Ab Initio Quantum Dynamics of Plasmonic Charge Carriers

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Abstract

Surface plasmons respond strongly to electric fields and generate energetic (hot) charge carriers that can be used in optoelectronic devices. However, utilization of hot carriers has to outcompete fast carrier relaxation in metals. Often, the reported efficiencies of nanoscale devices based on plasmon excitations are low, and the mechanisms of device operation remain inconsistent within the field. Further developments hinge on fundamental understanding the nature and kinetics of plasmon decay processes. We provide an overview of time-domain *ab initio* modelling of hot carrier dynamics, demonstrating that atomistic details of the surface structure of plasmonic materials, and their chemical interaction with semiconducting and molecular charge acceptors and substrates play key roles in governing the dynamics pathways. Considered case studies represent various dynamics channels and illustrate solar energy and optoelectronic applications.

Plasmonic Excitations Efficiently Generate Hot Charge Carriers

Charge transfer across metal/semiconductor interfaces is central to optoelectronic functions of many applications, including photovoltaics, detection, catalysis, etc.[1–6] Charge transfer should be fast to compete with other photophysical processes, such as carrier thermalization, energy relaxation, charge trapping, diffusion, and recombination. Various approaches have been utilized to accelerate the charge transfer process. Plasmonic devices, typically based on nanostructures of silver, gold, and copper, have attracted strong interest. Surface plasmon resonance (SPR) is the collective oscillation of charges due to strong light-matter interaction occurring in metallic structures, Figure 1. Many experiments have focused on SPR excitations in plasmonic systems. A plasmonic charge wave can decay radiatively, via emission a photon (i.e., photoluminescence) or nonradiatively in a process called **Landau damping** (dephasing). Nonradiative decay of SPR generates the highly energetic plasmonic state, i.e., hot charge carriers. High-energy hot carriers quickly scatter off each other, creating a Fermi-Dirac energy distribution at an elevated temperature. Subsequently, on a slower timescale, the charges relax and recombine by coupling to phonons. This timescale separation has given rise to the **two-temperature model**.[7] Great attention has been focused on the utilization of hot carriers for applications, including initiating photochemical reactions and increasing the efficiency of solar cells. Transfer of hot carriers from metallic particles to chemically attached acceptors provide an efficient route to stabilize and utilize hot carriers, Figure 2. The separated charges cannot recombine, and the recombination of charges across forbidden gaps in semiconductor acceptors is slow. There has been a tremendous number of experimental works devoted to developing materials involving plasmonic hot carriers.[8–11] Nevertheless, most reported energy conversion efficiencies have remained low, usually less than 1%,[12] limiting applications. The underlying physical limitations are not fully established. A fundamental understanding of the mechanisms, timescales, and efficiencies of plasmon-induced hot-carriers dynamics remains of significant interest, since it can identify and rationalize the factors governing optoelectronic performance.

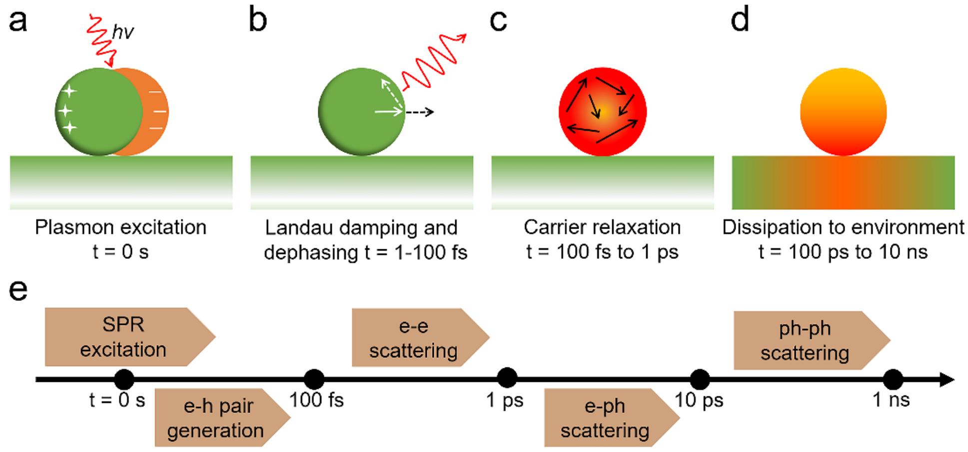

Figure 1. Electron-vibrational dynamics induced by a plasmon excitation. **(a)** Excitation of a surface plasmon resonance (SPR) creates a coherent oscillation of electronic charge density. **(b)** The charge density wave is dampened and loses coherence (dephases) generating uncorrelated charge carriers. **(c)** Charge carriers relax by electron-electron (e-e) and electron-phonon (e-ph) scattering. **(d)** The excess energy is dissipated to environment. **(e)** Timescale graph for the processes illustrated in parts (a-d).

