

Review

Review of Experimental Setups for Plasmonic Photocatalytic Reactions

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Received: 13 November 2019; Accepted: 26 December 2019; Published: 31 December 2019



Abstract: Plasmonic photocatalytic reactions have been substantially developed. However, the mechanism underlying the enhancement of such reactions is confusing in relevant studies. The plasmonic enhancements of photocatalytic reactions are hard to identify by processing chemically or physically. This review discusses the noteworthy experimental setups or designs for reactors that process various energy transformation paths for enhancing plasmonic photocatalytic reactions. Specially designed experimental setups can help characterize near-field optical responses in inducing plasmons and transformation of light energy. Electrochemical measurements, dark-field imaging, spectral measurements, and matched coupling of wavevectors lead to further understanding of the mechanism underlying plasmonic enhancement. The discussions herein can provide valuable ideas for advanced future studies.

Keywords: plasmonic photocatalytic reactions; photocatalytic reactors; instrumentation

1. Introduction

Applications of photocatalytic reactions have developed extensively since Fujishima and Honda presented their work in the electrochemical photolysis of water in a semiconductor electrode in 1972 [1]. The improvement of processing efficiency was started with the modification of photocatalysts. One modification approach entails loading metal nanoparticles on the surface of photocatalysts [2]. Researchers developing plasmonics perceived a possible breakthrough in plasmonic photocatalytic reactions after the work presented by Awazu et al. [3]. Several studies and reviews related to plasmonic photocatalytic reactions have been published, particularly in the past 3 years [4–21].

Plasmonic photocatalytic reactions are useful in various applications, such as antibiotics [5], photo-deposition [6], H₂ generation [22], and plasmon-induced dissociation of H₂ on Au through the generation of hot electrons [23]. The plasmonic enhancement of photocatalytic reactions is also affected by various experimental conditions. A study reported that in the photocatalytic degradation of methyl orange through a spinning disk reactor [24], the final reserved concentration ratios (C/C₀) for TiO₂ under illumination from a 4-W mercury tube lamp with and without an additional red

light-emitting diode (LED; 637 nm) were 0.71 and 0.62, respectively. The red light slightly suppressed the photocatalytic reactions by interfering with the movement of generated hot charges under ultraviolet (UV) light. However, the final reserved C/C_0 observed for Au-TiO₂ with and without an additional red LED are 0.54 and 0.65, respectively. The Au-TiO₂ hybrid photocatalyst under UV light and additional 637 nm light exhibited approximately 24% greater activity than did the TiO₂ photocatalyst under only UV light. The red light introduced plasmons on the Au side and enhanced photocatalytic reactions. The visible light affects not only the free electrons in the metal nanoparticles, but also hot charges generated in the photocatalyst under UV light illumination. This could occasionally engender ambiguity in the identification of plasmonic effects on photocatalytic reactions.

Plasmonic effects engender not only enhanced photocatalytic reactions but also product selectivity. Cui et al. presented selectivity of benzyl alcohol oxidation reaction products, namely benzaldehyde, benzyl benzoate, and benzoic acid, in plasmonic photocatalytic reactions [25]. A 1500-nm light source yielded 99.57% selectivity toward benzaldehyde, whereas 808 and 980 nm provided 95.87% and 93.43% selectivity, respectively. Moreover, the observed selectivity toward benzyl benzoate changed substantially with light wavelengths. A selectivity of 3.90% was obtained for the 808-nm trial, 5.62% for the 980-nm trial, and only 0.28% for the 1500-nm trial.

This review presents a brief discussion of experimental designs providing plasmonic enhancements of photocatalytic reactions, particle reactors and measurements. Plasmonic enhancement must occur through the light-induced generation of plasmons, such as volume plasmons (VPs), surface plasmons (SPs), or localized surface plasmon (LSPs), to improve processing efficiency in photocatalytic reactions with various plasmonic energy transformation paths [19]. In addition, this review introduces various reactors and identification methods to provide a brief overview of models of plasmonic photocatalytic reactions. In plasmonics, the generation of plasmons, especially SPs and LSPs, must typically match specific coupling conditions to achieve high light-to-plasmon conversion efficiency. Stronger or higher concentration of plasmons, increase the corresponding plasmonic enhancement.

It is confused to identify the plasmonic enhancements of photocatalytic reactions processed chemically or physically. Typically, a chemically plasmonic-enhanced photocatalytic reaction includes the migration of induced hot charges. A physically plasmonic-enhanced photocatalytic reaction goes through “electromagnetic field-enhancement” in the process. This review also briefly identifies how various energy transformation paths enhanced the photocatalytic reaction in chemically plasmonic or physically plasmonic enhancement pathways.

2. Energy Transformation Path of Plasmonic Photocatalytic Reactions

Plasmons are collective oscillations of free electrons at a metal-dielectric interface and are induced by external electromagnetic waves [26,27]. In general, plasmons can be roughly categorized into three types; i.e., VPs, SPs, and LSPs. According to the Drude model, VPs are induced when free electrons in bulk metal resist the penetration of external electromagnetic waves within an extremely small depth. The plasma or natural frequency, $\omega_{pe} = \sqrt{n_e e^2 / m^* \epsilon_0}$ describes the oscillation of electron density that allows wide variations in light transparency. SPs [28,29] are transformed modes of light wave propagating at the interface between negative (metal) and positive (dielectric or semiconductor) permittivity materials. A SP typically has a higher wavevector than that of light propagating in vacuum and in air. Therefore, the SPs generation require a special coupling method, such as the Otto configuration, Kretschmann configuration, grating or rough surface coupling [28]. LSPs are collective oscillation of free electrons generated and localized in a small region under external illumination. Sharp surface structures, such as nanoparticles or edges, gaps, nanometer-sized bumps, and valleys on a metal surface and silver colloid fractal clusters [30], provide a wide range of spatial frequency that can generate plasmon hot spots.

Regarding plasmonic photocatalytic reactions, this review restricts its scope to reactions that involve light harvest through the generation of various plasmons (Figure 1). In such plasmonic photocatalytic reactions, plasmons can modulate photocatalysis through the following effects: (i)

strong light absorption, (ii) intensive far-field light-scattering, (iii) near-field electromagnetic field strengthening, (iii) abundant hot carrier generation and (iv) plasmonic heating effects [19,31].

Light-induced plasmons can elastically or inelastically transform to light again (Figure 1), a phenomenon that is normally viewed as a scattering process. The induced plasmon energy on a metal nanoparticle can be delivered elastically as transferring light energy to nearby bulk materials or dielectric, semiconductor, or metal nanoparticles. Light energy scattering and trapping from metal nanoparticles can increase the photon flux flow through photocatalytic nanoparticles [19,32,33] thus plasmonically enhancing the photocatalytic reaction. The plasmon energy may trigger a photocatalytic reaction as it propagates through a photocatalytic nanoparticle [3]. In this type of plasmonic photocatalytic reaction, the light that can originally excite the reaction on the photocatalyst is focused through the metal nanoparticle and has a relatively higher power intensity. The distance between the metal nanoparticles and the nano photocatalyst is approximately 100 nm or shorter, but direct contact is not necessary. Most studies on plasmonic photocatalytic reactions have used lamps also delivering UV light (e.g., mercury lamp, xenon lamp) for direct energy transformation process.

