

Supporting Information

Hairy Hybrid Microrattles of Metal Nanocore with Functional Polymer Shell and Brushes

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Experimental Section

Materials

Gold (III) chloride trihydrate (99%), silver nitrate (99%), 4-nitrophenol (98%), tetraethyl orthosilicate (TEOS, 98%), 3-(trimethoxysilyl)propylmethacrylate (MPS, 98%), *O*-[2-(3-mercaptopropionylamino)ethyl]-*O'*-methylpolyethylene glycol 5,000 (PEG-SH, $M_n = 5,000$ g/mol), and *N*-isopropylacrylamide (NIPAM, 97%) were used as received from Sigma-Aldrich Chemical Co. Methacrylic acid (MAA, 99%, Sigma-Aldrich) was purified by vacuum distillation. Divinylbenzene (DVB80, Fluka, containing 80% divinylbenzene isomers) was washed with 5% aqueous sodium hydroxide and water and then dried over anhydrous magnesium sulfate. 2,2'-Azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized from methanol. The thiol-terminated poly(*N*-isopropylacrylamide) (PNIPAM-SH) chains were synthesized according to procedures reported in the literature¹ (from gel permeation chromatography or GPC measurements: $M_n = 11,600$ g/mol, polydispersity index or PDI = 1.32). Polyvinylpyrrolidone (PVP, 40,000 g/mol, Fluka), formaldehyde (37%, Nacalai Tesque), hydrofluoric acid (HF, 48%, Riedel-de Haen), ammonia solution (25 wt%, Merck), sodium borohydride (NaBH₄, Merck), acetonitrile (HPLC grade, Merck) were all used without further purification.

Synthesis of the Au@SiO₂-MPS and Ag@SiO₂-MPS Core-shell Nanoparticles via the Sol-gel Reaction

Gold nanoparticles (Au NPs) were prepared according to the standard sodium citrate reduction method.^{2,3} Briefly, 30 mL of aqueous solution of hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O, 0.022 g, 0.056 mmol) in a 50 mL round bottom glass flask was heated to reflux under magnetic stirring, followed by addition of a given volume of freshly

prepared aqueous solution of trisodium citrate. The reduction of HAuCl_4 was then initiated by trisodium citrate. The reaction was allowed to proceed under reflux for 0.5 h. About 4 mg of PVP was added to the mixture to stabilize the Au NPs as the reaction mixture was cooled to ambient temperature. Au NPs of different sizes were produced using similar procedures by varying the ratio of sodium tricitrate to gold (III) chloride trihydrate. Thus, Au NPs of 18, 23 and 45 nm in average diameters were obtained using trisodium citrate concentration of 3.5, 2.0 and 1.5 mM, respectively.

3-(Trimethoxysilyl)propylmethacrylate-modified gold@silica core-shell microspheres ($\text{Au@SiO}_2\text{-MPS}$) were prepared according to the modified Stöber method. Briefly, 10 mL of the aqueous Au NPs was first mixed with 40 mL of ethanol and 0.15 mL (0.67 mmol) of TEOS. The reaction mixture was placed in an ultrasonic water bath for 15 min prior to the addition of 1.2 mL of ammonia solution (25 wt%). The reaction mixture was sealed and stirred for 6 h at room temperature to allow for the coating of silica on Au NPs. About 0.15 mL of MPS (0.63 mmol) was then added and the reaction mixture was stirred for an additional 18 h to allow for the modification of the silica surface with MPS. After the reaction, the resulting $\text{Au@SiO}_2\text{-MPS}$ core-shell nanospheres were cleaned three times by dispersing the particles in THF, followed by centrifugation using *n*-hexane as the precipitating agent. The purified $\text{Au@SiO}_2\text{-MPS}$ particles were dried in a vacuum oven at room temperature overnight. Thus the $\text{Au@SiO}_2\text{-MPS}$ core-shell particles of 59, 70 and 90 nm in shell-thicknesses were synthesized via the sol-gel process using initial TEOS feed concentrations of 0.15, 0.20 and 0.25 mL, respectively.

For the synthesis of silver nanoparticles (Ag NPs), silver nitrate was used as the precursor.⁴ About 0.85 g of AgNO₃, 1.1 g of PVP and 1.5 mL of formaldehyde were introduced into 50 mL of deionized water in a 100 mL round-bottom glass flask. About 0.30 g of anhydrous sodium hydroxide in 10 mL of water was then added into the reaction mixture. Upon addition of sodium hydroxide, the reaction mixture turned grey instantaneously. The synthesized silver NPs were separated from the solution by adding four times the volume of acetone. The mixture was then centrifuged at 6000 rpm for 6 min. The black precipitate was washed three times with an acetone/water mixture (v/v = 3/1). The synthesized 38-nm Ag NPs were finally re-dispersed into 80 mL of ethanol for the subsequent silica coating process.

