Hot Electrons in Catalysis

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INTRODUCTION

Hot electrons—electrons with energies far exceeding the thermal distribution—are generated in metallic nanostructures by light excitation or by non-thermal dynamics such as atomic and molecular scattering.[1] Hot electrons are typically produced in large numbers in metal nanostructures due to high densities of states and large absorption cross sections, in particular through the decay of surface plasmon polaritons; but they are very short-lived.[2–5]

Despite their short lifetimes, hot electrons (or holes) can induce chemical dynamics and catalytic processes. The ability of hot electrons to induce chemical dynamics has been an intense area of study since at least 1964 when the landmark papers of Redhead and Menzel and Gomer on desorption induced by electronic transitions or "DIET" appeared.[6,7] Many decades later, the study of hot electrons and photoexcited charge carriers spans chemical catalysis, condensed matter physics, and ultrafast science. In condensed matter physics, non-equilibrium electron distributions have been found to fundamentally alter materials properties through electron–phonon coupling. In catalysis, hot electrons generated by photoexcitation, especially in the presence of plasmon enhancement, are studied for their ability to selectively promote chemical reactions. Injection of hot electrons (or holes) into molecules from surfaces can induce chemical reactions at energies lower than those required for thermally overcoming activation barriers.[8,9] In ultrafast and non-linear spectroscopy, electronic excitations enhance signals and affect lineshapes.

A variety of synthetic, spectroscopic, and imaging techniques are being wielded to understand and control the coupling of excited electrons with dynamical processes in materials and at interfaces. The aspiration to control the generation of hot carriers and thereby achieve selective excitation of specific electronic or vibrational modes is driving the development and application of frontier methods of time-resolved spectroscopy. To resolve the different physical phenomena that underlie hot-electron and plasmonic effects in heterogeneous catalysis and reaction dynamics at surfaces, a suite of theoretical methods ranging from continuum electrodynamics, many-body condensed matter theory, to molecular simulations and open quantum system dynamics is being applied.

Different sub-disciplines of physical chemistry investigate hot-electron effects with different motivations, viewpoints, and methods. These previously disparate research communities are beginning to converge on a common paradigm and language. One of the motivations behind this virtual special issue arose from a Psi-K/CECAM Flagship Workshop on "Light-matter interaction and ultrafast nonequilibrium dynamics in plasmonic materials" that was held at the University of Warwick in July 2022.[10] This event was attended by many contributors of this VSI and had the specific goal of bringing diverse research communities in this area together. The aim of this workshop was to provide engagement between communities, to create space for cross-community collaboration, and to tackle the interdisciplinary, multitechnique, and multiphysics challenge associated with light- and electron-driven dynamics in nanostructured materials.

We are excited to introduce this Virtual Special Issue (VSI) on "Hot Electrons in Catalysis" in The Journal of Physical Chemistry that highlights exciting research on hot-electron phenomena across ultrafast spectroscopy, catalysis, and surface physics. The VSI features 28 contributions and presents a rich mix of perspectives and aspects of hot-electron effects in catalysis. In the following, we briefly review the contributions to this VSI classified by key sub-topics.

HOT-ELECRON GENERATION IN METALLIC NANOSTRUCTURES

The efficiency of hot-electron generation in metallic nanostructures is expected to depend on parameters that govern optical absorption and electron transport, such as the shape, composition, size, and morphology of the nanostructure. This dependence is explored by Kim et al.[11] The authors extract hot-carrier-generation efficiencies from rates of plasmon-induced conversion of 4-mercaptobenzoic acid to benzenethiol. They compare these efficiencies for different nanoparticle (NP) shapes, finding that Au nanorods outperform other shapes such as nanospheres, nanocubes and nanotriangular prisms. Li et al.[12] report that Ag nanoplates outperform Au nanoplates in plasmon-induced reduction of 4-nitrobenzenethiol to p,p'-dimercaptoazobisbenzene and bimetallic Ag–Pt and Ag–Pd nanostructures outperform analogous Au–Pt and Au–Pd nanostructures.

Lifetimes of hot electrons are an important design factor and are governed by different relaxation processes. Chiang et al.[13] find *via* ultrafast spectroscopy measurements of hot electron dynamics in Au NPs that the rate of electron–phonon cooling of the hot electron distribution is independent of whether hot electrons were generated by plasmon-resonant or off-resonant excitation. They note that the bulk electron–phonon lifetime represents the maximum timescale within which hot electrons must be extracted for driving chemistry.

Finally, Henrotte et al.[14] showcase the use of scanning photoelectrochemical microscopy for elucidating how surface defects in hybrid Au–TiO$_2$ nanostructures affect hot-carrier generation. This study also reveals a dependence of reactivity on the NP size and the excitation wavelength.