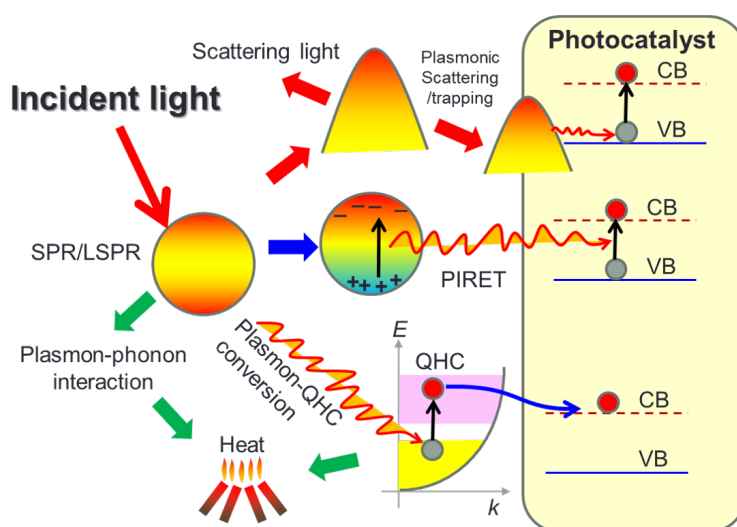


Figure 1. Various types of energy transformation in plasmonic photocatalytic reactions. Figure redrawn from reference [19].

Plasmonic energy in a metal may nonradiatively transfer to a photocatalyst in the near-field zone through a dipole-dipole interaction, and electron-hole pairs are thus generated in the photocatalyst (Figure 1) [19,34,35]. Plasmon-induced energy transformation (PIRET) [19] can occur even in the presence of an insulating space layer with a thickness of up to 25 nm between the plasmonic metal and the photocatalyst.

The plasmon energy can also nonradiatively decay to generate high-energy quantum hot charge carriers through Landau damping with intraband and interband electron transitions [19,36–38]. The hot electrons have a relatively high energy level and can be directly injected into the conduction band of the contacted photocatalyst (Figure 1) [19,39,40]. The electrons injected into the photocatalyst can still be regarded as hot carriers with an energy level higher than the conduction band level. In metal-photocatalyst heterostructures, hot electrons generated and transferred from the metal part exhibit longer excited-state lifetimes than do electrons photogenerated directly within photocatalysts through UV excitation [41]. Therefore, the metal and photocatalyst require only intimate contact for maximized electron injection. Govorov's group [31,42,43] and Kumarasinghe's group [44,45] have developed a single-electron model, involving the assumption of a noninteracting electron gas confined in a uniform background potential in metals. Their theories demonstrate that hot-electron generation and injection are highly sensitive to nanoparticle size and shape as well as "hot spot" presence.

A generated plasmon can inelastically decay to heat through a plasmon-phonon interaction. The local temperature can be substantially increased. The induced quantum hot carriers (QHCs) can also decay to convert energy to heat. The Arrhenius equation describes the positive exponential temperature-dependent processing efficiency of chemical reactions. Therefore, plasmonic heating also plays a crucial role in plasmonic photocatalytic reactions.

3. Types of Reactors for Photocatalytic Reactions

Photocatalytic reactions can be processed in various types of photocatalytic reactors (Figure 2). Slurry- and fixed-bed reactors are the most commonly used as shown in Figure 2a,c, respectively. In a slurry-bed reactor, the prepared photocatalysts are dispersed homogeneously in the target solution. Photocatalytic processing efficiency is typically further enhanced by mechanical stirring. The excitation light (e.g., mercury lamp, halogen lamp) illuminates from outside. A waterproof lamp (Figure 2d) or light guide might be placed in the solution to improve light excitation. Some photocatalysts are lost during recycling. Consequently, performing a sequential modification test on the same photocatalyst for comparison is difficult. Some studies have suggested using magnetic material, e.g., Fe, Co or Ni, to synthesize (composite) magnetic photocatalyst. Magnetic (composite) photocatalyst can be easily recycled using a magnet after use. However, this limits the material for photocatalyst fabrication. A notable modification to the slurry-bed reactors involves the use of a twin reactor (Figure 2b) to process separate photocatalytic reactions in two compartments using a membrane, [46–49]. The hydrogen and oxygen generation reactions in photocatalytic water splitting can be processed in separate compartments, thus eliminating costs associated with the separation process [46,47,50]. Moreover, advanced CO₂ reduction in the H₂ generation unit can also be processed as O₂ generation in another unit.

A fixed-bed reactor (Figure 2c) is convenient because it does not require recycling and is suitable for modification testing on the same photocatalyst for comparison. A light-transparent substrate can be used to deliver excitation light directly to the photocatalyst without absorption or scattering by the test solution. Figure 2e presents a tube reactor [51]. The inside of the light-transparent tube is coated with a photocatalyst and the tube is wrapped around the lamp to increase the surface contact area of the photocatalyst. Setups in Figure 2d,e improve light use efficiency. The slurry-bed reactor has a simple experimental setup but the tasks of collecting and recycling the photocatalyst after use are difficult. The fixed-bed reactor has disadvantages in its limited contact area. Few reactants can be degraded during long travel in solution before diffusing to the fixed photocatalyst located on the substrate. The electrochemical electrode is also a type of fixed-bed with similar disadvantages.

Several modified fixed-bed reactors (Figure 2f,g) are built to improve processing efficiency in photocatalytic reactions. In the reactors in Figure 2f,g the photocatalyst is deposited on multiple glass fibers [52–54] or inside a porous medium, respectively, to increase the surface contact area. The residence time of the target pollutants to the photocatalyst increases substantially. The excitation light is coupled outside the reactor and homogeneously delivered to the photocatalyst.

The aforementioned experimental setups are simple and easy to use. However, typical photocatalytic reactors (Figure 2a–g) may have disadvantages related to the final desorption step of photocatalytic reactions [16]. In slurry-bed reactors (Figure 2a) the photocatalyst moves with the flow carried by magnetic stirring. The suspended photocatalyst has low speed relative to the flow, and the mass transfer of the reactants and products relies only on diffusion in solution. In fixed-bed reactors (Figure 2c–g) the test solution flows over a surface deposited with photocatalysts. The flow speed in different fluidic layers changes widely according to the input flow speed and shape of the reaction chamber. The nonslip boundary condition considerably reduces the flow speed in the fluidic layer adjacent to the surface deposited with photocatalyst. The low-speed layer has a limited mass transfer of reactants and products diffused in the flow. Three alternatives, namely spinning or rotating disk reactor (SDR/RDR), Taylor vortex reactor, and micro-optofluidic chip (MOFC) reactor, have been developed for high-efficiency photocatalytic reactions. These reactors increase the flow speed around the surface of the photocatalyst-deposited layer.

