A Dual Catalyst with SERS Activity for Probing Stepwise Reduction and Oxidation Reactions

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Abstract: Aromatic azo compounds are high-value chemicals extensively used as pigments, drugs, and food additives, but their production typically requires stoichiometric amounts of environmentally unfriendly metals or nitrates. There is an urgent need to develop a dual catalytic system capable of reducing nitroaromatics to aromatic amines, followed by their oxidation to azo compounds. Here we report such a dual catalyst based on Ag@Pd-Ag core-frame nanocubes for the stepwise conversion of 4-nitrothiophenol to trans-4,4′-dimercaptoazobenzene under ambient conditions. Our in situ surface-enhanced Raman spectroscopy study reveals three sequential processes that include the Pd-catalyzed reduction of 4-nitrothiophenol to 4-aminothiophenol by hydrogen, a period during which the 4-aminothiophenol remain unchanged until all hydrogen has depleted, and the Ag-catalyzed oxidation of 4-aminothiophenol to trans-4,4′-dimercaptoazobenzene by the O2 from air. This work will lead to an environmentally friendly and sustainable approach to the production of aromatic azo compounds.

With the recent advances in engineered nanomaterials, Corma and co-workers discovered that Au nanoparticles supported on TiO2 or Fe3O4 powders could serve as a catalyst for the reduction of nitroaromatics to aromatic amines by H2, followed by the oxidation of aromatic amines to aromatic azo compounds by O2 at 100–120 °C.[1] In parallel, many other groups have explored the reduction of 4-nitrophenol by NaBH4 as a model system to investigate the reaction mechanism.[2–4] Significantly, when functionalized with a thiol group, the aromatic nitro- or amine- molecules can be chemically linked to the surface of Au nanoparticles to facilitate the investigation of reaction mechanisms using surface-enhanced Raman spectroscopy (SERS). As a vibrational spectroscopy method, SERS can reveal the “fingerprints” of molecular species for identifying the intermediates and products involved in a catalytic reaction.[5,6]

As revealed by SERS, the Au-catalyzed reduction of 4-nitrothiophenol (4-NTP) by NaBH4 follows a condensation route, involving the formation of 4,4′-dimercaptoazobenzene (DMAB) and 4-aminothiophenol (4-ATP) as an intermediate and final product, respectively.[7–10] In comparison, Ag nanoparticles were found to have no catalytic effect on the reduction reaction under similar conditions,[11] although Ag is a much better SERS substrate than Au.[12] When switched to Pd or Pt nanoparticles, it was shown that the reduction would occur at a much faster rate than the Au-based system, making it challenging to capture the intermediate.[13–15] On the other hand, there are a number of reports on the formation of DMAB from 4-ATP immobilized on the surfaces of Au or Ag nanoparticles through oxidation under ambient conditions.[16,17] In this case, it is well-known that primary aromatic amines can react with molecular oxygen to form azobenzene derivatives.[18] Alternatively, it was proposed that the Au or Ag nanoparticles could interact with light through the excitation of localized surface plasmon resonance for the generation of hot electrons, which then reacted with O2 to generate active oxygen species in the presence of H2O and thereby enable the oxidation of 4-ATP to DMAB.[17,19–22] Despite these developments, none of the previous studies were able to observe the reduction of 4-NTP to 4-ATP and the subsequent oxidation of 4-ATP to DMAB on a catalyst based on a single noble metal. A potential solution to this problem is to develop a dual catalyst comprising two noble metals, with one of them catalyzing the reduction reaction and the other the oxidation reaction.

