



NRL/MR/6178--20-10,036

Directing Optical Energy in Plasmonic Nanohybrids for Local Chemistry

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February 8, 2021

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 08-02-2021		2. REPORT TYPE NRL Memorandum Report		3. DATES COVERED (From - To) 10/2014 – 9/2019	
4. TITLE AND SUBTITLE Directing Optical Energy in Plasmonic Nanohybrids for Local Chemistry				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61153N	
6. AUTHOR(S) Pehr E. Pehrsson*, Blake S. Simpkins, Daniel R. Ratchford, and Jefferey C. Owrutsky				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 1B86	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6171--20-10,036	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR / MONITOR'S ACRONYM(S)	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: Approved for public release distribution is unlimited.					
13. SUPPLEMENTARY NOTES *Retired					
14. ABSTRACT This program elucidates the steps involved in plasmonically driven photochemistry, specifically hot carriers (both electrons and holes) created by the decay of plasmons into one or more electron-hole pairs. The plasmons provide a way to efficiently capture light and convert into a number of different energy storage forms. The energetic carriers resulting from plasmon decay are available to drive chemical reactions that would otherwise be energetically inaccessible, slow, or nonspecific. As such, it will have implications for significant efficiency gains in a wide range of chemistries relevant to the areas listed below. However, this program focuses on the mechanistic fundamentals, rather than a specific chemistry.					
15. SUBJECT TERMS Plasmonics photocatalysis Nano nanowires SERS surface enhancement					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Unclassified Unlimited	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON Blake Simpkins
a. REPORT Unclassified Unlimited	b. ABSTRACT Unclassified Unlimited	c. THIS PAGE Unclassified Unlimited			19b. TELEPHONE NUMBER (include area code) (202) 404-1901

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1. NAVAL/MARINE CORPS NEEDS

This program attempted to elucidate the steps involved in plasmonically driven photochemistry, specifically the promotion of hot carriers (both electrons and holes), created by the decay of plasmons, into one or more electron-hole pairs. The plasmons provide a way to efficiently capture light and convert into a number of different energy storage forms. The energetic carriers resulting from plasmon decay are then available to drive chemical reactions that would otherwise be energetically inaccessible, slow, or nonspecific. As such, technologies based on plasmon-derived reactive carriers will have implications for significant efficiency gains in a wide range of chemistries relevant to the areas listed below. This completed program focused on the mechanistic fundamentals, rather than a specific chemistry.

Power and Energy: alternative fuels

1. CO₂ reduction for hydrocarbon generation
2. H₂O splitting for fuel cells

Expeditionary and Irregular Warfare (& others): nm-scale electronic devices and sensors

1. Sterilization and remediation of groundwater
2. Semiconductor etching for scalable nano-optics & nanoelectronics (sensors)
3. Photodetection: Avalanche photodiode

2. TECHNICAL OBJECTIVE

Our objective was to use tunable, reproducible and scalable plasmonic nanohybrids to systematically understand and control the mechanisms of plasmon decay, hot carrier generation and transport, with the ultimate goal of understanding how plasmonically created hot carriers drive carrier-mediated photocatalytic chemistries. Plasmonic photocatalysis holds great promise for enhanced photon-to-reactant coupling, by generating photocarriers (*i.e.*, electrons and/or holes) that initiate critical chemistries important to energy generation and storageⁱ, chemical and biological sensing,ⁱⁱ photoelectrochemical etching of semiconductorsⁱⁱⁱ, and contaminant remediation, as well as non-chemical applications in photovoltaics and light detection. These chemistries are critical to the Navy's S&T plan, especially for Power and Energy. However, the fundamental carrier generation and relaxation mechanisms were poorly understood,^{iv} largely because of the inhomogeneous materials and system geometries formed *via* traditional wet-chemistry fabrication methods. We combined new nanoscale fabrication methods, nanoplasmonic architectures and characterization approaches in an attempt to surmount this roadblock.

