Center For Nanoscale Materials - Proposal #49346

Proposal Title: Scattering-mediated hot-electron transfer

Principal Investigator/Spokesperson

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Collaborators

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General Information

Contact Name: Stephen Gray

Selected Theme(s): Theory and Modeling
Field(s) of Research: Physics (not condensed matter physics), Chemistry (not materials chemistry), Optics
Funding Source(s): DOE, Office of Basic Energy Science
How many visits are needed to complete the experiment? 0.0
How many days per visit? 0.0
Timeframe for entire project in months? 12.0
Are you collaborating with CNM personnel in performing this work or experiment? No
Do you plan to perform this work or experiment with assistance from CNM personnel? No
Is it acceptable to disclose the scientific content of this proposal to CNM personnel prior to experimental approval? Yes
Have you contacted CNM scientific staff to discuss the feasibility of your proposal? Yes
Will the data collected be considered proprietary? No
How did you first hear about the applicability of CNM to your research?
Former Staff Member

Abstract

Light can be seen as a powerful and abundant reagent in chemistry, having both the ability to steer chemical transformations in desired directions, as well as to report back information on chemical structure and dynamics. The capacity to perform highly-efficient and cost-effective solar energy conversion, the ability to reliably and safely diagnose and treat complex diseases like cancer, and the ability to peer into the atomistic details of complex chemical systems can be advanced by the capability to precisely control the behavior of light on nanoscale and molecular dimensions. The fundamental ways in which matter interacts with light changes as one or more of the features of that matter approach the nanoscale (1e-9 m).
Nanostructured matter can have a profound impact on light, having the potential to confine it well beyond the diffraction limit, slow it down to speed much slower than the speed of light in a vacuum, and impart to it much more momentum than it would carry while propagating freely. Considerable effort has gone into developing new ways to detect, image, and control chemical

systems with ever greater precision by exploiting the various new ways in which light behaves when it interacts with nanostructured matter. We aim to advance a new approach for precisely controlling the interactions between visible light and chemical systems that we believe can open up opportunities for applications ranging from solar energy conversion to photodynamic therapy. This research proposes to study the fundamental properties of composite nanostructures made of two fundamental building blocks: large dielectric nanospheres decorated with small metal nanoparticles. We conjecture that these composite nanostructures can support a new phenomenon known as Scattering-Mediated Hot-Electron Transfer (SMHET) that opens up new opportunities to control the interaction between light and matter.

Description of Research

1. Describe the scientific or technical purpose and the importance of the proposed research.

The purpose of the proposed research is to elucidate a new mechanism of light-initiated energetic electron transfer that we believe open up new opportunities for enabling high-efficiency photocatalysis and solar energy conversion.

Light-initiated energetic electron transfer has attracted considerable attention as an emerging paradigm for photocatalysis and solar energy conversion, and involves a structure that can efficiently harvest solar photons and invest their energy into electronic motion. Subsequently, the energetic electrons excited on the harvesting structure deposit energy into nearby molecules, photovoltaic cells, or other energy-accepting materials. Noble metal nanoparticles, which support plasmon excitations (collective oscillations of conduction electrons driven by visible light), have been widely studied as materials to harvest visible photons and mediate energy transfer events. Recently, we have shown that composite nanostructures consisting of large dielectric nanostructures (e.g. silicon dioxide) decorated with small metal nanoparticles are capable of a unique mechanism of light-initiated energetic electron transfer that completely circumvents plasmon excitation. We conjecture that the nearfields created by scattering resonances in the large dielectric nanoparticle can directly excite energetic electrons on the metal nanoparticles, and that these energetic electrons can be transferred to accepting materials with high efficiency.

The proposed research aims to provide a quantum dynamical picture of the excitation and subsequent transfer of hot electrons within these composite nanostructures. Our work views the particular geometry and composition of the composite nanostructure as key ingredients in determining these dynamics because of the unique way in which the geometry and composition direct the evolution of incident optical fields in time and space. For example, a properly designed composite nanostructure can selectively harvest photons of a desired frequency and bandwidth from broad and diffuse light sources (e.g. solar radiation), and can shape these spectrally tailored fields in ways that direct their energy towards the small metal particles decorating the surface. We have demonstrated the ability to rationally design the absorption spectra of composite nanostructures using this paradigm, which we term scattering mediated absorption.

