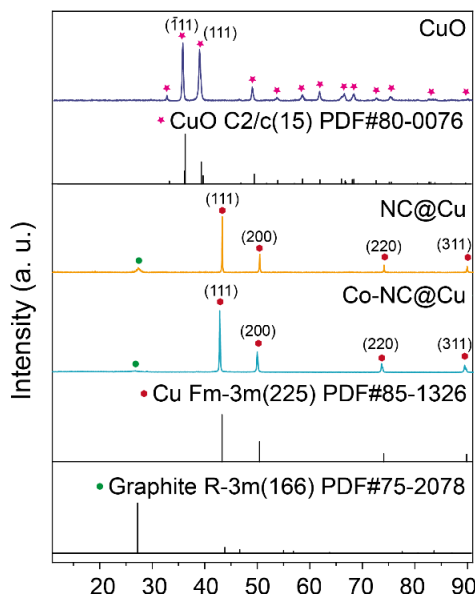


Figure 3-2 XRD patterns of CuO, NC@Cu, Co-NC@Cu and the corresponding standard PDF cards.

Therefore, a core-shell structure has been proposed, comprising a Co-N coordination-based Co-NC shell covering the Cu NPs core. The X-ray diffraction (XRD) results (Figure 3-2) reveal that the main diffraction peaks of the core component for both NC@Cu and Co-NC@Cu samples match with face centered cubic Cu, without any apparent peaks corresponding to CuO substances. This implied that the initial CuO NPs were successfully reduced to Cu NPs. Furthermore, the XRD patterns of NC@Cu and Co-NC@Cu showed a weak C peak, which is associated with the NC shell layer.

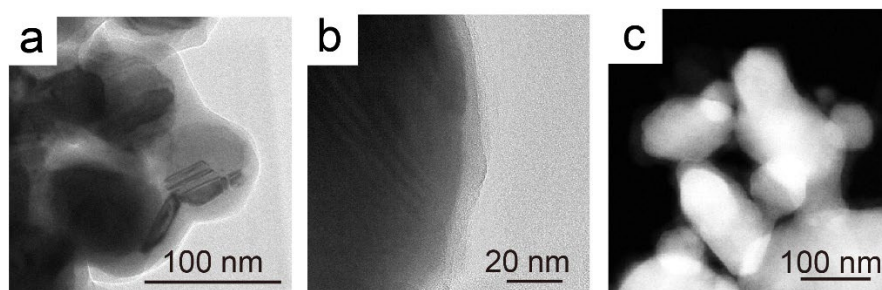


Figure 3-3 TEM images of a) Co-NC@Cu and b) zoomed-in image of a Cu NP edge. c) The HADDF-STEM of Co-NC@Cu.

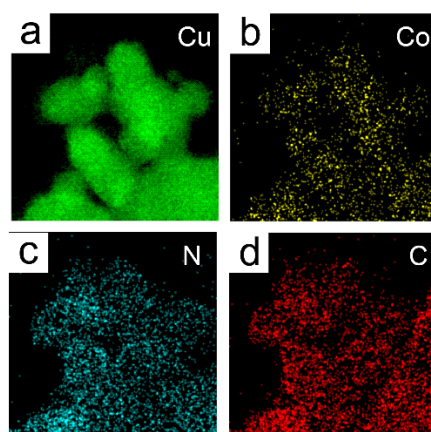


Figure 3-4 EDS element mapping of Co-NC@Cu for a) Cu, b) Co, c) N, and d) C.

Transmission electron microscopy (TEM) images (Figure 3-3) depicted the surface of Cu NPs was covered by thin NC layer. To further determine the dispersion and position of Co atoms, we characterized the Co-NC@Cu on an aberration-corrected TEM (AC-TEM), using high-angle annular dark-field scanning TEM (HAADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 3-4) and atomic-resolution HAADF-STEM imaging. These results further affirmed the dispersion of Co atoms on the NC layer, with Co atoms appearing as isolated bright spots (as indicated by the yellow circles in Figure 3-5). No Co nanoparticles or clusters were observed. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis revealed that the actual Co loading was 0.40 wt% (Table 3-1). Highly crystalline Cu lattices of the face-centered cubic (fcc) structure is evident in the atomic-resolution STEM image shown in Figure 3-5b and Figure 3-6.²⁴⁶

Table 3-1 The Co loadings of Co-NC@Cu, determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

Sample	Co (wt %)
Co-NC@Cu-50	0.30

Co-NC@Cu-100	0.40
Co-NC@Cu-250	0.49

Note: As Co-NC@Cu-100 for example, -100 means the precursor amount is 100 mg used for synthesis.

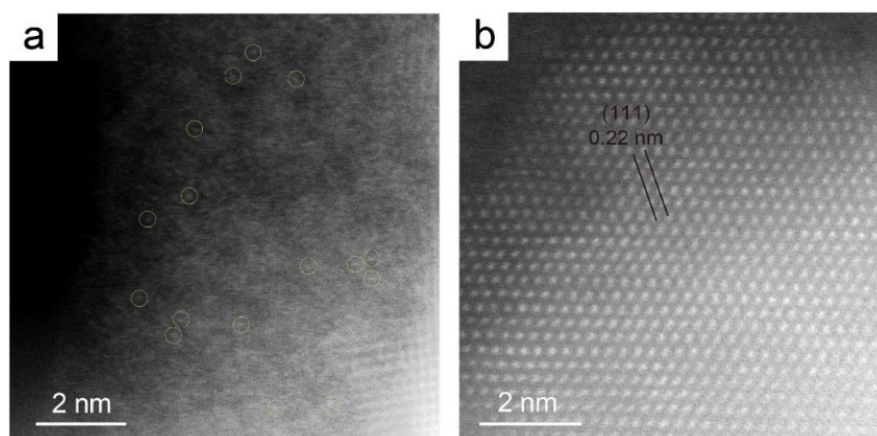


Figure 3-5 The AC HADDF-STEM local images of a) Co single atoms anchored N-doped carbon shell (i.e., Co-NC), and b) the core Cu.

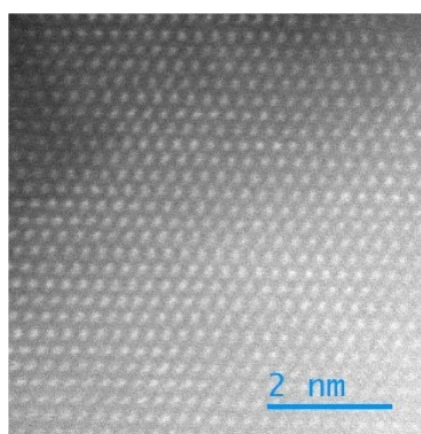


Figure 3-6 The AC HADDF-STEM local image of core Cu. The NP is viewed down a fcc<110> zone axis.

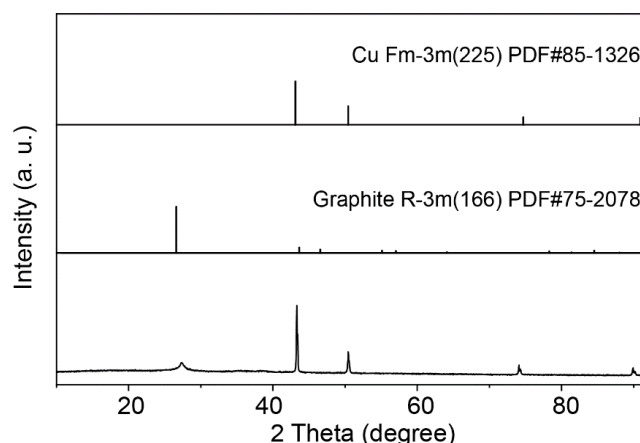


Figure 3-7 The XRD patterns of Co-NC@Cu after the 343-hour reaction.

After long-term (343 hours) stability tests, the characteristic XRD peaks of Cu and C in Figure 3.7 remain comparable to the pristine Co-NC@Cu sample (Figure 3-2). The lack of Cu core's oxidation after prolonged seawater splitting indicates the NC shell's effective protective attributes. The EDS elemental mapping results (Figure 3-8) confirm that the sample maintained the presence of constituent elements, notably Co, which remains well-dispersed throughout the material without any observable signs of aggregation.

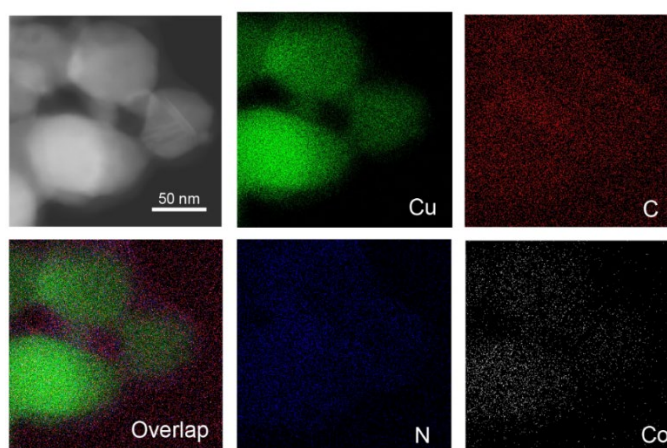


Figure 3-8 The HADF-STEM and EDS element mapping of Co-NC@Cu for Cu, Co, N, and C. Due to the use of Ni/C mesh for sample preparation, the signal for C element mapping is affected. In the manuscript, we avoid the use of grids containing C for preparing TEM samples.

X-ray absorption spectroscopy (XAS) analysis was conducted to investigate the coordination environment of Co, providing further confirmation of the atomic dispersed Co in Co-NC@Cu and offering deeper insights into the catalyst structure. The acquired data were compared with Co foil and CoPc as reference materials. The normalized X-ray absorption near-edge structure (XANES) spectra of the Co K-edge is depicted in Figure 3-9a. As indicated by the XANES spectra, the comparison of near-edge adsorption energy between Co-NC@Cu, CoPc, and Co foil, indicates that the Co K-edge energy of Co-NC@Cu is comparable with that of CoPc. This result suggests the similar chemical states of Co between Co-NC@Cu and CoPc. In addition, Co-NC@Cu exhibits similar pre-edge profile to that of CoPc for Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) spectra in Figure 3-9b. In the FT-EXAFS Co K-edge, a prominent peak at $\approx 1.43 \text{ \AA}$ corresponds to the first-shell coordination of the Co-N bond,²⁴⁷ mirroring the contribution observed in the CoPc reference value. Notably, no discernible Co-Co peak was detected at $\approx 2.17 \text{ \AA}$, indicating the negligible presence of metallic Co species.²⁴⁸ These findings corroborated the atomic dispersion of the Co-N coordination in Co-NC@Cu, aligning with the results of Co atomic dispersion observed in the HAADF-STEM image as discussed above. The wavelet transform EXAFS (WT-EXAFS) spectra (Figure 3-9c) illustrated that Co foil exhibited distinct sharp regions, representing Co-Co metal bonds.²⁴⁹ The contour plots for Co-NC@Cu in Figure 3-9d and CoPc in Figure 3-9e exhibit similar features, further supporting the formation of Co-N coordination in the Co-NC@Cu catalyst.

Additionally, X-ray photoelectron spectroscopy (XPS) in Figure 3-10-3-12 was employed to investigate the valence states of elements. The Co 2p spectra of Co-NC@Cu exhibited two characteristic main peaks at 796.0 eV and 780.3 eV corresponding to the Co 2p_{3/2} and Co 2p_{1/2} orbitals before and after reaction.²⁵⁰ The peaks of N1s corresponding to graphite N (401.1 eV), pyridinic N (398.6 eV), pyrrolic N (400.1 eV), and N-metal species (399.4 eV, corresponding to Co-N interaction) can be resolved in N 1s XPS spectra (Figures 3-13).²⁵¹

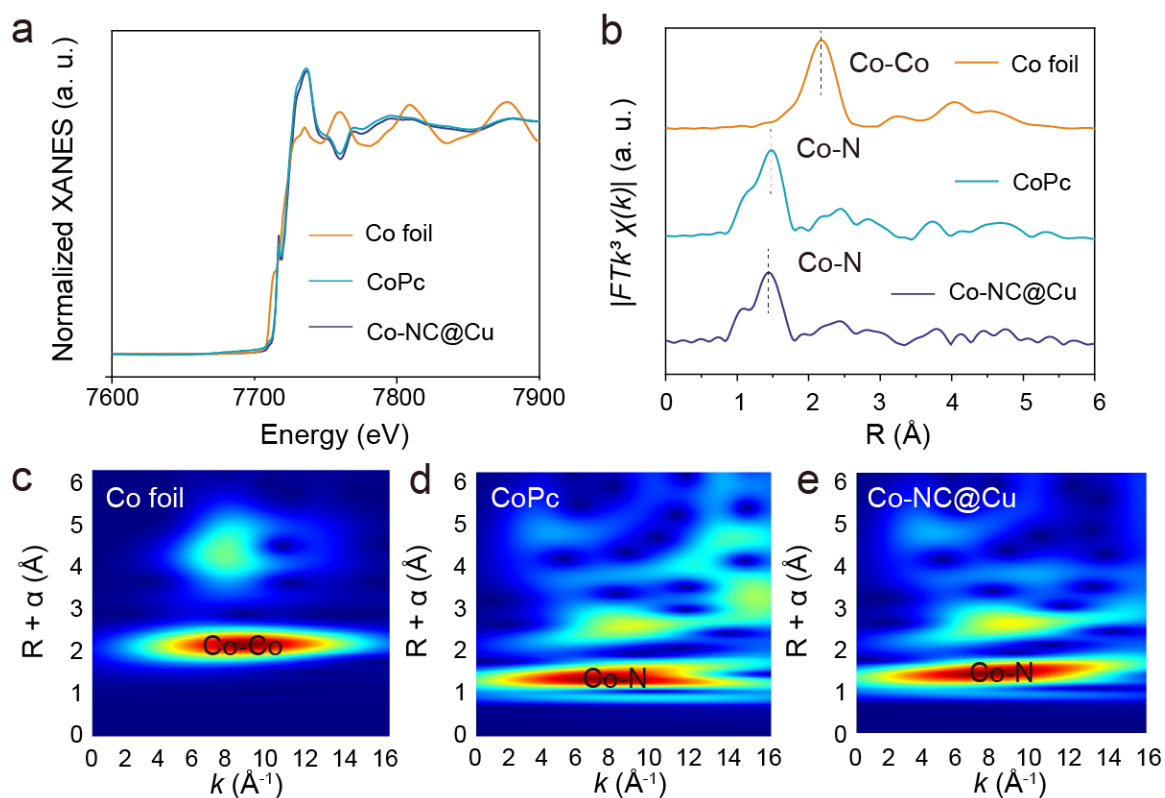


Figure 3-9 (a) The XANES and b) FT-EXAFS of Co K-edge for Co foil, CoPc and Co-NC@Cu. WT-EXAFS for (c) Co foil, (d) CoPc and (e) Co-NC@Cu.

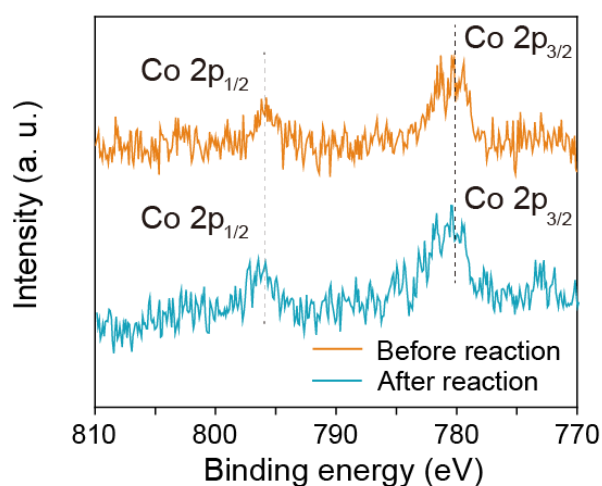


Figure 3-10 XPS spectra for Co 2p before (left) and after (right) the reaction.

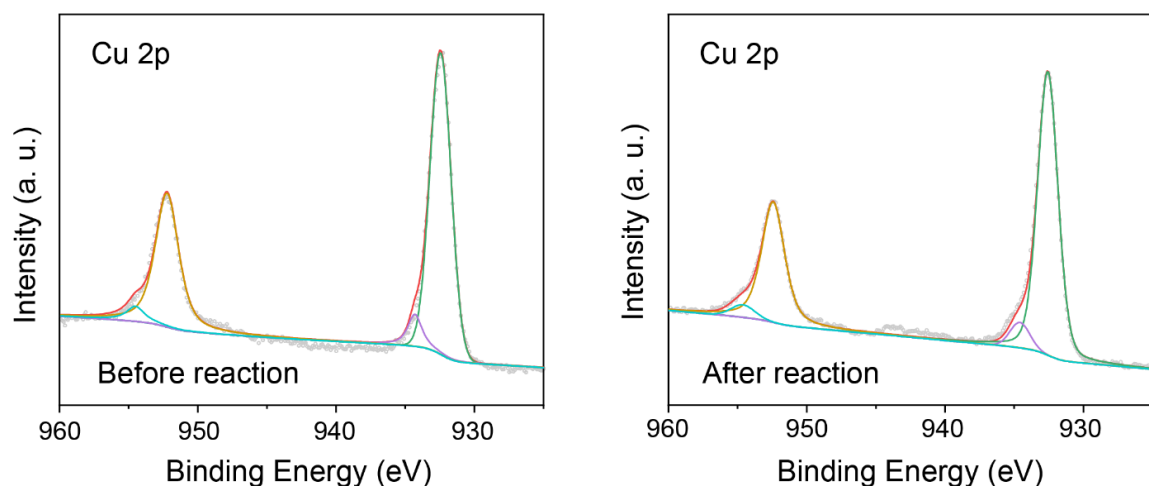


Figure 3-11 XPS spectra for Cu 2p before (left) and after (right) the reaction.

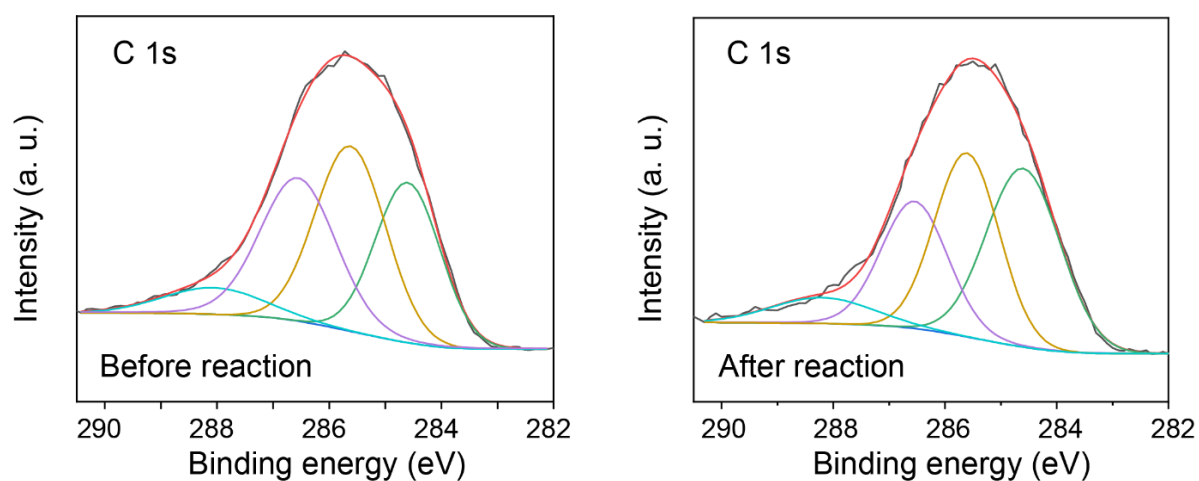


Figure 3-12 XPS spectra for C 1s before (left) and after (right) the reaction.

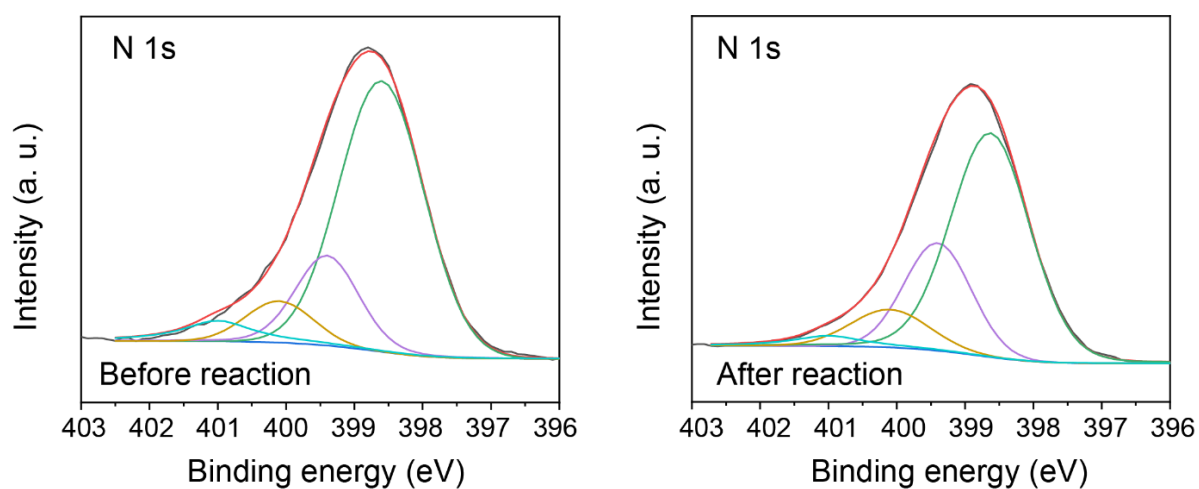


Figure 3-13 XPS spectra for N 1s before (left) and after (right) the reaction.

Furthermore, Raman spectroscopy (Figure 3-14) confirmed the presence of graphitic carbon structure. The D band at 1433 cm^{-1} is attributed to in-plane vibrations of sp_2 carbon atoms in graphite structure, while the G band at 1678 cm^{-1} originates from defects in graphene.²⁵² The electron paramagnetic resonance (EPR, Figure 3-15) spectrum revealed the presence of N defects (i.e., the doped N) in Co-NC@Cu. The observed signal at $g = 2.003$ confirmed these N defects in the sample, suggesting atomic-level coordination of Co atoms with N within NC@Cu.²⁵³ The above results have proved Co single atoms were successfully coordinated with N rather than forming the NPs.

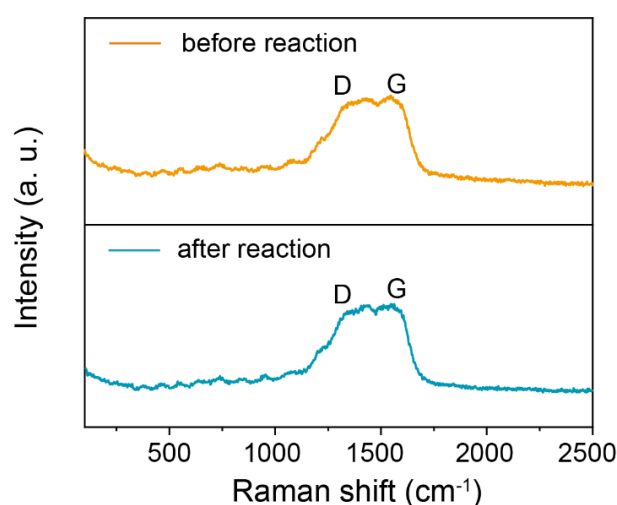


Figure 3-14 Raman spectra for Co-NC@Cu before and after 343-hour reaction.