The specifics of the plasmon decay, carrier-generation and charge separation and transport processes can dramatically affect ultimate chemical efficiency. We were able to address fundamental questions about these mechanisms because our nanohybrid structures were *tailored, tunable, and scalable* resulting in photo-carrier generation on a controllable platform that can be tailored to favor one energy transduction process over another. For example, we revealed that when plasmons decay in metal nanoparticles, the resulting energy distribution of those carriers, and how quickly they decay through coupling into other modes like phonons, determine how effectively one might collect and utilize these energetic carriers. We were also able to track the injection of hot carriers created in a metal, across an interface and into a proximal semiconductor, as well as hot-carrier creation directly in the semiconductor (the so-called field enhancement mechanism). The chemical activity of these hot-carriers were directly measured in a 3-electrode spectro-electrochemical cell specifically designed and fabricated for this program. Although we focus on the fundamental mechanisms in the questions above, the ability to efficiently generate reactive charge carriers in plasmonic nanohybrids and move them to the surface will ultimately have a broad impact in many important chemistries driven by hot carriers (CO₂ reduction and water splitting are prominent examples).

[i] Mukherjee et al., Nano Letters, 13, 240 (2013)

[ii] Wu et al., Nanotechnology, 23, 055201 (2012)

[iii] Huang et al., Advanced Materials, 23, 285 (2011)

[iv] Christopher et al., Nature Materials, 11, 1044 (2012)

3. TECHNICAL APPROACH

Heightened control of the plasmonic nanohybrid's characteristics permits us to systematically design for and address each step leading to carrier-driven chemistry (carrier generation, transport, and surface reaction). Our approach relied on new or modified nanofabrication methods to create **tunable, reproducible and scalable** nanohybrids and enabled us to understand and control charge generation, transport, and interfacial redox-chemistry mechanisms in plasmonic photocatalysts. This is a paradigmatic shift from the disordered, random jumbles of components previously used by many research groups. This high degree of randomness sharply limits the ability to systematically control, and hence understand, the mechanisms involved. Using a broad range of expertise in nanofabrication, theory, and characterization enabled us to surmount that limitation. We tuned the nanohybrid's resonance energy to direct optical energy into local or extended modes to control the location and energy distribution of hot carrier generation. Excited electrons and holes experience several stages of energy equilibration, each with characteristic timescales that determine their spatial distribution, residence time, and availability for surface chemistry. We used transient spectroscopies to elucidate the carrier lifetimes / migration distances, and the factors that control carrier transport. Finally, we determined the carrier flux, lifetime and energy-distribution at the nanohybrid's surface. These control the surface chemical reaction kinetics/thresholds, e.g., the formation of reaction intermediates such as transient negative ions and the chemical stability of the resonator surfaces.

4. TECHNICAL PROGRESS

The overall goal of this research were to gain a mechanistic understanding of the fundamental processes that drive plasmonic photocatalysis.

Theory

Theoretical approaches were used to (i) understand optical resonances in nanoscale plasmonic resonators and (2) to reveal charge injection mechanisms in planar plasmon-supporting systems. We first describe COMSOL simulations of nanoscale hybrid plasmonic resonators. The COMSOL finite-element simulations, with convergence testing, were performed for arrays of Si-pillar-based nanocrescents defined by Au coatings on the floors (at the base of the nanowires), nanowire sidewalls, and nanowire caps. The reflection spectra at and away from normal incidence were simulated with the polarization along the short and long axes of the nanocrescent. The resonant modes in the infrared (IR) spectral range can be identified from the dips of the reflection spectrum and the associated field profiles. It was established that the existing modes are the result of hybridization between the elemental modes of the simpler structures such as a metal floor without the crescent, a Si pillar with the metal floor, a Si cavity surrounded by the metal shell, and a solid metal pillar. The strong interactions between these modes owing to the small diameter and the thin crescent structure give rise to the observed mode structure for the full experimental structure that include the pillar, the crescent, and the metal cap.

