

# Investigations of Multi-Metallic Nanocatalysts for Promoting Plasmon-Augmented Chemical Energy Conversion

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## Abstract

*Plasmonically-sensitized nanocatalysts were investigated for their photocatalytic and photo-electrochemical oxidation of ethanol (EtOH), with an emphasis on breaking the carbon-carbon bond, under solar simulated-light. Material approaches included the (i) surface plasmon resonance (SPR)-functionalization of a traditional metal oxide semiconductor and (ii) bimetallic nanocatalysts composed of noble metals. Results are correlated with nanocatalyst morphology, composition, and homogeneity to maintain plasmon-induced light absorption, enhance the photo-oxidation of EtOH, and mitigate poisoning of the catalyst. Photo-electrochemical measurements were complimented with single-particle spectroscopic measurements to understand the energy conversion pathways for the extraction and utilization of SPR-excited "hot" carriers. EtOH oxidation was achieved, yielding a light-enhanced method for low temperature, complete photo-oxidation of high specific energy hydrocarbon fuels. Further, we have constructed in situ liquid phase transmission electron microscopy (LP-TEM) experiments to study the reduction of a secondary metal onto gold nanorods (AuNRs) under plasmonic excitation to visualize single particle-level processes in solution in real time.*

## Keywords

Energy conversion; light-matter interactions; plasmon resonance; nanoscale; catalysis; microscopy

## Introduction

Light stimulated localized surface plasmon resonance (LSPR) in metallic nanomaterials can promote the excitation of energetic, or "hot", charge carriers that can be locally transferred or thermally dissipated to augment energy conversion processes.<sup>1, 2</sup> Selectively driving energy-intensive industrial scale catalytic reactions at low-temperatures can be enabled at the nanoscale by locally activating adsorbed reactants and accelerating surface kinetics.<sup>1-3</sup> Excitation of surface plasmons further amplifies local electric fields, enhances far-field light scattering, increases the absorption cross section, and produces local

thermal gradients.<sup>1, 2</sup> In addition to initiating energy conversion chemical reactions, plasmonic energetic hot carriers can catalyze growth of secondary metals on the surface of plasmonic nanostructures using surface-adsorbed metal salt precursors.<sup>4-8</sup> Plasmonic photodeposition enables targeted nucleation/growth of secondary metals at specific active surface sites, such as the controlled deposition of catalytic metals (e.g., Pd or Pt) on the ends of AuNRs.<sup>5-8</sup> Gold nanoparticles (AuNPs) are excellent model systems as they exhibit highly tunable particle characteristics (i.e., size and morphology) and LSPR-induced optical properties across the electromagnetic spectrum.<sup>1-4, 9</sup> Controlled assembly of multi-metallic plasmonic nanostructures driven by LSPR excitation can couple plasmonic absorbers with co-catalysts. Hybrid plasmonic nanomaterials can be utilized to photosensitize substrates and to provide increased photocatalytic activity *via* hot carriers and localized photothermal heating.<sup>1-3, 5-8, 10, 11</sup>

Plasmonic nanoparticles (NPs) hold promise for several important technological areas, such as information encryption, chemical catalysis, novel manufacturing methods, energy scavenging, theranostics (therapeutics and diagnostics), optical/optoelectronic materials, and uncooled infrared photodetectors. The realization of plasmonics for new technologies necessitates advances in the design and optimization of plasmonic materials, morphologies, synthesis techniques, and spectroscopies with enhanced spatiotemporal resolution to better understand the dynamic behavior of plasmonic hot carriers.<sup>12</sup> Hot carriers and photothermal heating are of significant interest in the catalysis field due to their potential ability to drive chemical reactions, such as catalytic conversion of organic molecules into chemical fuels.<sup>3, 10, 11, 13</sup> Current approaches for measuring these two phenomena utilize ensemble averaged characterization techniques. The relative ratio of the electron decay *via* hot electron generation and thermal dissipation is determined by the NP size, shape, composition, and local environment.<sup>1, 2</sup> There remains a lack of experimental observations of hot electron generation and photothermal heating on single plasmonic NPs. Poor understanding of

