Electronic Supplementary Information (ESI)

Glucose-mediated catalysis of Au nanoparticles in microgels

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SI 1. Experimental Procedures

1.1. Materials

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$), sodium borohydride ($NaBH_4$), trihydrate citrate dehydrate (Tc), 4-vinylbenzeneboronic acid (VPBA), acrylamide (AAm), sodium dodecyl sulfate (SDS), *N*-isopropylacrylamide (NIPAM), *N,N′*-methylenebisacrylamide (MBAAm), and 2,2-azobis (2-methylpropionamidine) dihydrochloride (AAPH) were purchased from Aldrich. 4-Nitrophenol (4-NP) and nitrobenzene (NB) were purchased from Sinopharm Chemical Reagent Co. Ltd. NIPAM was recrystallized from a hexane-acetone (a 1:1 volume ratio) mixture and dried in a vacuum. All other chemicals were used as received without further purified. The water used in all experiments was of Millipore Milli-Q grade.

1.2 *Synthesis of Au nanoparticles*

Citrate-stabilized Au nanoparticles were first prepared by dropwise addition of fresh $NaBH_4$ solution (10.6 mM, 2.5 mL) to an aqueous solution of $HAuCl_4$ (0.1 mM, 200.0 mL) in the presence of sodium citrate (0.1 mM) under vigorous stirring. The resultant solution was stirred for 1 h and aged for 7 days at ambient conditions before use. The long aging time is necessary for completely degrading the reducing agent of $NaBH_4$.

1.3 Synthesis of Au@pPBA microgels

AAm (1.03×10^{-1} g, 1.450 mmol) was dropwise added into 100.0 mL of aqueous solution of citrate-stabilized Ag nanoparticles in a 250 mL round-bottom flask. After stirring for 1 h, SDS (6.0×10^{-2} g, 0.184 mmol) was added. This mixture was further stirred overnight. After addition of NIPAM (3.3×10^{-1}

g, 2.900 mmol), MBAAm (3.2×10^{-2} g, 0.2087mmol), and VPBA (3.2×10^{-2} g, 0.219 mmol), the mixture was purged with N_2 for 30 min and then heated to 70 °C. The polymerization was initiated by adding AAPH (1.68×10^{-2} g, 0.062 mmol). The red solution became turbid within 10 min and the reaction was allowed to proceed for totally 5 h. The product was purified by centrifugation (8000rpm, 30 min, 25°C) and redispersed in water (50.0 mL) for three times, followed by 3 days of dialysis against water.

1.4 Experiments on the model Au-catalyzed chemical reactions

The model chemical reactions were conducted in a quartz cuvette, which was placed inside a UV-vis spectrophotometer equipped with a temperature controller (±0.1 °C). Typically, the microgels (0.5 mL, 2.9×10^{16} Au-atoms/mL) and $NaBH_4$ (0.5 mL, 0.15 M) were mixed with 2.0 mL PBS buffers with pH of 7.4 and a designed glucose concentration in the quartz cuvette at 30.0 °C for 5 min. 4-NP and/or NB (30.0 μL, 0.01 M) was then added into the mixture. During the course of the reaction, the progress was in situ monitored by measuring UV-Vis absorption spectra. Experiments were reproducible to within 5%. The data was then analyzed by using the 4-NP/NB absorption.

1.5 Characterizations

FTIR spectra were recorded with a Thermo Electron Corporation Nicolet 380 Fourier transform infrared spectrometer. TEM images were taken on a JEOL JEM-1400 transmission electron microscope at an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) images were obtained on Hitachi S4800 scanning electron microscope with a field emission electron gun. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. The pH value was measured on a EUTECH PH 700 instruments. Dynamic light scattering (DLS) was performed on a 90Plus multi angle particle sizing analyzer equipped with a BI-9000AT digital autocorrelator (Brookhaven Instruments, Inc.). A He-Ne laser (35 mW, 659 nm) was used as the light source. All samples were passed through Millipore Millex-HV filters with a pore size of 0.80 μm to remove dust before the DLS measurements. The contents of Au in the microgels were determined by using ICP-OES.

SI2. Figures.