For the planar plasmonic systems, [Ahn, et. al. *Nanoscale*, **2017**, 9, 3010-3022 and Ahn, et. al. *J. Mater. Chem. A*, **2019**, 7, 7015-7024] which support traveling plasmon polaritons across a wide range of resonance frequencies, calculations of the generation, transport, and injection efficiency of the hot holes were carried out. In these systems, hot carriers produced by the decay of surface plasmon polaritons in Au and Ag films on a TiO₂ thin film were modeled assuming smooth films, which leads to a convenient conservation of in-plane momentum and allowed for the identification two charge transport regimes; a tunneling regime and a Schottky barrier-mediated transport regime. These calculation agreed well with experimental observations and bolstered our mechanistic interpretations. The transport efficiency of the hot carriers generated in small (~10 nm) Au nanoparticles embedded into a TiO₂ thin film were also carried out and revealed the origin of high transport efficiencies. [Ratchford, et. al. *Nano Lett.*, **2017**, 17, 6047-6055] This particular result is important to transitioning plasmonic technologies to energy-generation or chemical storage concepts. All

of these calculations compare favorably to the experimental results obtained under this program and were key to validating our hypothetical mechanisms.

Fabrication

We start by describing our simplest, yet informative, system. Planar films of Ag or Au support continuously tunable plasmonic resonances. This attribute allowed for the testing of charge injection (rates, efficiencies) as a function of plasmon, and therefore hot carrier, energy. Nanoparticle resonators do not allow one to tune plasmon resonance energy so easily. By tuning the plasmon energy across the Schottky barrier, we revealed two distinct charge transport regimes governed by different mechanisms. [Ahn, et. al. *J. Mater. Chem. A*, **2019**, 7, 7015-7024] This would be very difficult to do with conventional plasmonic materials and was an important discovery aiding efforts to increase plasmonic charge collection efficiency.

We have also fabricated several different types of semiconductor-plasmonic hybrid nanostructures for optical and transient optical spectroscopy, including layered materials incorporating nanoparticles (NPs), and three-dimensional gold nanocrescents of gold on Si nanowires and nanopillars. The latter were fabricated by evaporating gold on cm^2 arrays of Si nanowires and nanopillars, with independent control over polar and azimuthal degrees of freedom of the array with respect to the direction of evaporation. The resulting individual hybrid nanostructure consists of a metallic cap and crescent over each Si nanopillar. To delineate the plasmonic nature of resonances previously observed in the semiconductor nanopillar-metallic shell hybrids, we fabricated a series of the hybrids with systematic variation of the shell. These structures include: 1) a Si substrate supporting a periodic array of Si nanopillars, and a continuous gold ‘floor’ covering the substrate between the nanopillars; 2) the Si substrate supporting the Si nanopillar array, and the gold ‘floor’ covering the substrate and a gold cap on top of each nanopillar; 3) the Si substrate supporting the Si nanopillar array, with the gold cap on top and gold crescent over sidewall of each nanopillar.

Lastly, we made multi-layered stacks of Au NPs sandwiched in between TiO_2 atomic layer deposited (ALD) thin films (< 20 nm). The Au NPs were deposited using ebeam evaporation, which produced a high volume density of NPs with typical diameters of 10 nm. These samples have strong optical absorption due to a high NP density, and as discussed below, exhibit large hot-electron injection efficiencies because the NPs are small compared to the mean free path of an electron in gold. [Ratchford, et. al. *Nano Lett.*, **2017**, 17, 6047-6055]

