Supporting Information

Tuning the hydride reductions catalyzed on metal nanoparticle surfaces

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Experimental methods

Materials. Silver nitrate (anhydrous, 99.999%), 4-nitrophenol ($\geq$ 99%), sodium borohydride (powder, $\geq$ 98.0%), potassium tetrachloroplatinate(II), gold(III) chloride trihydrate, poly(acrylic acid) (average Mn 1800, powder), sodium citrate tribasic dihydrate ($\geq$ 99%) and poly(ethyleneimine) solution (average Mn ~1,200, 50 wt. % in H_2O) were purchased from Sigma-Aldrich and used without further purification. TEM grids (Carbon Grid Type-A, 300 Mesh, Cu) were purchased from TedPella.

Instruments. HRTEM images were obtained on a JEM 3010 high resolution transmission electron microscope. Absorption spectrum was obtained on a Sinco S-4100 with a kinetic model that enabled the time-resolved spectrum measurement. Zeta potential was analyzed with a Zetasizer Nano 2000 (Malvern Instruments, USA). IR spectrum was obtained with TENSOR27 (Bruker) FT-IR Fourier transform infrared spectrometer.

UV-Visible spectrum. UV-Visible spectrum was obtained on SCINCO S-4100 Scan UV-visible spectrophotometer at the kinetic model, by which full absorption spectrum was recorded at a 1200 ms interval. The kinetic data was obtained at the same time.

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IR spectrum. Nanoparticles were collected by centrifugation. The precipitates were washed with de-ionized water and collected by centrifugation again. The same procedure was repeated twice. The collected nanoparticles were dissolved in water and its IR spectrum was obtained by subtracting the background signal of water.

Preparation of stock solutions

Metal ion stock solutions (14 mM), poly(acylic acid) (PA) stock solution (1.1 mM), and polyethyleneimine (PEI) (2.4 M) were prepared in deionized water and kept in refrigerator. Sodium borohydride stock solution (1 mg/mL) was prepared in deionized and used instantly.

Synthesis of PA-AgNPs

$AgNO_3$ solution (3 mM, 630 μL) and poly(acrylic acid) (1.1 mg) were mixed in DI water (5370 μL) and left in the dark with stirring for 1 hour, followed by reducing with fresh sodium borohydride stock solution (210 μL).

The sample was used after an overnight incubation in the dark. The sample was then diluted in DI water.

Synthesis of PEI-AuNPs

Poly(ethyleneimine) solution (2.4 M, 66.7 μL) was added dropwise into pre-heated gold(III) chloride trihydrate solution (0.34 mM, 6 mL) with stirring in the dark for 5 minutes at 75℃. After cooling down for 25 minutes in the dark.The sample was diluted and used after 1 hour incubation in the dark with stirring. 5 nm, 14 nm and 26 nm gold nanoparticles were prepared at a PEI gold ratio of 3, 21 and 27, respectively.

Synthesis of PA-AuNPs

Briefly, a mixture of gold(III) chloride trihydrate solution (6.2 mM, 3.5 mL) and sodium citrate tribasic dihydrate (6.2 mM, 3.5 mL) were heated at 75℃ in the dark with stirring for 10 minutes to make citrate-AuNPs. After cooling down for 1 hour in the dark, a mixture of PA (0.0185 g, 210 μL) and sodium carbonate (0.0311 g) in DI water (3 mL) was added dropwise into citrate-AuNPs (7 mL). The sample was used after an overnight incubation in the dark.

Synthesis of PA-AuNPs with varied PA concentration

The above PA-AuNPs was added with 0 mg, 0.7 mg, 2.9 mg, and 10.6 mg of PA , respectively. The samples were diluted and used after 1 hour incubation in the dark with stirring.

Synthesis of PA-PtNPs

A mixture of potassium tetrachloroplatinate(II) solution (2.4 mg) and poly(acrylic acid) (1.5 mg) were mixed in DI water (8 mL) and left in the dark with continuous nitrogen bubbling for 20 minutes, followed by reducing with fresh sodium borohydride stock solution (66 μL).   The sample was used after an overnight incubation in the dark.

Comparison of catalytic ability

The concentrations of each component were kept throughout except where indicated. In a quartz cuvette (10 mm), DI water (1 mL), catalyst (0.3 mM, 1 mL) and 4-nitrophenol stock solution (30 μL) were mixed. Sodium borohydride stock solution (50 μL) for 4NP reduction was then added into the mixture, followed by a quick shake of the cuvette. The absorption spectra were then recorded on a SCINCO S-4100 Scan UV-visible spectrophotometer at room temperature. The concentration of silver ions was decreased to 0.1 mM to show the significance of aging time when comparing the impact of the aging time on the induction time.

The reduction can be visualized by the vanishing of the 400 nm peak of 4NP with the appearance of a new peak at 300 nm of 4AP. We observed the kinetics of the reaction by recording the change in the absorbance of the p-nitrophenolate ions at 400 nm (Figure S1).

Comparison of hydrogen generation from samples

Briefly, catalyst (3 mL) was put in a round-bottom flask with a sidearm. Detergent solution (30 μL) was injected into a burette (0.8 cm in diameter) to make a thin bubble film at a specific mark. The burette was connected to the sidearm of the flask with the hose sealed well with paraffin. Sodium borohydride stock solution (50 μL) was added into the catalyst and the lid of flask was closed. The bubble film went up as hydrogen gas was generated from the decomposition of $NaBH_4$. The volume of the bubbles was recorded once every 3 seconds.

Hydrogen reduction

Zinc metal drops were added into sulfuric acid ($Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$) in the sealed flask with sidearm.

The hydrogen was pumped into the 4NP solution in the presence of silver nanoparticles.
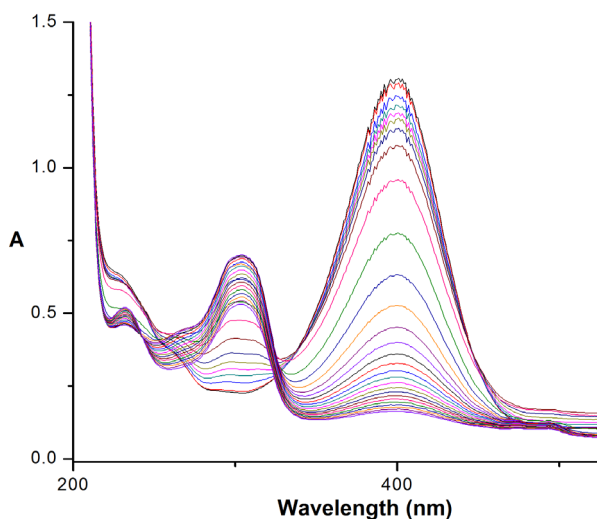

Fig. S1 Catalytic reduction of 4-nitrophenol with sodium borohydride. Absorption spectra at different reaction time. The disappearance of the peak for 4-nitrophenol (400 nm) due to the reduction of $-NO_2$ group to $-NH_2$ group; such a transition was reflected from its photos (inset).
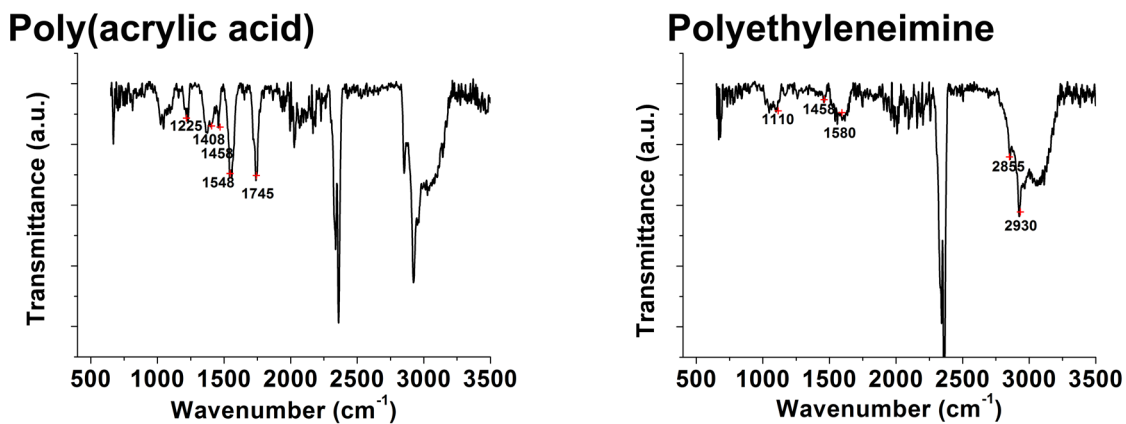

Fig. S2 IR spectra of poly(acrylic acid) and polyethyleneimine protected gold nanoparticles. A mixture of carbonyl stretch (C=O) at 1745 cm^{-1}, CH_2 stretching at 1458 cm^{-1}, and the C=O stretch at 1225 cm^{-1} and the symmetric and antisymmetric stretching frequencies of the carboxylate ion (COO^-) at 1408 and 1548 cm^{-1} were observed from the poly(acrylic acid)-stabilized gold nanoparticles. Characteristic peaks of polyethyleneimine were observed from the polyethyleneimine-stabilized gold nanoparticles: the bending vibration of the NH group and the stretching vibration of the C-N groups at 1580 cm^{-1} and 1110 cm^{-1}.
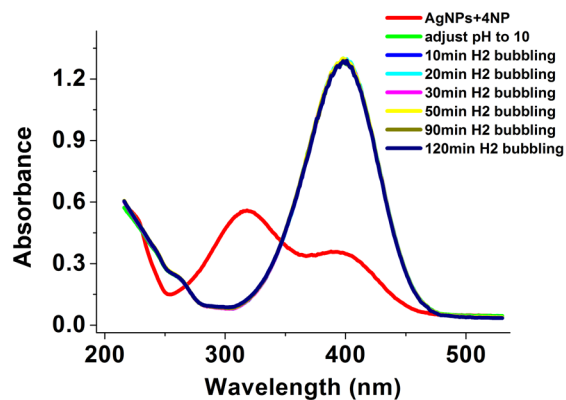
Fig. S3 Absorption spectra of 4-nitrophenol bubbled with hydrogen gas in the presence of gold nanoparticles.
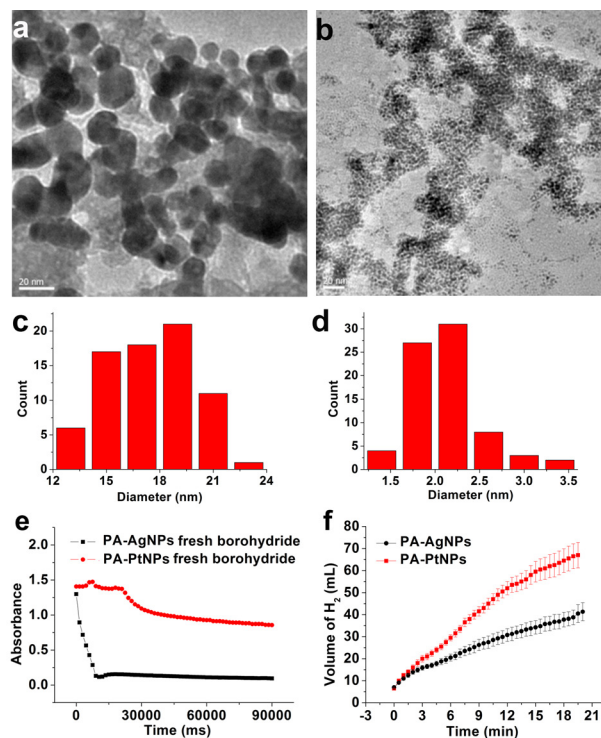

Fig. S4 Comparison of nitrophenol reduction and hydrogen generation between PA-stabilized platinum nanoparticles and PA-stabilized silver nanoparticles. **a** and **b**, TEM images of silver nanoparticles (**a**) and platinum nanoparticles (**b**). Their size distributions are shown in **c** and **d**, respectively. **e**, Absorbance at 400 nm as a function of time in the presence of silver and platinum nanoparticles when reducing 4-nitrophenol with fresh sodium borohydride. **f**, Volume of hydrogen generated via hydrolysis of sodium borohydride in the presence of above nanoparticles. The error bars indicate the standard deviation. The concentration of each of the ions was 0.3 mM. Scale bar: 20 nm.