In SDRs (Figure 2h and Figure 3a) [24,55–61], a reaction disk rotates to drive the fluid to move on top of it. The fluidic layer near the deposited photocatalyst moves faster than other layers above. A higher rotating speed of the reaction disk also introduces larger shear force and friction between adjacent fluidic layers and generates more microvortices. The mass transfer rate of molecules dissolved in water greatly increased. The microvortices can rapidly strip off the products of the photocatalytic reactions from the surface of the deposited photocatalyst on the rotating disk. The processing efficiency of the photocatalytic reactions is greatly enhanced. In the reference work by Huang et al. [24], 10 μ M methyl orange solution degraded to approximately 15% of its original concentration in only a single run of treatment. The photocatalytic degradation process for every drop of test solution was completed within less than 0.1 s. Notably, the disk was made of polycarbonate, which can be recycled from optical storage waste, making it environmentally beneficial.

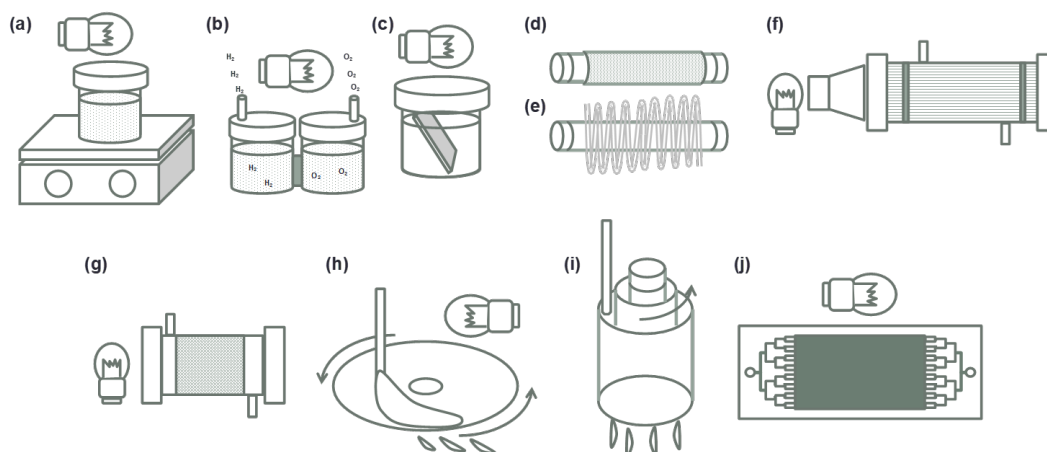


Figure 2. Various photocatalytic reactors: (a) slurry-bed reactor, (b) twin reactor, (c) plate fixed-bed reactor, (d) photocatalyst coated on the surface (or material covering the surface) of the light tube, (e) tube reactor, (f) fiber reactor, (g) photocatalyst deposited inside large surface area material or packed bed reactor, (h) spinning disk reactor, (i) Taylor vortex reactor, and (j) micro-optical fluidic chip reactor.

A Taylor vortex reactor [62–69] includes two cylinders that are arranged in symmetrically and can be oriented vertically (Figure 3a) or horizontally. Typically, the inner cylinder rotates at a high speed relative to the outer fixed cylinder. The test fluid (gas or liquid) is injected through the fixed outer cylinder and flow into the gap between the two cylinders. The rotating inner cylinder causes the test solution to also move in its rotation direction. Simultaneously, forces of centrifugal, Coriolis and gravitational are generated to move the fluid rapidly in relation to the outside cylinder. The faster the inside cylinder rotates, the more unstable the flow becomes. This thus produces an eddy current flow in the shape of rings stacked along the rotating axis. This is typically called Taylor flow. Numerous microvortices are generated from the friction and shear force in the vigorous agitated flow. The related setup is also called a Taylor vortex reactor.

In general, a Taylor vortex reactor is typical highly efficient [62–67] and the photocatalyst can be deposited on the outer surface of the rotating inner cylinder. A tube lamp can provide excitation light from the inside. The eddy current flow with numerous vortices can strip off high-affinity products generated by the photocatalytic reaction. Concurrently, reactants can be rapidly introduced, thus considerably increasing the mass transfer rate in the flow and resulting in enhanced photocatalytic reactions. Although the SDR and the Taylor vortex reactor are typically called microreactors, their processing capacity introduced by their high processing efficiency is comparable to that of a large tank reactor. These reactors characterized by a small size, low power consumption, and waste reduction properties, rendering them green technologies.

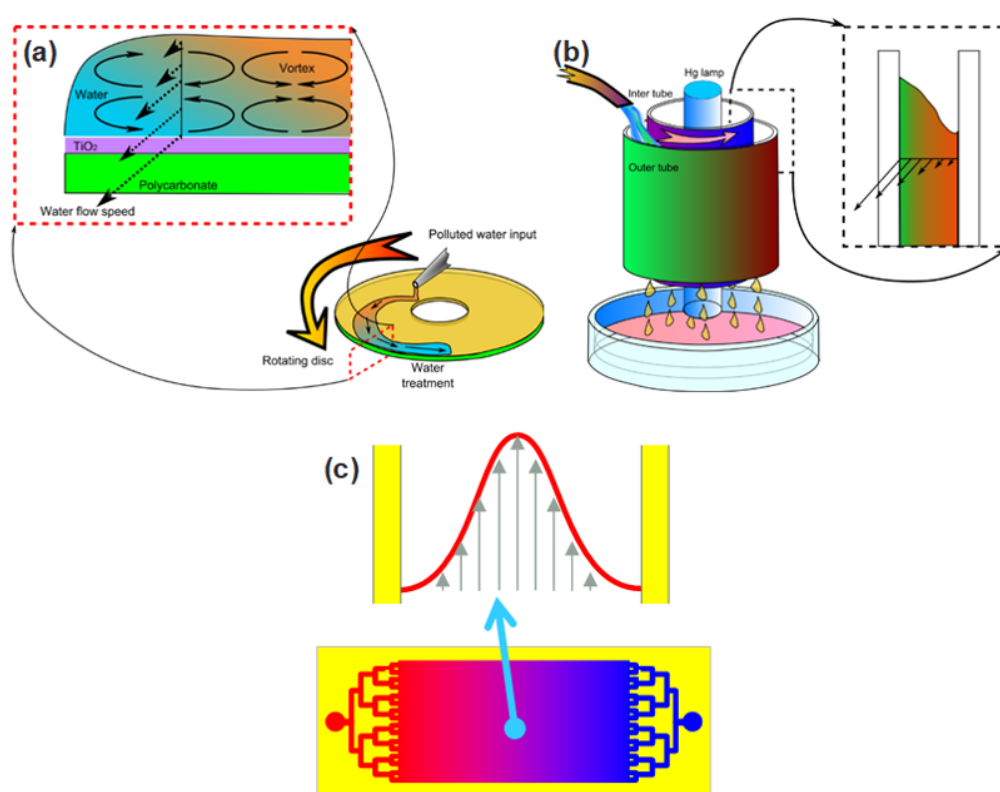


Figure 3. High-efficiency photocatalytic reactors: (a) spinning disk reactor, (b) Taylor vortex reactor, and (c) micro-optofluidic chip reactor.