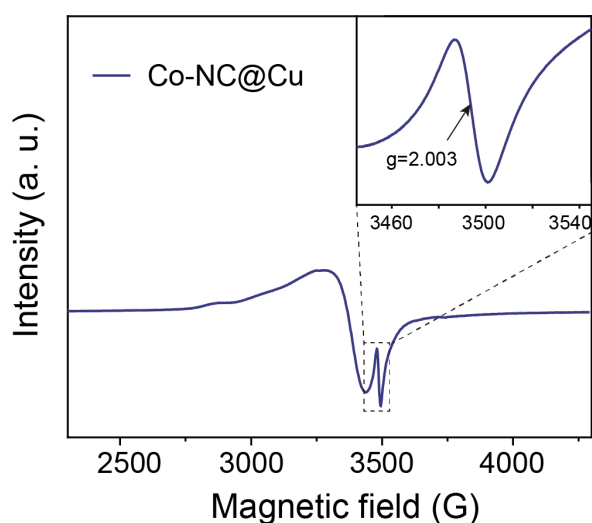


Figure 3-15 EPR spectra for Co-NC@Cu.

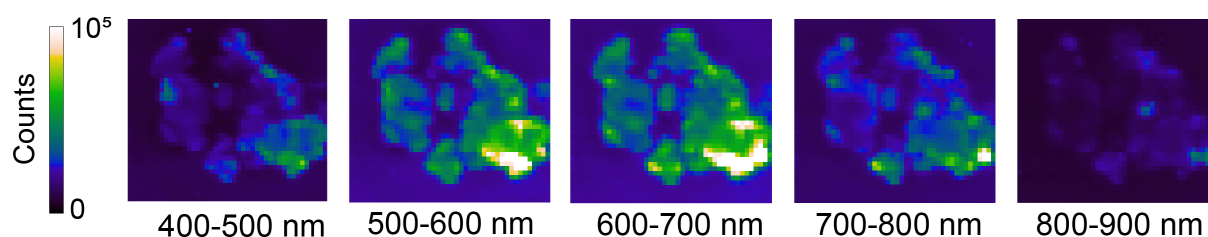


Figure 3-16 CL intensity maps integrated across different wavelength ranges from 400 to 900 nm.

The spatial and energy distribution of the resonances in Co-NC@Cu was investigated using spatially resolved cathodoluminescence (CL) spectroscopy. The CL signal was analyzed by integrating it across different wavelength ranges from 400 to 900 nm. Figure 3-16 illustrates the intensity maps obtained by integrating the CL emission across different wavelength ranges. The core-shell NPs with varied particle sizes (Figure 3-17) results in broadband absorption in the visible and near-infrared regions. This phenomenon arises from the existence of multiple plasmon modes excited within the differently sized plasmonic NPs.²⁵⁴

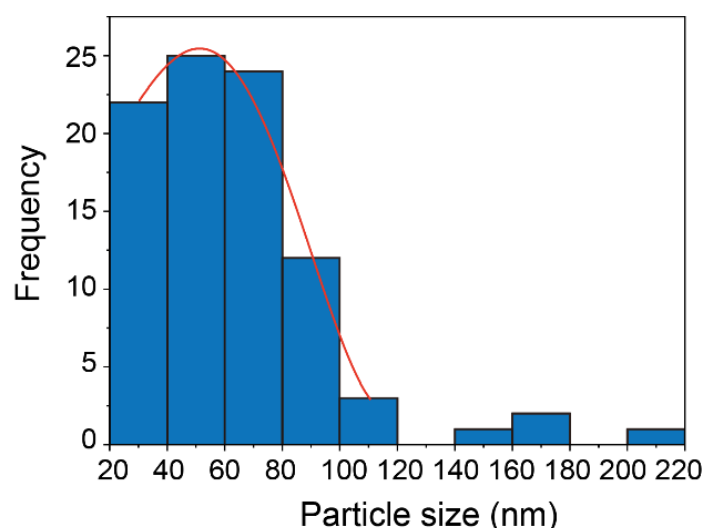


Figure 3-17 Size distribution histograms obtained from TEM images for Co-NC@Cu.

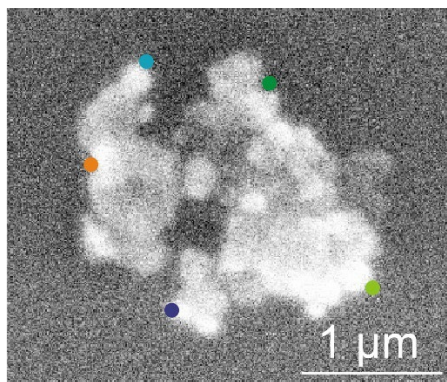


Figure 3-18 CL emission signal for Co-NC@Cu with the corresponding SEM image.

Figure 3-18 distinctly depicts the CL emission signal reflected from the brightened regions, indicating that the area of strong CL signal covers multiple nanoparticles. CL measurements were conducted in raster scanning mode, locally exciting the nanostructure, and acquiring the full spectra of each pixel of the scanned image as shown in Figure 3-18.

The CL spectra from different regions of the sample are represented in the sub-figures of Figure 3-19-3-21. The analysis of the CL signals at different edge sites (shown with different colours in Figure 3-18) revealed one or more peaks in the spectral region of 500-750 nm, where the signals exhibit relatively stronger intensity. This analysis further highlights the generation of multiple resonances at different wavelengths by the different sized Cu cores in the Co-NC@Cu catalyst sample.²¹⁷ The multiple resonances contribute to an overall broadband absorption in the visible and near-infrared spectra.²¹⁸

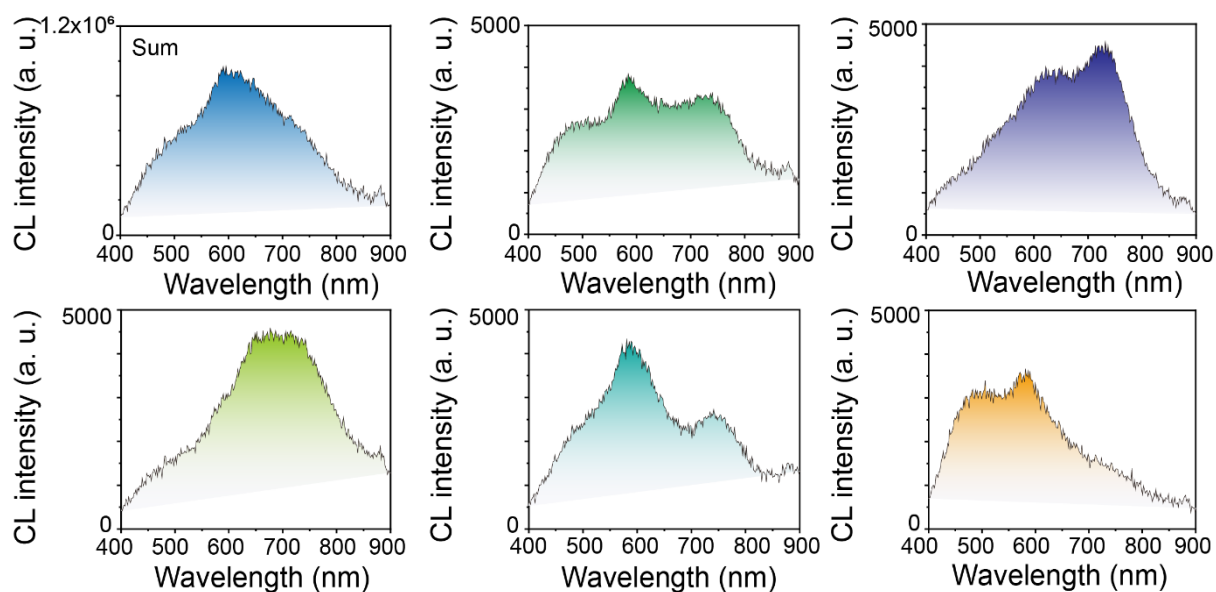


Figure 3-19 CL emission full/Sum spectrum (blue) and the spectra at the different sites indicated in Figure 3-18 with the corresponding colors.

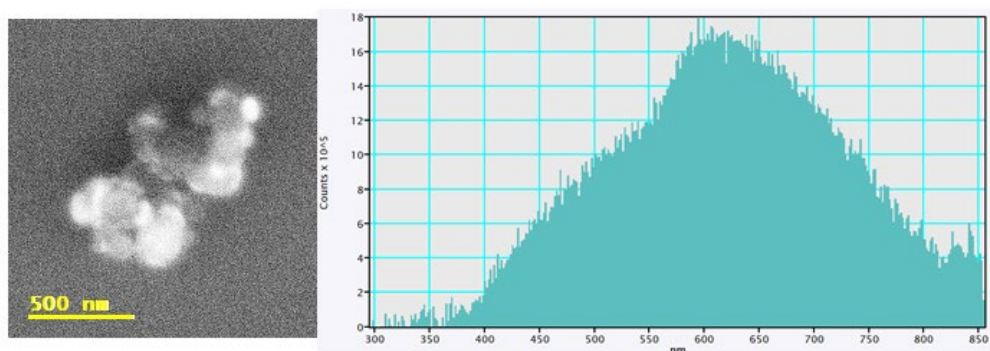


Figure 3-20 CL emission signal for Co-NC@Cu based on the corresponding SEM image and corresponding emission spectra.

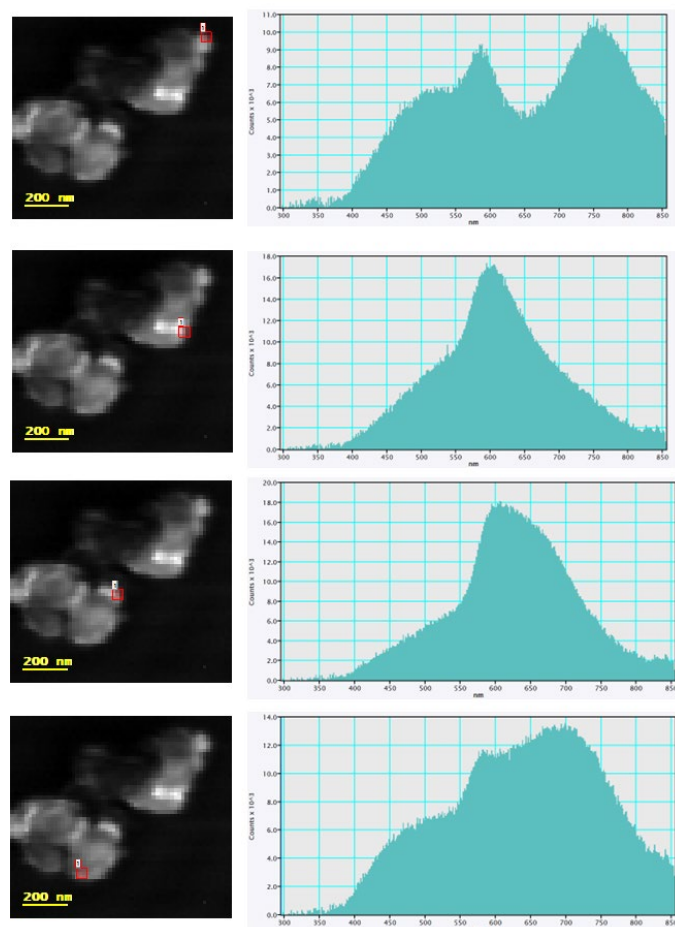


Figure 3-21 CL emission spectra at the different sites.

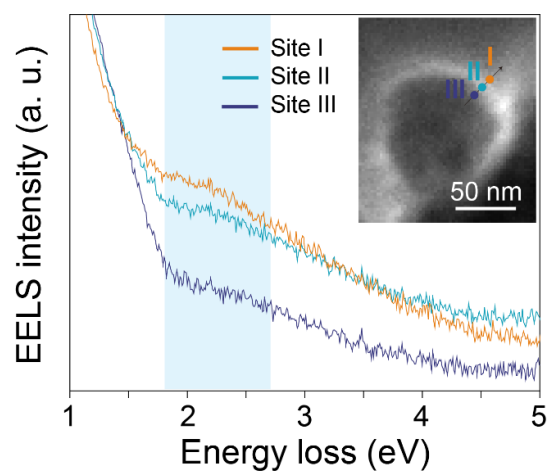


Figure 3-22 EELS spectra obtained from sites I, II, and III as indicated in the inset image.

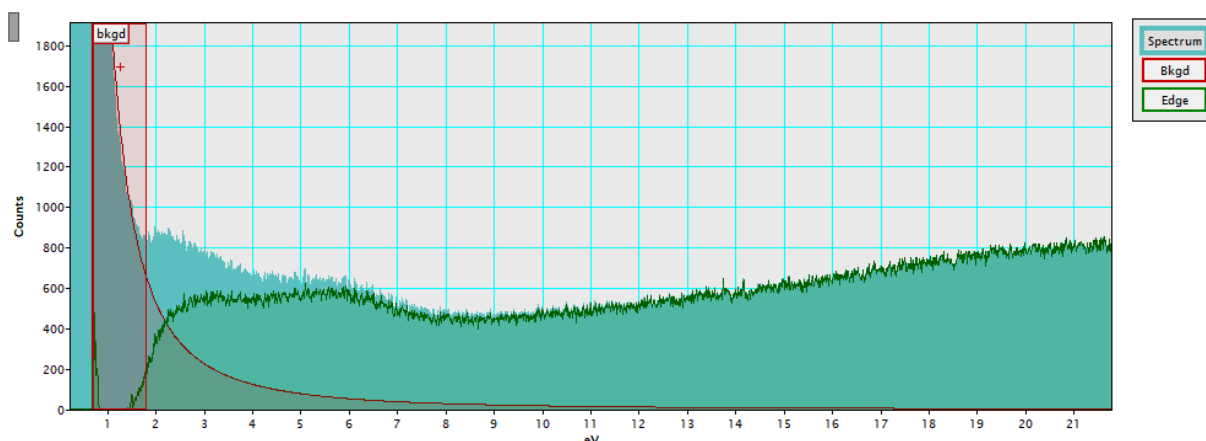


Figure 3-23 Plasmon signal mapping. Data was collected with a high dispersion for the highest resolution (0.4 eV). The ZLP was aligned post-acquisition, and the background was modelled as a power law leaving behind the signal from the plasmons. The broad peak is observed: at ~ 2 eV. The ~ 2 eV peak is attributed to the surface plasmon. The plasmon signals have been extracted and mapped using 0.2 eV wide windows located around the centre of the peak position as shown in the spectrum. Likewise, for the ~ 2 eV plasmon, however, as would be expected for a plasmon resonance this is more diffuse and extends further into the vacuum.

To gain insights into the enhancement of optical absorption by plasmonic Cu NPs, electron energy loss spectroscopy (EELS) was coupled with STEM-HAADF imaging to measure the local optical response.²¹⁹ In Figure 3-22-3-24, the EELS spectra of Co-NC@Cu particles is depicted, exhibiting a distinctive absorption shoulder. In the line scan, optical absorption in the range of 1.8-2.7 eV is depicted, corresponding to wavelengths between 459-689 nm (illustrated in the blue-shaded region in Figure 3-22). This range matches the complete Sum spectra of CL presented in Figure 3-19-3-20. Note that in Figure 3-22, the intensity at position I (near the edge of the NC shell) is higher than that at position II (within the NC shell), both of which are further higher than the intensity at position III (within the copper core).

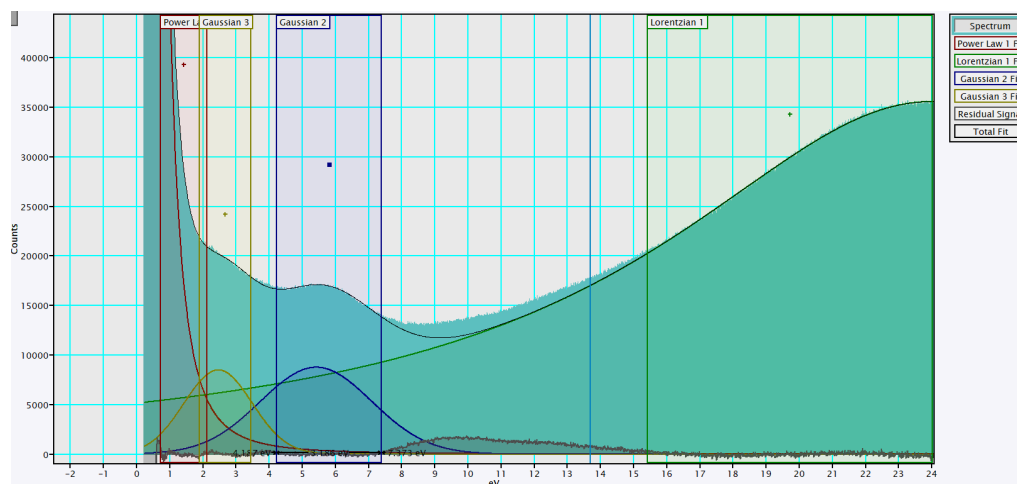


Figure 3-24 Fitting of line scan for EELS results. Fit the background as a power law spectrum; Fit the big plasmon at ~ 24 eV as a Lorentzian; One peak (orange curve) at ~ 2 eV fitted as gaussians; ~ 2 eV peak is attributed to the Cu NPs surface plasmon; Fitting shows good match, with small residuals.

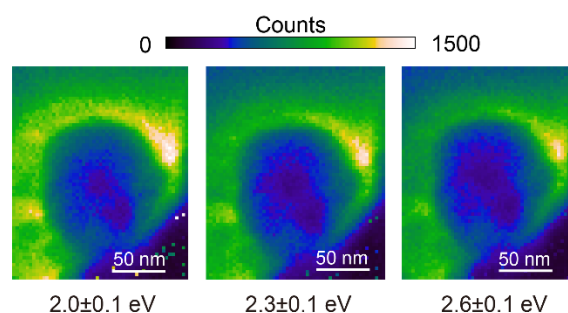


Figure 3-25 EELS mapping of Co-NC@Cu NPs at 2.0 ± 0.1 eV, 2.3 ± 0.1 eV and 2.6 ± 0.1 eV, corresponding to the blue-shaded peak region in the EELS spectra in Figure 3-22.

These results, combined with the EELS maps in Figure 3-25, confirm the LSPR effect in the Co-NC@Cu NPs, which is well-distributed around the Co-NC@Cu NPs without quenching. The above results highlight that Co-NC@Cu NPs possess the capability to absorb broad light from the visible to near-infrared regions, endowing this core-shell structure with enhanced light absorption across a wider wavelength range.²³⁶ The combined CL and EELS studies presented

here provide robust evidence for the LSPR phenomenon in Co-NC@Cu and its broad light harvesting capabilities.

3.2.2 Seawater Splitting Performance of Co-NC@Cu Catalysts

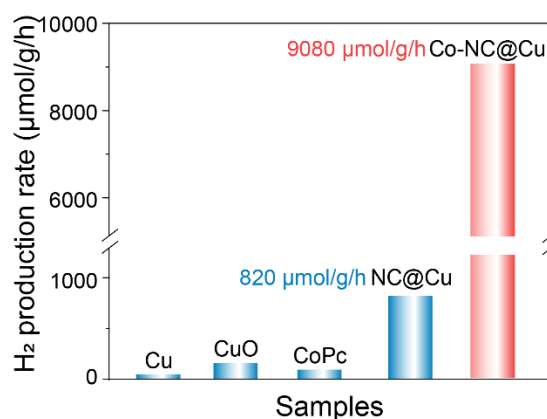


Figure 3-26 Comparison of the H₂ production rate from light-driven seawater splitting between Co-NC@Cu and its control samples.

To comprehensively study the light-driven seawater splitting performance of the synthesized Co-NC@Cu, the Xenon light source equipped with a condenser lens is utilized, which generated a spot with a diameter of 1.6 cm and a light intensity of 600 mW·cm⁻² (AM 1.5G). Notably, no sacrificial reagents and external heat source were used throughout the process. Photocatalytic seawater splitting performance of different samples was compared using gas products collected by gas chromatography (GC), as depicted in Figure 3-26. Notably, bare Cu, CuO and CoPc consistently show poor hydrogen production for photocatalytic seawater splitting. In contrast, Co-NC@Cu with Co single atoms anchored on the NC shell outperforms NC@Cu without Co single atoms by over 10 times. Accordingly, by controlling different CoCl₂ precursors during the synthesis process to optimize the Co loading (Figure 3-27), the optimized Co-NC@Cu sample achieves the highest H₂ production rate of 9080 μmol g⁻¹h⁻¹ in 1M NaCl seawater, demonstrating advanced performance in a noble metal-free, sacrificial agent-free photocatalytic seawater splitting system.

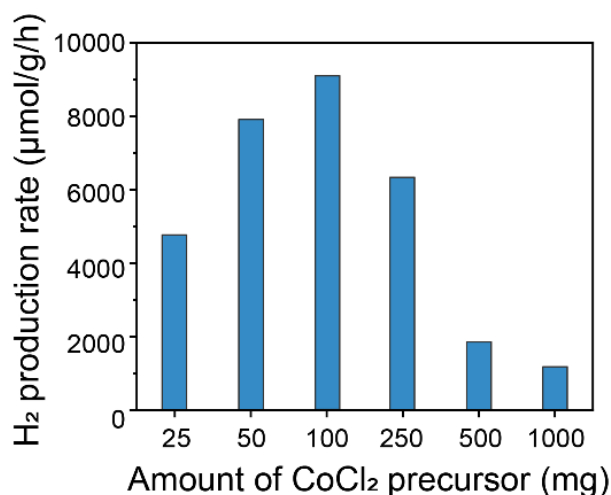


Figure 3-27 The reference experiments related to the optimization of Co loading.

To explore the potential roles of light and heat in the seawater splitting, additional experiments were conducted (Figure 3-28). The results indicated that only low-yield H₂ products were obtained under unfocused normal solar illumination, while no H₂ or O₂ products were detected when we solely heated the catalysts up to 150 °C. Additional reference experiments indicate that, when controlling for the same enhanced incident light/photons, the reaction environment temperature is related to H₂ generation (Figure 3-29a). This suggests that the thermal effect contributes to H₂ production, rather than the increase in H₂ generation being solely due to enhanced incident light/photons. Additionally, the relationship between H₂ yield and wavelength of light was investigated (see Figure 3-29b). The results indicate that the correlation between H₂ yield and wavelength aligns with the results from CL spectroscopy and EELS, illustrating that the optical absorption in the range of 459-689 nm corresponds to the highest H₂ production rates. These results imply that the photocatalytic reaction is driven by a combination of solar illumination and the light-focusing induced photothermal effect, rather than thermal or solar input alone. The photothermal effect arises from reaction-environment heating,²⁵⁵ increased light-induced hot carriers,²⁵⁶ and the higher thermal conductivity of seawater,²⁵⁷ collectively facilitating the photoreaction and enhancing the H₂ production rate.²³⁹

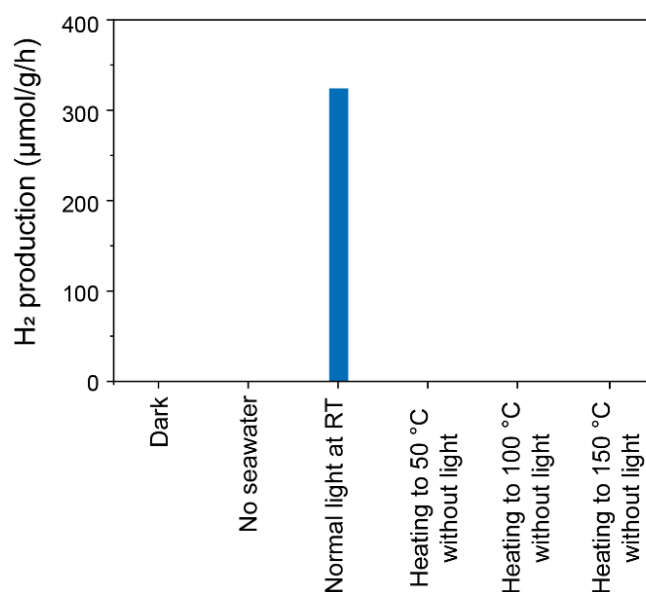


Figure 3-28 The reference for photocatalytic hydrogen production by seawater. Dark: without light and heat; No seawater: without any liquid, only powder samples; Normal light: 1 sun with 100 mW cm^{-2} ; RT: Room temperature; Heating was achieved by hot plate.

