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Mechanistic Study of Plasmon Driven Surface Chemistry and Quantum Plasmonics

Habteyes, Terefe
UNIVERSITY OF NEW MEXICO
1700 LOMAS BLVD NE
ALBUQUERQUE, NM,
US

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14. ABSTRACT

In this research project, significant experimental advances have been achieved at the frontiers of plasmon enhanced photochemistry, plasmon nanocavity resonances and plasmon enhanced light emission. The absorption bands of model organic molecules have been determined based on a novel approach that involves extracting electronic transition bands of adsorbates from molecule–plasmon excitation coupling. In contrast to past speculations that new electronic states are formed when organic dyes are adsorbed on metal surfaces, our experimental results show that the absorption bands of ï•°-conjugated organic dyes has the general shape of the corresponding absorption bands in solution apart from expected peak wavelength red-shifting and spectral broadening depending on the strength of the surface-molecule interaction. Establishing the absorption band has been foundational for our wavelength dependent analysis of plasmonenhanced photochemistry. By comparing the photochemistry of a model molecule (methylene blue) on gold nanoparticles at five excitation wavelengths (561, 633, 671, 785 and 808 nm) at different adsorption conditions, we have demonstrated that the reaction mechanism can be switched from charge transfer to adsorbate electronic excitation using surface ligands as metal-molecule spacer and dipole orienting scaffold. This has led to a new understanding that hot electrons may simply play a role of preparing anion intermediates that have accessible electronic transitions in the visible spectral region as the PI Habteyes has highlighted in a recent invited perspective article in the Journal of Physical Chemistry. This advance has built on our proposed mechanism that involves plasmon-pumped adsorbate intramolecular electronic excitation. New findings have also been reported in quantum plasmonics and plasmon enhanced light emission. Tuning plasmonic coupling from capacitive to the quantum tunneling regimes via atomic control of dielectric spacing, we have reported the observation of abrupt transition of resonance energy and spectral shape as the interaction transitions from capacitive to charge transfer, which is in contrast to the trends observed previous reports. By analyzing the temperature dependence of photoluminescence from semiconductor heterostructures coupled to plasmonic nanostructures, we have quantified contribution of plasmon enhanced absorption and spontaneous emission enhancement factors.

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Mechanistic Study of Plasmon Driven Surface Chemistry and Quantum Plasmonic

Grant FA9550-18-1-0512

Final Report

Air Force Office of Scientific Research
Attn: Dr. Michael Berman

PI: Terefe G Habteyes, Associate Professor
Department of Chemistry and Chemical Biology
Center for High Technology Materials
University of New Mexico
Albuquerque, NM 87106
Phone: 505-272-7504
Emails: habteyes@unm.edu

Abstract

In this research project, significant experimental advances have been achieved at the frontiers of plasmon enhanced photochemistry, plasmon nanocavity resonances and plasmon enhanced light emission. The absorption bands of model organic molecules have been determined based on a novel approach that involves extracting electronic transition bands of adsorbates from molecule–plasmon excitation coupling. In contrast to past speculations that new electronic states are formed when organic dyes are adsorbed on metal surfaces, our experimental results show that the absorption bands of π-conjugated organic dyes has the general shape of the corresponding absorption bands in solution apart from expected peak wavelength red-shifting and spectral broadening depending on the strength of the surface-molecule interaction. Establishing the absorption band has been foundational for our wavelength dependent analysis of plasmon-enhanced photochemistry. By comparing the photochemistry of a model molecule (methylene blue) on gold nanoparticles at five excitation wavelengths (561, 633, 671, 785 and 808 nm) at different adsorption conditions, we have demonstrated that the reaction mechanism can be switched from charge transfer to adsorbate electronic excitation using surface ligands as metal-molecule spacer and dipole orienting scaffold. This has led to a new understanding that hot electrons may simply play a role of preparing anion intermediates that have accessible electronic transitions in the visible spectral region as the PI Habteyes has highlighted in a recent invited perspective article in the Journal of Physical Chemistry. This advance has built on our proposed mechanism that involves plasmon-pumped adsorbate intramolecular electronic excitation. New findings have also been reported in quantum plasmonics and plasmon enhanced light emission. Tuning plasmonic coupling from capacitive to the quantum tunneling regimes via atomic control of dielectric spacing, we have reported the observation of abrupt transition of resonance energy and spectral shape as the interaction transitions from capacitive to charge transfer, which is in contrast to the trends observed previous reports. By analyzing the temperature dependence of photoluminescence from semiconductor heterostructures coupled to plasmonic nanostructures, we have quantified contribution of plasmon enhanced absorption and spontaneous emission enhancement factors.

