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

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Electronic Supplementary Information (ESI)

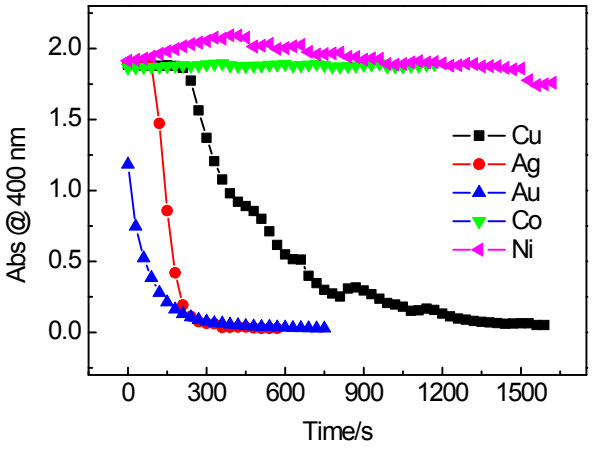

Fig. S1 Comparison of time-dependent UV-*vis* absorption spectra of 4-NP in the presence of $NaBH_4$ and metal ions (Cu^{2+}, Ag^{+}, $AuCl_4^{-}$, Co^{2+} and Ni^{2+}). [4-NP] = 0.1 mM; [$NaBH_4$] = 25 mM; [Metal ions] = 2 μM; T = 22.4°C.

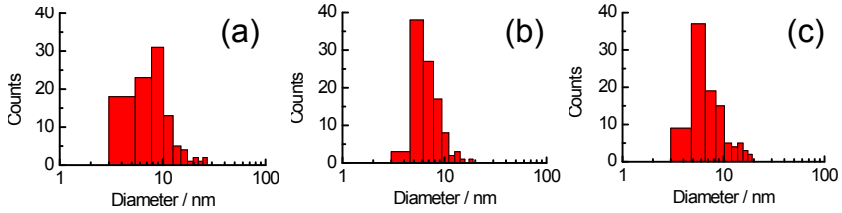

Fig. S2 The size distribution of *in situ* formed Cu (a), Ag (b) and Au (c) nanoparticles obtained from TEM experiments.

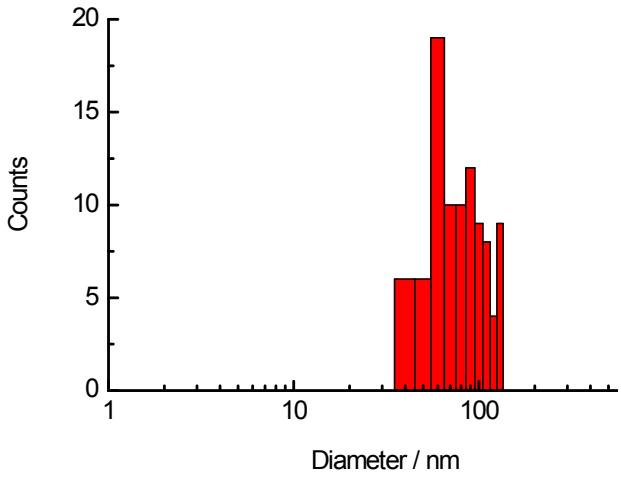

Fig. S3 The size distribution of *in situ* formed Ni nanoparticles obtained from TEM experiments.

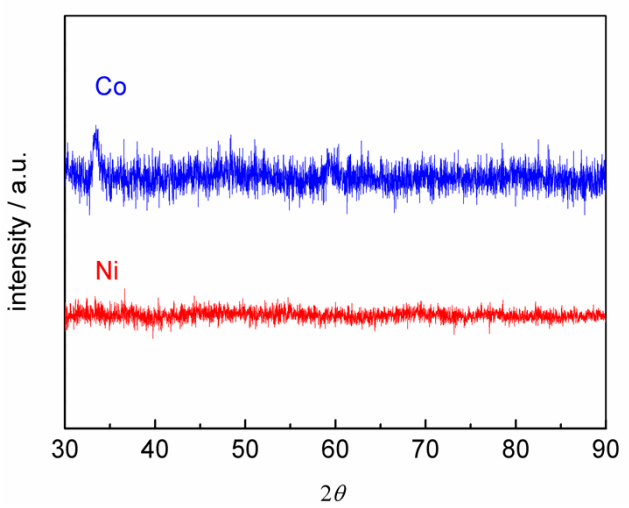

Fig. S4 XRD patterns of the *in situ* formed Co and Ni nanoparticles.

Table S1: The reaction time for fitting $\ln(C_t/C_0)$ versus t to obtain K.

	Time for Fig. 4/s		Time for Fig. 5/s		Time for Fig. 6/s		Time for Fig. 10/s
Cu	80~320(10 mM) 20~200(30 mM) 30~190(50 mM） 160~450(60 mM)	Cu	30~180(70 μM) 20~200(0.1 mM) 20~140(0.13 mM)	Cu	70~250(1 μM) 20~200(2 μM) 0~40(4 μM)	Cu	20~200(24 °C) 0~80(30 °C) 0~40(35 °C)
Ag	200~400(10 mM) 190~300(20 mM) 190~320(30 mM) 130~250(40 mM)	Ag	250~350(70 μM) 190~300(0.1 mM) 140~210(0.13 mM)	Ag	400~510(0.5 μM) 190~300(1 μM) 0~30(2 μM)	Ag	80~180(19 °C) 190~300(24°C) 80~120(29 °C)
Au	50~400(5 mM) 30~300(10 mM) 50~200(20 mM) 60~200(30 mM)	Au	50~200(70 μM) 50~200(0.1 mM) 10~180(0.13 mM)	Au	40~300(0.3 μM) 50~200(0.67 μM) 10~100(1 μM)	Au	50~200(24°C) 10~200(30°C) 10~100(35°C)
Co	50~170(10 mM) 30~150(20 mM) 30~150(30 mM) 30~150(40 mM)	Co	30~150(70 μM) 30~150(0.1 mM) 40~170(0.13 mM)	Co	40~160(50 μM) 30~150(100 μM) 20~110(150 μM)	Co	30~150(24°C) 30~150(30°C) 0~80(35 °C)
Ni	720~920(20 mM) 550~800(30 mM) 370~550(40 mM) 330~490(60 mM)	Ni	230~550(70 μM) 550~800(0.1 mM) 250~450(0.13 mM)	Ni	1070~1180(30 μM) 550~800(47 μM) 390~550(80 μM)	Ni	550~800(24°C) 280~360(30°C) 160~210(35°C)

Table S2: The diameters of *in situ* formed metal nanoparticles obtained from Scherrer equation.

	β/°	θ/°	D/nm
Cu	0.235	19.104	27.8
Ag	0.304	21.695	8.8
Au	0.6	19.18	13.8

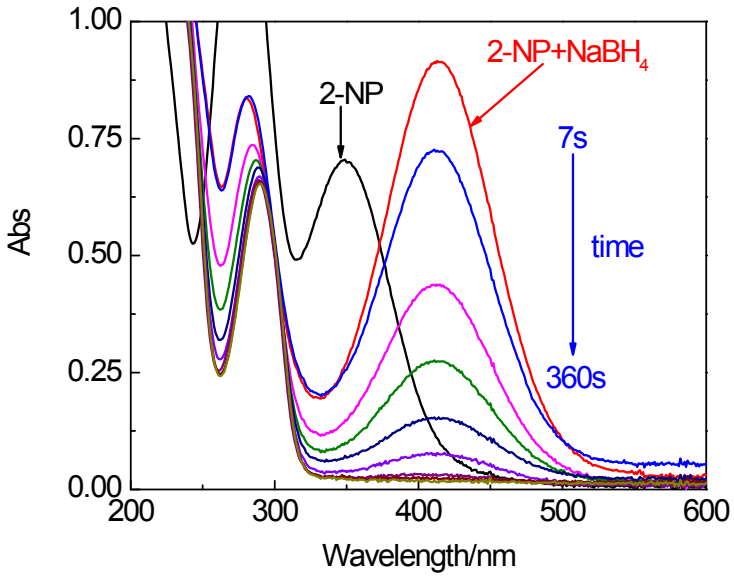

Fig. S5 Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of $NaBH_4$ and Cu^{2+}. [2-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Cu^{2+}] = 2.7×10^{-6} M; T = 24 ^{o}C. The time interval is 60 seconds between two sequential lines.

