Supporting Information to:

Theoretical Study of Plasmon-enhanced Surface Catalytic Coupling Reactions of Aromatic Amines and Nitro Compounds

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A. Computational Details

The metallic cluster model was used to investigate the reactions of PATP and PNTP on silver and gold surfaces. Molecules adsorbed on metal electrodes or nanoparticle surfaces were modeled as metal-molecule complexes \( M_5 \)-PATP(PNTP). The surface activated oxygen and hydrogen species were modeled as \( M_2 \)O and \( M_3 \)H cluster. Density functional theory (DFT) calculations were carried out with the hybrid exchange–correlation functional B3LYP.\(^1\)\(^-\)\(^2\) The basis sets for C, H, N, O, and S atoms of investigated molecules were 6-311+G(d, p), including a polarization function to all the atoms and a diffuse function to C, N, O, and S atoms.\(^3\)\(^-\)\(^4\) For all metal atoms, the valence electrons and the innershells were described by the basis set, LANL2DZ, and the corresponding relativistic effective core potentials, respectively.\(^5\)\(^-\)\(^6\) The solvent effect was considered by integral equation formalism polarization continuum model (PCM).\(^7\) All calculations including structure optimization and thermodynamic energy computation were carried out by using Gaussian 09 package.\(^8\)

The frequency calculations were performed on all the intermediates and transition states. For stable intermediate geometries, we verified that there is no imaginary frequency. In the case of the transition states we verified that there is only one imaginary frequency corresponding to the reaction coordinate. These frequency calculations also provided us with the thermochemical analysis at a pressure of 1 atm and temperature of 298.15 K. Electronic excitation was studied within the time-dependent DFT (TD-DFT) approaches, which is an efficient method and offers an orbital picture for a physical understanding of the electronic excitation process.\(^9\)

Figure S1. Optimized structures of surface complexes \( M_5 \)-PATP and \( M_5 \)-PNTP and surface activated oxygen and hydrogen species \( M_2 \)O and \( M_3 \)H.
### B. Molecular Abbreviation

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-aminothiophenol</td>
<td>PATP</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>p-nitrothiophenol</td>
<td>PNTP</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>p-nitrosothiophenol</td>
<td>PNSTP</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>p-hydroxyaminothiophenol</td>
<td>PHATP</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>p-nitrenethiophenol</td>
<td>PNETP</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>p,p’-dimercaptoazobenzene</td>
<td>DMAB</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>p,p’-dimercaptoazoxybenzene</td>
<td>DMAOB</td>
<td><img src="image7" alt="Structure" /></td>
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<tr>
<td>p,p’-dimercapthydroazobenzene</td>
<td>DMHAB</td>
<td><img src="image8" alt="Structure" /></td>
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</table>
C. Plasmon-driven photoreduction of PNTP

Figure S2 shows the Gibbs free energies as a function of irradiation wavelength for photocatalysis of PNTP to DMAB in neutral solution. The reaction mechanism of photoreduction of PNTP to DMAB has been proposed in our previous study. Under visible light irradiation, PNTP is reduced to nitroso compound PNSTP and hydroxylamine compound PHATP in sequence. PHATP is not able to undergo further photoreduction to produce amine compound PATP because of its high LUMO level. In contrast, PHATP re-oxidizes to PNSTP via photoinduced molecule-to-metal CT. The PNSTP/PHATP redox pair accumulated on surface undergoes condensation reaction to produce an azoxy compound DMAOB, which can be further reduced to DMAB (see Figure 4). As seen from Figure 5, the one electron-one proton reduction of PNTP to PNTP(H) (reaction 13) is the most difficult step during the overall processes of PNTP reduction. The calculated reduction potentials are -0.88 and -0.78 V vs. SHE at pH = 7 on silver and gold electrodes, respectively. On the silver electrode, the reduction of PNTP to PNTP(H) can be driven by 514 nm and 633 nm irradiation. However, such reaction cannot take place on gold by the selected four wavelength because of the low Fermi level of gold substrate.
D. Surface Catalytic Oxidation of PATP

Figure S3. Proposed Reaction Mechanism for Surface Catalytic Oxidation of PATP. M denotes metallic clusters of Ag5 and Au5 here.
Figure S4. Potential energy surface of the oxidation coupling reaction of PATP to DMAB catalyzed by $\text{M}_2\text{O}$.
E. Direct oxygenation of adsorbed PATP

Figure S5. Proposed Reaction Mechanism for Direct Oxygenation of PATP. M denotes metallic clusters of Ag5 and Au5 here.

\[
\begin{align*}
\text{M}_5\text{PATP} + O_2 & \rightarrow \text{M}_5\text{PATP(H)} + O_2H \\
\text{M}_5\text{PATP} + O_2H & \rightarrow \text{M}_5\text{PATP(H)} + O_2H_2 \\
\text{M}_5\text{PATP(H)} + O_2H_2 & \rightarrow \text{M}_5\text{PNETP} + OH + H_2O \\
\text{M}_5\text{PNETP} + OH & \rightarrow \text{M}_5\text{ADMABAM} + H_2O \\
\end{align*}
\]

(S1A1) (S1A2) (S1A3) (S1A4) (S1A5) (S1A6)

Table S1. Calculated Gibbs Free Energies (\(\Delta G\)) and Activation Energies (\(E_a\)) for Reaction 1 to 6

