PHOTOCATALYSIS DRIVEN BY PLASMONICS

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The light absorbing property and the availability of catalytically active sites make plasmonic nanostructures ideal candidate for the enhancement in photocatalysis rate. Plasmonic nanostructures can concentrate otherwise diffused visible illumination of photons to drive chemical transformations. This also results into introduction of different pathways to control the selectivity of the reactions. Here, fundamental photophysics in chemical reactions driven by localized surface plasmon resonance (LSPR) have been discussed. Some of the selected notable works on plasmon mediated direct plasmon catalysis achieved so far have been reviewed. Variation in the rate of photocatalysis due to the variation in illumination intensity and photon energy has been discussed in terms of the mechanisms of photocatalysis. Though there are a lot more work needed to confirm the selectivity in plasmonic photocatalysis, the evidence of the role of plasmon nanostructures in enhancing the rate of photocatalytic reactions can be obtained from both intensity and wavelength dependent rate of catalysis, thereby giving an alternative to the conventional thermally mediated heterogeneous catalysis.

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I. INTRODUCTION

Harvesting of solar energy to carry out catalytic chemical transformations has been viewed as a sustainable potential alternative to thermally driven heterogeneous catalysis.[1,2] Originally diffuse in nature, sunlight, when concentrated are capable to drive chemical transformations that are not easily attainable via thermo-mediated catalytic processes.[3] Splitting of H_2O and reduction of CO_2 are some of the commonly studied catalytic systems, where conversion of solar energy to chemical energy takes place to get stored in the form of chemical bonds.[4,5] The desired task of selectivity in chemical transformation can also be achieved with the efficient utilization of photocatalysts which is otherwise not possible via thermal catalysis.[6] One of the major drawbacks of thermal catalytic processes is that the product selectivity lies on manipulation of activation energy barriers and adsorption energies of the intermediates. This limits catalytic selectivity as manipulation of energetics of an elementary step will affect the energetics of other steps.[7] On the contrary, careful and specific design of the photocatalyst will allow us to potentially control the energetics of single elementary step via the involvement of its surface to deposit photon energy selectively into targeted orbitals of the adsorbate that are responsible for desired chemical bond activation.[8] This chapter includes some of the recent examples of photocatalysis mediated by noble metal (Ag, Au and Cu) nanoparticles by virtue of localized surface plasmon resonance (LSPR). Role of LSPR in photocatalysis can be either indirect or direct. In indirect plasmonic photocatalysis, transfer of photon energy takes place from excited plasmons to nearby moieties like semiconductors, molecular reactants, other metals etc. to drive the reaction remotely. But in direct photocatalysis, plasmonic nanoparticles first absorb the incoming light to drive chemical transformation on its surface under the influence of LSPR post photoexcitation. This proves the role of the nanoparticle as a catalytically active site.[9,10] Here, the emphasis has been given on direct plasmonic photocatalysis in presence of low-intensity visible photons.[11] Initially, direct plasmonic photocatalysis has been considered to be improbable because of the high quenching rate of excited adsorbates on plasmonic surface and short lifetimes of the charge carriers produced.[12]

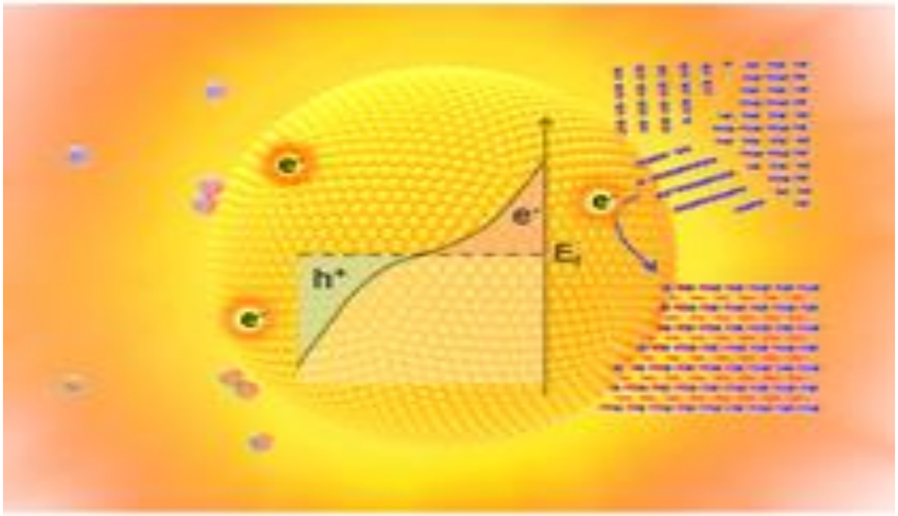

Figure 1: Schematic of plasmonic nanoparticle induced photocatalysis. It is reproduced with permission from ref. 2. Copyright 2019 American Chemical Society.

