In situ forming metal nanoparticles systems for catalytic reduction of nitroaromatic compounds

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Electronic Supplementary Information (ESI)
**Fig. S1** Comparison of time-dependent UV-vis absorption spectra of 4-NP in the presence of NaBH$_4$ and metal ions (Cu$^{2+}$, Ag$^+$, AuCl$_4^-$, Co$^{2+}$ and Ni$^{2+}$). [4-NP] = 0.1 mM; [NaBH$_4$] = 25 mM; [Metal ions] = 2 µM; T = 22.4°C.

**Fig. S2** The size distribution of *in situ* formed Cu (a), Ag (b) and Au (c) nanoparticles obtained from TEM experiments.
**Fig. S3** The size distribution of *in situ* formed Ni nanoparticles obtained from TEM experiments.

**Fig. S4** XRD patterns of the *in situ* formed Co and Ni nanoparticles.
**Table S1**: The reaction time for fitting $\ln(C_t/C_0)$ versus $t$ to obtain $K$.

<table>
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<tr>
<th></th>
<th>Time for Fig. 4/s</th>
<th>Time for Fig. 5/s</th>
<th>Time for Fig. 6/s</th>
<th>Time for Fig. 10/s</th>
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<tr>
<td><strong>Cu</strong></td>
<td>80–320(10 mM)</td>
<td>20–200(30 mM)</td>
<td>30–190(50 mM)</td>
<td>160–450(60 mM)</td>
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<td></td>
<td>20–140(0.13 mM)</td>
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<tr>
<td><strong>Ag</strong></td>
<td>200–400(10 mM)</td>
<td>190–300(20 mM)</td>
<td>190–320(30 mM)</td>
<td>130–250(40 mM)</td>
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<tr>
<td></td>
<td>190–300(0.1 mM)</td>
<td>140–210(0.13 mM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Au</strong></td>
<td>50–400(5 mM)</td>
<td>50–200(10 mM)</td>
<td>50–200(70 μM)</td>
<td>50–200(0.1 mM)</td>
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<tr>
<td></td>
<td>30–150(20 mM)</td>
<td>30–150(0.13 mM)</td>
<td>40–170(0.13 mM)</td>
<td>40–160(50 μM)</td>
</tr>
<tr>
<td><strong>Co</strong></td>
<td>50–170(10 mM)</td>
<td>30–150(20 mM)</td>
<td>30–150(30 mM)</td>
<td>30–150(300 μM)</td>
</tr>
<tr>
<td></td>
<td>30–150(0.13 mM)</td>
<td>40–170(0.13 mM)</td>
<td>40–170(0.13 mM)</td>
<td>40–160(100 μM)</td>
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<tr>
<td><strong>Ni</strong></td>
<td>720–920(20 mM)</td>
<td>230–550(70 μM)</td>
<td>1070–1180(30 μM)</td>
<td>550–800(20 μM)</td>
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<td>550–800(0.1 mM)</td>
<td>550–800(0.1 μM)</td>
<td>550–800(47 μM)</td>
<td>280–360(30 μM)</td>
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<td>370–550(40 mM)</td>
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<td>550–800(80 μM)</td>
<td>160–210(35 μC)</td>
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<td></td>
<td>330–490(60 mM)</td>
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**Table S2**: The diameters of *in situ* formed metal nanoparticles obtained from Scherrer equation.

<table>
<thead>
<tr>
<th></th>
<th>$\beta/^{\circ}$</th>
<th>$\theta/^{\circ}$</th>
<th>D/nm</th>
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<tr>
<td><strong>Cu</strong></td>
<td>0.235</td>
<td>19.104</td>
<td>27.8</td>
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<tr>
<td><strong>Ag</strong></td>
<td>0.304</td>
<td>21.695</td>
<td>8.8</td>
</tr>
<tr>
<td><strong>Au</strong></td>
<td>0.6</td>
<td>19.18</td>
<td>13.8</td>
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</table>
Fig. S5 Time-dependent UV-vis absorption spectra of 2-NP in the presence of NaBH$_4$ and Cu$^{2+}$.  [2-NP] = 2×10$^{-4}$ M; [NaBH$_4$] = 2×10$^{-2}$ M; [Cu$^{2+}$] = 2.7×10$^{-6}$ M; T = 24 °C.  The time interval is 60 seconds between two sequential lines.