The Ag@SiO₂-MPS core-shell NPs were synthesized by the sol-gel process, similar to that used for the fabrication of Au@SiO₂-MPS core-shell NPs. About 8 mL of the ethanol dispersion of Ag NP seeds, 5 mL of deionized water, 14 mL of ethanol and 0.10 mL (0.44 mmol) of TEOS were introduced into a 25 mL round bottom flask. The mixture was stirred for 10 min prior to adding 0.8 mL of ammonia solution (25 wt%, Merck) and the reaction mixture was stirred for 6 h. 0.1 mL of MPS was then added and the resulting mixture was left stirring for an additional 18 h. The reaction mixture was centrifuged at 8200 rpm for 10 min. The resultant Ag@SiO₂-MPS core-shell microspheres were cleaned and dried using procedures similar to those used for the Ag@SiO₂-MPS core-shell NPs.

Synthesis of the Au@SiO₂@Poly(methacrylic acid-co-divinylbenzene) (Au@SiO₂@P(MAA-co-DVB)) and Ag@SiO₂@P(MAA-co-DVB) Core-Double Shell

Microspheres via Distillation-Precipitation Polymerization

For the synthesis of Au@SiO₂@P(MAA-*co*-DVB) (or Ag@SiO₂@P(MAA-*co*-DVB)) core-double shell microspheres,^{5,6} About 0.02 g of the Au@SiO₂-MPS (or Ag@SiO₂-MPS) core-shell microspheres were dispersed into 10 mL of acetonitrile under ultrasonication. A mixture of methacrylic acid (MAA, 60 μL, 0.70 mmol), divinylbenzene (DVB, a crosslinking agent, 40 μL, 0.29 mmol) and 2,2'-azobisisobutyronitrile (AIBN, 2.0 mg, 0.012 mmol) were then introduced into the flask to initiate the polymerization. The polymerization reaction was allowed to proceed under reflux for 4 h. The Au@SiO₂@P(MAA-*co*-DVB) (or Ag@SiO₂@P(MAA-*co*-DVB)) core-double shell microspheres were purified by extraction three times with acetonitrile and ethanol to remove the un-reacted monomers and oligomers.

Synthesis of the Au@SiO₂@P(MAA-*co*-DVB)-*click*-PEG and Ag@SiO₂@P(MAA-*co*-DVB)-*click*-PNIPAM Hairy Core-Double Shell Microspheres via the Thiol-ene Surface Click Reaction

About 0.02 g of the Au@SiO₂@P(MAA-*co*-DVB) microspheres and 0.10 g of the PEG-SH (or PNIPAM-SH) were introduced into 10 mL of acetonitrile in a reaction flask under vigorous stirring. After degassing by argon for 15 min, 0.020 g of the AIBN initiator was added into the reaction mixture. The flask was sealed and the thiol-ene click reaction was allowed to proceed at 75°C for 48 h. The resulting Au@SiO₂@P(MAA-*co*-DVB)-*click*-PEG microspheres were purified three times with ethanol to remove the un-reacted PEG-SH chains. Similar procedures were used for the preparation of the hairy Ag@SiO₂@P(MAA-*co*-DVB)-*click*-PNIPAM core-double shell microspheres from the surface 'click' reaction between the Ag@SiO₂@P(MAA-*co*-DVB) core-double shell microspheres and PNIPAM-SH homopolymer chains.

Preparation of the Hairy Hybrid Microrattles by HF Etching of the Hairy Core-double Shell Microspheres

The hairy Au@air@P(MAA-co-DVB)-click-PEG (or Ag@air@P(MAA-co-DVB)-click-PNIPAM) hybrid microrattles were prepared by selective removal of the silica inner-shell from the respective Au@SiO₂@P(MAA-co-DVB)-click-PEG (or Ag@ SiO₂@P(MAA-co-DVB)-click-PNIPAM) hybrid microspheres in 24% HF for 6 h. The etching process was repeated twice to ensure the complete removal of the silica inner-shell. The resulting hybrid microrattles were cleaned by dialysis until the pH of medium became constant upon the complete removal of residual HF and SiF₄ from the system.

Catalytic Reduction of *p*-Nitrophenol in the Hairy Au@air@P(MAA-co-DVB)-click-PEG Hybrid Microrattles

For the spatially confined catalytic reduction of *p*-nitrophenol in the microrattles, about 0.50 mL of the Au@air@P(MAA-co-DVB)-click-PEG microrattles suspension (5.6×10^{-6} M with respect to the gold precursor concentration) in de-ionized water was added to 1 mL of NaBH₄ (Merck, 0.6 M) in a quartz cell. The mixture was magnetically stirred for 30 min at room temperature. *p*-Nitrophenol (1.5 mL, 1.7×10^{-4} M) was then quickly added to the reaction mixture. The progress of the catalytic reaction was monitored by UV-visible absorption at the wavelength of 400 nm at an interval of 6 min. The yellow solution turned colorless slowly with the progress of the catalytic reaction.