However, the requirements of long-lived excited states or charge carriers are found to be not necessary for photocatalytic activity in the course of time with numerous demonstrations of plasmon driven direct photocatalysis. This book chapter is organized in a way to first focus on the fundamental concepts of LSPR excitation followed by a brief review of the necessary photophysics required to understand the role of LSPR excitation on direct plasmonic photocatalysis.

A brief overview of some of the recent demonstrations of direct plasmonic photocatalysis via LSPR has been included. Further, mechanisms responsible for LSPR mediated direct photocatalysis have been critically analyzed to understand the experimental observations. The crucial role plasmon excitation has been discussed by taking examples of different model reactions. It is concluded by giving an outlook of the future directions of this field along with some of the unanswered questions.[8]

1. **Localized surface plasmon resonance:** Understanding the effect of plasmonic nanostructure on photocatalysis requires a discussion on LSPR excitation. The origin of LSPR is based on the matching of the frequency of incoming radiation with that of the plasmons originated due to the restoring force exerted by the positively charged nuclei. For noble metal nanoparticles, the frequency of plasmon resonance lies in the visible region of the spectrum. Coherent oscillation of electrons in space and energy as a result of interaction of resonant photons and surface electrons makes the photon energy to be confined for a longer period of time to the surface of nanostructure as compared to the time spent by photons travelling at the speed of light in the same control volume. The outcome is that the absorption coefficient of photons has a very high value resulting large buildup of photon intensity (strong electric fields) and a high concentration of hot electrons at nanostructured surfaces.[13,14] Under the influence of plasmon excitation, electrons undergo a coherent oscillation with a lifetime of ∼5−100 fs.[15] Dephasing of this oscillation takes place through three different mechanisms. (i) elastic reemission of photons which is radiative in nature, (ii) non-radiative Landau damping, resulting in the excitation of hot electrons and holes in the metal nanoparticle, and (iii) direct injection of electron into the acceptor states of the adsorbate through the interaction of excited surface plasmons with unpopulated adsorbate acceptor states, called chemical interface damping (CID) (Figure 2).[8,16] The geometry, composition and local environment of the nanostructure determine the magnitude of enhancement in local electric field, resonant wavelength and fraction of plasmon excitations decaying through mechanisms (i)-(iii). All of these dephasing mechanisms result into deposition of energy into the adsorbates resulting photocatalytic reactions. Various mechanisms have been proposed for the energy transfer from excited surface plasmons to adsorbates: In the radiative decay of plasmons, (i), energy is obtained by the adsorbate molecules from intense photon fluxes due to plasmonic nanostructure. For this mechanism to be operative, the energy of allowed electronic transition in the adsorbate to be similar to that of the reradiated photons resulting vibronic energy exchange involving the adsorbate molecule. This way, the plasmonic nanostructure is responsible for the alteration of internal molecular electronic transition energy of a chemisorbed molecule (Figure 2). Exchange of energy to the adsorbates by plasmon decay process (ii) can occur through transient transfer of hot electrons and holes from surface of plasmonic nanostructure to the orbitals of the adsorbed species. In this process (ii), Landau damping (~ 10 fs) leads to dissipation of plasmon acquired energy which is eventually used for generation of electron/hole pairs.[17]

