Nanocatalytic Activity of Gold and Gold–Palladium Nanostructures Revealed by Tip-Enhanced Raman Spectroscopy

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ABSTRACT: The new paradigm of solid-state catalysis is that coupling of plasmonic and catalytic metals can be used to achieve much higher catalytic efficiency relative to their counterparts. Chemical reactions on such bimetallic nanostructures are light-driven, which essentially enables "green catalysis" in organic synthesis. The catalytic efficiency of bimetallic platforms directly depends on their nanoscale structures, which remain poorly understood. We used tip-enhanced Raman spectroscopy (TERS) to investigate nanoscale plasmonic and photocatalytic properties of novel gold–palladium microplates (Au@PdMPs), along with their monometallic counterparts. We found that 4-nitrobenzenethiol (4-NBT) can be catalyzed to 4'-dimercaptoazobisbenzene (DMAB) and 4-aminothiophenol (4-ATP) on Au@PdMPs, whereas monometallic AuMPs produce exclusively DMAB as a result of such photocatalytic reduction of 4-NBT. Using 4-NBT as a molecular reporter, we found that the efficiency of these catalytic reactions has strong correlation with the nanoscale structure of microplates. Coupling TERS to GC-MS, we also found that Au@PdMPs were capable of catalyzing the Suzuki–Miyaura coupling reaction.
This high confinement of the electromagnetic field allows subnanometer spatial resolution upon TERS imaging. For instance, the Datta group recently used TERS as a probe to capture the buckling distortions in silicene. The El-Khoury group used TERS to investigate spatial variations in optical fields on the surface of Ag nanoparticles (NPs). It has been shown that edges of AgNPs exhibit higher signals in comparison to their center. Similar plasmonic enhancement has been also observed on the edges of AgNWs. Using ultrahigh vacuum (UHV) TERS, the Ren group investigated edge effects on a submonolayer of Pd on a Au surface. Using phenyl isocyanide (PIC) as a molecular reporter, the researchers showed that in TERS spectra collected at Pd edges, the C≡N vibrational of the PIC was red-shifted by 60 cm⁻¹ relative to molecules located on the Pd terrace. These results indicated that a degree of back-donation from the d band of the metal to the antibonding π* orbital of PIC at the step site is greater than at the terrace sites. This suggests that molecules located at Pd edges have higher reactivity relative to Pd atoms in terraces. A recent work from our group revealed that Au@Pt nanoparticles (Au@PtNPs) exhibited drastically different catalytic activity and selectivity compared to their monometallic analogues. Li and Kurouski showed that selectivity of Au@PtNPs originated from LSPR damping in such bimetallic nanostructures due to increased probability of interband transitions (close energy levels of d-bands and Fermi levels in Pt). This allowed for stepwise photoconversion of 4-ATP first to 4-NBT and then to DMAB, whereas on AuNPs, 4-ATP reduction proceeded instantaneously to DMAB. These results show that TERS is ideally suited for visualization of nanoscale catalytic properties of mono- and bimetallic nanostructures.

In this work, we used TERS to investigate nanoscale photocatalytic properties of Au@Pd microplates (Au@PdMPs) and their monometallic counterpart, AuMPs. We determined catalytically active and inactive nanostructures on the surfaces of Au@PdMPs and...
revealed structures of photocatalytic products of 4-nitrobenzenethiol (4-NBT) reduction and Suzuki–Miyaura coupling reaction on this novel class of bimetallic nanostructures.

The TERS spectrum of 4-nitrobenzenethiol (4-NBT) has three distinct vibrational bands centered at 1083, 1339, and 1575 cm\(^{-1}\). On Au nanostructures, 4-NBT can be photochemically reduced to \( p,p'-\text{dimercaptoazobisbenzene (DMAB)} \), which exhibits vibrational bands at 1147 cm\(^{-1}\) and a doublet at 1397 and 1441 cm\(^{-1}\).\(^{1,3,4,34}\) Macroscale TER imaging of Au@PdMPs (Figures 1a–d and S3) revealed random spots of DMAB formation without clear localization of reduction sites that were observed at the edges and tip of AuMPs (Figure 1e). We also found that Au@PdMPs overall exhibited lower 4-NBT-to-DMAB reduction activity in comparison to AuMPs. This could be explained by LSPRs damping in such bimetallic nanostructures due to increased probability of interband transitions. The last can be attributed to close energy levels of d-bands and Fermi levels in Pd.\(^{20}\)

Nanoscale TER imaging of Au@PdMPs revealed spherical and rod-like patterns of Pd on Au surface, which exhibited high 4-NBT intensity relative to the underlying surface of Au@PdMPs (Figures 1h and S4). We found that the edges of such spherical and rod-like Pd nanostructures exhibited high photocatalytic efficiency of 4-NBT reduction to DMAB. It should be noted that such photocatalytic reactivity has been previously known only for noble metals, such as Ag and Au. To the best of our knowledge, this is the first experimental evidence of 4-NBT-to-DMAB reduction on Pd. Our results suggest that Pd–Au coupling on one microplate allows for a transfer of photocatalytic properties that has been characterized for noble metals to catalytic metals. It should be noted that “nanolakes” between the spherical nanoscale structures on the surface of Au@PdMPs remained catalytically inactive. We did not observe 4-NBT or DMAB signals on those nanolake regions.

