

Supporting Information

Robust Hybrid Nanostructures Comprising Gold and Thiol-Functionalized Polymer Nanoparticles: Facile Preparation, Diverse Morphologies and Unique Properties

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Experimental

Materials

Pentaerythritol tetra(3-mercaptopropionate) (>85%), 1,4-butanedithiol (97%), and tetrakis(hydroxymethyl)phosphonium chloride (THPC, ca. 80% in water) were purchased from Aldrich or TCI and used as received without purification. 1-Dodecylamine (98%), sodium borohydride, and chloroauric acid were purchased from Shanghai Chemical Reagents Co, and used as received without purification. LCHBP was synthesized via tandem ring-opening metathesis polymerization and acyclic diene metathesis polymerization as previously reported procedure,¹ having an absolute molecular weight of 89.3 kDa with a polydispersity of 2.02 analyzed by gel permeation chromatography with multiangle laser light scattering. Solvents were distilled over drying agents under nitrogen prior to use: chloroform (CHCl₃) from calcium hydride, and tetrahydrofuran (THF) from sodium/benzophenone.

Characterization

FTIR spectra were recorded on a Nicolet Nexus 670 in the region of 4000–400 cm⁻¹ using KBr pellets. UV–vis absorption spectra were measured on a UV-1900PC spectrometer. ¹H (500 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ at 25 °C on a Bruker DPX spectrometer. The

hydrodynamic diameter was determined by means of dynamic light scattering (DLS) analysis using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW). Atom force microscopy (AFM) observations were performed on SPM AJ-III atomic force microscope at a measure rate of 1.0005 Hz in the tapping mode, and the AFM images were obtained at room temperature in air. Transmission electron microscopy (TEM) was performed on a JEM-200CX microscope operating at an acceleration voltage of 200 kV. Elemental analysis (EA) was conducted with a varioe EL III. X-ray diffraction (XRD) analyses were carried out on a Bruker D8 Advance, X-ray diffractometer with Cu K α radiation at a wavelength of 1.54 Å. The step size and scan rate were 0.02 and 2° min⁻¹, respectively. Thermal gravimetric analysis (TGA) was performed using an SDTA851e/SF/1100 TGA Instrument under N₂ flow at a heating rate of 10 °C/min from 25 to 800 °C. X-ray photoelectron spectroscopy (XPS) was performed on an ESCA Lab MK II instrument with Al K α radiation as the excitation source (1486.6 eV). All the spectra were recorded under ambient conditions. Cryogenic transmission electron microscopy (cryo-TEM) was performed to characterize the morphology of nanohybrids. A small droplet of solution was placed on a holey carbon film, which was further supported on a TEM copper grid. The droplet was then blotted to form a film of solution on the grid and allowed to equilibrate. The sample-loaded grid was then plunged into liquid nitrogen, and the solvent was vitrified. The sample was then transported under liquid nitrogen and mounted onto a cryogenic sample holder of the TEM. During the entire measurement, the sample was under vacuum and the temperature was maintained at -178 °C. All the images were acquired in a JEOL 1210 TEM, operating at 120 kV. To minimize beam damage, the samples were imaged under minimal electron dose (MDS) conditions.

Transformation of Reactive LCHBPs to the Crosslinked Polymer Nanoparticles with Various Thiol Groups

For 1a: LCHBP (90 mg) and 1,4-butanedithiol (110 mg) (1 : 2.5 molar ratio) were dissolved in dried THF (120 mL, $C = 8 \times 10^{-6}$ mol/L) at room temperature under N₂ atmosphere. 1-Dodecylamine (9 mg, 10 wt%) was added as a catalyst and the mixture was stirred for 4 h. The solution was concentrated under vacuum and precipitated into an excess of methanol, and the precipitate was isolated, dried under vacuum for 24 h to give a solid polymer. ¹H NMR (500 MHz, CDCl₃): 6.98–6.92 (m, CH₂OOCCH=CHCH₂O), 6.44–6.41 (d, HCH=CHCOOCH₂), 6.16–6.10 (m,

CH₂=CHCOOCH₂), 5.88–5.86 (d, HCH=CHCOOCH₂, CH₂=CHCH₂OCH₂, *trans*-CH=CH on polymer chain, CH₂OOCCH=CHCH₂O), 5.60 (s, *cis*-CH=CH on polymer chain), 5.23–5.18 (m, CH₂=CHCH₂OCH₂, *cis*-CHOCH), 4.70 (s, *trans*-CHOCH), 4.32–4.21 (m, OCOCH₂CH₂OCO), 4.00–3.95 (m, CH₂=CHCH₂OCH₂CH=CH), 3.12 (s, OOCCHCH), 2.85–2.76 (m, OOCCH₂CH₂SCH₂), 2.59–2.42 (m, HSCH₂CH₂CH₂CH₂SCH₂), 1.71–1.57 (m, HSCH₂CH₂CH₂CH₂SCH₂). Elemental analysis found: C, 53.1; H, 6.1; O, 28.5; S, 12.3 %.

