Supporting Information

Lattice Contracted AgPt Nanoparticles

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Experimental Section

Materials. Platinum acetylacetonate [Pt(acac)$_2$, Strem Chemicals, 98 %], silver stearate (Alfa Aesar) and nitric acid (HNO$_3$, 6.00N) were purchased through VWR. Oleic acid (90 %, technical grade), oleylamine (70 %, technical grade), 1,2-hexadecanediol (HDD, 90 %, technical grade), diphenyl ether (DPE, 99 %, ReagentPlus®), sodium borohydride (NaBH$_4$, ≥98 %) and *p*-nitrophenol (99%, ReagentPlus®) were purchased from Aldrich. All chemicals and reagents were used as received.

Synthesis. In a typical procedure, a mixture of Pt(acac)$_2$ (0.025 g or 64 μmol) and silver stearate (0.025 g or 64 μmol) was dissolved in DPE (1 mL or 31.5 mmol) at 85 °C for 15 min. This mixture was then added into a 25-mL three-neck round-bottom flask which contained oleic acid (0.3 mL or 0.9 mmol), oleylamine (0.3 mL or 0.9 mmol), and DPE (4 mL or 25.2 mmol), and was preheated at 180 °C. The reaction was carried out at 180 °C for 1 h under argon atmosphere. After the reaction, nanoparticles were separated by dispersing the reaction mixture in 2 mL of hexane and then 8 mL of ethanol followed by the centrifugation at 6000 rpm for 5 min.

Preparation of carbon-supported AgPt (AgPt/C) catalysts. Carbon black (Vulcan XC-72, 0.16 g) was dispersed in 12 mL of hexane via sonication for 60 min. The AgPt nanoparticles (a batch of product, about 25mg metal) were then added in 4 mL of hexane and mixed with 12 mL of the above dispersion of carbon black. The resulting mixture was sonicated for 60 min and then stirred for 12 h using a magnetic stirrer. The carbon-supported AgPt nanoparticles were separated out using a centrifuge at 5000 rpm for 5 min and air-dried.

Acid treatment. Carbon-supported AgPt nanoparticles (0.05g) were immersed in 5 mL of concentrated nitric acid (69.8%) for 1 h, followed by the addition of 5 mL of deionized (DI)

water (Aqua, 18 MΩ). The mixture was then separated using a centrifuge at 5000 rpm for 5 min. The powder was washed with DI water three additional times.

Catalytic study. The reduction of *p*-nitrophenol by NaBH$_4$ was used as a model system to quantitatively evaluate the catalytic property. The carbon-supported Pt reference catalyst used was from TKK. The as-made nanoparticles underwent a ligand exchange with butylamine in the preparation of carbon-supported AgPt catalysts.[1] In the procedure, the solid product of AgPt catalysts from a batch was re-dispersed in 12 mL of n-butylamine. The solution mixture was kept under stirring for 3 days. The final product was separated using a centrifuge at a rate of 5000 rpm for 5 min. The precipitate was washed with methanol three times. The precipitate was re-dispersed in 10 ml methanol by sonicating for 15 min and then separated by centrifugation with a rate of 5000 rpm for 10 min.

The metal loading of the catalysts was 45.9% for Pt/C and 13.1% for AgPt/C based on the metal amount. For the preparation of catalyst, 4 mg of carbon-supported nanoparticles was dispersed in 10 mL of DI water and sonicated for 10 min. In a typical procedure, 30 mL DI water was mixed with 0.3 mL of freshly made 1 mM p-nitrophenol solution. In this solution, 1 mL of freshly-made 1.5 M sodium borohydride (NaBH$_4$) aqueous solution was added. Finally, a solution of 250 μL of Pt/C or 50 μL of AgPt/C catalyst was injected into the mixture. The reaction was monitored using UV-vis spectroscopy (Ocean Optics, USB 2000) at 50 s interval for about 15-30 min.

The catalytic reduction of *p*-nitrophenol NaBH$_4$ is a first-order reaction based on the following equation:[2]

$$\ln \frac{C_t}{C_0} = -k_{app} t \qquad\qquad\qquad (S1)$$

where C_o and C_t are concentrations at the initial and a given time t, respectively. From this equation, we got the apparent rate constant, k_{app}. Basing on nanoparticle model built using Material Studio, we found that there were 959 atoms in a 2.8-nm Pt nanoparticle (Pt reference catalyst from TKK) and among them 32% of the atoms was on the surface. Similarly, 42% and 48% of the total atoms should locate on the nanoparticle surfaces for the 2-nm as-made AgPt and 1.8-nm acid-treated AgPt nanoparticles, respectively. The turnover frequency (TOF) is defined as moles (or numbers) of the product generated per moles (or numbers) of surface atoms of the catalysts. For the first-order reaction, the raw is written as:

$$-\frac{dC}{dt} = k_{app}C \tag{S2}$$

Thus, the turnover frequency (TOF) was calculated using the moles of product molecules divided by moles of metal atoms on particles surface using the following equation:[2]

$$-\frac{dC_t}{dt} = k_{app}C_t = k_1 S C_t \tag{S3}$$

where k_1 is the surface-related reaction rate constant, *i.e.*, the apparent rate constant normalized to surface area to volume ratio, S. The calculated results were summarized in Table S1.

Characterizations. Powder X-ray diffraction (PXRD) patterns were obtained using a Philips MPD diffractometer with a Cu Kα X-ray source (λ=1.5405Å). Electron microscopy specimens were prepared by dispersing the particles in hexane and drop-casting onto carbon-coated copper grids. TEM and HRTEM images were taken on a JEOL JEM 2000EX microscope at an accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) analysis was carried out on

a field emission scanning electron microscope (FE-SEM, Zeiss-LEO DSM 982) operating at 20 kV.

Reference:

1 J. Wu, J. Zhang, Z. Peng, S. Yang, F. T. Wagner, H. Yang, *J. Am. Chem. Soc.* 2010, **132**, 4984.

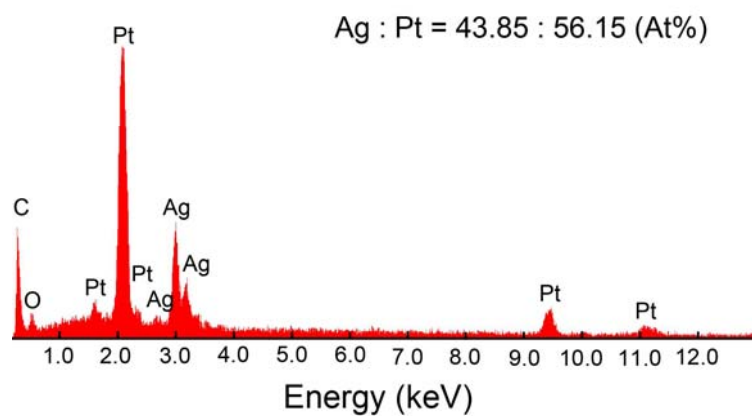2 Y. Mei, Y. Lu, F. Polzer, M. Ballauff, M. Drechsler, *Chem. Mater.*, 2007, **19**, 1062.

Figures

Ag : Pt = 43.85 : 56.15 (At%)

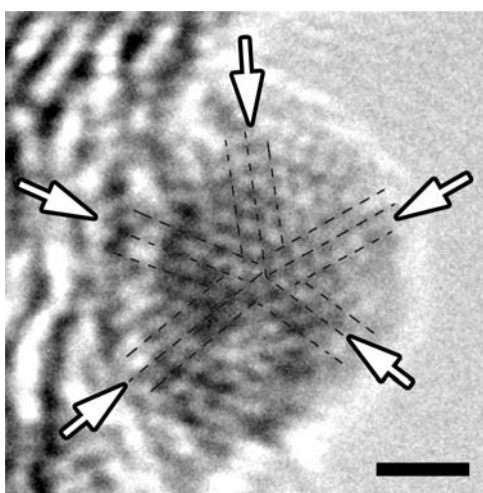**Fig. S1** EDX analysis of as-made AgPt nanoparticles.

