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Plasmon-driven charge dynamics in MXene-semiconductor heterojunctions: Synergistic SPR effects for photocatalysis

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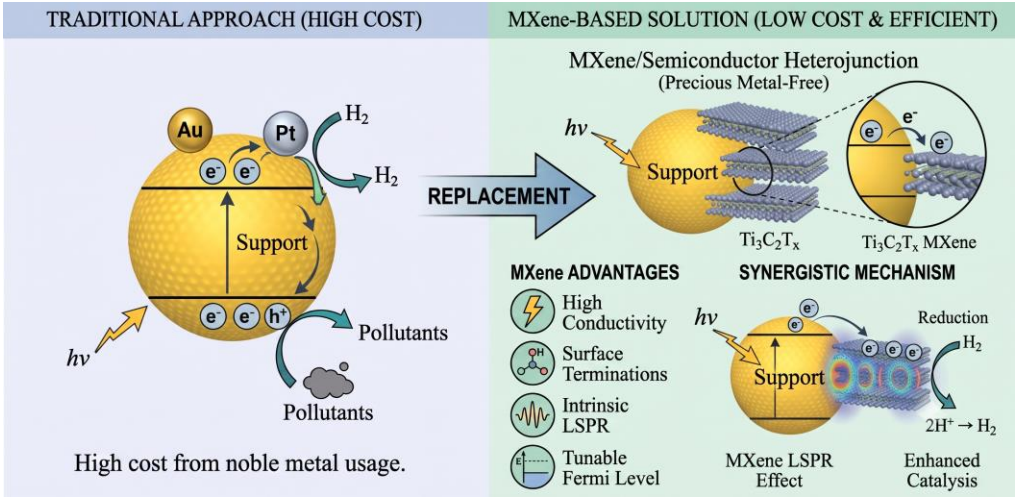
Abstract

The intensifying worldwide energy crisis and significant environmental deterioration require sophisticated, sustainable photocatalytic technology for solar-to-chemical energy conversion. Conventional semiconductor photocatalysts often experience swift electron-hole recombination and constrained visible-light absorption, limiting their practical efficacy. In appropriately engineered MXene-semiconductor heterojunctions, these limitations can be mitigated through specific mechanisms that may operate individually or synergistically, depending on the system design: localized surface plasmon resonance (LSPR)-induced hot-carrier transfer, efficient charge extraction by the conductive MXene network, and Schottky-barrier-mediated spatial charge separation. This review clarifies that alongside their established role as conductive supports, certain MXenes subject to specific compositions, carrier densities, and morphological conditions can exhibit experimentally demonstrated intrinsic LSPR features within the visible and near-infrared (NIR) regions, distinct from ordinary broadband photothermal absorption. Furthermore, adjusting surface terminal groups (Tx) can modify the electronic structure and optical properties of these 2D materials, thereby influencing their overall plasmonic response. To address the inherent oxidative instability of MXenes under severe aqueous conditions, strategies such as fluorine-induced surface passivation have emerged as promising approaches to improve long-term photostability. We rigorously analyze sophisticated synthesis methodologies and their influence on thermodynamically challenging multi-electron reactions, including photocatalytic hydrogen production, carbon dioxide reduction, nitrogen fixation, and the mineralization of persistent pharmaceutical contaminants. By integrating robust 2D/2D heterojunction engineering with demonstrated plasmonic effects, MXene-based nanocomposites provide an efficient, highly tunable, and potentially noble-metal-free platform for advanced energy conversion and environmental remediation technologies.

Graphical Abstract



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1. Introduction

The increasing worldwide energy demand, along with the significant environmental catastrophe caused by excessive fossil fuel consumption and human-induced climate change, presents an unparalleled challenge to human societies. In this context, the advancement of clean, sustainable, and renewable energy technology has become an essential requirement for the survival and future prosperity of our planet. Among several clean energy sources, solar energy emerges as the foremost alternative to the carbon-based economy owing to its vast availability, global accessibility, and intrinsically clean characteristics. Thus, creating effective technologies to directly transform this abundant solar energy into chemical energy and storable fuels has become a key and significant research frontier in advanced materials and energy science[1-4].

Among the different ways for capturing solar irradiation, semiconductor photocatalysis has been proposed as a particularly sustainable and promising approach. This method conceptually shares mechanistic similarities with natural photosynthesis and allows the use of sunlight photons to drive thermodynamically difficult chemical reactions without the need for secondary energy expenditure. The major applications in this field are in hydrogen generation by water splitting (HER), carbon dioxide reduction to useful solar fuels (CO_2RR), and detoxification of persistent organic and pharmacological contaminants[5]. The potential to achieve complete mineralization with minimal toxic secondary byproducts and their enormous potential in sustainable energy storage have made photocatalytic devices the focus of attention of materials scientists and environmental engineers worldwide.

Despite this unparalleled potential, traditional single-component photocatalysts and conventional semiconductors face severe structural and physical bottlenecks that drastically limit their overall efficiency on a practical scale. One of the major physical obstacles to the commercialization of these materials is the extremely high rate of photogenerated charge carrier (electron-hole pair) recombination before they can migrate to the catalyst surface to participate in redox reactions, a phenomenon that dissipates most of the absorbed energy as heat. Furthermore, the wide bandgap and susceptibility to severe photo-corrosion observed in specific classes of photocatalysts (such as certain metal sulfides and wide-bandgap oxides like TiO_2) restrict their long-term operational stability and limit their absorption capacity to a narrow fraction of the ultraviolet spectrum, leaving them incapable of harvesting photons across the broader visible and near-infrared (NIR) ranges[6-8].

To overcome these physical and thermodynamic limitations, the rational design of advanced heterojunctions, particularly the integration of semiconductors with two-dimensional transition metal carbides or nitrides (MXenes) and plasmonic nanostructures has emerged as a state-of-the-art solution. Benefiting from exceptional metallic-like electrical conductivity, a highly accessible surface area, and highly tunable surface functionalities (Tx, such as -O, -OH, and -F), MXenes can act as an effective conductive substrate and a promising electron sink, depending on the specific system configuration [9, 10]. Modulating these terminal groups (e.g., altering the [O]/[F] ratio) can modify the material's work function and interfacial chemistry. This modulation, alongside semiconductor electron affinity, defect states, and Fermi-level pinning, plays a crucial role in configuring the Schottky barrier, which can potentially suppress electron backflow. Concurrently, the localized surface plasmon resonance (LSPR) effect, whether originating from decorated noble metal nanoparticles or demonstrated intrinsic plasmonic properties of specific highly conductive MXenes, substantially broadens visible and NIR light harvesting. In experimentally verified systems, this plasmonic phenomenon creates a remarkable synergy by amplifying the localized electromagnetic near-field and inducing the generation of highly energetic hot electrons. In appropriately coupled architectures, these hot carriers have the potential to traverse the interfacial barrier, thereby accelerating surface redox kinetics and preventing recombination [10-12].