Characterization

Reflectivity measured from the semiconductor-nanopillar-metallic shell hybrids tracks resonances as the shape of the shell is systematically varied. Observed reflectivity changes – assisted by numerical simulations – suggest that the lowest energy resonance is due to a cavity plasmon. In the full hybrid structure, consisting of the gold cap and crescent over each Si nanopillar and the continuous gold floor between the nanopillars, the cavity plasmon involves strong concentration of electromagnetic energy by the metallic shell into the semiconductor nanopillar core. In contrast to traditional plasmonic nanostructures characterized by strong field concentration inside the metal and subsequent high losses, this new resonance concentrates the field inside the semiconductor where it can be usefully utilized. Reflectivity recorded from the hybrid nanostructure arrays in the spectral range $0.35\text{--}5\ \mu\text{m}$ demonstrated excitation of several resonant modes by the incident radiation. The resonances exhibited strong polarization dependence and were excited only when the incident radiation was linearly polarized either parallel or perpendicular to the direction passing through the tips of the crescent. Accordingly, the resonances were identified as localized plasmon modes involving oscillations in the crescent component of the nanostructure. Spectral positions of the resonances could be shifted by variation in both the diameter and the height of the nanostructure. To demonstrate concentration of electromagnetic field inside the semiconductor component of the hybrid nanostructure by the plasmonic resonances, Si Raman signal was recorded from the arrays using 633 nm and 785 nm laser radiation. A strong Raman enhancement – up to a factor of 8 – was observed when the incident laser radiation matched the wavelength and polarization of a plasmonic resonance.

One of the most important factors determining the efficiency of plasmonic photocatalysis is the charge injection efficiency from the metal NP into the semiconductor, however, the achievable injection efficiency from plasmonic devices remains unclear. We used free carrier absorption to determine the electron injection efficiency from the Au NPs to the TiO₂ in the multi-layered Au NP – TiO₂ films. Free carrier absorption in the TiO₂ was measured after exciting carriers in the nanoparticles. The transient signal magnitude vs. pump wavelength tracked with the plasmon resonance, confirming charge injection from the Au into the TiO₂. We used the free carrier absorption response to estimate the injection efficiency, which ranged from about 25% - 40%, monotonically decreasing with pump wavelength. [Ratchford, et. al. *Nano Lett.*, **2017**, 17, 6047-6055] While large, the measured injection efficiency is in good agreement with an upper bound injection estimate based on a simple approximation for the Au hot electron energy distribution. The measured injection efficiencies were corroborated by a separate experiment wherein the electron-phonon coupling times of the Au NPs were shown to be faster for NPs embedded in TiO₂ versus Al₂O₃, which is consistent with a reduced Au electron temperature due to electron injection. These results have important implications for understanding the achievable injection efficiencies for Au NPs fully embedded within a semiconductor with dimensions the Au electron mean free path. They show that the injection efficiency is largely dictated by the excited Au electron energy distribution. In addition to the pump-probe spectroscopies, we have recently acquired an incident photon to current efficiency (IPCE) instrument (Newport QEPVSI-b) to measure the external quantum efficiency of our samples. In agreement with the pump-probe spectroscopies, we have shown that the photoconductivity of the Au-TiO₂ stacks tracks with the plasmon resonance as a function of wavelength. The devices were shown to have an external quantum efficiency of 0.22% at an applied voltage of 1V.

We measured plasmon-induced methanol reduction on both TiO₂ and pure Ag in an in-situ spectroelectrochemical cell, which allows for a broadly tunable plasmon polariton to be launched while simultaneously measuring electrochemical response. Charge transfer associated with reactions in this system reveals itself as shifts in the open-circuit potential, and closely follows the polariton dispersion, thus verifying that the polariton mediates the optically-driven chemistry. These observations are important for two reasons. First, we believe they represent the first measurement of plasmon-induced chemistry from surface plasmon polaritons, [Ahn, et. al. *Nanoscale*, **2017**, 9, 3010-3022] and secondly, the broad tunability of such a system (across nearly the entire visible spectrum) offers the unique opportunity to evaluate plasmon-induced charge transfer as a function of continuously variable plasmon resonance energy; all within a single thin film structure. This tunability may make possible evaluation of resonant hot electron charge transfer from a metal film to a surface-bound molecule as a function of molecular orbital alignment. We have characterized the efficiency of hot carrier driven chemistry as a function of excitation energy, solution pH, and working electrode bias. [Ahn, et. al. *J. Mater. Chem. A*, **2019**, 7, 7015-7024] This work has revealed that hot holes are excited over the TiO₂ barrier and into solution for reaction. The power-dependence of this process has also been measured and verifies a photo-carrier driven process rather than a thermally-driven process.