To date, various ultrafast time-resolved spectroscopic techniques have been the primary tool for understanding the behavior of hot carriers, providing huge amounts of data used for phenomenological interpretations. While general behavior of hot carriers is established well, detailed mechanisms responsible for hot carrier evolution in plasmonic nanostructures remain elusive, because important photophysical and photochemical processes lack clear optical fingerprints in experiments. An atomistic description of the plasmon-induced hot carriers dynamics is increasingly necessary, while it presents a major challenge for current computational methods. Early works involve the development of semi-phenomenological models capable of describing the relaxations of plasmonic hot charges.[13] *Ab initio* calculations, requiring few assumptions and containing no empirical parameters, have been used to account for the mechanisms of plasmon decay and gauge their relative contributions in different materials,[14–16] but *ab initio* calculations are limited to small and simple systems due to the large computational cost. Plasmons have also been investigated using jellium-type or noninteracting electron models,[17] linear response **time-dependent density functional theory (TD-DFT)**,[18] perturbation theories such as Fermi's golden rule,[19] and nonequilibrium Green function formalism in the framework of many-body perturbation theory.[20] Our group has developed an approach combining **nonadiabatic molecular dynamics (NA-MD)** and TD-DFT,[21–24] allowing us to mimic the time-resolved experiments directly in the time-domain and at the atomistic level, characterizing explicitly a broad range of nonequilibrium processes in a variety of nanoscale materials.[25–29]

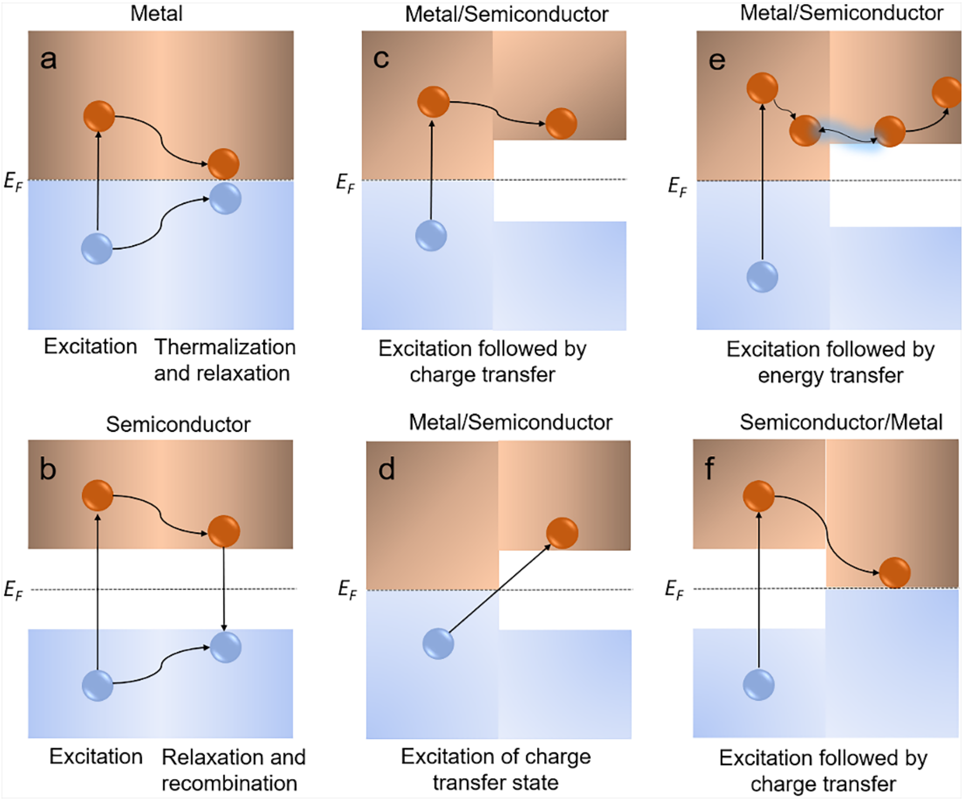

Figure 2. Plasmon-induced dynamics of hot carriers at metal and semiconductor interfaces. **(a)** Excitation of plasmons in a metallic system generates hot electrons and holes that relax and recombine rapidly in the absence of an energy gap. **(b)** Hot charge carriers in a semiconductor relax rapidly to the edges of the conduction and valence bands but take a long time to recombine. **(c)** Charge carriers generated in a metal by plasmon excitation can transfer to a semiconductor prior to relaxing and recombining. **(d)** If metal and semiconductor are strongly coupled, photoexcitation can create a charge-separated state. **(e)** Charges in a metal can exchange energy with charges in doped semiconductors, leading to energy rather than charge transfer. **(f)** Plasmon states increase efficiency of charge transfer from a semiconductor to a weakly coupled metal.

Ab Initio Quantum Dynamics Simulations Capture Atomistic Details of Plasmon-Driven Processes

Ab initio quantum dynamics simulations provide a unique perspective on the evolution of plasmonic hot carriers by creating an atomistic description and describing the processes in the time domain, most closely mimicking time-resolved experiments. The state-of-the-art methodology, developed by the Prezhdo group,[21–24] combines real-time TD-DFT for the evolution of the electrons with NA-MD for the evolution of ionic cores and electron-ion interactions. The electrons are treated quantum mechanically by solving the time-dependent Schrodinger equation, $i\hbar\frac{\partial\Psi(r,R,t)}{\partial t} = H(r,R,t)\Psi(r,R,t)$, which depends parametrically on the classical ionic coordinates, R. The ion motions are described classically by MD with semiclassical corrections.[30] The electron-vibrational coupling matrix elements, $d_{kj} = \langle\varphi_k(r,R(t))\big|\nabla_R\big|\varphi_j(r,R(t))\rangle$, are computed on-the-fly along the trajectories. Charge-charge scattering is described by the screened Coulomb interaction.[31,32] Quantum transitions between electronic states are modelled by **surface hopping**,[24,33] which can be viewed as a **master equation** with nonperturbative, configuration- and time-dependent transition rates. The NA-MD/TD-DFT methodology is complementary to the Boltzmann transport equation (BTE) with electron-electron and electron-phonon scattering rates obtained by DFT.[34,35] While perturbative and employing the harmonic approximation for atomic motions, the BTE allows one to perform longer and larger scale simulations. It also enables fine sampling of electron and phonon momenta, and recent NA-MD developments are dedicated to achieving a similar goal.[36,37] **Machine learning (ML)** tools are being used actively to increase the efficiency and scope of the NA-MD calculations. Ab initio DFT provides input to train ML force fields and generate long MD trajectories,[38–40] and to develop large-scale models of electronic Hamiltonians.[41] ML allows one to predict long-time quantities from limited data[42] and to analyze the simulation results.[43] The NA-MD/TD-DFT methodology has been successfully applied to study excited state dynamics in a broad range of nanoscale and condensed matter systems.[25–29]