Fig. S2 Magnified HRTEM micrograph of AgPt nanoparticles. The arrows indicate the twin planes, and the dotted lines indicate the lattices near the twin planes. The scale bar represents 1 nm.
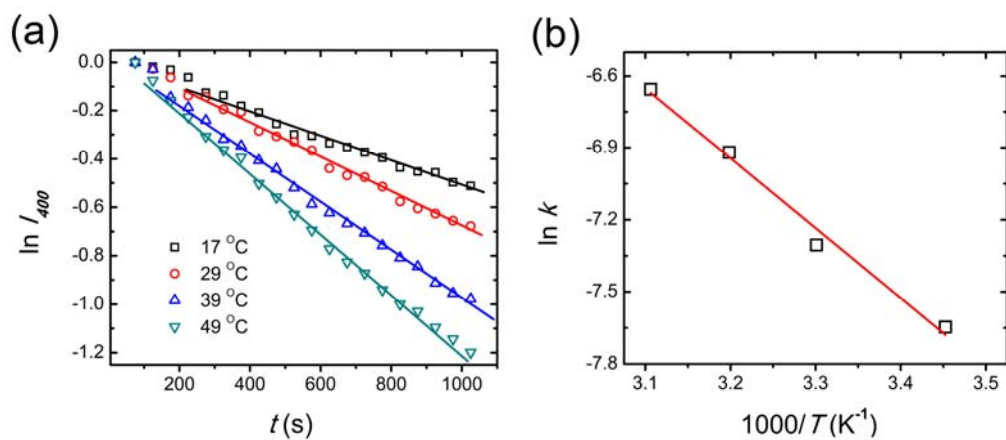
Fig. S3 Catalytic activity of Pt reference catalysts in the reduction of *p*-nitrophenol by NaBH$_4$:

(a) *ln I$_{400}$ - t,* and (b) the corresponding Arrhenius plots. *I$_{400}$* is the extinction at 400 nm.
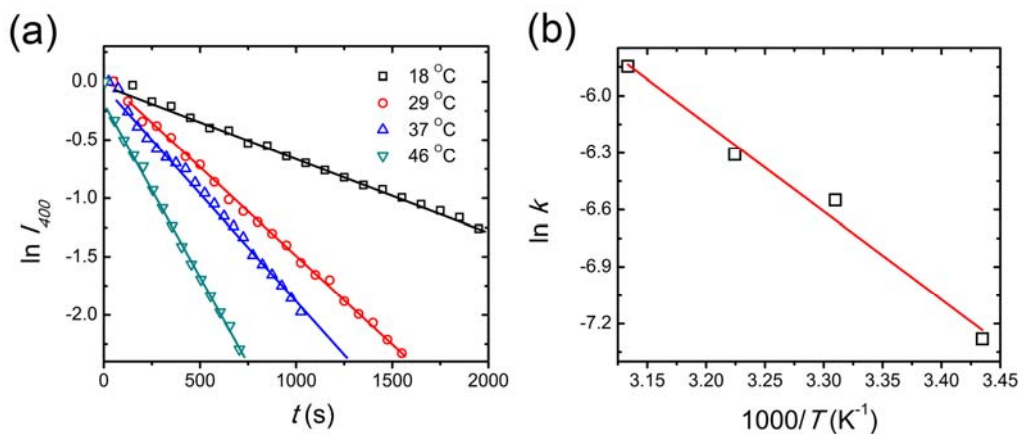

Fig. S4 Catalytic activity of acid-treated AgPt nanoparticle catalysts in the reduction of *p*-nitrophenol by NaBH$_4$: (a) *ln I$_{400}$ - t,* and (b) the corresponding Arrhenius plots.

Table S1. Apparent Rate Constant (k_{app}), Number of Moles on Surface (N), Tornover Frequency (TOF), Surface Area Normalized to Volume (S), and Rate Constant (k_1) for the Catalysts.

Sample	k_{app} (s^{-1})	N (mol)	TOF (s^{-1})	S (m^2/L)	k_1 ($s^{-1}\ m^{-2}\ L$)
AgPt (as made)	1.5×10^{-2}	2.7×10^{-8}	540	5.8×10^{-2}	2.5×10^{-1}
AgPt (after treatment)	6.9×10^{-4}	2.6×10^{-8}	26.2	5.5×10^{-2}	1.2×10^{-2}
Pt (reference)	4.2×10^{-4}	1.6×10^{-8}	25.5	3.3×10^{-2}	1.3×10^{-2}