CHEMICAL EFFECTS OF LIGHT ON NANOSCALE METAL PARTICLES

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Abstract:

Brightened metallic nanoparticles serve to catalyse chemical processes that hold significant implications for both industrial applications and societal advancement. The utilization of light in chemical reactions presents an intriguing replacement to petroleum, considering its prevalence as a sustainable energy medium. Light facilitates the unlocking of electronic improvements to chemical reactions by generating and activating hot carriers on molecular adsorbates, a process not accessible through conventional thermochemical conversions. This Perspective aims to offer a comprehensive overview of significant techniques and findings from many years of surface research in science that have established the groundwork for contemporary investigations into hot carrier photochemistry. Recent developments in nanoscience and heterogeneous catalysis have led to the emergence of novel materials, especially metal nanoparticles that maintain collective electronic oscillations when exposed to light (plasmon resonances), which can be utilized as effective photo-catalysts. Plasmonic photo-catalysts exhibit significant optical absorption and can be meticulously engineered via Landau damping to optimize hot carrier generation within a specified volume, thereby enhancing their application in relevant reactions. Photo Chemistry holds significant importance in numerous facets of this research domain. This tool serves a distinctive purpose in the synthesis of metal nanoparticles and plays a crucial role in exploring the underlying mechanisms of their formation.

Keywords: Photo Chemistry, heavy metals, Plasmonic methods, photo-catalysts, nano metal particles

Introduction:

The study of the photochemistry of small molecules on precisely characterized metal surfaces has captivated researchers for over thirty years. This domain captivates attention due to its foundation on the interplay of two distinct influences. On the other side, the potential for new reaction channels emerges through electronic excitation, which typically remain unattainable via thermal activation. Conversely, in contrast to molecular photochemistry occurring in the gas phase, the interactions between molecules and solid substrates unveil distinctive avenues for photoexcitation and photoreaction that remain unattainable in homogeneous reactions. This phenomenon arises chiefly from the influence of bonding interactions with the substrate, which alter both the ground state and the electronically excited states of the adsorbates. Furthermore, the swift transfer of energy from excitation among adsorbates and substrates, especially on metal as well semiconductor surfaces, may result in the immediate extinction of excited adsorbate states through the transfer of charge or otherwise energy from the adsorbates to the substrate (Henriksen and Hansen, 2019; Jiang et. al., 2018; Shaikhutdinov S, 2018).

Moreover, the excitation of adsorbates by hot electrons generated through photo absorption in the substrate is significant, as it facilitates charge as well energy transfer in the reverse direction, from the substrate to the adsorbates. Precisely defined metallic surfaces adorned with adsorbate layers in ultrahigh vacuum (UHV) conditions present systems that are thoroughly characterized in all dimensions, especially concerning their geometry as well electronic structure. The existence of layers typically composed of molecules that are inherently aligned on the surface renders surface photochemistry a compelling alternative to the stereo-dynamic manipulation of chemical reactions via optically aligned molecular beams. Three Clearly delineated adsorbate systems consequently offer distinctive environments for the exploration of surface photochemistry (Van Spronsen et. al., 2017).

Driven by the necessity to connect surface science conducted under ultra-high vacuum conditions with the operations of actual catalysts, simulation frameworks for different types of catalysis have undergone thorough investigation over the past ten years. Typically, these systems are composed of metal particles at the nanometre scale, which are supported by thin layers of oxide. The aim of these investigations extends beyond a thorough examination of actual catalysts; it encompasses an aspiration to enhance the regulation of the chemical, physical, as well catalytic characteristics of nanoparticle systems (Sun et. al., 2020).

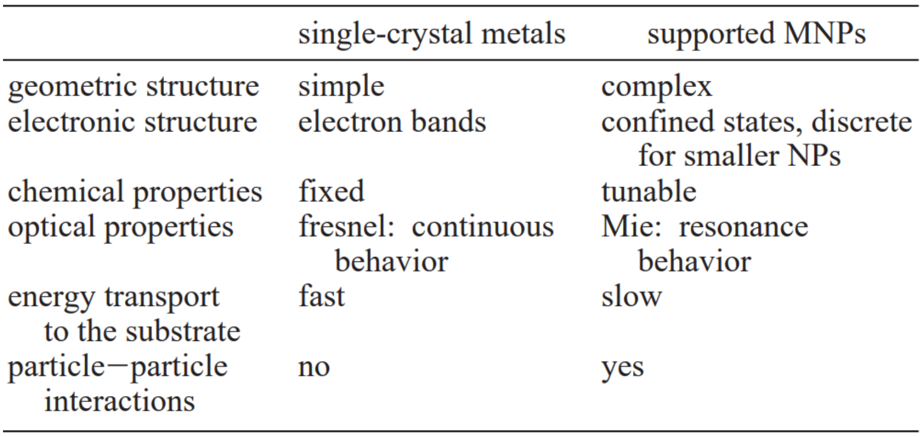
In this context, we refer to metallic particles that are characterized by dimensions within the nanometre scale as metal nanoparticles (MNP). The term metal cluster is often employed, more or less interchangeably. Nonetheless, this terminology is typically applied to a wider spectrum of sizes, beginning with diminutive aggregates comprising three atoms (trimer) and extending to particulates of micrometre dimensions. The minor clusters that exhibit the influences of molecular along with shell structures are unlikely to have significance in our discussion. The synthesis as well as applications of size-controlled ligand-stabilized magnetic nanoparticles, exemplified by Au55, represent a significant area of research (Luo et. al., 2016; Antonello and Maran, 2017). Nonetheless, they fall beyond the purview of this review.