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Electron Dynamics Following Plasmonic Excitation Occurs on Multiple Timescales

Excitation of a plasmon resonance leads to a cascade of decay events according to the following scenario, Figure 1. Landau damping transforms the collective state into an ensemble of hot electron-hole pairs within tens of femtoseconds. Hot carriers lose coherence and exchange energy through electron-electron scattering within several hundreds of femtoseconds. The non-equilibrium state relaxes to a quasi-equilibrium Fermi-Dirac distribution corresponding to a high effective carrier temperature.[7]

Subsequently, the carriers relax by scattering with phonons within several picoseconds, dissipating energy to heat. Finally, the energy is transferred to the surrounding matrix within hundreds of picoseconds, dissipating heat from the metal to the environment. Prior to the thermalization, hot charge carriers can be extracted to an active medium to drive a chemical reaction or an optoelectronic device. The main challenges for the efficient charge extraction stem from the weak electronic coupling between metals and charge acceptors, and the ultrafast energy dissipation in the metal. Thus, it is particularly important to determine the special conditions required for rapid extraction of excited electrons while they are still “hot”. The decay dynamics can be strongly influenced by realistic aspects of the systems, including shape, size, and composition of nanostructures, temperature, surface and defect states, surface passivation, chemical surrounding, etc. Understanding the dynamics and competition of different pathways is crucial for utilizing the plasmonic energy.

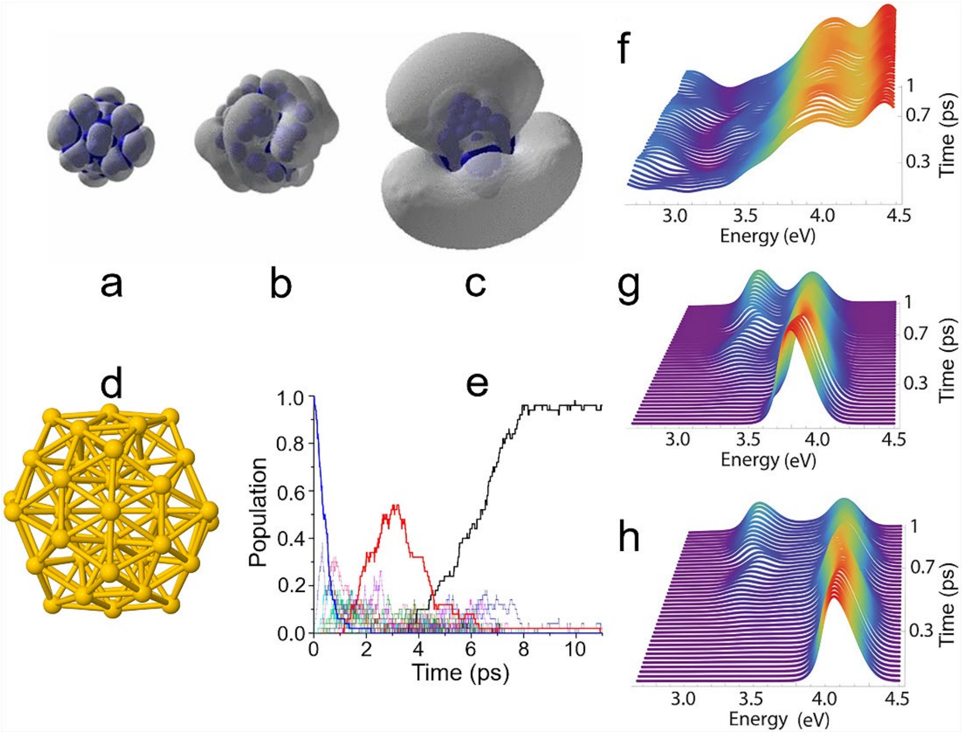

Figure 3. Plasmon initiated dynamics in metallic particles. Typical charge densities of **(a)** bulk, **(b)** surface, and **(c)** plasmon orbitals states in the Ag_{104} cluster. Reproduced, with permission, from [44]. **(d)** Optimized structure for the Au_{55} cluster. **(e)** Evolution of populations of electronic states in the Au_{55} cluster. While most states are populated only transiently and are short-lived, there exists a special state (red line) that is populated for a relatively long time, which may be sufficient to initiate a photochemical reaction. Reproduced, with permission, from [45]. **(f)** Evolution of the electronic density of states in the

Ag_{68} cluster. Decay of **(g)** lower and **(h)** higher energy plasmon excitations. No special states are seen in the Ag_{68} example. The population leaves the initial state, spreads over many states, and ultimately accumulates at the Fermi energy. Reproduced, with permission, from [46].