We have recently developed a novel class of bimetallic catalysts that could fulfill the dual requirements mentioned above.[11] Among all noble metals, Pd has the lowest energy barrier to the dissociation of H2 into atomic hydrogen (H) for the hydrogenation (or reduction) reaction of unsaturated compounds.[23] On the other hand, Ag is a well-known component of the industrial catalysts used for the epoxidation of ethylene by O2.[24] Conceptually, integration of Pd with Ag would give
a promising dual-catalytic system for the reduction of 4-NTP to 4-ATP (as catalyzed by Pd) and subsequent oxidation of 4-ATP to DMAB (as catalyzed by Ag). In an initial study, we fabricated the bimetallic nanocrystals as Ag@Pd-Ag core-frame for in situ monitoring of Pd-catalyzed reduction of 4-NTP to 4-ATP by NaBH₄. However, we did not observe the formation of DMAB via the oxidation of 4-ATP because the SERS measurements were stopped once the conversion from 4-NTP to 4-ATP was completed.¹¹¹

Herein we demonstrate, for the first time, the formation of trans-DMAB during the reduction of 4-NTP by NaBH₄ under ambient conditions when Ag@Pd-Ag core-frame nanocubes were employed as a dual catalyst and an active SERS substrate. Remarkably, our time-dependent SERS spectra clearly reveal three sequential steps involved in the transformation from 4-NTP to trans-DMAB on the surface of the bimetallic catalyst. The first step involves the Pd-catalyzed reduction of 4-NTP to 4-ATP without the detection of DMAB. Next, the 4-ATP molecules derived from 4-NTP can retain their identity without undergoing any changes as long as there is NaBH₄ in the reaction solution. The duration of this “stable” period is essentially independent of the Pd content deposited on the Ag nanocubes. Finally, upon the complete decomposition of NaBH₄, the 4-ATP is quickly transformed to trans-DMAB by the O₂ from air. In the last step, Ag enables the oxidation reaction by activating the dissociation of O₂ into atomic oxygen. Collectively, this work presents a new catalytic system based on Pd and Ag that embraces a great promise for producing aromatic azo compounds from nitroaromatics.

We generated Ag@Pd-Ag core-frame nanocubes by co-titrating Na₃PdCl₄ and AgNO₃ solutions into an aqueous suspension of Ag nanocubes (Figure S1 in the Supporting Information, 39.2 ± 1.6 nm in edge length) in the presence of ascorbic acid (AA) and poly(vinyl pyrrolidone) (PVP). We could control the Pd content, as well as the Pd to Ag ratio, in the final catalyst by simply varying the titration volume for each precursor solution. When the co-titration volume was increased from 0.1 to 0.2 and 0.3 mL (for each precursor), the Pd content was increased from 2.2 ± 0.2 to 3.6 ± 0.3, and 4.6 ± 0.3 wt.%.[11] Figure 1a,b shows aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the bimetallic nanocubes obtained at a co-titration volume of 0.2 mL for each precursor. As confirmed by energy dispersive X-ray spectroscopy (EDS) mapping (Figure 1c,d), the Pd atoms were preferentially deposited at the edge and corner sites of a Ag nanocube, leading to the formation of a core-frame structure.