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A meticulous examination of this paradigm is indispensable for researchers, engineers, and specialized audiences in the field of renewable energy. Moving beyond conventional statistical reports, this work addresses the profound gaps in the mechanistic understanding of charge carrier dynamics within these ternary and plasmonic nanostructures. With a specific focus on Plasmon-Driven Charge Dynamics in MXene-Semiconductor Heterojunctions: Synergistic SPR Effects for Photocatalytic Energy Conversion, this paper establishes, for the first time, a comprehensive roadmap of plasmon-driven charge transfer and synergistic LSPR effects that have not been previously elucidated in an integrated manner. By engaging with this article, readers will not only attain a deep understanding of the physical mechanisms governing interfacial charge dynamics but will also master the principles of intelligently designing highly stable, next-generation photocatalysts for industrial applications. This contribution ultimately cements this research as a unique, inspiring, and indispensable reference in contemporary scientific literature.

2. Fundamentals of Plasmonic MXene-Semiconductor Heterojunctions

A profound understanding of the photocatalytic behavior of advanced nanocomposites necessitates a meticulous dissection of the structural and electronic properties of their constituent components. MXenes represent a prominent class of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides governed by the general formula $M_{n+1}X_nT_x$, where M represents an early transition metal, X stands for carbon and/or nitrogen, and Tx denotes the surface terminal groups. From a solid-state physics perspective, many of these 2D materials exhibit metallic-like conductivity, although these electrical properties vary substantially depending on the specific MXene composition, surface termination, defect density, thickness, and oxidation state. Not every MXene behaves as a simple metallic conductor. In appropriately synthesized metallic MXenes, a remarkably high density of states (DOS) near the Fermi level transforms them into promising candidates for extracting photogenerated electrons, provided that the interfacial charge-transfer kinetics are optimized [13, 14].

In addition to their distinctive electronic structure, the surface chemical properties of MXenes play a pivotal role in promoting the charge dynamics of the catalyst. The synthesis processes naturally saturate their basal planes with abundant functional terminations, such as oxygen (-O), hydroxyl (-OH), and fluorine (-F). These moieties impart a profoundly hydrophilic nature to the 2D sheets, promoting dispersibility and facilitating interfacial contact with semiconductors, although practical synthesis often introduces challenges such as restacking, wrinkles, vacancies, and incomplete contact. More importantly, these surface terminations are not merely passive structural features; they serve as critical tuning knobs for the material's optoelectronic and plasmonic behavior. Modulating the [O]/[F] ratio on the MXene surface can influence its free electron density and modify the subsequent plasmonic resonance properties, such as shifting the resonance frequency or altering the damping rate depending on the specific system. This control over surface chemistry directly translates into an enhanced ability to tune the fundamental electronic and optical properties of the material[15, 16]. A comprehensive summary of these tunable termination effects and their corresponding band alignment dynamics is presented in **Table 1.**

On the other side of this architecture lies the physical phenomenon of localized surface plasmon resonance (LSPR), which serves as the primary driver for enhanced light absorption. While LSPR has historically been harnessed using noble metal nanoparticles, groundbreaking advancements have demonstrated that specific MXenes (particularly Ti3C2Tx) have been reported to exhibit intrinsic LSPR across a broad spectral range. However, this plasmonic response must be carefully distinguished from Drude-like free-carrier absorption or ordinary photothermal effects, as it is highly dependent on sample quality and optical geometry. Owing to their inherently high carrier density, incident photons can trigger collective

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oscillations of free electrons in MXenes, which may manifest as specific surface plasmon resonances depending on the geometry, anisotropy, thickness, and electromagnetic boundary conditions. The non-radiative decay of these plasmons can generate highly energetic charge carriers, specifically hot electrons and hot holes, although the existence, energy distribution, and lifetime of these hot carriers must be experimentally demonstrated (e.g., via ultrafast spectroscopy) to distinguish them from ordinary photogenerated carriers [18, 19].

Table1. Tunable Surface Terminations and Band Alignment.

Termination Effect	Mechanism	Functional Consequence	Ref.
–O vs. –OH conductivity	–O termination lowers conductivity relative to –OH; ratio-dependent	In-plane conductivity tunable for specific catalytic needs	[14]
Work function modulation	Terminations shift Fermi level via p–d orbital hybridization (up to 0.8 eV range)	Controls Schottky vs. ohmic contact with semiconductors	[10, 12]
De-functionalization	Vacuum annealing removes terminations, increasing conductivity	Metallic transport enhanced; intercalation can induce semiconductor-like transitions	[17]
Bandgap tuning	Theoretical predictions and specific experimental conditions indicate tunable bandgaps (e.g., 0.92–1.75 eV) for specific non-metallic or highly functionalized MXene compositions (e.g., specific oxygen-terminated structures).	Enables visible-light absorption and heterojunction design with TiO_2, g-C_3N_4, and Cu_2O in systems transitioning from metallic to semiconductor-like behavior.	[11, 12]

When the metallic MXene and the semiconductor phase are brought into physical contact, the system initiates an interfacial band alignment process to reach thermodynamic equilibrium. Since the work function of specific metallic MXenes is typically larger than the work function (and corresponding Fermi level position relative to the vacuum level) of certain conventional n-type semiconductors, the resulting potential difference can drive a flow of electrons from the semiconductor toward the MXene. This charge migration theoretically persists until the Fermi levels approach equilibrium, potentially leading to upward band bending in the semiconductor and the formation of a Schottky barrier at the interface; however, in practical heterojunctions, surface termination inhomogeneity, interfacial dipole layers, Fermi-level pinning, and defect states frequently govern the actual barrier height and band alignment. This Schottky barrier functions as an energy barrier where charge transport is typically thermally activated or tunneling-assisted; it permits photoexcited electrons to flow from the semiconductor to the MXene layer with a reduced recombination probability, while simultaneously creating a high energy barrier against their reverse flow. Operating under a plasmon-driven regime, this synergistic configuration can facilitate directional charge carrier separation, as evidenced in specific systems characterized by lifetime measurements or transient absorption, effectively prolonging carrier lifetimes and supplying an abundance of electroactive sites for surface redox reactions[20, 21].