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta G / \text{kcal\cdotmol}^{-1})</th>
<th>(E_a / \text{kcal\cdotmol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td>S1-1</td>
<td>37.65</td>
<td>35.80</td>
</tr>
<tr>
<td>S1-2</td>
<td>4.76</td>
<td>2.91</td>
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<td>S1-3</td>
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<td>S1-4</td>
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<td>-28.06</td>
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<td>S1-5</td>
<td>-11.21</td>
<td>-13.47</td>
</tr>
<tr>
<td>S1-6</td>
<td>-60.90</td>
<td>-59.99</td>
</tr>
</tbody>
</table>

Figure S6 presents the potential energy curves for oxygenation of PATP to DMAB in three different pathways. The calculated \(\Delta G\) and \(E_a\) for reaction S1-1 to S1-6 are listed in Table S1. Reactions 1 to 3 are endothermic and reactions 4 to 6 are exergonic. The activation energies of reaction 2, 4, and 6 are much lower than reaction 1, 3, and 5. This means that the oxidative ability...
of radical ·O$_2$H and ·OH are stronger than O$_2$ and H$_2$O$_2$ molecules. Reaction 3 has the largest activation energy value for path1 and path2, the RDS for path 3 is reaction 1a. The reaction barrier for path3 is lower than path1 and path2, so path3 is the most possible reaction route for oxygenation of PATP to DMAB. In this reaction route, PATP firstly loss one hydrogen atom to transform to its neutral radical PATP(H). Then, A ring coupling reaction between two molecules of PATP(H) gives a hydrazo species DMHAB. Finally DMAB is formed after two consecutive dehydrogenation steps of DMHAB. From Table S3, we find that both the Gibbs free energies and the activation energies of reaction 1a to 1f have approximate values for reaction occurred on gold and silver, except that the activation energy of 3 on silver is about 10 kcal/mol larger than gold.

Figure S6. Potential energy surfaces for reaction network of oxygenation of PATP through three different reaction pathways: path 1 (A, gold, B, silver), path 2 (C, gold, D, silver), and path 3 (E, gold, F silver)
F. Surface Catalytic Reduction of PNTP

Figure S7. Proposed Reaction Mechanism for Surface Catalytic Reduction of PNTP.
G. Direct Hydrogenation of adsorbed PNTP

Figure S8. Proposed Reaction Mechanism for Direct Hydrogenation of PNTP. M denotes metallic clusters of Ag5 and Au5 here.

\[
\begin{align*}
M_5\text{-PNTP} + H_2 & \rightarrow M_5\text{-PNSTP} + H_2O & (S2A1) \\
M_5\text{-PNTP} + H_2 & \rightarrow M_5\text{-PHATP} & (S2A2) \\
M_5\text{-PHATP} + H_2 & \rightarrow M_5\text{-PATP} + H_2O & (S2A3) \\
M_5\text{-DMAOB-M}_5 + H_2 & \rightarrow M_5\text{-DMAB-M}_5 + H_2O & (S2A4) \\
M_5\text{-DMAB-M}_5 + H_2 & \rightarrow M_5\text{-DMHAB-M}_5 & (S2A5) \\
M_5\text{-DMHAB-M}_5 + H_2 & \rightarrow 2M_5\text{-PATP} & (S2A6)
\end{align*}
\]

Table S2. Calculated Gibbs Free Energies for Hydrogenation of PNTP on Gold and Silver

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta G / \text{kcal\cdot mol}^{-1})</th>
<th>(E_a / \text{kcal\cdot mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td>S2-1</td>
<td>-27.16</td>
<td>-27.21</td>
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<tr>
<td>S2-2</td>
<td>-16.12</td>
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<td>S2-3</td>
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<td>S2-4</td>
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<td>S2-5</td>
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<td>-8.56</td>
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<tr>
<td>S2-6</td>
<td>-42.39</td>
<td>-43.28</td>
</tr>
</tbody>
</table>

Figure S9 presents the potential energy curves for hydrogenation of PNTP in different pathways. The calculated \(\Delta G\) and \(E_a\) for reaction S2-1 to S2-6 are listed in Table S2.
In the direct route, the initial step of reduction of PNTP is a hydrogen abstraction to form PNTP(2H). The activation energy for this step is about 58 kcal/mol. PNTP(2H) then loses one molecule of water to produce PNSTP. PNSTP is subsequently reduced to PHATP through PNSTP(H). The activation energy of TS2 is about 44 kcal/mol. The N-O bond of PHATP breaks to produce PATP(H). The activation energy of N-O bond cleavage is about 50 kcal/mol. The final step is formation of PATP from PATP(H). This hydrogen abstraction has a relative low activation energy of about 28 kcal/mol.

The condensation route starts from the ring coupling product DMAOB. DMAOB abstracts hydrogen to produce DMAOB(H) radical, which reacts with the left hydrogen atom to produce DMAB. The activation energy of TS4 is about 62 kcal/mol. DMAB undergoes subsequent hydrogenation reaction to form DMHAB. The activation energy of TS5 is lower than TS4, about 47 kcal/mol. Cleavage of N-N bond in DMHAB produces two molecules free radical PATP(H), which is finally reduced to PATP. The Gibbs free energies and activation energies of involved reactions are listed in Table S1. DMAB is not a stable product during PNTP reduction.

Figure S9. Potential energy surfaces of hydrogenation of PNTP through direct pathway on gold (A) and silver (B) and condensation pathway on gold (C) and silver (D)
H. Reference


