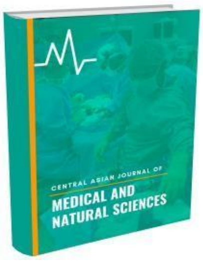

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Article

Recent Progress in Plasmonic Nanomaterials and Their Physicochemical Applications

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Abstract: Localized surface plasmon resonance (LSPR) is a phenomenon that is unique to plasmonic nanomaterials and has been the subject of considerable scientific interest due to the material's optical, electronic, thermal and physicochemical properties. In particular these nanostructures are characterized by exciting interactions with electromagnetic radiation, which allows for a wide range of applications in the field of sensing, catalysis, biomedicine, environmental treatment, and solar energy conversion. The synthesis techniques have advanced significantly in recent years which has resulted in better control over the size, morphology, composition, and surface functionalization of the nanoparticles, and in more stable and tunable plasmonic properties. Moreover, application of plasmonic nanomaterials with semiconductors, polymers, and hybrid nanostructures have provided the enhanced photocatalytic activity, photothermal conversion, and biosensing sensitivity. In the biomedical field, plasmonic nanoparticles have proven to play a promising role in targeted drug delivery, cancer photothermal therapy, molecular imaging and diagnostic biosensors. Moreover, their physicochemical properties are helpful for the charge transfer process, hot electron generation and better catalytic reaction process in environmental and energy-related technologies. Nevertheless, issues concerning toxicity, large-scale fabrication, reproducibility, and long term stability are still major concerns to address for practical and clinical implementation. The present review emphasizes the recent advances on plasmonic nanomaterials with respect to their physicochemical properties, synthesis methods and novel multifunctional applications in diverse fields of science and technology.

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1. Introduction

Plasmonic nanomaterials occupy a prominent position among nanostructured materials, enabling surface catalytic reactions, sensing of trace molecular species or disease markers, increased efficiency in solar energy harvesting and storage for sustainable energy conversion, and biomedicine. Nevertheless, many fundamental aspects of their interaction with matter at the nanoscale are unresolved, restricting their usage in advanced applications. Plasmonic phenomena emerge from the collective oscillation of conduction-band electrons. Surface plasmon resonance (SPR) manifests at a metal/dielectric interface, while localized surface plasmon resonance (LSPR) arises in individual metal nanostructures or closely spaced assemblies. The LSPR frequency depends on the size, shape, and surrounding dielectric; closed porous systems provide a versatile means of tuning. Only a few materials exhibit SPR and LSPR in the visible to near-infrared range:Molecular plasmons are surface-bound excitations at a lower dimension like monolayers or polymers. LSPR adheres to Maxwell's theory, yet quantum-size and nonlocal effects remain areas of extensive investigation [1]. The ability of plasmonic nanomaterials to concentrate and detect light locally at the single-molecule level facilitates detection in the parts-per-quadrillion range 2. Intensified processes driven by non-radiative electron and energy transfer to adjacent reactants have also been observed [2].

Physicochemical interface catalysis, digital information transmission at the nanoscale, enhancement of light absorption and exciton generation in solar cells, and photothermal therapy are recognized as important applications of plasmonic nanomaterials. Important criteria for distinct physicochemical applications include material composition, structure, spatial configuration, size, and shape, which influence plasmon resonance, degradation pathways, and toxicity. Significant figures-of-merit have been established to rationalize and optimize these systems [3].

Fundamentals of Plasmonic Nanomaterials

Plasmonic nanomaterials leverage collective excitations of free electrons to produce optical effects that are sensitive to size, shape, composition, and the dielectric environment. These excitations are governed by Maxwell’s equations and arise from the polarization of conduction-band electrons in metallic materials. In small particles, the excitation is known as localized surface plasmon resonance (LSPR); in extended structures, the excitation is termed surface plasmon resonance (SPR). Nanoplatelets produce several collective modes associated with distinct LSPR and SPR bands. Collective interactions scale with n1/3, where n is particle number density. Changes in dielectric environment are quantitatively analyzed using effective medium theory; particle-particle coupling is described using coupled-dipole theory [4,5].