As comprehensively illustrated in **Fig.1** (Bibliometric analysis and prominent research trends of MXenes in energy and photocatalysis), the profound optoelectronic properties and tunable surface chemistry of MXenes have catalyzed an explosive, exponential growth in global research interest.

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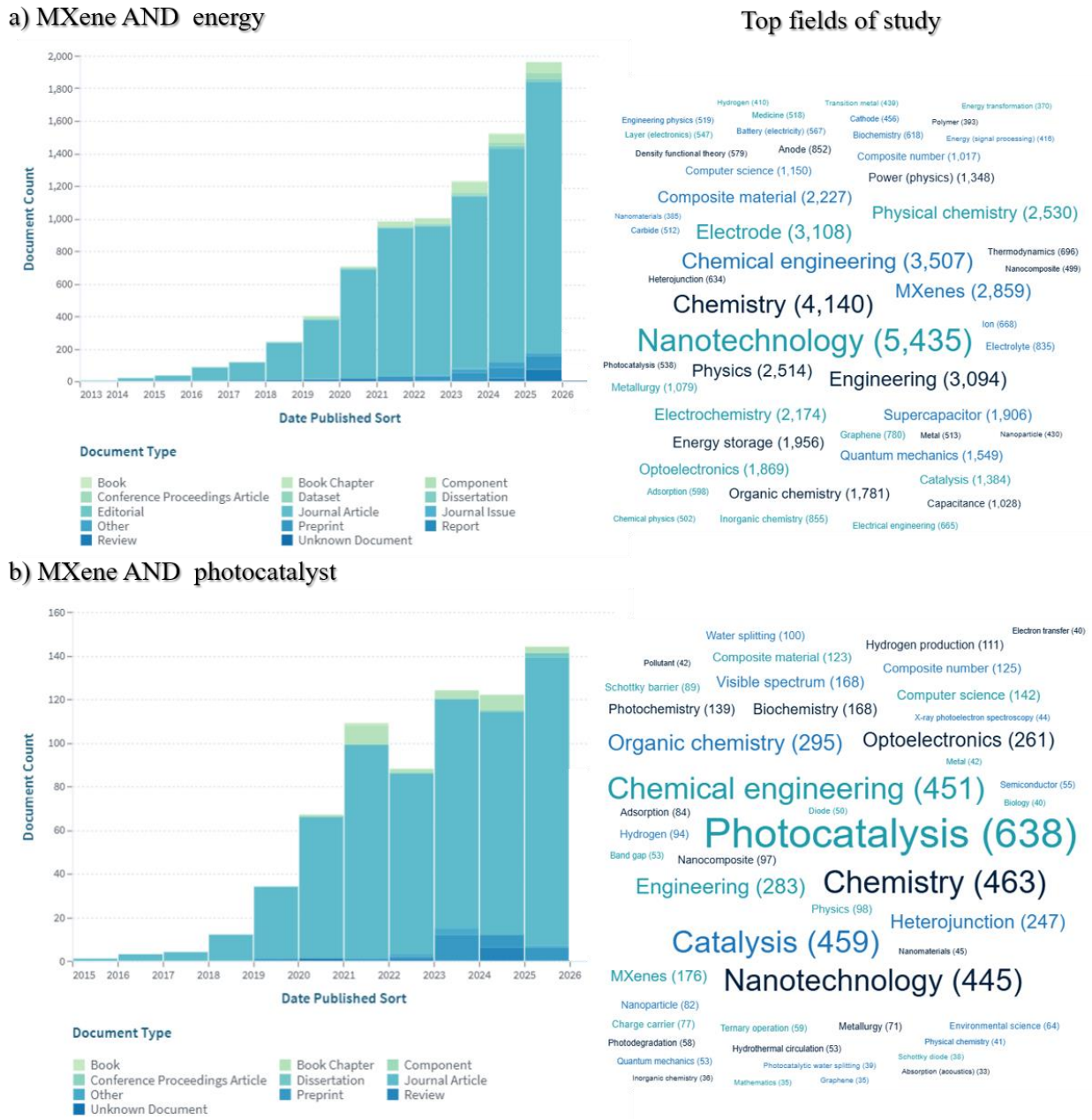

Fig. 1. Bibliometric analysis and prominent research trends of MXenes: (a) Exponential growth and keyword word cloud for MXene applications in the energy sector, and (b) targeted publication trends and word cloud specifically focusing on MXene-based photocatalysts.

To quantitatively assess this trajectory, a bibliometric analysis was conducted using the Lens.org scholarly database (spanning the publication years 2013 to 2026). The data retrieval was executed using two specific Boolean search queries across the Title, Abstract, Keyword, and Field of Study metadata fields: (1) (MXene) AND (energy), which yielded 9,513 scholarly works (Figure 1a), and (2) (MXene) AND (photocatalyst), which yielded 804 targeted publications (Figure 1b). The built-in analytical and visualization tools of the Lens.org platform were utilized to filter the records, categorize document types (primarily journal articles, reviews, book chapters, and conference proceedings), and generate the corresponding keyword frequency word clouds. This quantitative analysis reveals a striking trajectory: while the broader integration of MXenes within general energy-related fields has reached a state of substantial maturity, the specific rational design of MXene-based photocatalysts remains a rapidly evolving frontier.

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A granular examination of the word clouds within this specialized domain elucidates the scientific community's precise theoretical and practical focus. The prominent frequency of core conceptual keywords most notably "heterojunction," "Schottky barrier," "charge carrier," and "visible spectrum," indicates a strong thematic concentration in the analyzed literature, highlighting that interfacial engineering and decoupling charge transfer dynamics are central considerations for suppressing rapid electron-hole recombination. Consequently, this targeted optimization at the nanoscale directly fuels the most prevalent applied research vectors, predominantly "water splitting," "hydrogen production," and advanced "photodegradation." This statistical and thematic evidence underscores the theoretical importance of constructing rationally designed MXene-semiconductor architectures as a highly promising approach to addressing the thermodynamic barriers of traditional solar-to-chemical energy conversion.

