INVESTIGATION OF PLASMON-DRIVEN REACTIONS OF 4-MERCAPTOPHENYLBORONIC ACID ON SILVER NANOPARTICLES: A SERS STUDY

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Abstract

This work presents a preliminary SERS spectroscopy screening of plasmon-induced transformations of arylboronic compounds on silver-based nanostructures. The primary objective was to evaluate the feasibility of monitoring the Suzuki–Miyaura cross-coupling reaction (SMCR) on an exploratory AgPd bimetallic substrate under 532 nm excitation, aiming to overcome the high intrinsic plasmon damping of conventional transition-metal catalysts. Initial trends indicate that transitioning from strongly chemisorbed to weakly bound, physisorbed reactants successfully resolve spectral ambiguities and enhance reaction pathways. Additionally, baseline tracking of independent 4-mercaptophenylboronic acid (MPBA) behavior under basic conditions revealed pronounced side reactions; along with expected protodeboronation, unexpected homocoupling to 4,4′-biphenyldithiol and a nitration pathway driven by residual nitrite species were identified. Overall, these initial models demonstrate the potential of silver-assisted plasmonic substrates for the exploratory tracking of transition-metal-catalyzed surface reactions.

1 Introduction

Plasmon-driven reactions have emerged as a significant field of study over the past two decades, largely enabled by plasmon-enhanced spectroscopies on nanostructured materials. When electron oscillations are confined to a nanostructure, localized surface plasmon resonance (LSPR) occurs, which can both enhance chemical reactivity and enable monitoring of surface reactions as well [1]. A typical system for studying plasmonic reactions via surface-enhanced Raman scattering (SERS) spectroscopy relies on anchored substrates via a thiol group to the surface of the plasmonic material. Well-studied benchmark reactions include the conversion of 4-nitrothiophenol (NTP) to 4,4′-dimercaptoazobenzene (DMAB) [2] and the reduction of NO_2 groups to NH_2 in dinitroazobenzene compounds [3]. Cross-coupling reactions, such as the Suzuki-Miyaura cross-coupling reaction (SMCR), which forms biaryl compounds from aryl boronic acids and aryl halides, are also of high interest [4,5].

The primary mechanisms driving plasmonic catalysis are the hot carrier mechanism and the thermal pathway, alongside direct charge transfer as a distinct mechanism. To distinguish between hot carrier and thermal mechanisms, kinetic data fitting is commonly employed: the fitting curve for the hot carrier mechanism follows a linear function, whereas the thermal mechanism is characterized by an exponential function [6].

The primary objective of this study was to optimize the SMCR for real-time SERS monitoring on hydroxylamine-reduced silver nanoparticles (AgNH). Although the SMCR conventionally proceeds in non-aqueous media, its feasibility in eco-friendly aqueous environments catalyzed by AgPd

nanoparticles [7] and on palladium (Pd) or bimetallic gold-palladium (AuPd) nanoparticles together with monitoring the reaction by SERS had already been documented [1]. Nevertheless, neither AgPd, AuPd nor Pd nanoparticles are substrates achieving high SERS enhancement. Therefore, in this study we tried adapting this transition metal catalysis to a silver-based plasmonic substrate for SERS investigation. We investigate the chemical behavior of 4-mercaptophenylboronic acid (MPBA) on silver nanoparticles, focusing on the undesirable deboronation reaction that leads to the loss of the reactive $–B(OH)_2$ group [8,9]. To find ways to suppress this reaction, SERS was utilized to monitor MPBA deboronation under various experimental conditions. Surprisingly, we detected not only the expected product, thiophenol (TP), but also other reaction products such as 4,4′-biphenyldithiol (BPDT) resulting from a plasmon-driven homocoupling pathway, and in some cases, NTP. The latter points to an unexpected nitration reaction driven by residual nitrite species from the nanoparticle synthesis [8].

2 Results and Discussion

2.1 Characterization of SERS active systems and initial SMCR studies

To establish a suitable catalytic platform for monitoring the SMCR via SERS spectroscopy, initial feasibility studies focused on balancing surface conditions and reactant binding. A bimetallic framework consisting of palladium-modified silver nanoparticles (AgNH/Pd) was prepared as an exploratory substrate. Preliminary TEM (**Figure 1.**) and XPS (**Figure 2.**) measurements provided baseline confirmation of the decoration of AgNH with Pd species. Furthermore, UV-Vis spectroscopy revealed a qualitative redshift in the localized surface plasmon resonance (LSPR) maximum from 411 nm for bare AgNH to 423 nm after the addition of Pd ions, indicating a clear modification of the nanoparticle surface. All exploratory SERS evaluations were conducted under 532 nm laser excitation.

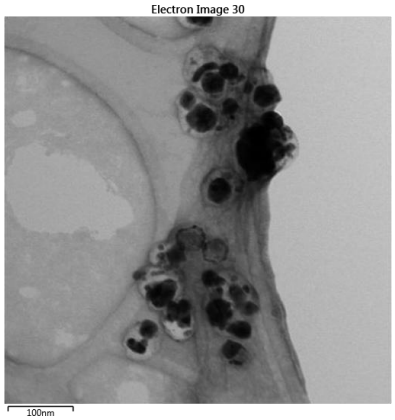


Figure 1. TEM micrograph of AgNH/Pd NPs.

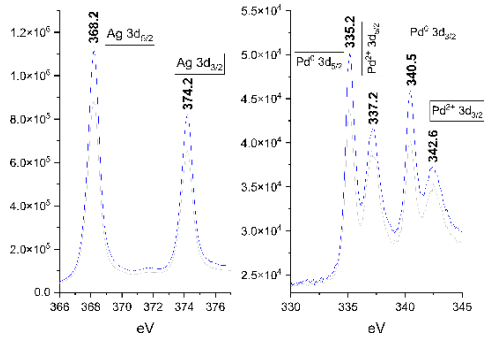


Figure 2. XPS spectra of AgNH/Pd NPs.

In the initial screening phase, the reaction was evaluated using a fully chemisorbed model system consisting of AgNH treated with MPBA, 4-bromothiophenol (BTP), an aqueous NaOH base, and a K_2PdCl_4 ([Pd]) catalyst source (**Figure 3.**). However, under these preliminary testing conditions, the spectral fingerprints of the cross-coupling and competing homocoupling pathways (Scheme 1) could not be unambiguously differentiated; in these initial trials, BPDT emerged as the dominant spectral product. To address this ambiguity in subsequent proof-of-concept tests, MPBA was replaced with phenylboronic acid (PBA), which lacks the thiol anchoring group. This modified system AgNH/BPT/PBA/NaOH/[Pd]) successfully yielded spectral features consistent with the distinct SMCR cross-coupling product, biphenyl-4-thiol (BPT) (**Figure 4.**), offering a preliminary baseline for comparison with literature data where Au/Pd nanoparticles were utilized as catalysts [4].

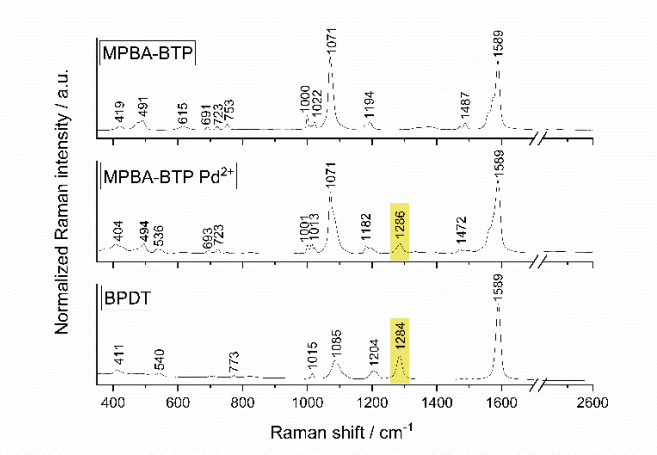


Figure 3. SERS spectra of reaction mixture before after reaction and standard spectrum of biphenyl.

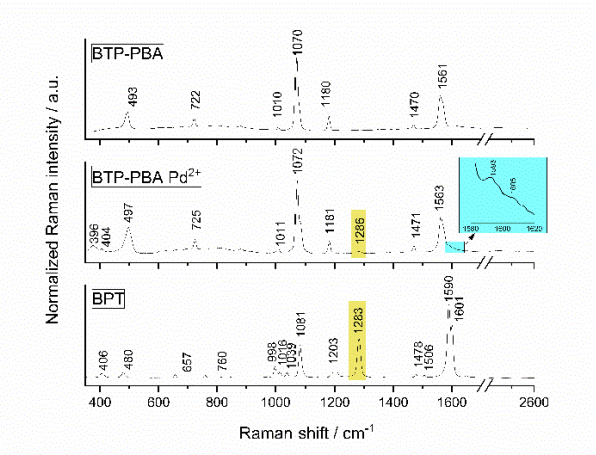
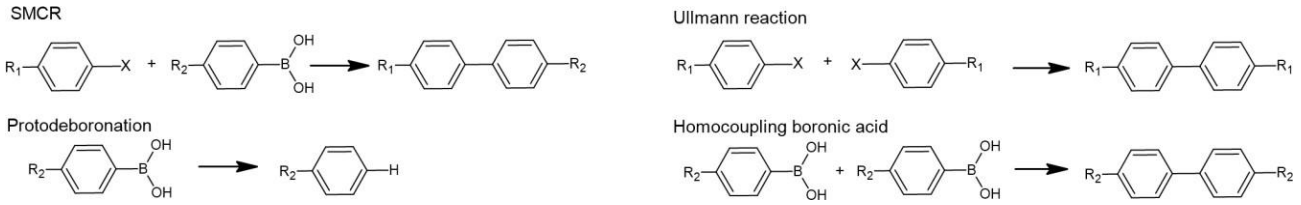


