# Laboratory Directed Research and Development

**Proposal Title:** In-situ Single Particle Plasmon Catalysis

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<td><strong>Proposal Term</strong></td>
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<td>Extension of LDRD from 2011-2012 on “High frequency magnetic metamaterials for tunable light harvesting and emission”</td>
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Abstract

We propose to explore energy-relevant catalytic processes – particularly photocatalytic water splitting – on single nanoparticles using in-situ microscopy and spectroscopy. Our goal is to understand the interplay of photocatalyst structure and function, in order to improve catalytic efficiencies.

Summary of Proposal

Description of Project

Designing an efficient photocatalytic system requires careful consideration of the optical, electronic, and kinetic aspects of redox reactions. These aspects have been challenging to control in ensemble measurements, where photocatalyst heterogeneity conceals many important and interesting structure-dependent catalytic properties. For example, the photocatalyst dimensions, surface structure, and the catalyst-support interface could all have profound consequences for catalytic activities. Accordingly, there is significant reason to explore photocatalytic reactions on single particles, in-situ and in real time. This proposal will explore structure-function relations in water-splitting catalysts by studying photocatalytic reactions on a single nanoparticle. Attention will be given to developing optical and electronic probes of photocatalytic activity that can readily monitor single-particle redox reactions, with the potential for single-electron precision. We will initially focus on hydrogen evolution from photoreduction of water, as probed using plasmonics. We will synthesize Ag-core, TiO₂ shell nanoparticles that are catalytically active under ultraviolet illumination. Both optical and electronic spectroscopy will be used to detect shifts in the plasmon resonances of these particles, which can serve as direct probes of charge transfer during catalysis. Our investigation of these novel catalytic materials will use the facilities in Stanford’s NanoCenter and in the SIMES research labs at SLAC.
Expected Results

This project will address two outstanding questions in photocatalysis:

1) What are the quantum-optical and quantum-electronic properties of catalytically-active nanomaterials? Most efficient catalysts have dimensions between 1 and 20 nm – bridging classical and quantum realms. In this meso-scale, the optical and electronic properties of catalysts are poorly understood. Our spectroscopic techniques will provide direct insight into these properties.

2) What is the role of nanoparticle geometry, surface-structure, and substrate on catalytic activity? By focusing on single-particle measurements, our experiments will disentangle structure-dependent catalytic processes.

Ultimately, our project will enable development of new and optimized catalyst geometries for renewable energy generation and storage.

Proposal Narrative

Purpose/Goals

The goal of this proposal is to explore structure-function relations in water-splitting catalysts by studying photocatalytic reactions on a single nanoparticle. Attention will be given to hydrogen evolution from photo-reduction of water, as probed using plasmonics. Both optical and electron spectroscopy will be used to probe shifts in the nanoparticle’s plasmon resonance during catalysis, which can give direct insight into charge transfer during redox reactions. This proposal is well-aligned with the DOE’s mission to “develop and explore a broad spectrum of new materials that have novel properties, such as catalysis, electrothermal behavior, radiation resistance or strength or otherwise contribute to the advancement of energy technologies by 2020.”

Approach/Methods

The plasmon resonances of metallic nanoparticles will be exploited to probe catalysis. In metallic nanoparticles, an incident electromagnetic wave can couple to the free conduction electrons of the metal, exciting a localized surface plasmon. As seen in Figure 1, surface plasmons give rise to strong scattering and absorption of light at frequencies that depend on the size, shape, and charge of the nanoparticle as well as on the dielectric properties of the metal and the surrounding medium. For the most commonly used plasmonic metals (Ag and Au), resonances occur near visible frequencies and are therefore easily
detectable with standard optical or electronic spectroscopy techniques. Further, the strong localization of the electromagnetic radiation near the metal nanoparticle surface gives rise to local high field intensities.