In addition to DMAB, we also observed spectroscopic signatures of 4-aminothiophenol (4-ATP) (4-ATP) (Figures 1i and S5) on the surface of Au@PdMPs. Some 4-ATP sites spatially overlap with the sites of DMAB formation, whereas other do not have such spatial co-localization. It should be noted that 4-ATP was not detected on AuMPs.\(^{33}\) One may wonder what are the underlying physical factors that determine formation of DMAB versus 4-ATP on Au@PdMPs surfaces. To answer this question, we compared the yield of 4-ATP and DMAB on the surfaces of Au@PdMPs and their monometallic counterparts (AuMPs) (Figure 2 and Table S2).

We found that reduction of 4-NTP yields around 5.6% of 4-ATP on Au@PdMPs, whereas no 4-ATP was formed on AuMPs. This observation can be explained from a perspective of the strength of the electric field in the tip–sample junction. A theoretical explanation of this phenomenon was developed by the Tian and Ren groups.\(^{36,37}\) According to this theory, the ratio of DMAB to 4-ATP on plasmonic surfaces is determined by the strength of the electric field in the tip–sample junction. The larger the localized electric field, the higher the ratio of DMAB to 4-ATP should be expected. On the basis of this theory, one can expect an electric field damping on Au@PdMPs due to interband transitions of Pd.\(^{38}\) At the same time, no LSPR damping is taking place on monometallic nanostructures (AuMPs). Indeed, these structures provide so-called gap-mode effect, enhancing the electric field in the tip–sample junction.\(^{38}\) Thus, high plasmon energy (electric field) results in formation of DMAB from 4-NBT, whereas low plasmon energy in the tip–sample junction leads to formation of 4-ATP (Scheme 1). It should be noted that a similar LSPR damping phenomenon was recently reported for Au@PtNPs.\(^{33}\)

![Figure 2](https://dx.doi.org/10.1021/acs.jpcl.0c01631)

**Scheme 1. Potential Energy Landscape of 4-ATP, 4-NBT, and DMAB**

**Figure 2.** Catalytic property of AuMPs and Au@PdMPs. The catalytic probability of each type was obtained by counting the catalytic site number of azo (blue bar) and amino (orange bar) and calculating the occurrence ratio of azo or amino in all catalytic events.

**AE** is the abbreviation for activation energy.

Li and Kurouski showed that LSPR damping can be used to enhance the selectivity of bimetallic nanostructures. Specifically, it has been shown that Au@PtNPs were capable of 4-ATP reduction to 4-NBT and then to DMAB, whereas 4-ATP photoreduction immediately resulted in DAMB on the surface of AuNPs. These results also suggest that an increase in the electric field may increase catalytic rates of the plasmonic reactions discussed above. In fact, the Datta group recently demonstrated that an electric field can be used to control the rate of metal-free azide–alkyne click reaction. Specifically, the researchers showed that an increase in the electric field would lower the activation energy of such reaction, facilitating the catalytic reaction.\(^{39}\) Therefore, we investigated how the electric field changes rates of catalytic reactions on the AuMPs and Au@PdMPs. We performed kinetic measurements of 4-
We measured a change in intensities of 1441 cm$^{-1}$ (DMAB) versus 1339 cm$^{-1}$ (4-NTP) and plotted a natural logarithm of their ratio at different points (eq 1 and Figure 4). We found that an increase in the electric field causes the increase in the reaction rate of 4-NBT to DMAB conversion. We also found that a relationship between the electric field and the rate constants of the above-mentioned reaction is linear. At the same time, the rate is different for AuMPs and Au@PdMPs at a given laser power: $k_{Au30\mu w} = 0.126$ s$^{-1}$, $k_{Au90\mu w} = 0.343$ s$^{-1}$, and $k_{Au150\mu w} = 0.819$ s$^{-1}$ for AuMPs; $k_{Au@Pd30\mu w} = 0.071$ s$^{-1}$, $k_{Au@Pd90\mu w} = 0.235$ s$^{-1}$, and $k_{Au@Pd150\mu w} = 0.477$ s$^{-1}$ for Au@PdMPs. On the basis of these results, we can conclude that hot-carrier driven reduction rates of 4-NBT to DMAB are greater on AuMPs than on Au@PdMPs.