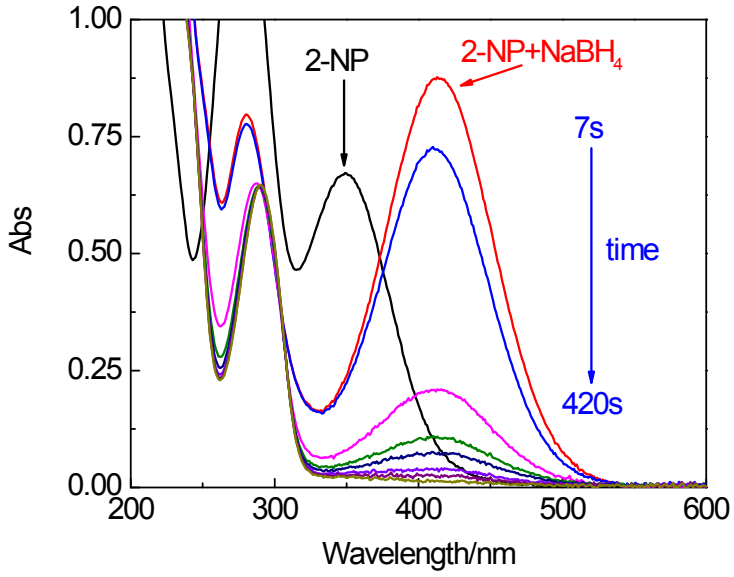

Fig. S6 Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of $NaBH_4$ and Ag^{+}. [2-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ag^{+}] = 1.2×10^{-6} M; T = 24 ^{o}C. The time interval is 60 seconds between two sequential lines.

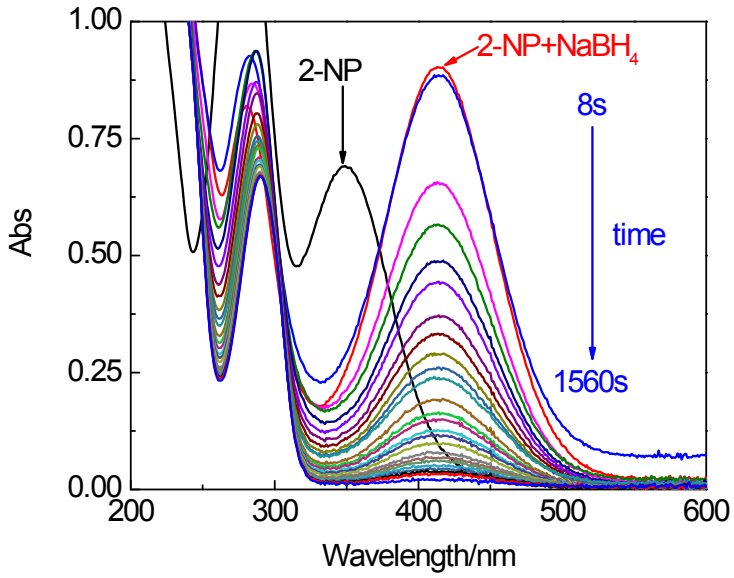

Fig. S7 Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of $NaBH_4$ and $AuCl_4^-$. [2-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [$AuCl_4^-$] = 6.7×10^{-7} M; T = 24 ^oC. The time interval is 60 seconds between two sequential lines.

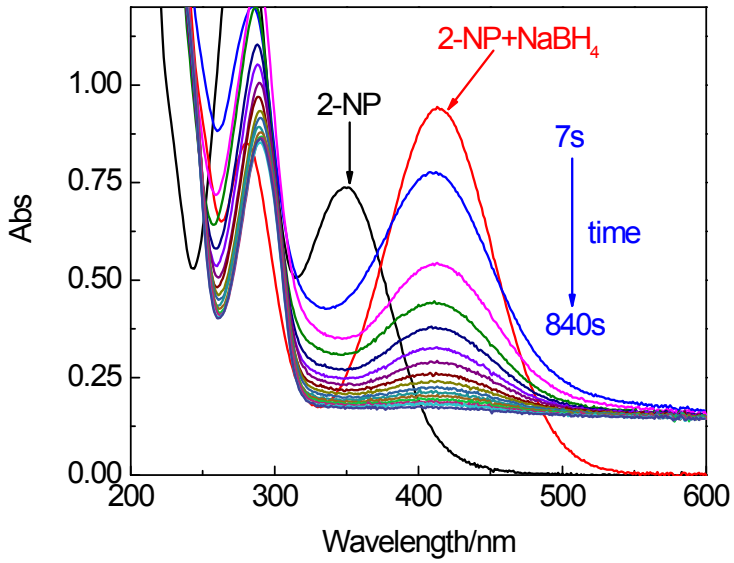

Fig. S8 Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of $NaBH_4$ and Co^{2+}. [2-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Co^{2+}] = 1×10^{-4} M; T = 24 ^oC. The time interval is 60 seconds between two sequential lines.

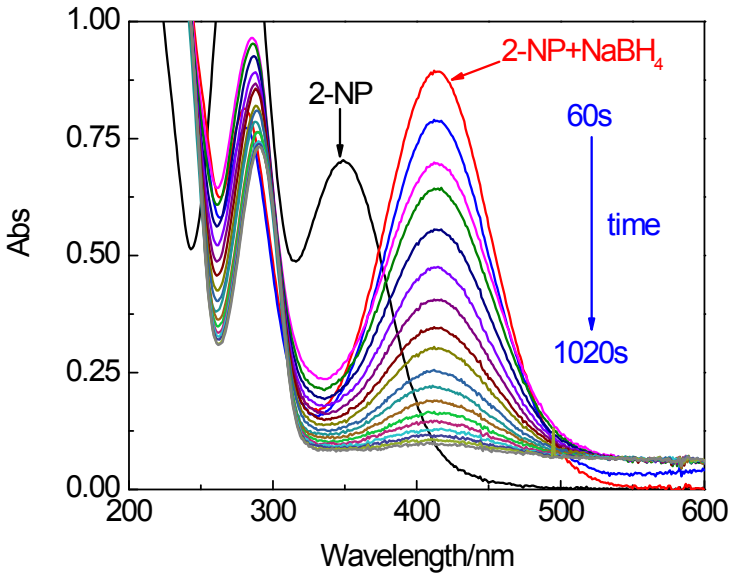

Fig. S9 Time-dependent UV-*vis* absorption spectra of 2-NP in the presence of $NaBH_4$ and Ni^{2+}. [2-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ni^{2+}] = 4.7×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines. The time interval is 60 seconds between two sequential lines.

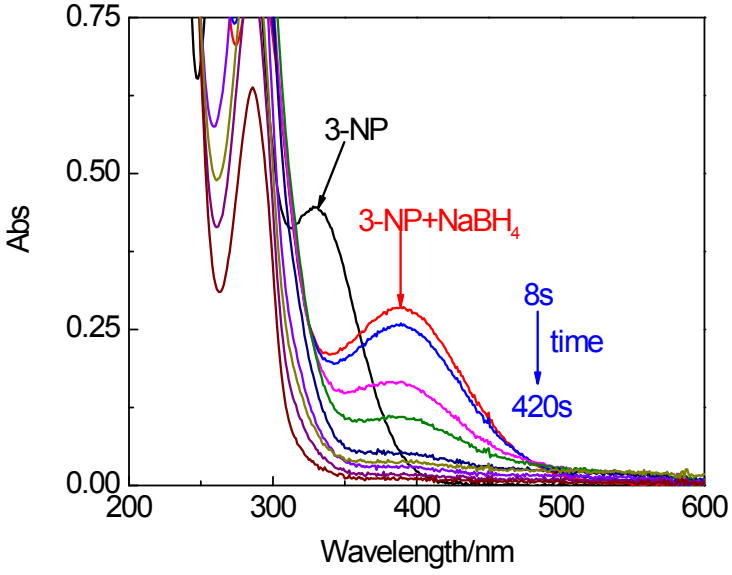

Fig. S10 Time-dependent UV-*vis* absorption spectra of 3-NP in the presence of $NaBH_4$ and Cu^{2+}. [3-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Cu^{2+}] = 2×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines. The time interval

is 60 seconds between two sequential lines.