Plasmonic nanomaterials can be broadly classified into noble metals (silver, gold, copper, platinum), metal alloys (silver-gold, silver-copper, and gold-copper), transition metal nitrides (TiN, NbN), and doped semiconductors (ZnO, TiO2, SnO2, TiN). The combination of low loss and high field enhancement makes noble metals the standard benchmark in plasmonics [6]. Absorption loss depends on the interband transition and is more significant in materials with a small band gap. Common synthesis routes include chemical and physical methods and templated preparations. Morphology control is achieved through seed-mediated growth, etching, and simple chemical reactions. Figures of merit (efficiency, stability, toxicity) are used to choose suitable materials for physicochemical applications [7,8].

Surface Plasmon Resonance Principles

Surface plasmon resonance (SPR) refers to the electronic oscillation of free electrons within a continuous metallic structure excited by incident electromagnetic radiation at the interface between a metal and a dielectric medium. In contrast, localized surface plasmon resonance (LSPR) describes the collective electronic oscillation of free electrons confined to nanometric metallic structures. When the energy of incident photons matches the energy of inter-band electronic transitions, the excitation of collective electron oscillation occurs and leads to electronic transitions that can be observed as additional optical response [9,10]. The SPR phenomenon predominantly occurs in the ultraviolet region, while the LSPR phenomenon can be activated in the entire ultraviolet-visible near-infrared (UV-Vis-NIR range) region. These excitation modes are intrinsic properties of metallic materials and are strongly influenced by the material type, shape, size, and dielectric environments of metallic particles 9. Plasmonic nanoparticles have been extensively investigated as optical structures due to their localized surface plasmon resonance (LSPR), which can be excited by light at wavelength ranging from ultraviolet to infrared [11,12].

Graphene has been widely used as a plasmonic material. It can excite a plasmonic resonance peak ranging from its UV-Visible NIR (near infrared) and electromagnetic enhancement can be perceived from first principle simulation. However, the lack of adequate accessibility of dielectric molecules to graphene and highly spontaneous oxidation as well as surface modification limit the utilization of the material in photo-thermal applications. Nevertheless, plasmons excited from the two-dimensional carbon nanomaterials and plays an important additional role in enhancing the light-matter coupling in these materials [13]. Plasmonic nanomaterials possess an unexplored capacity for novel applications such as photocatalysis, chemical transformations, wide-field imaging/photothermal therapy and SERS. Plasmonic nanomaterials utilize hot carriers from enhanced local electromagnetic field in the accessible UV-Vis-NIR. An exciting application of plasmonic nanomaterials is the detection of chemical vapour and the detection limit is among the requirement for application for sensor. Moreover, these nanoparticles can also act as stable SERS substrates at elevated temperature. Thus, addressing the key gaps in the understanding of fundamental and material aspects of plasmonic nanomaterials enables the exploration of the unique functionalities. It can also extend their applications to catalysis and chemical transformations [14,15].

Material Classes and Optical Properties

Plasmonic nanomaterials encompass metals and other materials supporting addressed localized surface plasmon resonance (LSPR) modes. Plasmonic LSPRs appear when free charge carriers exist at certain frequencies. Hence, plasmonic nanomaterials must also have suitable electronic band structures and engineering principles allow some semiconductors to meet these criteria 16. All plasmonic materials exhibit sharp and strong optical resonances, while materials that do not support plasmons exhibit weak, broad, and adjacent nonlinear optical responses [16,17].

Noble metals such as silver and gold are well-established plasmonic materials for confined surface plasmons and supported Au, Ag, and their alloy nanoprisms [18,19]. Conductive oxides and oxides of noble metals with sufficient free charge carriers fall into this category but remain underexplored. First-order phase transition metal-nitride plasmonic nanocrystals of titanium nitride (TiN) exhibit unique hot-carrier generation as well as stable LSPRs that can be tailored by alloying Fe and co-fabrication of controlled TiO2-semiconductor-precursor oxide plasmonic TiN. Composite plasmonic Ag–TiN nanocrystals further combine multiple functionalities detected in locally captured photothermal activities in Cu2O and TiO2 plasmon-enhanced photocatalysis, UV–Vis – NIR CO2 plasmonic nanodot and hydride sunlight, and enhanced catalysis with plasmon-induced titania coupling plasmonic TiN and TiN/substrate Cu0 boron-doped nanocrystals [20,21].