Characterization

Field-emission scanning electron microscopy (FESEM) images were obtained on a JEOL JSM-6700 SEM. Transmission electron microscopy (TEM) images were obtained on a JEOL

JEM-2100F field emission TEM. Fourier transform infrared spectroscopy (FT-IR) analysis was carried out on a Shimadzu FT-IR-8400 spectrophotometer, and the samples were scanned over the range of 4000-400 cm^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS Ultra HSA spectrometer equipped with a monochromatized Al $K\alpha$ X-ray source (1468.6 eV photons). Gel permeation chromatography (GPC) measurements were performed on Waters GPC system, equipped with a Waters 1515 isocratic HPLC pump, a Waters 717 plus Autosampler injector, a Waters 2414 refractive index detector and a series of three linear Jordi columns (Jordi Gel DVB 1000A, 300 x 7.8 mm, Cat. No. 10512, Serial No. 15072-17, packed with 5 μm PDVB particles), using THF as the eluent at a flow rate of 1.0 mL min^{-1} . The calibration curve was generated using polystyrene standards. The dynamic laser scattering (DLS) measurements were performed on a Brookhaven 90 plus laser light scattering spectrometer at the scattering angle of $\theta=90^\circ$. The hydrodynamic diameter of microspheres was obtained by averaging the values from five measurements. The UV-visible absorption spectra in the wavelength range of 200 to 800 nm were obtained on a Shimadzu UV-3101PC spectrophotometer. The polydispersity index (PDI) of the microspheres was calculated from the following statistical formulae⁷:

$$PDI = D_w / D_n \quad D_n = \sum_{i=1}^k n_i D_i / \sum_{i=1}^k n_i \quad D_w = \sum_{i=1}^k n_i D_i^4 / \sum_{i=1}^k n_i D_i^3$$

where *PDI* is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, and D_i is the diameter of the microspheres. In each case, about 50-100 particles in the FESEM image were used for the determination of average diameter. Coefficient of variation (CV), defined as the ratio of standard deviation (δ) to the mean (D_n) ($CV = \delta/D_n$), was used to estimate the error in microsphere size.

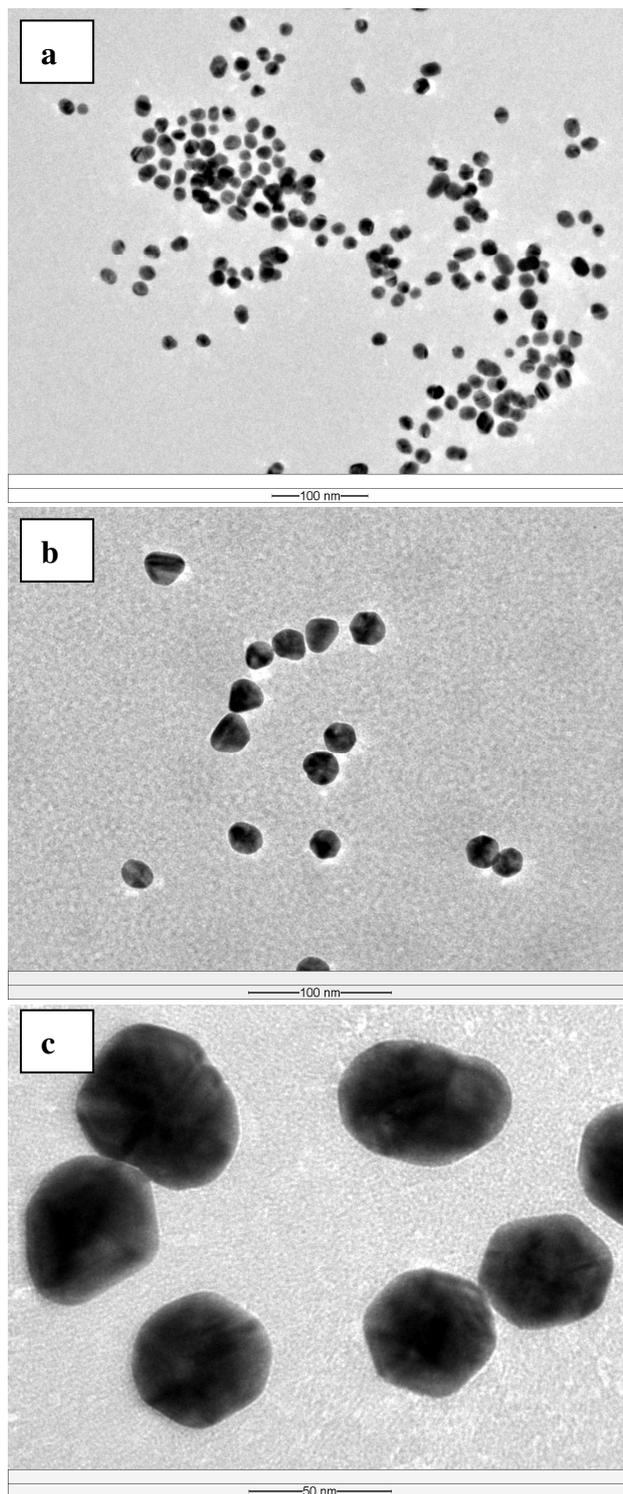


Figure S1 TEM images of the Au nanoparticles (NPs) with average diameters of (a) 18, (b) 23 and (c) 45 nm by adjusting sodium citrate concentration from 3.5 to 2 and 1.5 mM, respectively. The respective scale bars for (a)-(c) are 100, 100 and 50 nm.