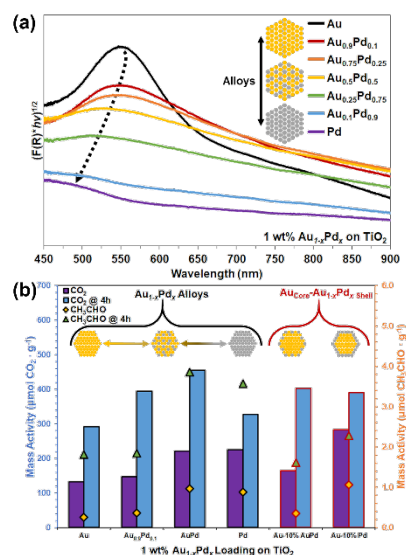
these two phenomena has limited their application.

Our work has focused on using light to drive energy-intensive photochemical reactions at low temperatures by investigating the ability of plasmonic nanocatalysts to drive the ethanol oxidation reaction (EOR) at plasmonic interfaces. Liquid hydrocarbons are of interest as a fuel source because they have high gravimetric and volumetric energy, are easy to store, and to transport. In our work we utilize EtOH oxidation as the model hydrocarbon reaction. Current challenges associated with using hydrocarbons as fuels are that its energetically unfavorable to cleave the carbon-carbon (C-C) bond, the C-C bond cleavage rate is negligible at ambient conditions, and incomplete oxidation typically yields intermediates, like acetaldehyde ( $\text{CH}_3\text{CHO}$ ), with only 4 out of 12 electrons extracted from EtOH.<sup>5, 13, 14</sup> Current materials suffer from low activity and a strong tendency towards adsorbed intermediates, leading to catalyst poisoning. Therefore, high temperatures are typically needed to drive the EOR thermo-electrochemically.

### Plasmonic Interfaces for Ethanol Oxidation

The activity for the EOR was compared using plasmonic Au nanospheres and nanorods coupled to titanium dioxide ( $\text{TiO}_2$ ).<sup>3</sup> Plasmonic contributions to the EtOH oxidation process were distinguished by targeting the excitation of high energy interband transitions and low energy intraband transitions. Higher energy interband transitions (<600 nm) correspond to the transverse SPR, which we found enabled the oxidation of formic acid and single-carbon intermediates to carbon dioxide ( $\text{CO}_2$ ). Lower energy intraband transitions (>600 nm) for the longitudinal SPR in the AuNRs facilitated (1) desorbing intermediates and (2) breaking the C-C bond. Plasmon resonance enhanced C-C bond cleavage and complete EtOH oxidation to  $\text{CO}_2$  by generating hot carriers and local heating.<sup>3</sup> However, Au alone is not a sufficient catalyst for EtOH oxidation, and a secondary catalytic metal is necessary to efficiently drive EOR.

In a second study, we explored a combination of Au, a plasmonic antenna, with palladium (Pd), an active EOR catalyst that suffers from poisoning effects from carbon monoxide.<sup>10</sup> We systematically varied the composition and structure (alloy vs core-shell) of Au-Pd and studied their ability to improve EtOH oxidation activity and inhibit the poisoning of Pd. The compositional range was developed for colloidal NPs from pure Au to pure Pd for homogenous alloys. Microscopy and elemental mapping showed that the nanospheres maintain their morphology and composition after loading onto  $\text{TiO}_2$ . Ultraviolet-visible (UV-Vis) spectra (Fig. 1a) show that as the composition was altered from Au-rich to Pd-rich, the SPR was significantly dampened and the maximum absorbance of the SPR peak was shifted to lower wavelengths as more Pd is incorporated. Core-shell NPs were synthesized with a Au core and a thin AuPd or Pd shell, and were embedded on a  $\text{TiO}_2$  support. In contrast to the alloys, the AuPd core-shell NPs retained a strong plasmon resonance with little dampening owing to maintaining a sub-2 nm shell.<sup>10</sup>