For 1b: LCHBP (90 mg) and pentaerythritol tetra(3-mercaptopropionate) (240 mg) (1 : 2.5 molar ratio) were dissolved in dried THF (150 mL, $C = 6 \times 10^{-6}$ mol/L) at room temperature under N₂ atmosphere. After adding the catalyst 1-dodecylamine (9 mg, 10 wt%), the mixture was stirred for 2 h. The solution was concentrated under vacuum and precipitated into an excess of ethyl acetate, the precipitate was isolated, dried under vacuum for 24 h to give a solid polymer. ¹H NMR (500 MHz, CDCl₃): 6.99–6.94 (m, CH₂OOCCH=CHCH₂O), 6.42–6.35 (d, HCH=CHCOOCH₂), 6.21–6.13 (m, CH₂=CHCOOCH₂), 6.02–5.86 (d, HCH=CHCOOCH₂, CH₂=CHCH₂OCH₂, *trans*-CH=CH on polymer chain, CH₂OOCCH=CHCH₂O), 5.69–5.60 (s, *cis*-CH=CH on polymer chain), 5.32–5.17 (m, CH₂=CHCH₂OCH₂, *cis*-CHOCH), 4.75–4.68 (s, *trans*-CHOCH), 4.39–4.20 (m, OCOCH₂CH₂OCO), 4.00–3.91 (m, CH₂=CHCH₂OCH₂CH=CH), 3.82–3.76 (m, (CCH₂OCOCH₂)₄), 3.16–3.05 (s, OOCCHCH), 2.87–2.81 (m, OOCCH₂CH₂SCH₂), 2.71–2.59 (m, CH₂SCH₂), 2.41–2.52 (m, COOCH₂CH₂SH), 1.68–1.47 (m, OOCCH₂CH₂SH). Elemental analysis found: C, 49.8; H, 6.8; O, 18.9; S, 24.5 %.

Synthesis of Gold Nanoparticles

Au NPs were prepared by the Duff method.² 1.0 M NaOH (3.0 mL) and THPC solution (2.0 mL), which had been prepared by mixing THPC solution (24 μL, 80%) with water (2.0 mL), were added into deionized water (91.0 mL). The mixture was vigorously stirred for 5 min, followed by the rapid addition H₂AuCl₄ aqueous solution (4.0 mL, 1 wt%), the color of the solution changed to dark brown immediately. After the reaction mixture was stirred for another 2 h, the solution was concentrated under vacuum, filtered through an Isopore polycarbonate filter membrane of 0.2 μm nominal pore size, and then stored at 4 °C prior to further use. The average size of the as-prepared Au NPs was determined using TEM to be about 5 nm.

Conjugation of Gold Nanoparticles onto Thiol-Functionalized Polymer Nanoparticles

A solution of the crosslinked LCHBP **1a** or **1b** in THF (2 mL) at a concentration of 0.5 mg/mL and the aqueous solution of Au NPs (about 5 mL) were mixed with vigorous stirring for 4 h in the dark at room temperature, leading to the attachment of Au NPs on the thiol groups of the crosslinked LCHBP **1a** or **1b**. To remove the remaining free Au NPs, the above solution was centrifuged. After decanting the supernatant, the precipitate was washed with deionized water for 4 times, and then collected the product to be dried for 3 days.

Catalytic Reduction of 4-Nitrophenol

Au/crosslinked LCHBP nanohybrids **2b** (10 mg) was mixed with freshly prepared aqueous solution of NaBH₄ (10 mL, 1.2 M), 4-nitrophenol solution (10 mL, 3.4 mM) was then added with constant magnetic stirring at room temperature. The color of the solution changed gradually from yellow to transparent as the reaction proceeded. At every 60 s interval, a 100 µL aliquot of the reaction mixture was taken out, diluted to 2 mL and analyzed using UV–vis spectroscopy.

Recycling of Gold/Crosslinked LCHBP Nanohybrid Catalyst

After the first batch of 4-nitrophenol reduction with Au/crosslinked LCHBP nanohybrids **2b** ([Au] = 0.085 mg/mL), the solid mass was isolated from the reaction mixture by centrifugation at 9000 rpm for 15 min. The collected product was purified using two cycles of centrifugation, supernatant removal, and re-suspension in water. The recovered nanohybrids **2b** was then used for further catalytic reduction of 4-nitrophenol with NaBH₄ maintaining similar reaction conditions. This process was repeated for five times.