In the first set of SERS measurements, we used the bimetallic nanocubes with 2.2 wt.% Pd obtained at a co-titration volume of 0.1 mL for each precursor. Figure 2 shows the SERS spectra recorded from an aqueous suspension of the 4-NTP-functionalized nanocubes at different time intervals after the introduction of NaBH₄. At t = 0 min, the spectrum shows three vibrational bands of 4-NTP (marked by dashed blue lines) at 1108 cm⁻¹ (C–N stretching, νCN), 1336 cm⁻¹ (O–N–O stretching, νONO), and 1572 cm⁻¹ (C–C stretching phenyl-ring, νCC).[18,21] The peak located at 1080 cm⁻¹ can be assigned to the C–S stretching, νCS. At t = 2 min, the νNO2 band was shifted to 1330 cm⁻¹, together with slight decrease in intensity. The blue-shift for the νNO2 band indicates a change to the symmetric stretching of NO2 due to the onset of reduction. Other bands remained essentially the same in peak positions but indicated some decrease in peak intensity. The spectrum showed almost no changes until t = 6 min when a shoulder peak appeared at 1595 cm⁻¹ (marked by a dashed orange line), which can be assigned to the νCC of 4-ATP.[16] As the reaction progressed to 15 and 30 min, the three bands associated with 4-NTP began to decrease in intensity while the peak assigned to the νCC of 4-ATP increased its intensity accordingly. At t = 40 min, all the bands associated with 4-NTP disappeared, and the two major peaks at 1078 cm⁻¹ and 1595 cm⁻¹ can be assigned to the νCS and νCC of 4-ATP, respectively. This result indicates the completion of the transformation from 4-NTP to 4-ATP by this time point. It is also worth noting that the intensity of νCC for 4-ATP was weaker than that of νCC for 4-NTP due to possible desorption of ATP from the surface in the presence of NaBH₄.[28] From 40 to 60 min, the bands of 4-ATP showed little change in terms of position, suggesting that the 4-ATP molecules remained on the bimetallic nanocubes. However, there was a noticeable increase in intensity for these bands, probably due to the formation of hot spots caused by particle aggregation. At t = 70 min, three bands appeared at 1142 cm⁻¹, 1388 cm⁻¹, and 1429 cm⁻¹ (marked by dashed red lines), which can be assigned to the νCH₂ + δCH₂, νNN + νNN, and νNN + δCH₂ of trans-DMAB, respectively.[16,25] This observation suggests that the 4-ATP adsorbed on the surface of bimetallic nanocubes with a Pd content of 2.2 wt.% could be oxidized by the O₂ from air to generate trans-DMAB once the reduction of 4-NTP has been completed and all the NaBH₄ in the solution had decomposed. The spectrum remained essentially the same until t = 90 min, apart from slight increase in intensity for the peaks.

Next, we switched to the bimetallic nanocubes with 4.6 wt.% Pd prepared by increasing the co-titration volume to
0.3 mL for each precursor. In this case, the Pd atoms were still mainly deposited on the edge and corner sites of each Ag nanocube, only with some spreading to the side faces due to surface migration. We also collected SERS spectra at different reaction times (Figure 3) and then compared them with the data shown in Figure 2. At \( t = 0 \) min, we observed a 20% decrease in intensity for the 4-NTP peak at 1572 cm\(^{-1}\) (\( \nu_{CS} \)). It is anticipated that the deposition of more Pd atoms on each Ag nanocube could deteriorate the SERS activity of Ag. The drop in peak intensity might also indicate weaker binding of 4-NTP molecules to the Pd surface. At \( t = 2 \) min, we observed four bands that can be assigned to 4-NTP and 4-ATP. As the reaction progressed to 4 min, we only observed the bands of 4-ATP, indicating the complete reduction of 4-NTP to 4-ATP at this time point. In contrast, the reduction was not completed until \( t = 40 \) min when the Pd content was at 2.21 wt% (see Figure 2). Taken together, we believe that the reduction of 4-NTP by NaBH\(_4\) can be accelerated by increasing the proportion of Pd atoms on the surface of a catalytic particle. From 4 to 20 min, the spectrum remained essentially unaltered, echoing the “stable” period shown in Figure 2. At \( t = 30 \) min, three bands characteristic of trans-DMAB appeared. Again, 4-ATP was oxidized within a 10 min window \((t = 20–30 \text{ min})\), similar to the case with a lower Pd content (Figure 2, 60–70 min). At \( t = 60 \) min, the \( \nu_{CS} \) band remained essentially the same but the intensities of other trans-DMAB bands increased, indicating the possible formation of hot spots due to particle aggregation. These data suggest that the oxidation of 4-ATP by the O\(_2\) from the air proceeded at comparable rate for both catalysts, with no correlation with the Pd content. We believe it is Ag that is responsible for the activation of O\(_2\) dissolved in the reaction solution for the oxidation of 4-ATP to trans-DMAB.