Figure 4. SERS spectra of reaction mixture addition of catalyst, before addition catalyst, after reaction and standard spectrum of biphenyl.



Scheme 1 – Scheme of SMCR and s side reactions.

22 Optimization: Transition from chemisorbed to physisorbed reactants

Based on initial observations suggesting that replacing strongly chemisorbed reactants might influence reaction kinetics, a preliminary screening strategy was altered by shifting from a strongly chemisorbed (thiol-anchored) state to a weaker bound or physisorbed state.

For these exploratory trials, BTP was replaced with 4-iodobenzonitrile (IBN), and MPBA was substituted with either PBA or 4-(methylthio)phenylboronic acid (MTPBA). Two new reaction series were monitored to assess qualitative trends using AgNH, the respective reactants, bases (NaOH or K_2CO_3), and [Pd] catalyst: (i) The PBA series: AgNH + IBN + PBA + bases + [Pd] (**Figure 5., 6.**), which indicated spectral features corresponding to 4-cyanobiphenyl as the potential SMCR product.

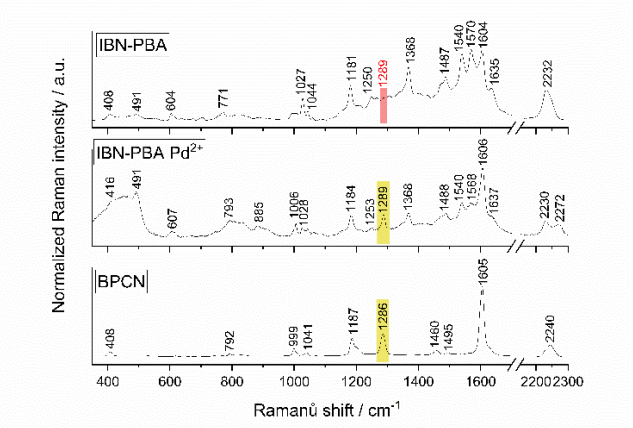


Figure 5. SERS spectra of reaction mixture with before addition of catalyst, after reaction spectrum of biphenyl.

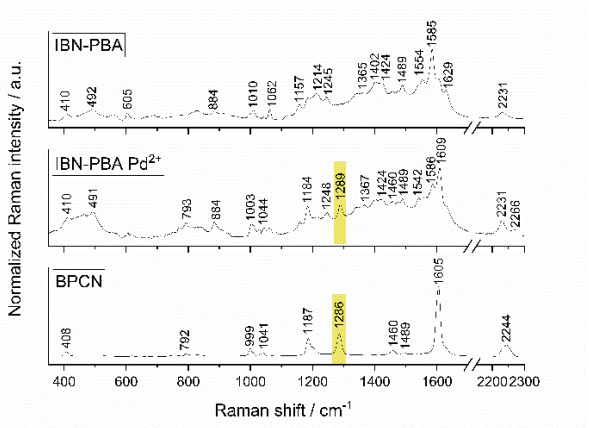


Figure 6. SERS spectra of reaction mixture with NaOH K2CO3 before addition catalyst, after reaction and standard and standard spectrum of biphenyl.

(ii) The MTPBA series: AgNH + IBN + MTBA + bases + [Pd] (**Figure 7., 8.**), which showed trends toward the formation of 4′-(methylthio)biphenyl-4-carbonitrile. In these preliminary screening steps, the series utilizing IBN qualitatively suggested a faster spectral evolution compared to the thiol-anchored precursors. However, when K_2CO_3 was introduced as the base in combination with IBN, spectral indications of a competing Ullmann-type homocoupling pathway were detected in both test systems.