The generated charge carriers create a constant probability distribution between energies E_f and $E_f + h\nu$, where E_f is the energy of the metal Fermi level. Variation in the probability distribution is very less because of the intraband nature of Landau damping where transition occurs between two states of sp character having density of a few eV above and below E_f in coinage metals.[8] The energy of the primary electrons spreads across many electrons via inelastic scattering with other electrons. Unlike semiconductors, the correlation between electrons and holes in metal nanoparticles are not intrinsic, which makes electron-hole recombination a non-efficient pathway for relaxation of plasmons. For the first few hundred fs, there is an "athermal" distribution of electron energies not following thermal Fermi−Dirac distribution.[18,19] The cascading exchange of electron energy results into its temporal evolution in the nanostructure. Experimental measurement of the temporal evolution of electron distribution can be done with the help of time-resolved two-photon photoemission spectroscopy (2PPE) where evolution of electron energies is monitored as a function of time delays between the pump and the probe pulse of the femtosecond laser (Figure 2).[8] This provides the required time for the transient charge transfer from plasmonic nanostructures to the adsorbate molecules. Spreading of electron energy through cascading effect is followed by electron-phonon coupling of low energy electrons with lattice phonons results into heating up of the metal lattice in a time scale of ∼1 ps. The remaining heat is dissipated to the surrounding environment in a time scale of 10-100 ps.[19] Such heating of nanostructure as a result of the plasmon decay could result in transfer of energy to the adsorbates to drive chemical transformations. Theoretical and experimental studies reveal that for an illumination intensity of 100 mW/cm^2, the maximum extent of increase in transient temperature is ~ 10-20 K.[20] If it is assumed that there is a double increase in the rate of a thermal reaction with a 10 K increase in operating temperature (apparent activation barrier of ∼100 kJ/mol), then 10^6 mW/cm^2 illumination intensity would be required to increase the rate of the reaction by 2-fold through plasmon heating. This makes consideration of plasmonic heating redundant in isothermal environments with low intensity of illumination.

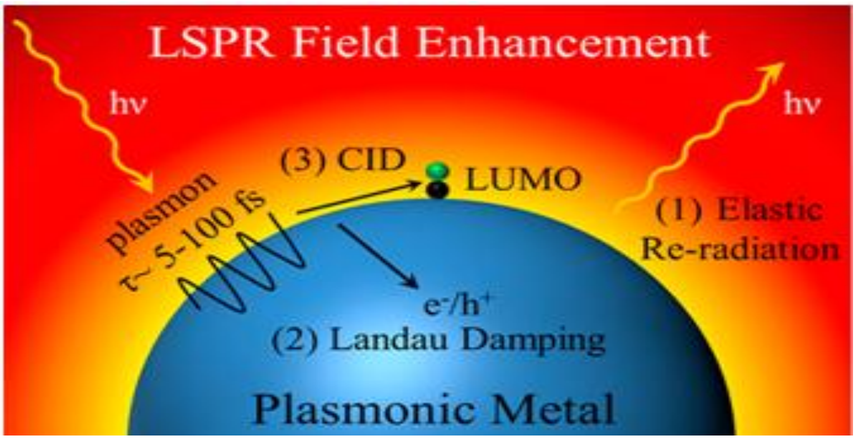

Figure 2: Schematic of different pathways for plasmon dephasing. Reproduced with permission from ref. 8. Copyright 2014 American Chemical Society.

The above discussed both plasmon decay mechanisms are found to be independent of the environmental conditions and addition of adsorbates to plasmonic nanostructures' surface opens up an ultrafast pathway for dephasing in the scale of few femtoseconds, through CID, (iii).[8,21] Here, the interaction between the oscillating plasmons and the unpopulated electronic states of the adsorbates results into dephasing of plasmons via transfer of hot charge carriers to unpopulated adsorbate states directly (Figure 2). Though there is some similarity between CID and Landau damping for plasmon dephasing, the major differences are the time scales of the processes, coherent transfer of energy and potentially resonant wavelength dependent energy transfer efficiency. Mechanisms (ii) and (iii) discussed above for electronic energy transfer to adsorbate mainly differs by whether there is an initial generation of hot electrons in the metal because of Landau damping and subsequently scattering into adsorbate states, (ii), or there is instantaneous direct hot electron injection into the states of adsorbate during plasmon dephasing, (iii). The distinction between the two mechanisms is physically manifested as a large difference in electron energy distribution experienced by the adsorbates depending on whether there is direct energy transfer or it occurs sometime after dephasing. This difference in electron energy distribution through various mechanisms may results into different efficiencies of photocatalysis and mechanistic characteristics.[8]

2. **Examples of plasmonic photocatalysis on metallic nanoparticles:** On the perspective of efficiency, there are two broad heads into which these different mechanistic insights can be provided.