Synthesis and Morphology Control

Plasmonic nanomaterials are materials that can support plasmonic or plasmon-like excitations, which also include phononic, excitonic, and magnonic modes [22]. Plasmonic nanomaterials are classified as metal-like systems (noble metals, alloys, transition metal nitrides, doped semiconductors) and metal-free systems (metal oxides, carbon nanomaterials, dielectrics, semiconductors), before becoming a generic term including materials that can be synthesized in controlled manner at nanoscale [23,24]. Metal-nanostructure-based plasmonic and molecular self-assembly approach as well as growth of size-controlled plasmonic metal core from self-assembled nanodots develop great interest in nanomaterial synthesis. Synthesis procedure can be divided into chemical (solution-based or gas-phase approach), physical (vapor-phase, wet-chemical and in-situ growth) templated top-down (moulding, etching, and lithography), and secondary growth methods [25,26].

2. Materials and Methods

According to the review article methodology, it was a literature-review methodology for the purpose of reviewing on the developments related to plasmonic nanomaterials and its physicochemical applications. Plasmonics: The relevant peer-reviewed researches, reviews, and scientific reports were systematically identified followed by integration to gain a better understanding of plasmonic nanomaterials with an emphasis on localized surface plasmon resonance (LSPR). This review focused on the aspects such as basic principles of surface plasmon resonance, classification of materials, synthetic strategies, morphology modulation techniques followed by physicochemical characterization methods and computational modeling methods from the selected literature. Optical, thermal, electronic and catalytic properties of studies addressing noble metals, metal alloys, transition metal nitrides and doped semiconductors and hybrid plasmonic systems were examined. Special consideration has been given to different synthesis methods like chemical, physical, templated and seed-mediated approach and characterization techniques such as UV–Vis–NIR spectroscopy, FTIR, Raman spectroscopy, SEM, TEM, AFM and electron energy-loss spectroscopies. Over the years, this information was analyzed to correlate nanoparticle composition, size and shape with their plasmonic performance in various dielectric environments. Moreover, you were also surveyed to find the new trends and developments in photocatalysis, electrocatalysis, biosensing photothermal therapy, biomedical imaging, solar energy conversion as well as hydrogen evolution and carbon dioxide reduction. Other aspects include toxicity, environmental compatibility, stability over time, reproducibility and scalability were also evaluated 13. The methodology allowed a comprehensive assessment of the status and progress of plasmonic nanomaterials, covering major breakthroughs, bottlenecks for implementation, and research outlooks necessary to advance their use towards scientific, industrial, environmental or biomedical applications by synthesizing results from multiple different studies.

3. Results and Discussion

Physicochemical Characterization Techniques

Physicochemical characterization techniques are essential for understanding the fundamental principles underlying plasmonic nanomaterials and relevant information can be extracted using various methods [27,28]. Approaches can be broadly classified into spectroscopic techniques, imaging techniques, and surface/interface studies. Characterization with ultraviolet-visible-near-infrared (UV-Vis-NIR), Fourier-transform infrared (FTIR), Raman, and pump-probe spectroscopies aims to extract the plasmon energy, lifetime, and nonradiative losses of plasmonic nanomaterials. Microscopy techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and electron energy loss spectroscopy (EELS) allow the morphology and crystallinity of the materials to be analyzed and enable mapping of the plasmonic field [29,30]. Surface chemistry and interface studies involve the investigation of ligand binding, charge transfer at the interface, work function, and surface passivation, influencing the stability and reactivity of plasmonic materials [31].