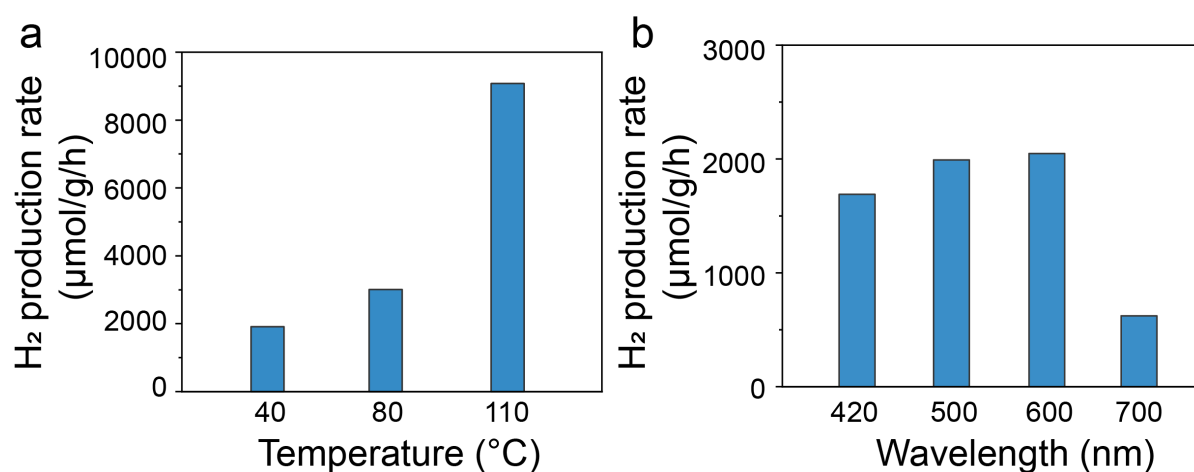


Figure 3-29 (a) Temperature-dependent photocatalytic seawater splitting for H₂ production. The experiment was studied by adjusting the reaction environment temperature using a water bath for the reactor while maintaining the same enhanced incident light conditions. (b) Wavelength-dependent photocatalytic seawater splitting for H₂ production.

Moreover, the effect of NaCl concentration on H₂ production rate and reaction temperature was studied (Figure 3-30). As NaCl concentration increases from 0 M to 1 M, the temperature rises to ~110 °C (bottom sub-figure), accompanying an increase in H₂ production rate to 9080 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (top sub-figure). Further increasing NaCl concentration only slightly impacts temperature and H₂ production, eventually reaching saturation.

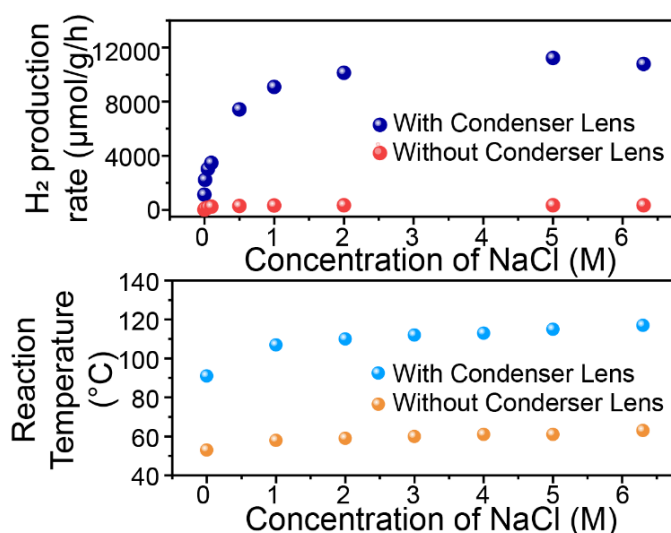


Figure 3-30 The H₂ production rate and reaction temperature as dependent on the NaCl concentration.

Time-resolved photoluminescence (TRPL) measurements (Figure 3-31) and density functional theory (DFT) calculations (Figure 3-32-3-35) were further employed to study the effect of NaCl content on photocatalytic seawater splitting. The DFT analysis shows traditionally inert cations/anions in seawater, such as Cl⁻, Na⁺, hydrated Cl⁻ and hydrated Na⁺ adsorb onto the surface of Co-NC@Cu, inducing charge polarization. The fitting of the TRPL spectra revealed an increase in carrier lifetime (Table 3-2), which can be attributed to the suppression of charge recombination due to the local polarization effect introduced near the surface by the adsorbed ionic species.²³² Therefore, the saline content in seawater can significantly enhance the performance of thermal-assisted photocatalytic seawater splitting by inducing strong charge polarization, and thereby prolonging carrier lifetimes.²³²

Table 3-2 The fitting of TRPL about carrier lifetime. The average carrier lifetime was calculated by using the following equation:

$$\tau_{\text{average}} = \frac{(A_1 \times \tau_1^2 + A_2 \times \tau_2^2)}{(A_1 \times \tau_1 + A_2 \times \tau_2)}$$

	τ_1	A_1	τ_2	A_2	τ_{average}
Pure water	1.67	1.02	15.62	0.31	11.99
1 M NaCl	2.21	1.10	18.81	0.43	14.97
5 M NaCl	5.52	0.47	25.2	0.38	21.00

The unit of τ is ns.

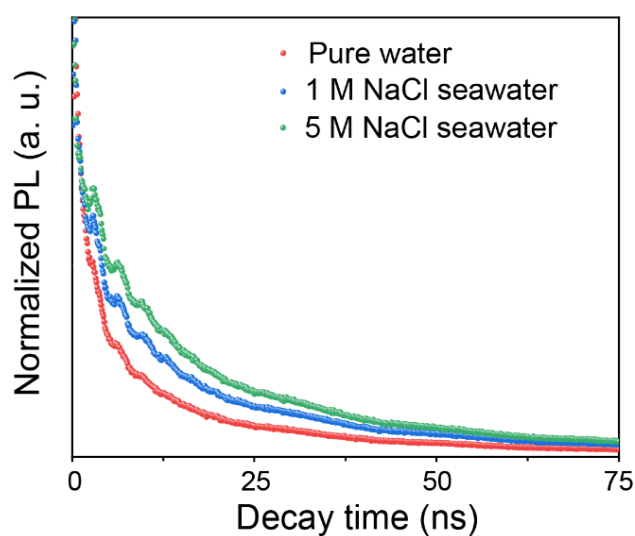


Figure 3-31 TRPL spectra of the Co-NC@Cu tested in NaCl solutions at the concentrations of 0, 1, and 5 mol L⁻¹, respectively. The excitation wavelength is 485 nm.

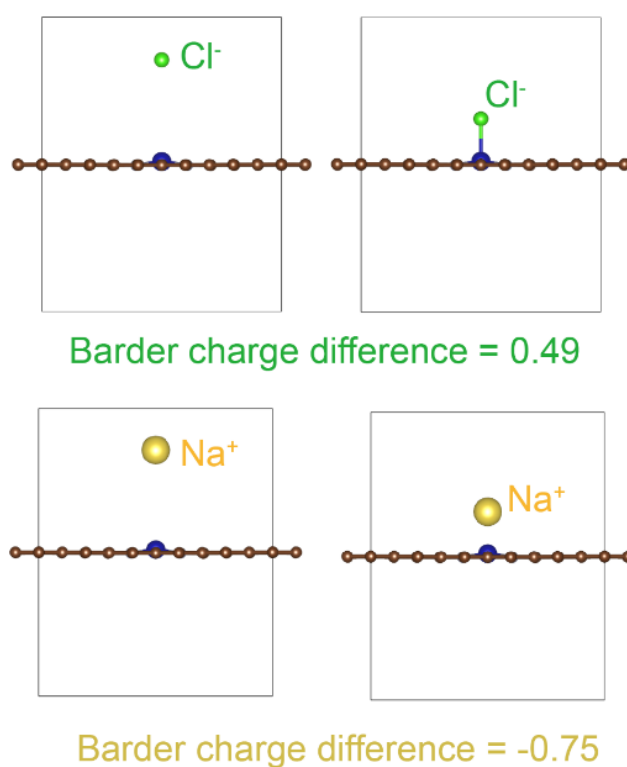


Figure 3-32 Calculated structures and Bader charges of Cl^- and Na^+ adsorption on the Co-NC.

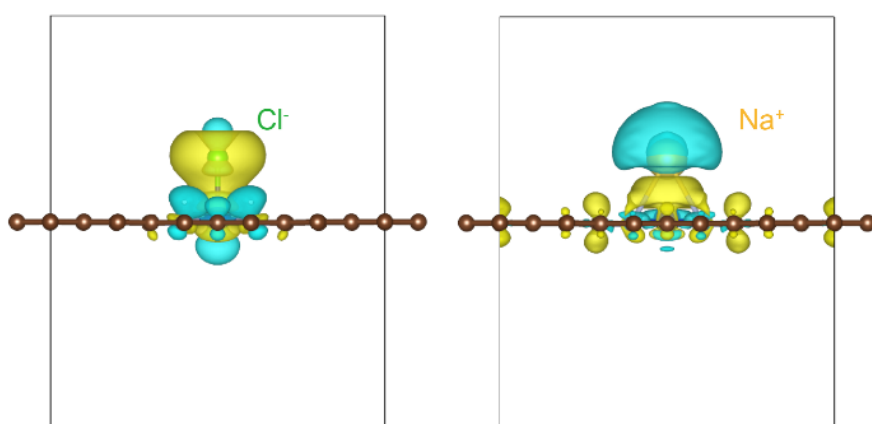


Figure 3-33 Calculated charge density difference plots for Cl^- and Na^+ adsorption on the Co-NC. The charge density isosurfaces are plotted at a value of $0.001 \text{ e}/\text{\AA}^3$. Blue and yellow isosurfaces represent charge loss and charge accumulation, respectively.

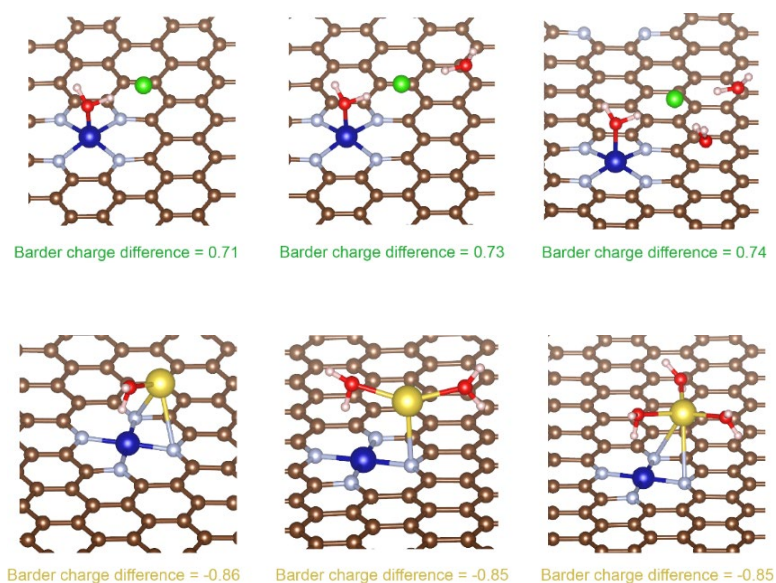


Figure 3-34 Calculated structures and Bader charges of hydrated Cl^- and Na^+ adsorption on the Co-NC. The results show that hydrated Na^+ ions are more inclined to adsorb onto the active sites around the Co-N-C coordination environment rather than the Co top site. Simultaneously, considering the adsorption of hydrated Cl^- ions, the competitive process between Cl^- and H_2O for the Co top site through slab adsorption model. The results indicate that H_2O molecules preferentially occupy the Co top adsorption site.

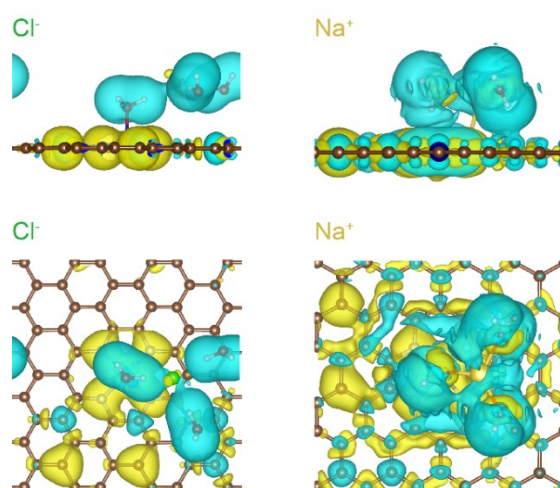


Figure 3-35 Calculated charge density difference plots for hydrated Cl^- and Na^+ adsorption on the Co-NC. The charge density isosurfaces are plotted at a value of $0.01 \text{ e}/\text{\AA}^3$. Blue and yellow isosurfaces represent charge loss and charge accumulation, respectively.

By recording the performance tests every 2 hours during the first 44-hour reaction, the received average STH reaches 4.78% (Figure 3-36a). The Co-NC@Cu sample also exhibits remarkable long-term stability and consistent photoactivity over 340 hours (Figure 3-36b), with the yield of H_2 and O_2 remaining close to the stoichiometric 2:1 ratio, demonstrating its overall water splitting capability and long-term stability. The STH result and long-term stability of Co-NC@Cu.

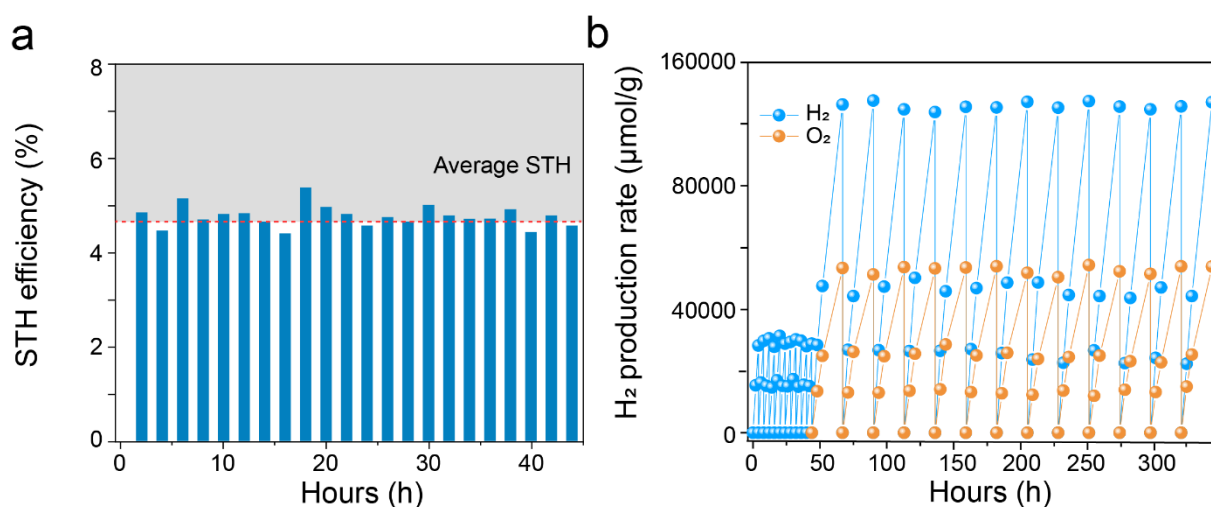


Figure 3-36 (a) STH efficiency recorded every 2 hours in the first 44-hour reaction. (b) Long-term stability tests up to 343 hours.

3.2.3 Theoretical Calculations

To gain deeper insights into the local E-field distribution associated with the plasmonic properties of Co-NC@Cu, DFT calculations were conducted to predict optical properties (Figure 3-37-3-39) and compared to Finite Difference Time Domain (FDTD) simulations were conducted by structural modelling based on the STEM-HAADF results.

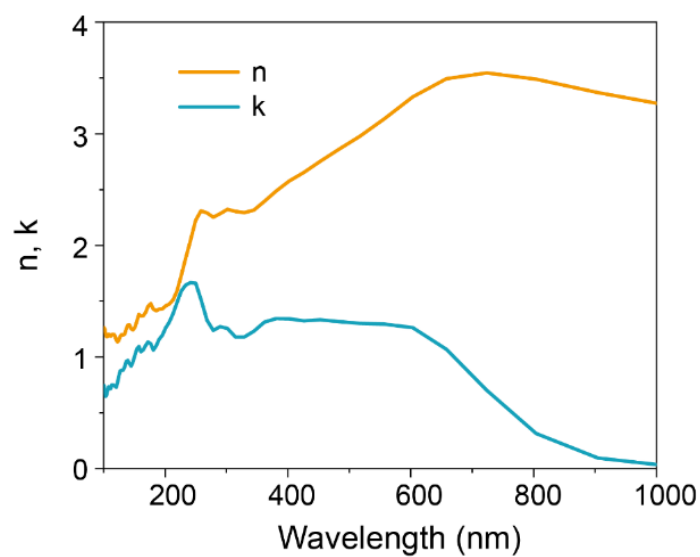


Figure 3-37 Refractive index (n) and extinction co-efficient (k) versus wavelength of Cu.

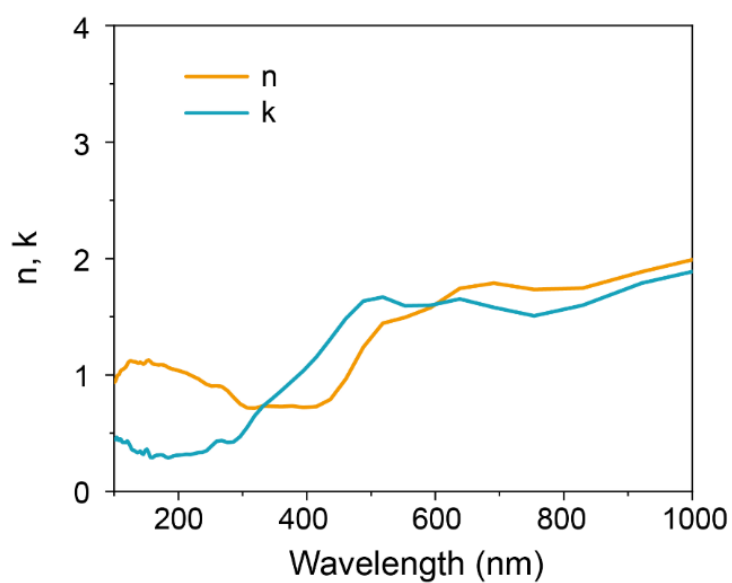


Figure 3-38 Refractive index (n) and extinction co-efficient (k) versus wavelength of Co-NC along *in-plane* direction.

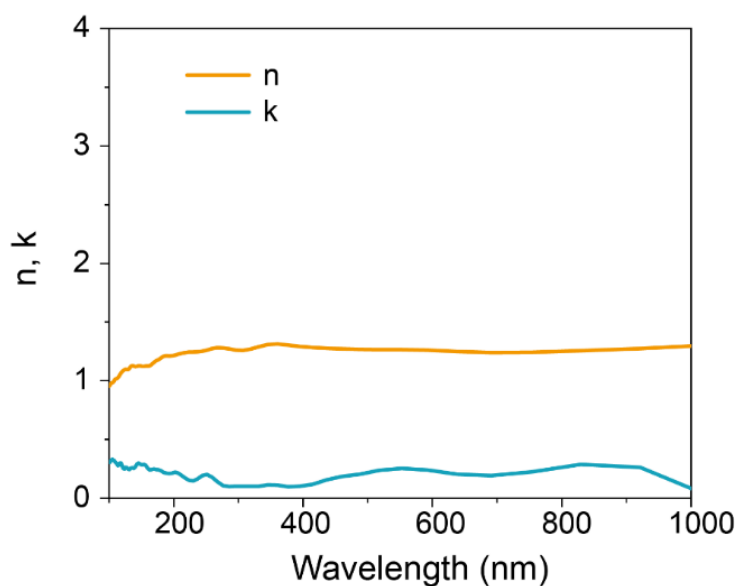


Figure 3-39 Refractive index (n) and extinction co-efficient (k) versus wavelength of Co-NC along *out-of-plane* direction.

As depicted in Figure 3-40a-d and Figure 3-41-43, FDTD simulation offers more information of the local E-field enhancement induced by the LSPR effect across the entire Co-NC@Cu system. Figure 3-40a illustrates the simulated local E-field distribution of Co-NC@Cu with a 50 nm Cu NP core and 10 nm NC shell at five different wavelengths. The E-field enhancement is particularly prominent from the visible and near-infrared range, with their negligible quenching phenomenon observed on the thin Co-NC shell. The characteristics of the local electromagnetic field arising from the plasmon resonance of the material surface in the core-shell structure can be affected by performing different radius of the metallic core or the thickness of the carbon shell.²¹⁹ As evidenced by the spectra in Figure 3-40b-d, enlarging the size of the Cu NPs core results in a red shift of the dominated resonant peaks. The increase in the core size of Cu NPs forms a larger plasmon resonator, thereby reducing the plasmon frequency and energy. Figures 3-40c-d demonstrate that increasing the Co-NC shell thickness (5 nm and 10 nm) also leads to a minor red shift in peak energy and a slight decrease in E-field intensity, while still maintaining over $\times 10$ local E-field enhancement when Cu NP size exceeds 30 nm under full-spectrum solar illumination. Therefore, the enhanced local E-field of

the Cu NP core effectively transfers to the Co-NC shell surface without significant quenching by the shell.