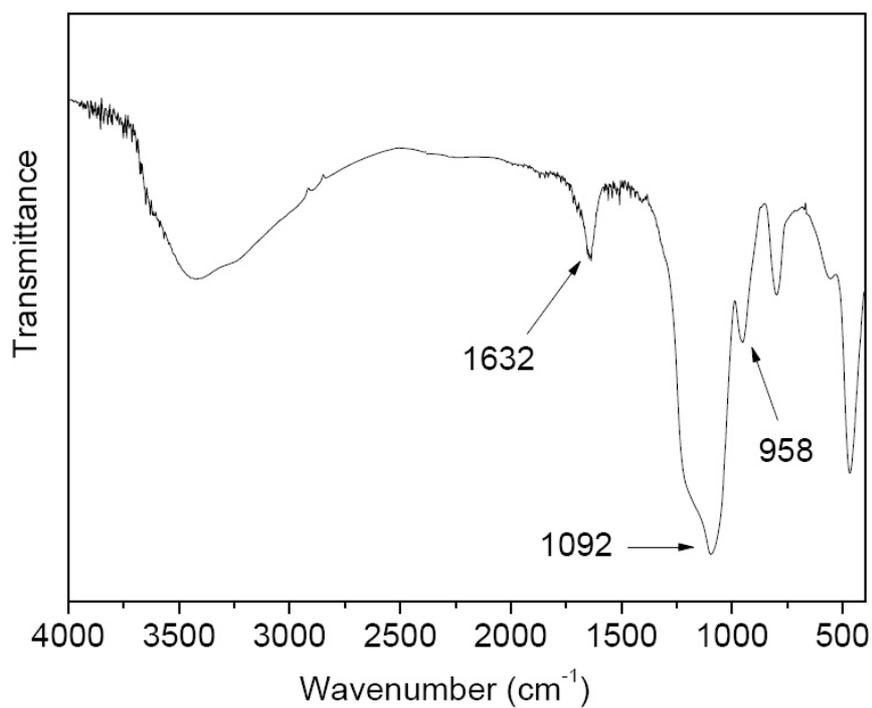


Figure S2 FT-IR absorption spectrum of the Au@SiO₂-MPS core-shell NPs template. The absorption peaks at 958 and 1092 cm⁻¹ are assigned to the characteristic stretching vibration of Si-OH and Si-O-Si groups respectively. The peak at 1632 cm⁻¹ is associated with the vinyl groups from MPS on the surfaces of the core-shell NPs. (MPS: 3-(trimethoxysilyl)propyl methacrylate).