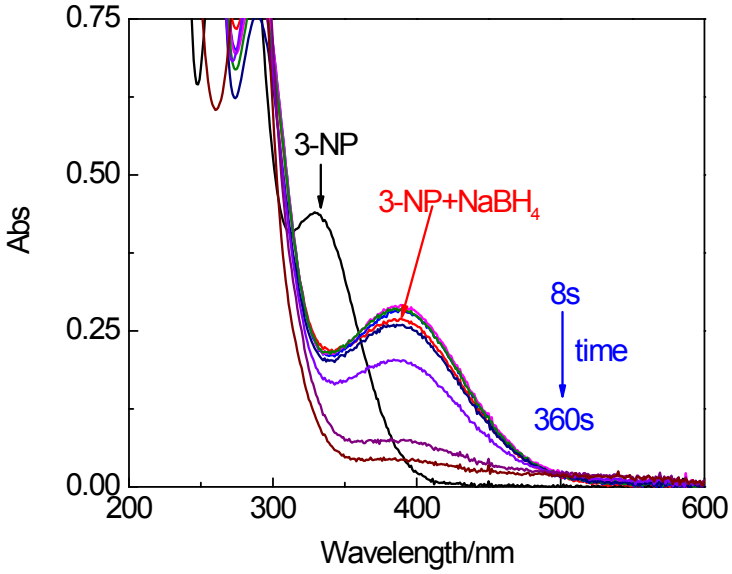

Fig. S11 Time-dependent UV-*vis* absorption spectra of 3-NP in the presence of $NaBH_4$ and Ag^+. [3-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ag^+] = 1×10^{-6} M; T = 24 ^oC. The time interval is 60 seconds between two sequential lines.

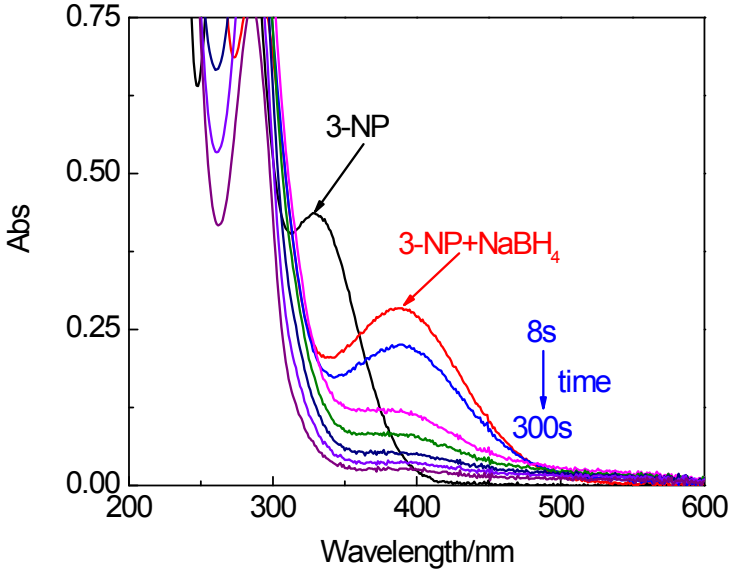

Fig. S12 Time-dependent UV-*vis* absorption spectra of 3-NP in the presence of $NaBH_4$ and $AuCl_4^-$. [3-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [$AuCl_4^-$] = 6.7×10^{-7} M; T = 24 ^oC. The time interval is 60 seconds between two sequential lines.

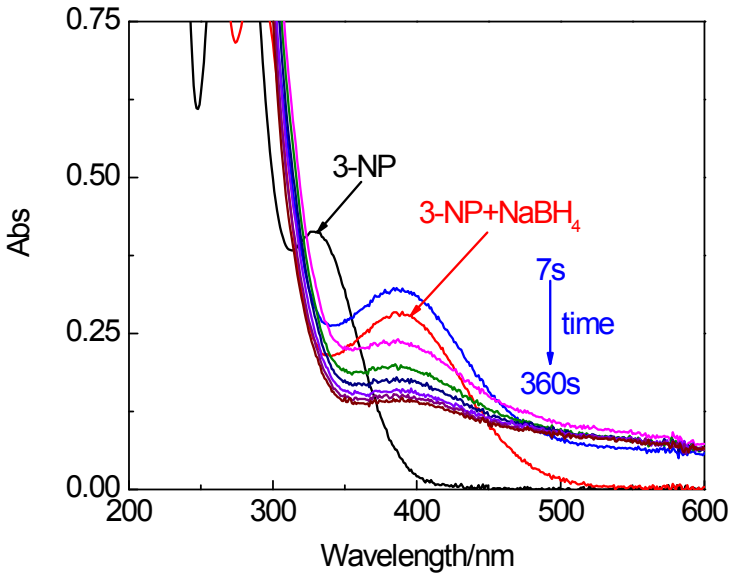

Fig. S13 Time-dependent UV-*vis* absorption spectra of 3-NP in the presence of $NaBH_4$ and Co^{2+}. [3-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Co^{2+}] = 3.3×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

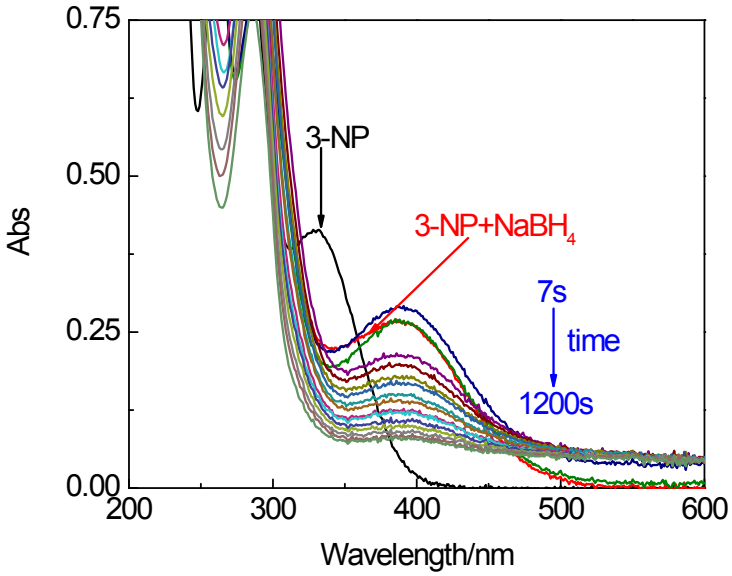

Fig. S14 Time-dependent UV-*vis* absorption spectra of 3-NP in the presence of $NaBH_4$ and Ni^{2+}. [3-NP] = 2×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ni^{2+}] = 4×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

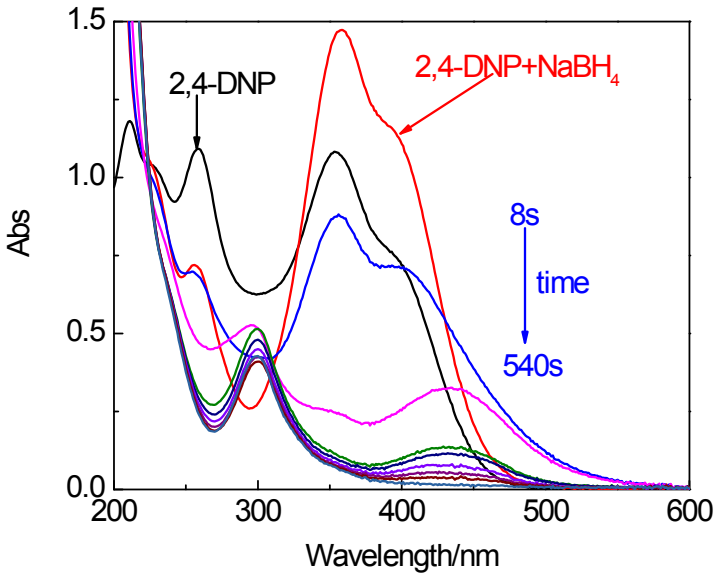

Fig. S15 Time-dependent UV-*vis* absorption spectra of 2,4-DNP in the presence of $NaBH_4$ and Cu^{2+}. [2,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Cu^{2+}] = 2×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