To execute our investigation, we will develop a multi-scale modeling methodology that uses classical electrodynamics to model the way in which the composite nanostructure shapes incident electromagnetic fields, and utilizes real-time-dependent electronic structure methods to model the way that these shaped electromagnetic fields drive the dynamics of energetic electrons in the small metal nanostructures that comprise components of the composite nanostructures. These studies will provide information about how the transfer of hot electrons from harvesting composite structure to acceptor structures occurs, and upon which properties it is dependent. It will yield a wealth of information about the dynamics of the energetic electrons themselves: the lifetime of their excitations, the quantity of energy they possess, and their pathways of relaxation and transfer.

This project will provide essential insight into dynamics of energetic electrons involved in light-initiated energy transfer events which has so far been missing in the field, both in the context of energetic electrons resulting from plasmon excitation and from the novel scattering-mediated mechanism we have recently described. We hypothesize that energetic electrons generated by scattering mediated absorption will have several advantages over those generated by plasmon excitation, namely longer lifetimes and greater selectivity in their energy distributions.

2. Describe and justify the relevance of the proposed research to nanoscience/nanotechnology.

One of the great promises of nanoscience and nanotechnology is the ability to precisely control optical energy and information flow at nanoscale dimensions. This level of control opens up new possibilities for controlling how light interacts with matter on the molecular scale, and can lead to significant advances in both fundamental and applied nanoscience. This level of control is accomplished by exploiting a variety of nanophotonics phenomena that occur when light interacts with nanostructured

matter. This work is of great relevance because it will provide a novel approach for studying the real-time dynamics of energetic carriers that are born from these phenomena, including plasmon excitation and scattering-mediated absorption. In the context of the class of composite nanostructures that we conjecture can enable scattering-mediated hot-electron transfer, our investigation will provide essential knowledge about the energetics and lifetimes of the hot-electrons, and will elucidate key distinguishing factors between scattering mediated hot electrons and their counterparts generated by plasmon excitation.

We hypothesize that energetic electrons generated by scattering mediated absorption will have several advantages over those generated by plasmon excitation, namely longer lifetimes and greater selectivity in their energy distributions. If true, the use of scattering mediated absorption could open up many new opportunities for highly efficient solar energy conversion and selective photochemistry. The theoretical results we will obtain will be crucial for helping us to assess the validity of this hypothesis.

3. Provide a justification for requesting CNM resources and the particular capabilities chosen, especially if you have similar instruments in your institution.

The use of the CNM high performance computing cluster (Carbon) and software resources will be critical to the success of this project. Time-domain simulation of the interaction between incident electromagnetic fields and the composite nanostructures is a key requirement for our modeling methodology. The investigation of the dynamics of energetic electrons driven by the unique fields scattered by the composite nanostructures depends upon accurate information about these scattered-fields in the time-domain. The finite-difference time-domain method, available through the Lumerical software on Carbon, represents a unique computational tool for obtaining the requisite time-domain scattered fields. Due to the multi-scale nature of the composite nanostructures we will study, these calculations must be done in a highly parallel environment using efficient software. The composite nanostructures are large in totality (several microns in diameter), and the smallest features (the small decorating metal nanoparticles) are on the order of 5 nanometers. In order to accurately capture the behavior of the electromagnetic fields, spatial grids smaller than the smallest feature size are required. Furthermore, the spectrally-selective scattering resonances that give rise to the scattering-mediated absorption behavior we are interested are long-lived phenomena, so long simulation times will be required. The combination of large structures with small features and long simulation times will lead to simulations that are both CPU and memory intensive. In order to perform systematic investigations of this system, substantial cumulative time and storage will be required. These requirements will significantly exceed those of our local computational resources at William Paterson University, but will be within the resources available on Carbon.

4. Describe your samples and procedures, and explain the basis for the time request(s).

We will study composite nanostructures that consist of two fundamental building blocks: a large dielectric nanosphere (dielectric core), and small metal nanoparticles that decorate (or reside just below) the surface of the dielectric nanosphere (see Figure 1 in ancillary file). The size of the dielectric nanosphere, and its specific composition (via its dielectric constant) are critical parameters for determining the resonant scattering properties of the composite nanostructure, and these resonant scattering properties in turn dictate the scattering-mediated absorption behavior of the composite. That is, the large dielectric nanospheres on their own have distinct scattering spectra and can have many scattering peaks across the visible spectrum, however the large dielectric nanosphere does not absorb visible light. The small metal nanospheres on their own scatter light very weakly, and may not have any visible absorption peaks in the visible spectrum.