5. TRANSITIONS

This program has led to an Invention Disclosure: "Hybrid Si core-plasmonic shell nanopillar structures for efficient room temperature luminescence generation", S. Tsoi, D.C. Ratchford, I. Vurgaftman, P.E. Pehrsson, invention disclosure presented to IEB, [STRN: NRL/O/6170-17-106, Navy Case #108501] Sept. 20, 2018

6. PLANNED TRANSITIONS

Budgeted Transitions

N/A

Potential Transitions

Insight into optical emission from the hybrid nanostructures has led to a Nanoscience Institute proposal currently under RAC consideration. “Plasmonically-Enhanced Radiative Transition in Semiconductors” is led by S. Tsoi and includes participants from the current program.

7. PUBLICATIONS/PATENTS

1. Ratchford, D. C. Plasmon-induced charge transfer: Challenges and Outlook, *ACS Nano*, under review, **2019** [Invited Perspective Article]
2. Zhang, Y.; Mandal, R.; Ratchford, D.C.; Anthony, R.; Yeom, J. ZnO nanowires/Si nanocrystals hybrid structures as immobilized photocatalysts for photodegradation, *Sci. Rep.*, under review, **2019**
3. Ahn, W.; Vurgaftman, I.; Pietron, J. J.; Pehrsson, P. E.; Simpkins, B. S. Energy-Tunable Photocatalysis by Hot Carriers Generated by Surface Plasmon Polaritons, *J. Mater. Chem. A*, **2019**, 7, 7015-7024
4. Ratchford, D. C.; Dunkelberger, A. D.; Owrutsky, J. C.; Pehrsson, P. E. Quantification of efficient plasmonic hot-electron injection in gold nanoparticle – TiO₂ films, *Nano Lett.*, **2017**, 17, 6047-6055
[2017 Berman Award Winner]
5. Ahn, W., Ratchford, D. C., Pehrsson, P. E., and Simpkins, B. S., Surface Plasmon-Polariton Induced Hot Carrier Generation for Photocatalysis, *Nanoscale*, **2017**, 9, 3010-3022
6. Saydjari, A., Pietron, J. J., Simpkins, B. S., Electrochemical Deposition and Spectroelectrochemical Response of Bromophenol Blue Films on Gold, *Electroanalysis*, **2015**, 27, 1960-1967
7. Kim, W., Simpkins, B. S., Long, J. P., Zhang, B., and Guo, J., Localized and non-localized plasmon resonance enhanced light absorption in metal-insulator-metal nanostructures, *J. Optical Society of America B*, **2015**, 32, 1686-1692 cited as a “top 10 Downloaded Article” August 2015
8. Tsoi, S.; Ratchford, D. C.; Vurgaftman, I.; Pehrsson, P. E., Hybrid Si core-plasmonic shell nanopillar structures for efficient room temperature luminescence generation, Invention disclosure presented to IEB, [STRN: NRL/O/6170-17-106, Navy Case #108501] Sept. 20, 2018

9. RECOGNITION

1. Received the 2017 Alan Berman Basic Research Publication Award for Ratchford, et. al, *Nano Lett.*, **2017**, 17, 6047-6055
2. Dr. Ratchford was invited to write a Perspective article in *ACS Nano* describing his impressions of plasmon-mediated charge transfer processes

10. CONTRACTS

N/A

11. ADDITIONAL INFORMATION

N/A

12. KEYWORDS

Plasmonics Photocatalysis
Nano Nanowires
SERS Surface Enhancement

13. DUAL USE

The ultimate uses envisioned for the results of this research have obvious applications in both the DOD and civilian arenas. For example, power and energy are critical to both sectors, and the efficiency improvements anticipated from this work will be of direct benefit, as will improvements in semiconductor processing and sensor technologies. The potential transitions include solar fuels, organic remediation, and semiconductor processing, as well as related work in light detection and photovoltaics.

14. DOD SUBJECT CATEGORY

Non-Electrical Energy
Conversion
Physical Chemistry
Energy Storage

15. 6.1 BRP/6.2 DTAP

Chemistry