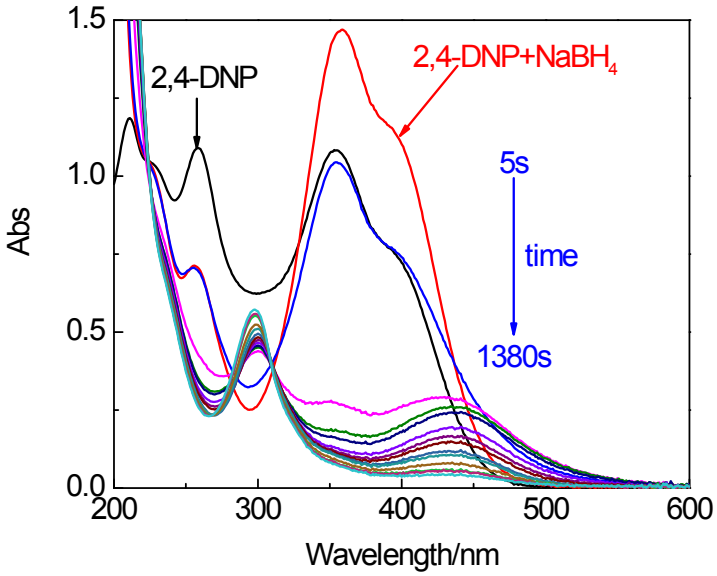

Fig. S16 Time-dependent UV-*vis* absorption spectra of 2,4-DNP in the presence of $NaBH_4$ and Ag^{+}. [2,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ag^{+}] = 1×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

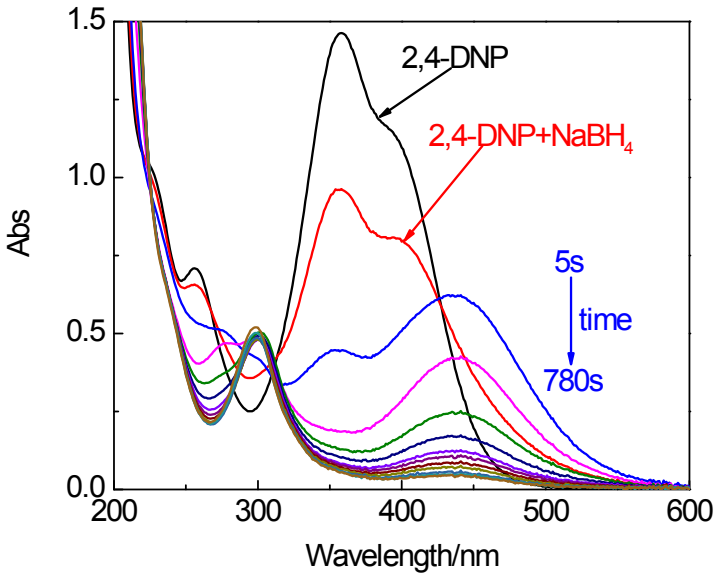

Fig. S17 Time-dependent UV-*vis* absorption spectra of 2,4-DNP in the presence of $NaBH_4$ and $AuCl_4^-$. [2,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [$AuCl_4^-$] = 6.7×10^{-7} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

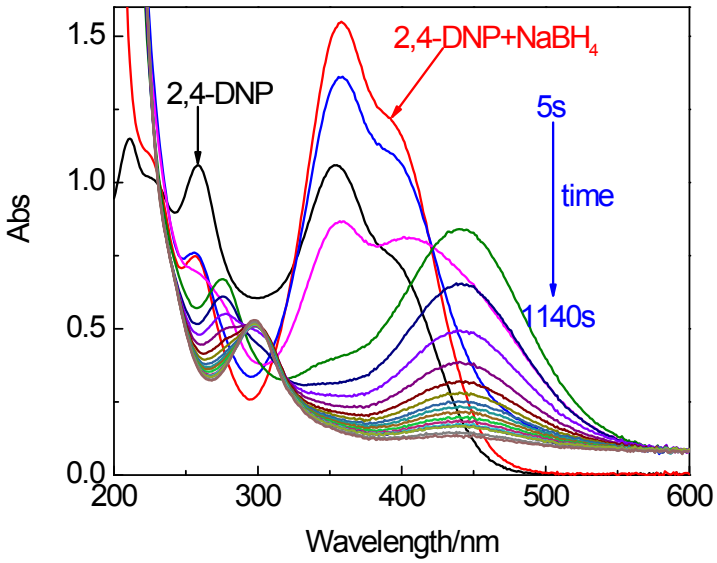

Fig. S18 Time-dependent UV-*vis* absorption spectra of 2,4-DNP in the presence of $NaBH_4$ and Co^{2+}. [2,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Co^{2+}] = 1×10^{-4} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

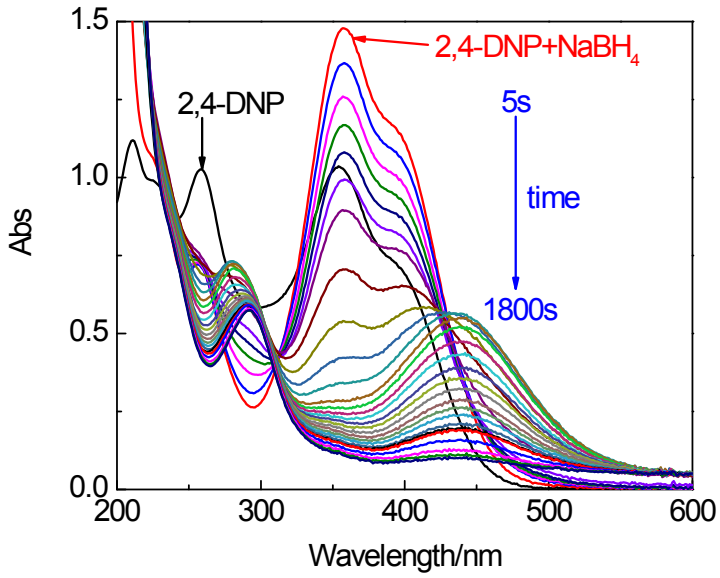

Fig. S19 Time-dependent UV-*vis* absorption spectra of 2,4-DNP in the presence of $NaBH_4$ and Ni^{2+}. [2,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ni^{2+}] = 4.7×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

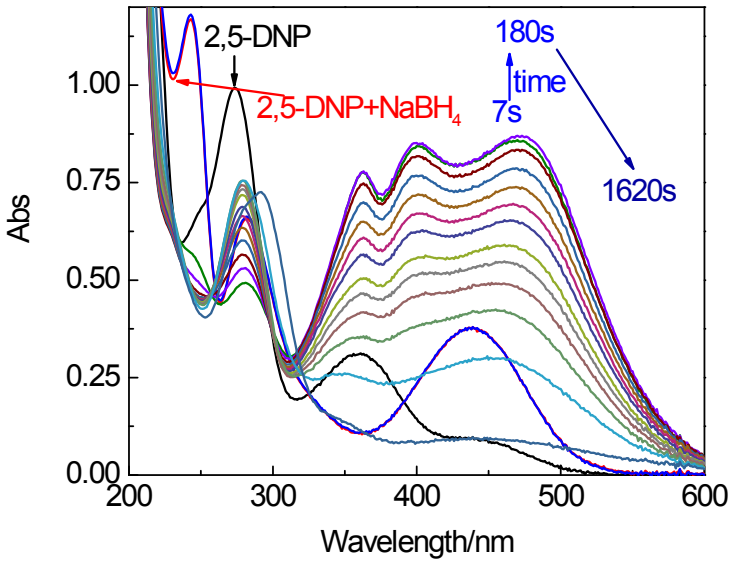

Fig. S20 Time-dependent UV-*vis* absorption spectra of 2,5-DNP in the presence of $NaBH_4$ and Cu^{2+}. [2,5-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Cu^{2+}] = 2×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