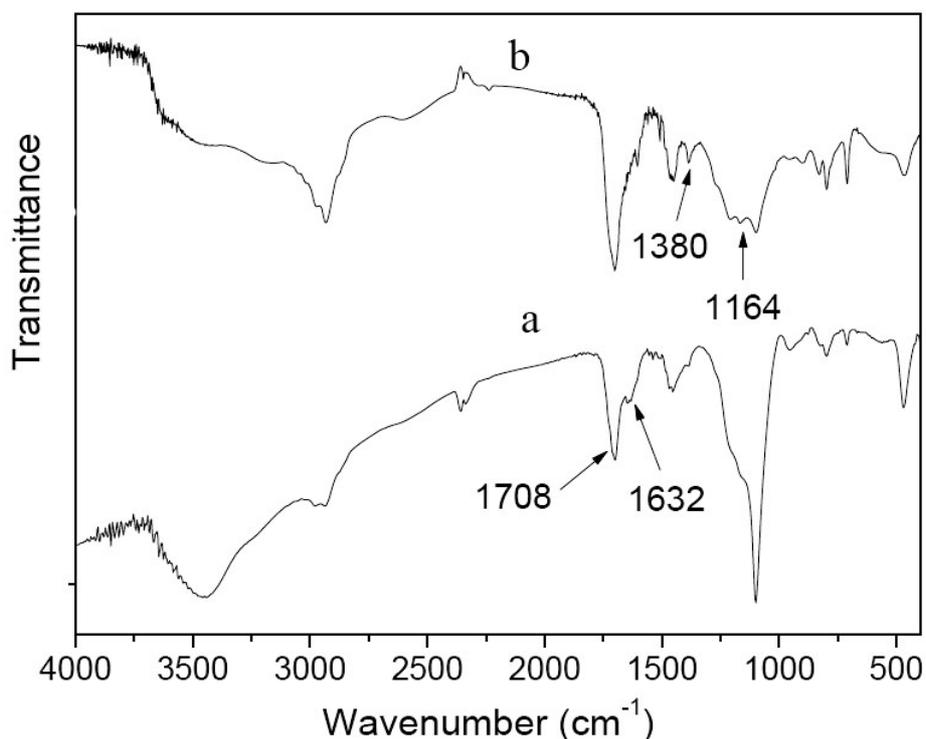


Figure S3 FT-IR absorption spectra of the (a) Au@SiO₂@P(MAA-co-DVB) and (b) Au@SiO₂@P(MAA-co-DVB)-click-PEG microspheres. The absorption peak at 1708 cm⁻¹ corresponds to the stretching vibration of the carboxylic acid groups from PMAA segment. The absorption peak at 1632 cm⁻¹ is assigned to the C=C stretching vibration from the PDVB segments. The absorption peaks at 1164 and 1380 cm⁻¹ are associated with the vibration of C-O and -CH₃ groups from the grafted PEG brushes on the exterior surface of the core-double shell microspheres. (MPS: 3-(trimethoxysilyl)propyl methacrylate; MAA: methacrylic acid; DVB: divinylbenzene; PEG: polyethylene glycol).

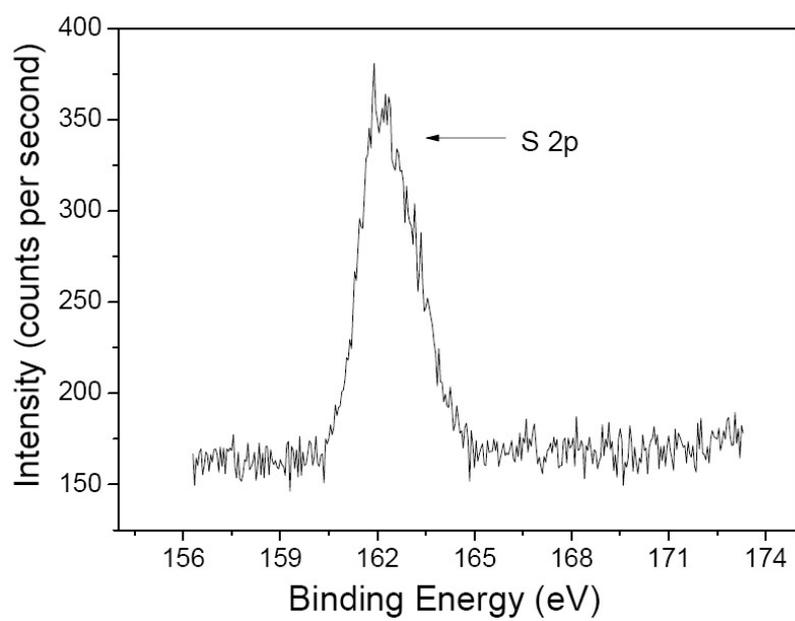


Figure S4 XPS S 2p core-level spectrum of the thiol-terminated poly(ethylene glycol) (PEG-SH) chains.