Effect of illumination intensity: Earlier studies of surface mediated heterogeneous photocatalysis reveal that microscopic mechanistic information can be obtained from macroscopically observed illumination intensity dependent photocatalytic rate.[22] The illumination intensity (I) dependent photocatalytic rate can be divided into 4 categories: sublinear (Rate ∝ In, n < 1), linear (Rate ∝ I), superlinear (Rate ∝ In, n > 1), and exponential (Rate ∝ ef (I)). These dependencies can be derived mathematically from the rate equations of the elementary steps of the photocatalytic cycle thereby giving information about the photon utilization mechanism in the photocatalytic process. Except for the sublinear dependency, the other dependencies have been found to occur in direct plasmon driven photocatalysis under different operating conditions. However, the sublinear dependency is only observed in semiconductor photocatalysis in presence of bulk electron-hole recombination. An occurrence of thermally driven chemical reaction can be predicted by observing exponential change of photocatalytic rate with respect to the change in illumination intensity.[20] Both theoretical and experimental studies reveal that during plasmon excitation, the heating of the nanoparticle results in a change in its surface temperature which varies linearly with the change in illumination intensity.[23] Combination of this linearity with Arrhenius expression for thermally controlled chemical reactions reveals that rate of plasmon mediated reactions changes exponentially with the change in illumination intensity. In a recent study, for example, the rate of production of CO from CO_2 and H_2 in presence of Au/ZnO shows exponential dependency on laser intensity, quantitatively matching the expected results in a thermally driven process.[24] Besides, the high band gap of ZnO (~3.3 eV) is an evidence that visible light absorption in these experiments occurred only through Au nanostructures. For conversion of CO_2 to CO, the intensity required is 250 W/cm^2, which is 3 orders of magnitude higher intensity than that of average solar irradiance. However, because of the high absorption coefficient of the plasmonic nanostructures, it will be difficult to observe the exponential dependence of rate on intensity at low illumination intensity of photons in temperature regulated reactors. In addition to that there is always the problem of selectivity in such thermally driven reactions.

Generally, the linear dependence of catalytic rate on intensity of illumination, (Rate $\propto$ I) is the most commonly observed intensity dependent plasmon mediated photocatalytic rate. Some of the linear relationship, for example, are Ag nanocube mediated ethylene epoxidation,[20] desorption of NO from Ag nanoparticles,[25] dissociation of H_2 and D_2 to form H-D on Au nanoparticles etc.[26] These observations have been found to be relevant for photon intensities and catalyst geometries over a wide range making it difficult to optimize the best condition for direct plasmonic photocatalysis. Isotopic labeling experiments give additional evidence of the linear-dependence of rate on illumination intensity in an electron driven process. The rate limiting step in a thermally driven catalytic process has been measured through the kinetic isotope effect (KIE) via isotopic labeling of the reactants. The measurement of the change in rate of catalysis in presence of the labeled reactant is used to obtain the KIE which can be predicted theoretically through the transition state theory. It is evident from experiments that electron driven processes at the surface of metal display KIEs more prominently when compared to the thermally driven reactions. For example, KIE measurement of Ag nanocube mediated ethylene epoxidation through O_2^{16} and O_2^{18} shows higher KIE = 1.19 value for plasmon involvement than KIE = 1.06 for the thermal reaction. This signifies that the hot electrons generated via LSPR excitation facilitates dissociation of O_2 which is the rate limiting step in epoxidation of ethylene.[8,27]