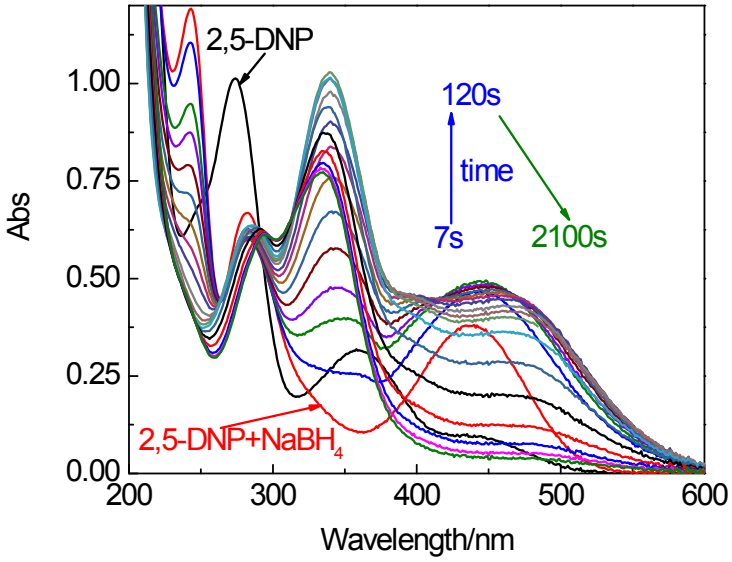

Fig. S21 Time-dependent UV-*vis* absorption spectra of 2,5-DNP in the presence of $NaBH_4$ and Ag^+. [2,5-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ag^+] = 1.3×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

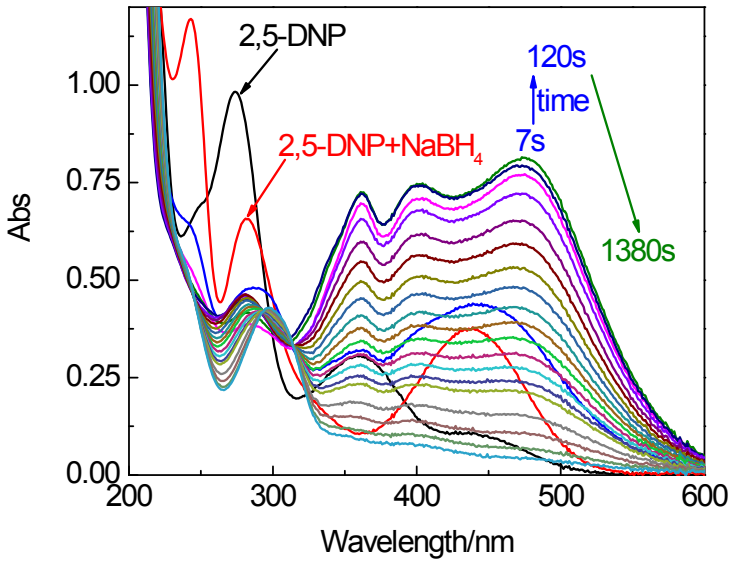

Fig. S22 Time-dependent UV-*vis* absorption spectra of 2,5-DNP in the presence of $NaBH_4$ and $AuCl_4^-$. [2,5-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [$AuCl_4^-$] = 6.7×10^{-7} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

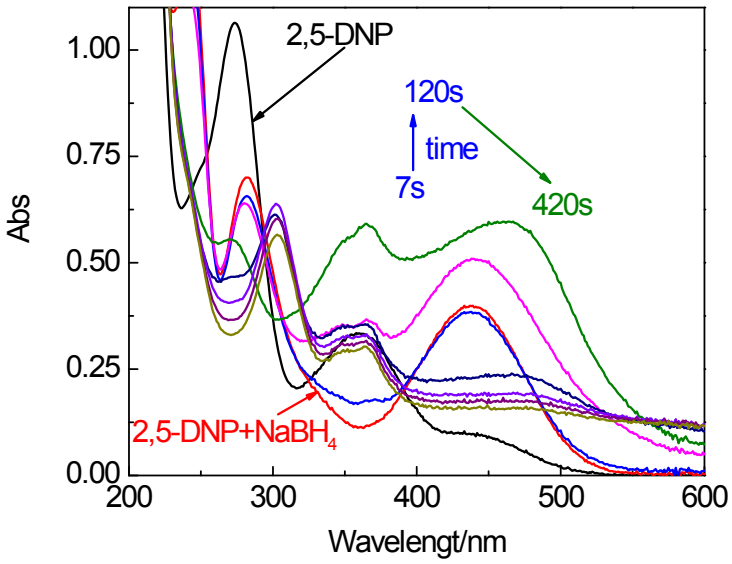

Fig. S23 Time-dependent UV-*vis* absorption spectra of 2,5-DNP in the presence of $NaBH_4$ and Co^{2+}. [2,5-DNP] = 1×10^{-4} M; [$NaBH_4$] = 4×10^{-2} M; [Co^{2+}] = 1×10^{-4} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

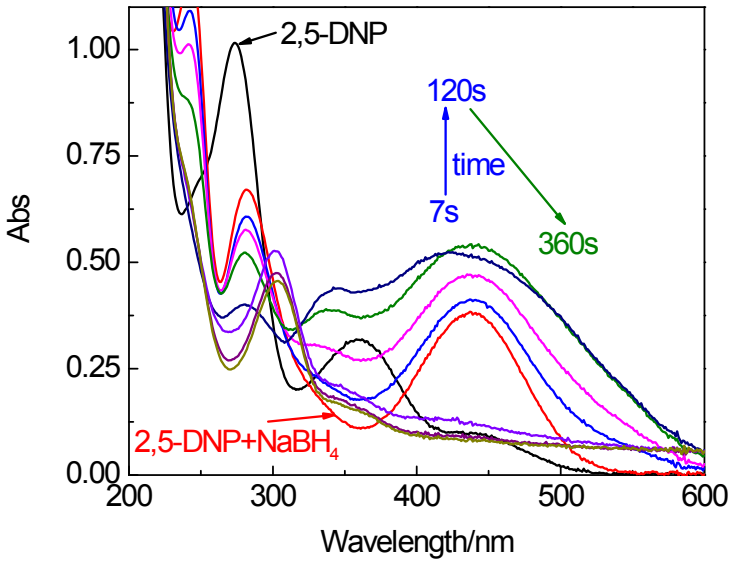

Fig. S24 Time-dependent UV-*vis* absorption spectra of 2,5-DNP in the presence of $NaBH_4$ and Ni^{2+}. [2,5-DNP] = 1×10^{-4} M; [$NaBH_4$] = 4×10^{-2} M; [Ni^{2+}] = 4.7×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

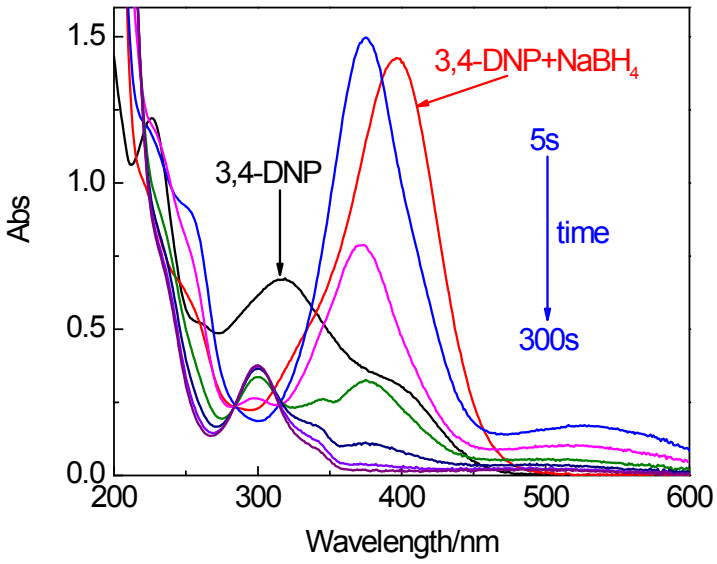

Fig. S25 Time-dependent UV-*vis* absorption spectra of 3,4-DNP in the presence of $NaBH_4$ and Cu^{2+}. [3,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Cu^{2+}] = 2×10^{-6} M; 24 °C. The time interval is 60 seconds between two sequential lines.