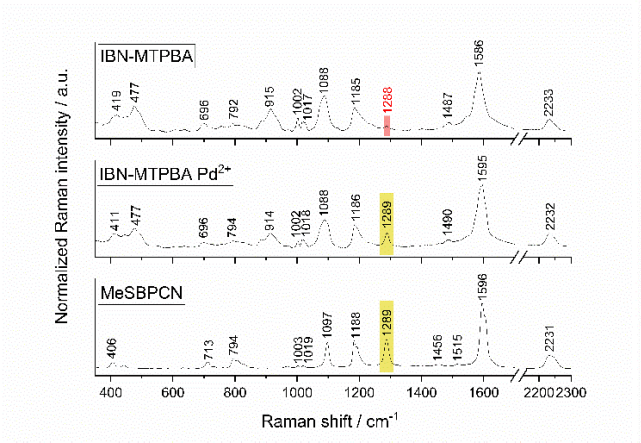


Figure 7. SERS spectra of reaction mixture with before addition of catalyst, after reaction spectrum of biphenyl.

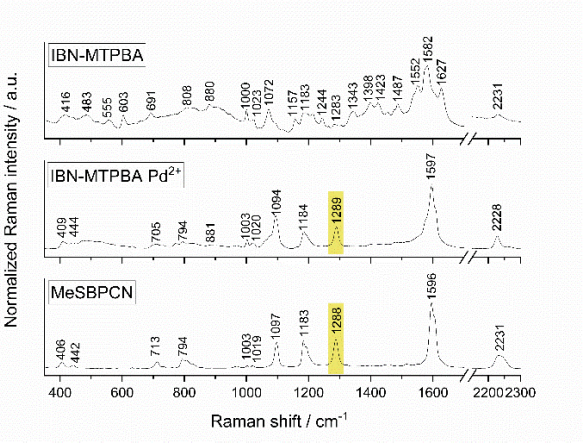


Figure 8. SERS spectra of reaction mixture with NaOH K2CO3 before addition catalyst, after reaction and standard and standard spectrum of biphenyl.

Ultimately, these initial screening models indicated that the 532 nm excitation wavelength is a promising candidate for this platform, providing sufficient SERS enhancement for baseline evaluation with viable signal-to-noise ratios and short accumulation times. This performance highlights the potential of silver-based substrates over conventional catalytic platforms based on pure Pd or Au/Pd nanoparticles. While silver possesses exceptional plasmonic efficiency in the visible range, transition metals like Pd and their alloys with gold suffer from high intrinsic damping and unfavorable dielectric properties in this spectral region [10,11].

2.3 MPBA side reactions

In parallel, the independent chemical behavior of MPBA on bare AgNH under basic conditions was studied to clarify the background processes. Importantly, it was found that chemisorbed MPBA on AgNH under 532 nm excitation exhibits pronounced side reactions, most notably deboronation. While this laser-induced protodeboronation of MPBA is well-documented in the literature [9], our SERS experiments revealed additional, unexpected spectral features.

Apart from the expected deboronation, we observed bands around 1280 cm^{-1} corresponding to the C–C inter-ring vibration of BPDT, confirming a plasmon-driven homocoupling pathway (not shown here, [8]). More surprisingly, an intense band at approximately 1330 cm^{-1} appeared in several spectra, which was assigned to the symmetric stretching mode of a nitro group NO_2. Subsequent factor analysis isolated a spectral component matching the reference spectrum of 4-nitrothiophenol (NTP) [8]. To determine the origin of this unexpected nitration, we first tested nitrate ions (NO_3^-), as $AgNO_3$ is used during the synthesis of AgNH; however, the addition of KNO_3 did not induce the appearance of the nitro band. The only other nitrogen-containing compound in the system was the reducing agent, hydroxylamine hydrochloride. According to the literature [12,13], the autooxidation of hydroxylamine yields nitrite anions (NO_2^-). To confirm our hypothesis that the reducing agent acts as the ultimate source of the nitro group, we used freshly prepared AgNH, and the 1330 cm^{-1} band was clearly detected in the AgNH/MPBA system. Finally, this mechanism was verified by the intentional addition of sodium nitrite ($NaNO_2$), which successfully replicated the nitration reaction [9].

3 Summary and further research

In this work, a bimetallic AgNH /Pd platform was pre-screened for monitoring the Suzuki- Miyaura cross-coupling reaction (SMCR) via SERS spectroscopy under 532 nm excitation. Preliminary trials showed that shifting from strongly chemisorbed to weakly bound reactants (using IBN) successfully resolves spectral ambiguities and improves reaction trends. This approach takes advantage of silver's higher plasmonic efficiency upon excitation in the visible region compared to Pd or Au/Pd systems. Furthermore, preliminary studies of the behavior of isolated MPBAs revealed significant side reactions, including protodeboration and an unexpected nitration pathway triggered by residual nitrites.

Future research will focus on the comprehensive, quantitative optimization of this bimetallic platform. Detailed kinetic studies are underway to precisely evaluate the impact of reaction conditions (laser power, temperature, and base strength) on reaction yields, alongside advanced chemometric modeling to resolve overlapping spectral features for a definitive publication.

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