Phonon-Mediated Relaxation of Plasmonic Charge Carriers is Relatively Slow

Electron-vibrational interactions produce elastic and inelastic scattering. Inelastic scattering involves electronic and vibrational energy exchange, while elastic scattering induces loss of phase information and coherence. The decoherence time can be quantified as the **pure-dephasing** time,[47] whose inverse gives the homogenous (single particle) optical linewidth. Classic theories of surface plasmons consider plasmon-surface scattering to be the fastest contribution to plasmon dephasing.[48] Elastic electron-phonon scattering processes may[49] or may not[50] lead to pure-dephasing of plasmons. Phonon-induced pure-dephasing of plasmon, surface and bulk excitations in silver clusters, Figure 3a-c, was modelled using *ab initio* MD.[44] Since **plasmon orbitals** are localized away from the atoms, the electron-phonon coupling is much weaker for plasmons than bulk and surface states. Phonon-induced pure-dephasing of plasmons took 30-40 fs and showed modest size-dependence, electron-phonon coupling being stronger in smaller clusters. Both plasmon and non-plasmon states coupled primarily to low-frequency acoustic-phonons that modulated size and shape of the nanoparticles and were sensitive to temperature variations, because the frequencies of acoustic phonons in metallic clusters are comparable to the thermal energy, k_bT.

Electron-phonon relaxation following plasmon excitation of the Ag_{68} particle was studied by ab initio TD-DFT/NA-MD,[46] Figure 3f-h. The inelastic scattering process took picoseconds, two orders of magnitude longer than the elastic plasmon-phonon scattering. The coupling to phonons was weak because plasmon orbitals were spatially delocalized away from the particles, Figure 3c. Higher energy plasmon orbitals were delocalized farther away from the cores, and hence, exhibited weaker coupling to phonons and decayed more slowly than lower energy plasmons, rationalizing the difference in the decay of low- and high-energy excitations observed in experiments.[51,52] The picosecond **lifetime** of hot electrons generated by plasmon excitations can be sufficient to allow charge extraction or initiation of elementary photochemical events associated with bond breaking, formation or rearrangement.

Charge-phonon relaxation in metallic films is generally similar to that in clusters. The study on gold films[53] showed that, with increasing temperature, both inelastic and elastic electron-phonon scattering accelerated and involved broader ranges of phonon modes due to enhanced anharmonicity. The inelastic scattering was strongest between states with small energy gaps, because the NA electron-vibrational coupling is inversely proportional to the energy gap.[22] The elastic scattering was fastest between pairs of states that were distant in energy, because it is proportional to the energy gap fluctuation, which is generally larger for larger gaps.[54] The electron-phonon interactions exhibited mild dependence on excitation energy, in agreement with the experimental linear dependence of the reflectance coefficients on electron temperature.[55]

Metallic Particles Support Special, Longer-Lived Electronic States

Metallic particles contain a variety of structural motifs on the surface, and particular structures can give rise to special states that partly decouple from the quasi-continuum of metal states and trap charges for relatively long times. The situation is known in catalysis, which often occurs on point or extended defects in metals, or at single metal atoms or small metal clusters.[56] The quantum dynamics modeling of hot electron relaxation in the Au_{55} cluster[45] following plasmon excitation found a long, 3.6 ps electron relaxation time, which was independent of the initial energy. The slow relaxation originated from a long-lived intermediate state located 0.8 eV above the Fermi energy, Figure 3d,e. The intermediate state facilitated charge and energy transfer from the Au_{55} nanoparticle into TiO_2 due to proper energy alignment with the TiO_2 conduction band edge. These results ruled out the often assumed molecular-like relaxation in metallic clusters, because the relaxation happened via a quasi-continuum manifold of states. Interestingly, excited state dynamics in the Ru_{10}/TiO_2 system was reported to occur on a 1-2 ps timescale,[57] while the Au_{20}/TiO_2 system showed a 100 fs relaxation time.[58] The differences can be linked to the cluster shape. Both Ru_{10} and Au_{55} were spherical particles and generated picosecond relaxation times, while the Au_{20} particle was a pyramid and showed sub-picosecond relaxation.

Ab initio MD simulations are limited to picoseconds, while metallic clusters can undergo atomic rearrangements on longer timescales. ML is a useful tool for developing *ab initio* level force fields that can be used to produce much longer trajectories.[38,39] This approach was used to study excited state quantum dynamics in the pyramidal Pt_{20} cluster adsorbed on the MoS_2 substrate,[59] Figure 4a-c. The top atom of the pyramid was oscillating between two configurations on a hundred picosecond timescale. The perfectly pyramidal Pt_{20} particle produced rapid electron-phonon relaxation. However, when the top atom was partially detached from the rest of the pyramid, it introduced unsaturated chemical bonds that supported a localized electron trap state with reduced coupling to the rest of the system. The trap state extended the hot electron lifetime 3-fold, creating favorable conditions for a catalytic process. Photochemistry of molecules adsorbed on periodic surfaces depends strongly on lifetime of transiently populated molecular electronic states, and even short lifetimes can be sufficient.[60] Whether or not the trap state on the Pt_{20} cluster was populated depended on the initial energy of the electron as it was entering the Pt_{20} particle. Higher energy initial states had access to additional relaxation pathways bypassing the trap state. The transient structural distortion of Pt_{20}, supporting a longer-lived electron trap, provided an example of potentially many analogous scenarios that may play key roles in metal cluster catalysis driven by hot electrons.