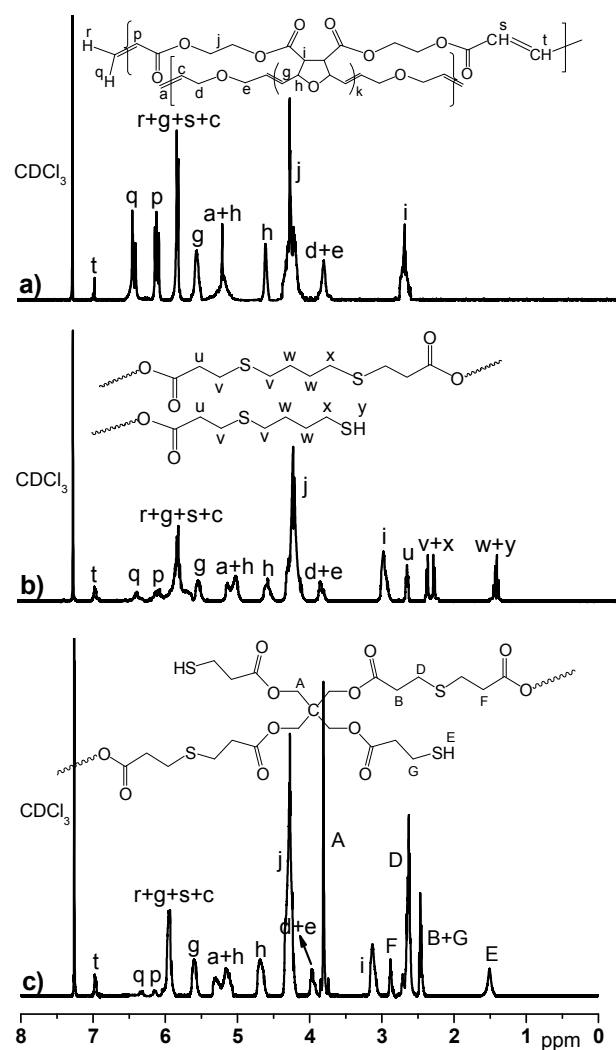


Fig. S1 ^1H NMR spectra of (a) LCHBPs, (b) crosslinked LCHBPs **1a**, and (c) crosslinked LCHBPs **1b**.

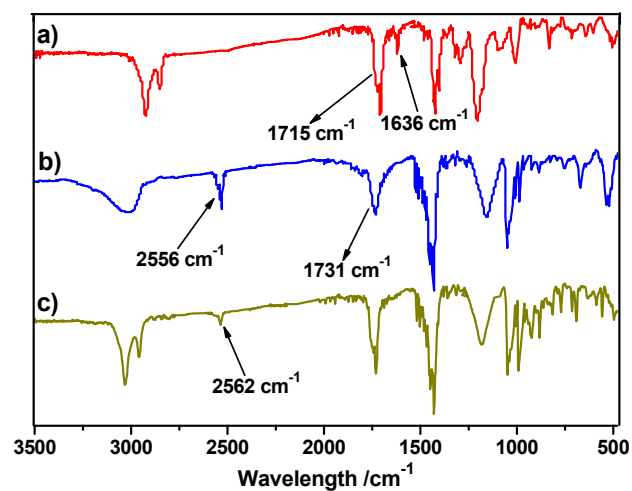


Fig. S2 FTIR spectra for (a) LCHBP, (b) crosslinked LCHBP **1a**, and (c) Au/crosslinked LCHBP **2a**.

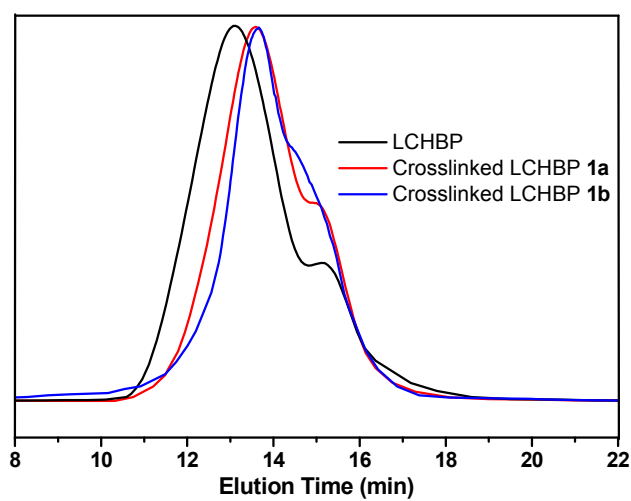


Fig. S3 GPC traces of LCHBP and crosslinked polymer nanoparticles **1**.