The mechanism that has been proposed to explain the LSPR mediated 1st order intensity dependent photocatalysis is analogous to electronic transition induced desorption.[8] When the charge carriers generated via plasmon excitation have energetic and spatial overlap with unpopulated electronic state of the adsorbate, then transient transfer to the adsorbate states at a timescale of ~1-20 fs results in the formation of a transient negative ion (TNI) adsorbate.[28] This TNI formation is followed by transient of the adsorbate to the TNI PES. Typically, the equilibrium bond distance of TNI PES is different from that of the ground state PES. This leads to acceleration of the adsorbate along a particular nuclear degree of freedom resulting either a chemical transformation of the TNI PES, or a gain in vibrational energy when it returns back to ground state PES, i.e., decaying of the electron back to the metal.[29,30] The gained vibrational energy is dissipated via coupling to the metal surface at a time scale of 1-10 ps. The first order dependence of rate on intensity indicates that there is dissipation of the gained vibrational energy by the ground state PES to the metal prior to electron scattering. The efficiency of chemical transformation occurring through transient electron transfer are dependent upon various factors. Firstly, the probability of electron transfer from metal to the adsorbate is governed by the efficiency of the electron transfer coupling.[31] Secondly, the amount of gained energy required to induce the chemical reaction which is governed by the activation barrier for the reaction and the temperature of the system.[32] The temperature of the system plays a role in controlling the required energy gain for the reaction based on the exponential increase in the population of higher energy vibrational states with temperature. At higher temperature, molecules will be present in the vibrational states near the activation energy threshold and so require less energy from electron scattering to overcome the activation barrier. Thirdly, amount of deposited energy into the molecule through TNI which depends upon the shapes of the PES for ground state and TNI, electronic state lifetime, the congruence of energy of the scattering electron and unpopulated energy level of the adsorbate, and the system's temperature.[33] The nature of the adsorbate affects many of these factors such as the coupling efficiency, PES shape and the unpopulated adsorbate energy level. All these factors may result into unique selectivity compared to a pure thermal process via favorable interactions between plasmon derived charge carriers and the adsorbate.

The mechanism of superlinear dependency of photocatalytic rate on intensity has found similarity with that of the linear dependency. Some of examples of superlinear relationship are Au nanoparticle mediated dissociated of H_2 and D_2 to form H-D,[26] Ag nanocube cluster mediated ethylene epoxidation.[20] In both the cases, at low photon intensity, the photocatalytic rate shows linear dependency on intensity which converts into superlinear dependency at higher intensity. These observations have been explained by considering two different aspects. In case of Au mediated H-D formation, superlinearity behavior has been attributed to the heating of the nanoparticle, though no evidence could be provided to support it.[26] But for epoxidation of ethylene, it is found to be impossible to explain the superlinearity based on superposition of linear and exponential (heating process) functions thereby ruling out possibility of a nanoparticle heating-based mechanism. A non-thermal based transition from linear to superlinear dependency is further confirmed by the fact that the measured KIE for Ag nanocube cluster mediated epoxidation of ethylene and the used intensity of illumination during the transition from linear to superlinear behavior are positively related.[32]

Both linear and superlinear dependency of rate of photocatalysis on illumination intensity have been found on single crystal metal surfaces at much higher illumination intensity and low quantum yield as compared to that with plasmonic nanostructures. For example, Ag mediated O_2 dissociation during ethylene epoxidation transitioned from linear to superlinear at 10^9 times lower intensity of illumination compared to that on single crystal Pt.[8,32] Significant enhancement in the efficiency of photocatalysis in presence of plasmonic nanostructures as compared to the efficiency due to single crystal surfaces can be attributed to several factors. First, the significant enhancement of absorption coefficient in presence of plasmonic nanostructures compared to the single crystal metals. Secondly, the selective absorption of resonant photons at the surface of plasmonic nanostructures which have similar length scales as compared to the mean free path of electrons in them results into high probability of interaction of the hot electrons with the adsorbate. On the other hand, photon absorption by the single crystal occurs in the bulk and their large thickness hinders the charge carriers to reach the surface of the crystal. The third factor is the generation of hot spots, small tiny volumes created at the junction of two plasmonic nanostructures which can channelize the photon energies for very efficient photocatalysis.[34] The fourth and the last factor is light absorption by plasmonic nanostructure covered with the adsorbate may have a higher value of cross section for direct injection of charge into the adsorbate, compared to single crystals covered with the adsorbate thereby making the photocatalysis very efficient. Though these mechanisms have been explored in various contexts, but a quantitative description about them in connection with direct plasmonic photocatalysis is still to be achieved.

Effect of wavelength on plasmonic photocatalysis: The relation between photon absorption properties of photocatalysts to their performance can be well explored with wavelength dependent photocatalytic measurements. Also, the adsorbate's impact on the efficiency of a photocatalyst can be obtained from comparison of wavelength dependence of two different photocatalytic reactions on the same catalyst. This is based on the principle of activation of different bonds in the rate limiting or selectivity controlling steps at different excitation wavelengths. This adsorbate-specific bond activation at different wavelengths in electron driven reactions on metal surfaces can be explained with two primary mechanisms. The first mechanism emphasizes for similar qualitative trends in wavelength dependence of photocatalytic rate in different reactions, but different magnitudes in efficiency.[33] This difference in photocatalytic efficiencies suggests that electron scattering efficiency is adsorbate dependent which could be due to various factors like efficiency of coupling, shape of the PESs etc. The second mechanism is proposed in a case where the photocatalytic rates of the two reactions may display different qualitative trends or shapes at different wavelengths. This difference infers to the impact that the adsorbates have on absorption of photon which will drive the process. It is expected that if direct injection of charge into the adsorbate results in plasmon dephasing rather than through an indirect injection, i.e., first into the metal followed by transfer to the adsorbate, then the wavelength dependence would resemble an overlap of the LSPR spectrum and the molecular resonance absorption spectrum. Though adsorbate dependent effects could not provide conclusive information on the wavelength dependent photocatalysis, but the unsolved mechanisms may point towards the selective activation of specific bonds through the above-mentioned mechanisms. The dependence of rate of direct plasmonic photocatalysis on the wavelength has been explored for Ag nanocube cluster mediated ethylene epoxidation,[32] Au nanoparticle driven H-D formation through H_2 and D_2 dissociation,[26] etc. For the epoxidation of ethylene, the rate of photocatalytic reaction is measured as a function of long pass filter energy. Comparison of the derivative of this dependence to the relative plasmon intensity, obtained through overlap integral of intensity of the source and the nanocube's UV-vis spectrum, provides a measure of the plasmon excitation rate. At constant power, action spectrum reveals a reasonable agreement between the wavelength dependent photocatalytic rate and the plasmon intensity.[32] A similar agreement has been observed between the rate of photocatalysis and the catalyst's action spectrum during H-D formation in Au surface.[26] By observing the similarity between the absorption spectrum of the plasmonic photocatalyst and the wavelength dependent rates of catalysis, it can be argued with evidence that LSPR excitation is responsible for the photocatalytic activity. Moreover, combination of these wavelength dependent results with a linear dependence of photocatalytic rate on intensity infers to the involvement of an electronic (nonthermal) mechanism in LSPR driven photocatalysis. However, these results are not enough to clarify whether photocatalysis is driven by direct injection of charge into adsorbate states, CID, or through the interaction of adsorbates with hot electrons in the metal produced through Landau damping. Studies show that formation of covalent bonds between the adsorbate and the surface of the plasmonic nanostructure results into the shift in energy of the plasmons which is attributed to surface electronic structure modification near E_f that are responsible for supporting oscillating surface plasmons.[35] Though the rate of photocatalysis gets affected by plasmon oscillation and direct charge transfer into adsorbate states, but the wavelength dependent measurements performed till now mainly focus on activation of weakly bound adsorbates and are not expected to show a significant deviation from the LSPR spectrum.

Therefore, measurements involving tightly bound adsorbates which can perturb the electronic structure of the plasmonic surface may provide the information regarding efficacy of CID to drive photocatalysis. However, the evidence of role of plasmonic nanostructure in direct plasmonic photocatalysis is obtained from the wavelength dependent studies.[8] But the inference on whether charge injection into adsorbates occurs at the instant of plasmon dephasing or sometime after dephasing is limited by few studies on this which also makes it difficult to predict the possible effectiveness of using LSPR excitations to modulate selectivity through adsorbate specific activation. More careful further studies on this topic would provide clear insights into the unanswered questions.

II. CONCLUSIONS

The role of plasmonic nanostructures in heterogeneous catalysis has been discussed in detail. The reactions that can be catalyzed through the involvement of plasmonic surfaces have become wider over the years. The rate of chemical reactions taking place on the surfaces of Ag, Au, Cu etc. shows significant enhancement at low intensity visible photon illumination. This has been inferred to the focusing of photon energy by LSPR leading to the enhancement of rate limiting steps in various reactions. To some extent, selectivity in chemical reactions can also be achieved with the help of plasmonic nanostructures. Study of the mechanisms reveals that transient hot electron transfer to the adsorbate orbitals is responsible for most of the reported direct plasmonic photocatalysis where the nature of the adsorbate plays significant role in catalytic efficiency. The conclusive evidence of the role of plasmonic nanostructures in photocatalysis can be obtained through both intensity and wavelength dependent photocatalytic rate.

