

Hot carrier flow in catalysis

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Nanoscale materials that contain metallic components can be designed to have excellent light-harvesting capabilities, and can also be used to direct the flow of energy from incident photons into small molecules at or near the surface of metal nanoparticles. One promising route for energy flow is through so-called hot charge carriers, which are optically excited on metal nanoparticles and subsequently transferred to molecules / materials that share an interface with the metal. Here we provide a brief overview of the fundamentals of hot carrier generation and transfer, discuss both theoretical and experimental means for interrogating these processes, and discuss several potential societally-important applications of hot-carrier driven chemistry to solar fuels, and sustainable chemistry.

Keywords: Nanostructure, Photonics, Photocatalysis, Plasmonics, Sustainability

Introduction

The understanding of the dual particle-wave nature of light and matter was a watershed moment in our basic understanding of how energy flows in the universe, and has been leveraged extensively in advancing experimental and theoretical tools to elucidate, and even control, the flow of energy in chemical and material systems where light and matter converge [1]. Hot-carrier driven catalysis represents a curious trinity of energy flow – incoming light imparts energy into electronic degrees of freedom, which in turn impart energy into nuclear degrees of freedom. Not only is this interplay between photonic, electronic, and

phononic/nuclear energy fundamentally interesting, it shows potential to enable technologies that are capable of efficiently harvesting energy from solar photons or using low-intensity light sources to drive photochemical transformations under mild conditions, which are both important from the point of view of sustainability [2-4]. Here we will focus on metal nanoparticles as sources of hot carriers; such nanoparticle systems may derive their efficient hot carrier generation properties from intrinsic optical resonances (such as localized surface plasmon resonance, LSPR [2-4]) or emergent optical resonances (such as scattering mediated absorption, SMA [5,6]).

Hot-carrier generation and transfer

Hot-carrier transfer from metal nanoparticles to molecules to initiate photocatalytic reactions is an intrinsically multi-scale problem, the constituents span multiple length scales and the energy transfer events span multiple time-scales. On the shortest timescale (~ 10 fs), electromagnetic energy flows into the electronic degrees of freedom of the nanoparticle(s) and molecule(s) subject to their mutual physio-chemical interactions; these interactions may have a small or large impact on the electronic degrees of freedom depending on the identity of the metal and the molecules [4]. Plasmonic excitation and decay also occurs on this timescale [2-4]. On slightly longer timescale (10s to 100s of fs) sees evolution of the hot-carrier distributions, including thermalization through electron-electron scattering, decay through electron-phonon scattering, and transfer to molecular adsorbates [4,7]; the transfer of charge from the metal to the molecule both deposits energy into the molecules degrees of freedom, but also fundamentally changes the potential energy surface that govern the nuclear dynamics of the molecule. Nuclear motion of the adsorbate molecules evolves on potential energy surface(s) which correspond to excited and/or ionized states of the adsorbate molecule, and typically occurs on slower timescales (~ 100 s – 1000 s of fs), though theoretical studies have suggested ultra-fast (~ 30 fs) nuclear dynamics following plasmon-induced electron transfer may occur in water splitting reactions [8]. These timescales are illustrated schematically in Figure 1.

Theory and simulation of hot-carrier driven catalysis

It is interesting to imagine what a comprehensive predictive computational model of hot-carrier driven catalysis would look like. In our view, upon specification of materials and geometry of the nanostructure and adsorbed molecule(s) and details of the illumination source, such a tool would predict the flow of electromagnetic energy into the electronic degrees of freedom of the nanoparticle and molecule

subject to their mutual physio-chemical interactions, subsequently predict the electronic motion of the excited system, and finally predict the nuclear motion to allow inference into the potential reactive probabilities and pathways. At this point, there exist no routine comprehensive theoretical/computational approaches; though at current one can simulate each sub-process on its own temporal timescale and gain some insight into the integrated processes. This suggests that continued progress, particularly along the direction of multi-scale theory and simulation, will yield theoretical/computational tools that can provide insights and aid in the design of systems for performing desired hot-carrier induced catalysis.