3. Synthesis Strategies and Structural Design

The rational design and precise engineering of the structural architecture in plasmonic MXene-semiconductor heterojunctions necessitate controlled synthesis strategies with nanometric precision. The synergistic performance of surface plasmon resonance (SPR) and charge transfer dynamics is fundamentally dependent on the quality of interfacial contact, the spatial distribution of the active phases, and the strategic preservation or modification of the two-dimensional (2D) MXene framework during fabrication. Consequently, the materials engineering community places significant emphasis on developing synthesis methodologies that offer high reproducibility, structural integrity, and scalability for industrial applications. Among various approaches, hydrothermal/solvothermal synthesis, electrostatic self-assembly, and photo-deposition have emerged as extensively studied and widely adopted strategies for constructing these advanced photocatalytic systems[20, 22].

This approach is extensively utilized for the direct *in-situ* growth of semiconductor nanostructures (e.g., TiO_2, CdS, or MoS_2) onto MXene nanosheets. By employing confined reaction environments under elevated temperatures and pressures, this method imparts exceptional crystallinity to the semiconductor phase. Historically, a primary challenge associated with the hydrothermal technique has been the inherent susceptibility of MXenes (such as Ti_3C_2Tx) to structural degradation and uncontrolled oxidation in high-temperature aqueous media. However, recent advanced structural designs have ingeniously turned this vulnerability into a synthetic opportunity. Through meticulously controlled hydrothermal oxidation, a portion of the MXene network can be deliberately oxidized to form tightly integrated semiconductor phases (e.g., anatase TiO_2 nanosheets). It is important to note that distinguishing controlled partial oxidation from uncontrolled degradation requires rigorous evidence of interface orientation and phase purity to verify the formation of robust, seamlessly integrated heterojunctions such as (001)TiO_2/Ti_3C_2. To prevent excessive oxidation and maintain the intrinsic electrical conductivity of the core MXene network, researchers frequently substitute water with organic solvents (solvothermal routes) or strictly optimize the reaction time and temperature [23-25].

Electrostatic self-assembly represents a mild, room-temperature, and highly efficient strategy for heterojunction construction, particularly ideal for preserving the delicate electronic properties of MXenes. The fundamental principle of this technique relies on the Coulombic interactions between components bearing opposite surface charges. Due to the abundance of terminal functional groups (e.g., -O, -OH, and -F), MXenes can exhibit a highly negative zeta potential in aqueous solutions, although this is strongly dependent on pH, ionic strength, concentration, and electrolyte composition. By systematically adjusting the pH or utilizing appropriate surface modifiers (such as $-NH_2$ groups), 2D semiconductor nanostructures like ultrathin C_3N_4 or CdS nanoflowers can be endowed with a positive surface charge. The subsequent mixing of these tailored suspensions triggers a rapid, homogeneous self-assembly of the components. This method

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establishes a favorable face-to-face (2D/2D) physical contact, which is an important structural prerequisite, though not independently sufficient, without appropriate electronic coupling and band alignment for facilitating hot-carrier transfer, reducing interfacial charge resistance, and maximizing the active surface area in the plasmonic regime [26-28].

To further quantify the mechanistic superiorities of this face-to-face configuration, **Table 2** provides a comprehensive comparative analysis of the interfacial contact and charge transfer dynamics between 2D/2D electrostatic assembly and conventional mixed-dimensional (0D/2D or 1D/2D) geometries. Specifically, it highlights the advantages in contact area, carrier separation distance, and scalability.

Table2. Interfacial Contact and Charge Transfer Dynamics.

Dimension	**2D/2D Electrostatic Assembly**	**Conventional 0D/2D or 1D/2D**	**Ref.**
Contact Area	Large face-to-face interface	Limited point or line contact	[29, 30]
Charge Transfer Distance	Potentially minimized depending on interface quality	Longer, bulk-dependent	[31, 32]
Carrier Separation	Facilitated by internal electric fields (requires verification via band bending or Kelvin-probe data)	Weaker interfacial coupling	[33, 34]
Restacking Prevention	May reduce restacking under optimized preparation conditions	Partial coverage only	[35, 36]
Scalability	Solution-based, surfactant-free	Often requires templates	[37, 38]

For traditional ternary systems requiring the precise loading of noble metal nanoparticles (such as Au, Ag, or Pd), photo-deposition is widely recognized as a highly effective technique, though not without its limitations regarding precise control over particle-size distribution and nucleation-site reproducibility. In this photochemical process, the primary semiconductor is subjected to ultraviolet light irradiation, generating photogenerated electrons that rapidly migrate toward electron-rich defect sites on the MXene. While these sites are often assumed to be electron-rich defects that can reduce metal precursor ions into metallic nanoparticles, it requires careful experimental verification to ensure such defects do not inadvertently function as trapping or recombination centers. However, emerging paradigms in materials science emphasize leveraging the *intrinsic* LSPR properties of highly conductive MXenes themselves. Provided the intrinsic MXene exhibits a robust plasmonic response rather than merely acting as a conductive cocatalyst, the need for the complex and costly photo-deposition of noble metals can potentially be bypassed. This noble-metal-free approach reduces material costs, although significant scale-up challenges such as synthesis reproducibility, oxidation stability, flake size control, and etching wastewater management must still be addressed to establish true industrial feasibility [19, 39].

The strategic integration of these synthesis approaches culminates in the development of sophisticated architectures, including 2D/2D sandwich-like heterostructures, 3D porous frameworks, and core-shell configurations. Encapsulating the plasmonic site, whether intrinsic MXene domains or noble metal nanoparticles within ultrathin semiconductor layers maximizes the localized surface plasmon resonance (LSPR) near-field enhancement while effectively preventing the agglomeration and chemical degradation of the active phases. Such hierarchical designs can expand the electrochemically active surface area (a property that should be corroborated by quantitative structural characterizations like BET or ECSA measurements), shorten the diffusion pathways for reactants, and ultimately deliver an unparalleled synergy for efficient solar-to-chemical energy conversion and environmental remediation [40-42].