Figure 4 outlines the proposed mechanism to decipher the reaction of 4-NTP by NaBH\(_4\) for the production of trans-DMAB on the surfaces of Ag@Pd-Ag nanocubes as a dual catalyst. Because the SERS spectra indicate that the \( \nu_{CS} \) peaks of 4-NTP, 4-ATP, and trans-DMAB essentially remained unchanged during the reaction, we assume that these molecules are preferentially adsorbed at a configuration parallel to the Au surface through the Au–S linkage. It is also worth noting that the assignment of SERS peaks to trans-DMAB rather than cis-DMAB supports our argument about a parallel configuration for the molecules on a surface rather than a vertical configuration. Upon the addition of NaBH\(_4\) to an aqueous suspension of 4-NTP functionalized bimetallic nanocubes under ambient conditions, NaBH\(_4\) decomposes for the generation of H\(_2\). It is well-known that H\(_2\)
By assuming atomic hydrogen would become available upon decomposition of NaBH₄, leading to the rapid production of H₂, which is completely different in the aqueous solution for the Ag-catalyzed oxidation of 4-ATP to trans-DMAB. We believe that during our experiments the reduction of 4-NTP to 4-ATP occurred in the presence of excess NaBH₄ (or H₂). In this case, atomic hydrogen on the surfaces could prevent the oxidation of as-prepared 4-ATP by O₂ dissolved in the aqueous solution, leading to the “stable” period of 4-ATP molecules attached to the surfaces of bimetallic nanocubes. As the decomposition of NaBH₄ (or the release of H₂) ended, the adsorption of H on the Pd layer stopped and the desorption of atomic hydrogen at room temperature began. Upon desorption of hydrogen atoms, Ag atoms would activate O₂ for a thermodynamically spontaneous oxidation of 4-ATP to the production of trans-DMAB on the surfaces of Ag@Pd-Ag nanocubes, which is supported by other findings. By using the solubility of O₂ in DI water, we estimated that 1.1 x 10⁻⁷ mol of O₂ would become available to react with 4-ATP molecules that were present in the order of 10⁻¹⁰ mol, leading to the rapid production of trans-DMAB from 4-ATP.

It is also interesting to acknowledge that we could cycle the reaction of 4-ATP to and from trans-DMAB through the re-addition of NaBH₄. Figure S4 shows SERS spectra collected from the 4-NTP molecules adsorbed on the surfaces of bimetallic nanocubes prepared by a co-titration volume of 0.2 mL for each precursor. After the first introduction of NaBH₄, we observed the formation of trans-DMAB on the surfaces at t = 100 min. Upon the second addition of NaBH₄ to our reaction solution, at t = 5 min we noticed the formation of 4-ATP with an extremely weak SERS signal, likely due to the desorption of 4-ATP from the surfaces of nanocubes in the presence of NaBH₄. It appears that after full decomposition of NaBH₄, the 4-ATP was then oxidized to form trans-DMAB. These results support our argument that Ag would catalyze the oxidation reaction of 4-ATP upon the completion of further adsorption of H atoms on the surfaces of bimetallic nanocubes.

In summary, we have demonstrated the use of Ag@Pd-Ag nanocubes as dual catalyst and a unique SERS probe for monitoring the reduction of 4-NTP to 4-ATP by NaBH₄ and the subsequent oxidation of 4-ATP to trans-DMAB by O₂ under ambient conditions. We identify that Pd atoms could catalyze the reduction of 4-NTP toward 4-ATP without the observation of DMAB as an intermediate. Because of the adsorption of H₂ on Pd atoms for the generation of atomic hydrogen, the reduction would progress more rapidly when more Pd atoms are deposited on the bimetallic nanocubes. Upon the completion of reduction, 4-ATP molecules derived from 4-NTP would remain attached to the catalytic surface due to the excess amount of H₂ involved in the reaction and the presence of H atoms. Once H atoms desorb at room temperature, Ag would enable the activation of O₂ in the aqueous solution for the Ag-catalyzed oxid-
dation reaction of 4-ATP to trans-DMAB. This work establishes a new catalytic system based on Pd and Ag atoms on a single nanocrystal for producing aromatic azo compounds from nitroaromatics.

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