The investigation of thermally triggered chemical reactions has been conducted on mass-selected metal clusters, both in the gas phase and following their gentle deposition onto solid surfaces. In the latter scenario, catalytic cycles have indeed been observed. Conversely, the body of research concerning the photochemistry of compounds adsorbed on clusters of metal within the gas phase remains notably limited. As far as we are aware, the photocatalytic characteristics of mass-selected metal clusters that have been soft-landed on surfaces remain unexamined to date. The process of submitting small, mass-selected aggregations onto substrates followed by examining their size-specific properties can be characterized as a 'bottom-up approach'. This technique would enable an exceptional level of control, provided one could ascertain the quality of the surface as well densities of specific imperfections with remarkable precision. Given that this is often not the situation, it is necessary to characterize the system following cluster deposition, a practice that is typically overlooked, especially concerning oxide surfaces (Wang et. al., 2019; Khetrapal et. al., 2018).

Characterization using scanning tunnelling microscopy was, nonetheless, pursued for diminutive metal clusters comprising several tens of atoms on Pt(111), Si(111), and graphite substrates. An alternative methodology involves the vapour deposition of metallic atoms onto substrates, subsequently leading to their aggregation into either crystalline or amorphous nanoparticles. This method demonstrates exceptional adaptability in constructing particle systems with diverse topographic and electronic characteristics, facilitating the examination of size-selected, deposited clusters through local probe spectroscopies. In the two methods, comparing findings among experimental as well theoretical results, along with data gathered on planar surfaces, holds significant interest as well importance. This is especially true when the presence of nanoparticles gives rise to subjectively novel behaviours, such as particle size effects, cluster-support interactions, or specific collective excitations in the individual magnetic nanoparticles or in the ensemble (O'Donovan et. al., 2002; Wang and Laskin, 2009).

Table 1 presents a comparison of the distinctive properties of single-crystal surfaces of metal along with supported metal nanoparticles. The latter reveals an array of novel physical as well as chemical characteristics alongside the established characteristics of single-crystal conduct. Notably, this includes a more intricate geometrical structure as well the quantization of electronic states within spatially restricted networks, which consequently results in a reduction in electrical transfer into the substrate. The unique chemical as well catalyst characteristics are largely influenced by the novel morphology of nano-sized particles ensembles, which arise from significant surface-to-volume percentages and constrained particle dimensions (Fukui and Yasumatsu, 2017; Dong et. al., 2017).

Table 1: Elements Influencing Photochemical Reactions on Metals with Single-Crystal as well Metallic Nanoparticles (MNPs) Supported



	single-crystal metals	supported MNPs
geometric structure	simple	complex
electronic structure	electron bands	confined states, discrete for smaller NPs
chemical properties	fixed	tunable
optical properties	fresnel: continuous behavior	Mie: resonance behavior
energy transport to the substrate	fast	slow
particle−particle interactions	no	yes

By adjusting the preparation conditions, one can effectively tailor the system properties to meet the requirements of a particular chemical reaction. Moreover, the unique optical properties of nano sized metal particles exert a significant impact on photochemistry. The interplay of these variables influences the engagement of MNPs with adsorbed molecules, thereby affecting their efficacy in photochemical reactions.

The turn able morphology of particle systems, encompassing aspects such as shape, size, and environmental conditions of the MNPs, presents a significant opportunity to customize and refine their optical properties in comparison to bulk crystals. Specifically, novel collective modes in electron excitations, characterized as Mie-type surface Plasmon polarities, hold significant importance in facilitating photochemical reactions. Utilizing the significant field enhancement brought about by particle Plasmon resonances, initial investigations into the photochemistry on metallic nanoparticles were conducted in the mid-1980s (Zhao et. al., 2018).

The experiments conducted during this period were motivated by the insights and consequences obtained from surface-enhanced Raman spectroscopy (SERS), a technique that employs the Plasmon prompted electromagnetic near field to provoke opto-vibrational excitations in adsorbed molecules. The topology of MNP ensembles is recognized as significant for thermally induced catalysis, as it affects the transport of chemical species between MNPs and the support, a phenomenon known as the spill-over effect. This principle should likewise apply to photochemical reactions, further enhancing the advantages already conferred by the unique optical characteristics of MNP ensembles, as influenced by their topography and interactions with the support. A comprehensive exploration of the interconnections among these facets remains an area requiring additional investigation (Zhan et. al., 2018).

The present article examines the photochemistry of metal nanoparticles, which were synthesized in ultrahigh vacuum on precisely defined metal or insulator substrates and analysed using standard surface science methodologies. Our focus will not extend to ultra-small clusters, specifically those comprising fewer than approximately 100 atoms. Instead, we will concentrate primarily on the diameter range of 2 to 20 nm, which corresponds to several hundred to around 10^5 atoms. In this context, we will employ the nomenclature MNPs. Nevertheless, given that the majority of foundational concepts have been established with incorporated particles or those prepared under less rigorous conditions, significant studies utilizing these types of samples will also be referenced as necessary (Spreafico et. al., 2017; Zhan et. al., 2020). We meticulously examine the distinct variations among bulk surfaces of metal as well MNPs.

Characteristics of Nanoparticles Composed of Metals:

The characterization along with preparation of a specimen hold paramount significance in the investigation of photochemistry on MNPs. This document provides a concise overview of the experimental methodologies employed in the synthesis of magnetic nanoparticles on precisely defined substrates. Furthermore, it examines their pertinent characteristics in the realm of photochemistry, including geometrical configuration and electronic as well as optical properties, as elucidated through a range of surface analytical techniques. The majority of the experimental techniques employed bear a resemblance to those utilized in photochemical investigations of single-crystal surfaces. Typically, they integrate traditional surface analysis methodologies with appropriate illumination sources (She et. al., 2017; Sjakste et. al., 2018).

The primary distinction between single-crystal and MNP studies lies in the unique methodologies employed for the preparation of the particle ensembles. Regarding the optical properties of MNPs, a multitude of studies exists that cannot be thoroughly addressed within the confines of this review. Moreover, numerous prior studies focused on embedded particles; thus, their findings may not be readily applicable to UHV-prepared systems, despite the foundational concepts that emerged from those investigations (Zhang et. al., 2017). This document endeavours to present a comprehensive overview of the current understanding derived from a selection of both experimental as well as theoretical investigational publications. Our primary emphasis lies on the ultrafast electron dynamics occurring within MNPs, as this is expected to significantly influence photochemistry. We also engage with subjects pertaining to plasmonics, as we anticipate that the collective excitations will be pivotal in surface photochemistry involving combinations of optically associated MNPs.

Formulation with Geometric Configuration of Metal Nano-particles on Precisely Demarcated Shells:

Several investigations have been conducted in order to prepare and evaluate MNPs on properly organized oxide films, with the objective of creating model systems for catalysis that is heterogeneous. Common substrates include thin oxide films developed on metallic supports, exemplified by a two-layer Al2O3 film on NiAl (110k) and a MgO film on Mo (100k). On a chemical level, inactive bulk supports, including strongly oriented pyrolytic graphite (HOPG) as well quartz, are being utilized as well. Given that particles typically nucleate at point and line defects; substrates are occasionally subjected to ion sputtering before metal deposition. This process aims to create well-defined locations for binding and enhance the resilience of the particles. Metal atoms are typically deposited using an electron beam evaporator, with the flux being meticulously calibrated by a microbalance composed of quartz crystals (QCM). The manipulation of the temperature of the substrate along with surface concentration defect allows for precise control over the size and morphology of the MNPs (Yu et. al., 2016).

For instance, palladium exhibits growth at low temperatures (100K) into diminutive amorphous clusters on Al2O3/NiAl (110k), whereas at ambient temperature (300K), it develops into comparatively larger and crystalline nanoparticles characterized by predominantly (111k) oriented top and side facets, alongside a lesser presence of (100k) facets. Gold nanoparticles exhibit a growth behavior that closely resembles that of palladium, with the notable distinction that the greater mobility of gold necessitates lower temperatures to achieve particle sizes comparable to those of palladium. It is important to note that the nucleation of gold on Al2O3 represents a unique scenario and should not be directly compared to the nucleation of palladium. Conversely, the crystallization of Ag NPs presents greater challenges. Standard cluster densities are approximately 10 particles per cm^2 (Jakob and Nilius, 2020).

The distribution of sizes among MNPs tends to exhibit a broad spectrum when they are deposited on oxide surfaces. For MNPs exhibiting plasmon resonances within the visible spectrum, such as Ag NPs, the pattern of distribution of size can be considerably refined through the innovative 'laser shaping' technique pioneered by Trager and colleagues. This method involves the resonant heating of magnetic nanoparticles through laser pulses that are precisely tuned to the plasmon energy. As a result, smaller particles gradually evaporate, while larger particles experience a reduction in size during the laser treatment process. MNPs with mean diameters exceeding 50-100 nm can be produced through lithographic techniques, which provide remarkable precision in controlling particle sizes, shapes, and their spatial arrangement on surfaces. Nevertheless, the NPs prepared through lithography exceed the size parameters outlined in this review, and the issue of particle cleanliness poses a significant challenge for precise photochemical studies (Zhao et. al., 2019).

The geometric configurations of MNPs may be examined using many methods, including scanning tunneling microscopy (STM), atomic force microscopy (AFM), transmission electron microscopy (TEM), including spot profile analysis of low-energy electron diffraction (SPA-LEED). STM as well AFM provide localized structural insights at the atomic scale. Figure 1 displays characteristic STM images of Pd and Ag nano particles (Hansen et. al., 1999). SPA-LEED offers data on coverage, particle size, including inter-particle distances standardized throughout a sample area corresponding to the diameter of the electron beam (less than 1 mm, roughly encompassing 10 particles). Following the rectification of tip convolution effects intrinsically associated with scanning probe methodologies, a strong concordance was achieved between SPA-LEED and STM/AFM findings. A supplementary method that offers atomic resolution is Transmission Electron Microscopy (TEM). Nevertheless, its ex-situ nature, resulting from the typical process of transporting the sample via air, restricts its use for the characterisation of ultra-high vacuum (UHV)-prepared magnetic nanoparticles (Biswas et. al., 2020; Freund et. al., 1993).

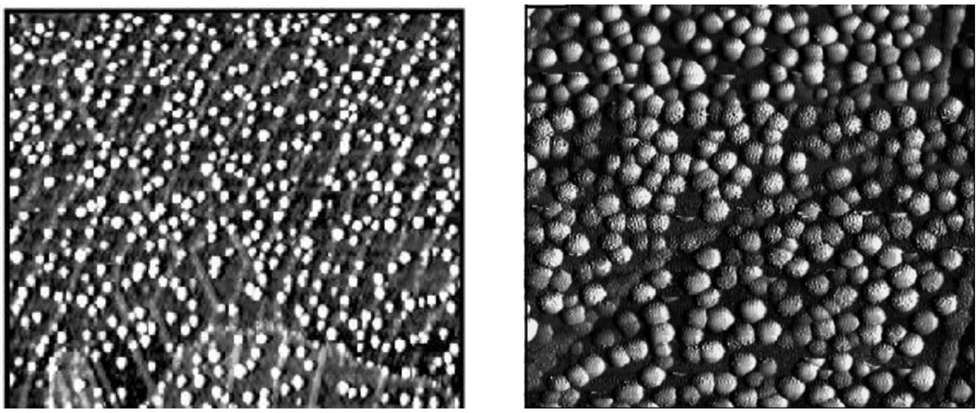


Figure 1: Scanning tunnelling microscopy pictures of (a) palladium and (b) silver nanoparticles on Al2O3/NiAl (110) (Hansen et. al., 1999).