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4. Synergistic SPR Effects in Boosting Photocatalytic Performance

The enhanced photocatalytic efficiency of MXene-based heterojunctions is fundamentally rooted in the synergistic interplay between localized surface plasmon resonance (LSPR), efficient charge carrier separation, and rapid interfacial electron transport. This triad of mechanisms is proposed to enhance the solar-to-chemical energy conversion process, often surpassing the baseline performance of pristine semiconductor-based photocatalysts [43, 44].

The charge transfer process initiates with the LSPR effect, which can originate either from decorated noble metal nanoparticles (e.g., Au, Ag, or Pd) or intrinsically from the highly conductive MXene matrix itself. Under visible and near-infrared (NIR) light irradiation, the collective oscillation of conduction-band electrons in these metallic domains generates a high-intensity localized electromagnetic near-field. Depending on the specific system's quantum yield and competitive direct photoexcitation pathways, a fraction of these excited plasmons can undergo rapid non-radiative decay, resulting in the generation of highly energetic charge carriers termed hot electrons. These hot electrons can potentially surmount the interfacial potential barrier, provided there is appropriate energetic overlap between the hot-carrier distribution and receiving states, sufficient interface coupling, and a suitable barrier height. This hot electron injection pathway may allow a significant fraction of these carriers to be extracted before the ultrafast electron-electron and electron-phonon thermalization processes dominate, driving thermodynamically demanding redox reactions that are otherwise unattainable under standard, non-plasmonic photocatalytic conditions [45-47].

The most pervasive limitation in traditional photocatalytic systems is the rapid recombination of photogenerated electron-hole pairs, which severely curtails overall efficiency. In these meticulously designed heterojunctions, the MXene nanosheets serve an indispensable dual role. Owing to their inherent metallic-like conductivity and a remarkably high density of states (DOS) near the Fermi level, MXenes function as a highly conductive pathway. It is important to note that while this bulk conductivity is distinct from ultrafast interfacial charge-transfer kinetics, it fundamentally facilitates subsequent carrier transport. Once the photogenerated or plasmon-induced electrons populate the semiconductor's conduction band, they are rapidly extracted (a dynamic process that ideally requires verification via femtosecond-scale transient measurements) by the intimately interfaced MXene sheets. This charge separation process effectively prevents the deleterious accumulation of electrons within the semiconductor matrix, thereby potentially extending the lifetime of spatially separated carriers. In essence, under favorable interfacial energetics, the MXene can facilitate the extraction of electrons away from the semiconductor, mitigating carrier recombination, while its intrinsic LSPR may simultaneously act as an optical amplifier in verified plasmonic systems [48-50].

This profound synergistic effect is governed by the internal electric field established at the heterojunction interfaces. Assuming a favorable band alignment which necessitates systematic experimental verification of work functions, valence-band, and conduction-band positions for each specific system this structure can promote spatial and directional separation of charge carriers: electrons are preferentially channeled toward the MXene interface, while holes may remain localized on the semiconductor surface (a dynamic that requires experimental validation rather than being inferred solely from idealized band diagrams). This highly directional transport is further amplified by the modulation of MXene surface functional groups (e.g., tuning the [O]/[F] ratio), which has been proposed to fine-tune the local electrostatic field and minimizes interfacial resistance in certain studies, though establishing a precise quantitative relationship remains an ongoing challenge. Furthermore, the intense localized electric field and localized photothermal heating provided by the LSPR can influence reaction kinetics; however, carefully designed temperature-controlled experiments are critical to explicitly decouple these distinct photothermal contributions from pure plasmonic charge-transfer mechanisms [51-53].

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The spatially separated and long-lived charge carriers increase the probability of participating in targeted surface redox reactions with remarkable efficiency. The accumulated electrons on the catalytically active surface of the MXene must remain available for reduction reactions without becoming trapped or recombining a condition that strongly depends on identifying and establishing the exact location of the catalytic reduction sites. When optimized, these electrons are consumed by adsorbed species (reducing O_2 to superoxide radicals O_2^- or H^+ to H_2 gas), while the holes powerfully drive oxidation half-reactions (oxidizing OH^- to hydroxyl radicals OH or directly degrading persistent organic pollutants). By ingeniously decoupling the specific sites of electron and hole consumption through this rational architecture, the system achieves a state of prolonged carrier longevity. It is important to clarify that while this separation significantly increases the probability that carriers participate in reactions, the thermodynamic redox potentials themselves remain determined by the intrinsic electronic structure and reaction conditions. Consequently, the plasmonic MXene-semiconductor nanocomposite exhibits a triple-threat advantage: amplified broad-spectrum light harvesting via SPR, rapid and directional charge separation via the tunable MXene sink, and enhanced surface reaction kinetics, culminating in highly competitive photocatalytic performance for advanced energy conversion and environmental remediation [54-56].

5. Advanced Energy and Environmental Applications

In order to alleviate the worldwide energy problem and to mitigate the deterioration of the environment, the rational design of plasmonic MXene-semiconductor heterojunctions offers highly promising pathways. In well-engineered systems, key photophysical features such as broadband light absorption, improved charge carrier dynamics, and tailored interfacial stability can collectively contribute to enhanced catalytic performance. Recent research has concentrated a great deal of attention on harnessing these composites for thermodynamically challenging, multi-electron photocatalytic energy conversion processes. Additionally, sophisticated environmental cleanup under full-spectrum irradiation has also been carried out. This is in response to the urgent demand for sustainable energy paradigms [12, 57, 58].

Water splitting for green hydrogen (H_2) production represents the cornerstone of sustainable energy technologies. However, the sluggish kinetics of the hydrogen evolution reaction (HER) typically require expensive platinum-group co-catalysts [59-61]. Plasmonic MXene-semiconductor composites have emerged as highly efficient, noble-metal-sparing, or entirely noble-metal-free alternatives. In these architectures, the MXene surface acts as a macroscopic catalytic terminal; its inherently low work function and precisely tuned hydrophilic terminal groups (-O and -F) can potentially provide a high density of catalytically active sites. However, surface hydrophilicity does not automatically imply a favorable Gibbs free energy for hydrogen adsorption (ΔG_{H^*}); rather, ΔG_{H^*} is highly site-specific and must be rigorously determined through experimental measurements or computational modeling for each specific architecture [62, 63].