MOFC reactors [70–85] have been used in some photocatalytic reactions. Although they have low processing volume, MOFC reactors have features that contribute to high processing efficiency in many applications: (i) Their small fluid channel size results in a high mass transfer rate, thus enabling effective transportation of reactants and products. (ii) The plasmon or light converted into heat results in increased temperature in localized area in micro fluids that further enhances mass transfer in fluidics. (iii) The external magnetic field and large variation in flow speed in the fluid channel lead to distinctive ion condensation of OH^- , thus enhancing active OH^* radical generation [85]. (iv) Their highly efficient light illumination engenders low energy loss.

4. Measurements in Plasmonic Photocatalytic Reactions

As presented in Figure 1, this review focused on photocatalytic reactions that involve light energy harvesting through generation of plasmons through several direct or indirect paths. Approaches for examining plasmonic enhancement in photocatalytic reactions can be categorized as follows: use of (i) plasmonic photocatalytic electrochemical measurements, (ii) scavengers and specially fabricated samples, (iii) optical measurements, and (iv) plasmonic light-to-heat conversion. Photocatalytic electrochemical measurements contribute the best means of examining plasmonic enhancement in photocatalytic reactions because the effect of light illumination can be easily depicted using photocurrent variations or deviations in characteristic cyclic voltammetry traces. The study of plasmonic effects is typically related to nanomaterial optical responses, and optical measurements are vital approaches for energy transformation in near-field zone. Therefore, electrochemical and optical measurements are crucial methods for characterizing plasmonic enhancements in photocatalytic reactions.

4.1. Plasmonic Photocatalytic Electrochemical Measurements

Photocatalytic technology was developed from the electrochemical photolysis of water by Fujishima and Honda in 1972 [1]. Photoelectrochemical techniques remain a powerful and direct

tool for examining plasmonic enhancement in photocatalytic reactions [20]. Various types of metallic samples, such as nanoparticles [39,86,87], dendritic nanoforests [88–90], and photonic crystal [7,91], are used for examining plasmonic photocatalytic electrochemical reactions. The energy levels of reactive intermediates can be determined by monitoring overpotentials [92]. The photocurrent measurement provides real-time monitoring of the triggering enhancements [22,93]. Li et al. fabricated TiO₂ nanorods selectively planted inside an Au nanohole array [91]. The photocurrent enhancement factor was measured as a function of the wavelength and were consistent with the absorption section. Kim et al. applied a temperature-dependent photocatalytic measurement approach to acquire the activation enthalpy [87]. They observed that a reduction in activation enthalpy reduction was directly related to the photoelectrochemical potential accumulation on the Au nanoparticle under steady-state light excitation, a phenomenon analogous to electrochemical activation. Their findings are compatible with the phenomenon of additional energy compensation engendered by extra plasmonic enhancement of the photocatalytic endothermic oxidation of NH₄⁺ in an SDR [94].

Plasmonic responses are typically determined using dark-field imaging (Figure 4) and optical microscopy entails monitoring scattering spectra for a plasmonic sample [38,95]. Dark-field imaging does not involve light illumination (Figure 4b) in contrast to bright-field imaging (Figure 4a). Plasmonic responses can be easily observed in dark-field imaging. Therefore, combining electrochemical measurements with dark-field microscopy [96–98], particularly hyperspectral dark-field imaging is valuable [99]. The charge carrier density can be precisely controlled by altering the applied potential and allowing for real-time optical monitoring of the affected LSP resonance responses [97,98,100]. Using hyperspectral dark-field imaging, Byers et al. [99] demonstrated that upon electrochemical tuning, a population of nanoparticles can undergo several processes ranging from nanoparticle charging to electrochemical reactions, such as chloride ion oxidation and hydrogen evolution reaction. These optical and chemical responses are altered on the base of a combination of nanoparticle or nanoparticle-substrate properties that undergo either nanoparticle charging or charge transfer in plasmon-enhanced photocatalytic reactions. Cell illumination leads to several deviations from conventional cyclic voltammetry characteristic traces, such as discrete shifts in onset potential for half reactions and an increase in the photocurrent, which provide useful information on the energy barriers for the reaction [101]. This is consistent with the quantized size dependence of light-to-heat energy transformation through a Pt thin film with a thickness of several nanometers [102]. QHC generation through the excitation of d-band electrons may be confined by selection rules.

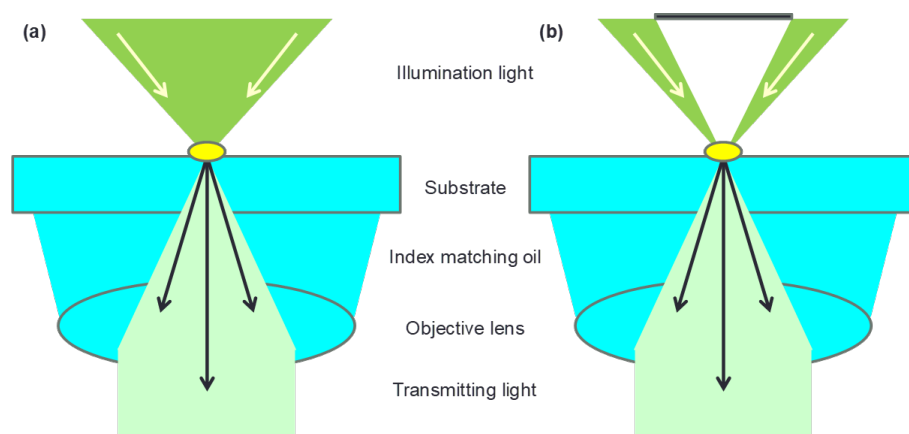


Figure 4. Optical microscopy in a (a) bright field and (b) dark field.

4.2. Optical Measurements

Optical measurements, such as transmission or absorption spectroscopy [9,22,23,25,35,37,88,103–110], Raman spectroscopy [111], and pump-probe measurements, are used for imaging optical effects in enhanced photocatalytic reactions.

The plasmonic responses of nanometallics materials are typically presented as variation in relatively broad transmission or absorption features in optical transmission spectra. The size, structure, or material change of nanometallic materials can be directly determined by feature shifts. Light-scattering spectroscopy of individual Au nanoparticles was reported to reveal the dephasing of particle plasmons in dark-field imaging [38]. A substantial reduction of the plasmon dephasing rate in nanorods as compared with small nanospheres could be attributed to a suppression of interband damping. A comparison with theory revealed that pure dephasing and interface damping negligibly contribute to the total plasmon dephasing rate.

The coating of metal nanoparticles on photocatalysts results in different optical transmission spectra that resemble those associated with typical plasmonics. Therefore, many studies have used transmission spectroscopy data to confirm the mechanism of plasmonic photocatalytic reactions. However, an action spectrum is required for further understanding how various light wavelengths are used in processing the plasmonic enhancement of photocatalytic reactions [23,89,91,112]. By using super-continuum laser, Mukherjee et al. [23] declared that “hot electrons do the impossible: plasmon-induced dissociation of H_2 on Au”. Seven bandpass filters ranging from 500 to 800 nm, each with a wavelength spacing of 50 nm, were used to measure the wavelength dependence of the photocatalytic H_2 dissociation rate. The wavelength dependence of hydrogen deuteride (HD) generation was related to H_2 dissociation and was comparable to the calculated absorption cross section of Au (7 nm)- TiO_2 (30 nm) and to the diffuse reflectance spectrum. Visible light ranging from 500 to 800 nm cannot induce excitation or generation of hot charges in TiO_2 nanoparticles but can generate plasmons on Au nanoparticles. Some studies have adopted wavelength-dependent photocurrents in electrochemical measurements [88,91,93] to explain the mechanism of plasmon-enhanced photocatalytic reactions. These derived action spectra provided evidence of plasmon-induced photocatalytic reactions.