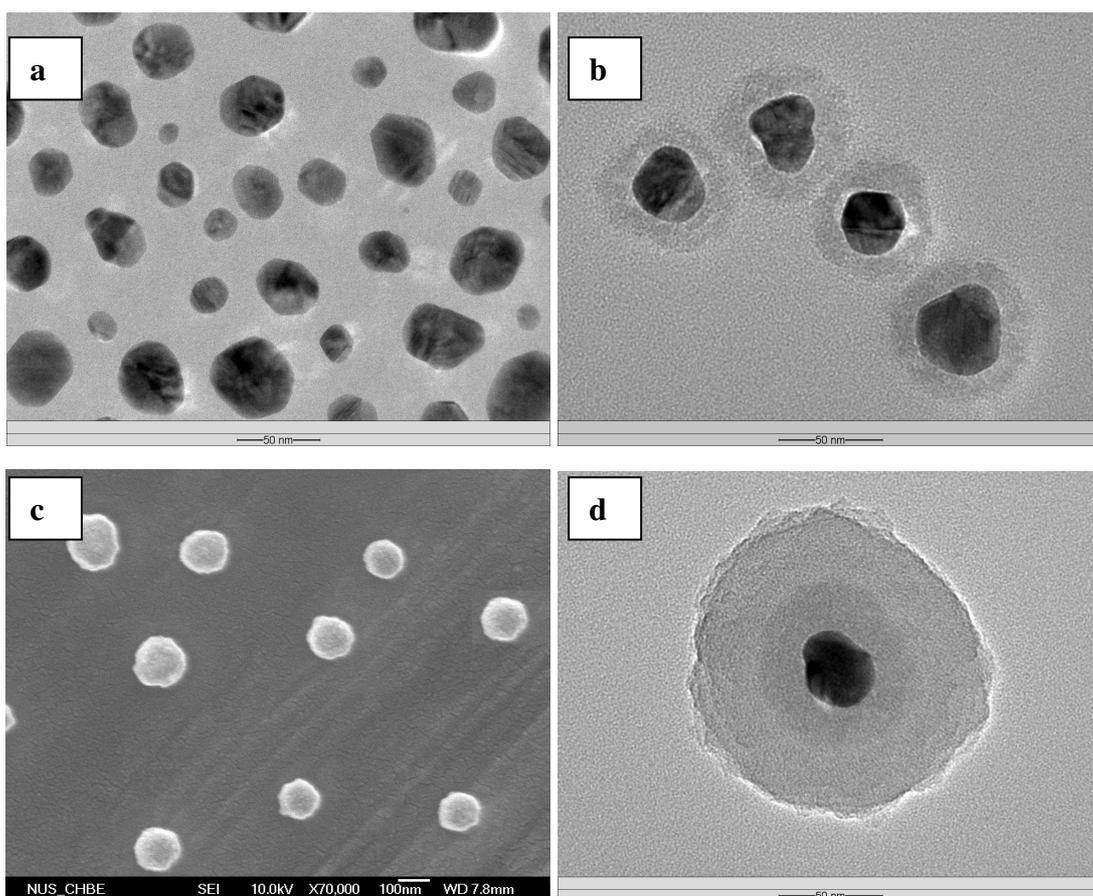


Figure S5 (a) TEM images of the Ag nanocores, (b) TEM images of the Ag@SiO₂-MPS core-shell nanoparticles, and (c) FESEM and (d) TEM images of the Ag@SiO₂@P(MAA-co-DVB) core-double shell microspheres. (MPS: 3-(trimethoxysilyl)propyl methacrylate; MAA: methacrylic acid; DVB: divinylbenzene). The respective scale bars for (a)-(d) are 50, 50, 100 and 50 nm.

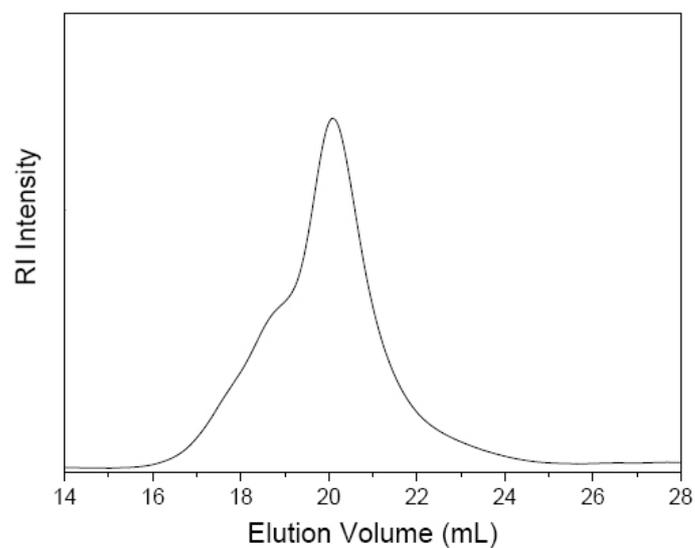


Figure S6 Gel permeation chromatography (GPC) elution curve of the thiol-terminated poly(*N*-isopropylacrylamide) (PNIPAM-SH) chains in *N,N*-dimethylformamide (DMF) at a flow rate of 1.0 mL min⁻¹. The appearance of a shoulder (high molecular weight fraction) in the elution curve is probably due to the formation of some S-S coupling of polymer chains during the reduction process

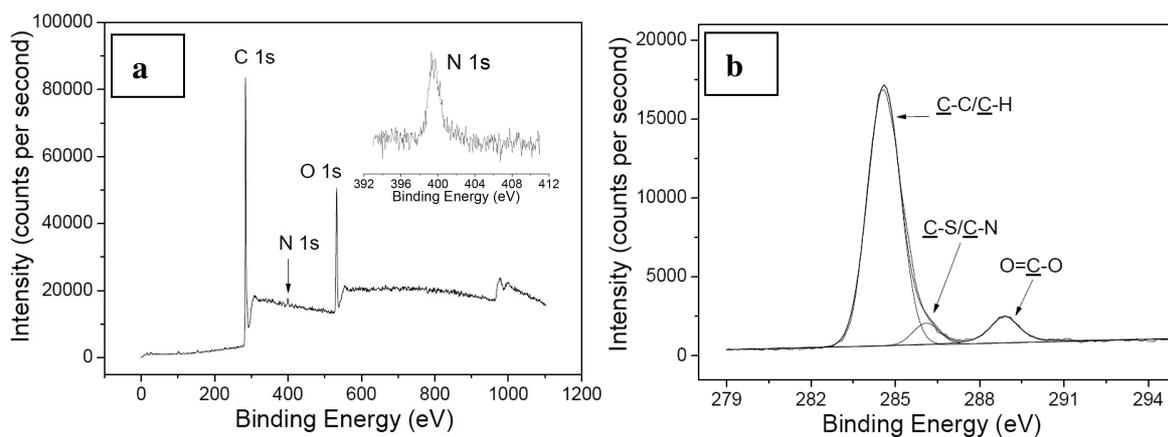


Figure S7 XPS wide-scan (a) and C 1s core-level (b) spectra of the Ag@SiO₂@P(MAA-co-DVB)-click-PNIPAM microspheres. (MAA: methacrylic acid; DVB: divinylbenzene; PNIPAM: poly(*N*-isopropylacrylamide)).