Monometallic Pd and Au@Pd bimetallic nanostructures have a unique property to catalyze Suzuki–Miyaura coupling reactions. As a result of such reactions, organoboron species and halides are cross-coupled. We investigated whether Au@PdMPs were capable of catalyzing Suzuki–Miyaura reaction. We deposited a monolayer of para-bromobenzenethiol (BrBT) on the surface of Au@PdMPs and added them to the solution of phenylboronic acid (PHBA). Using gas chromatography coupled to mass spectroscopy (GC-MS), we detected the formation of biphenyl-4-thiol (BPT, see Figure S6). The yield of the product directly correlated with the amount of the reagent. Specifically, with 0.5 and 20 mmol of BrBT, we get 0.26 $\mu$mol and 14.3 $\mu$mol of product, respectively (see Table S1). This corresponds to 0.5% and 0.7% of reaction yield, respectively. It should be noted that we did not aim to compare the yield of the Suzuki–Miyaura coupling reaction on Au@PdMPs relative to their monometallic analogues (PdMPs). One can envision that such comparison is nearly impossible to make because the yield of chemical reactions.

\[ \ln \left( \frac{c(4\text{-NBT})_t}{c(4\text{-NBT})_0} \right) = \ln \left( \frac{I_{1441}/I_{1339}}{I_{1441}/I_{1339}} \right) = kt \]

where $c(4\text{-NBT})_t$ and $c(4\text{-NBT})_0$ represent the concentration of 4-NBT at different reaction times. $I_{1441}$ and $I_{1339}$ are the intensities of the bands at 1441 cm$^{-1}$ (DMAB) and 1339 cm$^{-1}$ (NO$_2$), respectively. $k$ is the rate constant, and $t$ is the reaction time.

Figure 3. TERS kinetic measurements of 4-NBT to DMAB reduction at different laser powers: 30, 90, and 150 $\mu$w on (a–c) AuMPs and (d–e) Au@PdMPs.
directly depends on the amount of MPs, which is impossible to measure precisely in the reaction mixture. Nevertheless, this proof-of-principle study demonstrates that Au@PdMPs can be used to perform Suzuki−Miyaura coupling reaction.

One may wonder whether TERS can be used to identify active sites on the surface of Au@PdMPs that perform this coupling reaction. To answer this question, we used TERS to image the surface of Au@PdMPs with a monolayer of BrBT (Figure S7). The TERS spectrum of BrBT has two vibrational bands at 1065 and 1558 cm$^{-1}$, which can be assigned to C−Br and C−C ring vibration, respectively.42 Next, TERS was used to image the surface of Au@PdMPs after Suzuki−Miyaura reaction (Figure 5). In the collected TERS spectra, we found no evidence of BrBT presence on the surface. Instead, we observed the vibrational band at 1594 cm$^{-1}$, which can be assigned to the vibration mode of benzene rings on biphenyl (Figures S8 and S9). We found that edges of Au@PdMPs exhibited higher intensity of BPT relative to the flat terrace. This suggests that Au@PdMPs edges have the highest catalytic efficiency of Suzuki−Miyaura coupling reaction. It should be noted that Au@PdMPs edges also exhibited the high rates of 4-NBT reduction activity to DMAB and 4-ATP (Figure S3c,f,i). Additional microscopic examination and theoretical calculations are required to fully elucidate the facet structure of these edges to explain their high catalytic activity, which are beyond the scope of the current work.

Summarizing, we have systematically investigated the nanoscale plasmonic and photocatalytic properties of novel bimetallic nanostructures, Au@PdMPs, along with their monometallic counterparts, AuMPs. We found that 4-NBT can be catalyzed both to DMAB and 4-ATP on the bimetallic structures, whereas monometallic AuMPs produce exclusively DMAB as a result of such photocatalytic reduction of 4-NBT. The efficiency of these catalytic reactions has strong correlation with nanoscale structure of microplates. Coupling TERS to GC-MS, we found that Au@PdMPs were capable of catalyzing the Suzuki−Miyaura coupling reaction. TERS imaging of these new types of plasmonic nanostructures with unique catalytic properties allows for establishing a relationship between nanoscale structural characterization and catalytic reactivity. Furthermore, our results should aid in enlightening the design of more bimetallic structures with a more rational strategy.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01631.

Detailed description of sample preparation, spectra acquisition methods, and instrumentation (PDF)

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**Figure 4.** Rate constants of 4-NBT to DMAB reduction based on the intensity ratio of the band of 1441 cm$^{-1}$(DMAB) and 1339 cm$^{-1}$(NO$_2$) in TERS spectra obtained with AuMPs (blue trace) and Au@PdMPs (black trace). Each trace was fitted with a linear model according to eq 1.

**Figure 5.** (a) Chemical equation of Suzuki−Miyaura reaction. (b) Typical TERS spectra of the Suzuki−Miyaura reaction product, BPT. (c) TERS mapping of BPT on Au@PdMPs (50 nm per pixel). The intensity of the 1594 cm$^{-1}$ band of BPT is shown in red. (d) Corresponding AFM image of Au@PdMPs.
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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
We are grateful to AgriLife Research of Texas A&M for the provided financial support. We also acknowledge the Governor's University Research Initiative (GURI) grant program of Texas A&M University, GURI Grant Agreement No. 12-2016, M1700437. We thank Zachary Gorman and Professor Michael V. Kolomiets for their kind help with GC-MS characterization; we also appreciate Dr. Patrick Z. El-Khoury’s help with calculating the Raman spectrum of 4-ATP and BPT.

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