As a model nanoparticle photocatalytic system, we will consider a Ag nanoparticle core functionalized with a light-absorbing TiO₂ shell. We will prepare highly dispersed Ag@TiO₂ core-shell nanostructures using colloidal synthesis and study their catalytic efficiency *in-situ* by both dark-field optical microscopy and electron microscopy at the single particle level. As seen in Figure 1, the function of the Ag core is three-fold. First, it provides a direct probe of the number of photogenerated electrons, since its plasmon resonance depends sensitively on the number of electrons in the Ag. Second, as recently demonstrated by our ensemble measurements, the Ag serves as a reservoir for photo-generated electrons. Therefore, it could prevent electron-hole recombination prior to catalysis. Third, via plasmon resonances, it could enhance the absorption cross-section of the photocatalytic particle, locally concentrating light onto the catalyst and improving catalytic activity.

**Optical spectroscopic probes of photocatalysis:**
We will explore 10-20 nm diameter Ag@TiO₂ nanoparticle photocatalysts using optical spectroscopy. As a first experiment, we will study the photocatalytic properties of individual Ag@TiO₂ structures under ultraviolet illumination. Upon irradiation, electron-hole pairs are generated in the TiO₂. The conduction band alignment of Ag and TiO₂ enables fast transfer of the photogenerated electron into the Ag,³⁴ which results in a blue-shift of the Ag plasmon resonance. Dark-field microscopy will be used to study this plasmon resonance shift of individual nanoparticles during catalysis. The particles will be dispersed in a home-built quartz flow cell that allows both UV transmission and a steady flow of solvent (ethanol), used as electron donor. Subsequently, the surface of the Ag@TiO₂ shell will be functionalized with a commercially available dye (N3 dye, the ruthenium complex cis-RuL₂(NCS)₂) to extend the absorptance of the nanoparticles into the visible, past 600 nm.

Our single-particle optical spectroscopy will be correlated with electron microscopy measurements of particle structure, including scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM). This approach will unveil the structure-function correlations that are usually
Figure 1: Localized surface plasmon resonance (LSPR) spectroscopy can monitor catalytic reactions on individual particles in situ. As seen in (a) and (b), small noble-metal nanoparticles can locally enhance electric fields and are extremely sensitive to charge transfer. Ag nanoparticles coated with a photosensitive shell (TiO₂) exhibit a strong blue-shift in their plasmon resonance, indicative of electrons added to the Ag core during catalytic redox reactions (c).

blurred in an ensemble measurement and give unprecedented insight into the effects of nanoparticle shape, size, and interface on the photocatalytic properties of the core-shell structures. Via these single-particle studies, we aim to clarify the charge transfer processes occurring at or near the surface of a TiO₂-based water-splitting photocatalyst.

In-situ electron spectroscopic probes of photocatalysis:
We will explore sub 10-nm Ag-core nanoparticle catalysts using in-situ TEM and electron energy loss spectroscopy. Unlike larger particles, these smaller particles only weakly scatter light, making them difficult to experimentally observe with single particle optical techniques. In fact, for the past four decades, there has been substantial debate over the plasmonic properties of these small particles.

Recently, we have disentangled the competing effects of quantum confinement and surface scattering of plasmon resonances in catalytically-active nanoparticles, as small as 1 nm in diameter. Using electron energy loss spectroscopy (EELS), we experimentally collected individual nanoparticle plasmon resonances while imaging them with atomic-scale resolution. This study allowed the first comprehensive understanding of the quantum plasmon modes of individual noble-metal nanoparticles. In this proposal, we will explore catalysis with quantum-confined Ag core, TiO₂-shell nanoparticles using in-situ, liquid-cell TEM EELS. This approach will allow us to simultaneously observe and spectrally analyze catalytic reactions in their native environment.
Specific Location of Work

Synthesis and characterization will be performed in SIMES (nanoparticle synthesis), at Stanford in the Durand Building, Room 190 (optical characterization), and in the Stanford Nano Center (electron beam excitation and characterization using a combination of EELS, nanodiffraction, holography, and tomography).