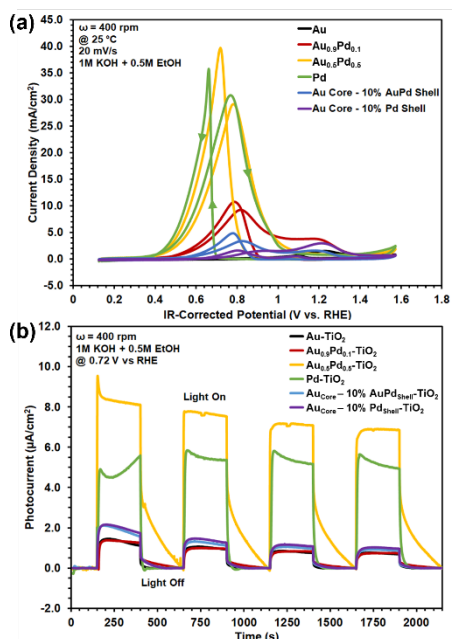


**Figure 1.** (a) UV-Vis spectra of 1 weight (wt. %) AuPd alloy NPs on  $\text{TiO}_2$ . (b) Photo-oxidation of EtOH to  $\text{CO}_2$  and/or  $\text{CH}_3\text{CHO}$  for AuPd alloy and core-shell NPs on  $\text{TiO}_2$  under irradiation.  $\text{CO}_2$  is plotted on the left axis with purple (1 h) and blue (4 h) bars.  $\text{CH}_3\text{CHO}$  is plotted on the right axis with orange diamond (1 h) and green triangle (4 h) markers.

A series of AuPd alloy and core-shell NPs loaded on  $\text{TiO}_2$  supports were suspended and irradiated in solution with solar simulated light (AM1.5G), the gaseous products were measured by gas chromatography mass spectrometry. Photocatalytic measurements (Fig. 1b) were performed to probe the catalysts' structure and composition to optimize and improve plasmonic enhancement of the EOR. Mass activity for 1h shows that the production of acetaldehyde (orange markers) and  $\text{CO}_2$  (purple bars), from complete EtOH oxidation, for AuPd alloys increased with increasing Pd concentration until about 50% Pd, where the activity leveled off. Core-shell NPs with a 10% Pd shell exhibited the highest activity overall. Catalysts that were irradiated for longer periods (4h) showed a linear increase in acetaldehyde (green markers) production over time, while  $\text{CO}_2$  (blue bars) production slowed for some compositions. The 1:1 AuPd alloy exhibited the highest overall rate of complete EtOH oxidation to  $\text{CO}_2$  and partial oxidation to the acetaldehyde intermediate. Pure Au and Pd showed the lowest rates of long-term oxidation of EtOH to  $\text{CO}_2$ . Alloy ( $\text{Au}_{0.9}\text{Pd}_{0.1}$ ) and core-shell NPs with 10% Pd concentration exhibited similar prolonged activity with improved selectivity towards complete EtOH oxidation, as shown by the lower rates of acetaldehyde formation in comparison to AuPd and Pd. Therefore, EtOH photo-oxidation activity was improved by combining a plasmonic antenna and a catalytic metal reactor with the appropriate composition and structure.<sup>10</sup>

Plasmonic AuPd alloys and core-shell NPs were studied using rotating disk electrochemistry (RDE) methods. Working electrodes were 20 wt.% AuPd NPs loaded on conductive carbon supports with a Nafion binder onto a glassy carbon disk. Cyclic voltammetry (CV) measurements (Fig. 2a) generate EOR current by scanning anodically up to