Fig. S6 Time-dependent UV-vis absorption spectra of 2-NP in the presence of NaBH$_4$ and Ag$^+$.  [2-NP] = 2×10$^{-4}$ M; [NaBH$_4$] = 2×10$^{-2}$ M; [Ag$^+$] = 1.2×10$^{-6}$ M; T = 24 °C.  The time interval is 60 seconds between two sequential lines.
**Fig. S7** Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of NaBH₄ and AuCl₄⁻. [2-NP] = 2×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [AuCl₄⁻] = 6.7×10⁻⁷ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S8** Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of NaBH₄ and Co²⁺. [2-NP] = 2×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Co²⁺] = 1×10⁻⁴ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S9** Time-dependent UV-vis absorption spectra of 2-NP in the presence of NaBH$_4$ and Ni$^{2+}$. [2-NP] = 2×10^{-4} M; [NaBH$_4$] = 2×10^{-2} M; [Ni$^{2+}$] = 4.7×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines. The time interval is 60 seconds between two sequential lines.

**Fig. S10** Time-dependent UV-vis absorption spectra of 3-NP in the presence of NaBH$_4$ and Cu$^{2+}$. [3-NP] = 2×10^{-4} M; [NaBH$_4$] = 2×10^{-2} M; [Cu$^{2+}$] = 2×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines. The time interval
Fig. S11 Time-dependent UV-vis absorption spectra of 3-NP in the presence of NaBH₄ and Ag⁺. [3-NP] = 2×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Ag⁺] = 1×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S12 Time-dependent UV-vis absorption spectra of 3-NP in the presence of NaBH₄ and AuCl₄⁻. [3-NP] = 2×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [AuCl₄⁻] = 6.7×10⁻⁷ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S13 Time-dependent UV-vis absorption spectra of 3-NP in the presence of NaBH₄ and Co²⁺. [3-NP] = 2×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Co²⁺] = 3.3×10⁻⁵ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S14 Time-dependent UV-vis absorption spectra of 3-NP in the presence of NaBH₄ and Ni²⁺. [3-NP] = 2×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Ni²⁺] = 4×10⁻⁵ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S15** Time-dependent UV-vis absorption spectra of 2,4-DNP in the presence of NaBH$_4$ and Cu$^{2+}$. [2,4-DNP] = $1 \times 10^{-4}$ M; [NaBH$_4$] = $2 \times 10^{-2}$ M; [Cu$^{2+}$] = $2 \times 10^{-6}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S16** Time-dependent UV-vis absorption spectra of 2,4-DNP in the presence of NaBH$_4$ and Ag$^+$. [2,4-DNP] = $1 \times 10^{-4}$ M; [NaBH$_4$] = $2 \times 10^{-2}$ M; [Ag$^+$] = $1 \times 10^{-6}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S17** Time-dependent UV-visible absorption spectra of 2,4-DNP in the presence of NaBH₄ and AuCl₄⁻: [2,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [AuCl₄⁻] = 6.7×10⁻⁷ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S18** Time-dependent UV-visible absorption spectra of 2,4-DNP in the presence of NaBH₄ and Co²⁺: [2,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Co²⁺] = 1×10⁻⁴ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S19 Time-dependent UV-vis absorption spectra of 2,4-DNP in the presence of NaBH$_4$ and Ni$^{2+}$. [2,4-DNP] = 1×10$^{-4}$ M; [NaBH$_4$] = 2×10$^{-2}$ M; [Ni$^{2+}$] = 4.7×10$^{-5}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S20 Time-dependent UV-vis absorption spectra of 2,5-DNP in the presence of NaBH$_4$ and Cu$^{2+}$. [2,5-DNP] = 1×10$^{-4}$ M; [NaBH$_4$] = 2×10$^{-2}$ M; [Cu$^{2+}$] = 2×10$^{-6}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S21 Time-dependent UV-vis absorption spectra of 2,5-DNP in the presence of NaBH₄ and Ag⁺. [2,5-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Ag⁺] = 1.3×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S22 Time-dependent UV-vis absorption spectra of 2,5-DNP in the presence of NaBH₄ and AuCl₄⁻. [2,5-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [AuCl₄⁻] = 6.7×10⁻⁷ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S23 Time-dependent UV-vis absorption spectra of 2,5-DNP in the presence of NaBH$_4$ and Co$^{2+}$. [2,5-DNP] = 1×10$^{-4}$ M; [NaBH$_4$] = 4×10$^{-2}$ M; [Co$^{2+}$] = 1×10$^{-4}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S24 Time-dependent UV-vis absorption spectra of 2,5-DNP in the presence of NaBH$_4$ and Ni$^{2+}$. [2,5-DNP] = 1×10$^{-4}$ M; [NaBH$_4$] = 4×10$^{-2}$ M; [Ni$^{2+}$] = 4.7×10$^{-5}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S25 Time-dependent UV-vis absorption spectra of 3,4-DNP in the presence of NaBH₄ and Cu²⁺. [3,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Cu²⁺] = 2×10⁻⁶ M; 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S26 Time-dependent UV-vis absorption spectra of 3,4-DNP in the presence of NaBH₄ and Ag⁺. [3,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [Ag⁺] = 1×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S27** Time-dependent UV-vis absorption spectra of 3,4-DNP in the presence of NaBH₄ and AuCl₄⁻. [3,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 2×10⁻² M; [AuCl₄⁻] = 6.7×10⁻⁷ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S28** Time-dependent UV-vis absorption spectra of 3,4-DNP in the presence of NaBH₄ and Co²⁺. [3,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 4×10⁻² M; [Co²⁺] = 1.4×10⁻⁴ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S29** Time-dependent UV-vis absorption spectra of 3,4-DNP in the presence of NaBH₄ and Ni²⁺. [3,4-DNP] = 1×10⁻⁴ M; [NaBH₄] = 4×10⁻² M; [Ni²⁺] = 4.7×10⁻⁵ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S30** Time-dependent UV-vis absorption spectra of 2,4,6-tNP in the presence of NaBH₄ and Cu²⁺. [2,4,6-tNP] = 5×10⁻⁵ M; [NaBH₄] = 3×10⁻² M; [Cu²⁺] = 6×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S31** Time-dependent UV-vis absorption spectra of 2,4,6-tNP in the presence of NaBH₄ and Ag⁺. [2,4,6-tNP] = 5×10⁻⁵ M; [NaBH₄] = 3×10⁻² M; [Ag⁺] = 3×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S32** Time-dependent UV-vis absorption spectra of 2,4,6-tNP in the presence of NaBH₄ and AuCl₄⁻. [2,4,6-tNP] = 5×10⁻⁵ M; [NaBH₄] = 3×10⁻² M; [AuCl₄⁻] = 1.7×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S33 Time-dependent UV-vis absorption spectra of 2,4,6-tNP in the presence of NaBH$_4$ and Co$^{2+}$. [2,4,6-tNP] = 5×10$^{-5}$ M; [NaBH$_4$] = 6×10$^{-2}$ M; [Co$^{2+}$] = 1.5×10$^{-4}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S34 Time-dependent UV-vis absorption spectra of 2,4,6-tNP in the presence of NaBH$_4$ and Ni$^{2+}$. [2,4,6-tNP] = 5×10$^{-5}$ M; [NaBH$_4$] = 6×10$^{-2}$ M; [Ni$^{2+}$] = 4×10$^{-5}$ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
**Fig. S35** Time-dependent UV-vis absorption spectra of 2,4,6-tNT in the presence of NaBH₄ and Cu²⁺. [2,4,6-tNT] = 5×10⁻⁵ M; [NaBH₄] = 2×10⁻² M; [Cu²⁺] = 2×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