Electronic Characteristics

The electrical configuration of MNPs holds significant implications for their photochemical performance and thus warrants meticulous study. The electronic properties of MNPs are investigated primarily through two methodologies: photoelectron spectroscopy, which serves as a non-local approach, and scanning tunnelling spectroscopy, which functions as a local approach. A variety of variants of each type, each with different benefits and drawbacks for the examination of MNPs on surfaces, have been developed to date, which are succinctly reviewed in the following discussion.

Structure of Electrons

Figure 2 provides a schematic representation of the alterations in electronic structure that occur during the transition from an individual atom to a more extensive metal crystal. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) are commonly employed to investigate the electronic structure of MNPs. On a single side, a progressive emergence of metallic bands from individual atomic orbitals is noted in the valence band region as cluster size increases. Furthermore, a clearly delineated Fermi edge emerges in clusters comprising several thousand atoms, effectively distinguishing between occupied as well as unoccupied electronic states. The emergence of metallic properties is observed at approximately 1 nm, while a bulk-like band structure develops at around 3 nm in diameter. Conversely, notable alterations in the binding energy (BE) of core as well valence electrons are observed (Guo et. al., 2016; Vallée F, 2018).

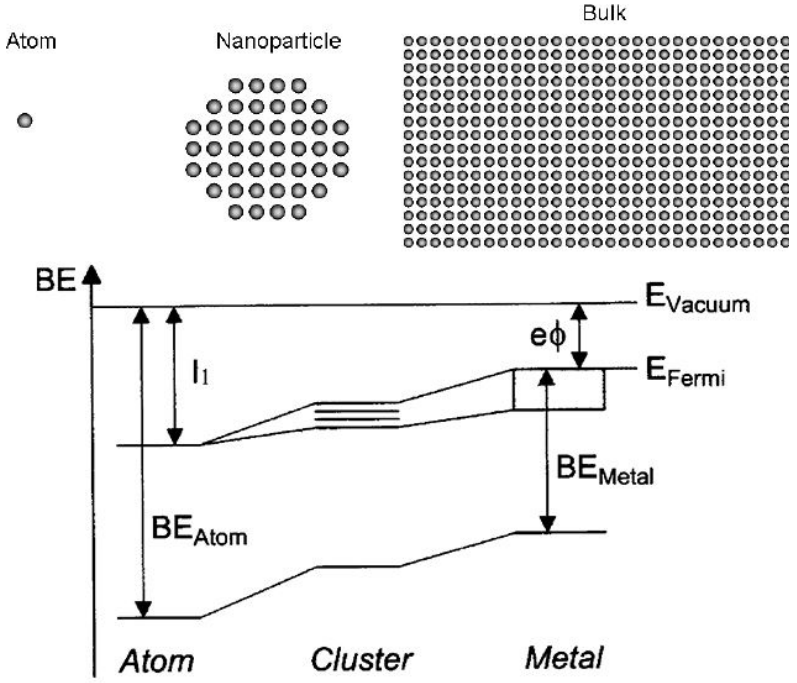


Figure 2: alterations in electronic structure in formation of metal from an atom (Santra AK, Goodman, 2002)

The shifts encompass chemical consequences in the starting situation and unfinished screening impacts to the final state, arising from the constraints imposed by the limited size of cluster. The influence on photoemission observed in this context is absent in extended metallic systems, highlighting the distinct screening as well delocalization characteristics of the positive charge remaining on the overall system during and/or following electron emission. The final state effect leads to a displacement of the complete photoelectron spectrum, which is determined by the Coulomb energy interaction between the localized charge on the cluster and the photoelectron, thus exhibiting a proportional relationship to the inverse of the particle diameter. Recently, the phenomenon of lattice strain in magnetic nanoparticles has been examined as a contributing factor to binding energy shifts (Dong et. al., 2020).

The UPS/XPS data serve as a valuable tool for assessing the influence of electronic coupling within the metal substrate that supports the oxide film and the magnetic nanoparticles. For instance, in the case of Pd as well Rh deposits on slender alumina films on NiAl (110), the influence of the transfer of charges from the substrate was minimal within the time frame of the core ionization process (10^-17 to 10^-15 s, varying with the type and mode of excitation). Furthermore, an analysis of the Auger and auto-ionization spectra of CO-covered Pd particles demonstrated that, even within the temporal confines of the core-hole lifetime (approximately 10^-15 seconds), there is no observable charge transfer taking place (Tal et. al., 2017).

As illustrated in Figure 3, one can confidently exclude electron tunnelling from the NiAl substrate when analysing sufficiently rapid disruptions in the electrical composition of metal deposits, such as the formation of core holes (Watanabe et. al., 2006). Conversely, the rapid charge transport through the thin oxide effectively inhibits ongoing charging of the MNPs. It is essential to recognize that the conclusions derived for ultrathin Al2O3 films may not universally apply to all thin-film supports and metal-oxide film combinations, necessitating verification for each specific instance.