REFERENCES

[1] Y. Zhao, W. Gao, S. Li, G.R. Williams, A.H. Mahadi, D. Ma, "Solar- versus Thermal-Driven Catalysis for Energy Conversion," Joule, vol. 3, pp. 920-937, 2019.
[2] (Z. Zhang, C. Zhang, H. Zheng, H. Xu, "Plasmon-Driven Catalysis on Molecules and Nanomaterials," Acc. Chem. Res., vol. 52, pp. 2506-2515, 2019.
[3] J. Wang, T. Ding, K. Wu, "Coulomb Barrier for Sequential Two-Electron Transfer in a Nanoengineered Photocatalyst," J. Am. Chem. Soc., vol. 142, pp. 13934-13940, 2020.
[4] Kazuhiko Maeda, Kentaro Teramura, Daling Lu, Tsuyoshi Takata, Nobuo Saito, Y. I. & K. D. "Photocatalyst Releasing Hydrogen from Water," Nature, vol. 440, pp. 295, 2006.
[5] B. Tang, F. X. Xiao, "An Overview of Solar-Driven Photoelectrochemical CO_2 Conversion to Chemical Fuels," ACS Catal., vol. 12, pp. 9023-9057, 2022.
[6] G. M. Bonn, S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf, G. Ertl, "Phonon- versus Electron-Mediated Desorption and Oxidation of CO on Ru(0001)," Science, vol. 285, pp. 1042-1050, 1999.
[7] F. Abild-Pedersen, J. Greeley, F. Studt, J. Rossmeisl, T. R. Munter, P. G. Moses, E. Skúlason, T. Bligaard, and J. K. N, "Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces," Phys. Rev. Lett., vol. 99, pp. 016105_1-016105_4, 2007.
[8] M. J. Kale, T. Avanesian, P. Christopher, "Direct Photocatalysis by Plasmonic Nanostructures," ACS Catal., vol. 4, pp. 116-128, 2013.
[9] Y. Wang, I. Aravind, Z. Cai, L. Shen, B. Zhang, B. Wang, J. Chen, B. Zhao, H. Shi, et al., "In Situ Investigation of Ultrafast Dynamics of Hot Electron-Driven Photocatalysis in Plasmon-Resonant Grating Structures," J. Am. Chem. Soc., vol. 144, pp. 3517-3526, 2022.
[10] (Y. Negrín-Montecelo, X. T. Kong, L. V. Besteiro, E. Carbó-Argibay, Z. M. Wang, M. Pérez-