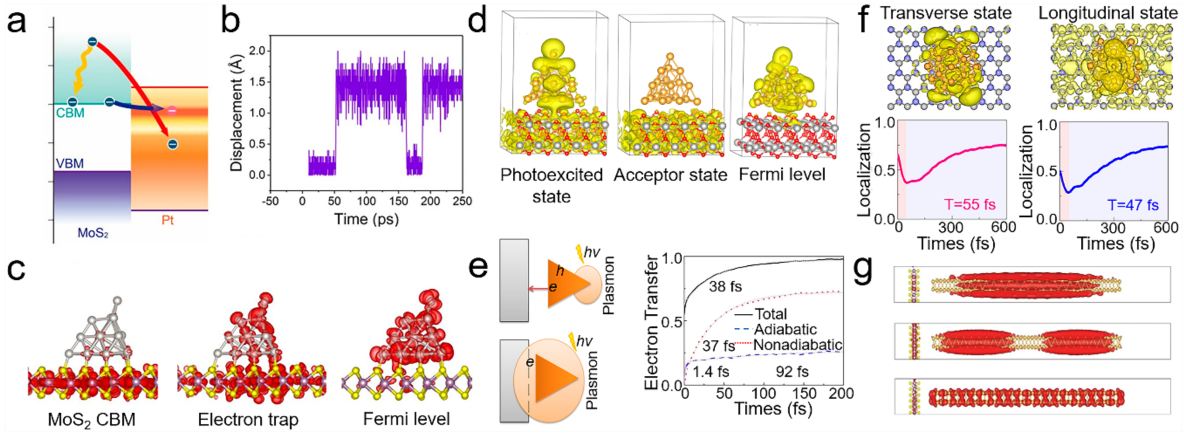

Figure 4. Charge transfer processes at interfaces between metallic particles and semiconductors. **(a)** Hot electron injection and relaxation in Pt_{20}/MoS_2. Electron transferred from the MoS_2 conduction band minimum (CBM) into Pt_{20} gets transiently trapped in the state depicted in part (c). However, electron transferred from a higher energy in MoS_2 bypasses the trap. **(b)** The top atom of the Pt_{20} pyramid, shown in part (c), fluctuates on a 100 ps timescale, creating the trap state. **(c)** The initial, trap and final states for the electron transfer dynamics in Pt_{20}/MoS_2. Reproduced, with permission, from [59]. **(d)** The photoexcited, acceptor and Fermi level states in Au_{20}/TiO_2. Because TiO_2 is a three-dimensional material, its surface has unsaturated chemical bonds that interact strongly with Au_{20}. The strong interaction enables plasmonic excitation of a state with a large charge transfer character. The theoretical prediction [58] was demonstrated experimentally [10]. **(e)** Traditional (top) and charge transfer excitation (bottom) mechanisms of plasmon-driven charge separation. About 60% of the electron is already transferred from

Au_{20} to TiO_2 during photoexcitation (right), and the remaining 40% of the electron transfer to TiO_2 within 40 fs by nonadiabatic transitions. Reproduced, with permission, from [58]. **(f)** The extent of charge transfer occurring during photoexcitation of Au_{55}/MoS_2 and Ag_{55}/MoS_2 depends on light polarization. Longitudinal excitation gives more charge transfer than transverse excitation. Reproduced, with permission, from [61]. **(g)** Plasmon (top and middle) and bulk (bottom) excitations in Au_{100}/MoS_2. Because MoS_2 has no unsaturated chemical bonds on the surface, and plasmonic excitations in the Au_{100} rods are localized away from MoS_2, the photoexcited states exhibit very little charge transfer character. Reproduced, with permission, from [62].

Substrates Can Strongly Influence Charge Carrier Dynamics in Metals

Substrates and adhesion layers are commonly used to assemble complex nanostructures, to achieve advanced optical and electronic functionalities. The electronic response of metal/substrate composites can be much different from that of free-standing structures. Interaction between a metal and a conducting substrate may give rise to composite plasmon-plasmon resonances.[63] Inclusion of adhesion layers,[64] surface adsorbates,[8] and molecules[65] between metal films and semiconducting or dielectric substrates help to enhance charge and energy flow across interfaces.

Thin titanium (Ti) and titanium oxide (TiO_x) films have been used as adhesion layers between metal films and dielectric substrates to improve thermal transport. Experiments[66] showed that inclusion of a Ti layer between Au films and dielectric substrates increased the interfacial bonding and accelerated the energy flow. Ab initio quantum dynamics calculations,[67] Figure 5a,b, identified the reasons. The Ti layer greatly enhanced the density of states in the relevant energy window. In addition, Ti atoms were much lighter than Au atoms, creating strong electron-phonon coupling. By contrast, semiconducting substrates, such as Si, SiO_2, or Al_2O_3, had no effect on electron-phonon dynamics, even though they are also composed of light atoms. This is because they have almost no contribution to the states near the Fermi level. Further calculations[68] demonstrated that the hot electron relaxation was robust to partial alloying between Ti adhesion layers and Au films. Similar results were established for holes.[69] The influence of the Ti adhesion layer on the hole-phonon relaxation showed strong energy dependence, because the electronic density of states exhibited a sharp step below the Fermi energy, due to contributions of different atomic orbitals to the electronic energy bands in the metal.