+1.5 V, which coincided with an oxide layer formation on the metal NPs. Peak anodic current is followed by a current drop due to passivation of the electrode. Coverage of the active sites and competition with oxide forming species results in this passivation. Cathodically sweeping the potential from +1.5 V to +0.1 V, reduced the oxide species and EtOH oxidation resumed. The 1:1 AuPd alloy exhibited the highest EOR activity, comparable to pure Pd. In contrast, pure Au, alloyed AuPd with low Pd composition, and core-shell NPs exhibited poor electrochemical EOR activity.<sup>10</sup>

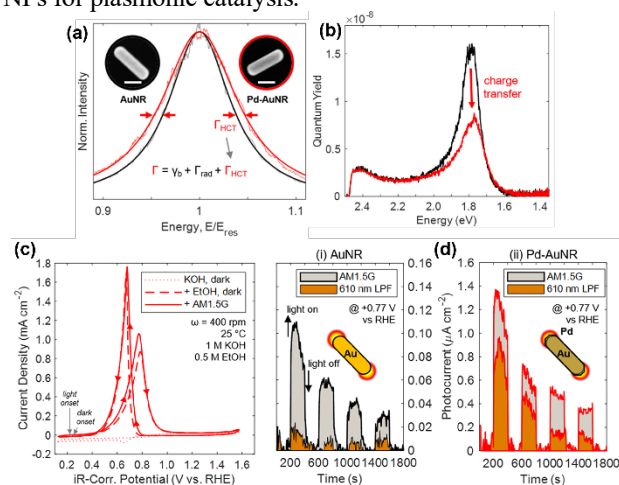


**Figure 2.** (a) Electrochemical CVs using 20 wt.% AuPd alloy and core-shell NPs on carbon. (b) Photoelectrochemical CAs using 1 wt.% AuPd alloy and core-shell NPs on TiO<sub>2</sub>, held at +0.72 V under 250s on/off chopped light, baseline (i.e., 0 μA cm<sup>-2</sup>) is the dark current. Nanocatalysts deposited onto a rotating disk, glassy carbon working electrode. Reference (Ag/AgCl) and counter (Pt) electrodes used in 0.5 M EtOH with 1 M KOH electrolyte.

Photo-electrochemical studies were performed with 1 wt.% plasmonic NPs on TiO<sub>2</sub> with chronoamperometric (CA) measurements (Fig. 2b) with chopped solar simulated light. Light-induced current (photocurrent) density (mA/cm<sup>2</sup>) for each electrode was measured over 2000+ s. Low photocurrent with a 40-53% retention over 2000s was observed for Au-rich compositions. In contrast, Pd is a good EOR catalyst that improves charge separation and transfer, with an 84% photocurrent retention over 2000s. The 1:1 AuPd alloy exhibited the highest prolonged photocurrent activity with 72% retention, which was postulated to be due to injection of hot carriers from Au to Pd active sites, outperforming the EOR activity of pure Au and Pd, as well as other alloy, and core-shell compositions.<sup>10</sup>

Subsequently we investigated using SPR excitation to transfer hot carriers to facilitate the deposition of secondary catalytic metals on anisotropic nanostructures.<sup>13</sup> Gold nanorods (AuNRs) provide a method to target the reductive

photodeposition at specific sites at ambient conditions for growth by either interacting with hot carriers or heat dissipated from the metal lattice. We focused on targeting Pd via metal salt reactants due to their well-understood chemistry. The photo-chemical deposition method was tailored to grow a sub-2 nm Pd shell absent of lattice defects via hot carriers generated from longitudinal SPR excitation in the presence of [PdCl<sub>4</sub>]<sup>2-</sup>. The growth was accomplished with a 1:5 Pd: Au atomic ratio, resulting in an undamped LSPR response and provided a method to develop bimetallic NPs for plasmonic catalysis.<sup>13</sup>



**Figure 3.** (a) Dark field scattering spectra show plasmon linewidth,  $\Gamma$ , expands and (b) luminescence spectra show decrease in quantum yield of AuNRs (black) upon adding Pd (red). Electrochemical EOR used 20 μg Pd-AuNRs (red) and AuNRs (black). (b) CVs of Pd-AuNRs without (dotted) and with EtOH under dark and light (solid) conditions. (c) Photoinduced CAs with (i) AuNR and (ii) Pd-AuNR NPs held at +0.77 V under 200s on/off chopped light (gray shaded) and 610 nm long pass filtered (LPF) light (orange shaded).