HOT-ELECTRON TRANSPORT ACROSS HETEROSTRUCTURES

For hot electrons to be harvested, they often need to be transferred across metal–semiconductor and metal–molecule junctions. It is therefore essential to understand how electronic interactions and couplings across such interfaces govern hot electron dynamics. For example,

the ability of a molecular adsorbate to capture hot electrons sensitively depends on the nature and strength of the molecule–metal bond and the alignment of electronic energy levels of the metal and molecule. Chen and Wang[15] show this for plasmon-induced reductive coupling of *para*-substituted nitrophenyl derivatives as they vary the chemical linker group that anchors the molecules on the Ag NP surface.

By finely tuned design of composite and hybrid catalyst architectures, it is possible to simultaneously optimise hot-carrier lifetimes and catalytic properties. Furthermore, hybrid constructs also allow light absorption properties to be optimized for maximizing solar-to-chemical energy conversion. Many contributions of this VSI show that heterostructuring paves the path to longer-lived charge carriers. Vo and Chang[16] study a hybrid system composed of Au nanorods and carbon films. From spectral linewidths, they deduce that hot electrons generated by plasmonic excitation of the nanorods are transferred to the carbon film, potentially extending the lifetime of the charge carriers. An et al.[17] report the fabrication of plasmonic metal–semiconductor photoelectrodes that generate hot electrons under visible-light excitation and achieve efficient splitting of seawater. Geng et al.[18] report that by hybridizing rhodium nanoparticles with solar absorbers such as titanium nitride (TiN), plasmonic CO_2 reduction catalysis can be achieved with milder degrees of heating and light illumination. Ma et al.[19] present solar-powered redox cells based on TiO_2 nanostructures functionalised with Au NPs. Au NPs enhance light absorption and interfacial hot carrier transfer, which increases photocurrents compared to bare TiO_2 nanostructures. Mohanty et al.[20] present heterostructures comprised of Au NP-decorated strontium titanate ($SrTiO_3$) and titanium carbide (Ti_3C_2) MXenes, which exhibit broad spectrum absorption, effective hot carrier separation, and efficient transport. These hybrid photocatalysts are deployed for sunlight-driven degradation of pharmaceutical pollutants via plasmonic enhancement.

Finally, following up on a recent report of photoelectrocatalytic production of ammonia from nitrate on Au NPs,[21] Silveira et al.,[22] show that a hybrid NiO–Au NP–TiO_2 structure allows such production at neutral pH, making the process compatible with agricultural use of ammonium. Hot electrons generated by visible-light excitation of the hybrid system are injected into the TiO_2 electrode where they enhance the rate of nitrate conversion while hot holes are harvested by NiO.

IMAGING OF HOT-ELECTRON DYNAMICS

In addition to spectroscopic probing, high-spatial-resolution imaging techniques are being increasingly applied for gaining insights into plasmon-induced, hot-electron-driven dynamics. For example, real-space observations using high-resolution scanning tunnelling microscopy with plasmonic tips provide information on electron-induced dynamics of adsorbates as Kazuma et al.[23] show for single O_2 molecules on a Ag(110) surface. Alcorn et al.[24] uncover that apart from driving chemical reactions, hot electrons can induce restructuring of the NPs themselves. Specifically, the authors observed by in-situ transmission electron microscopy that plasmon excitation of Au–Cu alloy NPs induces their Ostwald ripening, which is a nonthermal process driven by excited carriers. Continuous-wave photoexcitation might therefore lead to morphological changes of plasmonic catalysts and alter their optical and catalytic properties under operating conditions.

MECHANISTIC STUDIES OF HOT-ELECTRON CATALYSIS

While photoinduced enhancement of catalytic rates has been observed for a variety of systems, true photochemical effects are difficult to discern from an ordinary effect of photothermal heating. As a result, the contribution of hot electrons in catalysis is "hotly" debated[25,26] and requires elucidation of the enhancement mechanism. The VSI features a number of insightful mechanistic studies of plasmon-induced catalysis. Mantilla et al.[27] report differences between Au and Ag NPs in chemical selectivity of plasmon-induced transformations of 4-ATP: on Ag NPs, plasmon-induced oxidation of 4-ATP is favored, whereas dimerization is favored on Au NPs. This difference likely originates from the abundance of surface oxygen on Ag. Sarhan et al.[28] show that broadband absorption of colloidal black Au NPs enables hot-electron-driven dimerization and cross-linking of 4-nitrothiophenol. Kumar et al.[29] show that near-infrared (NIR) light excitation of NIR-resonant triangular Au nanoprisms induces the hydrolysis of dimethylphenylsilane, but likely does so via a photothermal effect rather than photochemical enhancement. Zang et al.[30] show that photoelectrochemical water splitting can be enhanced by strong coupling of localized surface plasmon resonances (LSPRs) with a Fabry–Pérot nanocavity. Lee at al.[31] present plasmon-induced polymerisation of acrylic acid on Au NPs where they find that the polymer thickness depends on the excitation wavelength, illumination power, and sacrificial hole scavenger. The authors attribute photopolymerization activity to plasmon-induced generation of monomer radicals and deem local photothermal heating to play a negligible role. Lee and Ha[32] employed single-nanoparticle studies to elucidate hot-electron-mediated reduction of Ag onto Au nanorods without a reducing agent.