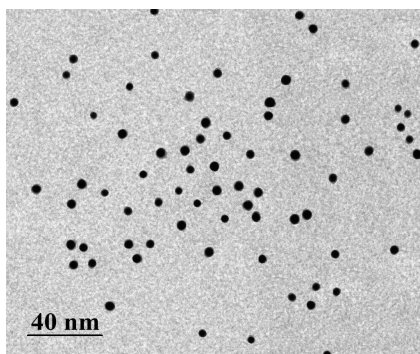


Fig. S4 TEM image of Au nanoparticles.

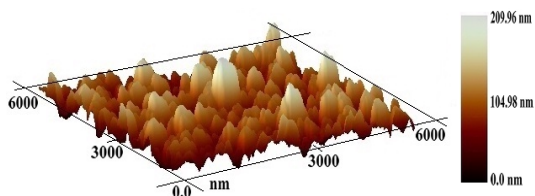


Fig. S5 AFM height image of crosslinked LCHBP nanoparticles **1a** with a concentration of 0.02 mg/mL.

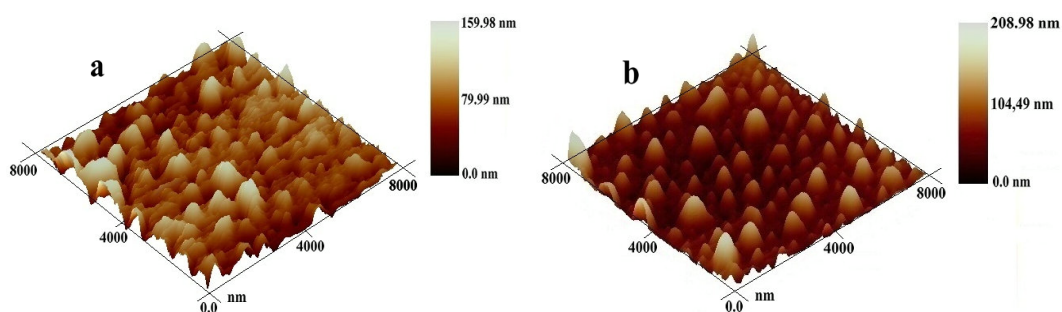


Fig. S6 AFM height images of crosslinked LCHBP nanoparticles **1b** with different concentrations of (a) 0.01 mg/mL and (b) 0.02 mg/mL.

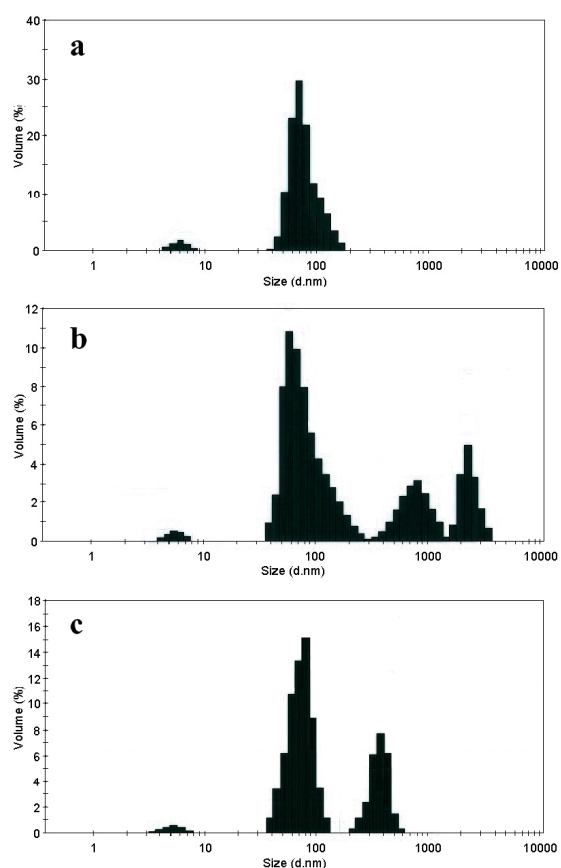


Fig. S7 Size and distribution of Au/crosslinked LCHBP nanohybrids **2b** determined by means of DLS with different concentrations of (a) 0.005 mg/mL, (b) 0.01 mg/mL, and (c) 0.02 mg/mL in THF.