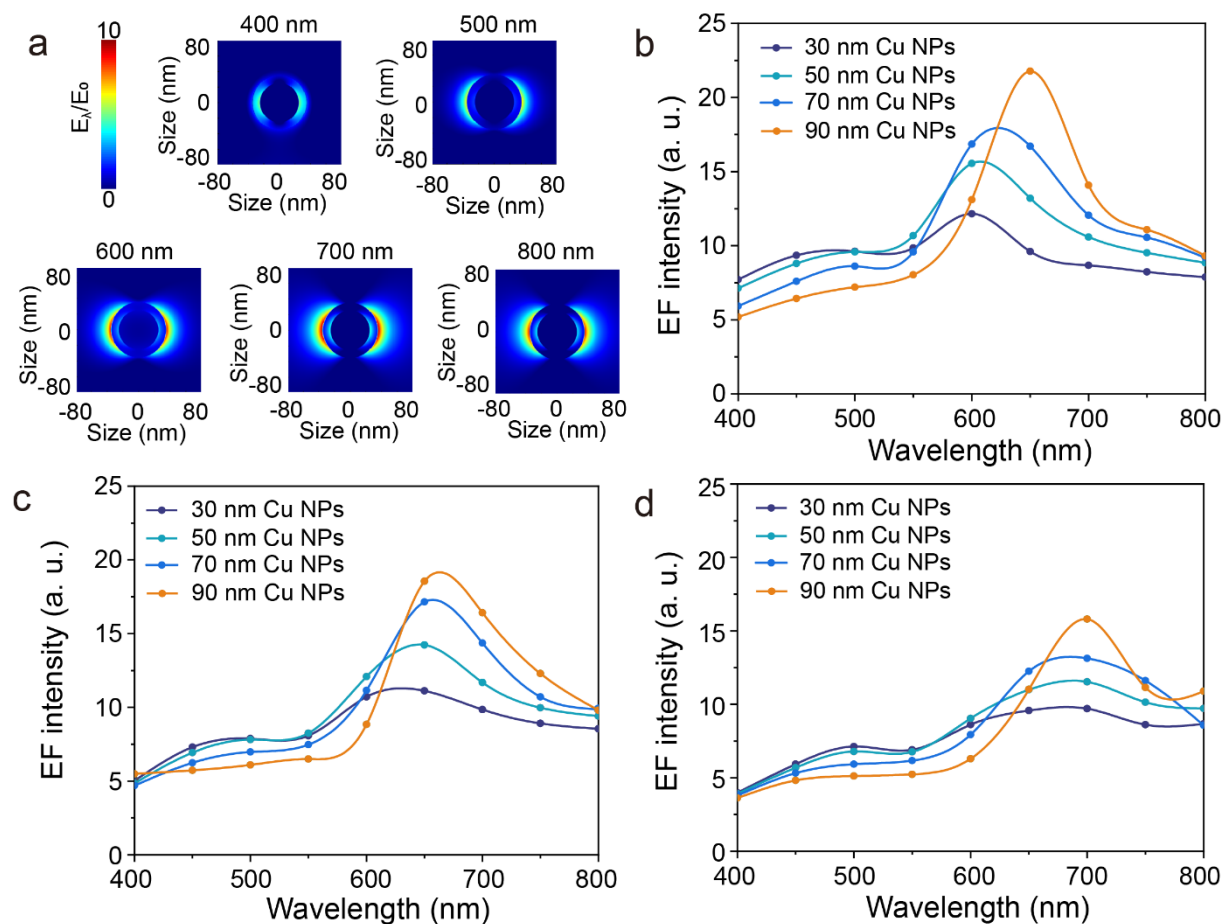


Figure 3-40 (a) The simulated E-field distribution of Co-NC@Cu under light irradiation at different wavelength ranges using FDTD simulations. (b) The maximum E-field (EF) intensity vs. incident light wavelengths for Cu NPs with different size. (c) The maximum E-field intensity vs. incident light wavelengths for Co-NC@Cu with (c) 5 nm and (d) 10 nm shell thickness. The E-field intensity of the incident light was set to 1 V/m, and the incident light intensity was set to $600 \text{ mW} \cdot \text{cm}^{-2}$.

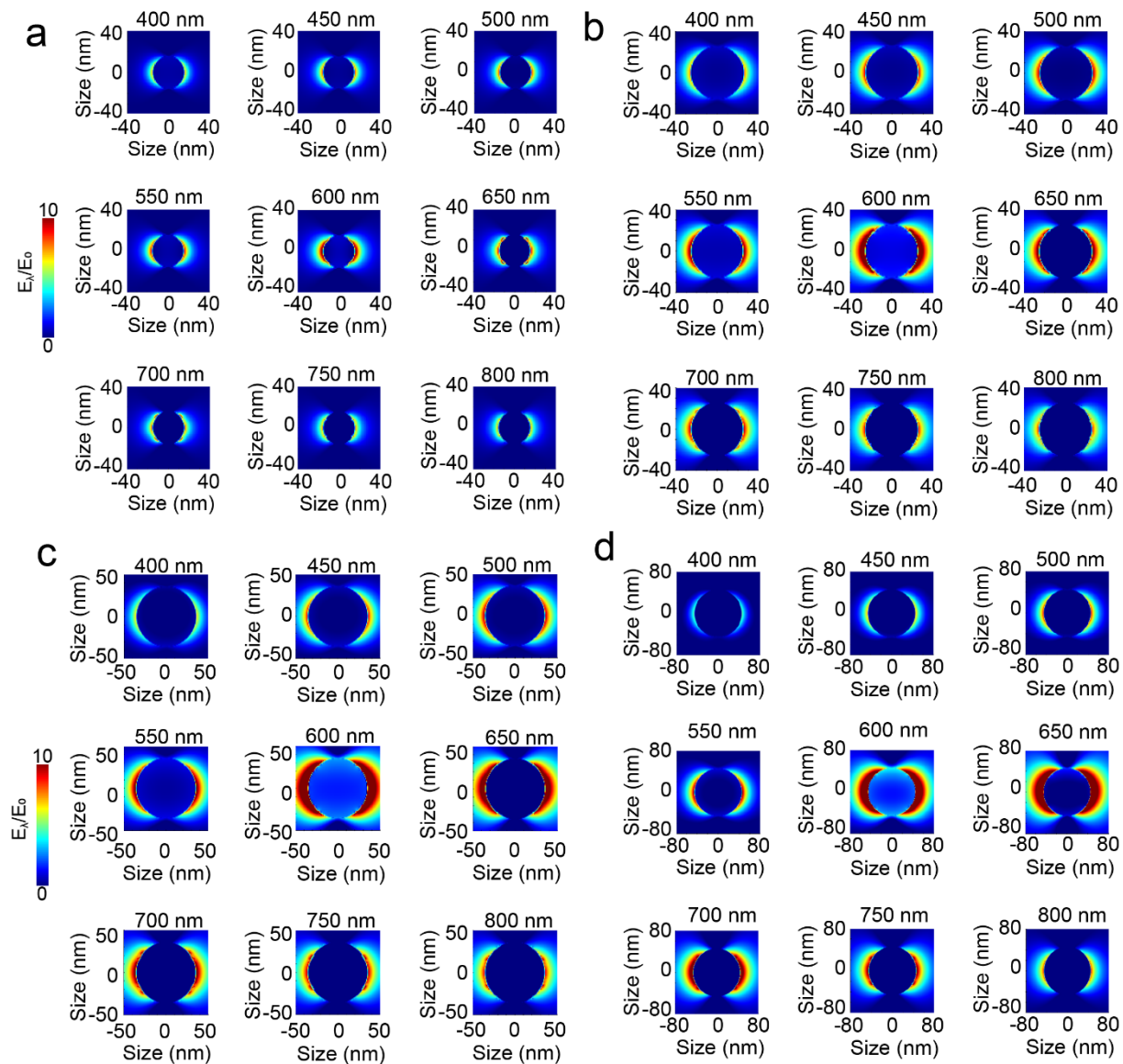


Figure 3-41 The simulated E-field distribution of Cu NPs under light irradiation at different wavelength ranges using FDTD simulations for a) 30 nm, b) 50 nm, c) 70 nm and d) 90 nm Cu NPs.

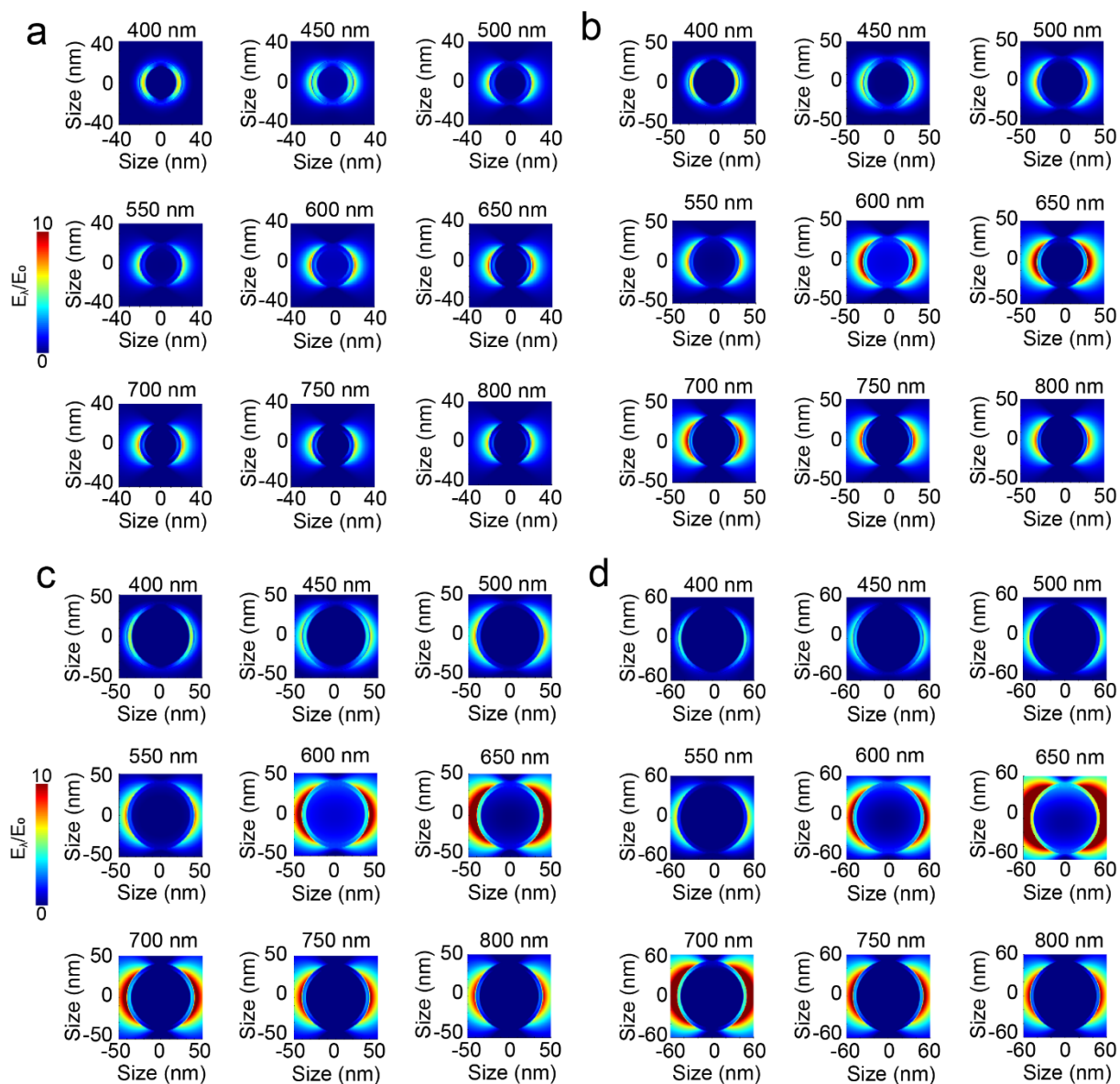


Figure 3-42 The simulated E-field distribution of Co-NC@Cu NPs with 5 nm thickness of NC layer under light irradiation at different wavelength ranges using FDTD simulations for a) 30 nm, b) 50 nm, c) 70 nm and d) 90 nm Cu NPs.

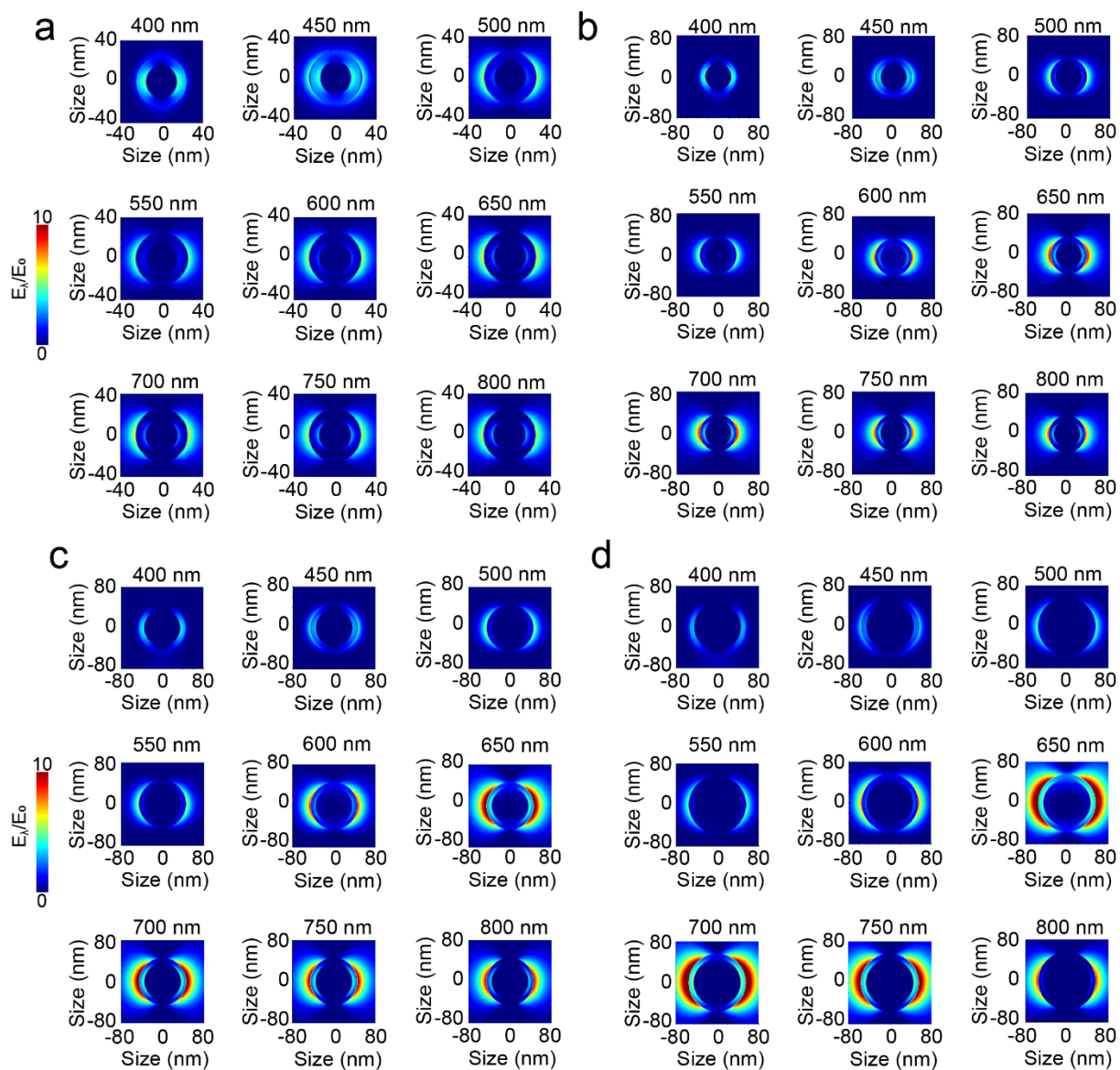


Figure 3-43 The simulated E-field distribution of Co-NC@Cu NPs with 10 nm thickness of NC layer under light irradiation at different wavelength ranges using FDTD simulations for a) 30 nm, b) 50 nm, c) 70 nm and d) 90 nm Cu NPs.

The local E-field profoundly influences the desorption and adsorption of intermediates during the reaction steps, thereby activating the chemical bonds and energy of the intermediates and subsequently modulating the Gibbs free energy and reaction activity. The previous studies have validated that plasmonic E-fields can thermodynamically regulate reaction pathways.²⁰² As depicted in Figure 3.44a-b, Figure 3-45-3-46 and Table 3-3, our investigation examines the effect of the E-field on the Gibbs free energy of each reaction step for NC shells with or without Co atoms as catalytic reaction sites. HER (hydrogen evolution reaction) is typically described as a three-step process: the initial state $H^+ + e^-$, the intermediate adsorbed H^* , and the free energy of the final product $\frac{1}{2}H_2$, and the ΔG_{H^*} is considered to describe the activity.²⁵⁸⁻²⁶⁰ Co-NC were found to be more thermodynamically favourable for H_2 production compared to the sole NC shown in Figure 3-44a. This provides a foundation for prioritizing the design of catalysts with Co-N coordination as ideal water-splitting catalysts. It is worth noting here that the applied E-field further reduces the ΔG_{H^*} for Co-NC under E-field perturbation.

Table 3-3 The relevant DFT calculation results of adsorption energies on various possible absorbers on NC and Co-NC.

	N-doped Carbon		Co-N-doped Carbon	
	Eads	Gads	Eads	Gads
Slab	-551.94		-537.42	
*O ₂	-561.99	-562.12	-548.17	-548.17
*O ₂ +*H	-564.26	-564.39	-550.65	-550.39
*OOH	-565.88	-565.55	-552.11	-551.80
*OOH+*H	-568.07	-567.57	-554.58	-554.29
*O+H ₂ O	-570.73	-570.26	-556.23	-555.61
*O	-556.65	-556.60	-542.40	-542.39
*O+*H	-558.95	-558.94	-544.93	-544.92
*OH	-561.68	-561.37	-547.05	-546.82
*OH+*H	-563.82	-563.50	-549.97	-549.42
*H ₂ O	-566.24	-565.84	-551.86	-551.38

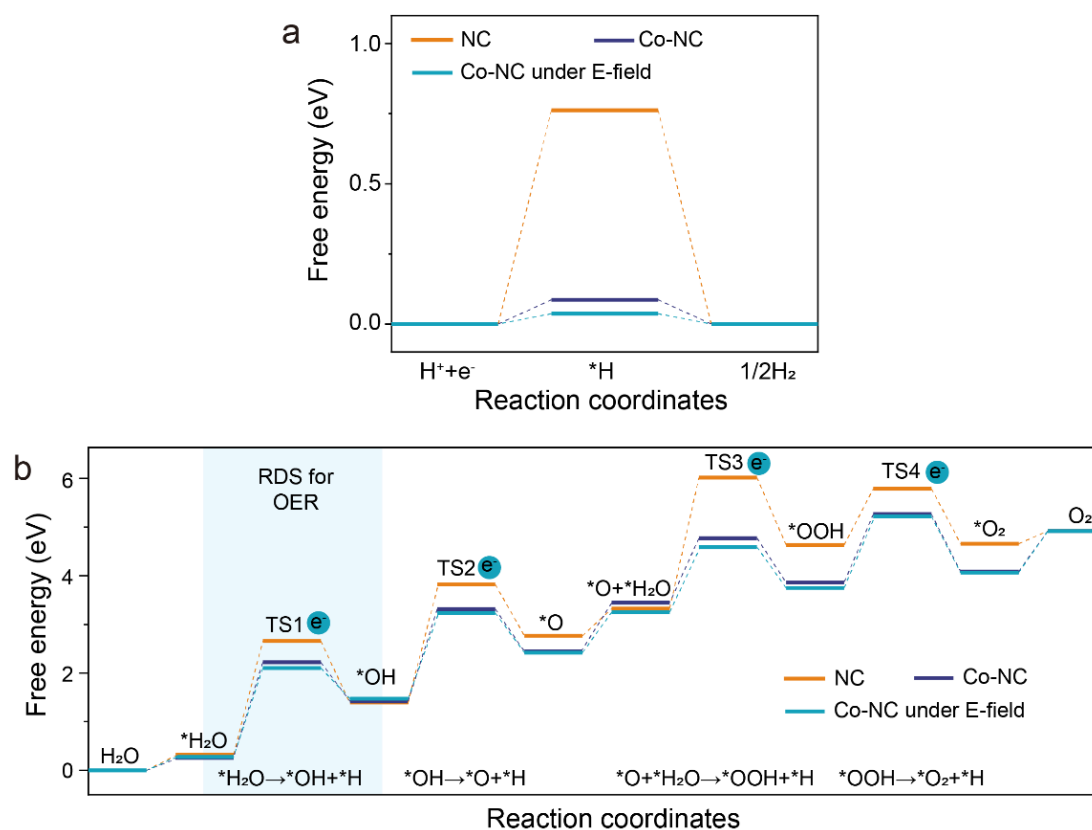


Figure 3-44 Calculated Gibbs free energy of (a) HER and (b) OER on Co-NC@Cu, with E-field perturbation included if mentioned.

In the DFT model described in Figure 3-44b, which involves the OER (oxygen evolution reaction) mechanism involving four concerted proton-electron transfer steps, we investigated the impact of the E-field on the Gibbs free energy of each reaction step in the OER. The reaction barriers and rate-determining steps (RDS) are crucial descriptors for assessing OER performance, and we modelled the intermediate adsorption structures for all potential sites in Figure 3-46. The free energy reaction pathway results indicate that Co-NC exhibits better oxidation reaction activity compared to NC alone. This is due to the lower free energy barrier of the OER process for Co-NC compared to NC from a thermodynamic perspective shown in Figure 3-44b. Furthermore, the transition state calculations reveal that the $*OH \rightarrow *O + *H$ step is considered the RDS (Figure 3-47). Although the change in Gibbs free energy of Co-NC during OER reaction steps under E-field perturbation is slight, it is noteworthy that the energy

barrier of RDS decreases from 1.96 eV under no E-field to 1.83 eV under $\times 10$ E-field perturbation, which favors the activity of the oxidation reaction. Therefore, the NC with Co single atoms was found to exhibit thermodynamically favourable OER under E-field. The calculations show perturbing E-fields play a crucial role in achieving ideal photocatalytic water splitting performance, particularly for the LSPR-active Co-NC@Cu core-shell.

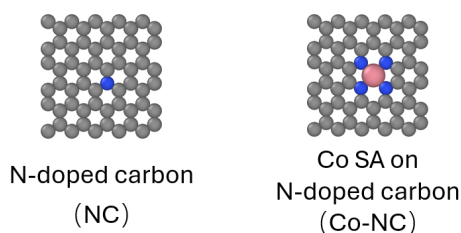


Figure 3-45 DFT modeling for NC and Co-NC. The colors of elements represent: Co, pink; N, blue; C, gray.

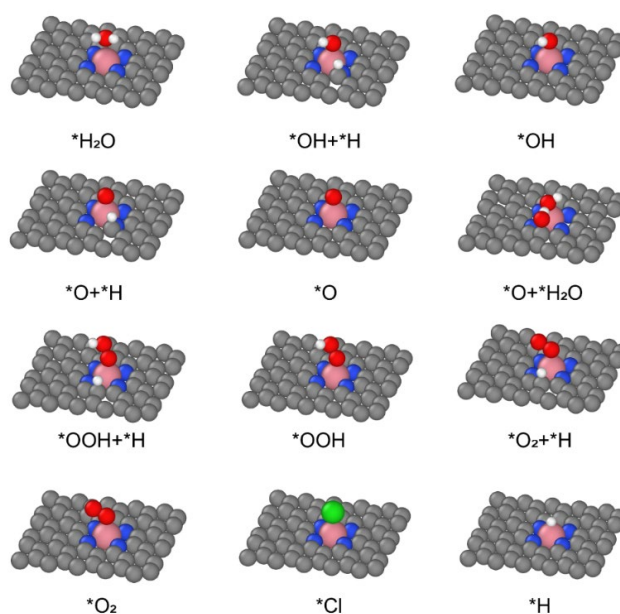


Figure 3-46 The optimized structure with intermediates adsorption for Co-NC@Cu. The colors of elements represent: Co, pink; N, blue; H, white; O, red; C, gray; Cl, green.

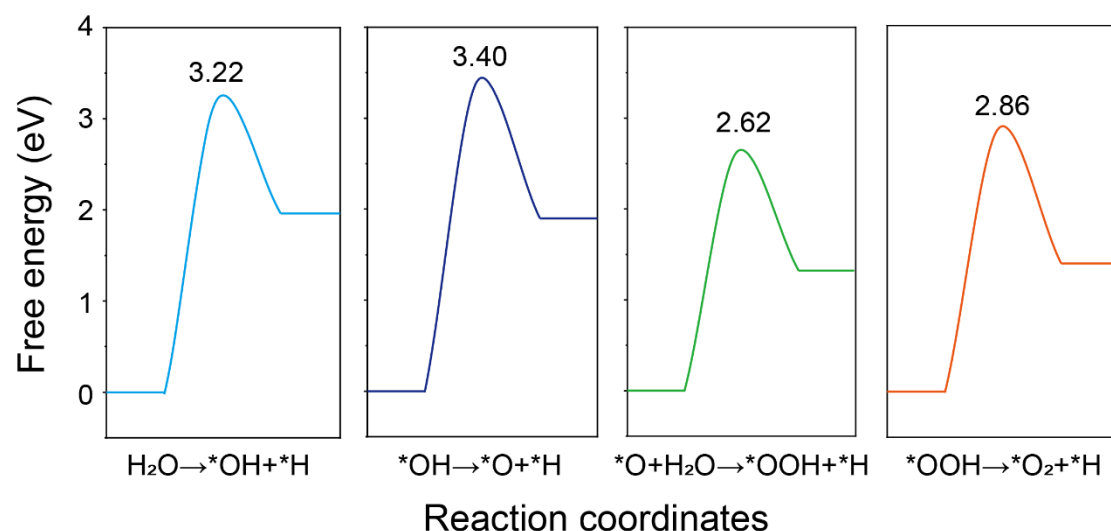


Figure 3-47 The transition-state (TS) energies are calculated for OER on Co-NC@Cu. The TS results show that the step of $*OH \rightarrow *O + *H$ was considered as the RDS.

3.3 Conclusion

In conclusion, we present a novel atomic Co dispersed on an NC@Cu core-shell structure catalyst for efficient photocatalytic seawater splitting to generate H_2 , without requiring sacrificial agents or noble metal co-catalysts. Comprehensive characterization confirms the successful synthesis of the core-shell structure with Co single atoms. Reaction environment analysis reveals that the focus-light-driven thermal effects and salt-ion-induced charge polarization contribute to enhancing photocatalytic performance. Further investigations demonstrate that this catalyst exhibits broad-spectrum light absorption ability, facilitating increased participation of photogenerated charge carriers in reactions. Besides, the LSPR effect originated from the core Cu NPs in Co-NC@Cu is not quenched by the embraced NC shell. Theoretical calculations support that the Co-NC single atoms provide ideal active sites for water splitting, with reduced energy barriers for both reduction and oxidation reactions under the local E-field perturbation induced by LSPR, further boosting photocatalytic activity. Consequently, Co-NC@Cu achieves high STH efficiency with long-term stability in seawater splitting for hydrogen production. This presents a promising strategy utilizing non-noble metal plasmonic NPs for

efficient solar-driven hydrogen generation from abundant saline resources. The insights from this study will be useful for developing other noble metal-free, sacrificial agent-free, single-atom based and plasmonic photocatalysts. Importantly, the strategies established here align closely with the overarching theme of photocatalyst design explored in this thesis, providing universal insights for constructing efficient and stable photocatalysts applicable across various solar-driven energy conversion processes.

Chapter 4 Machine learning aided design of single atom based monolayer Janus for photocatalytic CO₂ reduction

4. Introduction

The development of sustainable and clean electrochemical energy conversion technology is a key step in coping with the challenges of energy shortage and environmental pollution²⁶¹. The exploration and development of new electrocatalysts with excellent performance and low cost will promote the commercial application of these energy conversion technologies. With the development of theoretical computations and in situ/operando experiments, the structure, performance and reaction mechanism of single-atom catalysis (SAC) in electrochemistry have been unveiled in recent years²⁶². The development of SACs can make the rational use of metal resources and maximize the atom to promote the atom economy-utilization efficiency. The unique electronic structure and unsaturated coordination environment of the active center in SACs have been shown to improve the catalytic activity in various reactions²⁶³⁻²⁶⁵. The active sites and geometric structure of SACs show that the similarity with their homogeneous catalyst analogs makes them have great potential to improve selectivity²⁶⁶. In addition, the simple structure helps to accurately identify and characterize active sites. In turn, the advantage of SACs helps research fully understand the correlation between structure and catalytic performance and helps to achieve a reasonable catalyst design for the target reaction on the atomic scale. With the largest atom utilization efficiency, SAC are becoming a rising star in chemical science.

The strategy of combining Density functional theory (DFT) and machine learning methods pave the way to explore catalytic performance of single atom catalyst^{41, 161}. Besides, there is a lack of systematic design principles to provide a general descriptor of the relationship between the intrinsic characteristics of single atom catalyst and the prediction of catalytic activity, especially the complex effects of coordination environment, reaction mechanism, and interaction between polymetallic atoms on the redox reactions in energy

conversion, such as hydrogen evolution reaction, oxygen evolution reaction, CO₂ reduction reaction, and/or nitrogen reduction reaction. N element is well known in providing coordination environment for single atoms. Recently, elements S^[1,2], and P^[3] were also, respectively, used to coordinate single atoms; furthermore, N-S elements co-coordinated single atoms were reported. Note here, the economical, eco-friendly waste biomasses could be used to derive active carbon skeletons with containing N, S and/or P elements. There are C, H, O, N, S, P, Cl etc. elements in biomass.[6] Carbonisation of biomasses through pyrolysis is a facile way to remove H, O, Cl with producing activated carbon, while keeping desired amounts of N, S and/or P to provide the coordination environment for single atoms. However, the multi-element (N, S, and/or P) coordinated single atom catalysts have not yet been systematically screened out theoretically, not to mention experimentally.

Transition metal dichalcogenides (TMDs) monolayers are of two-dimensional (2D) X–M–X structures, with a hexagonally packed plane of transition metal atoms (Mo, W, etc.) sandwiched between two planes of chalcogen atoms (S, Se, or Te).²⁶⁷ This provides the opportunity to design two different anionic chalcogen atoms/layers bonded onto two sides of the middle transition metal layer. Recently, structural symmetry breaking of TMD monolayers to form "Janus TMDs", such as a sandwiched S-Mo-Se structure, showed potential application in electrocatalysis.²⁶⁸⁻²⁷¹ Unlike MoS₂, MoSe₂, or randomly alloyed MoSSe, the Janus MoSSe is highly asymmetric along the c-axis direction.²⁷² Such structural configuration endows its endogenous strain within the Janus monolayer, thus providing an additional degree of freedom to tune the electronic structures and carrier mobility. It is worth noting that the first-principles calculations have revealed that Janus TMDs with unconventional 1T' phase possessed superior properties such as high stability and ultra-high carrier mobility.²⁷³ Nevertheless, the aforementioned experimental studies of Janus TMDs are based on the 2H phase,^{268, 270, 272, 274-}
²⁷⁶ 1T' phase Janus TMDs are still in the theoretical stage and have not been synthesized experimentally.^{273, 277}

For the monolayer of Janus 2H-TMDs, taking 2H-MoSSe as an example, it can be prepared mainly through two different synthetic routes. One method is to first prepare the MoS₂ monolayer on a substrate by the chemical vapor deposition (CVD) method, and then the top S atoms of the MoS₂ monolayer are stripped off and replaced with other heteroatoms, such as H atoms. Subsequently, thermal selenization is performed to form a structurally stable Janus S-Mo-Se monolayer.²⁷² Another method is also to first grow the TMDs monolayer on a substrate using the CVD method, followed by direct sulfidation or selenization of the top layer atoms via CVD or pulsed laser deposition (PLD).^{272, 278} For obtained Janus MoSSe monolayers by the aforementioned CVD methods, Mo atoms are covalently bonded to underlying S/Se and top layer Se/S atoms. However, both CVD-based techniques require precise control of experimental conditions, such as H₂-plasma power for stripping off S atoms, selenization/sulfuration temperature, and atmospheric pressure, otherwise, it is easy to destroy the 2D structure or form random MoSSe alloy structures. More importantly, Janus MoSSe prepared by the above high-temperature CVD method is a 2H phase, due to the metastable phase (1T/1T') transition temperature of ~60 °C to ~150 °C for MoS₂ and MoSe₂.²⁷⁹⁻²⁸⁰ Accordingly, developing a simple, efficient, and easily scalable strategy for the synthesis of Janus MoSSe monolayer that is not limited to the 2H phase, and investigating their corresponding physicochemical properties for advanced applications will fill the important gap in the study of unconventional phase Janus TMDs.

The primary objective of this work is to accelerate the discovery and screening of functional single-atom based two-dimensional (2D) for energy conversion applications through high-throughput density functional theory (DFT) calculations and data-driven methodologies. This project aims to initiate two key steps. The first step will build upon an database of 20,000 single-atom based 2D Janus configurations. This dataset will include comprehensive information on the electronic properties, catalytic characteristics, and other relevant features of these materials. These expansive datasets will support the training of machine learning (ML)

models designed to accelerate the prediction and screening of effective single-atom based catalysts for energy conversion applications. The second step will focus on experimental synthesis and design for applications in CO₂RR. Based on the ML-aided computational predictions, the project will synthesize multiple candidate single-atom based catalysts and explore their practical applications in energy conversion.

4.1 Methods

Software

DFT has been widely used in describing and predict the structural, electronic, optical, and thermal properties of many fundamental and complex materials in chemical, physical, and material science in recent years. The premise basis of DFT is to consider electrons and atoms separately instead of a wave function. Here they use the Vienna Ab initio Simulation Package (VASP) (<https://www.vasp.at/documentation/>), which is a computer program for atomic scale materials modeling. VASP obtains an approximate solution by calculating the many-body Schrodinger equation and obtains the electronic structure and ground state energy of the system. In addition, VASP also has a hybrid functional that combines the Hartree-Fock method with DFT. VASP also provides Green's function method (GW quasiparticle and ACFDT-RPA) and many-body perturbation theory (second-order Møller-Plesset). In VASP, single-electron orbits, charge density, and local potential are all represented by plane wave basis sets. The interaction between electrons and ions is described using gauge conservation or super soft pseudopotential or projected enhanced wave methods. To determine the electronic ground state in the calculated system, VASP uses an efficient iterative matrix diagonalization method, such as the minimization method or the Davidson algorithm.

Vienna ab initio Simulation Package (VASP) code was performed in this work to describe the calculated models^{208, 281}. And the projector Augmented Wave (PAW) pseudopotentials²⁸² were used to describe the valence electrons and frozen cores, and the Perdew-Burke-

Ernzerhof (PBE) function of the generalized gradient approximation (GGA)²⁸³ was used to describe the exchange-correlation functional component of the Hamiltonian. The kinetic cutoff energy of the plane wave basis was set to 400 eV, and geometry convergence tolerance for energy and force was less than 10^{-4} eV and 0.02 eV/Å, respectively. In addition, the van der Waals (vdW) correction was corrected for the dispersion correction using Grimme's DFT-D3 method²⁸⁴ as implemented in VASP. When building models of different configurations, the constructed slab model for calculating adsorption energy was guaranteed to be larger than 15 Å in the c direction to avoid the interlayer interactions caused by periodicity. The Brillouin zone was sampled with $3 \times 3 \times 1$ Monkhorst-Pack grids for calculating free energy. Additionally, ab initio Molecular-Dynamics (AIMD) simulations of 4 ps with a time step of 1 fs at 300 K and 600 K within the canonical ensemble (NVT) with a N ose–Hoover heat bath scheme were employed to evaluate the dynamic stability of the structure²⁸⁵.

The work function Φ is defined by $\Phi = E_{\text{vac}} - E_{\text{F}}$, where E_{vac} is defined as the value of the converged electrostatic potential sufficiently far from the terminating surface of interest such that the restoring force on an emitted electron is negligible. E_{F} is the Fermi level (electrochemical potential of electrons) inside the material. Hydrogen adsorption energy ΔE_{ads} is defined as $\Delta E_{\text{ads}} = E_{\text{ads}} - E_{\text{slab}} - \frac{1}{2}E_{\text{H}_2}$, where E_{ads} and E_{slab} represent the total energy of the Au@MoSe₂, Au@MoOSe, or Au@MoSSe with and without adsorption hydrogen atoms. E_{H_2} is the total energy of the H₂ gas molecule. The ΔG_{H} is defined as $\Delta G_{\text{H}} = \Delta E_{\text{ads}} + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE_{ZPE} is the difference corresponding to the zero point energy between the adsorbed state and the gas phase, T is the temperature, $T\Delta S$ is the difference corresponding to the entropy ($T = 298.15$ K)²⁸⁶.

Workflow

A workflow for generating datasets of single-atoms based catalyst through high-throughput DFT computation has been established. This process consists of Python-based code and VASP software (licensed). For one material, structural information required for calculations can

be directly obtained from the open-access database or derived through space group information. The Python code automatically adjusts the parameters of input in VASP and job scripts based on selected elements, structures, and other information. Once all input files are prepared, the initial rough optimization of structures is performed. Following optimization, adsorption models for all possible intermediates are computed based on the type of redox reactions. Adsorption configurations are considered for all possible adsorption sites, and the code determines adsorption types and configurations based on structural symmetry. After job submission, and upon completion, the code checks for energy convergence. If convergence is achieved, the calculation stops; otherwise, it is marked as incomplete and further assessment is needed to determine structure stability or model validity. The completed calculation is then labeled and processed to extract descriptors using output analysis, resulting in the construction of a dataset.

All above steps, including automated calculations, automated data processing, and automated data collection, are fully implemented through Python code developed by their group. With the support of computational resources, this workflow supports the rapid construction of large number of materials datasets based on different applications. Finally, the data generated by this workflow will be used for training ML to expand results to more materials, thereby accelerating the discovery of single-atoms catalysts for energy conversion.

We have developed python-based code to realize from material optimization to adsorption site determination to thermodynamic correction to reaction path calculation. Therefore, this code will also apply to multi-element coordinated single atom catalyst for redox reactions. In addition, we also have experience in machine learning, including the prediction of crystal facet and facet junction through ANN²⁸⁷ and the analysis of the relationship between multi-factor synthesis conditions in material synthesis and the morphology of synthetic materials through SISO. With the support from NCI computing resources, we will accelerate the screening of candidates for high-performance single atom catalysts for future energy applications.

Data Preparation

The dataset used in this study was initially uploaded and processed from a tab-delimited file containing four columns: Molecule, Atom, Substrate, and Adsorption Energy. After loading the data, rows without adsorption energy values were removed. To enable numerical computation, categorical columns (Molecule, Atom, Substrate) were encoded using one-hot encoding. The resulting numerical features, along with the adsorption energy column, were standardized using the StandardScaler to ensure that all features contributed equally to the model's performance.

Neural Network Architecture

A deep neural network model was designed and implemented using TensorFlow/Keras. The architecture consists of three fully connected layers with the following specifications:

The first layer contains 512 neurons with ReLU activation and L2 regularization, followed by a dropout layer with a dropout rate of 0.4.

The second layer consists of 256 neurons with ReLU activation and L2 regularization, followed by another dropout layer with the same dropout rate.

The third layer contains 64 neurons with ReLU activation and L2 regularization.

The final output layer contains a single neuron to predict the adsorption energy.

The Adam optimizer was used for training with a learning rate of 0.0001, and the loss function was set to mean squared error (MSE).

Outlier Removal

To ensure robust model performance, an initial training was performed to identify and remove outliers. The process involved:

Training the neural network on the full dataset for 200 epochs with a batch size of 64.

Predicting adsorption energy values for the training set and calculating the absolute prediction errors.

Identifying outliers with prediction errors exceeding a predefined threshold (0.5). These outliers were removed from the dataset, resulting in a filtered dataset for subsequent training.

Cross-Validation

A 5-fold cross-validation was employed to evaluate model performance on the filtered dataset:

The dataset was split into five folds using KFold with shuffling and a random seed of 42.

For each fold, the model was trained on the training subset and validated on the held-out subset. Each fold was trained for 200 epochs with a batch size of 64.

Training and validation losses (MSE) were recorded for each epoch, and fold-wise mean squared error (MSE) and R² scores were computed to evaluate performance.

Final Model Training and Prediction

After cross-validation, the final model was retrained on the entire filtered dataset for 200 epochs. Predictions were made using the final model, and the mean squared error (MSE) and R² score were calculated to assess the overall performance.

Visualization and Results

Training and validation losses for each epoch during cross-validation were averaged across folds and plotted to illustrate model convergence. A final prediction vs. real value comparison was conducted to analyze the model's predictive accuracy.

Experimental procedures

Chemical

Hydrogen tetrachloroaurate(III) tetrahydrate ($\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$, 98%, Innochem), molybdenum(V) chloride (MoCl_5 , 99.6%, Alfa), oleylamine (OM, technical grade, 70%, Sigma-Aldrich), 1-octadecene (ODE, technical grade, 90%, Sigma-Aldrich), diphenyl diselenide (PDSe, 98%, Sigma-Aldrich), acetic acid (glacial, analytical grade, 99.7%), hexane (technical grade, $\geq 99\%$), and ethanol (AR) were used as received without further purification.

Synthesis of Au NPs

Dissolved 16 mg of $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ in 6 mL of OM in a 20 mL glass bottle by stirring. The sealed glass vial was then heated in an oil bath at 140 °C for 30 min. After cooling to room temperature, collected the product by centrifugation and then redispersed in 10 mL of OM and 10 mL of ODE for further use.

Colloidal synthesis of Au@MoSe₂ core@shell heterostructures

1.0 mL of ODE and 4.0 mL of the prepared Au NPs dispersion were placed in a 100 mL three-necked flask and degassed under vacuum at 120 °C with magnetically stirring for 30 min. Subsequently, the mixture with argon continued heating to 300 °C and rapidly injected 200 μL of MoCl_5 -OM solution (50 mM) and 200 μL of PDSe-OM solution (50 mM) into the above mixture for 2 min of reaction. After cooling to room temperature, the Au@MoSe₂ core@shell heterostructure was obtained by centrifugation.

Synthesis of Au@MoOSe core@shell heterostructures

The Au@MoOSe core@shell heterostructures were obtained by the electrochemical oxidation method. Typically, the anodic oxidation of Au@MoSe₂ core@shell heterostructures was conducted by using cyclic voltammetry with a scan rate of 10 mV/s for 10 cycles in the range of +0.273 - +1.273 V vs. RHE. in 0.5 M H_2SO_4 electrolyte.

Synthesis of Pt SA on 1T'-MoOSe@Au

The synthesis of Pt single-atom catalysts on 1T'-MoOSe@Au was conducted in a sealed 50 mL reaction vessel. The precursor solution was prepared by dissolving 50 μ L of 0.1 M H₂PtCl₆·6H₂O in a mixed solvent of 4.5 mL deionized water and 0.45 mL ethylene glycol (EG), followed by stirring at 600 rpm for 5 min (denoted as Solution A).

In parallel, 50 mg of 1T'-MoOSe@Au was dispersed in 15 mL of EG and stirred at 600 rpm for 1 h in the reaction vessel. Subsequently, 5 mL of Solution A was added to the reaction vessel, resulting in a total reaction volume of 20 mL. Immediately after addition, the vessel was wrapped with aluminum foil to prevent light exposure. The system was degassed under an Ar atmosphere for 20 min, with Ar gas flowing below the liquid surface for inlet and above the surface for outlet, while maintaining continuous stirring at 600 rpm. After degassing, the reaction proceeded in the dark under continuous stirring for 24 h.

The resultant mixture was centrifuged at 6000 rpm for 10 min, and the precipitate was washed three times with ethanol and deionized water. The washed sample was dried in a vacuum oven at 70°C to obtain the final Pt SA on 1T'-MoOSe@Au powder.

Synthesis of Pt SA on 2H-MoOSe@Au

The conversion of Pt SA on 1T'-MoOSe@Au to Pt SA on 2H-MoOSe@Au was achieved via annealing. The Pt SA on 1T'-MoOSe@Au powder was subjected to calcination at 400°C for 2 h in an Ar atmosphere using a tube furnace, with a heating rate of 5°C/min.

4.2 Results and Discussion

4.2.1 ML and DFT aided design

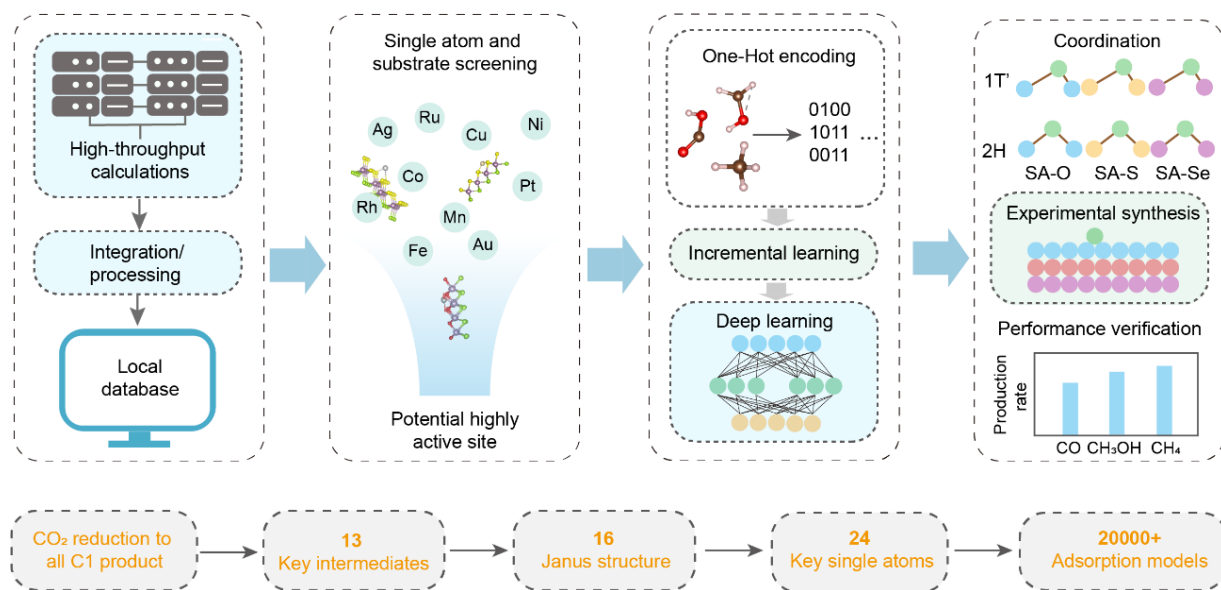


Figure 4-1 A comprehensive workflow for the expansion and development of single-atom based 2D materials for catalytic applications in energy conversion. The process begins with high-throughput DFT calculations, which generate a local database of atomic configurations and properties. This database serves as a foundation for single-atom and substrate screening, focusing on transition metals (e.g., Ag, Co, Fe, Mn, etc.) anchored on 2D materials like TMD Janus structures, MXenes, oxides, and carbon-based supports. The data is then processed using ML techniques, including one-hot encoding, incremental learning, and deep learning, to accelerate predictions of catalytic activity. Promising configurations undergo further coordination analysis (e.g., SA-O, SA-S) and experimental synthesis for performance verification, targeting reactions like HER, CO₂RR, and NRR, etc. The workflow outlines steps for dataset expansion to include 13 key intermediates, 16 Janus structures, 24 single-atom species, and over 20,000 adsorption models, enabling efficient catalyst discovery for sustainable energy applications.

Figure 4-1 shows a comprehensive and innovative workflow for the systematic expansion of single-atom-based 2D TMD materials and the development of machine learning (ML) models aimed at accelerating the discovery of efficient catalysts for energy conversion applications, building on the developed single-atom-based Janus-TMD material datasets. The

workflow begins with high-throughput DFT calculations, which are the basis for generating a local database of atomic configurations. This database provides important information including the electronic structure, thermodynamic stability, and catalytic properties of single atom-based systems. The current data set consists of more than 20,000 configurations representing a wide variety of transition metal atoms (Ag, Co, Mn, Fe, Ru, Ni, etc.) fixed on a variety of 2D material substrates such as Janus-TMD structures. These calculations serve as the basis for identifying the most promising candidates for further research.

The scalability of this database is an important highlight. By systematically expanding the scope of application to include additional configurations, intermediates, and substrates, the database will target hundreds of thousands of entries in the near future, which will ensure a comprehensive search of the design space and allow the identification of single atomic catalysts tailored to specific energy conversion reactions. The integration of ML technology into this workflow represents a paradigm shift in catalyst discovery. By adopting one-hot encoding and incremental learning of molecular structures and adopting advanced deep learning models, the project achieves significant computational efficiency and prediction accuracy. Compared to the traditional DFT approach, the ML extended workflow provides an amazing speed boost. This ML-driven approach not only accelerates the screening process, but also facilitates the discovery of patterns and insights that may not be apparent in purely theoretical calculations. The model can predict adsorption energy, reaction intermediates, and key catalytic properties with minimal computational overhead, enabling rapid evaluation of thousands of candidate configurations.