Spectroscopic Methods

Plasmonic materials have drawn extensive interest due to their strong light confinement and scattering at sizes smaller than the excitation wavelength [32]. Early on, considerable efforts focused on characterization of collective oscillation modes of free-electron gas in metallic systems, later termed surface plasmon polaritons (SPPs), localized surface plasmon resonances (LSPRs), and nanoplasmonics, respectively [33]. Plasmon resonances can be coupled via various exterior stimuli, covering the entire electromagnetic spectrum from microwave to terahertz. A broad spectrum of new designs exploiting wavelength, duty cycle, and symmetry has further emerged. Electrons in highdimensional materials can be confined in nanoscale metallic particles and two-dimensional materials, enabling light-matter interaction on a single-atom level [34]. Converted energy loss can trigger chemical reaction and energy transfer, always monitoring behavior evolution. Reactions related to polymeric organic materials, catalytic processes, biomass conversion, and target by-products achieved in the last decade have uncovered plasmonics chemistry that greatly widen preparation limit and fabrication capability. Many fields, including catalysis, energy, biomedicine, chemical detection, and imaging, can benefit from a broad choice metallic nanoparticles, film, nanowires, and porous structure—to facilitate system development [35].

Absorption wavelength, lifetime, and loss rate reflect the intrinsic information of materials without any modification and apply to either material screening or device service. Numerous spectroscopic methods, which provides both temporal and spectral resolution from femtosecond to microsecond, are established to achieve such capability. Plasmonic nanomaterials have demonstrated their tremendous potential in various applications ranging from chemical sensing, biomedicine, photocatalysis, and photocurrent generation. Plasmonic sharing can remarkably enhance the efficiency of these systems, yet the structure and morphology exhibit substantial influence on the effect and are regulated by multiple tuning parameters. Plasmonics evolves to non-thermalized light-matter science. Direct coupling strength of nanolights is governed by superradiance and subradiance play a more deterministic role to predict complex physicochemical platforms [36].

Microscopy and Structural Analysis

The interaction of light with plasmonic nanostructures leads to multiple phenomena, such as localized surface plasmon resonances, surface-enhanced Raman scattering, guided surface-plasmon waves, and many more. A combined understanding of their morphology (size, shape, structure, agglomeration degree, etc.) and their optical responses is critical for a rational design of plasmonic devices. The characterization of such objects, particularly at the nanoscale, remains challenging [37,38]. Therefore, a thorough examination of established and emerging techniques is of paramount importance. Several studies propose a classification of plasmonic phenomena based on the dimensionality of structures (zero-, one-, two, and three-dimensional). In this context, zero-dimensional (0D) particles includes isotropic systems, like spherical nanoparticles, which support size-dependent plasmonic colouration. Conversely, elongated objects such as nanorods or nanowires that exhibit shape-dependent surface plasmon resonances correspond to one-dimensional (1D) objects. Two-dimensional (2D) systems encompass different geometries like solid or nanopatterned films, which control the propagation of surface plasmons [39,40]. Finally, three-dimensional (3D) hollow structures allow for the study of multilayered materials and a greater number of surface plasmon modes and coupling between different layers [41].

Surface Chemistry and Interface Studies

Surface chemistry and interface studies of plasmonic nanostructures play a vital role in applications such as plasmonic sensors, molecular spectroscopy, and catalysis. These studies investigate ligand–metal interactions, charge transfer, work function modulation, and passivation effects. Controlling the formation and distribution of hotspots during nanostructure fabrication enables precise optimization for enhanced surface-enhanced Raman scattering (SERS) responses, which support early diagnosis of liver cancer. High-fidelity fabrication of complex geometries is therefore crucial, yet conventional techniques such as electron-beam lithography remain time-consuming and may introduce unwanted contaminants that hinder the performance of nanoscale devices [42,43].