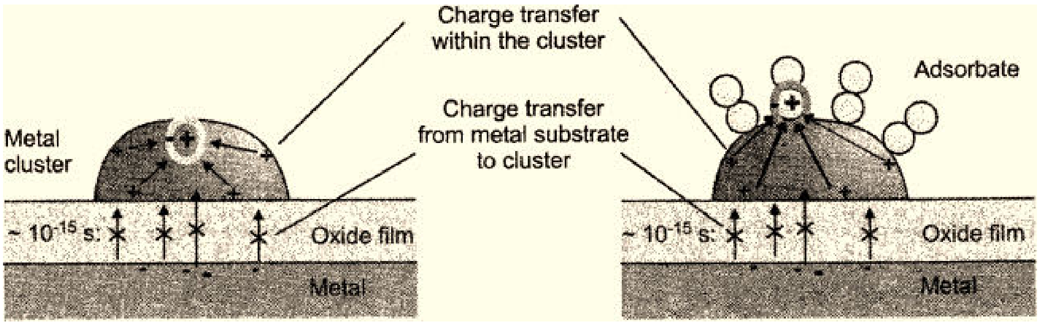


Figure 3: The screening processes after the formation of a core hole inside a cluster (in left side), in addition to an adsorbate layer (in right side) (Watanabe et. al., 2006).

Dynamics of Electrons

The behaviour of hot electrons produced in MNPs is pivotal in influencing the kinetics of chemical reactions on their surfaces, provided these hot electrons initiate the chemical processes in the adsorbates. We thus provide a succinct overview of the present understanding about these processes.

The temporal process of photoexcitation and relaxation of electrons in an MNP may be delineated into many stages (Aikens, 2018; Ionin et. al., 2016).

Step 1: The absorption of a photon excites an electron situated below the Fermi level of a metal nanoparticle, resulting in the formation of an electron-hole pair.

Step 2: This generates a temporary a thermal electron-hole distribution that evolves swiftly by electron-electron scattering, has a downward energy shift, and undergoes broadening. The temporal dynamics of these processes is highly contingent upon the energy of hot electrons, occurring rapidly (under 10 fs) at elevated energies (2-3 eV) relative to the Fermi level, and decelerating (to tens of femtoseconds) as energy diminishes. This relationship may be approximated using Fermi liquid theory in bulk crystals or thick films.

Step 3: Within a temporal range of about 100 fs to 1 ps, a quasithermal distribution characterized by a specific electron temperature is attained, significantly exceeding the lattice temperature.

Step 4: The resultant thermal hot electron distribution undergoes additional cooling by electron-phonon interactions, a process that transpires over a time scale ranging from few to several hundred picoseconds or more. The two-temperature model is applicable in this situation.

Following step 1, the succeeding phases temporally overlap and progress in a linked manner. The intermixing mechanisms are significant for surface photochemistry on MNPs. The relaxation processes of hot electrons in implanted metallic nanoparticles have been investigated using sub-pico-second pump-probe experiments and theoretical analysis.

In general, the disparities in electron-electron scattering among bulk materials and sufficiently large metal nanoparticles (d > 2 nm) of the same substance are not significant when compared to the variations observed between different materials, provided that surface discrepancies or states of defect are disregarded. In actuality, the behaviour may be influenced mostly by defect contributions, resulting in both elastic and non-elastic dispersion events.

The hot electron dynamics in heavy metal interfaces have been thoroughly examined using both theoretical approaches and two-photon photoemission (2PPE) experiments. Equivalent investigations for magnetic nanoparticles (MNPs) are limited, despite existing research on silver and gold nanoparticles (NPs) on highly ordered pyrolytic graphite (HOPG) conducted by Pfeiffer and colleagues using two-photon photoemission (2PPE). Conversely, the electron dynamics of metal nanoparticles (MNPs) embedded in a matrix or supported on a solid substrate have been investigated by optical spectroscopic techniques and theoretical approaches.

Disagreement exists over the alterations in hot electron cooling durations caused by finite particle size, particularly when the particle diameter is less than the electron means free path. It must be acknowledged that within our size range, the standard attenuation lengths and the photon wavelength significantly exceed the particle diameter. The primary assertion is that the surface introduces supplementary scattering centers (surface states, defects, irregularities); thus, when the mean bulk scattering lengths surpass the particle's diameter, scattering should augment with the surface-to-volume ratio as size diminishes, specifically scaling with 1/R. This outcome has been achieved in several theoretical studies (Jimenez-Villacorta et. al., 2016).

You X, Ramakrishna and Seideman, recently provided an analysis of the progression of processes of relaxation of hot electrons in relation to photochemistry at MNPs. Forty-three It was noted that it is essential to differentiate between a low excitation regime, where the aforementioned considerations seem relevant, and a high excitation density regime, in which the cooling of electron temperature occurs at a significantly slower rate due to confinement effects (You et. al., 2018).

At elevated excitation densities, the thermal dynamics of molecules that are absorbed on magnetic nanoparticles may rival or even surpass the significance of photochemical procedures. Consequently, it is crucial for the field of photochemistry concerning MNPs to differentiate between photochemical and thermal processes. The heating of magnetic nanoparticles, along with bulk metals, through the application of short laser pulses has been examined with considerable depth.

Optical Characteristics

The optical features of MNPs result from their unique electrical and geometric characteristics, which are particularly significant for surface photochemistry. They have undergone significant study. The significant study by Tang and his group examined prior findings. The primary issues are the dependencies of the absorption spectra of MNPs on their dimensions and morphologies, inter-particle interactions, and their surrounding surroundings. A substantial amount of data exists for supported as well embedded granules of alkalis, silver, and gold, which underpins the majority of the aforementioned features. Recent information has emerged from time-resolved laser spectroscopy (Tang et. al., 2018).

Enhancement of Plasmonics Fields

An exceptional phenomenon in the optical response of metallic nanoparticles (MNPs) is the size and shape dependent collective electrical stimulation known as Mie plasmon. This results in significant field enhancement around the particles, which is very crucial in surface-enhanced Raman spectroscopy (SERS). It accounts for a significant increase in absorbency seen in all photo-induced phenomena. The very potent plasmon modes in silver and gold nanoparticles have been used since the Middle Ages to create the vivid hues in stained glass. They have been scientifically investigated, primarily in the condensed phase. This excitation is used in numerous sensors for medical as well biological applications, where, in addition to field augmentation, the sensitivity of the plasmon to changes in the dielectric properties of the material around the MNPs is leveraged. Both effects are anticipated to influence MNP photochemistry.