**Fig. S36** Time-dependent UV-vis absorption spectra of 2,4,6-tNT in the presence of NaBH₄ and Ag⁺. [2,4,6-tNT] = 5×10⁻⁵ M; [NaBH₄] = 2×10⁻² M; [Ag⁺] = 1×10⁻⁶ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S37 Time-dependent UV-vis absorption spectra of 2,4,6-tNT in the presence of NaBH₄ and AuCl₄⁻. [2,4,6-tNT] = 5×10⁻⁵ M; [NaBH₄] = 2×10⁻² M; [AuCl₄⁻] = 6.7×10⁻⁷ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S38 Time-dependent UV-vis absorption spectra of 2,4,6-tNT in the presence of NaBH₄ and Co²⁺. [2,4,6-tNT] = 5×10⁻⁵ M; [NaBH₄] = 4×10⁻² M; [Co²⁺] = 1×10⁻⁴ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.
Fig. S39 Time-dependent UV-vis absorption spectra of 2,4,6-tNT in the presence of NaBH₄ and Ni²⁺. [2,4,6-tNT] = 5×10⁻⁵ M; [NaBH₄] = 4×10⁻² M; [Ni²⁺] = 3.3×10⁻⁵ M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

Fig. S40 Time-dependent UV-vis absorption spectra of 2,4,6-tNT in the presence of NaBH₄ only. [2,4,6-tNT] = 5×10⁻⁵ M; [NaBH₄] = 4×10⁻² M; T = 24 °C. The time interval is 60 seconds between two sequential lines.