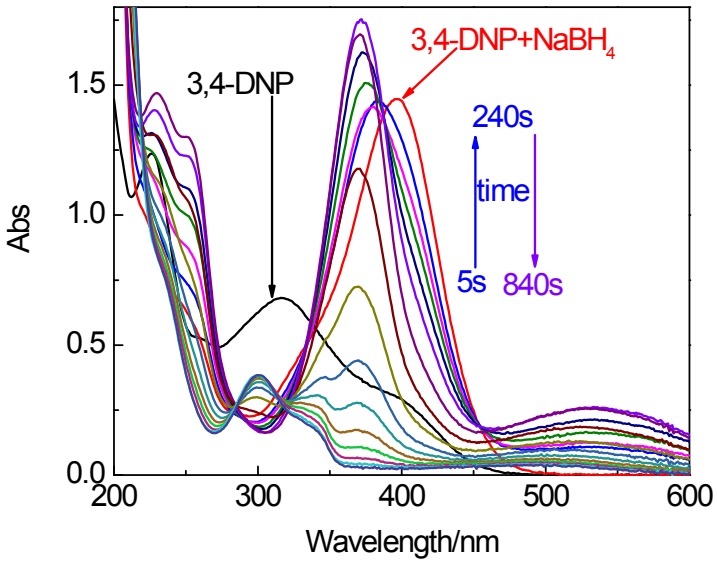

Fig. S26 Time-dependent UV-*vis* absorption spectra of 3,4-DNP in the presence of $NaBH_4$ and Ag^{+}. [3,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [Ag^{+}] = 1×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

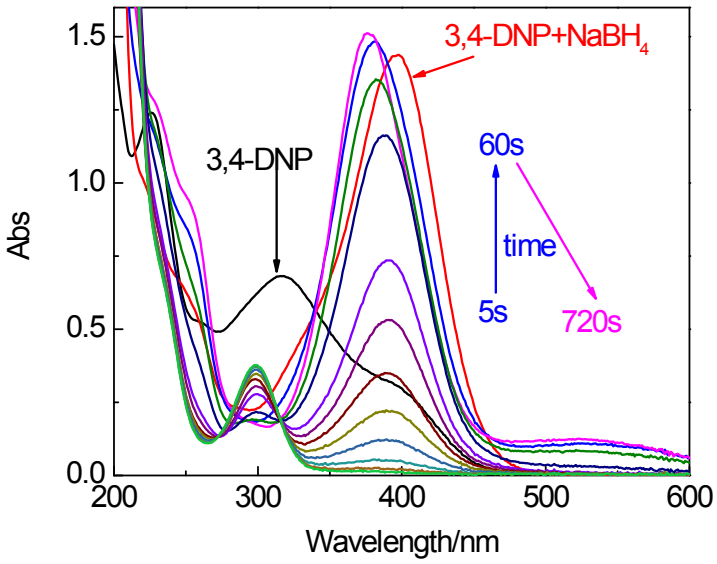

Fig. S27 Time-dependent UV-*vis* absorption spectra of 3,4-DNP in the presence of $NaBH_4$ and $AuCl_4^-$. [3,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 2×10^{-2} M; [$AuCl_4^-$] = 6.7×10^{-7} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

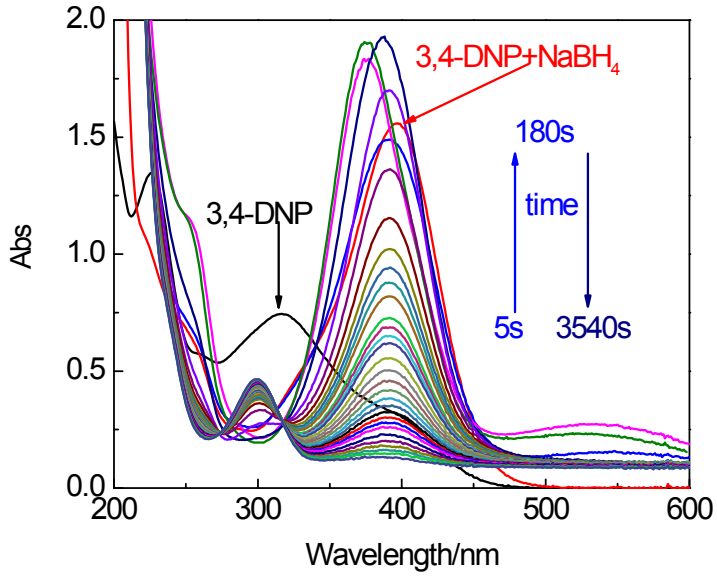

Fig. S28 Time-dependent UV-*vis* absorption spectra of 3,4-DNP in the presence of $NaBH_4$ and Co^{2+}. [3,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 4×10^{-2} M; [Co^{2+}] = 1.4×10^{-4} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

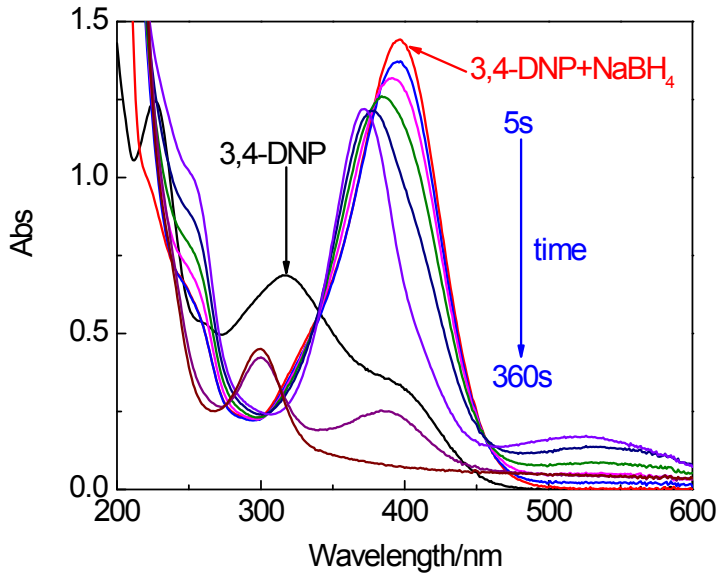

Fig. S29 Time-dependent UV-*vis* absorption spectra of 3,4-DNP in the presence of $NaBH_4$ and Ni^{2+}. [3,4-DNP] = 1×10^{-4} M; [$NaBH_4$] = 4×10^{-2} M; [Ni^{2+}] = 4.7×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

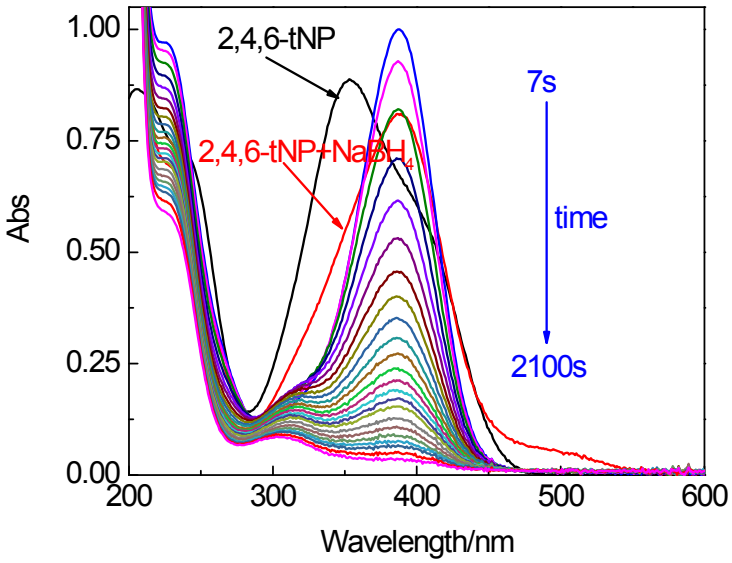

Fig. S30 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNP in the presence of $NaBH_4$ and Cu^{2+}. [2,4,6-tNP] = 5×10^{-5} M; [$NaBH_4$] = 3×10^{-2} M; [Cu^{2+}] = 6×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