The resonant absorption in the composite structures had been observed to closely mimics the resonant scattering behavior of the large dielectric nanostructure (see Figure 2 in ancillary file). We will vary the size of the dielectric nanospheres and the composition of the small metal nanoparticles. The latter parameter will modulate the scattering spectrum, and the former will determine the extent to which the absorption behavior of the composite is driven by the dielectric scattering spectrum alone.

We will consider a variety of scenarios in our calculations to elucidate the impact of the size of the dielectric nanosphere and the composition of the small metal nanoparticles on the resulting dynamics of the hot electrons derived from scattering-mediated absorption. We will perform calculations with metals that support plasmon resonance at visible wavelengths (e.g. silver and gold), as well as metals that do not support visible plasmons (e.g. iron and platinum). We will consider a variety of environments in which to embed or support the small metal nanoparticles, including large (>500 nm) dielectric nanoshperes which support high quality-factor visible scattering resonances known as whispering gallery modes, moderate (200-500 nm) dielectric nanospheres which support lower quality-factor visible scattering resonances known as Fabry-Perot modes, and continuous dielectric substrates which do not support scattering resonances.

Computational work performed through a previous CNM proposal (#44191) showed that fundamentally new photophysics can emerge from the interaction between distinct optical resonances in composite nanostructures we have described in this proposal. Lumerical calculations on these systems typically required between 5,000 and 10,000 CPU hours, and data storage for the results typically required 40 GB.

It was also experimentally demonstrated that the emergent photophysics can be leveraged for solar-to-chemical energy conversion. In particular, scattering resonances excited on large dielectric nanoparticles can mediate spectrally selective absorption events on small metal nanoparticles that decorate the surface of the dielectric nanostructure, which was termed “scattering-mediated absorption”. For example, this phenomenon was leveraged to induce strong resonant absorption of visible light by small platinum nanoparticles decorating the surface of large SiO2 nanospheres, whereas small colloidal platinum nanoparticles alone show no resonant visible absorption.

Our goal for the proposed work is to investigate the conjecture that the intense nearfields generated by ścattering resonances can drive energetic electron transfer events between metals and adsorbate molecules. Our work views the particular geometry and composition of the composite nanostructure as key ingredients in determining the dynamics of these transfer events because of the unique way in which the geometry and composition direct the evolution of incident optical fields in time and space. The requested allotment of resources on Carbon will enable us to perform a preliminary exploration of this vast parameter space of geometries and compositions.

Our procedures include the use of the Lumerical software, which will be used to compute the time-dependent electric field resulting from the interaction between a simulated solar spectrum and the composite nanostructures. We will use the time-dependent electric fields in our home-built code for evolving the metal nanoparticle electronic structure in a time-dependent configuration-interaction singles methodology performed within a suitably-chosen space of active orbitals to allow us to elucidate the dynamics of hot electrons excited by scattering-mediated absorption.

5. Describe all of the participants' previous experience relevant to the proposed research AND any preliminary research results obtained.

Prof. Jonathan Foley, PI on this proposal, has considerable experience developing and using theoretical methods to study light-matter interactions in nanostructured and molecular systems. He also has considerable experience using the high performance computing facilities and electrodynamics software resources available at the CNM: he has utilized these resources will working as a postdoctoral fellow in the CNM’s theory and modeling group, and also as a user (proposal #44191) where he conducted theory and modeling work investigating composite nanostructures that resulted in a publication in Nature Photonics.

Noor Eldabagh holds a B.S. in Biology and a minor in Chemistry from William Paterson University (WPU). She has been using theoretical and computational methods to investigate novel optical phenomena in a variety of different composite nanostructured systems. She has contributed to a book chapter on the nanophotonics of composite nanostructures that has been accepted for publication in a volume on Novel Nanoscale Hybrids by Wiley.

Jason Codrington is senior Chemistry major at WPU who has been working to elucidate the mechanism of scattering mediated absorption in composite nanostructures, in conjuction with work performed by the PI on proposal #44191. Jason was also a co-authored on the recent paper in Nature Photonics that resulted from proposal #44191.

Kimberly Fernando is a senior chemistry major at WPU who has been working to develop a real time-dependent configuration-interaction singles code for modeling hot-electron dynamics in metal nanoparticles.