Concurrently, the LSPR effect, originating either from the intrinsic plasmonic resonance of the MXene matrix itself or from integrated metallic nanoparticles, can promote the injection of high-energy hot electrons across the interfacial barrier under visible and near-infrared (NIR) irradiation. These energetic electrons are subsequently channeled by the MXene network. This synergistic process helps suppress charge recombination and supports H^+ reduction, resulting in significantly enhanced H_2 evolution rates compared to those of pristine semiconductors, provided that parameters such as catalyst loading, light intensity, and sacrificial agents are comprehensively optimized [64-66].

The artificial photosynthetic conversion of carbon dioxide (CO_2) into value-added chemical fuels (CH_4, CO, HCOOH, and CH_3OH) offers a dual-benefit solution: mitigating greenhouse gas emissions and storing intermittent solar energy in stable chemical bonds. Nevertheless, the CO_2 reduction reaction (CO_2RR) is severely bottlenecked by the high dissociation energy of the C=O bond and complex multi-electron transfer pathways. Ternary and intrinsic plasmonic MXene composites

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are being actively investigated to address these thermodynamic hurdles elegantly [67-69]. The localized photothermal heating induced by the non-radiative decay of plasmons can potentially accelerate the reaction kinetics and influence CO_2 mass transfer at the solid-liquid interface. Furthermore, the MXene support plays a pivotal dual role: its highly conductive network facilitates a continuous supply of the multiple electrons required for CO_2RR, while its surface functional groups (particularly -OH and -O species) can serve as superior CO_2 capturing sites. Depending on the specific surface chemistry and dynamic reaction conditions, these active sites strongly chemisorb CO_2 molecules and stabilize the crucial highly reactive intermediates (e.g., CO_2^- radicals). When properly optimized and experimentally validated via in-situ spectroscopic techniques, this can enhance both the overall conversion efficiency and the selectivity toward specific high-value solar fuels like methane [70-72].

Ammonia is a vital industrial chemical and a highly promising carbon-free energy carrier. The conventional Haber-Bosch process for NH_3 synthesis is heavily energy-intensive and environmentally taxing. Photocatalytic nitrogen fixation under ambient conditions is considered a holy grail in catalysis, primarily due to the immense energy required to cleave the highly stable N≡N triple bond (941 kJ mol^{-1}). Plasmonic MXene-semiconductor heterojunctions present a groundbreaking approach to overcoming this barrier. The intense localized electromagnetic fields (hot spots) and the injection of highly energetic hot electrons generated by the broadband SPR effect can provide essential energy to assist in the activation of the N≡N bond, typically promoting associative reaction pathways rather than direct dissociation. Simultaneously, the exposed transition metal atoms (Ti sites) and inherent structural defects on the MXene basal planes have been proposed as potential active sites for N_2 chemisorption and activation. However, it is crucial to recognize that the practical application of these sites in aqueous media is highly challenged by competitive hydrogen evolution and their susceptibility to poisoning by oxygen or water under ambient conditions. Overcoming these limitations through structural-plasmonic synergy can theoretically facilitate the sequential proton-coupled electron transfer steps, establishing a robust and sustainable pathway for artificial nitrogen fixation [58, 73, 74].

Beyond energy generation, the formidable redox capacity of these plasmonic heterojunctions is highly applicable to advanced environmental purification. Utilizing the full solar spectrum (UV-Vis-NIR), the synergistic charge separation mechanisms inherent to MXene-based Schottky or step-scheme (S-scheme) heterojunctions generate long-lived, highly reactive oxygen species (ROS) such as hydroxyl radicals (OH) and superoxide radicals (O_2^-). This enables the rapid and non-selective degradation of recalcitrant organic pollutants, including pharmaceutical residues (tetracyclines and antibiotics), endocrine-disrupting chemicals, and industrial dyes. The strong interfacial electric field ensures that the powerful oxidizing potential of the photogenerated holes in the semiconductor's valence band is strictly preserved, while the MXene's intrinsic plasmonic properties accelerate electron consumption. While the ultimate goal is the complete mineralization of toxic contaminants into harmless H_2O and CO_2, it is scientifically imperative to acknowledge that photocatalytic processes do not inherently guarantee the absence of toxic secondary products. Partial oxidation can frequently produce intermediate byproducts that are more persistent or toxic than the parent compounds. Therefore, rigorously tracking these intermediates (e.g., via liquid chromatography-mass spectrometry) and quantifying Total Organic Carbon (TOC) removal are essential prerequisites to verify true mineralization and provide a genuinely safe and efficient solution for advanced wastewater treatment [75-77].

6. Long-term Photostability and Reusability

A fundamental prerequisite for the practical implementation of photocatalysts in real-world energy conversion systems is ensuring their long-term photochemical stability and reusability. Although pristine MXenes exhibit extraordinary

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optoelectronic properties, they are inherently susceptible to structural degradation and oxidation in aqueous environments under harsh light irradiation. This oxidation not only deteriorates their metallic conductivity but also depletes the free electron density essential for sustaining their intrinsic localized surface plasmon resonance (LSPR) [78-80]. In unmodified or heavily oxygen-terminated MXenes, these functional groups can act as chemical bridges that inadvertently accelerate the adsorption and dissociation of water and oxygen molecules. This process activates the kinetics of spontaneous oxidation, gradually converting the MXene into structurally defective TiO_2, leading to a severe decline in performance, evidenced by up to a 36.7% drop in efficiency after only four consecutive cycles in certain reported systems [81, 82].

To overcome this critical structural limitation, surface passivation through the rational engineering of terminal moieties (T_x) has emerged as one possible stabilization strategy. Replacing these detrimental oxygen-dominated terminations with highly electronegative elements, such as fluorine (-F), can establish a defensive barrier against oxidative degradation. From a physicochemical perspective, the extreme electronegativity of fluorine (3.98) induces the formation of exceptionally strong polar bonds with the titanium (Ti) atoms in the outer layer of the MXene. These strong bonds effectively localize the d-orbital electrons of titanium, thereby reducing its thermodynamic tendency to participate in oxidation reactions [83, 84]. However, it is crucial to emphasize that fluorine termination cannot be described as a universal guarantee for long-term photostability. The actual stability of MXenes remains highly dependent on a complex interplay of factors, including specific composition, defect density, dissolved oxygen concentration, water content, illumination intensity, reaction temperature, initial surface chemistry, and their specific synthesis and storage history. Empirical evidence confirms this protective mechanism in specific experimental contexts; for instance, certain fluorine-rich MXenes exhibit distinguished structural stability, demonstrating a marginal efficiency loss of merely 7.9% after four consecutive photocatalytic cycles [16, 85, 86].