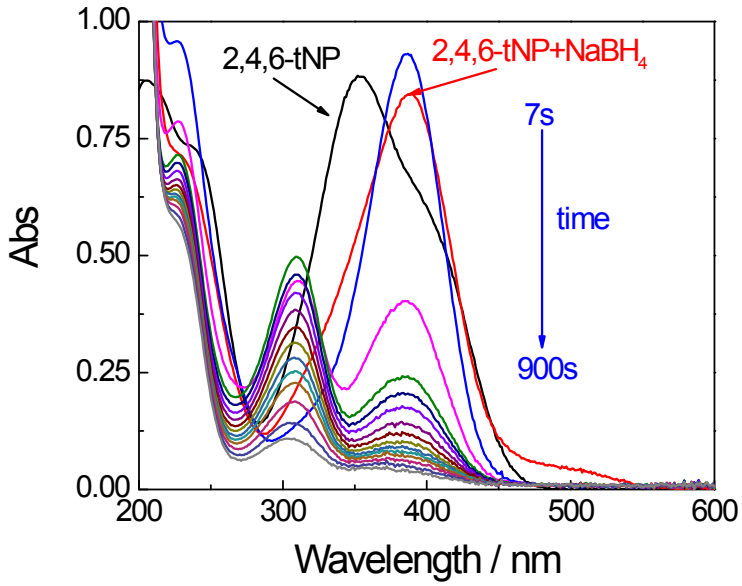

Fig. S31 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNP in the presence of $NaBH_4$ and Ag^+. [2,4,6-tNP] = 5×10^{-5} M; [$NaBH_4$] = 3×10^{-2} M; [Ag^+] = 3×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

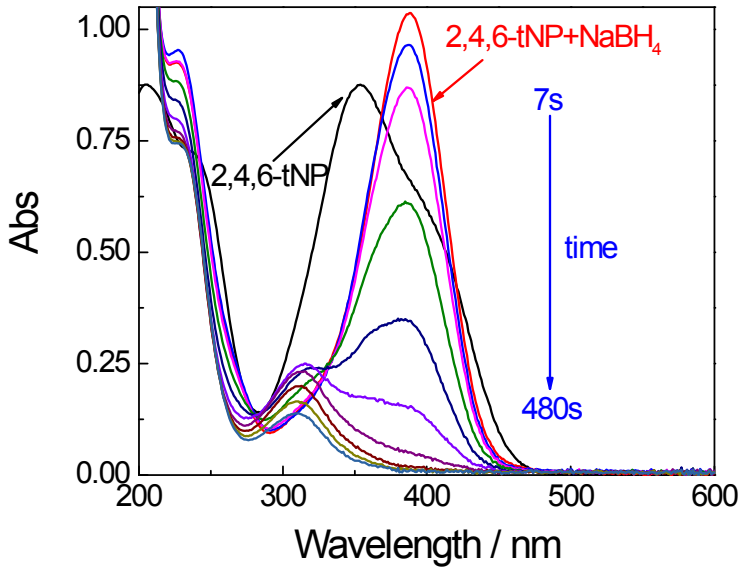

Fig. S32 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNP in the presence of $NaBH_4$ and $AuCl_4^-$. [2,4,6-tNP] = 5×10^{-5} M; [$NaBH_4$] = 3×10^{-2} M; [$AuCl_4^-$] = 1.7×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

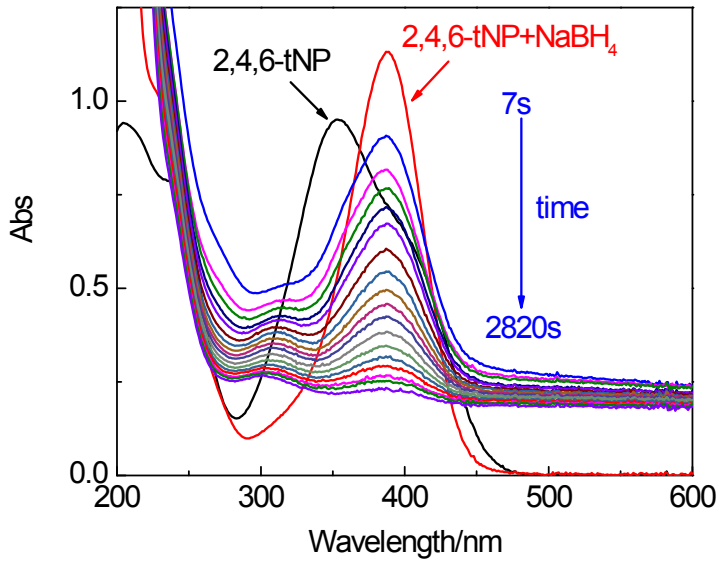

Fig. S33 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNP in the presence of $NaBH_4$ and Co^{2+}. [2,4,6-tNP] = 5×10^{-5} M; [$NaBH_4$] = 6×10^{-2} M; [Co^{2+}] = 1.5×10^{-4} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

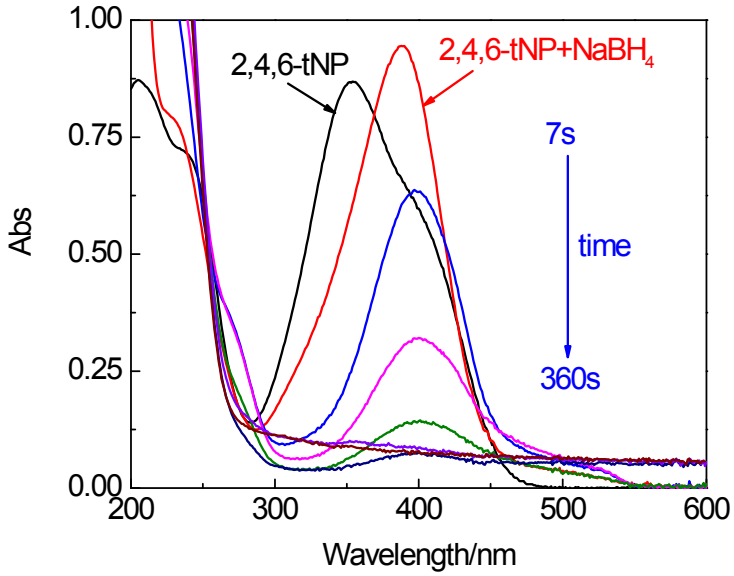

Fig. S34 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNP in the presence of $NaBH_4$ and Ni^{2+}. [2,4,6-tNP] = 5×10^{-5} M; [$NaBH_4$] = 6×10^{-2} M; [Ni^{2+}] = 4×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

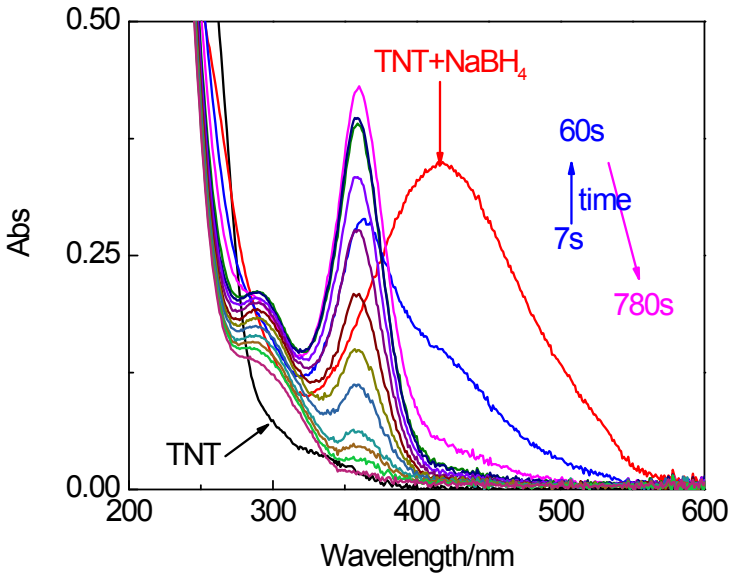

Fig. S35 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNT in the presence of $NaBH_4$ and Cu^{2+}. [2,4,6-tNT] = 5×10^{-5} M; [$NaBH_4$] = 2×10^{-2} M; [Cu^{2+}] = 2×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