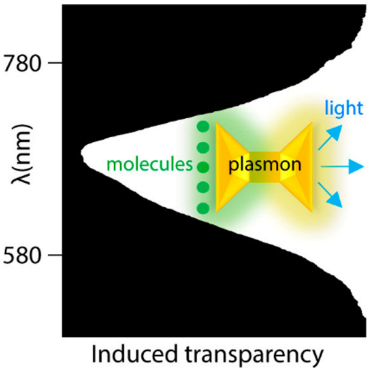
Summary of Published Results

1. Mechanistic Understanding of Plasmon Enhanced Photochemistry

Extracting Electronic Transition Bands of Adsorbates from Molecule–Plasmon Excitation Coupling

Tefera E. Tesema, Hamed Kookhaee, and Terefe G. Habteyes, *J. Phys. Chem. Lett.* **2020**, 11, 9, 3507–3514

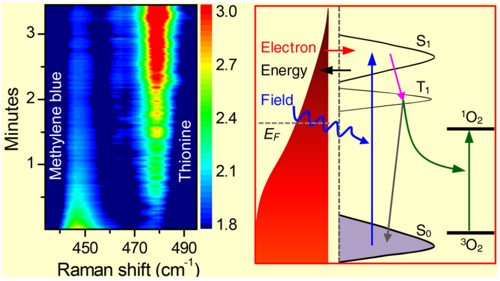
The coupling between molecular electronic and particle plasmon excitations can result in various intriguing outcomes depending on how strongly or weakly the excitations couple to compete with their respective decay rates. In this work, using methylene blue and thionine dyes as model systems, we show that the electronic absorption band of resonant adsorbates can be determined with submonolayer sensitivity from the weak molecule–plasmon excitation coupling that results in the attenuation on the plasmonic absorption band. The extracted spectra are strongly similar to the absorption spectra of the corresponding molecules in solution, apart from the expected spectral red-shift and broadening. Interestingly, the adsorption isotherms determined on the basis of the magnitude of the attenuation correlate linearly with that determined from the adsorbate-induced plasmon resonance red-shift. The results demonstrate that in the weak coupling regimes the plasmon modes can be considered as an environment that supplies energy to and takes energy from the adsorbates.



Plasmon-Driven Reaction Mechanisms: Hot Electron Transfer versus Plasmon-Pumped Adsorbate Excitation

Tefera E. Tesema, Bijesh Kafle, and Terefe G. Habteyes, *J. Phys. Chem. C* **2019**, 123, 14, 8469–8483. Invited Feature Article.

Photochemistry that can be driven at low incident photon flux on optically excited plasmonic nanoparticles is attracting increasing research interest because of the fundamental need to combine surface reaction and in situ spectroscopy as well as the opportunity that plasmon-driven reactions may offer a pathway for efficient conversion of solar energy into fuel. In mechanistic studies of plasmon-driven reactions to date, a great deal of emphasis is given to hot electron transfer. The results summarized in this Feature Article indicate that photochemistry on plasmonic nanoparticles can be induced by hot electron transfer from the nanoparticle to an unoccupied orbital of the adsorbate and/or by plasmon-pumped electron transition from an occupied molecular orbital to an unoccupied molecular orbital of the adsorbate. The branching photochemical reaction of para-aminothiophenol on the plasmonic gold surface depending on the presence

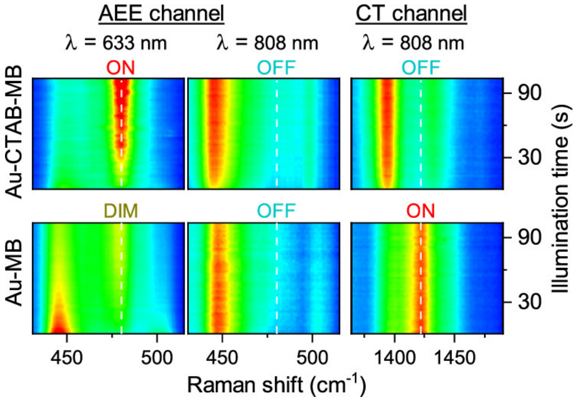


of a cetyltrimethylammonium bromide surface ligand that influences the hot electron concentration is used to highlight reactions driven by hot carriers. The importance of plasmon-pumped electronic excitation of adsorbates in initiating surface photochemistry is demonstrated based on the N-demethylation of methylene blue (MB) on gold nanostructures depending on excitation wavelengths. At excitation wavelength that overlaps with the resonances of MB and the gold nanoparticles, conversion of MB to thionine is observed in the presence of oxygen in the atmosphere and water in the surface–molecule complex. Considering that MB is a well-known photosensitizer, this observation suggests that the photochemical N-demethylation reaction involves singlet oxygen that can be generated via energy transfer from the MB triplet excited state to the O2 triplet ground state.

