Electronic Supplementary Information

In situ recyclable gold nanoparticles using CO₂-switchable polymers for catalytic reduction of 4-nitrophenol

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Experimental details

Materials: Gold plate target (99.99%), tetrohydrofuran (THF), sodium hydroxyl (NaOH), sodium borohydride (NaBH₄), butylamine (99%) 4-nitrophenol and deuterium chloroform (CDCl₃) were purchased from Sigma-Aldrich and used without further purification. 2-(Diethylamino)ethyl methacrylate (DEAEMA, 99%) purchased from Aldrich was passed through a column of basic aluminum oxide prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN) (Polysciences) was recrystallized twice from ethanol before use. The reversible addition-fragmentation chain transfer (RAFT) agent, 2-(2-cyanopropyl)dithiobenzoate (CPDB), was synthesized using a literature method.¹ Amicon Ultra-4 Ultracel-50K centrifuge filters (Millipore) were obtained from Fisher Scientific. Water was purified by a Millipore Ultrapure water system to have a resistivity of 18.2 M Ω ·cm at 25 °C.

Characterization: Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker 300MHz NMR spectrometer using CDCl₃ as solvent. A Waters size exclusion chromatograph (SEC) instrument, equipped with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector, was utilized to measure the number- and weight-average molecular weight (Mn and Mw) and the polydispersity index (PDI) using polystyrene (PSt) standards. The SEC measurements were conducted at 35 °C using one column (Waters Styragel HR4E, 7.8 mm × 300 mm, 5 μ m beads) and THF eluent (flow rate: 1.0 mL/min). A UV-Vis spectrometer (Varian 5000) was used to measure the absorption/transmittance spectra of AuNPs and 4-NP in catalytic reaction solution at room temperature. TEM images were taken with a JEOS-

2100F TEM (École Polytechnique de Montréal, Montréal, Canada) by drop casting AuNP dispersions on carbon-coated copper grids. Elemental analysis with neutron activation analysis (NAA) technique was performed using SLOWPOKE nuclear reactor (École Polytechnique de Montréal, Montréal, Canada) to quantify Au concentration in the Au colloidal solution for conjugation with the polymer and to determine the amount of Au catalysts used in the catalytic reaction. The pH values of the solutions were measured with a Mettler-Toledo FG2 pH meter.

Preparation of gold nanoparticles (AuNPs):¹ AuNPs were prepared using pused laser ablation in liquid (PLAL-AuNPs) on a bulk Au target with a KrF excimer laser (GSI Lumonics PM-846, wavelength: 248 nm, repetition rate 20 Hz). The laser beam was focused by an objective lens (focal length=7.5 cm) onto a gold plate, which was placed at the bottom of a 6 mL glass vessel filled with NaOH aqueous solution (pH≈10). The depth of the water layer above the target was ~10 mm. Laser fluence on the target was set at ~35.0 J/cm² throughout the ablation process. As-prepared PLAL-AuNPs were used directly for surface modification and relevant characterization.

Preparation of thiol-terminated poly(2-(diethylamino)ethyl methacrylate) (SH-PDEAEMA):² PDEAEMA with dithioester end group, PDEAEMA-C(=S)-S-Ph, was firstly prepared via RAFT polymerization of DEAEMA with CPDB as chain transfer agent and AIBN as initiator. The typical polymerization run was as follows. DEAEMA (6.0 g, 0.032 mol), AIBN (1.0 mg, 0.006 mmol), and CPDB (0.06 g, 0.27 mmol) were added into a 10 mL one-necked flask, followed by the addition of 5 mL of THF. After the solution under stirring was purged by argon flow for 20 min, the flask was sealed and

placed into an oil bath for reaction at 70 °C for 6 h. At the end of the reaction, the copolymer was purified by three times of precipitation from a dilute THF solution into cold hexane, and then it was collected/dried and characterized by ¹H-NMR and SEC (3.8 g, 63.3 % yield, M_n =18,600 g/mol, PDI=1.12). For preparation of thiol-terminated PDEAEMA (SH-PDEAEMA), the general procedure was as follows. Three grams of PDEAEMA-C(=S)-S-Ph was dissolved into 8.0 mL of THF. After the solution was purged by argon for half an hour, butylamine was then added. The reaction was stirred for 2 h under argon. The solution color changed from pink to light yellow during the aminolysis, which indicated the conversion of dithioester groups into thiol functionalities. The reaction mixture was then added dropwise to a 10-fold excess of cold hexane, and SH-PDEAEMA was collected and dried in a vacuum oven and characterized using ¹H-NMR and SEC.