Plasmonic scattering and trapping and PIRET processes can be controlled by the spectral overlap and physical contact between a metal and photocatalyst [113]. This can help identify the PIRET and plasmonic scattering and trapping processes. For example, Awazu et al. [3] presented a plasmonic photocatalyst comprising silver nanoparticles embedded in a silica (SiO_2) spacer layer under TiO_2 layer. Localized plasmon polariton excitation on the surface of Ag nanoparticles caused a substantial increase in the near-field amplitude at well-defined wavelengths in the near-UV range under plasmonic scattering and trapping processes. The photocatalytic behavior of TiO_2 was considerably improved by the enhanced near-field amplitudes of LSP. The SiO_2 shell covered the Ag core, preventing light-induced hot electrons flowing from the directly contacted TiO_2 . The optimized size of Ag NPs give rise to large LSP induced by the near-UV light can be explained by Mie scattering theory. This resulted in the seven times enhancement in photocatalytic decomposition of methylene blue. In addition, PIRET occurs in the Ag- SiO_2 - TiO_2 core-shell nanoparticles because of the spectral overlap between Ag and TiO_2 [113]. Nanometals can excite charge carriers in photocatalysts through PIRET and hot-electron injection processes. In Ag- SiO_2 - TiO_2 sandwich nanoparticles, the LSPs resonance band overlaps with the absorption band edge of TiO_2 , enabling PIRET, and the SiO_2 barrier prevents hot-electron transfer. In Au- TiO_2 , hot-electron injection occurs, but the lack of spectral overlap disables PIRET. In Ag- TiO_2 , both hot-electron transfer and PIRET occur.

Photoluminescence (PL) is also used in characterizing the effect of hot charge recombination in photocatalytic reactions [114–118]. Decreased PL peaks indicate suppressed recombination of photoinduced charge carriers, which can lead to an enhanced photocatalytic reactions. Gao et al. [118] used PL spectra to measure Lorentz force-assisted charge carrier separation enhancement in TiO_2 . They applied a magnetic field by placing a permanent magnet beneath the photocatalytic system. Studies on metal-decorated heterostructure photocatalyst have revealed that PL spectra of original photocatalysts had stronger signals than did those of metal-photocatalyst heterostructures [114–117]. This indicates the decreased recombination rate of photoinduced charge carriers and enhanced photocatalytic activity of metal-decorated nanoparticles. Charge carrier recombination could be effectively suppressed by introducing metal nanoparticles to the photocatalyst surface. This demonstrates a strong relationship

between PL intensity and photocatalytic activity. However, additional measurements are necessary to demonstrate whether photocatalytic reaction enhancement is maintained through plasmon generation.

Raman spectroscopy is a valuable optical measurement tool for measuring the inelastic scattering of photons by matter. The exchange of energy involves the gain or loss of vibrational energy by a molecule as incident photons from a visible laser shift to lower or higher energy states. Surface-enhanced Raman scattering (SERS) [111,119–122] involves the amplification of Raman scattering signals by SPs on a metallic surface with high charge carrier density. Brooks et al. conducted an in-depth review of Raman spectroscopy applications for understanding plasmon-mediated photocatalysis [20]. As sensitive spectroscopic techniques, SERS and tip-enhanced Raman spectroscopy (TERS) offers considerably more detailed information on molecular probe structure compare with electronic spectroscopic techniques [123–135]. SERS and TERS require metal nanostructures and a sharp metal tip, respectively, to induce strong LSPs and trigger large Raman scattering signals. Therefore, Raman spectroscopy is typically used with a metal photocatalyst.

Energy transformation in plasmonic material sensing (i.e., chemical and biosensing [136–141] and SERS [119–122]) resembles that in plasmonic photocatalytic reactions. Therefore, methods of obtaining larger or enhanced signal readings in plasmonic sensing resemble to a higher enhanced processing efficiency in plasmonic photocatalytic reactions. Size dependence is typically valuable in plasmonic responses and SERS [111]. For large-scale material sensing or photocatalytic reactions, array or condensed random structures can achieve relatively high light absorption [141–143] or can even be perfect absorbers [144,145]. Furthermore, array structures help in SERS [26,27] and ultrafast real-time bioassays [140]. Metallic or heterostructure materials can facilitate the achievement of multilevel [146] and recyclable functions [147], respectively. Plasmonic incidences is strongly affected by the wavevector of incident light [95]. Therefore, prism-based light incidence systems are frequently used in plasmonic material sensing [137–139]. Photocatalyst modification is also frequently used in the study of plasmonic photocatalytic reactions and is discussed in Section 5.1.

Time-dependent property of plasmonic photocatalytic reactions is crucial for understanding plasmon progression after excitation, [19,22,35,37,38,103,148–150] as shown schematically in Figure 1. Near-field dipole-dipole interactions, light-scattering, and hot carrier responses to incident light combines as plasmonic optical response [19]. The plasmon dephasing time, as determined by radiative and nonradiative damping mechanisms, directly determines which step in the plasmon evolution is dominant in photocatalytic reaction enhancements. Metal nanoparticle reflection can be altered by the variation in plasmonic responses with particle size [37,38,103,148]. A coherent SP can be generated by introducing an incident photon source that is on-resonant with the extinction spectrum of a nanoparticle. SPs maintains its coherence for 1–10 fs and then starts to undergo energy conversion by decaying through either radiative or nonradiative pathways [151]. After the surface plasmon loses coherence, the nonradiative decay pathway produces a distribution of hot carriers that may be used in initiating photocatalytic reactions. This multistep decay process occurs primarily through Landau damping [36], where energy is transferred from a coherent plasmon to individual electron-hole pair excitations. Initially, the hot carrier distribution is nonthermal and contains charged species that are far from the Fermi level of the material [152,153]. Hot electrons and holes then rapidly undergo thermalization, reaching a Fermi-Dirac distribution that corresponds to a high effective electron temperature. This initial thermalization occurs through energy redistribution in electron-electron scattering interactions over the next several hundred femtoseconds (1–100 fs) [38,148]. During this time, the hot electrons and holes may contain energies ranging from the Fermi level to the work function. These charge carriers are sufficient in quantity and lifetime to initiate external chemical processes [152]. The hot carriers further dephase through an additional relaxation mechanism consisting of electron-phonon interactions over 1–10 ps [154,155]. During these two time intervals, the charge carriers may contain sufficient energy to transfer to a nearby chemical species to initiate a single or multistep chemical reaction. In a pump-probe measurement executed in a previous study using femtosecond diffuse

reflectance spectroscopy, the transient absorption decay behavior of TiO_2 particles was determined to be independent of calcination temperature [156].