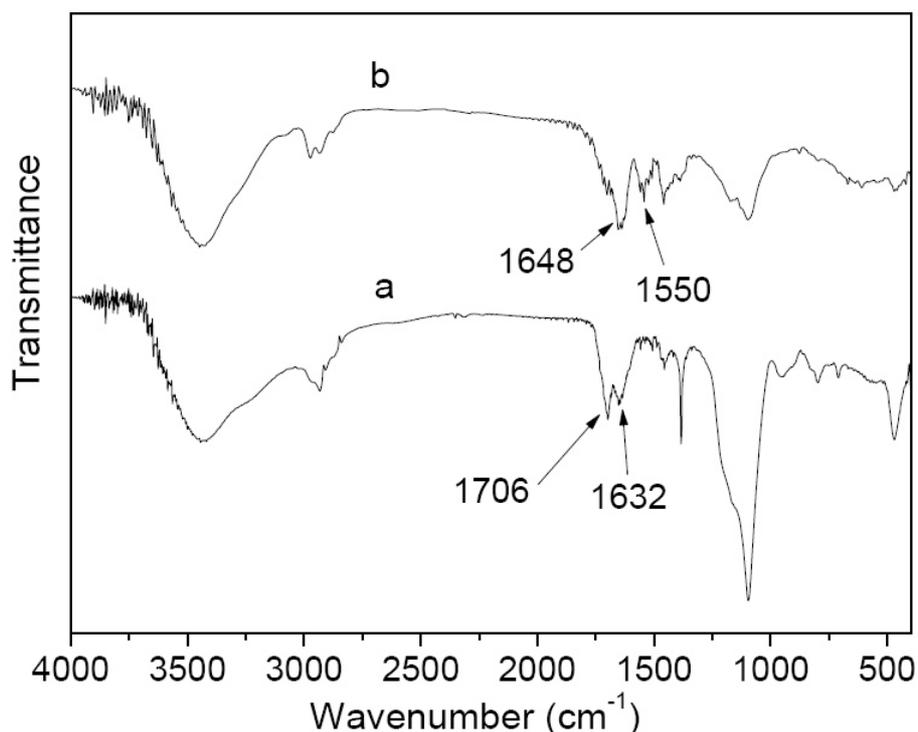


Figure S8 FT-IR spectra of the (a) Ag@SiO₂@P(MAA-co-DVB) microspheres and (b) Ag@SiO₂@P(MAA-co-DVB)-click-PNIPAM microspheres. For the Ag@SiO₂@P(MAA-co-DVB) microspheres, the absorption peak at 1706 cm⁻¹ is associated with the stretching vibration of carboxylic acid groups from PMAA segments. The absorption peak at 1632 cm⁻¹ corresponds to the absorption of vinyl groups from the PDVB segments. Upon grafting of the PNIPAM-SH brushes to the core-double shell microsphere surfaces, the FT-IR spectrum of hairy Ag@SiO₂@P(MAA-co-DVB)-click-PNIPAM core-double shell microspheres exhibit two new absorption peaks at 1648 cm⁻¹ (amide I mode of C=O) and 1550 cm⁻¹ (amide II mode of N-C=O), which are characteristic of the stretching vibration of the amide group from PNIPAM brushes. (MAA: methacrylic acid; DVB: divinylbenzene; PNIPAM: poly(*N*-isopropylacrylamide)).

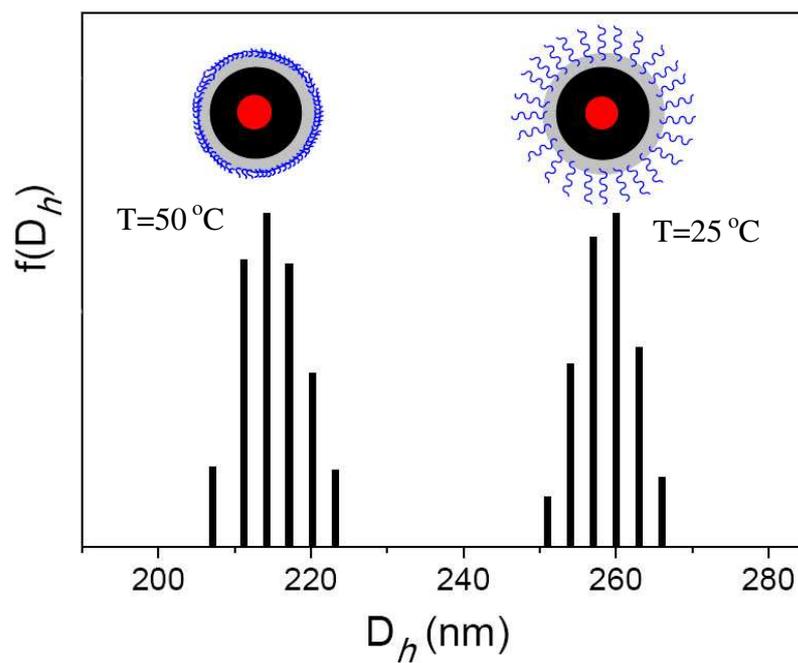


Figure S9 Hydrodynamic diameters (D_h) of the Ag@SiO₂@P(MAA-co-DVB)-click-PNIPAM hairy core-double shell microspheres in aqueous medium at temperature of 25 and 50°C, respectively. (MAA: methacrylic acid; DVB: divinylbenzene; PNIPAM: poly(*N*-isopropylacrylamide)).