Anticipated Outcomes/Results

This proposal will result in new, fundamental understanding of nanoparticle photocatalysts for solar-fuel generation. By investigating the plasmon resonances of individual the metal-core, semiconducting-shell nanoparticles, we will identify the unique quantum-optical and quantum-electronic properties of catalytically-active nanomaterials. Our results will highlight the role of nanoparticle geometry, surface-structure, and substrate on catalytic activity. Ultimately, this LDRD will enable development of new and optimized catalyst geometries for renewable energy generation and storage.

References

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Education and Training
2009-2010: Postdoctoral Fellow, University of CA, Berkeley and Lawrence Berkeley National Labs
2009: Ph.D., Applied Physics, California Institute of Technology, Pasadena, California
2005: M.S., Applied Physics, California Institute of Technology, Pasadena, California
2003: B.S., Physics, Washington University in St. Louis, St. Louis, Missouri
2003: B.S., Systems & Electrical Engineering, 2003, Washington University in St. Louis, St. Louis, Missouri

Major Honors and Awards
Stanford:
NSF CAREER Award, 2012
Technology Review TR35, 2011
Hellman Faculty Scholar, 2011
Air Force Office of Scientific Research Young Investigator Grant, 2010
Frederick E. Terman Fellow, Stanford University, 2010-2014
Robert N. Noyce Family Faculty Fellow, Stanford University, 2010-2014
Caltech:
Materials Research Society Gold Award, 2008
Everhart Lecturer, Caltech, 2008
Kavli Nanoscience Institute Graduate Award Winner, 2005
National Science Foundation Graduate Research Fellow, 2007-2009
WashU:
Outstanding Young Alumni Award, 2012
The Tau Beta Pi outstanding student award, 2003
The Systems & Electrical Engineering outstanding student award, 2003
The ODK outstanding student award for campus and community service
Research and Professional Experience

- **Stanford University, Assistant Professor of Materials Science and Affiliate Faculty of the Precourt Institute for Energy (2010 - present)**
  Principal Investigator of a team of 7 Ph.D. students and 3 postdoctoral fellows interested in exploring the fundamental electrodynamic properties of metamaterials and their applications to bioimaging and solar energy harvesting. Professor for "Materials Chemistry" and "Electronic Materials Engineering"

- **University of CA, Berkeley and Lawrence Berkeley National Labs (2009-2010)**
  Postdoctoral fellow in the laboratory of Professor Paul Alivisatos, investigating the optical and electronic properties of single nanoparticle hydrogen-evolving photocatalysts.

- **California Institute of Technology (2003-2009)**
  Graduate student in the laboratory of Professor Harry Atwater, investigating passive and active plasmonic devices, including negative refractive index materials and subwavelength plasmonic modulators.

Selected Publications, Patents, and Press

- 2 patents on plasmonic modulators and color displays, 1 pending on upconverting electrodes
- 17 journal publications with over 1100 combined citations; 1 book chapter
- Five selected publications:
**Synergistic Activities**

- Chair or Co-chair, Materials Research Society Symposium “Plasmonic Materials & Metamaterials,” Spring 2012 and Spring 2010
- Guest Editor, Materials Research Society Bulletin on Plasmonics (to be published, August 2012)
- Lawrence Berkeley National Lab Molecular Foundry Executive Committee (2012-present)
- New Student Orientation *Engaging with Faculty* lecture: “Global Challenges, Nanoscale Solutions” (2011)
- Pre-major advisor to Stanford freshman and sophomores, 2010-present
- Elementary and middle-school outreach aimed at solar-energy education at the Bay Area science Festival (2011) and through “Chemistry in the Classroom” and Career Day Outreach
- More than 50 invited talks and contributed presentations at conferences and workshops

**Budget Explanation**

The budget includes 7.5% effort for the PI, Jennifer Dionne and 62.5% effort for graduate student Jonathan Scholl. Materials and services, and user fees for shared facilities, are expected to cost $25k per year. The total cost in year one, including SLAC indirects would be $147k, and $146k in year two.

**Approvals**

Stephanie Carlson, Acting Business Manager, PSD

Tom Devereaux, Director, SIMES

Cynthia Friend, ALD, Photon Science