Many studies on mechanism of photocatalytic reaction enhancement have drawn conclusions after considering only a broad light absorption band of metal decorations. Such studies have not provided extra supporting experimental results. It is of concern that metal nanoparticles also responsible for accepting the light energy induced hot electrons from contacted photocatalysts (i.e., hot-electron injection model or chemical model of plasmonic photocatalytic reactions), thus reducing the recombination of the hot charge pairs.

5. Using Plasmonic Photocatalytic Reactions

Specially designed photocatalysts are typically examined using spectroscopy, selective photocatalytic reactions, pump-probe measurements, specially arranged light sources, and advanced reactors. Plasmonic light-to-heat conversion is also easily identified through temperature variation in reactions. This review considers only crucial emerging studies on plasmonic photocatalytic reactions that may provide suggestions for future studies.

5.1. Specially Fabricated Samples

Researchers have used various methods and materials to study and improve the photocatalytic processing efficiency of titanium dioxide, such as calcination temperature [156], TiO_x ($x < 2$) photocatalysts fabricated through flame aerosol synthesis [157], and oxygen vacancies obtained using plasma treatment [158]. Scavengers, such as EtOH [87], were used to reveal the role of hot charges in photocatalytic reactions. Bikondoa et al. [159] used a scanning tunneling microscope to directly visualize defect-mediated dissociation of water on $\text{TiO}_2(110)$. They demonstrated that defects play a key role in oxide surface reactions. Binary photocatalytic nanoparticles may also have high photocatalytic processing efficiency. Graphene is highly conductive in two specific dimensions and is largely used like metal decoration in binary nanophotocatalysts [160–164]. For advanced methods improving photocatalytic reactions, several studies have suggested ternary nanophotocatalysts, such as Ag- TiO_2 -graphene [165–167], Ag_2MoO_4 -AgBr-Ag [104], Ag-rGO- Bi_2MoO_6 [105], Ag-AgCl- TiO_2 [168], Ag-AgCl- $(\text{BiO})_2\text{CO}_3$ [106], ZnO-Ag-Ag $_2\text{WO}_4$ [107], Ag_2WO_4 -AgBr- TiO_2 ternary nanocomposites [108], Au- $\text{La}_2\text{Ti}_2\text{O}_7$ [169], and Au- TiO_2 -graphene [170]. Cu_7S_4 -Pd hetero-nanostructures were also reported to exhibit near-infrared solar energy harvesting, leading to highly efficient photocatalytic reactions. Pd nanoparticles act as acceptors of light-generated holes in this system.

A noteworthy modification is the binary Pt decorated TiO_2 nanophotocatalyst, whose advantages involve the effective separation of the photogenerated electrons and holes [2,171,172]. The photogenerated electrons move from the valence band of TiO_2 to the conduction band of Pt (Figure 5a). The electrons flow through the external circuit to the Pt cathode in which water molecules are reduced to hydrogen gas; the holes remain in the TiO_2 anode in which water molecules are oxidized to oxygen. However, higher content-loaded Pt nanoparticles can absorb more incident photons that do not contribute to photocatalytic efficiency. The highest photocatalytic activity for the Pt- TiO_2 nanohybrids on MB could be achieved at 1 at % Pt loading [172]. The hot-electron injection model successfully explains the photocatalytic process of metal-decorated photocatalysts. However, in 2008, Awazu et al. [3] presented a “plasmonic photocatalyst” consisting of silver nanoparticles embedded in titanium dioxide. Their experimental results demonstrated that 30–100-nm silver nanoparticles can enhance processing efficiency under near-UV illumination even when covered by a SiO_2 layer. This signifies that metal nanoparticles can help deliver light energy by inducing a large localized electric field rather than solely mediating the accept light-generated electrons. This was a valuable breakthrough in plasmonic photocatalytic reactions. Composite nanoparticles of photocatalysts and higher plasmonic response metals of various sizes [173] and shapes (e.g., nanospheres [37,174], stars [37], and rods [174]) are recommended for advanced photocatalytic reactions. Array structures can be fabricated on a substrate to achieve high light absorption efficiency [7,91,111,175] to enhance light energy use in

plasmonics. Adapting nanophotonics to photocatalysis introduces particularly slow photon effects and a strong light absorption and extinction band that enhances light harvesting [7]. Li et al. [91] fabricated TiO₂ nanorods selectively planted inside an Au nanohole array to enhance light capture and energy transfer to the plasmonic photocatalytic reaction through plasmon-induced resonant energy transfer.

In metal-photocatalyst heterojunctions, metal nanostructures may play multiple roles, including surface catalysis, surface passivation, Fermi level equilibration, and plasmonic enhancement [176]. The enhancement of photocatalytic activity or photocurrent is not solely due to the plasmonic enhancement effect of metal nanostructures. The effects of a metal nanostructure on plasmonic enhancement can be experimentally distinguished from other enhancement effects [176].

For future advanced applications in plasmonic photocatalytic reactions, a fabrication method that provides samples with stronger plasmon coupling and induction may induce a new breakthrough in plasmonic photocatalytic studies. Layered structures for creating plasmonic black absorber [93] and TiN materials for metal-like near-infrared plasmonics responses [177–182] are potential materials in relevant applications. Nanoparticles of various sizes and shapes [183,184] can achieve various plasmon modes for the target light absorption band. Dendritic nanoforests can achieve wide light absorption [185,186]. Both methods are also valuable for photochemical or photocatalytic applications.

In practical applications, it is difficult to identify a plasmonic enhancement mechanism apart trapping of light-excited hot electrons by the metal nanoparticle and longer recombination time with generated hot holes in metal-photocatalyst heterostructured nanomaterials. Therefore, it typically engenders ambiguity in determination of mechanisms underlying plasmonic enhancement in photocatalytic reactions.

5.2. Plasmonic Light-To-Heat Conversion

Light-to-heat energy conversion is a common concept, particularly under the warm sunlight at noon. When focused to a higher-order power density, this energy can even cut through steel. Light energy introduces VPs before being reflected by bulk metallic materials. However, “plasmonic” light-to-heat energy conversion is different, especially for nanomaterials [102]. Incident light excites SPs and LSPs on nanomaterials such as nanoparticles [187–191], nanorods [192], nanostars [193], nano particle arrays or networks [194,195], and nano-thin film [102] with an even higher electromagnetic field in the near-field zone. The effects of material, size, quantum, and structure result in a complex situation [102,189–191,193–197]. The size dependence of the quantum effect results in an even more complex situation when the size of the quantum well decreases to a few nanometers [102]. The harmless dosing power density for skin or tissue can be trapped or focus on a small area for detection and treatment in bioassay [140], bacterial [198], cancer cell [192,199–201], or as a nano or bulk cleavage [202]. Localized heat energy is strong and can be used to kill target cancer cells [203] while preserving the nearby cells [204].