Thermal and Optical Nonlinearities in Plasmonic Systems

Collective electron oscillations (surface plasmons) may be coupled to electromagnetic waves. Surface plasmon polaritons are coupled modes that propagate laterally along the metal/dielectric interface. Surface plasmon polaritons on bulk metals exist at infra-red wavelengths, whereas materials for visible wavelengths typically rely on localized surface plasmon resonances. These are supported by nano-dimensional metal particles instead of macroscopic interfaces. The resonance condition depends on particle size, shape, and dielectric environment, which control the particle geometry also dictates the particle geometry [44,45]. The dependences have been characterized experimentally for spheres (1 nm–1 μm)/spheroids (1 nm–10 μm) and nanorods (4–300 nm) [44]. The abundant phenomena lend themselves to a range of applications across catalysis, chemical sensing, energy conversion, and bio-imaging/therapy. Specific plasmonic material systems (gold, silver, and copper; supplementary alloys; certain transition metal nitrides; n-type/semiconductor detailed synthesis routes also underpin subgenus, complemented by templated approaches that exploit shadowing/projection deposition [46].

Plasmonic Nanomaterials in Catalysis and Chemical Transformations

Plasmonic nanomaterials play a significant role in catalysis and chemical transformations, related to hot-electron generation within metals absorbing visible light. Well-defined plasmonic systems can attain plasmon lifetimes longer than 100 fs, permitting hot-electron transfer to surrounding species which significantly enhances reactions. Plasmonic field-driven photocatalytic activity is often linked to the formation of hot electrons that are injected into the conduction bands of the semiconductor, while hot holes are injected into semiconductor valence bands. In this case, plasmonic-supported semiconductor systems can also enable plasmonic photothermal selenium electrocatalysis. Accordingly, a competitive tandem photoelectrocatalytic H2 evolution route is also reported in CoP/CoP2 heterostructured catalysts, where the CoP2 plays a crucial role in hot-carrier transport and CoP in subsequent H2 evolution [47,48].

Electrocatalysis and photoelectrochemical applications also benefit from plasmonic materials, supporting charge routing in electrocatalytic processes. Plasmon-induced charge separation within purely metallic Au nanocrystals and subsequently deposited catalysts also enables the transport of separated surface hot electrons toward catalytic reaction sites and adjustment of the effective overpotential. Charging–discharging processes and enhanced charge routing are crucial for boosting methanol oxidation and hydrogen evolution in plasmonic-elevated energy-storage systems. Furthermore, Co–Ni alloy-decorated plasmonic nanostructures enhance the light-activated electrochemical CO2 transformation efficiency of low-concentration CH4 in vapor–liquid–solid synthetic processes. The hierarchy of plasmonic cationic nanoparticles on large-area semiconducting matrices promotes efficient sunlight-conversion water-splitting systems via parallel hot-electron-transfer pathways and accelerates H2 generation [49].

Photocatalysis Mechanisms

Localized surface plasmon resonances (LSPRs) in metal nanoparticles can be excited by incident light, leading to collective oscillations of conduction electrons. Plasmonic nanomaterials support energetically accessible LSPR modes in the ultraviolet, visible, and near-infrared regions, which can couple to molecular vibrations, thereby facilitating light–matter interactions. Nanostructured systems such as metal/semiconductor composites or metal-coated semiconductor nanoparticles offer additional pathways for the efficient transfer of photogenerated electrons and elicit high photocatalytic activities [50]. Such systems exploit plasmonic charge separation, whereby electron transfer occurs from a plasmon-excited state in a noble metal to a semiconductor conduction band 50. Ultrafast spectroscopy has revealed that plasmon-induced charge carriers exhibit hot-electron characteristics and that the excited-state lifetime is similar to that of the LSPR. Hot carriers can participate in various follow-up processes, including further interfacial transfer, scattering back to the metal, or recombination with holes, and thus determine the overall efficiency of plasmonic-mediated photocatalytic processes [51,52].

Electrocatalysis and Photoelectrochemical Applications

Plasmonic nanomaterials have been shown to enhance the performance of multiple catalysed reactions by participating in photochemistry and photoelectrochemical processes [53]. Two mechanisms direct plasmon coupling and the generation of hot charge carriers have been proposed to describe the fundamental pathways involved in the participation of plasmonic materials in such processes. Because hot charge carriers possess excess energy, they can participate in thermodynamically unfavourable charge-transfer reactions. For instance, plasmonic nanomaterials have been demonstrated to increase the formation of hydroxyl radicals from the decomposition of superoxide radicals when they are coupled to TiO2 in visible light photocatalytic degradation systems. Plasmonic materials catalyse hydrogen generation from water splitting systems where hot electrons migrate from a gold surface to the conduction band of TiO2. Such an approach is effective because the band-edge energy of TiO2 combined with plasmonic nanomaterials creates a driving force for charge transfer at the interface. Chemical species such as oxygen and hydrogen facilitate the transfer of the other corresponding charge at the interface, and chemical and catalytic processes become decoupled, limiting the overall strategy to the transfer of the support charge [54]. A similar approach can be developed for plasmon-enhanced electrochemical reactions, but the involvement of an additional layer of chemical complexity makes it more complicated than photocatalysis. Interfacial energetic engineering, charge transport, and tandem photoactive mechanisms have been proposed as means of plasmonic enhancement in electrochemical and photoelectrochemical reactions [55,56].

Sensing, Imaging, and Biomedical Applications

Plasmonic nanomaterials have recently gained increased attention for their potential applications in sensing, imaging, and biomedicine. Devices such as surface plasmon resonance (SPR) biosensors exploit refractive index changes, while other setups leverage plasmon-enhanced scattering for single-molecule detection. Nanomaterials used in these sensing applications can be tailored to achieve low-detection limits in complex media 58. When modified with plasmon-sensitive chemical components, they can also interrogate local conditions, providing complementary yet still highly desired real-time information on selectivity and concentration [57].

Photothermal therapy is a widely studied concept in the biomedical community. Noble metal nanomaterials offer tunable optical absorption, enabling applications ranging from thermal-release drug delivery to DNA-release systems. In addition, photothermal agents that absorb in the near-infrared biowindows minimize photodamage to adjacent healthy tissue, and this infrared hydrophilic core-shell structure has also been incorporated for enhanced 2D and 3D imaging of photothermal therapy effect [58,59].

Biosensing Platforms

Recently, plasmonic nanostructures, including nanoparticles, nanodisks, nanoplates, and nanorods, have emerged as promising sensing platforms for biomolecules. These nanostructures undergo localized surface plasmon resonance (LSPR), depending on their size and shape, resulting in significant electromagnetic field enhancement that is sensitive to refractive index variations [60]. Consequently, they can act as highly selective refractive index and colorimetric biosensors, with detection limits down to 10−15 M 61. Furthermore, noble metal nanoparticles can accelerate surface-enhanced elastic scattering (SEES) and surface-enhanced Raman scattering (SERS), enabling detection of biomolecules like DNA, proteins, and viruses down to the single-molecule level. These sensors record bounce-back signals from LSPR and SERS, allowing precise analysis of target biomolecules [61,62].

Plasmonic nanostructures also serve as transducers to couple photoluminescence from quantum dots or organic dyes into the substrate through surface plasmon-coupled emission (SPCE) 63. Additionally, they optimise quantum-dot–metal and dye–metal separation distances by exploiting the long-range propagation of surface plasmon polaritons (SPPs). Plasmonic sensors based on optical waveguides and photonic circuits enable real-time, pluggable, and ultra-compact sensing platforms. Diverse fabrication options facilitate the integration of these devices with microfluidics or other lab-on-a-chip systems for on-site analysis beyond the laboratory setting [62].

Photothermal Therapy and Biomedical Imaging

Plasmonic nanoparticles can absorb and convert light energy into localized heat when illuminated at their resonance frequencies, making them useful for photothermal therapy [64]. Gold, a noble metal, is highly inert and suitable for PTT because of its low cytotoxicity and high photostability. Combining different nanostructures into nanohybrids enhances properties and functionalities for diagnostics, imaging, and cancer treatment. Stability, biocompatibility, and precise heating control are critical for clinical applications. Regulatory considerations are evolving to ensure safety before commercial use, providing a framework for the responsible development and application of plasmonic photothermal technologies [65,66].