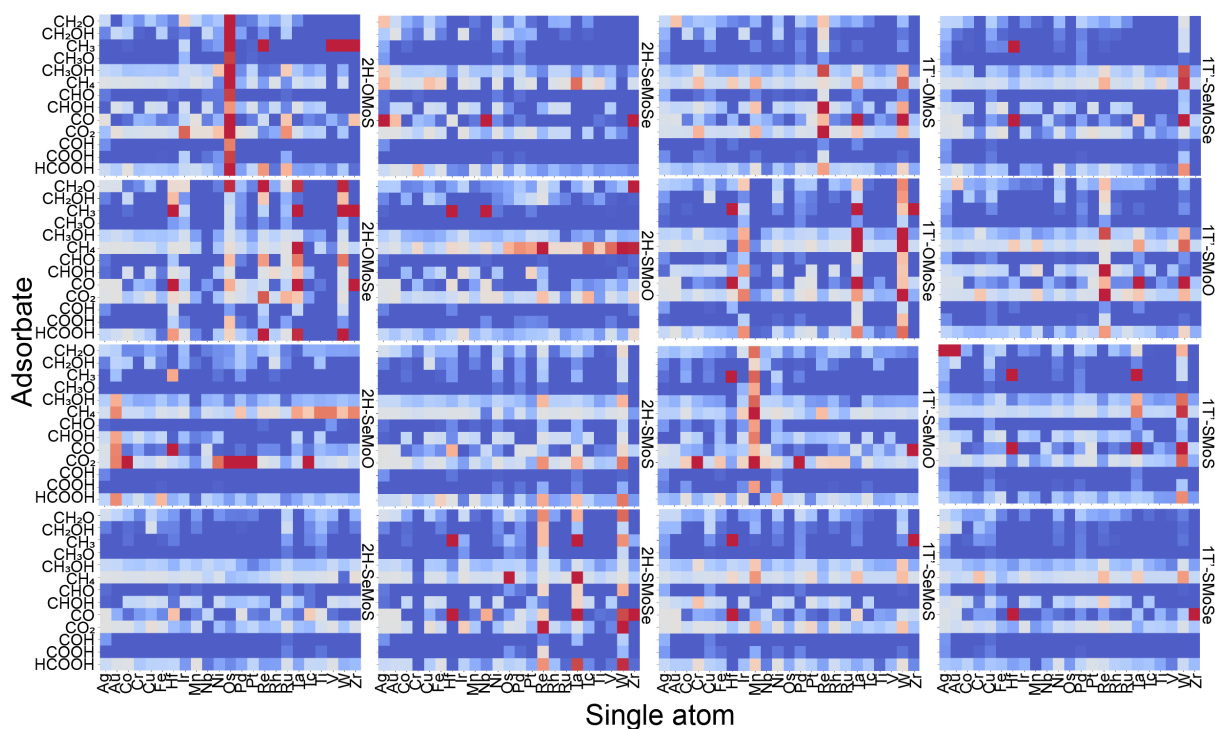


Figure 4-2 Adsorption energy prediction and screening.

Following ML prediction, the workflow focuses on identifying single atom and substrate combinations with the highest catalytic potential. Key indicators such as adsorption energy, selectivity, and activation barriers are used to prioritize candidates. These promising arrangements are subjected to detailed configuration analysis including coordination environments such as SA-O, SA-S, and SA-Se. The diversity of these coordination structures allows fine-tuning of catalytic properties, increasing both selectivity and efficiency of the target reaction. Workflows are designed to iteratively extend and improve both the dataset and the ML model. For example, the current database contains adsorption models of 13 major reaction intermediates and 16 Janus structures, and there are plans to significantly increase these numbers. In addition, the incremental learning framework enables new data to be seamlessly integrated, further enhancing the predictive power of ML models. The repetitive nature of this workflow allows for continuous purification of the catalyst. By incorporating the experimental results into the ML model, we create a feedback loop that bridges the theoretical and practical aspects of catalyst development. This integration of DFT, ML, and experimental verification

represents a holistic approach to catalyst discovery and ensures fast, scalable and accurate identification of materials for sustainable energy conversion.

Figure 4-2 provides a comprehensive visualization of the adsorption energy of a single atom catalyst supported on a Janus-TMD substrate for CO₂ reduction to C1 product. The vertical axis represents the major reaction intermediates (e.g. CHO, CHOOH, CO) and the horizontal axis represents single atomic species (e.g., Ag, Co, Mn) tested over different Janus structures. Each subplot corresponds to a specific Janus substrate that allows a detailed evaluation of the substrate's effect on adsorption behaviour. The heat map effectively captures the adsorption tendency, the blue area indicates that the adsorption energy is more negative, and the red area indicates that the adsorption energy is more positive. These changes are important for catalyst performance because adsorption energy is required to balance adsorption and desorption in the catalytic reaction. Excessively strong adsorption can interfere with the release of intermediates and cause multi- electron / hole reactions, and excessively weak adsorption can limit the stability of intermediates, so that produce the C1 product with lower electron / hole transfer, like CO and CH₄. The results show that the selection of Janus substrates, types of single atoms significantly affect the adsorption energy, and that certain substrates with single atom site exhibit stronger interactions with certain intermediates. In addition, interactions and intermediates between certain single atoms, such as Re, Ir, W, and Ta, exhibit more complex behaviours, emphasizing the role of single atom coordination in the regulation of catalytic properties. Intermediate adsorbents show a clear adsorption pattern compared to other adsorbents such as CO₂, CH₄, HCOOH, and CO. These results suggest that specific combinations of single atoms and substrates are suitable for specific catalytic steps and have moderate adsorption energies of key intermediates that show promising candidates for catalytic activity.

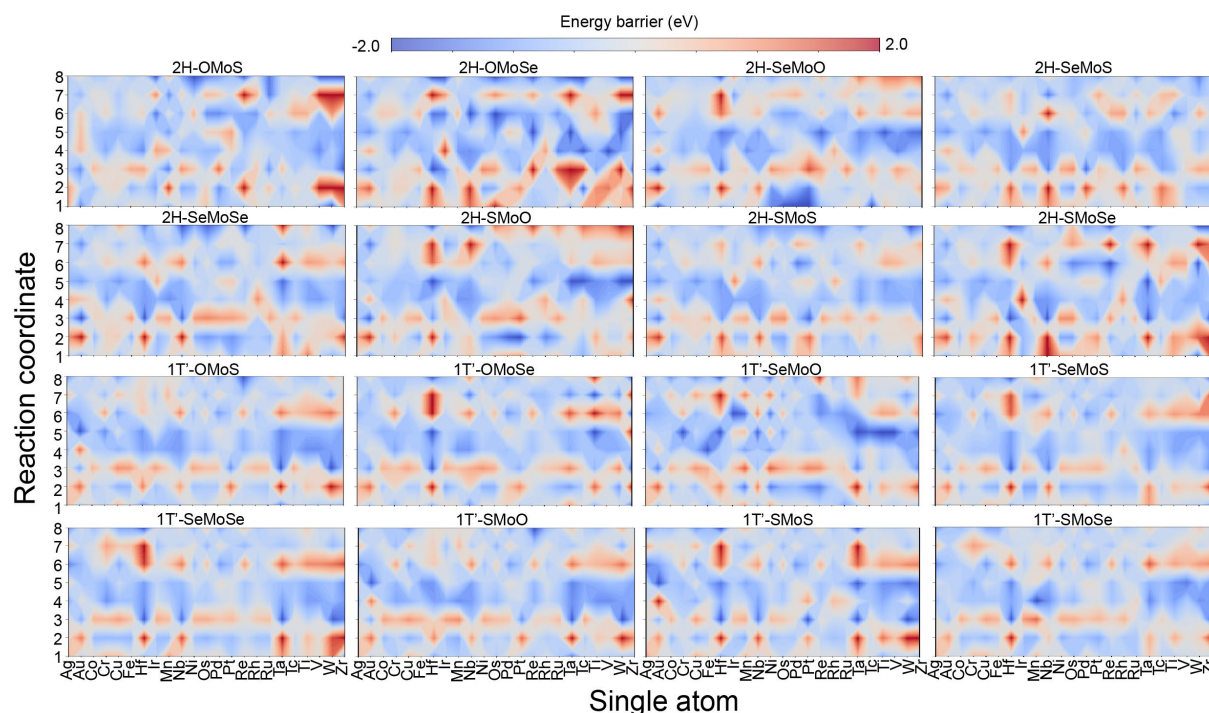


Figure 4-3 Reaction pathways prediction and screening. $\text{CO}_2^* + \text{e}^- + \text{H}^+ \rightarrow \text{COOH}^*$ (1); $\text{COOH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CO}^* + \text{H}_2\text{O}$ (2); $\text{CO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CHO}^*$ (3); $\text{CHO}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_2\text{O}^*$ (4); $\text{CH}_2\text{O}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3\text{O}^*$ (5); $\text{CH}_3\text{O}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3\text{OH}^*$ (6); $\text{CH}_3\text{OH}^* + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ (7); $\text{CH}_3 + \text{e}^- + \text{H}^+ \rightarrow \text{CH}_4$ (8).

The reaction pathways in Figure 4-3 highlights interactions between substrate phases, type of single atom, and chalcogen substitution in TMDs, and provides a comprehensive overview of reaction pathways and energy barriers for various single atom configurations across different reaction coordinates. Replacing selenium with sulfur and oxygen can further increase catalytic activity in certain systems, possibly the conductivity and electrodynamics introduced by these substitutions. In addition, single atom identity greatly affects the distribution of energy barriers on certain electron/hole transfer steps, noble metals single atoms show lower barriers in some cases, and certain transition metals (such as Hf and Ta) single atom have higher energy barrier. Moreover, the system demonstrates that most of the catalysts exhibit reaction energy barriers at steps 2, 3, and 6, providing predictions and guidance for further optimization to lower the reaction energy barriers. The results the importance of adjusting the material phase and selecting the appropriate single atom species to achieve the aimed activity.

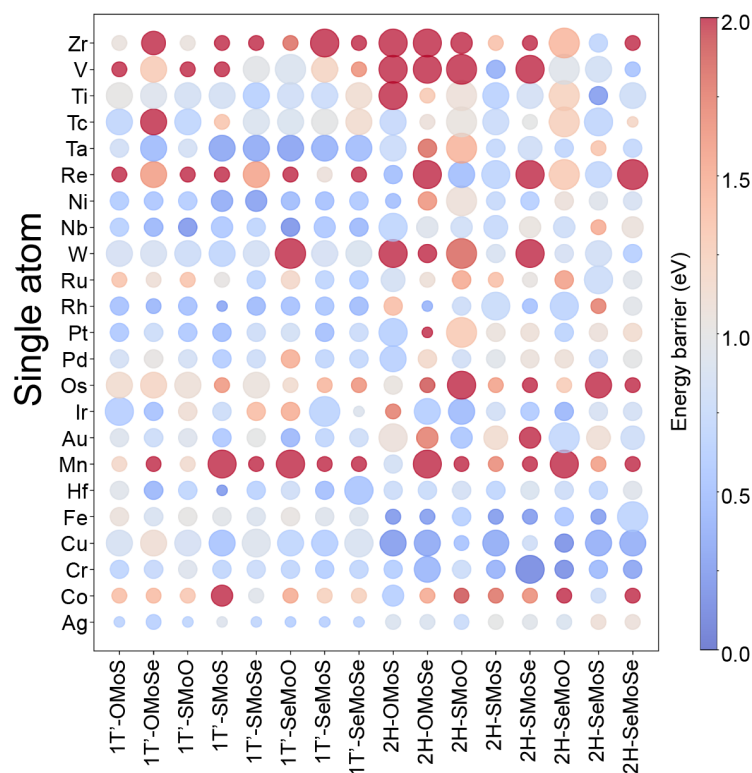


Figure 4-4 Bubble map for reaction energy barriers.

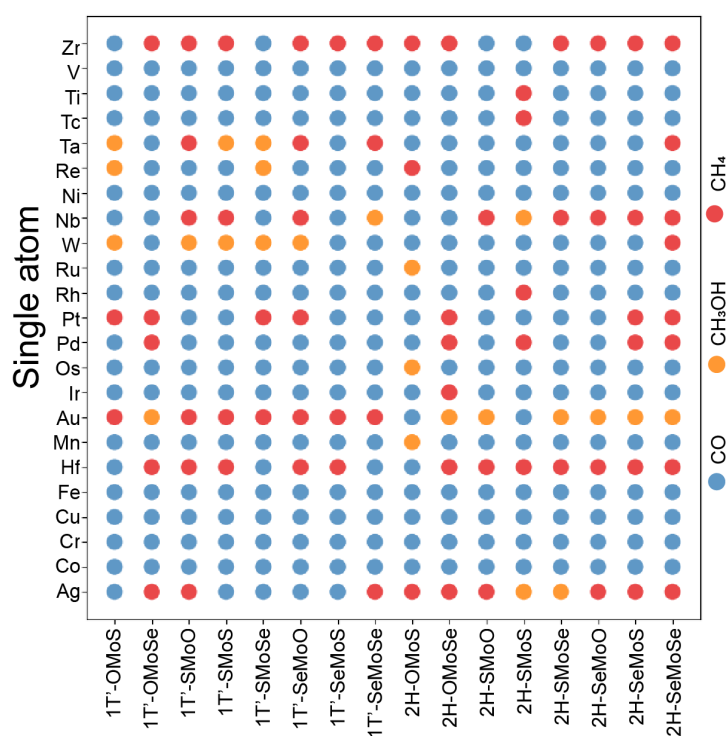


Figure 4-5 Production selectivity predicted by ML.

Figure 4-4 represents the energy barrier of different single atom/substrate combinations, bubble size reflects the degree of electron-proton transfer during the reaction, and bubble colour shows the size of the energy barrier. Noble metals such as Pt, Pd and Au tend to exhibit lower energy barriers across most substrates, highlighting their catalytic efficiency. On the other hand, transition metals such as hf and ta generally exhibit high energy barriers, indicating that the catalytic activity is limited under similar conditions. Changes in the energy barrier distribution underscore the importance of material selection affecting kinetics and efficiency. Figure 4-5 focuses on product selectivity and predicts the possibility of forming CH₄, CH₃OH, or CO under certain catalytic conditions. Selectivity is strongly influenced by the identity of the substrate and single atom, and certain single atom/substrate combinations prefer different products. For example, a single atom of Au tends to prefer CH₄ production, while other atoms such as Fe, Co, Ni, and Cu tend to produce CO. A more uniform distribution of CO as a product suggests that CO formation is a common intermediate or primary product for a wide range of materials.

The combined analysis reveals a clear relationship between minimizing the energy barrier and achieving product selectivity. Specific single atom and substrate combinations can be adjusted to optimize catalyst efficiency and the formation of the desired product. These findings provide important guidance for the design of selective single-atom catalysts and allow targeted coordination of reaction results through material and structural modifications. The visualization also highlights the potential for future use of high-throughput screening and ML to predict and refine selectivity for specific reactions.

4.2.2 Experimental verification

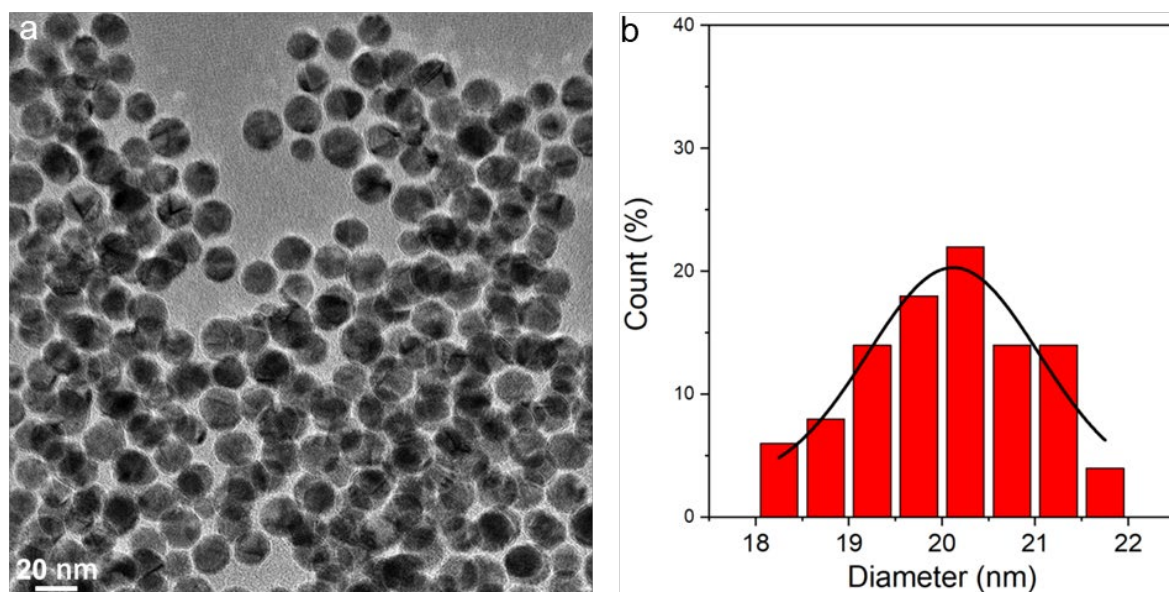


Figure 4-6 (a) TEM image of Au@MoSe₂ core@shell heterostructures. (b) Diameter size measured from (a), the mean size is ~20 nm.

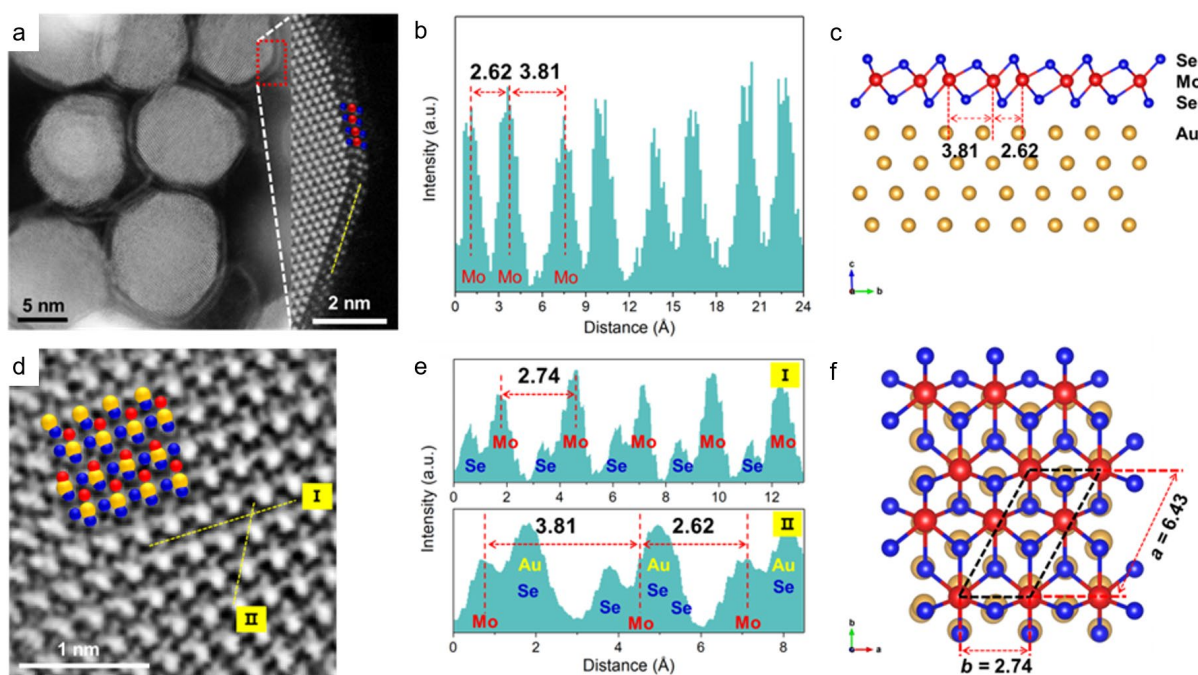


Figure 4-7 Synthesis of 1T'-MoSe₂ monolayers encapsulated on Au NPs. (a) Low-magnification and enlarged HAADF-STEM images obtained from the edge part of Au@MoSe₂. (b) Intensity profile extracted from the yellow line in (a). (c) Side view of the crystal structure of

1T'-MoSe₂ monolayer bonded to Au according to (a). (d) HAADF-STEM image of an Au@MoSe₂ acquired from the central part. (e) Intensity profiles extracted from the yellow lines of (I) and (II) in (d). (f) Top view of the crystal structure of 1T'-MoSe₂ monolayer bonded to Au according to (d).

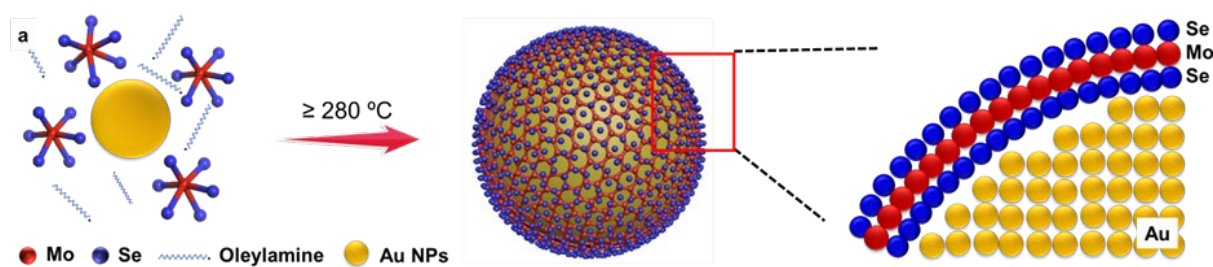


Figure 4-8 Proposed preparation scheme of synthesis of 1T'-MoSe₂ monolayers encapsulated on Au NPs.

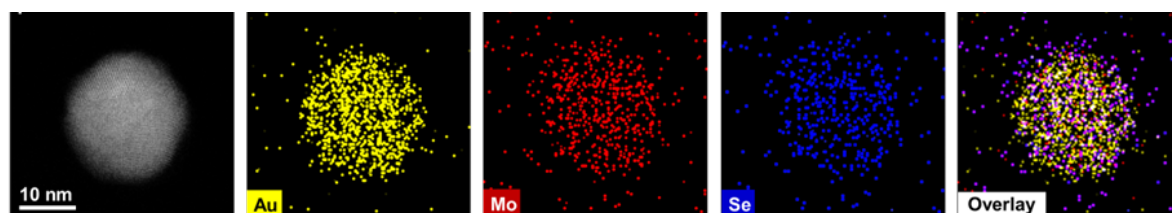


Figure 4-9 HAADF-STEM image and corresponding EDS elemental mappings of an individual Au@MoSe₂.