THEORY AND SIMULATION OF HOT-ELECTRON-DRIVEN DYNAMICS

The description and analysis of hot-electron-driven chemical dynamics at surfaces represents a true challenge for modern theory and simulation due to the need to account for nonadiabatic effects in coupled electron-nuclear dynamics, and the challenges associated with first-principles representations of hybrid metal–organic interfaces. To compare to measurable dynamic observables, accurate and efficient interatomic potentials and surrogate models are required for statistically significant sampling. This VSI features theoretical studies that explore several aspects of these challenges.

Mean-field dynamics simulations based on real-time time-dependent density functional theory provide important insights into the coupling between light, electrons, and molecular motion. Wang and Aikens[33] study light-induced H_2 activation on Au_6 and Ag_6 clusters and investigate how excitation frequency and polarization affect bond activation and hot-electron relaxation processes. Giri and Schatz[34] perform real-time time-dependent density functional tight-binding dynamics for H_2 photodissociation on larger Ag and Au NPs ranging from 19 to 489 atoms. Their work reveals that a threshold light intensity is required for initiating dissociation; this threshold depends on the size and composition of NPs and also on the wavelength.

Approximate mixed quantum–classical molecular dynamics (MD) methods such as the molecular-dynamics-with-electronic-friction (MDEF)[36,37] approach can be coupled with models of hot-electron dynamics, such as the two-temperature model (2TM), to study light-driven chemical dynamics at surfaces. Lindner et al.[38] present 2TM-MDEF simulations of

laser-induced recombinative desorption of hydrogen from a Ru(0001) surface. The approach uses interatomic potentials generated by machine learning, which enables the simulation of thousands of reaction events thereby allowing calculation of hot-electron-induced desorption probabilities and isotope ratios under various coverages and laser fluences. Tetenoire et al.[39] present ab-initio MDEF simulations of the photoinduced desorption and oxidation of CO on a Ru(0001) surface. They find that femtosecond-laser-generated hot-electron distributions predominantly induce CO desorption over the oxidation of CO to CO_2, which is consistent with experimental findings. Gardner et al.[40] systematically assess the limitations of different mixed quantum–classical methods such as MDEF, surface hopping MD, and Ehrenfest dynamics for nonadiabatic molecular scattering and non-thermal surface dynamics in which hot electrons play an important role. Dillon and Gieseking[35] report systematic convergence of nonadiabatic couplings in surface-hopping calculations using a plane-wave basis, which provides a particularly convenient approach for modeling nonadiabatic dynamics in condensed phase. It is shown that excited-state relaxation times can have significant discrepancies if the results are not converged with respect to the kinetic energy cutoff of the basis.

To fully understand ultrafast electron creation and relaxation, it is important to go beyond the 2TM picture of thermalized electrons in solids. João, et al.[41] present an atomistic approach to simulate light-driven hot electron generation in nanoparticles by combining real-time density matrix propagation with semi-empirical tight-binding electronic structure. They are able to predict hot-carrier generation rates for Au and Ag NPs of diameters up to 20 nm. The authors find that the hot-carrier distribution is sensitive to the NP size, particularly for Ag NPs. Seibel et al.[42] use full Boltzmann collision integrals to describe the ultrafast driven creation and subsequent thermalization of nonequilibrium electrons in Au. The authors find that the 2TM model significantly overestimates the creation of primary electrons, i.e., electrons directly created by photon absorption, but ignores the creation of secondary electrons, i.e., hot electrons generated by electron–electron scattering. The latter can affect the electron relaxation dynamics for picoseconds after the laser pulse has ended. Girotto, Caruso, and Novko[43] also go beyond the picture of thermalized hot electrons in their study of ultrafast light-driven phonon dynamics in MoS_2 monolayers. By coupling time-dependent electron and phonon populations from ab-initio time-dependent Boltzmann equation simulations with many-body phonon self-energy calculations, they study the ultrafast changes in frequencies and lifetimes of individual phonon modes. They find that photoexcited MoS_2 exhibits anisotropic phonon softening at specific points in the Brillouin zone due to population and depopulation of conduction and valence valleys in the band structure.

CONCLUSIONS

The study of electronic excitations at metal-organic interfaces provides a fertile ground for advancing the fundamental understanding and ultrafast control of light–matter interactions and the use of these interactions for selective catalysis and surface reaction dynamics. The intricate interplay of light, electrons, phonons and chemical dynamics require that this challenge be approached simultaneously from physics, chemistry, and materials science perspectives. The range of contributions in this VSI capture these different perspectives. In all, the advances

reported in this VSI enlighten our understanding of hot-electron phenomena and highlight avenues for further development.

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DATA AVAILBILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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