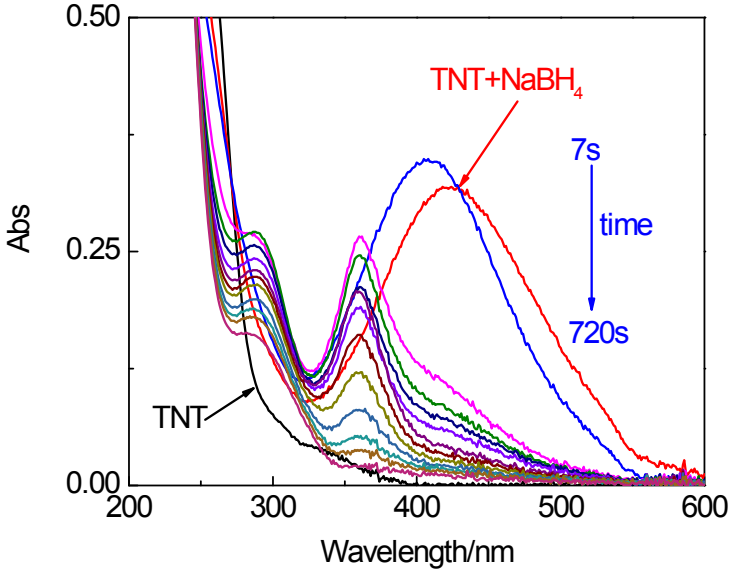

Fig. S36 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNT in the presence of $NaBH_4$ and Ag^{+}. [2,4,6-tNT] = 5×10^{-5} M; [$NaBH_4$] = 2×10^{-2} M; [Ag^{+}] = 1×10^{-6} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

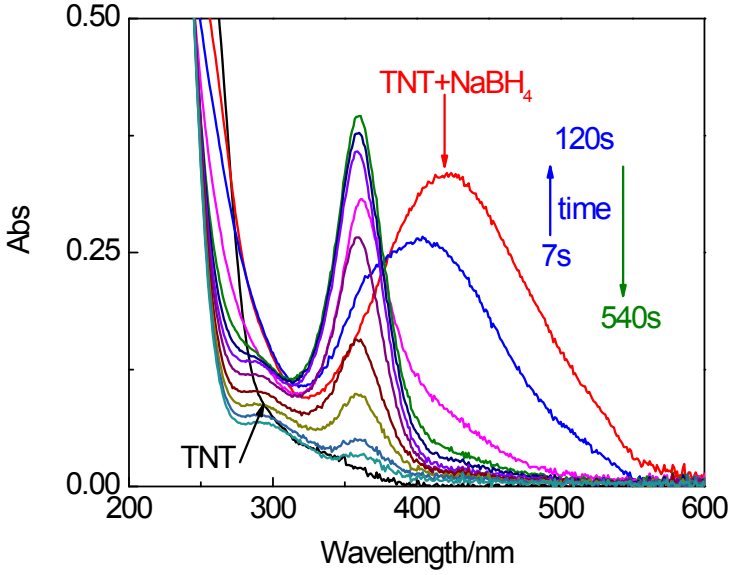

Fig. S37 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNT in the presence of $NaBH_4$ and $AuCl_4^-$. [2,4,6-tNT] = 5×10^{-5} M; [$NaBH_4$] = 2×10^{-2} M; [$AuCl_4^-$] = 6.7×10^{-7} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

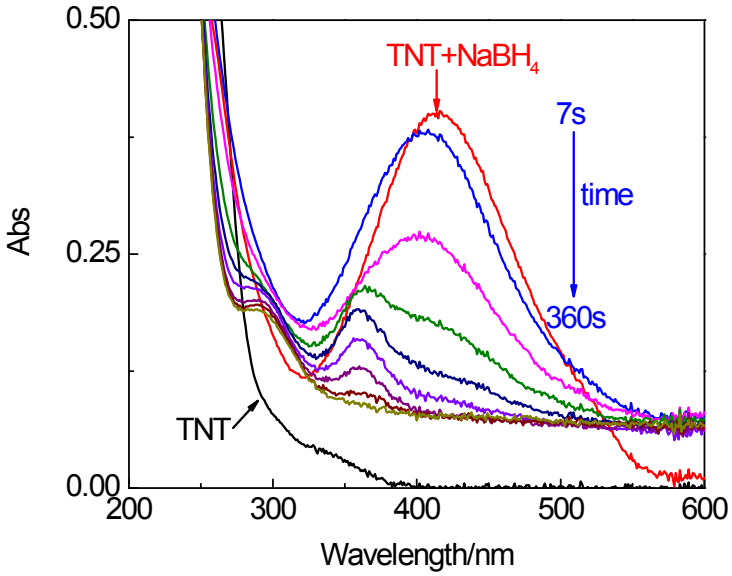

Fig. S38 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNT in the presence of $NaBH_4$ and Co^{2+}. [2,4,6-tNT] = 5×10^{-5} M; [$NaBH_4$] = 4×10^{-2} M; [Co^{2+}] = 1×10^{-4} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

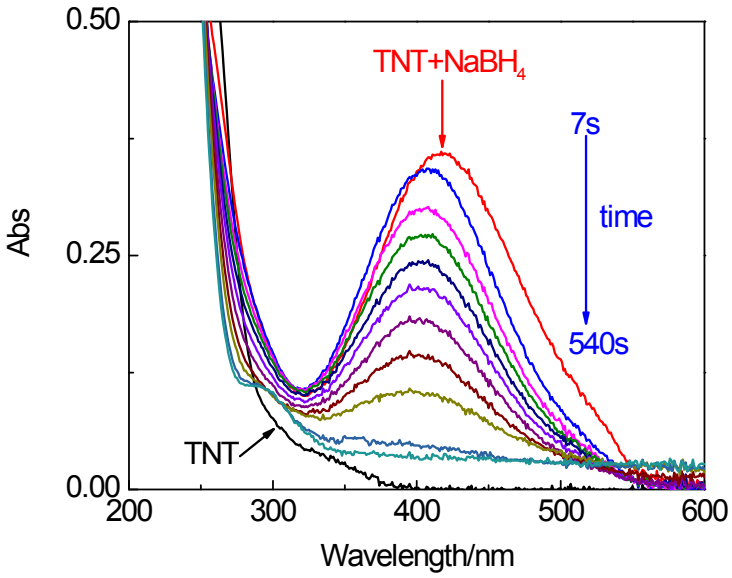

Fig. S39 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNT in the presence of $NaBH_4$ and Ni^{2+}. [2,4,6-tNT] = 5×10^{-5} M; [$NaBH_4$] = 4×10^{-2} M; [Ni^{2+}] = 3.3×10^{-5} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.

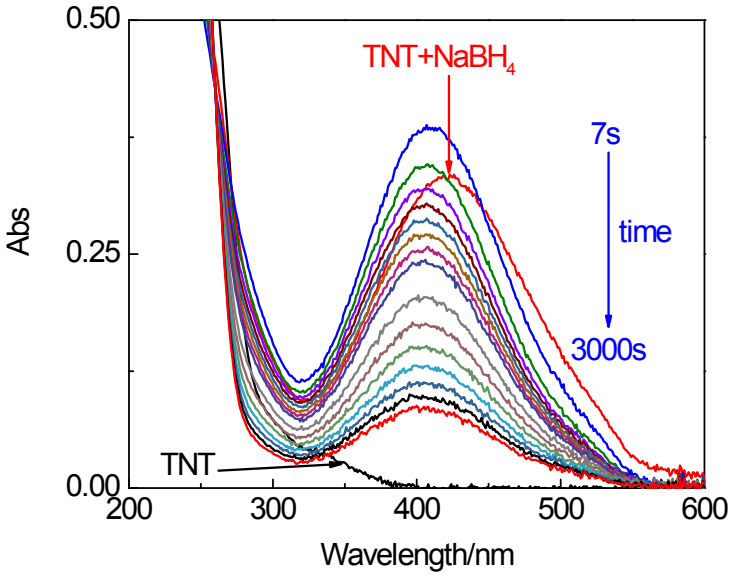

Fig. S40 Time-dependent UV-*vis* absorption spectra of 2,4,6-tNT in the presence of $NaBH_4$ only. [2,4,6-tNT] = 5×10^{-5} M; [$NaBH_4$] = 4×10^{-2} M; T = 24 °C. The time interval is 60 seconds between two sequential lines.