Plasmonic nanoparticle-based PTT can induce localized and irreversible damage to tumors by hyperthermia without harming surrounding healthy tissue [67]. A platform combining single-particle analysis and PET imaging quantifies heat generation and assesses therapeutic effectiveness. In vitro measurements of heat generation and absorption cross-section are compared to theoretical predictions. In vivo experiments monitor heat produced by irradiated nanoparticles in tumor xenografts with PET imaging. Near-infrared resonant silica–gold nanoshells demonstrate superior heating performance compared to colloidal spherical gold nanoparticles. PET imaging reliably indicates early treatment response. This approach benchmarks the photothermal efficiency of various plasmonic nanoparticles for cancer therapy [68].

Energy Conversion and Storage Implications

Plasmonic nanomaterials can also facilitate solar energy conversion processes that directly utilize energy from the sun or convert waste heat into electricity. In general, enhancing the activity of energy-related plasmonic processes remains one of the most active research directions in the field. Hot electron injection can drive plasmon-enhanced photocatalytic hydrogen evolution and CO2 reduction reactions at plasmonic interfaces, creating a pathway for solar energy storage or valorization in chemical feedstock. Recent advancements in this area centre on new structures, functionalization with additional catalysts or co-catalysts, or the additional engineering of carrier dynamics [69].

Plasmonic nanoparticles and other structures that support confined plasmons can create electromagnetic fields that facilitate the absorption of light in two-dimensional materials or semiconductor nanocrystals. This additional harvesting can be achieved via photothermal heating, hot-electron transfer, or the field versus energy-transfer mechanisms characteristic of energy-transfer processes. Picosecond laser pulses can also cause plasmonic nanostructures to generate electromagnetic pulses to couple to intersubband transitions in certain quantum wells, enhancing individual absorption in the far-infrared region beyond the fundamental limit of the two-dimensional material itself [70].

Plasmonic-Enhanced Photoelectrochemical Cells

Adding plasmonic nanostructures to photoelectrochemical cells can increase efficiency and expand the range of materials that function as semiconductors. Plasmonic nanomaterials improve light harvesting by enhancing near-field intensity and subsequently improving photocurrent generation at semiconducting photoanode/electrolyte interfaces [71,72]. Moreover, photogenerated hot electrons in plasmonic materials can be injected into the conduction band of a semiconductor, where they contribute to water-splitting reactions. For instance, gold nanoparticles incorporated into titanium dioxide or ferric oxide photoanodes enhance photocurrent via these mechanisms. CO2 reduction, previously limited to semiconductor catalysts, can now be performed at plasmonic deposits on ferroelectric photoanodes. Nanostructured copper, gold, and silver electrodes catalyze multi-step pathways, and the catalytic activity varies significantly with nano-morphology [73,74].

Hydrogen Evolution and CO2 Reduction Interfaces

Plasmonic nanomaterials show great potential in isolating and harvesting solar energy through hybrid plasmonic/co-catalytic materials for hydrogen evolution reaction (HER) and CO2 conversion routes. Plasmonic hybrid catalysts reduce solar-to-chemical-energy conversion overpotentials. Plasmonic catalysts generate hot carriers that can either promote surface reactions or be transferred to an adsorbate to drive surface reactions far from equilibrium. Complex hybrid structures facilitate the separation of the energized carrier from the plasmonic material and further transport it to the co-catalyst [75].

Stability, Toxicity, and Environmental Considerations

Plasmonic nanomaterials, owing to their unique properties, have found many applications in different fields. In biomedical applications, human exposure to their toxic side effects has been highlighted through ecotoxicity and theranostic studies. Various studies have identified toxic effects and cellular responses of gold and silver plasmonic nanomaterials in bacterial, fungi, viruses, and mammalian cell systems, as discussed in [76]. These findings should be taken into consideration when using plasmonic nanomaterials for further applications.