Switching a Plasmon-Driven Reaction Mechanism from Charge Transfer to Adsorbate Electronic Excitation Using Surface Ligands

Hamed Kookhaee, Tefera E. Tesema, and Terefe G. Habteyes, *J. Phys. Chem. C* **2020**, 124, 41, 22711–22720.

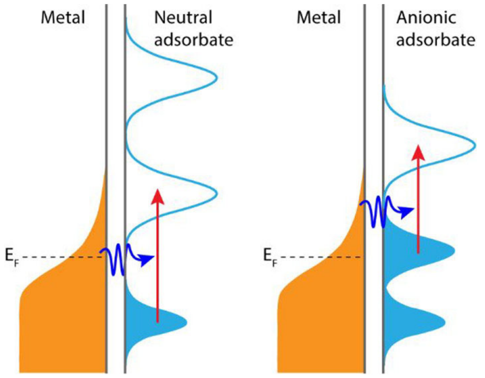
Understanding photocatalytic reaction conditions that selectively leads to a desired product on metal surfaces is a longstanding research problem in heterogeneous catalysis. Here, using plasmon-enhanced N-demethylation of methylene blue (MB) as model reaction, we show that a high degree of product selectivity can be achieved by switching the mechanism from charge transfer (CT) to adsorbate electronic excitation (AEE). In the presence of a cetyl trimethyl ammonium bromide (CTAB) surface ligand on gold nanoparticles, MB is selectively transformed to thionine at a 633 nm excitation wavelength that overlaps with the electronic transition of the adsorbate. The AEE mechanism involves near-field-enhanced intramolecular electronic excitation of the MB adsorbate, and this mechanism is favored by the presence of CTAB that appears to increase the rate of adsorbate excitation by orienting the molecular dipole along the driving surface field and to prolong the lifetime of the excited state by slowing down adsorbate-to-metal energy transfer. On the other hand, when MB is directly adsorbed on the nanoparticles, the mechanism involves electron transfer that may lead to the formation of an anionic complex. In situ surface-enhanced Raman scattering spectra suggest that the complex remains stable at long excitation wavelengths (808 and 785 nm), while at shorter wavelengths (671, 633, and 561 nm), it may undergo nonselective N-demethylation, yielding partially demethylated derivatives in addition to thionine. These experimental observations underscore the importance of adsorption condition in determining the mechanism of plasmon-enhanced photocatalytic reactions.



Anions as Intermediates in Plasmon Enhanced Photocatalytic Reactions

Terefe G. Habteyes, *J. Phys. Chem. C* **2020**, 124, 49, 26554–26564. Invited Perspective Article

Hot electron transfer to unoccupied molecular orbitals is the most popularized mechanism for plasmon enhanced photocatalytic reactions, while a few reactions have been attributed to near-field enhanced intramolecular adsorbate electronic photoexcitation. In this Perspective, it is argued that the role of hot electrons may be limited to preparing anionic complexes that can undergo further chemical transformation via photoexcitation to dissociative potential energy surfaces. The proposed mechanism is based on careful analysis of two different examples of plasmon mediated reactions: N-demethylation of methylene blue (MB) and dissociation of CO_2. In the case of MB N-demethylation, experimental evidence obtained from in situ surface enhanced Raman scattering (SERS) spectroscopy shows that MB converts selectively to thionine on gold nanoparticles (NPs) at optimal surface–molecule separation at an excitation wavelength that matches the electronic transition of the molecule. When MB is directly adsorbed on the metal NPs, the SERS spectra recorded at near-infrared wavelength indicate the formation of an anionic complex that can undergo nonselective N-demethylation when visible light is used. Similarly, comparison of the wavelength dependent plasmon mediated photocatalytic dissociation and hydrogenation of CO_2 on metal NPs to the related gas phase photochemistry suggests that the mechanism likely involves photoexcitation of surface bound CO_2^- anions prepared via metal to molecule electron transfer. In general, it is proposed that near-field enhanced direct electronic excitation of adsorbate or adsorbate–metal complex plays a critical role in most, if not all, plasmon mediated photochemical reactions, while hot electrons prepare reactive intermediate species.