6. Describe briefly the outcome of prior allocated proposals to the CNM that are not included above. This is mandatory if this proposal is a continuation of a previous CNM proposal. Include:

a. The previous proposal number(s).

b. Restate the purpose.
c. Briefly summarize the results and the role that CNM played.
d. Provide a list of your publications and presentations that contain data obtained from using the CNM.

a. The previous Proposal Number: 44191

b. The purpose of the proposal was to elucidate the photophysics of a class of hierarchical nanoparticles that showed exceptional promise for mediating photocatalytic reactions under simulated solar illumination.

c. Using the computing resources and electrodynamics software provided by the CNM, we were able to perform detailed investigation into the optical response of the hierarchical nanostructures of interest, particularly investigating the impact of various geometrical parameters on the optical properties. Based on these investigations, we developed a simplified model with predictive power that has helped to elucidate part of the underlying mechanism of photocatalysis, and may help us to optimize the resonant properties of these structures. The use of the computing resources and electrodynamic software provided by the CNM was also critical in allowing us to perform the large number of calculations required to validate our simplified model of the hierarchical nanostructures. We have published a paper in Nature Photonics based on these results and these model, as well as experimental results obtained by our collaborators.

d. Provide a list of publications and presentations that contained data obtained from using the CNM

i. Publication (investigators on this proposals in bold): N. Zhang, C. Han, Y.-H. Xu, J. J. Foley IV, D. Zhang, J. Codrington, S. K. Gray, Y. Sun, Nature Photonics, “Near-field dielectric scattering promotes optical absorption by platinum nanoparticles”, 2016, 10, 473-482

ii. Presentations:

a. Invited seminar at Middle-Atlantic Regional Meeting of the American Chemical Society, June 16, 2016, “Scattering Mediated Hot-Electron Transfer: A new paradigm for photocatalysis”, J. J. Foley IV
b. Nanoscience Poster Session at Middle-Atlantic Regional Meeting of the American Chemical Society, June 16, 2016, “ Leveraging Whispering Gallery Modes for Scattering Mediated Absorption “, N. Eldabagh
c. Nanoscience Poster Session at Middle-Atlantic Regional Meeting of the American Chemical Society, June 16, 2016, “Insert Title”, J. Codrington
d. 10th Annual Undergraduate Research Symposium, William Paterson University, April 9th 2016, “Scattering Mediated Hot Electron Transfer”, N. Eldabagh, J. Codrington

7. References, including relevant publications (Max 2000 characters)

[1] N. Zhang, C. Han, Y.-J. Xu, J. J. Foley IV, D. Zhang, J. Codrington, S. K. Gray, Y. Sun, “Near-field dielectric scattering promotes optical absorption by platinum nanoparticles”, Nature Photonics, 2016, 10, 473-482.
[2] H. A. Atwater, A. Polman. “Plasmonics for improved photovoltaic devices, Nat. Mater., 2010, 9, 205
[3] J. R. Cole, N. J. Halas, Optimized plasmonic nanoparticle distributions for solar spectrum harvesting”, Appl. Phys. Lett., 2006, 89, 153120
[4] B, O’Regan, M. Grätzel, “A low-cost, high-efficiency solar cell based on dye-sensizited colloidal TiO2 films”, Nature, 1991, 353, 737
[5] J. Huang, O. Buyukcakir, M. W. Mara, A. Coskun, N. M. Dimitrijevic, G. Barin, O. Kokhan, A. B. Stickrath, R. Ruppert, D. M. Tiede, J. F. Stoddart, J.-P. Sauvage, L. X. Chen, “Highly efficient ultrafast electron injection from the single MLCT excited state of Copper(I) Diimine complexes to TiO2 nanoparticles”, Angew. Chem. Int. Ed, 2012, 51, 12711

[6] J. J. Foley IV, C. Ungaro, K. Sun, M. C. Gupta, S. K. Gray, “Design of emitter structures based on resonant perfect absorption for thermophotovoltaic applications”, Opt. Express, 2015, 23, A1373
[7] S. Lal, S. E. Clare, N. J. Halas, “Nanoshell-enabled photothermal cancer therapy: impending clinical impact”, Acc. Chem. Res., 2008, 41, 1842

[8] X. Huang, M. A. El-Sayed, “Plasmonic photo-thermal therapy (PPTT)”, Alexandria J. Med., 2011, 47, 1
[9] D. K. Chatterjee, L. S. Fong, Y. Zhang, “Nanoparticles in photodynamic therapy: an emerging paradigm”, Adv. Drug. Deliv. Rev., 2008, 60, 1627
[10] L. Schermelleh, R. Heintzmann, H. Leonhardt,, “A guide to super-resolution fluorescence microscopy”, J. Cell. Bio., 2010, 190, 165
[11] H. K. Hunt, A. M. Armani, “Label-free biological and chemical sensors”, Nanoscale, 2010, 2, 1544