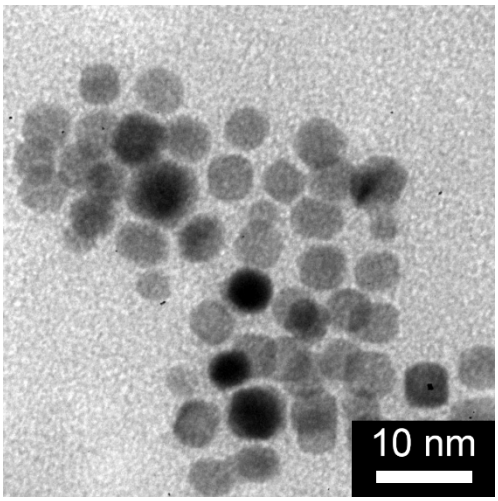

Fig. S1 Typical TEM image of Au nanoparticles.

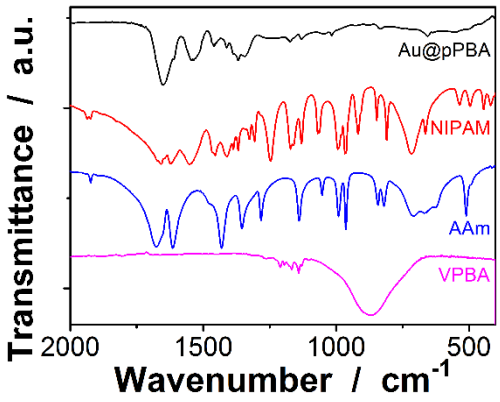

Fig. S2 IR spectra.

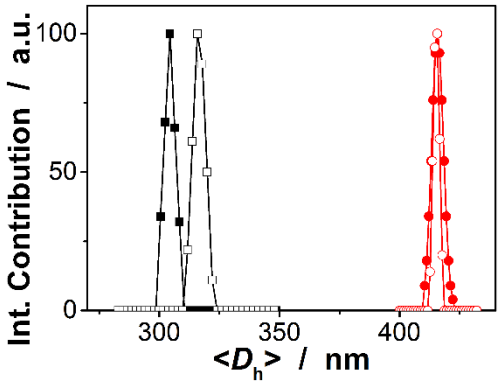

Fig. S3 DLS size distribution of the Au@pPBA before (■,●) and after (□,○) five cycles of adding ([Glu] = 5.0 mM: ●,○) and removing ([Glu] = 0.0 mM: ■,□) glucose.

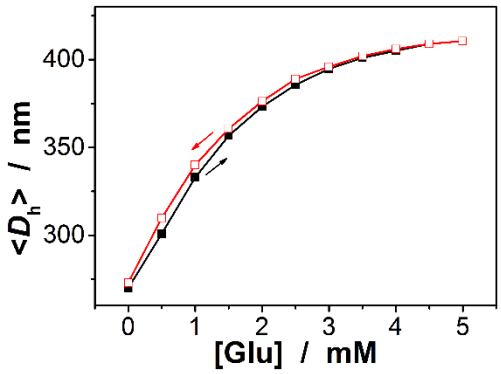

Fig. S4 Glucose-dependent $<D_h>$ of the polymer microgels made without Au nanoparticles.

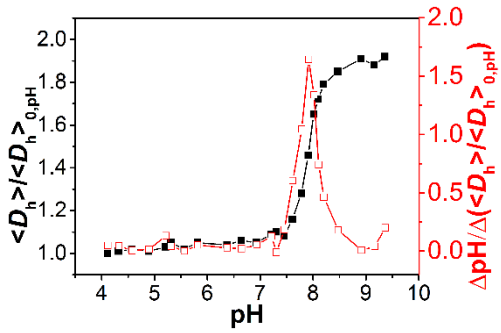

Fig. S5 The solution pH-dependent normalized hydrodynamic diameter, $<D_h>/<D_h>_{0,pH}$, of the Au@pPBA.

