Enhanced catalytic application of Au@polyphenol-metal nanocomposite synthesized by a facile and green method

Supplementary Information
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EXPERIMENTAL SECTION

Chemicals
Hydrogen tetrachloroaurate hydrate (HAuCl4·4H2O), ferric chloride hexahydrate (FeCl3·6H2O), 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), 4-nitrophenol (4-NP), and sodium hydrate (NaBH4) were purchased from Sinopharm Chemistry Reagent Co. Ltd. (Beijing, China). Tannic acid (TA), (-)-Epigallocatechin gallate (EGCG), and gallic acid (GA) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification. Ultrapure water was prepared in the laboratory using a Milli-Q SP reagent water system from Millipore (Milford, MA).

Synthesis of core-shell Au@ployphenol-Fe nanocatalyst
Au NPs were first prepared by simply mixing 1 mL of HAuCl4·4H2O (1mM) with 5 μL of TA (40 mg mL⁻¹) at room temperature. The suspension was vigorously mixed by a vortex mixer until the solution color changed red and kept constant. The obtained Au NPs were collected by centrifugation (10000 r min⁻¹) and washed with water to remove excess TA. To fabricate Au@ployphenol-Fe nanocatalyst, 10 μL of FeCl3·6H2O (1 mg mL⁻¹) was added into the 0.5 mL of Au NPs solution with a 30 s of vigorous mixing, followed by the addition of 10 μL of TA (4 mg mL⁻¹) with another 30 s mixing. After mingling of the above mixture with 0.5 mL Tris-HCl (pH = 8.5), the products were recovered by centrifugation and rinsed with water two times. The layer thickness can be controlled by selectively repeating the above cycle. For the assembly of other polyphenols-Fe layers, the synthetic procedures were same as described above except that EGCG and GA were used in place of TA at same concentration.

Catalytic reduction of 4-NP
The reduction of 4-NP in the presence of NaBH₄ was carried out to investigate the catalytic activity of the catalyst. Typically, 2 mL of deionized water, 1.0 mL of fresh NaBH₄ (0.2 M), and 0.1 mL 4-NP (5 mM) were added into a quartz cuvette in sequence, followed by the addition of 0.05 mL of catalyst (2 mM Au) to the mixture. The reaction progress was monitored by UV-vis spectroscopy at a certain time interval to obtain the successive information. When conduct the pH-dependent experiments, various buffer systems were applied to adjust the pH value: pH ~ 2, glycine - HCl (0.2 M); pH ~ 5.0, Na₂HPO₄ (0.2 M) - citric acid (0.1 M); pH ~ 8.5, Tris - HCl (10 mM).

Characterization
The size and morphology of the synthesized materials were surveyed by H-7500 transmission electron microscope (TEM, Tokyo, Japan) and Tecnai G2 F20 HRTEM with an energy dispersive X-ray spectrometry (HRTEM-EDX, FEI, Netherlands). X-Ray photoelectron spectroscopy (XPS) measurements were conducted by applying a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al Kα radiation (1486.6 eV). Zeta-potential measurements were conducted in water by using a Zetasizer Nano ZS (Malvern). UV-vis absorption tests were carried out on a 4802S UV-vis spectrophotometer (Shanghai Unico, China).
**Fig. S1** TEM image of bare Au NPs.

**Fig. S2** UV-vis spectra of bare Au NPs, Au@TA-Fe composites with 1, 2, and 3 assembly cycles. The inset shows the color of the corresponding solution.
Fig. S3 XPS spectrum of O 1s core-level.

Fig. S4 XPS spectrum of Au 4f core-level.
Fig. S5 pH-responsive character of TA-Fe$^{3+}$ layer.
**Fig. S6** Rate constant $k$ of different reuse cycle.

**Fig. S7** TEM image of Au@TA-Fe nanocatalyst after used.

**Table S1** Comparison of catalytic activity for 4-NP reduction by Au based nanocatalysts
<table>
<thead>
<tr>
<th>Catalyst structure</th>
<th>$k$ (min$^{-1}$)</th>
<th>$k_{\text{corr}}$ (min$^{-1}$ µmol$^{-1}$)</th>
<th>Ref. No.</th>
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</thead>
<tbody>
<tr>
<td>Au NPs/SiO$_2$-NTs</td>
<td>0.64</td>
<td>0.638</td>
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<tr>
<td>Au NPs@[Na]-HAMS</td>
<td>0.31</td>
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<td>2</td>
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<tr>
<td>AuNPs/Fe$_3$O$_4$-NPs</td>
<td>0.01</td>
<td>0.36</td>
<td>3</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$-Au@mSiO$_2$</td>
<td>0.35</td>
<td>1.05</td>
<td>4</td>
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<tr>
<td>Au NPs/TWEEN/GO</td>
<td>0.25</td>
<td>1.16</td>
<td>5</td>
</tr>
<tr>
<td>Au NPs/GO</td>
<td>0.18</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Au@MIL-100(Fe)</td>
<td>0.33</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Au-EGCG-CF</td>
<td>0.14</td>
<td>0.14</td>
<td>8</td>
</tr>
<tr>
<td>Dumbbell-like Fe$_3$O$_4$-Au</td>
<td>0.63</td>
<td>0.33</td>
<td>9</td>
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<td>PLAL-AuNPs/CeO$_2$-NTs</td>
<td>0.14</td>
<td>0.84</td>
<td>10</td>
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<td>Au@TA-Fe</td>
<td>0.37</td>
<td>3.7</td>
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References: