

Supporting Information

Insight into the Mechanism of Gold-Catalyzed Reduction of Nitroarenes Based on Substituent Effect and *in-situ* IR

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For the kinetic analysis in this work, two methods were applied for the nitroarenes with different groups. One is the monitor of the transformation by UV-vis for *p*-nitrophenol, *p*-nitrobenzenethiol, *p*- and *m*-nitroaniline. While, for *m*-nitrophenol, *m*- and *p*-nitrobenzoic acid, their UV-vis spectra are overlap with corresponding amino product, so HPLC was used to monitor the reduction process for these nitroarenes. A comparison between the reaction kinetics of same reaction using these two methods is needed, and the results of these two methods are similar, as shown in Figure S1.

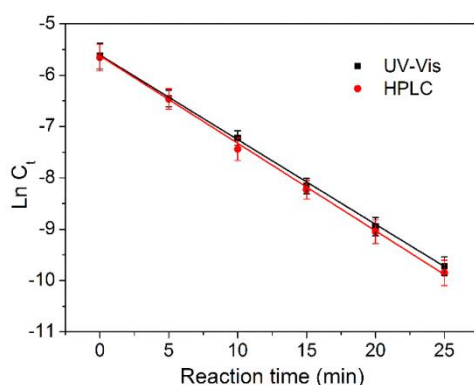


Figure S 1 Kinetic analyses of the reduction of *p*-Nip by both UV-vis and HPLC.

Reaction conditions: 50 mL of *p*-Nip solution (4 mmol/L in water), Au-SiO₂ (20 mg, 1 mol% Au), NaBH₄ (75 mg, 10-fold for *p*-Nip), at room temperature under air.

The effect of solution pH on the reduction was investigated by comparing the same reduction in the solution with different pH values and the results were listed in Table S1. It is worthy to note that the reaction rate is similar in the solutions with a pH value of 8.21, 9.17 and 9.26, while it obviously decreased when the pH value was up to 10.2, and the reduction needed a longer time for the solution with a pH 12.0. It was suggested that the protonation of solvent has a great effect on the reaction. At the same time, the kinetic analysis was investigated in the solutions with different pH values. As shown in Figure S2, all the catalytic reactions followed pseudo-first-order kinetics throughout the entire pH range from 8.21 to 12.0, which proved that the reaction kinetics were not affected by solution pH.

Table S 1 Effect of solution pH on the reduction.

$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{OH} \xrightarrow[\text{NaBH}_4 \text{ R.T.}]{\text{Au-SiO}_2} \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OH}$					
	Solvent	pH in reaction	Time (min)	Conversion (%)	Selectivity (%)
1	pH 6.86 buffer solution	8.21	23	99.3	>99
2	pH 9.18 buffer solution	9.26	28	99.2	>99
3	Water	9.17	25	98.8	>99
4	Water with NaOH	10.2	40	99.2	>99
5	Water with NaOH	12.0	90	98.2	>99

Reaction conditions: solvent 50 mL, *p*-Nip (28 mg, 0.2 mmol), Au-SiO₂ (20 mg, 1 mol% Au), NaBH₄ (75 mg, 10-fold for *p*-Nip), at room temperature under air. The pH value was detected by pH meter and the reaction process was detected by HPLC.

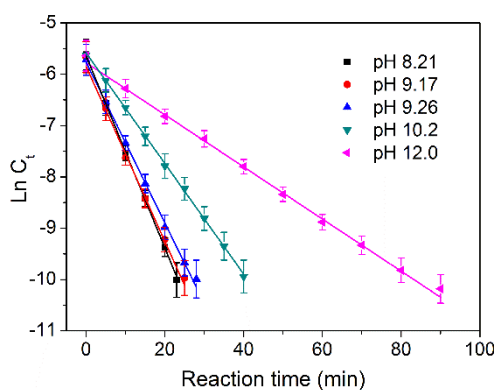


Figure S 2 The kinetic analysis of Au-SiO₂ catalyzed reduction of *p*-Nip in the solutions with

different pH values (the error bars represent the standard deviation of three measurements).

To verify the reusability of Au-SiO₂, five consecutive runs were carried out. All the runs could be finished in 25 minutes with almost 99% conversion and 99% selectivity.