Plasmon Longevity and Diminution

The influence of particle size on plasmon decay processes may be encapsulated as follows. For large MNPs with $R > 10$ nm, radiation damping mostly restricts the plasmon lifespan. At diminutive sizes (0.5 e $R < 2$ nm), the dissipation into electron-hole pairs (Landau damping) prevails. For intermediate dimensions, both effects are in competition. Most of these processes will remain active subsequent to non-resonant photon absorption. If significant photon emission contributions as the primary relaxation mechanism of plasmons can be discounted, the first outcome of plasmon decay is very energetic electron-hole (e-h) pairs, which will be the direct result of non-resonant excitations. The temporal sequences after the decomposition of plasmon excitations are potentially significant for surface photochemistry on MNPs.

Plasmon lifetimes, mostly obtained from resonance widths and hole-burning studies, have been determined to be quite brief. Plasmon dephasing in sodium clusters on a lithium fluoride substrate has been quantified at 15 femtoseconds by femtosecond time-resolved second-harmonic production. The breadth of Ag NPs on quartz and sapphire surfaces is influenced by their size, shape, and chemical surroundings (e.g., adsorbates or support), as shown by an amalgamation of persistent burning of spectral hole as well laser shaping techniques (Wilson and Jain, 2020).

The substrate's effect has been examined by reflectivity measurements and assessed via the stimulation of multipolar modes of plasmon for Ag nanoparticles on R-Al2O3(0001). The absorption spectra of individual gold nanoparticles with diameters as small as 5 nm have recently been recorded using a photo-thermal heterodyne visualization technique. Intrinsic size effects manifested as a widening of the outer layer of plasmon resonance; these data may be juxtaposed with those from the photon-STM discussed in the subsequent section.

Redmond and Brus conducted a thorough investigation of the dynamics and characteristic decay durations of plasmon excitations in Ag nanoparticles on HOPG, finding values on the order of a few femtoseconds. Plasmonics increases in the two-photon photo-emission (2PPE) yield were found for gold nanoparticles on highly oriented pyrolytic graphite (HOPG106) and silver nanoparticles on silicon (111) and thin alumina sheets. The size dependency of the 2PPE production was carefully examined in the latter scenario, and potential impacts on photochemistry were analysed (Redmond and Brus, 2007).

A combination of light emission spectroscopy with scanning tunnelling microscopy (STM) is known as "photon-STM" because it allows for the study of luminescence from individual MNPs (shown in Figure 4). This method injects field-emitted electrons into single-supported particles from a scanning tunnelling microscope (STM) tip, which acts as a local electron emitter, to promote photon emission. Figure 4 shows the process of collecting photons emitted by a scanning tunnelling microscope (STM): a parabolic mirror encircles the head of the microscope, optics guide the beam through the vacuum chamber's quartz view port, the beam is focussed onto a UV-vis grating spectrograph's slit, and a CCD camera chilled by liquid nitrogen is utilized for detection. This system allows for the imaging and spectroscopic study of individual particles on solidified surfaces to be conducted simultaneously.

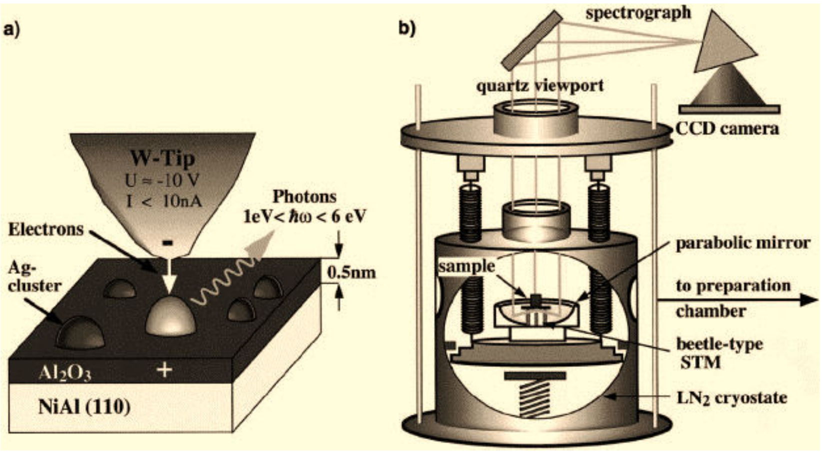


Figure 4: This is the experimental setup for the scanning tunnelling microscopy (STM) of individual Ag nanoparticles supported on a thin alumina sheet (0.5 nm). (a) A schematic showing the space under the tungsten tunnel's tip. The tip fields emit electrons into a single Ag nanoparticle with specified parameters (tunnel voltage, current), and then photons with energies between 1 and 6 eV are measured. (b) In the air, there is a grating spectrograph and a CCD camera, and within the UHV chamber is a beetle-type scanning tunnelling microscope (STM) with its tip pointing upwards. This is all part of the experimental setup for analysis. A transfer rod allows the sample to be transferred from the second chamber, where it is processed and described, to the UHV chamber (Nilius et. al., 2001**).**

Nanoparticle Photochemistry on Metals

The Introduction delineates that the fascination with photochemistry on MNPs stems from the anticipated alterations compared to photochemistry on single-crystal surfaces, brought about by the unique characteristics of MNPs. In order to establish a foundation for discourse, it is advantageous to succinctly outline the current state of single crystals before contemplating the anticipated developments. The comparison is succinctly encapsulated in Figure 5.