The MoSe₂ monolayers were initially synthesized on the surface of Au nanoparticles (NPs) to form core@shell heterostructures with an approximate size of 20 nm (Figure 4-6 and Figure 4-7a), employing a straightforward colloidal chemical synthesis method. In brief, molybdenum chloride (MoCl₅) and diphenyl diselenide dissolved in an oleylamine solution were injected into a hot mixture containing oleylamine, 1-octadecene, and Au NPs at 280 °C under an argon atmosphere (Figure 4-8). The as-grown MoSe₂ exhibits a highly efficient formation of uniform Se-Mo-Se monolayers on the surface of Au NPs, as depicted in Figure 4-7a-f. Additionally, the

thickness of the surface-grown MoSe₂ is measured to be ~0.8 nm. This observation confirms both the stability of Au NPs under mild synthesis conditions and that no diffusion of Au atoms occurred into the crystal structure of the surface-coated MoSe₂ monolayers (Figure 4-7a). STEM-energy-dispersive X-ray spectroscopy (EDS) line scanning spectra taken from HAADF-STEM image further confirm the core@shell structure of obtained Au@MoSe₂ heterostructure, with a molar ratio between Mo and Se estimated to be ~1:2 shown in Figure 4-9 and 4-10. The intensity profile (Figure 4-7b) extracted from the yellow line in Figure 4-7s reveals alternating Mo-Mo distances of ~2.62 and 3.81 Å, providing unequivocal evidence for the presence of a MoSe₂ monolayer with an unconventional 1T' phase.

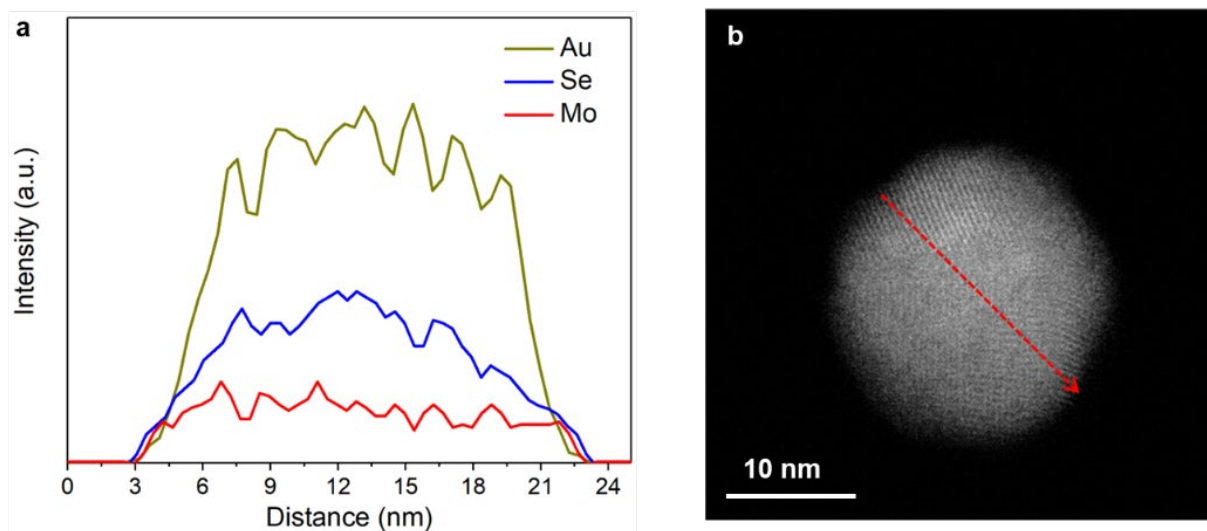


Figure 4-10 (a) STEM-EDS line scanning profiles of an individual Au@MoSe₂ core@shell heterostructure along the red arrow of (b).

Moreover, the atomic-resolution HAADF-STEM image (Figure 4-7d) acquired from the central region of the Au@MoSe₂ heterostructure is employed to further investigate the binding mode between the MoSe₂ monolayer and Au. The intensity profiles (Figure 4-7e) extracted from the yellow lines in Figure 4-7d reveal that the surface coated 1T'-MoSe₂ monolayer exhibits three distinct Mo-Mo distances of 2.74, 3.81, and 2.62 Å, suggesting structural parameters of $a = 6.43$ Å ($3.81 + 2.62$ Å) and $b = 2.74$ Å. Accordingly, a corresponding crystal

structure model is analyzed and fitted as shown in Figure 4-7f. The successful determination of the crystal structure for Au@MoSe₂ heterostructure provides a reliable framework for constructing *fcc*-metals@1T'-TMDs heterostructures. It is worth noting that lattice parameters measured for the 1T'-phase MoSe₂ monolayer are slightly smaller than theoretical values ($a = 6.87 \text{ \AA}$, $b = 3.27 \text{ \AA}$),²⁷⁹ possibly due to significant strains induced by bent lattices of MoSe₂. The STEM-EDS elemental mappings (Figure 4-9) support the uniform growth of the 1T'-MoSe₂ monolayer on the Au NP surface.

The term "exfoliation energy" encompasses two distinct definitions. In one context, it refers to the energy required to peel off the top layer from the surface of a crystalline block.²⁸⁸ Alternatively, in a different context, it represents the interlayer binding energy of layered materials, *i.e.*, the energy needed to separate layers from a bulk material.²⁸⁹ Here, the defined exfoliation energy serves as a metric for assessing the difficulty of exfoliating monolayer 1T'-MoSe₂ from Au@MoSe₂ and Au@bilayer MoSe₂.²⁹⁰ As anticipated, the calculated exfoliation energy tends to converge with increasing interfacial distance (Figure 4-11a). The results reveal that detaching a monolayer of 1T'-MoSe₂ from Au@MoSe₂ requires significantly more energy compared to peeling a monolayer from Au@bilayer MoSe₂. Furthermore, the strong interaction force between monolayer 1T'-MoSe₂ and the Au substrate, along with the interlayer weak interaction, is elucidated through potential energy wells (Figure 4-11b), representing the potential wells felt by Se atoms along the *zz* direction (due to atomic displacement). Specifically, one Se atom on Au@MoSe₂ but closest to the Au substrate is selected for movement, considering Se atoms in the unit cell are equivalent due to structural symmetry. The potential well of Au@MoSe₂ is asymmetric concerning positive and negative atomic displacements, indicating the asymmetry in the ability of atoms to vibrate around their equilibrium positions and a nonlinear dependence of ionic forces on displacement amplitudes.²⁹¹⁻²⁹² The findings demonstrate that when Se atoms in monolayer 1T'-MoSe₂ move negatively along the *zz* direction, the potential well deviates most from parabolic behavior, and the variation in potential

energy increases with atomic displacement, thereby confirming the strong interaction between Se atoms of monolayer 1T'-MoSe₂ and the Au substrate. In contrast, when Se atoms of bilayer 1T'-MoSe₂ move along the zz direction, the potential well is harmonic, and the variation in potential energy is weak, attributed to the weak interlayer van der Waals interaction.

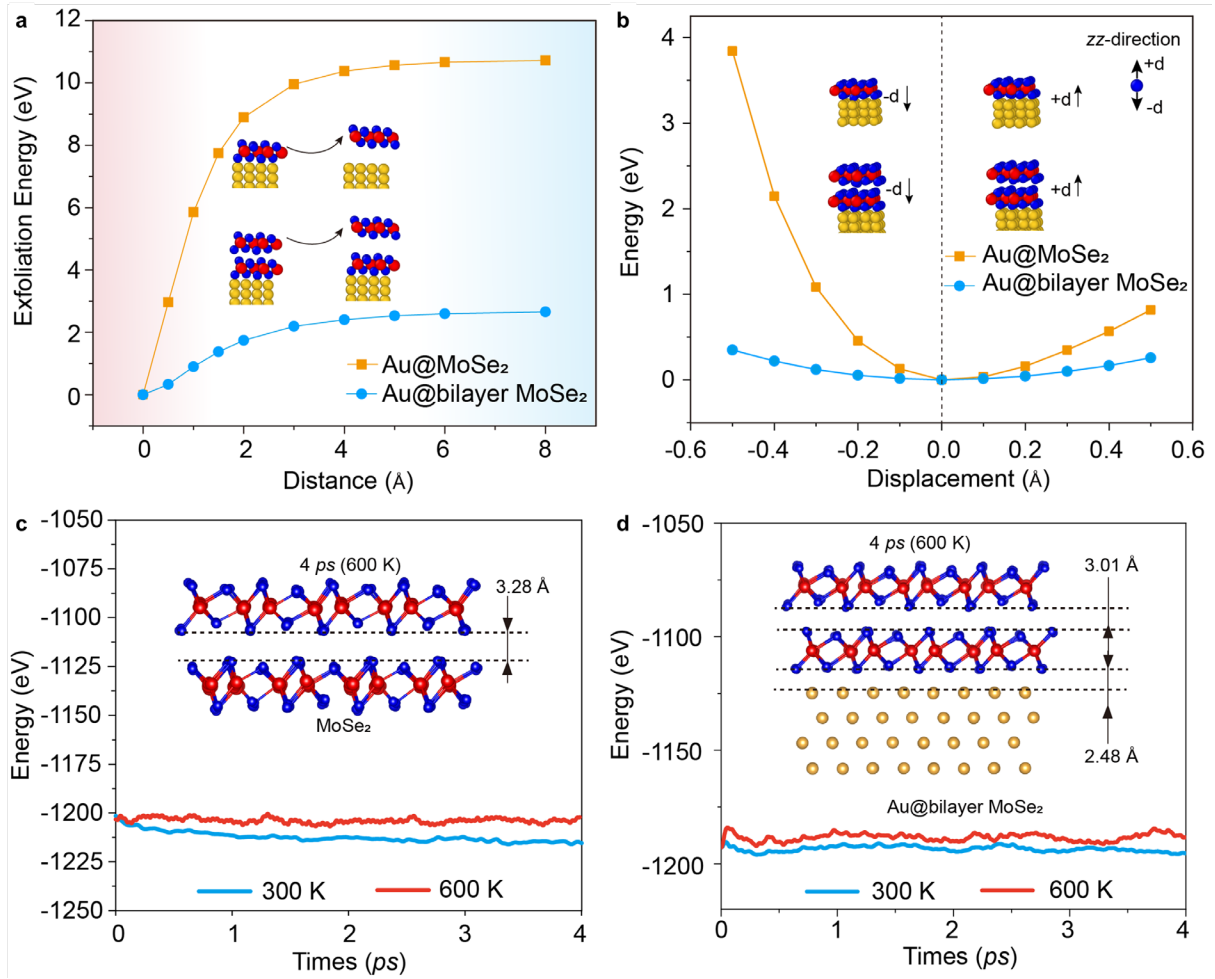


Figure 4-11 Synthesis mechanism investigation of monolayer 1T'-MoSe₂ growth on Au. (a) Exfoliation energies of monolayer 1T'-MoSe₂ from Au@MoSe₂ and Au@bilayer MoSe₂. (b) Potential energy change concerning displacement of the Se atom along the zz direction. AIMD simulations of the total energy for (c) bilayer 1T'-MoSe₂ and (d) Au@bilayer 1T'-MoSe₂ structure at 300 and 600 K, respectively. Internal diagram of the atomic structures for (c) bilayer

1T'-MoSe₂ and (d) Au@bilayer 1T'-MoSe₂ after an AIMD simulation period of 4 ps at 600 K, respectively.

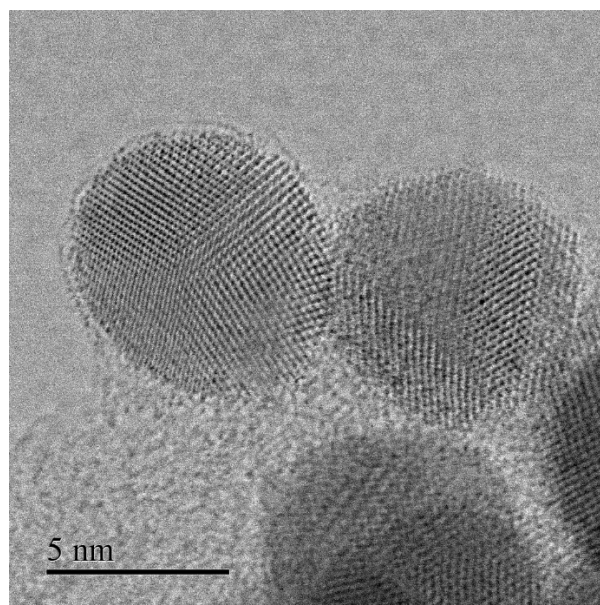


Figure 4-12 HRTEM image Au@MoSe₂ core@shell heterostructures after direct one-step oxidation.

Ab initio molecular dynamics (AIMD) simulations were further performed to investigate the synthesis mechanism and stability of monolayer 1T'-MoSe₂ on Au NP at temperatures of 300 K and 600 K (annealing temperature) with appropriate equilibration time. Figure 4-11c,d shows the side view of the structure evolution of bilayer 1T'-MoSe₂ and bilayer 1T'-MoSe₂ on Au substrate at 600 K, respectively, with a total time of 4 ps. The results indicate the distance between the Au substrate and 1T'-MoSe₂ is significantly smaller than the interlayer distance of the bilayer 1T'-MoSe₂, indicating the stronger interaction between Au substrate and 1T'-MoSe₂ compared to the weaker van der Waals (vdW) interaction of 1T'-MoSe₂ interlayers. The above results showed that the Au substrate immobilizes the 1T'-MoSe₂ monolayer and facilitates the interlayer separation of the 1T'-MoSe₂. Consequently, theoretical calculations align with experimental results, indicating that metastable 1T'-MoSe₂ monolayers can be

reliably coated onto the surface of Au NPs using our developed colloidal chemical synthesis method.

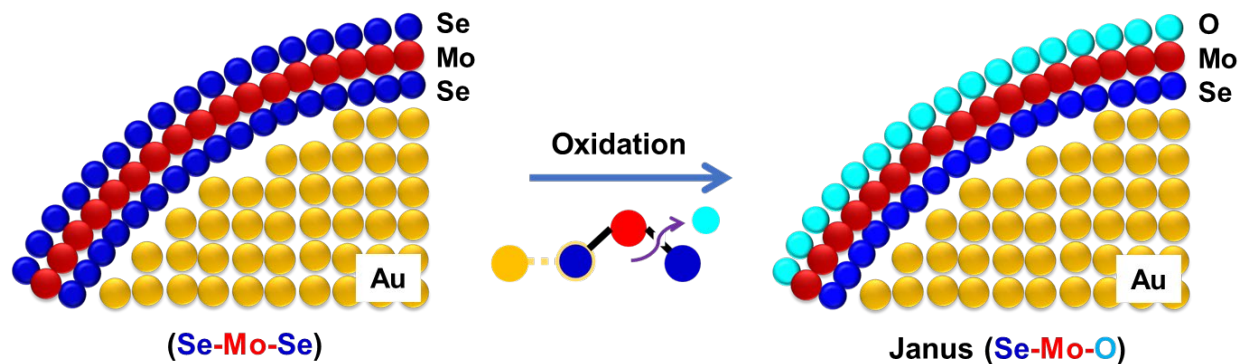


Figure 4-13 Proposed preparation scheme of synthesis of Janus 1T'-MoOSe monolayers encapsulated on Au NPs.

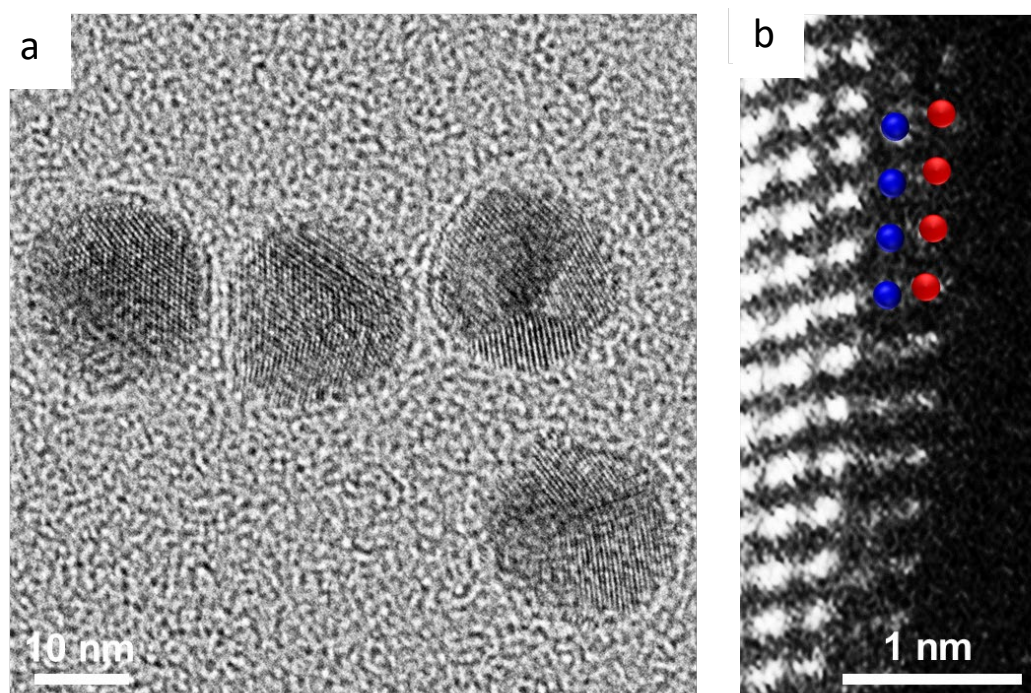


Figure 4-14 (a) Low-magnification TEM images and (b) HAADF-STEM images obtained from the edge part of Au@MoOSe.

In the subsequent synthesis of Janus Au@MoOSe, we initially attempted direct one-step oxidation using the colloid chemical synthesis method. However, it is observed that this

approach led to the destruction of the monolayer structure of MoSe₂ shells, as depicted in Figure 4-12. Previous studies have demonstrated the substitution of X (X = S or Se) atoms with O atoms on the MoX₂ basal plane,²⁹³⁻²⁹⁵ indicating the feasibility of fabricating Janus MoSSe structures through the design of intermediate Janus MoOSe structures. In this design, electrochemical oxidation was employed to replace the outer Se atoms of the MoSe₂ monolayer with O atoms (Figure 4-13), while ensuring the stability of the inner Se atoms due to Au NP protection. Low-magnification TEM image (Figure 4-14a) and HAADF-STEM image (Figure 4-14b) reveal the surface-coated MoOSe layer thickness < 1 nm after oxidation, confirming retention of monolayer structure.

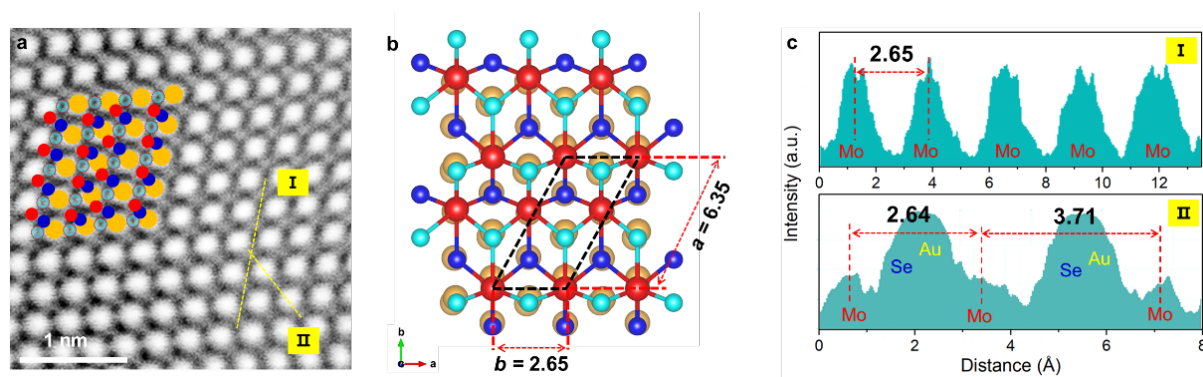


Figure 4-15 (a) HAADF-STEM image acquired from the central part of Au@MoOSe. (b) Corresponding crystal structure of Au@MoOSe, in which yellow balls represent Au atoms, red balls represent Mo atoms, blue balls represent Se atoms, and water blue balls represent O atoms. (c) Intensity profiles extracted from the yellow lines of (I) and (II) in (a).

Binding mode analysis between MoOSe and Au along with the corresponding crystal structure is also conducted (Figure 4-15a, b). The intensity profiles (Figure 4-15c) present three different Mo–Mo distances of 2.65, 2.64, and 3.71 Å, suggesting the structural parameters $a = 6.35$ Å ($2.64 + 3.71$ Å) and $b = 2.65$ Å for surface coated MoOSe monolayers. Additionally, the STEM-EDS elemental mappings presented in Figure 4-16 confirm the homogeneous distribution of Au, Mo, Se, and O elements throughout the Au@MoOSe heterostructure.

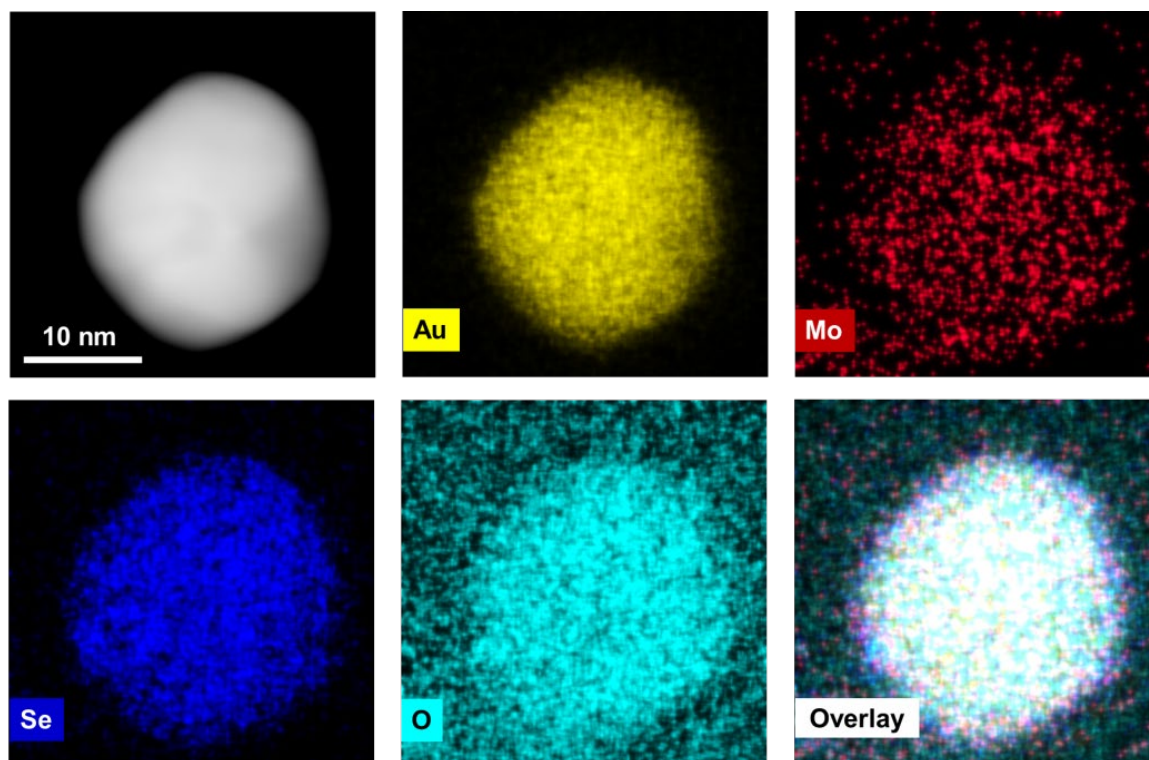


Figure 4-16 HAADF-STEM image and corresponding EDS elemental mappings of an individual Au@MoOSe.