A noteworthy application of plasmonic light-to-heat energy conversion is plasmonic polymerase chain reactions [205,206]. Enzymatic amplification of beta-globin genomic sequences, a process typically called a polymerase chain reaction, is crucial for various applications, including diagnosis, biomedical research, and criminal forensics. Most polymerase chain reaction methods rely on thermal heating and cooling cycles to induce DNA melting and enzyme-driven DNA replication. The treatment solution volume is normally small and is particularly suitable for MOFC reactor processing [207–217]. Plasmonic light-to-heat energy conversion contributed to a breakthrough ultrashort polymerase chain reaction cycle time of 30 cycles in 54 seconds [218]. This has induced more modifications with various plasmon generation methods, such as those involving the use of nanorods [219], Pt thin films [220], and Au thin films [221]. Plasmonic light-to-heat energy conversion is beneficial for rapid and precise heating in polymerase chain reaction.

Localized heating can be used in photocatalytic reactions [58,222,223]. Using a temperature-dependent photocatalytic measurement approach to acquire the activation enthalpy, Kim et al. [87] reported that reduction in activation enthalpy was directly related to the photoelectrochemical potential

accumulation on the Au nanoparticle under steady-state light excitation, another phenomenon analogous to electrochemical activation. Plasmonic light-to-heat conversion is particularly crucial for endothermic reactions such as ammonium decomposition in water. Ammonium decomposition is typically executed using wet air oxidation method at high temperatures and in a high-pressure sealed tank [224,225]. The process usually requires temperatures higher than 150 °C–200 °C to trigger efficient reactions. However, a large tank of sufficient treating volume is at risk of explosion and is characterized by high power consumption to maintain high pressure and temperature. A high-pressure environment is used to increase the reactant collision rate. Ammonium oxidation in an SDR mainly increases the mass transfer rate and collision rate of target reactants, which results in reactions under ambient conditions [58]. Providing an additional chemical-stabilized Pt thin film (8 nm) [226] could result in energy compensation in plasmonic endothermic reactions when compared with typical endothermic ammonium oxidation [223].

5.3. High-Efficiency Reactors

Slurry- and fixed-bed reactors are the widely used reactors in studies on plasmonic photocatalytic reactions. They have slightly different near-field optical responses (Figure 5a,b) that might affect plasmonic enhancement of photocatalytic reactions. Light is scattered in the elastic or inelastic decay path depending on the various matching conditions. However, typical processing setups do not consider optics for enhancing or identifying the mechanism underlying the “plasmonic enhancement” of photocatalytic reactions. Some reactors have features that enhance plasmonic responses in plasmonic photocatalytic reactions. In the study of plasmonics, the wavevector matches the plasmonic features (i.e., VPs, SPs, LSPs) and have substantial optical responses. In slurry-bed reactors, the wavevector of light is $k_{x-water} = \sin\theta n_{water} \lambda$ which is the product of the water refractive index n_{water} and light wavelength λ . In this case, $\sin\theta$ is typically 1 under conditions of diffuse scattering. This limits the wavevector of a specific wavelength of light to a fixed value. Light with a suitable “short” wavelength, typically UV light, for photocatalyst activation may not match the coupling condition of plasmonic features (i.e., size of the metallic decorations on a heterostructure photocatalyst). Therefore, the difference in plasmonic enhancement changed through the scattering and trapping path cannot be clearly observed. Only “long” wavelength lights, typically exhibiting visible or near-infrared absorption peaks, can couple to the decorated metallic nanoparticles and generate heat. The generated heat enhances the corresponding chemical reactions but the enhancement effect is not significant. Furthermore, the diffuse reflection of incident light by a high-density suspended photocatalyst substantially reduces the energy used in photocatalytic reactions. Diffuse light scattering can increase the chances of light absorption by photocatalysts but it may engender light decay as long-distance travel in water.

Fiber reactors [227–229] have optical advantages of delivering light with high efficiency. Glass optical fibers can deliver incident light to photocatalysts without substantial decay under diffuse scattering in water. Incident light from the glass side efficiently induces SPs and LSPs in high efficiency (Figure 5c,d). The wavevector of light propagating in an optical fiber is $k_{x-glass} = \sin\theta n_{glass} \lambda$, where λ is the same as that in water; $n_{glass} \sim 1.5 > n_{water} \sim 1.3$ and only slightly increases the wavevector. However, light propagating in the optical fiber can illuminate the photocatalyst fixed on the optical fiber various angles (θ) from within the glass component. Therefore, the variation in the incident light wavevector can increase the variation in the wavevector for a specific light wavelength. The incident light can have a wavevector that matches the coupling condition of plasmon generation. This increases the probability of light inducing photocatalytic reactions on the photocatalyst or inducing enhanced plasmonic responses on the decorated metallic nanoparticles. Plasmonic scattering and trapping, PIRET, QHCs and heat transformation (Figure 1) can all have enhanced responses.

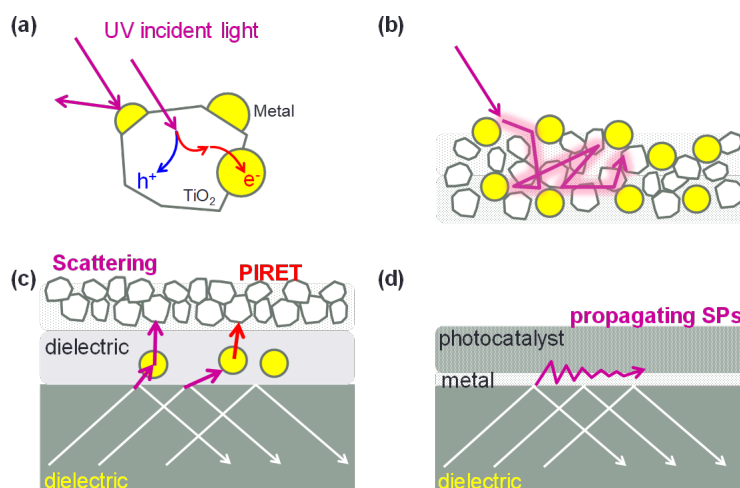


Figure 5. Near-field optical response of (a) binary heterogeneous photocatalyst, (b) binary polycrystalline photocatalyst deposited on substrate, (c) embedded metal nanoparticles beneath the deposited polycrystalline photocatalyst, and (d) metal thin film beneath the deposited photocatalyst layer. High-wavevector lights illuminating the substrate from below induce substantial coupling of light energy in (c) and (d).

Reactors with waveguide features or the potential to couple with light for an increased wavevector variation are particularly suitable for studying plasmonic photocatalytic reactions. Fixed-bed or MOFC reactors [71,81,85] with thin and flat glass substrates are also suitable for use as waveguides for delivering light energy. These reactors might help studies on plasmonic photocatalytic reactions. Light-transparent substrate-based SDRs are also crucial for high-efficiency plasmonic photocatalytic reaction studies. The degradation of methyl orange in water using a dual-light-source SDR (DL-SDR) and glass-embedded diffusion coupler demonstrated the mechanism underlying the enhancement of plasmonic photocatalytic reaction [24]. When visible light (637 ± 8 nm) from a spindle LED propagated in the circular polycarbonate disk waveguide of a DL-SDR, it gradually lost energy as absorbed by the Au-TiO₂ double-sphere nanoparticles deposited on top. This absorption enhanced the processing efficiency of the plasmonic photocatalytic reaction excited by the upper 254-nm light from a low-pressure mercury tube lamp. The additional visible light resulted in no difference in photocatalytic reactions with only TiO₂ nanoparticles. An experiment with multilayer reactors of aluminum disks and both visible and UV light from above reached the same conclusion [56]. Red visible light can induce plasmon on 20-nm Au nanoparticles but not in photocatalytic reactions. This is evident of plasmonic enhancement in photocatalytic reactions.