The photonic problem (shortest timescale), that is the interaction between light and the nanoscale components (i.e. solving for the electric field in the vicinity of the nanoparticle, \vec{E}_{NP} in Figure 1), can be accurately treated within classical electrodynamics. A wide variety of analytical and numerical techniques can be deployed to accurately simulate the flow of electromagnetic fields in the vicinity of nanomaterials. Analytical methods like Mie theory [10] and the T-Matrix scattering method [11] may be deployed if the nanoscale constituents can be modeled as lone spheres or as arrangements of spheres with non-overlapping boundaries. For arbitrary geometries, the discrete dipole approximation [12] and finite element method [13] may be used to solve for the behavior of the electromagnetic fields in the frequency domain, and the finite-difference time-domain method can be used to solve for the flow of the EM fields in the time-domain [14]. These techniques are critical for providing insight into how the nanoscale structure harvests and directs the flow of optical energy, which will influence the generation of hot carriers. All things being equal, nanoparticles which can more efficiency harvest and concentrate incident optical energy will see higher rates of hot-carrier generation [15], and nanoparticles with longer-lived optical resonances will see more persistent hot-carrier dynamics [6]. Modeling hot-electron dynamics (intermediate timescale) and transfer requires a quantum mechanical treatment of the electronic degrees of freedom of the metal and adsorbate molecule ($\Psi_{el,NP}$, $\Psi_{el,mol}$) respectively. A surge in computational advances in the efficiency of electronic structure methodologies, density functional theory in particular, have enabled detailed investigation of the electronic distributions and their dynamics (through the real-time implementation of time-dependent DFT) in small (~ 1 nm) metal nanoclusters [8], though application of *ab initio* methods to nanoparticles in general remains intractable. A variety of semi-empirical approaches, including the so-called Jellium model [6,15-16] and density functional theory tight-binding [17] have been employed to study larger nanoparticle systems since they effectively coarse grain over core electronic degrees of freedom; these methods are still limited by relatively steep (\sim quartic) scaling with the system size. Finally, progress has been made towards the treatment of nuclear dynamics on (perhaps multiple) excited-state or ionized potential energy surfaces, including the use of Ehrenfest dynamics [8] and fewest-switches surface hopping [9] in conjunction with time-dependent DFT. Also, impressive advances in wavefunction embedding theories has permitted the accurate mapping of relevant molecular potential energy surfaces with inclusion

of physio/chemical interactions with metal nanoparticle surfaces [18]. Wavefunction embedding approaches, more than density functional theory or semi-empirical approaches, offer a more systematic route to including high-level electronic correlation effects, which may be significant for accurately capturing the shape of excited-state potential energy surfaces which govern the reactivity in these processes.

Experimental characterization of hot-carrier driven catalysis

Experimental realization and characterization of efficient hot carrier platforms, i.e. plasmonic and other optical nanostructures, encompass a wide variety of sample fabrication approaches and experimental techniques. Typically, the samples used for characterization of hot carrier generation can be categorized into two groups: colloidal and nanofabricated. The colloidal approach has an advantage of using wet chemistry methods for tailoring the material composition and structure of the nanoparticles. Using this approach high quality nanoparticles with good crystalline structure can be obtained [19]. Using more sophisticated techniques, more complex hybrid nanoparticles with desired electronic and optical properties can be synthesized [20]. On the other hand, the top down approach used in nanofabrication offers a unique ability to control the size and shape, thereby imparting exquisite control of optical energy flow and confinement, owing to the flexibility of the lithographic and material deposition techniques [21]. Using this approaches, arbitrary shapes of plasmonic platforms can be fabricated which can allow to access new hot carrier generation mechanisms. For example, the ability to fabricate tapered nanostructures have allowed to study the hot carrier generation in adiabatically focusing plasmonic fields and to shape the momentum distribution of the hot carriers [22-23].

Various optical experimental approaches have been used to study the processes of photo-induced hot electron generation and injection in the temporal, spatial, and frequency domains. Because of the fleeting nature of hot-carriers it is usually necessary to employ time-resolved experimental techniques in order to observe the short-lived phenomena associated with them. Pump-probe transient spectroscopy has the advantage of offering ultrafast temporal resolution only limited by the pulse duration of the excitation source, i.e. from 10s to 100 fs [24]. This allows to access the fast dynamics of electron excitation and relaxation in nanostructures [25-26]. In a typical experiment the pump pulse excites the localized plasmonic resonance which leads to the production of energetic carriers in the system [21, 27]. The broadband probe pulse can subsequently probe the reflectivity of the system and gain access to the changes in the dielectric constant of the material caused by the excited hot carriers in the system [28]. Using these techniques the effects such as the field localization and the enhanced generation of hot electrons in nanometric gaps have been demonstrated [21]. This process can be understood in terms of Landau damping where the localization on the characteristic length scale in real space creates large field gradients leading to resonant dephasing of the plasmonic and free carrier intraband absorption in the metal [29]. The length scale in this process is given by the band curvature of the

conduction band (i.e. the Fermi velocity) and can be compared to the Kreibig term of the plasmonic damping of small nanoparticles [30]. Furthermore, the ultrafast transient absorption studies can uncover the mechanisms of hot carrier generation and injection in hybrid metal-semiconductor nanocomposite particles [31]. In such studies, typically, the probe pulse monitors the time-resolved absorption in the semiconductor at the corresponding bandgap energies and, thus, any transient changes in absorption can be indicative of hot carrier injection across the metal interface. Using similar approach, Lian *et al.*, reported direct decay of plasmons in colloidal metal nanoparticles into an excited carriers in an adjacent semiconductor, beating the conventional Fowler limit for a two-step generation and charge transfer mechanism in a typical Schottky injection scheme [20]. Pump-probe spectroscopy also enables studying the spatial distribution of excited hot carriers. Using this approach the diffusion of the generated carriers can be traced in the samples and the information about the spatio-temporal dynamics at different scales can be extracted [23, 32-33].

In the frequency domain, the hot carrier generation and transfer can be also studied using emission spectroscopy techniques. The particular emission spectrum can be used to garner information about the hot electron energy distribution and dynamics. Various physical processes have been used to describe the hot carrier distribution in nanoscale systems. Most commonly, photoluminescence spectroscopy is used to characterize hot electron generation in plasmonic structures [34]. In such studies, pulsed excitation laser sources are typically used to access the multi-photon regimes of the PL emission. However, recently it has been demonstrated that emission excited by continuous wave excitation can also produce invaluable information about the hot carrier distribution in the nanosystems [35]. Early studies on gold nanostructures attributed the emission at different spectral ranges to distinct physical processes [36]. Whereas the two-photon absorption induced luminescence at visible frequencies was thought to arise from intraband transition, the near-infrared emission was assigned to intraband absorption, i.e. hot electron generation. The latter, which scales linearly with the excitation power, is facilitated by plasmonic confinement which makes the resonant free carrier absorption possible in noble metals. This view was further developed in later studies where a continuous variation of emission power exponent was observed across the photoluminescence (PL) spectrum [34, 37]. Such non-integer values of the PL power exponent were assigned to the fact that the emission throughout the whole spectrum has the same origin, i.e. the radiative recombination of thermally equilibrated hot electron gas excited via intraband absorption. Later studies added novel dimensions to our understanding of hot electron-mediated emission by invoking other mechanisms for the observation of the broadband signals. Raman scattering has been used to explain some of the spectral features of plasmon-enhanced emission [35, 38]. In such a process the inelastic scattering occurs by exciting a conduction band electron and a lattice phonon. Thus, the hot electron energy distribution above the Fermi energy is imparted onto the Raman scattering spectrum, similar to PL emission.

Hot-carrier driven photocatalysis

The strategy of doing hot-carrier driven photocatalysis fits broadly within the push for advancing sustainable paradigms in chemistry [2-4,39]. Most directly, a tremendous amount of progress has been made towards developing photocatalytic and photoelectrochemical systems that leverage hot-carrier transfer to facilitate energy-intensive chemical reactions that produce chemical fuels, e.g. water splitting to H₂ and O₂ [4,8,40-42] or CO₂ reduction to CH₄ [43], or important feedstocks for fuels, including CO₂ reduction to CO [4,39]. Because plasmonic and other resonant metal nanoparticles are extremely efficient light harvesters, these reactions can be initiated with relatively low illumination conditions (~100 mW/cm², similar to solar illumination), which suggests the possibility for utilizing such paradigms for solar fuels. As one concrete example, Moscovits and co-workers reported plasmonic gold nanorod-based solar water splitting devices capable of yielding $5 \cdot 10^{13}$ H₂ molecules per second of operation per cm² of device coverage under solar illumination (around $1 \cdot 10^{18}$ visible photons per second per cm²) [39]. Under 3 sun illumination, the same system yielded about 2.8 mmol of H₂ per hour per gram of catalyst [39]; a similar yield (2 mmol of CH₄ per hour per gram of catalysis) was reported by Garcia and co-workers [43] using heterostructures involving plasmonic gold, copper, and titanium oxide whose selectivity for CO₂ to CH₄ was enhanced by hot-carrier injection from gold to copper. While these and other studies are extremely exciting, hot-carrier driven solar fuel generation remains relatively immature, and it is difficult to project cost competitiveness from lab-scale studies to date [39]. Important cost benchmarks include the price to generate these products using fossil fuels; for example fossil-fuel driven production of H₂ via steam methane reform is estimated to cost around \$1.40 / kg H₂ and production of CO from partial oxidation of fossil fuels is estimated to cost around \$0.19 / kg CO [39]. It is our view that continued research efforts, both in fundamental and applied domains, should keep in mind several important goals to (1) increase efficiencies of hot-carrier driven reactions (in terms of photon-to-chemical yields or chemical-yields to catalyst-mass, or both), (2) realize such reactions using little or no precious metals, (3) increasing the durability and lifetime of such catalytic systems, which can all positively impact cost competitiveness over the lifecycle of these systems. Critical economic analysis accompanying these efforts could be illuminating for the overall prospect of utilizing hot-carrier driven photochemistry at industrial scale.

Besides solar fuels, hot-carrier driven catalysis can also be used to increase the sustainability of chemical reactions more broadly, for example, by lowering the energy requirements of chemical reactions that are traditionally run at high temperatures, and/or by improving the selectivity of reactions that may undergo side reactions or degradation under high temperature conditions. For example, plasmon-induced hot electron injection from gold / palladium heterostructures has been suggested to efficiently activate the C-Br bond to facilitate a number of Suzuki coupling reactions, which are widely used in the pharmaceutical and industrial chemistry, and has resulted in 2-fold improvements in yields when compared to their thermally activated counterparts [44]. Recently, hydrogenation

of alkynes to alkenes and alkanes was demonstrated using hot-electrons from periodic gold / platinum heterosurfaces, where hot-electron generation results from surface plasmon polariton excitation on gold, and subsequent hot-carrier transfer and activation of alkyne triple bonds is facilitated by the platinum [45]. Such studies highlight the vast potential in functionality that can be realized by creating heterostructures with one or more components that serve as hot-carrier sources.

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Figure Captions

Figure 1. Schematic of hot-carrier driven catalysis with metal nanoparticles, with timescales and key quantities involved in each sub-process.

Figure 2. Illustrations of hot-carrier mediated chemistry for solar fuels (water splitting and CO₂ reduction) and for ubiquitous synthetic steps utilized across many industries (Suzuki coupling and hydrogenation reactions).