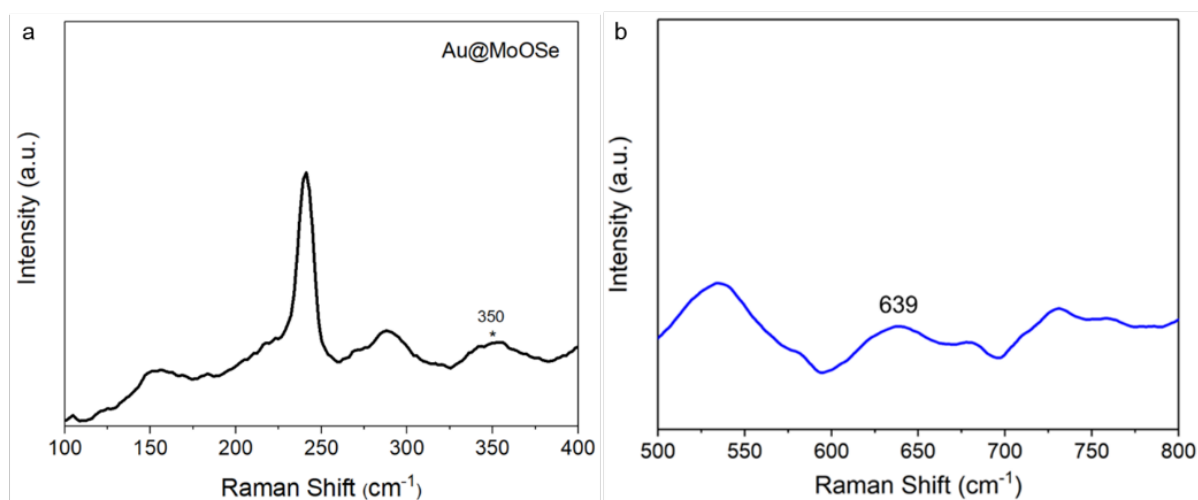


Figure 4-17 Raman spectrum of the Au@1T'-MoOSe in (a) low and (b) high frequency.

We successfully synthesized Au@MoS₂ with a high 1T'-phase purity of MoS₂. In contrast to the Au@MoSe₂ product, a new peak at 350 cm⁻¹ appears in the Raman spectrum of

Au@MoOSe (Figure 4-17a) due to in-plane opposite vibrations between Se and Mo-O pairs.²⁹⁶ Additionally, a relatively high-frequency peak at 639 cm^{-1} arising from stretching of the Mo-O bond is observed as well (Figure 4-17b),²⁹⁶ indicating successful preparation of Janus MoOSe monolayers derived from MoSe₂ monolayers. After electrochemical oxidation, the Mo core level region exhibits four peaks (Figure 4-18a), corresponding to MoO₂ (232.8 and 229.5 eV) and MoSe₂ (231.8 and 228.4 eV), indicating both Mo-O and Mo-Se bonds exist in Au@MoOSe samples. The up-shifts observed in the Mo 3d XPS spectra of Au@MoOSe samples suggest alterations in the chemical environment and electronic structures around the Mo atoms compared to Au@MoSe₂ counterparts. Furthermore, the O 1s XPS peak at a binding energy of 530.4 eV can be assigned to Mo(IV)-O bonds (Figure 4-18b).

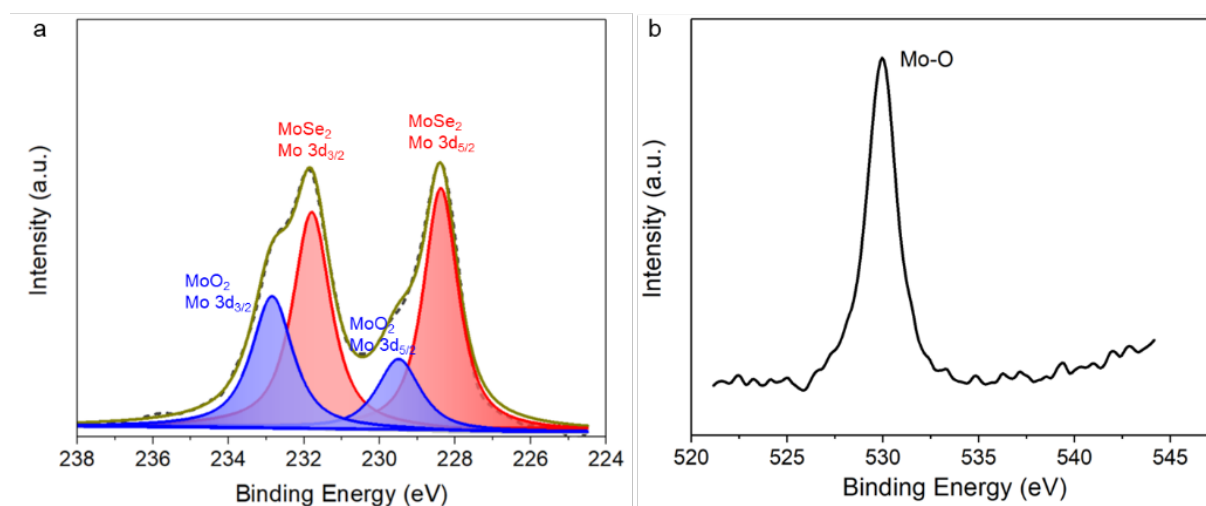


Figure 4-18 (a) Mo 3d and (b) O 1s XPS spectra of Au@MoOSe.

The Se 3d spectra of Au@MoOSe (Figure 4-19) exhibit two prominent peaks in the range of approximately 53.5 eV to 55.1 eV, corresponding to the selenides peak,²⁶⁸ confirming that surface-coated MoSe₂ monolayer has not undergone complete oxidation due to the protective effect of Au NP.

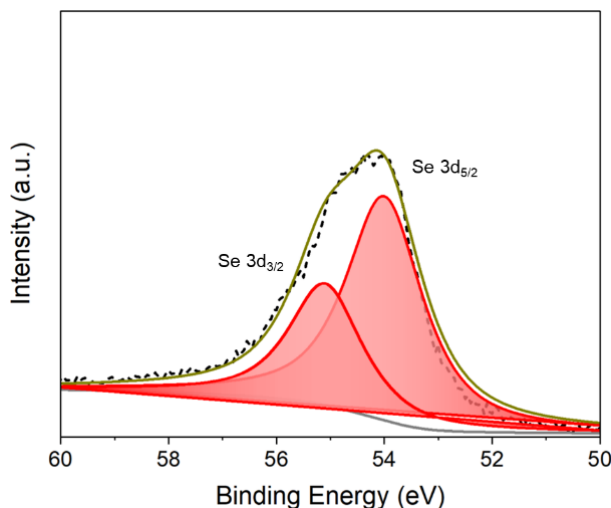


Figure 4-19 Se 3d XPS spectra of Au@MoOSe.

The XANES and EXAFS spectra provide insight into the local electronic structure and coordination environment of Pt single atoms (SAs) loading on different MoOSe substrates (1T' and 2H phases). In the normalized XANES spectrum (Figure 4-20a), Pt SA samples showed distinct characteristics compared to Pt foils and showed deviations from the properties of metal Pt. The white line intensity of Pt SA-1T'-MoOSe and Pt SA-2H-MoOSe is higher than that of Pt foil, suggesting that Pt in these samples is present in a more oxidized state. This observation is consistent with the electron interaction between Pt and MoOSe, which may stabilize Pt atoms in a lower coordination environment and a slightly positive oxidation state. EXAFS spectra (Figure 4-20b) further elucidate the local structure around Pt atoms. The Fourier transform EXAFS significantly reduced the intensity of the first shell peak of the Pt SA sample compared with the Pt foil, confirming the properties of single atoms of Pt in these systems. In particular, the first shell peak position of Pt SA-1T'-MoOSe and Pt SA-2H-MoOSe will shift to a lower position. The R value shows a shorter Pt-O bond distance to the Pt-Pt bond in the metal Pt as compared to the Pt foil. This observation further supports the unique local coordination of Pt atoms in MoOSe. In summary, XANES and EXAFS analyses confirm that Pt atoms are successfully stabilized as single atoms on MoOSe substrates and that the results of XAS with local electron and structural environments slightly different between the 1T' and

2H phases have succeeded in the synthesis of Pt single atoms on MoOSe substrates, providing important support for experimentally verifying the machine learning predictive catalytic performance of these systems.

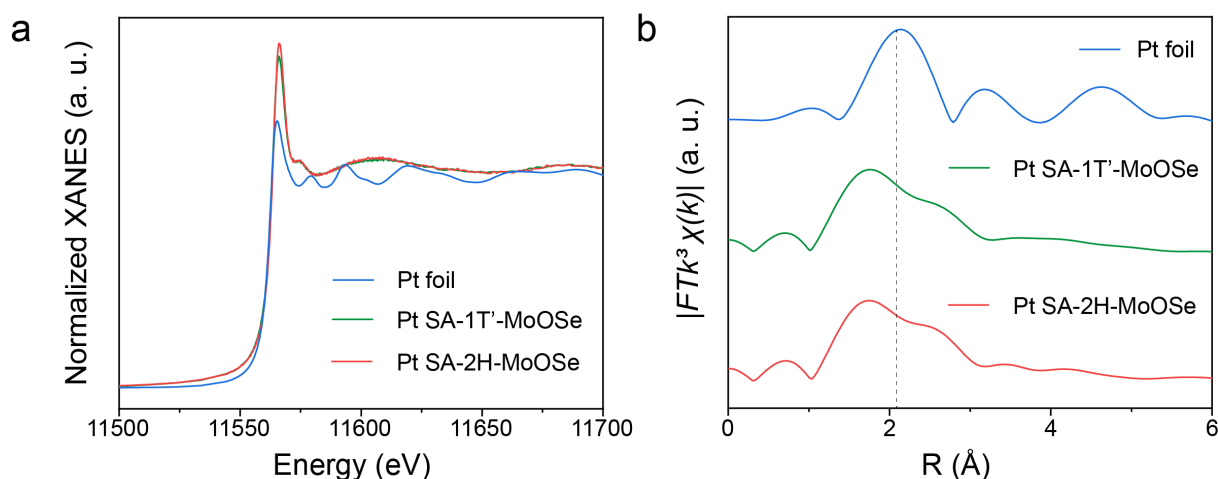


Figure 4-20 (a) XANES and (b) EXAFS spectra at the Pt L3-edge of 1T'-MoOSe and 2H-MoOSe.

Since we successfully synthesized Pt SA supported on 1T'-MoOSe and 2H-MoOSe, we go back to our ML predictions. Prior to experimental test, the ML results indicated that both catalysts would produce CH_4 as the primary CO_2 reduction product. Additionally, the ML model predicted that Pt SA on 1T'-MoOSe would exhibit lower reaction energy barriers compared to Pt SA on 2H-MoOSe, suggesting higher catalytic activity of Pt SA for the 1T' phase. The ML-predicted CH_4 production rate was expected to be higher for Pt SA-1T'-MoOSe than for Pt SA-2H-MoOSe, leading to subsequent photocatalytic testing to validate these predictions.

Figure 4-21 shows the experimentally measured production rates of CH_4 and CO for three materials: 1T'-MoOSe substrate, Pt SA-1T'-MoOSe and Pt SA-2H-MoOSe. 1T'-MoOSe substrate showed lowest photocatalytic performance, with small amounts of CH_4 and CO produced. In contrast, introducing Pt SA significantly enhanced the production rates of both CH_4 and CO, demonstrating the pivotal role of Pt single atoms in activating the substrate and

improving catalytic performance. Among the Pt SA on two different substrates, Pt SA-1T'-MoOSe exhibited the highest activity. This superior performance underscores the exceptional catalytic properties of the 1T' phase, likely due to its metallic nature, which facilitates electron transfer and enhances overall catalytic efficiency. While Pt SA-2H-MoOSe showed lower CH₄ and CO production rates than Pt SA-1T'-MoOSe, it still demonstrated significantly higher activity than 1T'-MoOSe substrate, validating the role of Pt single atoms in boosting the catalytic activity of the 2H phase. The experimental results validate the ML predictions, confirming the ability of the ML-trained database to predict catalytic performance effectively. Therefore, the integration of ML with experimental testing can accelerate the rational design of advanced single-atom catalysts, enabling efficient and selective CO₂ reduction. Further optimization of the ML model and exploration of additional phases or substrates could unlock new opportunities for catalytic system development.

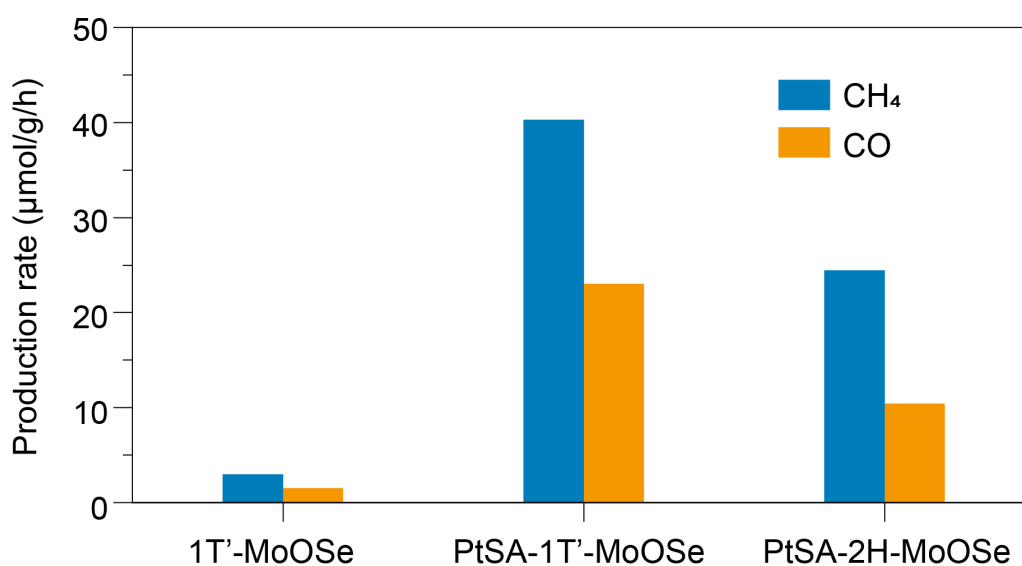


Figure 4-21 The photocatalytic performance test for CO₂ reduction.

4.3 Conclusion

In this chapter, we demonstrated a comprehensive workflow for expanding a SA-based 2D materials database and advancing ML models to accelerate efficient catalyst screening and discovery. Using a dataset of Janus-TMD materials as an example, this project adopted ML models trained on the dataset to identify high-activity catalytic sites and screen potential 2D Janus substrates for photocatalytic CO₂ reduction. The ML workflow integrated one-hot encoding of molecular structures, incremental learning, and deep learning models, which significantly improved prediction accuracy while reducing computational costs. Through the extended dataset and ML-driven predictions, the project successfully identified and prioritized optimal single-atom catalyst candidates for CO₂ reduction. Experimentally, three Janus substrates—1T'-MoSe₂, 1T'-MoOSe, and 1T'-MoSSe—were synthesized, and further growth of single-atom Pt on these substrates was achieved. Photocatalytic experiments validated the ML-predicted activity and selectivity, demonstrating the potential of ML models in guiding experimental designs and accelerating catalyst development. This combination of DFT and ML strategies has not only accelerated the rational design of single-atom catalysts but also expanded the potential applications of 2D materials in sustainable energy conversion. The growing dataset of atomic structures, intermediates, Janus configurations, and adsorption models provides a robust foundation for improving ML models and driving innovations in single-atom-based 2D materials discovery. These advancements pave the way for future breakthroughs in efficient and selective catalytic systems for sustainable energy applications. Crucially, the ML-driven design framework demonstrated in this chapter complements the experimental approaches discussed previously (Chapters 2 and 3), highlighting a coherent strategy to accelerate the discovery and optimization of photocatalysts for diverse renewable energy applications.

Chapter 5 Conclusion

In conclusion, this thesis systematically explored strategies for designing high-performance photocatalysts through microenvironment engineering, plasmonic effects, and single atom loading techniques. Each of these methodologies, while distinct, collectively addresses the unified goal of developing efficient, selective, and sustainable materials for renewable energy conversion applications. Chapters 2, 3, and 4 together form an integrated narrative highlighting experimental advancements and theoretical innovations essential for future catalyst development. We have also highlighted the role of DFT and data-driven design in accelerating photocatalyst discovery and supplementing experimental studies. Despite the burgeoning of novel photocatalyst design strategies over the past few years, we strongly believe that further improvements are still necessary, and that this research field will remain a hot topic. Therefore, we here highlight the opportunities and challenges of designing photocatalysts based on experimental and data-driven strategies:

In terms of experimental strategies, cocatalysts (especially noble-metal-based cocatalysts), single- or dual-atoms loading, and formation of defects/vacancies significantly improve the efficiency of CO₂ photoreduction in photocatalytic semiconductors by modulating the semiconductor valence band and acting as electrons-aggregation centers. Key areas for future research include: (1) seeking alternatives for noble-metal cocatalysts, (2) improving the stability of single-atom catalysts under light irradiation and (3) precisely controlling single atom construction. Other strategies, such as heterojunction construction, facet engineering of semiconductors and functional group modification also enhance the activity of CO₂ photoreduction to methane to a certain extent. Therefore, future studies should also more broadly consider the combination of multiple strategies to improve the activity of photocatalysts,^{190, 297} such as introducing cocatalysts on heterojunction photocatalysts,²⁹⁸ constructing functional group modification and defects on the surface of semiconductors,^{6, 81, 190, 297} nanocatalysts phase engineering,²⁹⁹⁻³⁰⁰ local surface plasmonic enhancement,³⁰¹⁻³⁰⁴ and

superlattice architectures,³⁰⁵ etc. These experimental strategies, including plasmonic engineering, single-atom catalysts, and core-shell designs, synergistically enhance photocatalytic performance by optimizing charge carrier dynamics and surface reaction environments, which have been systematically demonstrated through CO₂ reduction and seawater splitting studies in this work. At the same time, it is necessary to conduct rigorous investigations to examine the specific interactions and synergies between the multiple strategies employed and establish structure-activity relationships, including quantitative elucidation of mass transport effects and intrinsic chemical kinetics. Experimental strategies examined in this thesis demonstrate significant potential in improving photocatalytic processes. Specifically, plasmonic-metal oxide structures with localized surface plasmon resonance (LSPR), as detailed in Chapter 2, illustrate the importance of surface microenvironment control to achieve maximum selectivity and enhanced reaction rates in photocatalytic CO₂ reduction. Chapter 3 extended these insights by introducing atomic cobalt dispersed on NC@Cu core-shell structures, demonstrating efficient and stable hydrogen production from seawater. This approach successfully leveraged LSPR-induced local electric fields and single-atom active sites, offering valuable guidelines for constructing robust photocatalysts under challenging saline environments.

In tandem with the pursuit of photocatalysts with improved photocatalytic selectivity and yield, the overall process sustainability should also be an important concern, especially given the need for industrial application on a large scale to achieve carbon neutrality. While a detailed techno-economic analysis could be done to identify specific aspects of a given process that can be optimized, it is immediately clear that the cost and long-term stability of the catalyst as well as the environmental impact of its synthesis are important considerations. Thus, the potential for scalable, low-cost production should also be a focus of future catalyst engineering studies. Widely available and low-cost semiconducting materials, such as TiO₂ and ZnO, demonstrate high chemical- and photo-stability but usually have large bandgaps and limited

activity under visible light irradiation. Along these lines, a promising research direction could be to improve the properties of these materials through scalable post-synthetic modifications, such as thermal treatment to introduce defects and oxygen vacancies and subsequent addition of non-noble metal cocatalysts or surface functional groups.

Furthermore, in addition to the discovery and development of high-performance photocatalyst materials, successful commercialization also entails the integration of these materials into highly efficient photoreactors. This will require innovative reactor design, which has developed quickly in recent years,³⁰⁶ to achieve maximum efficiency and ease of operation at a low cost. The key design challenge is to optimize an optically and chemically engineered system that concentrates and homogenizes light intensity in an absorbing and scattering photocatalyst bed integrated within a photoreactor configuration. Of these requirements, maximizing the absorption of light by the photocatalyst is the most essential. Minimizing the unfavorable reflection, scattering, and transmission loss are also necessary since the photon utilization efficiency will be reduced. Although high light absorption is beneficial for a large number of electron-hole pairs and high photocatalytic activity, reflection and scattering effects limit the penetration depth of light throughout the active sites of the photocatalysts. Finally, the management of heat and mass transfer issues, such as reactant diffusion into the catalyst particle and product removal from the reactor, is also an important consideration in reactor design.³⁰⁷

Data-driven innovation supported by DFT calculations is a powerful solution to accelerate photocatalyst discovery. However, implementing a complete data-driven process from data generation to rational design and innovation is still laborious. Full DFT simulations are not always feasible especially for complex photocatalysts (e.g., multicomponent materials, amorphous materials, polycrystalline materials, etc.) and if the full reaction network (as opposed to the computation of simple descriptors) is to be simulated for all possible products. Researchers are working on developing new descriptors for photocatalytic CO₂ reduction, but

the development of descriptors also needs to be data-driven to validate their correlation with target properties. Fortunately, the combination of experimental studies with focused DFT calculations remains successful in revealing reaction mechanisms and rationalizing observed reactivity trends. In the future, screening and integration of multi-scale calculations with DFT calculations will guide the further understanding of photocatalytic CO₂ reduction. Beyond experimental methodologies, integrating computational techniques, particularly density functional theory (DFT) and machine learning (ML), plays a critical role in accelerating catalyst discovery and optimization. Chapter 4 provided a comprehensive demonstration of this integrated approach by employing advanced ML algorithms to rapidly screen and identify optimal single-atom loaded Janus two-dimensional (2D) materials for photocatalytic CO₂ reduction. This ML-driven approach substantially reduces computational efforts and experimental uncertainty, facilitating targeted synthesis and verification of promising candidates. Thus, this thesis underscores the necessity and efficacy of combining experimental data with computational predictions to accelerate the rational design of photocatalysts. Furthermore, the integration of ML-driven computational methods with experimental approaches, as highlighted in Chapter 4, provides a comprehensive pathway toward the accelerated discovery of advanced photocatalysts. This integrated approach bridges fundamental theoretical predictions with practical catalytic experiments, offering a unified strategy to overcome current challenges and significantly improve catalyst efficiency and selectivity.

In summary, the design of functional materials for energy conversion applications cannot be achieved without the integration of theoretical and experimental approaches. With the exponential growth of data, the use of ML to assist in catalyst design has become increasingly important. Following the completion of this dissertation, we will continue to explore the design of functional materials. Specifically, in Chapter 4, there remain valuable datasets yet to be explored and analysed. Moving forward, we will employ the previously developed ML models

to comprehensively screen the CO₂RR performance of various single-atom-loaded TMD monolayers, with a particular focus on predicting the formation of C₂ products and identifying optimal active sites with high selectivity and catalytic efficiency.

Moreover, this project will focus on extensively expanding the existing TMD database to enable predictions of a wide range of redox reactions beyond 2D TMD and CO₂ reduction. These include more typical 2D materials for the hydrogen evolution reaction (HER) for seawater/wastewater, CO₂RR, oxygen reduction reaction (ORR), nitrogen reduction reaction (NRR), organic waste oxidation (OWO), methane oxidation (MO), and other emerging energy conversion processes. Based on ML-assisted computational predictions, the project will synthesize multiple candidate single-atom catalysts and explore their practical applications in energy conversion. Our goal is to develop a versatile database capable of predicting catalytic behaviours for various oxidation and reduction processes. The ML models will be trained on this enriched dataset to enhance their capability to predict the catalytic activity, stability, and selectivity of a broader range of single-atom-loaded 2D materials. This comprehensive approach aims to pave the way for the rational design of advanced catalysts for future energy conversion technologies.

Moving forward, our research will continue to build upon the coherent framework established in this thesis, leveraging both experimental innovations and computational advancements. Future studies will further expand datasets and apply ML models to a wider range of catalytic processes beyond those explored here, solidifying a robust, integrative platform for rational photocatalyst design and sustainable energy applications.

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