SDRs could enhance mass transfer and result in ammonium oxidation at room temperature [58] through the use of a bare-glass disk that typically executed using wet air oxidation method in environment of high temperature and high pressure [224,225]. Depositing an additional 8-nm platinum thin film using plasma-enhanced atomic layer deposition (PE-ALD) [226] has been reported to further introduced plasmonic-enhanced photocatalytic ammonium oxidation in water [58,223]. The energy compensated in the plasmonic photocatalytic oxidation of ammonium is a quantized phenomenon independent of the incident light power density [94,230]. The quantized energy transformation [102] originates from the fixed quantum wavelength of the excited QHCs discussed in Section 5.2.

6. Models of Plasmonic Photocatalytic Reactions

In early studies, decorated metal nanoparticles were found to improve the photocatalytic processing efficiency of TiO₂. This can be explained by the lower energy level of metal conduction band than the excited band of photocatalyst that results in direct electron transfer (DET) model. However, it cannot sufficiently explain all the enhancement effects in photocatalytic reactions. The studies of

optical plasmonic effect start at around 1960s and booming at 1990s provide a substantial explanation of the enhanced processing efficiency of metal-photocatalyst composited nanomaterials. Typically, a chemically plasmonic or physically plasmonic enhancement of photocatalytic reactions are related to include the migration of induced hot charges or process through “electromagnetic field-enhancement,” respectively. Various energy transformation paths discussed above can enhance the photocatalytic reaction in chemically plasmonic or physically plasmonic enhancement pathways, as shown in Figure 6.

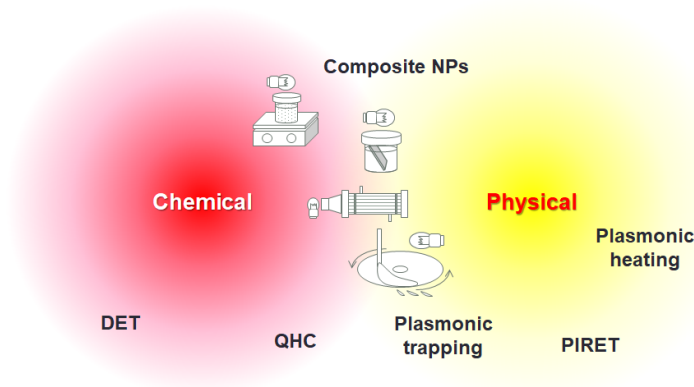


Figure 6. Chemically and physically plasmonic enhancement models of various types of energy transformation in plasmonic photocatalytic reactions.

In the metal-photocatalyst composited nanoparticles, the migrations of the ultraviolet light-induced hot-electron on the photocatalyst and plasmon-generated quantum hot electrons on the nano-metal results in reduced charge recombination rate. These are chemically plasmonic enhancements of photocatalytic reactions that need composite nanoparticles. The chemically plasmonic-enhanced photocatalytic reactions have relatively small facility-dependence and can conveniently process in various kinds of reactors.

The physically plasmonic enhancements are relatively tricky to identify clearly from the chemically plasmonic enhancements in photocatalytic reactions. Plasmonic scattering and trapping of the incident light, PIRET, and plasmonic heating were typically observed physically plasmonic enhancements in the specially arranged experiments. It usually needs some specially fabricated samples or specially arranged experimental setup to reveal the physically plasmonic enhancement in photocatalytic reactions. An insulator spacer in specially manufactured samples blocked the contact between photocatalyst and metal nanoparticles that also stop the electron migration [3]. In dual-light-source experiments [24,56], longer wavelength light has lower energy that not able to induce hot charges carriers in the photocatalysts. This can also demonstrate an extra physically plasmonic enhancement in the composited nanoparticles of no insulator spacer.

Normally, chemically plasmonic enhancements are undoubtedly processing in most of the photocatalytic reactions by metal-photocatalyst composite material. The studies in specially arranged experimental setups aiming at physically plasmonic enhancements are usually only for scientific studies. In practical applications, the plasmonic photocatalytic reactions are looking for the highest processing efficiency. It needs balanced effects from chemically plasmonic and physically plasmonic enhancements of photocatalytic reactions that also needs specially designed experimental setup. A specially designed experimental setup with high-efficiency reactor and optimized light energy delivering can thus provide further enhanced plasmonic photocatalytic reactions.

7. Conclusions

Studies on plasmonic enhancement of photocatalytic reactions are increasing in the recent years. Methods and reactors for processing the photocatalytic reactions are abundant. However, the mechanism underlying the plasmonic enhancement of photocatalytic reaction remains confusing.

Identifying a specific factor or mechanism including the greatest effects in plasmonic enhancements is difficult. This difficulty can be attributed to the complicated plasmonic optical responses as well as the complicated microchemical processes in photocatalytic reactions. The aim of this review is to highlight experimental methods used in studies in plasmonic photocatalytic reactions over the past decade and provide identifiable alternative mechanisms for theoretical modeling. To simplify plasmonic effect modeling in photocatalytic reactions, plasmonic photocatalytic reactions are defined as reactions enhanced through the light-induced generation of plasmons. The advantages of introducing plasmons in photocatalytic reactions are (i) strong light absorption, (ii) intensive far-field light-scattering, (iii) electromagnetic field strengthening in near-field zone, (iii) abundant hot carrier generation, and (iv) plasmonic heating effects. These inspired substantial research on improving the processing efficiency of photocatalytic reactions. The mechanisms of plasmonic enhancement in photocatalytic reaction systems is gradually becoming clear but remains vague in practice. This review may help to identify the plasmonic enhancement path in photocatalytic reaction from an instrumentation perspective.

Author Contributions: Conceptualization, H.J.H., J.C.-S.W., H.-P.C., Y.-F.C.C., and Y.-S.L.; reference collection, H.J.H., Y.H.W. and P.-J.C.; original draft preparation, H.J.H.; review and editing, H.J.H., J.C.-S.W., H.-P.C., Y.-F.C.C., Y.-S.L., Y.H.W. and P.-J.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Technology of Taiwan under the project number MOST 107-2622-E-492-022-CC3, MOST 108-2112-M-492-001, MOST 108-2221-E-239-005, MOST 108-2622-E-492-023-CC3, MOST 106-2112-M-019-005-MY3, MOST 108-2221-E-002-111-MY3, 108-2119-M-002-027, University Research Grant of Universiti Brunei Darussalam (Grant No. UBD/OAVCRI/CRGWG (004) /170101), and Taiwan Academic Sinica under the project number AS-KPQ-106-DDPP.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

VPs	Volume Plasmons
SPs	Surface Plasmons
LSPs	Localized Surface Plasmons
PIRET	Plasmon-Induced Energy Transformation
QHCs	Quantum Hot Charge carriers
SDR	Spinning Disk Reactor
MOFC	Micro Opto-Fluidic Chip
PL	Photo luminescence

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