Lorenzo, A. O. Govorov, M. M. A. C. D. Comesaña-Hermo, "Synergistic Combination of Charge Carriers and Energy-Transfer Processes in Plasmonic Photocatalysis," ACS Appl. Mater. Interfaces, vol. 14, pp. 35734-35744, 2022.
[11] S. C. Warren, E. Thimsen, "Plasmonic Solar Water Splitting," Energy Environ. Sci., vol. 5, pp. 5097-5460, 2012.
[12] A. Nitzan, L. E. Brus, "Theoretical Model for Enhanced Photochemistry on Rough Surfaces," J. Chem. Phys., vol. 75, pp. 2205-2214, 1981.
[13] S. Link, M. A. El-Sayed, "Shape and Size Dependence of Radiative, Nonradiative and Photothermal Properties of Gold Nanocrystals," Int. Rev. Phys. Chem., vol. 19, pp. 409-453, 2000.
[14] L. Brus, "Noble Metal Nanocrystals: Plasmon Electron Transfer Photochemistry and Single-Molecule Raman Spectroscopy," Acc. Chem. Res., vol. 41, pp. 1742-1749, 2008.
[15] S. Link, M. A. El-Sayed, "Size and Temperature Dependence of the Plasmon Absorption of Colloidal Gold Nanoparticles," J. Phys. Chem. B, vol. 103, pp. 4212-4217, 1999.
[16] K. Watanabe, D. Menzel, N. Nilius, H. J. Freund, "Photochemistry on Metal Nanoparticles," Chem. Rev., vol. 106, pp. 4301-4320, 2006.
[17] R. A. Molina, D. Weinmann, R. A. Jalabert, "Oscillatory Size Dependence of the Surface Plasmon Linewidth in Metallic Nanoparticles," Phys. Rev. B, vol. 65, pp. 155427, 2002.
[18] G. D.Valle, M. Conforti, S. Longhi, G. Cerullo, D. Brida, "Real-Time Optical Mapping of the Dynamics of Nonthermal Electrons in Thin Gold Films," Phys. Rev. B, vol. 86, pp. 155139, 2012.
[19] (C. Voisin, N. Del-Fatti, D. Christofilos, F. Vallée, "Ultrafast Electron Dynamics and Optical Nonlinearities in Metal Nanoparticles," J. Phys. Chem. B, vol. 105, pp. 2264-2280, 2001.
[20] P. Christopher, H. Xin, S. Linic, "Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures," Nat. Chem., vol. 3, pp. 467-472, 2011.
[21] B. N. J. Persson, "Polarizability of Small Spherical Metal Particles: Influence of the Matrix Environment," Surf. Sci., vol. 281, pp. 153-162, 1993.
[22] W. Ho, "Reactions at Metal Surfaces Induced by Femtosecond Lasers, Tunneling Electrons, and Heating," J. Phys. Chem., vol. 100, pp. 13050-13060, 1996.
[23] A. O. Govorov, H. H. Richardson, "Generating Heat with Metal Nanoparticles," Nano Today, vol. 2, pp. 30-38, 2007.
[24] C. Wang, O. Ranasingha, S. Natesakhawat, R. Paul, J. Ohodnicki, M. Andio, J. P. Lewisac, C. Matranga, "Visible Light Plasmonic Heating of Au–ZnO for the Catalytic Reduction of CO2," Nanoscale, vol. 5, pp. 6968-6974, 2013.
[25] K.H. Kim, K. Watanabe, D. Mulugeta, H.J. Freund, D. Menzel, "Enhanced Photoinduced Desorption from Metal Nanoparticles by Photoexcitation of Confined Hot Electrons Using Femtosecond Laser Pulses," Phys. Rev. Lett., vol. 107, pp. 047401, 2011.
[26] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, j. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, N. J. Halas, "Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H2 on Au," Nano Lett., vol. 13, pp. 240-247, 2013.
[27] D. N. Denzler, C. Frischkorn, C. Hess, M. Wolf, G. Ertl, "Electronic Excitation and Dynamic Promotion of a Surface Reaction," Phys. Rev. Lett., vol. 91, pp. 226102, 2003.
[28] F. M. Zimmermann, W. Ho, "State Resolved Studies of Photochemical Dynamics at Surfaces," Surf. Sci. Rep., vol. 22, pp. 127-247, 1995.
[29] D. Menzel, "Electronically Induced Surface Reactions: Evolution, Concepts, and Perspectives," J. Chem. Phys., vol. 137, pp. 091702, 2012.
[30] J. J. Czyzewski, T.E. Madey, J. T. Yates, "Angular Distributions of Electron-Stimulated-Desorption Ions: Oxygen on W(100)," Phys. Rev. Lett., vol. 32, pp. 777-780, 1974.
[31] C. D. Lindstrom, X. Y. Zhu, "Photoinduced Electron Transfer at Molecule−Metal Interfaces," Chem. Rev., vol. 106, pp. 4281-4300, 2006.
[32] P. Christopher, H. Xin, A. Marimuthu, S. Linic, "Singular Characteristics and Unique Chemical Bond Activation Mechanisms of Photocatalytic Reactions on Plasmonic Nanostructures," Nat. Mater., vol. 11, pp. 1044-1050, 2012.

[33] T. Olsen, J. Gavnholt, J. Schiøtz, "Hot-Electron-Mediated Desorption Rates Calculated from Excited-State Potential Energy Surfaces, " Phys. Rev. B, vol. 79, pp. 035403, 2009.
[34] A. M. Michaels, Jiang, L. Brus, "Ag Nanocrystal Junctions as the Site for Surface-Enhanced Raman Scattering of Single Rhodamine 6G Molecules," J. Phys. Chem. B, vol. 104, pp. 11965-11971, 2000.
[35] P. Mulvaney, "Surface Plasmon Spectroscopy of Nanosized Metal Particles," Langmuir, vol. 12, pp. 788--800, 1996.