Capabilities and Usage

Theory and Modeling

- CNM High Performance Computing Cluster (Carbon)
  - Total compute time requested (a value between 50,000 and 500,000 processor hours is typical): 325000
  - List Computer Codes to be used that are EXTERNAL to CNM and parallelization capabilities: Lumerical
  - Standard packages, compilers and libraries required: Lumerical
  - Typical number of processors per job (Note: each node has 8 processors): 256
  - Typical memory per compute node: 10 GB
  - Typical real-world time per job (hours): 80
  - Total storage capacity per job: 60 GB
  - For real-time analysis of experimental data provide description of or reference to experimental part, bandwidth requirement for storage and processing, and charateristics for realtime processing (where applicable): N/A
  - Expected number of production jobs: 15
  - Total persistent disk space required for project (GB): 600
- Computational Nanoscience Software
  - Will this be used on a computing facility external to CNM ?:
    No
  - MPI-based parallel versions of the nanophotonics
    - Will this be used on a computing facility external to CNM ?:
      No
  - Time-domain nanophotonics simulation package
    - Will this be used on a computing facility external to CNM ?:
      No

Safety

Will the proposed activity involve the use of carcinogens, mutagens, or reproductive hazards at the Argonne facility?
No

Will the proposed activity involve the use of biohazards at the Argonne facility?
No

Will the proposed activity involve the use of human tissue/materials/cells at the Argonne facility?
No

Will the proposed activity require the transport of USDOT Select Etiological Agents to the Argonne facility?
No

Will the proposed activity involve the use, characterization, or other handling of radioactive materials at the Argonne facility?
No

Will the proposed activity require the use of user-supplied equipment at the Argonne facility?
No

Will the proposed activity involve significant hazards (at the Argonne facility) that are not identified above?
No

Attachments

FIGS.pdf

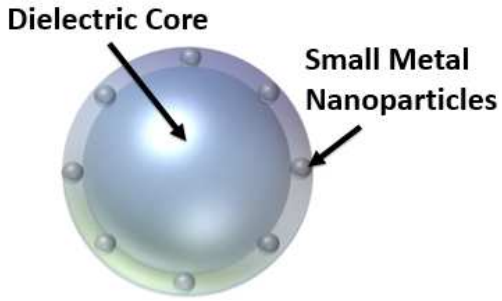

Figure 1: Schematic of composite nanostructures with a large dielectric core decorated with small metal nanoparticles.

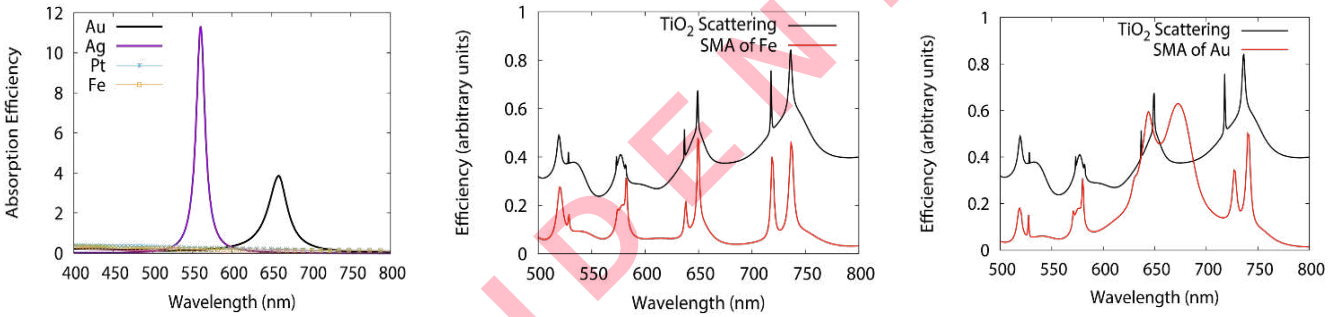

Figure 1: Illustration of absorption spectra of small metal nanoparticles embedded in a continuous titanium dioxide (TiO_2) background (left) compared to the absorption spectra of composite nanostructures where a 808 nm titanium dioxide nanosphere is decorated with small iron nanoparticles (center) and small gold nanoparticles (right). The scattering spectrum of the 808 nm TiO_2 sphere is superimposed on the absorption spectra of the composite structures, illustrating the way in which the composite nanostructure's absorption mimics the dielectric scattering spectrum in the Scattering Mediated Absorption mechanism.