TiO_x layers exhibit a range of stoichiometries, with *x* ranging from 0 to greater than 2. Experiments[70] indicated that TiO_x layers with relatively low oxygen content were beneficial for thermal boundary conductance. Kumar et al.[71] found experimentally that incorporation of non-stoichiometric TiO_x layers improved photocatalytic activity of plasmonic Au nanostructures. Lu et al.[72] demonstrated, using NA-MD/TD-DFT simulation, that the chemical composition and stoichiometry of the TiO_x layer strongly influenced the nonradiative electron-phonon relaxation processes. By changing the oxygen content in TiO_x, the hot carrier lifetimes can be strongly tuned. The control over a particular charge carrier and an energy range is related to the energy level alignment between the Au film and the TiO_x substrate, and to the strength of interfacial bonding, both factors influenced by the oxygen content. Oxygen-rich and oxygen-poor TiO_2 modulate the hole and electron relaxations, respectively, while Ti metal controls the relaxation of both charge carriers. The predictions obtained from the atomistic quantum dynamics simulations have been verified by experiments[73] and apply to other metal/substrate nanocomposites.

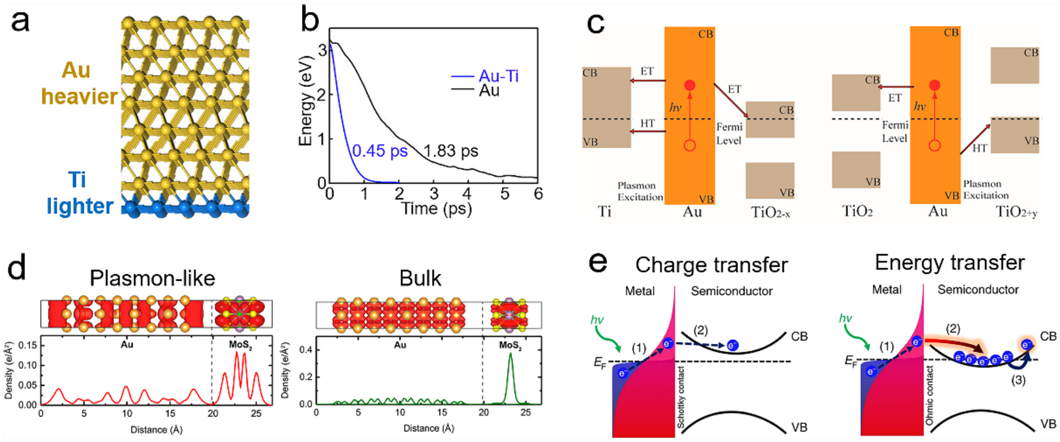

Figure 5. Charge and energy transfer processes between metal and semiconductor films. **(a)** Thin Ti adhesion layers are often placed between Au films and semiconductor substrates. **(b)** The thin Ti adhesion layer accelerates charge-phonon energy exchange nearly five-fold, because Ti atoms are much lighter than Au atoms, and the Ti layer has a large density of states near the Fermi energy. Reproduced, with permission, from [67]. **(c)** The charge-phonon energy relaxation rate can be controlled by the TiO_x substrate stoichiometry, which determines alignment of the Au and TiO_x the energy levels. The theoretical prediction [72] was later confirmed experimentally [73]. Reproduced, with permission, from [72]. **(d)** Plasmon orbitals (top) extend into the gap between the weakly interacting MoS_2 and Au films, facilitating charge transfer from MoS_2 to Au, as demonstrated by experiment and rationalized by theory [74]. Bulk orbitals (bottom) do not exhibit this property. Reproduced, with permission, from [74]. **(e)** In addition to

the plasmon-initiated charge transfer from a metal to a semiconductor (top), one can attain energy transfer (bottom) by scattering of hot electrons in the metal with conduction band electrons present in a doped semiconductor. While Coulomb attraction between the transferred electrons and remaining holes limits the charge transfer, the energy transfer does not have such limitation, and large amounts of energy can flow rapidly by the charge-charge scattering mechanism. Reproduced, with permission, from [75].

Sequential vs. Instantaneous Charge Transfer at Metal/Semiconductor Interfaces

Extraction of hot carriers following plasmonic excitation is a central question in applications. It is essential to extract the carriers within about a picosecond before they dissipate most of the excess energy to heat. There exists no "rule of thumb" regarding the charge transfer mechanism. Atomistic details of the interfacial interaction do matter and can be captured by an atomistic simulation. The conventional view involves the indirect **plasmon-induced hot-electron transfer (PHET)**: Hot carriers are generated in the metal by plasmon decay and then undergo charge transfer to a chemically attached acceptor. This process was verified experimentally in a simple system of Au nanorods coated with monolayer thiol molecules.[76] However, according to both experiment and theory, PHET is considered rather inefficient, since photoexcited electrons in a metal have short lifetimes due to high density of electronic states all the way from the initial excitation energy to the Fermi level, causing rapid charge relaxation and recombination. Often, such rapid relaxation contradicts observations, and one may wonder whether there is another mechanism that avoids hot carrier losses in the metal while maintaining fast charge transfer to the acceptor.