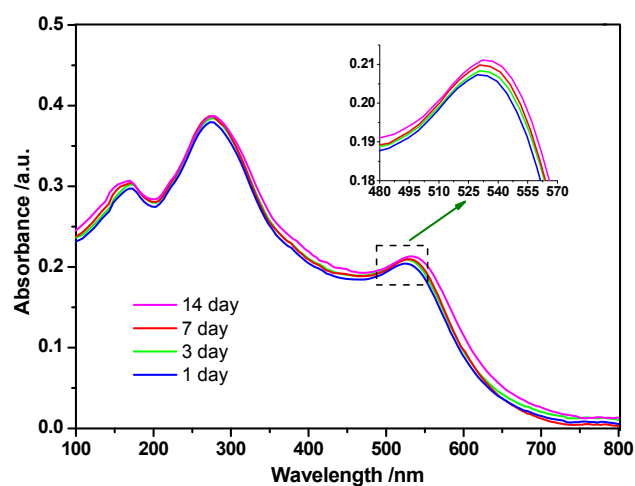


Fig. S8 UV-vis spectra of Au/crosslinked LCHBP nanohybrids **2b** under different storage time.

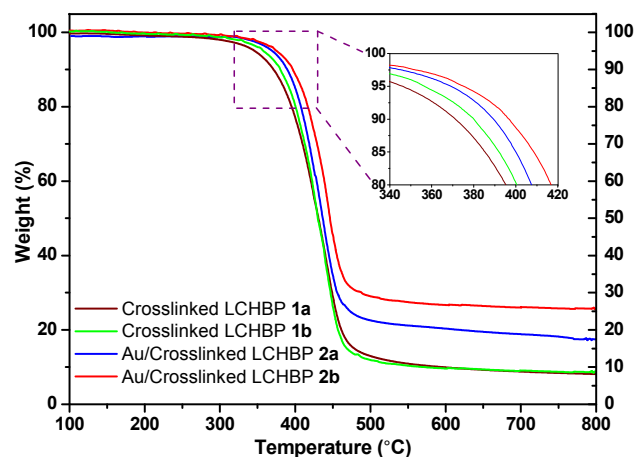


Fig. S9 TGA curves of crosslinked LCHBPs and Au/crosslinked LCHBP nanohybrids.

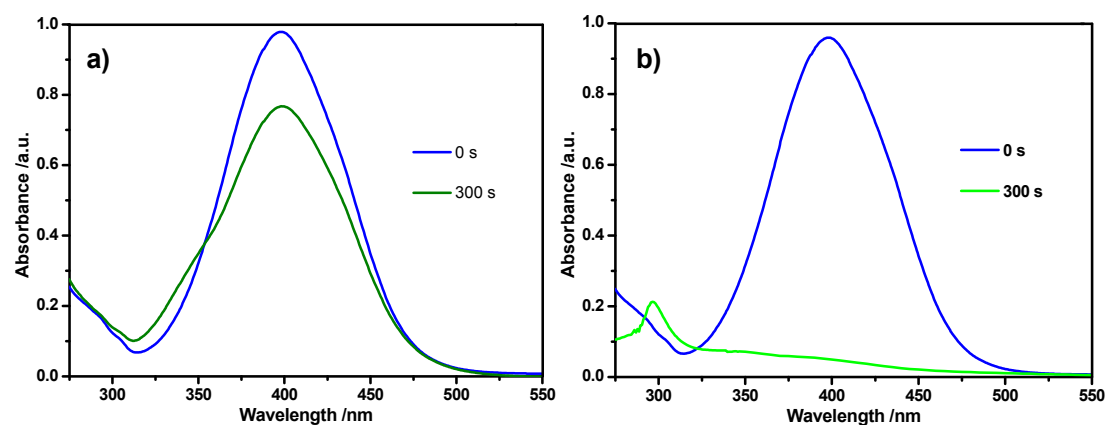


Fig. S10 UV-vis spectra for catalytic reduction of 4-nitrophenol by sodium borohydride using catalyst of (a) bare Au nanoparticles and (b) Au/polymer nanohybrids **2b** for the fifth recycle.

References

- 1 L. Ding, M. R. Xie, D. Yang and C. M. Song, *Macromolecules*, 2010, **43**, 10336.
- 2 (a) D. G. Duff, A. Baiker and P. P. Edwards, *Langmuir*, 1993, **9**, 2301. (b) D. G. Duff and A. Baiker, *Langmuir*, 1993, **9**, 2310. (c) C. C. Huang, C. T. Chen, Y. C. Shiang, Z. H. Lin and H. T. Chang, *Anal. Chem.*, 2009, **81**, 875.