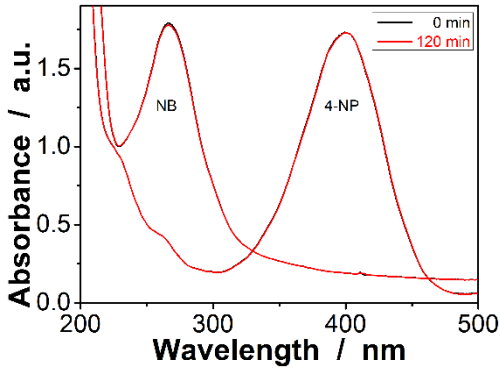

Fig. S6 UV-vis spectra of 4-NP and NB in the presence of glucose ([Glu] = 5.0 mM), without adding the Au@pPBA and Au nanoparticles.

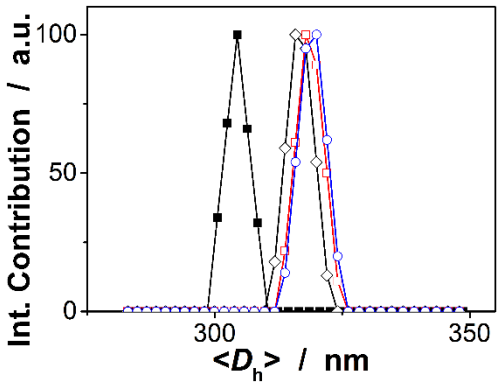

Fig. S7 DLS size distribution of the Au@pPBA before (■) and after ten cycles of use for the reduction of 4-NP (□) and NB (○). The size distribution for the Au@pPBA after ten cycles of adding ([Glu] = 5.0 mM) and removing ([Glu] = 0.0 mM) glucose is also presented for comparison (◊).

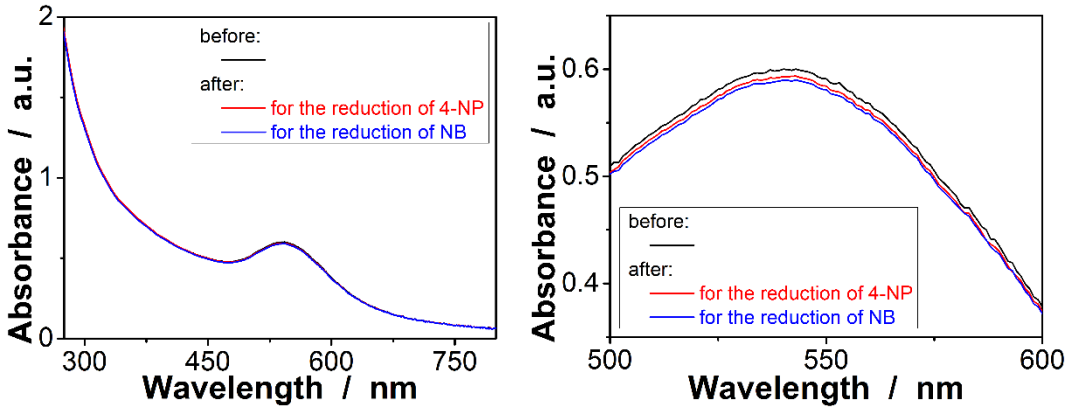

Fig. S8 UV-vis spectra of the Au@pPBA before and after ten cycles of use for the reduction of 4-NP and NB.

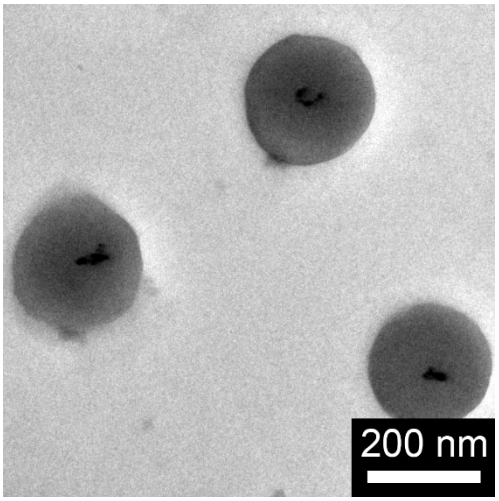

Fig. S9 Typical TEM image of the Au@pPBA after ten cycles of use.