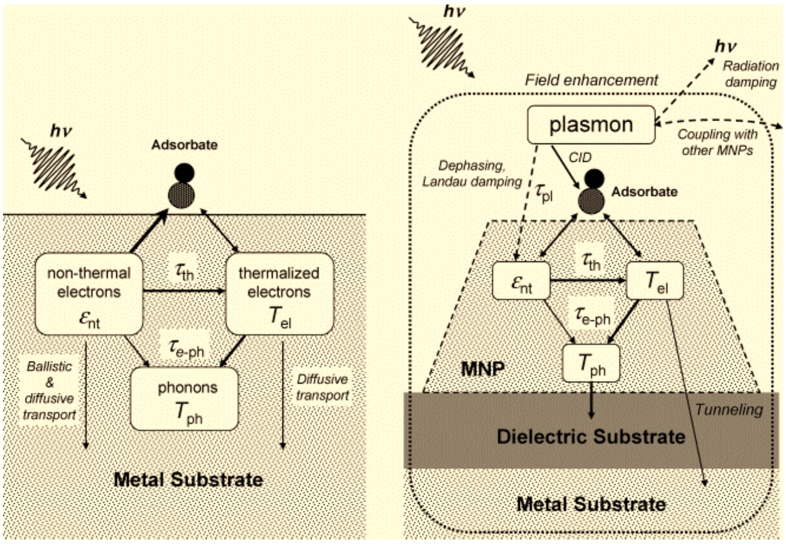


Figure 5: The progression of excitation subsequent to photon absorption for a molecule situated on a single-crystal surface (left) as well as a metal nanoparticle (Watanabe et. al., 2006).

To initiate photochemistry, that is, to transform electronic excitation energy into the energy of nuclear motion, an optical excitation must elevate the molecule in question to a potential-energy curve characterized by a significant slope in the Franck-Condon region, thereby enabling the atoms to be propelled along it. The most straightforward process often regarded is the desorption of an adsorbate or a portion thereof; in the context of a photochemical reaction, this may serve as the initial step. A comprehensive body of knowledge exists regarding these processes, commonly referred to as DIET (desorption induced by electronic transitions). On metal and semiconductor surfaces, electronically excited adsorbates undergo rapid de-excitation, significantly altering the desorption probability in comparison to the dissociation of a similar free molecule. The connection that may be severed can pertain to either the interaction between the adsorbate and the substrate or an intrinsic bond within the adsorbed molecule; subsequently, neutral or charged molecular and atomic fragments may depart from the surface, while some fragments may remain adsorbed.

A variety of mechanisms featuring distinct excitation and de-excitation processes have been suggested, among which the earliest is referred to as the MGR mechanism. At elevated excitation energies, specifically those involving multiple valence excitations or core excitations, typically exceeding 40 eV, primary excitations occurring in the adsorbed molecules may play a significant role, especially when they are induced in a selective and resonant manner. One hundred eighty at low energies, such as single valence excitations or even subthreshold excitations within the substrate, the primary mechanism for photo-desorption and reaction typically occurs through absorption in the substrate. This process leads to the formation of transient negative adsorbate ions via hot electron transfer, with atom acceleration taking place during their brief lifetime (Jiang et. al., 2019).

The phenomenon arises from the considerable penetration depth of photons within this energy spectrum, resulting in elevated concentrations of hot electrons possessing appropriate energy levels. The validity of this mechanism can be established through an examination of how the observed process correlates with the polarization of the light. The behaviour of bulk absorption typically exhibits a marked distinction from that observed in adsorbate complexes. Although the durations of these transient states, characterized by a hot electron localized on unoccupied orbitals of an adsorbate, are quite brief, the rate at which electrons oscillate between the substrate and the adsorbate is remarkably elevated.

Indeed, the renowned rapid quenching (below 1 fs) of excited molecular states at metal and semiconductor surfaces, as encapsulated in the MGR mechanism and now increasingly accessible to direct measurement, serves as evidence for this phenomenon, as it is intrinsically linked to the hot electron transfer through microscopic reversibility. Once more, the induced bond breaking may pertain to either the molecule-surface interaction or an intramolecular bond. In this instance, the process bears resemblance to dissociative electron attachment (DEA) in molecules, a phenomenon that has been thoroughly examined by numerous researchers in the context of condensed and adsorbed films (Chen et. al., 2019).

A probable series of occurrences involves the absorption of photons within the bulk, resulting in a significantly non-thermal hot electron distribution. This distribution subsequently cools through electron-electron interactions, with its peak shifting downward over a time scale of approximately 10 to 100 femtoseconds, a process that decelerates markedly as the energy of the hot electrons decreases. Ultimately, this leads to the establishment of a quasi-thermal distribution, which then interacts with the lattice via electron-phonon interactions, occurring over a time scale of several tens to hundreds of picoseconds.

Should the primary hot electrons align with the energy of the molecular negative ion resonance, a direct transfer can occur; however, if this alignment is absent due to the majority of hot electrons originating at excessively high energy levels, the subsequent step of energy redistribution becomes crucial, as it enables the hot electrons to undergo changes that ultimately lead to energy matching. The quasi-thermal distribution is unlikely to possess a sufficient number of electrons with the requisite energy to attain the transient molecular state, particularly in scenarios of low excitation. The CID, as previously mentioned, may possess the capability to direct hot electrons into the pertinent adsorbate orbitals.

These considerations hold relevance solely at low excitation densities (<10-4 electron/atom). Should the latter exceed the linear range, a scenario likely to arise with exceedingly brief pulses, nonlinear phenomena may become relevant, referred to as friction-induced desorption and DIMET (desorption induced by multiple electronic transitions). The notion of electronic friction in surface phenomena like desorption traces its origins to the 1970s. In the presence of a substantial density of excited electrons situated just above the Fermi level, these electrons can transfer kinetic energy to the atoms through a series of collisions, effectively propelling them over an activation barrier in a process reminiscent of friction (Futamata and Maruyama, 2008).