Beyond chemical surface passivation, the rational design of heterojunction architectures with robust semiconductors such as CdS, g-C_3N_4, or TiO_2 provides a synergistic dual-encapsulation and protection mechanism. In these composite systems, the spatial arrangement of the semiconductor phase acts as a physical shield, protecting the vulnerable MXene core from corrosive external environments [87, 88]. Reciprocally, this architecture profoundly alters the electron-hole dynamics to protect the semiconductor itself. By rapidly extracting photoexcited holes or electrons via the highly conductive MXene network, the system can effectively suppress the detrimental phenomenon of anodic photo-corrosion in vulnerable semiconductors such as CdS, thereby significantly enhancing the durability of the entire ternary nanocomposite. Systematic structural assessments of recycled composites frequently corroborate the validity of these protective strategies [89, 90]. Engineered nanocomposites, such as $Ti_3C_2T_x$/CdS and $Ti_3C_2T_x$/C_3N_4, have experienced negligible reductions in their reaction rate constants (k) merely 2.3% and 3.3%, respectively after extensive photodegradation cycling [91-93]. This exceptional stability is not an isolated phenomenon; it has been clearly documented in magnetized MXene structures over seven cycles, in Ag_3PO_4-based Schottky catalysts over eight cycles (maintaining an impressive efficiency of 68.4%) [94], and in $CdLa_2S_4$/Ti_3C_2 water-splitting systems following six continuous and demanding operational cycles [95]. Post-reaction analyses utilizing transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) are frequently employed to evaluate the structural retention of these composites. In several reported systems, such imaging and crystallographic data indicate that the 2D morphology, the layered structure of the MXene, and the phase architecture of the heterojunctions are largely preserved over multiple laboratory testing cycles (typically 4 to 8 runs), with minimal observable phase degradation. Nevertheless, because laboratory cycling tests cover relatively short operational durations, further extended durability studies under continuous, realistic operating conditions are still needed. Consequently, MXene-based photocatalysts, when integrated with surface passivation and heterojunction architectures,

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demonstrate promising improvements in structural integrity and photochemical stability, representing an important step toward their potential use in practical applications [96-98].

7. Future Perspectives and advancement applications

The rational integration of plasmonic phenomena with MXene-semiconductor heterojunctions represents a paradigm shift in the design of next-generation photocatalysts. As extensively discussed, the synergistic triad of LSPR-induced hot electron generation, the exceptional charge-channeling capability of the MXene electron sink, and the directional carrier separation at the heterojunction interface offers a promising pathway to address the thermodynamic and kinetic bottlenecks of traditional photocatalysis. These engineered architectures have demonstrated highly competitive efficiency in critical energy conversion processes, most notably photocatalytic hydrogen evolution and the reduction of CO_2 to solar fuels as well as in the advanced remediation of recalcitrant environmental pollutants. However, transitioning these highly engineered nanomaterials from laboratory-scale demonstrations to robust industrial-scale applications necessitates overcoming several formidable challenges [11, 19, 99].

7.1. Current Challenges and Limitations

Despite remarkable progress, the field of MXene-based plasmonic photocatalysis confronts critical challenges that must be urgently addressed for practical deployment. The most significant impediment to the long-term application of MXenes is their inherent susceptibility to oxidative degradation, particularly in aqueous environments and under the highly oxidative conditions characteristic of photocatalysis. Exposure to water, dissolved oxygen, and photogenerated reactive oxygen species (ROS) inevitably leads to the structural degradation of the MXene basal plane, frequently resulting in the transformation of $Ti_3C_2T_x$ into defective TiO_2 phases. This degradation drastically diminishes their metallic conductivity, curtails their function as efficient electron sinks, and dampens their intrinsic LSPR capabilities. While surface passivation provides preliminary protection, achieving absolute long-term operational stability remains a major concern.

Another formidable barrier is the economic viability associated with traditional plasmonic systems. Historically, the highest-performing plasmonic heterojunctions have relied heavily on noble metals, such as Au, Ag, and Pd, to harvest broadband light and generate hot electrons. However, the natural scarcity and exorbitant cost of these precious metals fundamentally limit the economic feasibility of deploying these photocatalytic systems on a massive, industrial scale. Consequently, finding cost-effective, scalable alternatives that can replicate or exceed the plasmonic enhancements traditionally provided by these expensive elements is a key challenge for large-scale applications.

Finally, the scalability and environmental impact of current synthesis protocols present complex engineering hurdles. Conventional synthesis methods for MXenes, such as the selective etching of MAX phases using concentrated hydrofluoric acid (HF), are highly hazardous, environmentally toxic, and prohibitively difficult to scale up safely. Furthermore, ensuring the uniform and reproducible deposition of semiconductor phases onto MXene nanosheets without inducing severe restacking or agglomeration at a commercial scale remains a significant challenge. Addressing these limitations through the development of greener, cost-effective synthesis methods and scalable assembly processes is absolutely essential for the future commercialization of MXene-based photocatalysts.

To unlock the full potential of plasmonic MXene-semiconductor heterojunctions and facilitate their real-world deployment, future research must prioritize the exploitation of intrinsic MXene plasmonics alongside sustainable synthesis protocols. A paramount objective is to completely phase out expensive noble metals by fully leveraging the intrinsic LSPR properties of highly conductive MXenes. This can be achieved by meticulously tuning their surface terminations, such as optimizing the [O]/[F] ratio, to modulate carrier densities and enhance the electromagnetic near-field without the need for precious

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metals [19, 100, 101]. Additionally, integrating earth-abundant plasmonic alternatives, such as transition metal nitrides (e.g., TiN or ZrN), offers robust LSPR effects in the visible and NIR regions and provides superior thermal stability for harsh photocatalytic conditions [102-104]. To complement this material optimization, addressing the toxicity and oxidative degradation associated with traditional synthesis is critical. Future designs must adopt fluorine-free, green synthesis methods, such as Lewis acidic molten salt etching, which have shown extraordinary promise in enhancing intrinsic oxidation stability while preserving catalytic activity [105, 106].