Excitation of the Au plasmon resonance in Au/TiO_2 heterostructures showed electron injection into the TiO_2 conduction band within 240 fs.[77] A similar, ultrafast charge transfer was seen in metal nanoparticle/CdS heterostructures.[9] To rationalize the sub-picosecond timescales, Long and Prezhdo[58] studied theoretically a Au_{20} nanoparticle absorbed on a TiO_2 surface, and observed direct **plasmon-induced charge transfer (PICT)** involving electronically excited states with a large fraction of charge density delocalized from Au_{20} onto TiO_2, Figure 4d. Upon plasmon photoexcitation, an electron appeared immediately inside TiO_2 in 60% of the cases, bypassing the intermediate step of charge thermalization inside the nanoparticle. In the remaining 40% of the cases, the electron injection into TiO_2 occurred on a 100 fs timescale by the nonadiabatic mechanism, i.e., by hops between electronic states localized in Au_{20} to electronic states of TiO_2, Figure 4e. The electron-phonon energy relaxation paralleled the electron injection but was slower. Following the generation of the charge separated state, the electron overcame attraction to the hole and delocalized into TiO_2 bulk driven by entropy due to a high number of accessible bulk TiO_2 states. Presence of structural defects in TiO_2 can trap the injected electron, enabling picosecond electron-hole recombination. The unconventional PICT mechanism was demonstrated experimentally a year later for an Au nanoparticle grown on a CdSe nanorod by Lian and co-workers.[10] These exciting findings called for more thorough understanding of plasmon-induced charge transfer via atomistic modeling.

Calculations show that plasmon-driven charge separation is strongly influenced by the interfacial interaction. Considering the same Au_{20} pyramid as well as Au_{100} nanorods interfaced with the MoS_2 substrate, Figure 4g, Long, Prezhdo and co-workers demonstrated that traditional PHET was the dominant mechanism.[62] The plasmonic excitation decayed into free-electron states within 30 fs after photoexcitation. Electron transfer from Au into MoS_2 followed within 100 fs, outcompeting energy relaxation within Au, requiring several 100 fs. In contrast to the Au_{20}/TiO_2 system, plasmonic charge-transfer excitations were not formed in Au_{20}/MoS_2 because the interfacial interaction was much weaker. The TiO_2 surface contains under-coordinated atoms that are eager to form chemical bonds with Au. In contrast, an intrinsically two-dimensional material, MoS_2 contains no under-coordinated atoms, and the Au/MoS_2 interaction is primarily van der Waals. The authors concluded that PHET dominates if the interaction with the metal is week, e.g. van der Waals, while PICT occurs when the interaction is strong, e.g. chemical bonding. In the experimental demonstration of PICT, the Au particle was chemically grown on the CdSe nanorod.[10] Considering electron injection from the Au_{55} and Ag_{55} metallic clusters into a MoS_2 monolayer, Zhang et al.[61] demonstrated that the PHET and PICT mechanisms can coexist even in weakly bound hybrids, both mechanisms leading to faster carrier transfer than carrier cooling. The relative contributions of the two mechanisms were sensitive to polarization of the incident light, Figure 4f. Kumar et al.[78] demonstrated that probabilities of PHET and PICT were also sensitive to other external stimuli such as strain. The plasmon excitation delocalized between the metal and the semiconductor established a novel concept for plasmonic photosensitization of wide band gap semiconductors,[10,58] leading to efficient conversion of photons to charge carriers for solar energy and optoelectronic applications.

Electron-Electron Scattering at Metal/Semiconductor Interfaces Rapidly Transfers Hot Electron Energy

Hot electrons in a metal can transfer energy across metal/semiconductor interfaces without transferring charge. Electron-vibrational relaxation heats up phonons, and phonons of a metal scatter with phonons in a semiconductor. Phonon-phonon scattering is relatively slow, compared to electron-electron scattering, and is harder to control.[79] If the semiconductor is intrinsically or extrinsically doped, hot electrons in the metal can scatter with charges in the semiconductor. Given a sufficiently high concentration of charge carriers in the semiconductor, significant amounts of energy can be rapidly transferred across the interface. The extend of the energy transfer can greatly exceed the amount of charge transfer, which is limited by attraction of the transferred electrons with the remaining holes across the interface. Charge-charge scattering between metal and semiconductor occurs via Coulomb coupling,[31] and ab initio quantum dynamics simulations require consideration of ensembles of electrons.[80] If the thickness of the metal layer is less than the electron scattering length for the metal, the energy transfer across the metal/semiconductor interface becomes ballistic and extremely fast.

Focusing on an Au/CdO interface, Tomko et al.[75] reported experimentally that in cases of strong non-equilibrium, photoexcited metals can undergo an electron-mediated ballistic energy transfer to a non-metal substrate, without charge injection. They termed this effect **ballistic thermal injection (BTI)**. BTI is different from the interfacial charge transfer caused by hot electrons traversing the **Schottky energy barrier**. Ab initio NA-MD simulation suggested that energy transfer from Au to CdO is mediated by hot electron energy coupling. The proposed BTI mechanism offers the possibility of remotely modulating the optical and electronic properties of non-metals without specific electronic excitations at the metal/semiconductor interfaces.