Table S 2 The reusability of Au-SiO₂.

$\text{HO}-\text{C}_6\text{H}_4-\text{NO}_2 \xrightarrow[\text{Water RT}]{1 \text{ mol\% Au-SiO}_2, \text{NaBH}_4} \text{HO}-\text{C}_6\text{H}_4-\text{NH}_2$		
Reuse	Conversion (%)	Selectivity (%)
1	>99	>99
2	>99	>99
3	>99	>99
4	98.9	>99
5	>99	>99

Reaction conditions: *p*-Nip (4 mmol/L, 50 mL), NaBH₄ (75 mg, 10-fold), Au-SiO₂ (20 mg, 1 mol% Au). The reactions were carried out at room temperature under air and the product was detected by HPLC-MS after 25 minutes.

The TEM images of ultra small Au-SiO₂ before and after five consecutive runs showed that there is no alteration of the catalysts.

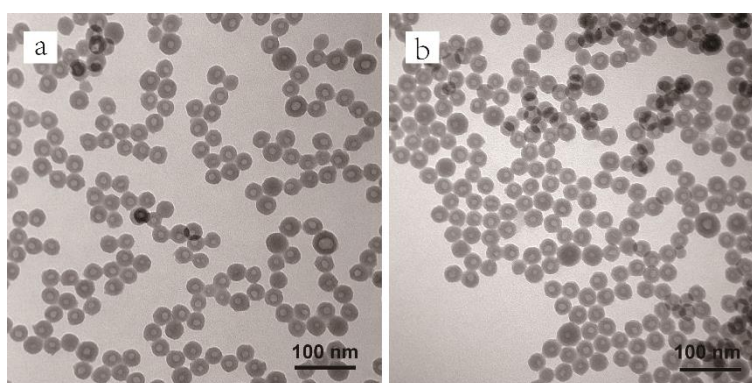


Figure S 3 TEM images of a) Au-SiO₂ synthesized and b) Au-SiO₂ after five recycle use.

Characterization of products

p-Aminophenol

¹H NMR (500 MHz, DMSO-d₆) δ 8.32 (s, 1H), 6.47 (dd, *J* = 8.8, 2.3 Hz, 2H), 6.44 – 6.38 (m, 2H), 4.39 (s, 2H). MS *m/z* 110 ([M+H]⁺)

m-Aminophenol

¹H NMR (500 MHz, DMSO-d₆) δ 8.82 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.22-5.90 (m,

3H), 4.85 (s, 2H). MS m/z 110([M+H]⁺)

p-Phenylenediamine

¹H NMR (500 MHz, DMSO-d₆) δ 6.57 (d, *J* = 1.6 Hz, 1H), 3.32 (s, 1H). MS m/z 109([M+H]⁺)

m-Phenylenediamine

¹H NMR (500 MHz, DMSO-d₆) δ 6.64 (t, *J* = 7.8 Hz, 1H), 5.80 (d, *J* = 1.8 Hz, 1H), 5.77 (dd, *J* = 7.8, 2.1 Hz, 2H), 4.64 (s, 4H). MS m/z 109([M+H]⁺)

p-Aminobenzoic acid

¹H NMR (500 MHz, DMSO-d₆) δ 11.92 (s, 1H), 7.61 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.54 (dd, *J* = 8.5, 1.6 Hz, 2H), 5.86 (s, 2H). MS m/z 136 ([M-H]⁻)

m-Aminobenzoic acid

¹H NMR (500 MHz, DMSO-d₆) δ 8.62 (s, 1H), 8.48 (d, *J* = 8.2 Hz, 1H), 8.35 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 1H), 6.52 (s, 2H). MS m/z 136 ([M-H]⁻)

p-Aminobenzenesulfonic acid

¹H NMR (500 MHz, DMSO-d₆) δ 7.61 (d, *J* = 1.8 Hz, 2H), 6.84 (d, *J* = 1.8 Hz, 2H), 4.86 (s, 2H). MS m/z 172([M-H]⁻)

p-Aminothiophenol

¹H NMR (500 MHz, DMSO-d₆) δ 7.06 (dd, *J* = 6.5, 4.7 Hz, 1H), 7.01-6.97 (m, 1H), 6.54-6.46 (m, 2H). MS m/z 125 ([M+H]⁺)