Single-particle spectroscopic measurements were performed on the AuNRs with Pd end coatings to determine the energy conversion pathway using dark field scattering (Fig. 3a) and photoluminescence (Fig. 3b).<sup>13</sup> Spectra showed quenching (decrease) in the overall radiative quantum yield after depositing Pd on the AuNRs. Measurement results were consistent with separation of intraband hot carriers across the Pd-Au interface, removing excited carriers that could recombine radiatively. Further studies were needed to answer: Are hot carriers the primary driving force for plasmonic energy conversion reactions? The EOR was investigated by CV (Fig. 3c) and CA (Fig. 3d) using the RDE setup and electrochemical conditions previously discussed. CVs showed characteristic redox peaks of EtOH oxidation shown in Fig. 2a for Au and Pd. Light-enhancement was observed for the Pd-AuNRs, with an increase in current density and an anodic shift in the onset potential (~35 mV) under irradiation. CAs showed an increase in the photocurrent density by an order of magnitude after depositing Pd. Plasmonic enhancement was mostly observed at longer wavelengths (>610 nm). Photodeposition of Pd onto AuNRs improved the EOR current in CA 13x under

solar-simulated light and 40x for longitudinal SPR-targeted irradiation conditions (>610 nm), revealing 4x more efficient utilization of excited intraband carriers. Corresponding absorbed photon-to-charge carrier efficiency (APCE) was calculated to be 50x improved after Pd photodeposition. The overall low APCE for the plasmonic NPs indicate that most of the excited carriers undergo electron-phonon scattering, resulting in primarily photothermal heating as the dominant mechanism.<sup>13</sup>

In summary, we determined that plasmonic photo-sensitization can enhance the visible-light activity to cleave C-C bonds for EOR. Plasmonic EOR activity can be optimized by modifying AuPd composition and structure. Plasmonic nanocatalysts have had favorable influence on mitigating catalyst poisoning, tuning the selectivity and conversion efficiency. The 1:1 AuPd alloy exhibited optimal mass activity, high electrochemical activity, and prolonged photocurrent for oxidizing EtOH. We developed a method for the targeted plasmonic photodeposition of secondary catalytic metals like Pd on active sites of AuNRs, identified hot carrier transfer from the AuNR to Pd using single particle spectroscopy, and determined the photo-electrochemical methods that photothermal heating may be the primary mechanism for EOR enhancement.

Recently, LP-TEM was utilized to visualize the formation of silver (Ag)-shell on AuNRs in situ in real-time where two distinct Ag shell morphologies, faceted bipyramidal and tip preferential shells, were identified.<sup>15</sup> Electron-beam-induced Ag deposition onto AuNRs observed by aqueous-phase LP-TEM was consistent with radiolysis-induced Ag reduction. Any plasmonic metal deposition via hot electron reduction occurring in aqueous phase LP-TEM imaging was obscured by rapid chemical radical-induced metal deposition as mediated by ligand coverage. An implication of this work is that aqueous-phase LP-TEM imaging is likely not capable of separating plasmon-induced metal reduction from radiolysis-induced processes due to the susceptibility of water to radiolysis and production of aggressive radical species. Instead, this work suggests a potential pathway for investigating plasmonic phenomena with LP-TEM is to utilize radiolysis resistant solvents.<sup>15</sup>

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