In typical thermal environments and with laser irradiation at low excitation densities, such processes do not compete with phonon-coupled processes; nonetheless, they may gain significance at elevated densities of (thermalized) hot electrons. DIMET was introduced as an alternative nonlinear DIET mechanism to elucidate the phenomena associated with nonlinear electronically induced desorption triggered by brief, intense laser pulses. This mechanism fundamentally operates as a sequential MGR process: even with swift de-excitation through quenching to the substrate, an excitation step may facilitate some acceleration of the adsorbate atoms along an excited-state curve. Should the subsequent excitation step transpire prior to the dissipation of atomic kinetic energy, the ramifications of repeated excitation and de-excitation cycles may accumulate, ultimately resulting in bond cleavage along that coordinate (Zama et. al., 2017).

The MNP-support interface could potentially serve as an impediment to the conduction of heat. The MNP could potentially reach elevated temperatures and maintain that heat for an extended duration, facilitating thermal desorption from a substrate that has been subjected to excessive heat. The existence of such an effect is contingent upon the underlying support. For

MNPs on alumina, given its commendable thermal conductivity, this aspect may be of little significance.

In these deliberations, we have posited that the excitation densities remain minimal. At elevated excitation densities, these concepts become inadequate, as mechanisms known as friction-induced desorption and DIMET will assume dominance. Within the domain of plasmon excitations, the metallic nanoparticles function as antennas, effectively concentrating energy within a limited surface area. Consequently, photon fluencies that result in low excitation densities, when distributed across the entire surface, may be adequate to reach this specific range. This suggests that phenomena occurring on single-crystal surfaces with femtosecond laser pulses could also manifest on MNPs when subjected to longer or less intense pulses. In such circumstances, the transient transfer into negative-ion resonances may assume greater significance. Furthermore, direct excitations of adsorbates, enhanced by plasmons, may increasingly surpass the significance of the substrate-mediated process. Conversely, the friction-mediated mechanism may also manifest at reduced photon fluencies for MNPs (Kazuma et. al., 2018).

The aforementioned considerations hold true even in the absence of coupling between MNPs. It is evident that they would experience frustration when engaging with MNP arrays, as the plasmonics fields of the individual MNPs can couple in a non-linear manner, resulting in significant spatial and temporal energy localization, often referred to as hot spots. It is entirely plausible that such circumstances could result in significant alterations to MNP photochemistry. There are no documented instances of such effects in the existing literature. Furthermore, all measurements conducted thus far have been analysed under the premise that the photoactive species reside on the surface of the MNP.

Conclusion and Future Perspectives

The dimensions and structural characteristics of MNPs undoubtedly exert a significant impact on the photochemical processes occurring at their surfaces. MNPs have the potential to introduce novel adsorption sites and unique electronic states that are not present on single-crystal surfaces. The unique photochemical processes taking place on MNPs are intrinsically linked to alterations in electronic structure and geometrical parameters, which are, naturally, interrelated. The distinct ground and excited electronic states, along with their respective lifetimes, lead to varying dynamics and kinetics on nanostructured surfaces.

This survey reveals that the specific photo-physical properties of MNPs are varied and intricate; however, given the extensive duration of their investigation, the amassed knowledge and comprehension is commendable. The restriction of excitations resulting from the diminutive dimensions of the MNPs is anticipated to enhance the efficacy of photochemical processes. The significance of plasmon excitation, when it occurs, along with the associated field enhancement, is quite evident; the temporal progression subsequent to the excitation is comprehended in principle. The pertinent parameters are typically well-defined, although their scale, relative significance, and interactions remain somewhat obscure. What remains to be addressed is the necessity of conducting all experiments on precisely characterized samples, where the dimensions and morphology of the individual particles, along with their arrangement on the support, are clearly defined. Although a bottom-up approach, characterized by the gentle deposition of mass-selected particles followed by in situ characterization, may seem more attractive in theory, the established methods for preparing defined samples through vapor deposition appear to be more advantageous in practice. The utilization of alloy nanoparticles, such as Au-Ag122, may facilitate the customization of plasmon enhancement, enabling specific chemical selectivity for surface photoreactions of particular interest.

When juxtaposed with the advancements achieved in photophysics, the exploration of photochemistry on precisely characterized samples remains in its nascent phase, evidenced by the relatively limited volume of publications in this domain. Once more, it is imperative to engage with meticulously delineated samples. The utilization of advanced laser techniques, along with their ongoing refinement towards shorter pulse durations, is poised to yield significant benefits.

The most promising methodology will involve an integration of photo-physical and photochemical investigations utilizing the same sample, thereby eliminating any potential impact of sample preparation on the transferability of results.

Numerous inquiries remain unresolved. The distinct contributions of the various outlined mechanisms, as well as potential new ones, must be systematically analysed, elucidated, and scrutinized for both low and high excitation densities. The impact of plasmon enhancement and the intricate dynamics of hot electrons on photochemical processes necessitates thorough examination for molecules interacting with MNPs. The influence of field enhancement for molecules that are not in direct contact with the MNPs could play a significant role in facilitating reactions on the oxide. The antenna effect of MNPs may facilitate the induction of spill-over effects of hot electrons, wherein the localized injection of electron-hole pairs into an appropriate oxide initiates photochemical reactivity on these oxides, potentially enabling the exploration of the length scale associated with such transfer processes. In every instance, the plasmonics interaction within a configuration of metallic nanoparticles and the resultant hotspot development may give rise to intriguing reactive phenomena. This research domain undoubtedly presents a captivating landscape, and one can anticipate intriguing findings in the near future.

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