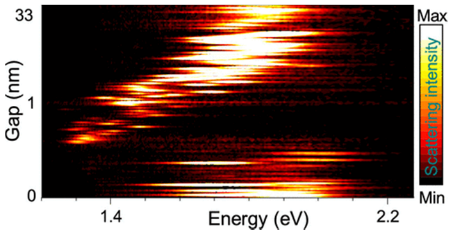


2. Trapping Electromagnetic Field on Polarizable Materials Using Plasmonic Nanoparticles

Tuning Plasmonic Coupling from Capacitive to Conductive Regimes via Atomic Control of Dielectric Spacing

Sharmin Haq, Tefera E. Tesema, Bisweswar Patra, Eric Gomez, and Terefe G. Habteyes, *ACS Photonics* **2020**, 7, 3, 622–629

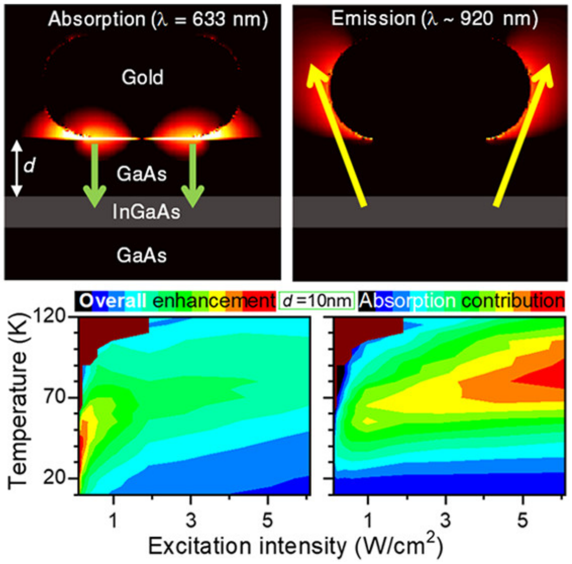
The gap length between plasmonic nanoparticles determines the strength of the optical coupling that results in electromagnetic field enhancement for spectroscopic and other applications. Although gap plasmon resonances have been the focus of increasing research interest, experimental observations have primarily been limited to the coupling of spherical nanoparticles that may not provide clear spectral contrast of the optical response as the interaction evolves from capacitive to charge transfer with the gap size decreasing to sub-nanometer. Here, by taking advantage of the sharp plasmon resonances of colloidal gold nanorods coupled to gold film, we present the spectral evolution of gap plasmon resonance as the particle–film spacing varies from over 30 nm to the touching limit. We find that the capacitive gap plasmon resonance of the coupled system red-shifts and narrows continuously until it vanishes at the quantum tunneling limit, in contrast to the nonlocal and Landau damping effects that are expected to result in relative blue-shifting and spectral broadening. When the spacer thickness is further decreased, high order cavity modes appear, and eventually single peak broad resonances that are characteristic of tunneling and direct contact particle–film interaction emerge. The experimental observations show that nanorods are better suited for creating cavity plasmon resonances with high quality factor, and the spectral contrast at the transition provides clarity to develop improved theoretical modeling of optical coupling at sub-nanometer gap lengths.



Revealing Temperature-Dependent Absorption and Emission Enhancement Factors in Plasmon Coupled Semiconductor Heterostructures

Chih-Feng Wang, Sadhvikas Addamane, Bisweswar Patra, Claudia Rivera Lebron, Sharmin Haq, Ganesh Balakrishnan, Kevin J. Malloy, and Terefe G. Habteyes, *ACS Appl. Electron. Mater.* **2019**, 1, 8, 1439–1448

Localized surface plasmon resonances can increase the quantum efficiency of photon emitters through both absorption and spontaneous emission enhancement effects. Despite extensive studies, experimental results that clearly distinguish the two plasmonic enhancement effects are rarely available. Here, we present clear spectral signatures of the plasmonic enhancement effects on the absorption (excitation) and spontaneous emission (Purcell factor) by analyzing the temperature-dependent photoluminescence (PL) properties of an InGaAs/GaAs single quantum well (QW) coupled to colloidal gold nanorods (AuNRs) at different GaAs capping layer thicknesses (d). We find that when the emitting InGaAs layer is close to the AuNRs (d = 5 nm), the plasmonic enhancement effect on the QW PL is dominated by the Purcell factor, which significantly increases the external quantum efficiency of the QW that otherwise barely emits. When d is increased to 10 nm, the temperature dependence of the PL enhancement factor (F) reflects absorption enhancement in the capping layer followed by carrier diffusion and capture by the well. First, F increases with temperature and then decreases following the temperature dependence of the carrier diffusion coefficient in GaAs. By factoring out the contribution of the captured carriers to F, it is shown that carrier



transfer to the well reaches saturation with increasing incident laser power. In addition to providing insight into the plasmonic enhancement mechanism, the results presented in this work suggest that colloidal plasmonic nanoparticles can be used as simple probes for understanding carrier transport phenomena in arbitrary semiconductor heterostructures.