Functionalization of AuNPs with PDEAEMA: PDEAEMA functionalized AuNPs (PDEAEMA-AuNPs) were achieved by slow, drop wise addition of 1 mL of Au colloidal solution ([Au]=40 ppm, measured by NAA) into 10 mL of ~0.625 mM SH-PDEAEMA THF solution under vigorous stirring. The solution was then continuously strongly stirred at room temperature for another ~72 h to complete the surface coupling process. After that, the solution was centrifuged at 2,000 rpm for 15 min to separate and remove aggregates. The light orange supernatant was collected and centrifuged again at 12,000 rpm for 30 min to collect AuNPs and separate them from excess SH-PDEAEMA polymers. The collected AuNPs were washed with THF twice and re-dispersed in THF. Finally the PDEAEMA-AuNP solution was concentrated by partially evaporating THF solvent.

Dispersion of PDEAEMA-AuNPs into water and their CO₂-Switchable tests: In a typical process, 2 mL of pure water was added into 1 mL of above concentrated PDEAEMA-AuNP THF solution and mixed. The solution mixture was bubbled with CO₂ (~60 mL/min) for ~ 3 hours to blow THF away and disperse PDEAEMA-AuNPs in water. Finally light wine-color, clear solution was obtained. This solution was then purged with CO₂ and N₂ (~60 mL/min) alternatively to estimate the CO₂-switchable property of the AuNPs.

Catalytic reduction of 4-nitrophenol (4-NP) over PDEAEMA-AuNP catalyst: Three mL of CO₂ purged PDEAEMA-AuNP clear aqueous solution ([Au]=19 ppm, confirmed by NAA) was mixed with 1 mL of 0.5 mM 4-NP solution. And then 4 mL of 5 mM NaBH₄ solution was added immediately and mixed. At certain time intervals, aliquots of the reaction mixture were taken out and injected into a quartz cuvette for monitoring the reaction process with UV-Vis absorption spectroscopy. After the reaction finished, the solution was bubbled with N₂ to form an opaque suspension. This suspension was allowed to stand without disturbing for a short time until the AuNPs float onto the solution surface, and then the clear solution containing products was gently extracted to separate the products and the floating layer containing the Au catalyst. The PDEAEMA-AuNPs were subsequently re-dispersed in water by CO₂ bubbling and re-used for the next round of catalytic reaction.



Fig. S1 (a) TEM image of as-prepared PLAL-AuNPs; (b) Histogram of NP size distribution.



Scheme 1. (a) Reactions of the side chains of PDEAEMA on AuNP surface upon CO_2 and N_2 bubbling. (b) Schematic illustration of catalytic cycles using PDEAEMA-AuNPs as catalyst via CO_2/N_2 bubbling.



Fig. S2 TEM images of PDEAEMA-AuNPs before (a) and after CO_2 bubbling (b); Insets show selected area electron diffraction (SAED) patterns; (c) and (d) show corresponding high-resolution TEM (HRTEM) images of (a) and (b), respectively. The spacing (0.234 nm) of lattice fringes in (c) and (d) matches the interplanar distance of the {111} crystal plane of face-centered cubic structure of Au, consistent with the crystalline structure shown in the SAED patterns.³ These results suggest that the crystalline structure does not change before and after CO_2 bubbling.



Fig. S3 UV-Vis absorption spectra of 4-NP in the presence of N_2 bubbled PDEAEMA-AuNPs and NaBH₄ for 60 min.

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