Table 3. Summary of Strategic Directions for MXene-Semiconductor Heterojunctions.

No.	Strategic Direction	Key Objectives	Expected Outcomes and Impact
1	Exploiting Intrinsic MXene Plasmonics & Earth-Abundant Alternatives	• Phase out expensive noble metals. • Tune **[O]/[F]** surface ratios and carrier densities. • Integrate transition metal nitrides (e.g., TiN, ZrN).	• Development of direct, noble-metal-free LSPR pathways. • Superior thermal and chemical stability under harsh photocatalytic conditions.
2	Advanced Interface Engineering & Green Synthesis	• Adopt fluorine-free, green synthesis (e.g., Lewis acidic molten salt etching). • Apply ALD conformal coatings. • Engineer Z-scheme and S-scheme architectures.	• Enhanced intrinsic oxidation stability with non-toxic fabrication. • Protection against oxidants while maintaining unimpeded charge tunneling.
3	Expansion of Multifunctional Environmental Applications	• Target the simultaneous treatment of mixed wastewater contaminants. • Combine antibiotic degradation with heavy metal reduction (e.g., Cr(VI) to Cr(III)).	• Comprehensive and synergistic environmental remediation. • Establishment of robust, scalable dual adsorption-photocatalysis technologies.
4	Integration with Advanced Characterization & Machine Learning	• Utilize *in situ* and *operando* spectroscopy (e.g., ultrafast transient absorption). • Apply Artificial Intelligence (AI) and Machine Learning (ML) algorithms.	• Explicit decoupling of nanoscale charge transfer and photothermal dynamics. • Intelligent, predictive design of optimal band alignments and material geometries.

Beyond synthesis, advancing structural design through interface engineering is essential for expanding the multifunctional environmental applications of these heterojunctions. Developing ultra-thin, conformal protective coatings via Atomic Layer Deposition (ALD) or engineering advanced Z-scheme and S-scheme charge transfer architectures can effectively shield the MXene from direct exposure to oxidants while maintaining unimpeded charge tunneling. These structurally robust and optimized architectures hold immense potential for the comprehensive remediation of complex, real-world wastewater. Consequently, future studies should focus on the simultaneous, synergistic treatment of mixed contaminants, leveraging the dual adsorption-photocatalysis capacity of MXenes. For instance, the concurrent degradation of pharmaceutical residues, such as antibiotics, coupled with the reduction of highly toxic heavy metal ions like Cr(VI) to Cr(III), will be a crucial milestone in developing highly efficient, scalable water purification technologies.

Finally, the rational design of the ultimate photocatalyst demands the integration of advanced characterization techniques with next-generation computational modeling. Researchers must increasingly leverage *in situ* and *operando* spectroscopic techniques, such as ultrafast transient absorption spectroscopy, to explicitly decouple the complex charge transfer dynamics and photothermal effects at the nanoscale. Coupling these advanced empirical diagnostics with Artificial Intelligence (AI) and Machine Learning (ML) algorithms will dramatically accelerate the discovery of optimal material combinations, structural geometries, and interfacial band alignments. This multidisciplinary approach will not only unravel the

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fundamental plasmon-driven charge kinetics but will also pave the way for the intelligent, predictive design of highly efficient, durable, and commercially viable plasmonic MXene-semiconductor systems for both energy conversion and environmental detoxification. A summary of Strategic Directions for MXene-Semiconductor Heterojunctions in the SPR concept is presented in **Table 3**.

8. Conclusion

The global imperative to transition toward sustainable, carbon-neutral energy paradigms and comprehensive environmental remediation has driven the rapid evolution of advanced photocatalytic technologies. This review has systematically examined how the integration of plasmonic phenomena with MXene-semiconductor heterojunctions offers a promising approach to mitigating the inherent bottlenecks of traditional photocatalysis, namely, sluggish charge transfer kinetics and rapid electron-hole recombination. The enhanced photocatalytic performance observed in specific engineered architectures arises from a conditional, multi-dimensional interplay of mechanisms. Plasmonic excitation, whether originating from integrated noble metal nanoparticles or harnessed from the intrinsic localized surface plasmon resonance (LSPR) of specific MXene compositions under appropriate morphological and optical conditions, can function as a potent optical amplifier. Where experimentally verified, this effect extends light absorption into the visible and near-infrared spectra and may facilitate the generation of energetic hot carriers capable of crossing interfacial barriers when properly energetically aligned.

Concurrently, 2D MXene nanosheets, endowed with variable but often high metallic-like conductivity, tunable surface terminations (such as modulated [O]/[F] ratios), and adjustable work functions, can serve multiple roles. Depending on the specific heterojunction design, they may act as optical absorbers and/or effective electron-extracting cocatalysts. Under favorable band alignment and minimal Fermi-level pinning, this configuration can promote directional charge carrier separation, extending carrier lifetimes and supplying electroactive sites for surface redox reactions. Consequently, appropriately designed MXene-semiconductor heterojunctions have demonstrated notable improvements in thermodynamically demanding, multi-electron energy conversion processes at the laboratory scale. As discussed, these systems can enhance photocatalytic hydrogen evolution rates, support the reduction of CO_2 into solar fuels, assist in ambient nitrogen fixation (NRR), and promote the degradation of recalcitrant environmental pollutants, provided that reaction parameters and intermediate toxic byproducts are rigorously monitored and managed.

Nevertheless, significant scientific and engineering challenges remain, most notably the intrinsic oxidative susceptibility of MXenes in aqueous media, the need to conclusively decouple plasmonic hot-carrier effects from photothermal contributions, the economic constraints of noble metal dependency, and the complexities of scalable, green synthesis. While emerging strategies such as surface termination engineering, protective 2D/2D interfacial encapsulation, and the exploration of earth-abundant plasmonic alternatives show encouraging laboratory-scale results, extensive long-term operational validation is still required. Ultimately, plasmonic MXene-semiconductor nanocomposites represent a dynamic research frontier in materials science, offering valuable mechanistic insights and design principles to guide the future development of solar-to-chemical energy conversion technologies.

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E. F.G.: Validation, Investigation, Data curation, Methodology, Writing – draft. **M.A.**: Validation, Supervision, Methodology, Writing – editing. **F. R.**: Validation, Supervision, Methodology, Writing – editing.

Declaration of Competing Interest

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

Data Availability

Data can be made available upon request.

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