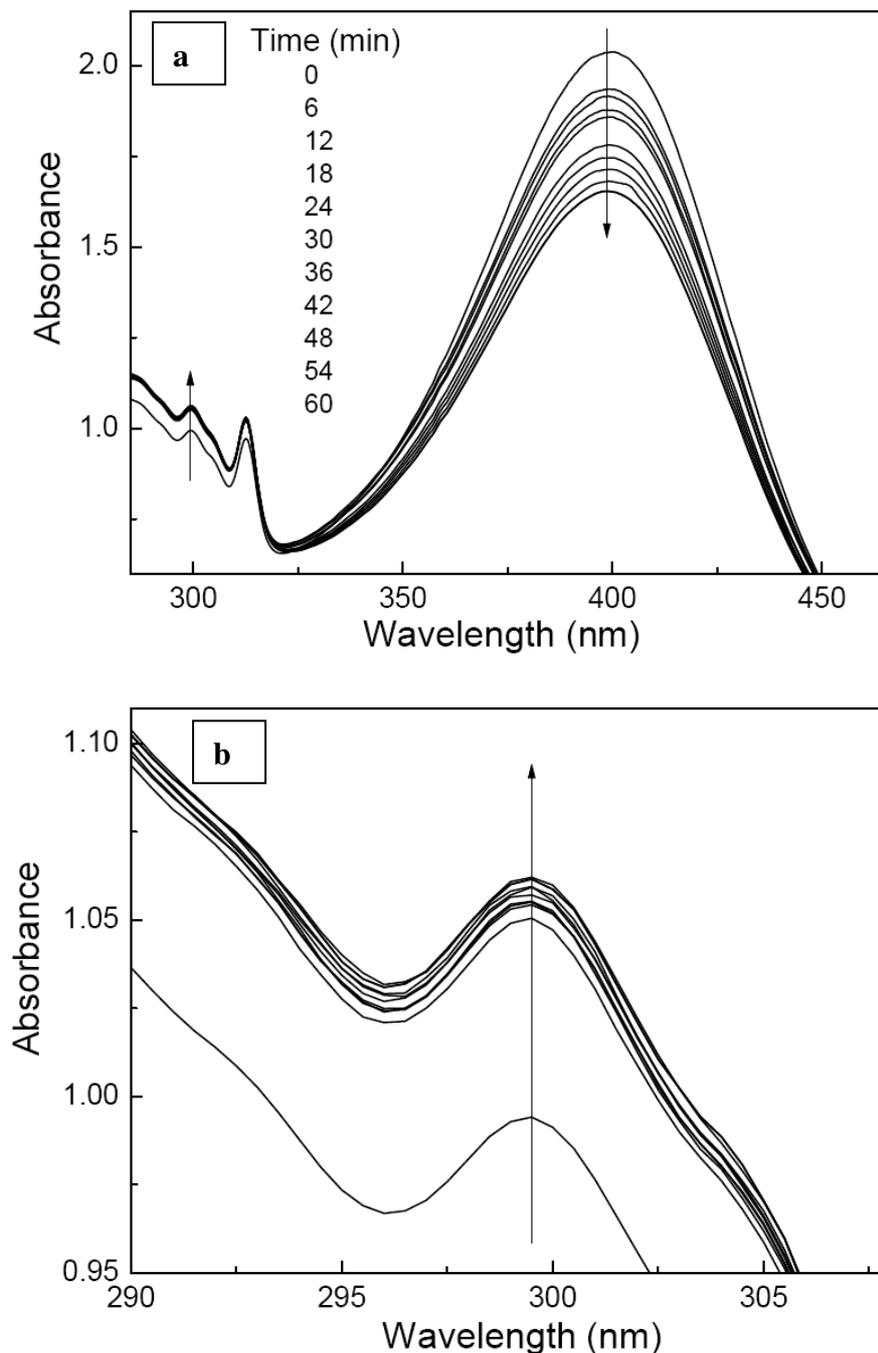


Figure S10 Catalytic reduction of *p*-nitrophenol to *p*-aminophenol ($C_0 = 8.5 \times 10^{-5} \text{ M}$) by the Au@air@P(MAA-*co*-DVB)-*click*-PEG hybrid microrattles as monitored by time-dependent UV-visible absorption spectra. As the catalytic reaction proceeds, the characteristic absorption peak of the reactant (*p*-nitrophenol) at 400 nm decreases with a concomitant increase in the absorption peak of the product (*p*-aminophenol) at 299 nm.⁸⁻¹¹ The product absorptions at high concentrations do not differ significantly from each other probably due to the limited solubility of *p*-aminophenol in the aqueous media.

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