Plasmon States Can Efficiently Accept Charges over Significant Distances

The examples discussed above focused on quantum dynamics of hot electrons generated in a metal. The opposite process, in which hot electrons generated in a semiconductor transfer charge or energy into a metal, is also important from both fundamental and applied points-of-view and can be facilitated by plasmon states. Xu et al.[74] carried out joint experimental and theoretical studies of distance dependent hot-electron-transfer dynamics at the MoS_2/Au interface using a combination of time-resolved photoemission electron microscopy and *ab initio* calculations, Figure 5d. They found that the electron injected into MoS_2 can undergo ultrafast transfer to the Au substrate within few hundreds of femtoseconds. The electron transfer rate was demonstrated to decrease exponentially as a function of the MoS_2-Au distance. Surprisingly, the attenuation coefficient was very small, 0.06 ± 0.01 Å^{-1}, indicating efficient electron injection into the metal over nearly a nanometer of vacuum. The rate decayed much more rapidly at larger MoS_2-Au separations. The experimental result was rationalized by the ab initio calculations showing that the transition from the slow to the rapid decay coincided with the reach of the Au plasmon orbitals into the vacuum, top panel of Figure 5d, and that the charge transfer proceeded via these states. The weak distance dependence of the interfacial electron transfer process, achieved through participation of plasmon states, suggested that the transfer should be robust against surface defects and corrugation – an important practical feature of optoelectronic devices.

Concluding Remarks

We have summarized the recent findings that shed light on the microscopic mechanisms underlying the evolution of plasmonic hot carriers in a diverse set of systems, motivated by hot carrier utilization in solar energy conversion and optoelectronics. The ab initio TD-DFT/NA-MD calculations consider the full set of processes occurring in systems composed of hundreds of atoms and on timescales from femto- to nanoseconds. The simulation methodology treats simultaneously the dynamics of coupled electronic and atomic systems, allows one to study complex far-from-equilibrium processes in real time and at the ab initio level, directly mimicking the time-resolved experiments. Particular focus has been given to the atomistic details that are responsible for funneling of plasmon energy into special, chemically active electronic states and determine interfacial interactions in nanoscale hybrids. The nature of plasmon-active electronic excitations, plasmon dephasing, charge-charge and charge-phonon scattering, hot carrier charge and energy transfer, and influence of substrates have been illustrated and discussed. The central questions explored are how the charge and energy extraction can effectively outcompete the intrinsic ultrafast energy relaxation in metals, and how the special features of plasmon electronic states can be utilized. Dynamics following plasmonic excitations occur on multiple length and time scales, and a variety of theoretical and experimental tools are required for a comprehensive understanding. These tools are developed in different scientific communities, and the need to connect the different descriptions into a unified picture provides exciting opportunities for future research (See Outstanding Questions). The atomistic modeling should be scaled up in size and time, to address more realistic and complex systems and processes relevant to the emerging technologies. The conclusions obtained with a few representative examples should be generalized to describe existing classes of materials and to predict behavior of novel materials. The fundamental understanding of the nature and dynamics of plasmonic charge carriers obtained by the ab initio quantum dynamics simulations provides valuable qualitative and quantitative insights into charge and energy flow in metallic and hybrid nanostructures, guiding new experiments and providing design principles for further improvement of materials and devices.

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Glossary

Time-dependent density functional theory (TD-DFT): an accurate and efficient technique to describe electronic structure of materials and molecules, and evolution of electrons in time subject to external electric fields, coupling to vibrations, etc.

Nonadiabatic molecular dynamics (NA-MD): an approach for describing evolution of coupled electronic and vibrational systems, with electrons treated quantum mechanically, e.g. by TD-DFT, and vibrations treated classically or semi-classically. All degrees of freedom are considered explicitly, and no other approximations, e.g., harmonic, weak coupling, are made.

Surface hopping: a commonly used family of NA-MD techniques designed to satisfy the key physical conditions, including probabilistic branching, thermal equilibration, and loss of coherence.

Master equation: a method for evolving ensembles of systems with rates obtained by perturbation theories, e.g., Fermi’s golden rule, or surface hopping.

Plasmon orbital: an electron orbital obtained from DFT calculation; a superposition of the plasmon orbitals gives rise to collective plasmonic excitation in TD-DFT calculations.

Two-temperature model: a phenomenological description for the evolution of energy (temperature) of electronic and vibrational degrees of freedom based on time-scale separation of the lighter (electrons) and heavier (atoms) particles.

Pure-dephasing: Loss of coherence within an (electronic) subsystem caused by coupling to an environment, e.g. vibrations.

Machine learning (ML): a family of hierarchical, non-linear fitting techniques that can be used to interpolate efficiently complex sets of data, e.g., obtain a force field for atomic evolution NA-MD or an electronic density functional for TD-DFT.

Plasmon-induced hot-electron transfer (PHET): a multi-step processes initiated by a collective plasmon excitation, which dephases into independent charge carriers, which transfer to another material or molecule.

Plasmon-induced charge transfer (PICT): a single step process resulting in charge transfer from a plasmonic material to another material or molecule already during photoexcitation.

Ballistic thermal injection (BTI): transport of hot carrier energy across an interface with another material by carrier-carrier scattering at the interface; BTI is particularly fast and efficient if electrons travel to the interface ballistically, i.e., without scattering with other electrons, phonons or defects.

Lifetime: the time during which an electronic state remains populated and a charge carrier retains its energy, before it loses energy by coupling to other degrees of freedom, e.g. phonons or another charge.

Landau damping: exponential relaxation of oscillation of the electron density wave (plasmon).

Schottky energy barrier: a potential energy barrier for motion of electrons across a metal/semiconductor interface.

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