Research studies have shown that plasmonic nanomaterials are capable of enhancing the performance of solar energy, photocatalysis, and batteries by overcoming bandgap limitations. Options for preventing such limitations are the use of other photocatalysts, dye sensitizing, and surface functionalization, the latter increasing lifetime through stabilization and decreasing transport and recombination efficiency. All chemical reactions and processes produce wastes at the end, highlighting the importance of life cycle assessment for new systems involving plasmonic material or devices. In addition to direct input and output, materials and solvents used for cleaning substrates and devices must also be accounted for in a comprehensive analysis [77,68].

Computational Modelling and Design Strategies

Plasmonic phenomena advance the development of next-generation devices and systems by offering new strategies to manipulate light at the nanoscale. Computational modelling provides a versatile toolbox to predict, design, and explore plasmonic nanomaterials and devices. Recent progress in understanding the fundamental principles of linear and nonlinear light-matter interactions enables advanced design methodologies for plasmonics. Computing power has made it possible to address large, complex systems of practical interest, significantly contributing to high-throughput screening and uncertainly quantification of material systems [79].

Computational electromagnetic modelling simulates the interaction of electromagnetic waves with nanoplasmonic structures to obtain relevant experimental measures, allowing theory-to-experiment work flow. Optical scatter and extinction spectra are two key targets obtained by modelling, from which comparison with experiment serves as one of the preliminary tests of accuracy of the model. Analyses of time-dependent near-field of the structure provide additional insight into the underlying mechanics of the system of interest, guiding further experiments for high-impact applications [80].

The wavelength scale of plasmonic systems requires consideration of large mesoscale systems of industrial relevance, leading to a shift toward atomistic modelling. The embrace of a wider variety of materials in plasmonic research motivates investigation of doped semiconductors and the incorporation of explicit solvent and ligands to access the aquatic environment and extend modelling to surface-enhanced Raman scattering systems [81,82].

Future Directions and Emerging Trends

Plasmonic nanomaterials, which harness localized surface plasmon resonances (LSPRs) to couple optical fields on the nanoscale, have become increasingly important for applications in catalysis, sensing, energy, and biomedicine. The relevant physicochemical phenomena at nanoscale interfaces have therefore received considerable attention, supported by advances in fabrication capabilities that allow systematic tuning of size, shape, composition, and architecture. Although substantial progress has been achieved in various areas, several critical challenges remain. Methodologies for quantifying optical properties and plasmonic figures of merit remain underdeveloped, particularly for innovative materials. Robust structure–function relationships that bridge composition, morphology, and electronic structure to plasmonic behavior have yet to be established for many emerging systems [83].

Catalysis continues to be a prominent area of plasmonic research, with photocatalysis and electrocatalysis demanding improved understanding of plasmon-driven mechanisms and plasmon-enhanced energy conversion pathways. Plasmonic materials also play essential roles in novel processes such as selective hydrogenation, polymerization, and CO oxidation and monitoring the dynamics of catalytic systems on the nanoscale remains a critical question. Although understanding the fundamental mechanisms of plasmon-assisted energy harvesting has advanced greatly in recent years, design criteria for efficient plasmonic nanostructures in photoelectrochemical cells, photocatalysis, and CO2 reduction remain illdefined. Meanwhile, demands for large-scale manufacture and eco-friendly materials push the application focus toward stable, non-toxic metals and environmentally benign ligands [84,85].

4. Conclusion

In conclusion, the development of the plasmonic nanomaterials has created many new opportunities for their physicochemical and technological applications in various scientific areas such as catalysis, biosensing, photothermal therapy, environmental remediation and solar energy conversion. Localized surface plasmon resonance (LSPR) has unique optical and electronic properties that have enabled unprecedented light harvesting, hot electron generation, stronger electromagnetic field modification, and photocatalytic efficiency. Recent developments in synthesis of nanoparticles, surface engineering, and hybrid plasmonic-semiconductor systems have further improved the stability, tunability and multifunctional properties of these materials. Nevertheless, there are key issues that need to be addressed for mass production, storage, biocompatibility, toxicity studies, and basic understanding of the plasmon-mediated processes. Further interdisciplinary research is needed to fine-tune plasmonic nanomaterials, and speed up their progression toward clinical, industrial, and environmental applications.

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