Supplementary Material (ESI) for Chemical Communications

Chiral gold nanoparticle-based electrochemical sensor for enantioselective recognition of 3,4-dihydroxyphenylalanine

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Experimental procedures

Chemicals

Enantiopure D-penicillamine (D-Pen, > 99 %), L-penicillamine (L-Pen, > 99 %), sodium borohydride ($NaBH_4$), 3,4-dihydroxyphenylalanine (DOPA) enantiomers (D- and L-form), and 1,4-butanedithiol (BDT) were obtained from Sigma-Aldrich and were used as received. Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$, 99 %) was purchased from Acros Organics. All other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared using deionized water (> 18 MΩ cm resistivity) purified in a Milli-Q system. Fresh DOPA solutions containing 0.25 M H_2SO_4 (pH 0.6) were prepared and thoroughly deaerated with highly pure nitrogen before electrochemical experiments.

Instrumentation

Electrochemical experiments were performed using a two-compartment three-electrode cell with a gold working electrode, a platinum wire auxiliary electrode, and a saturated Ag/AgCl reference electrode. A CHI660A electrochemical workstation (CH Instruments Co., USA) was used for electrochemical experiments. The size and morphology of synthesized Pen-AuNPs were investigated using a JEOL JEM-3010 transmission electron microscope (TEM) operated at an acceleration voltage of 100 kV. The mean diameters of Pen-AuNPs were estimated by measuring the diameters of 100 individual nanoparticles. The absorption spectra of Pen-AuNPs were obtained with a UV-vis absorption spectrometer (Scinco S-3100, Korea). Circular dichroism (CD) spectra were recorded with a JASCO J-715 spectropolarimeter using a bandwidth of 2 nm. The resolution for ellipticity was 0.01 mdeg. The CD spectra were obtained by averaging four scans.

Preparation of Pen-AuNPs

Pen-AuNPs were synthesized by a procedure reported previously.[1] Each of two kinds of penicillamine enantiomers (D- or L-form) was used as a capping ligand of AuNPs. Briefly, 0.5 mmol of $HAuCl_4$ dissolved in water (0.121 M) and 1.0 mmol of penicillamine were first mixed in methanol (100 mL). A freshly prepared 0.2 M aqueous $NaBH_4$ solution was rapidly added under vigorous stirring. After stirring for 2 h, the solution was stored overnight. Adding ethanol (300 mL) to the solution gave a dark-brown precipitate. The precipitate was thoroughly washed with water/ethanol (1:9) and ethanol, after which the precipitate was re-dissolved in ethanol. After centrifugation for 1 h, the precipitate was filtered using a 0.2 μm PTFE membrane and successively washed with water/ethanol (1:9, 1:1, 1:3, 1:4, and 1:9). Finally, a powder of Pen-AuNPs was obtained by a freeze-drying procedure. The powder was redispersed in distilled water prior to electrochemical experiments. The Pen-AuNP solutions were stored at 4℃ and were stable for a month without aggregation.

Preparation of Pen-AuNP-immobilized gold electrode

Gold electrodes 1.6 mm in diameter were polished using 0.3 μm alumina powder (Buehler, Lake Bluff, MN) and rinsed with deionized water. Residual alumina particles were thoroughly removed by sonicating the electrodes in ethanol and deionized water for 5 min, respectively. The electrodes were immersed in 0.5 M H_2SO_4, and subsequently, applied potential differences of +2.0 V for 5 s and -0.35 V for 10 s. They were electrochemically cleaned in 0.5 M H_2SO_4 by cycling the electrode potential between -0.3 and +1.55 V with a scan rate of 4 V/s until a reproducible cyclic voltammogram was obtained. Finally, they were checked by performing cyclic voltammetry in a fresh 0.5 M H_2SO_4 solution with a scan rate of 0.1 V/s between -0.3 and +1.55 V. The electrochemically cleaned gold electrodes were immersed in an ethanol solution containing 2 mM of BDT for 2 h. They were thoroughly rinsed with ethanol to remove the physically adsorbed BDT. The BDT-modified electrodes were subsequently soaked in the Pen-AuNP solution for 30 min. We found that 30 min was the optimal condition since differences in the anodic peak potentials between D- and L-DOPA (∆E) on Pen-AuNP-immobilized gold electrodes was maximized at 30 min. The Pen-AuNP-immobilized electrodes were washed with copious amount of water and used for electrochemical experiments.

Reference

1 a) H. Yao, K. Miki, N. Nishida, A. Sasaki and K. Kimura, *J. Am. Chem. Soc*. 2005, **127**, 15536; b) H. Yao, T. Fukui and K. Kimura, *J. Phys. Chem. C* 2007, **111**, 14968.

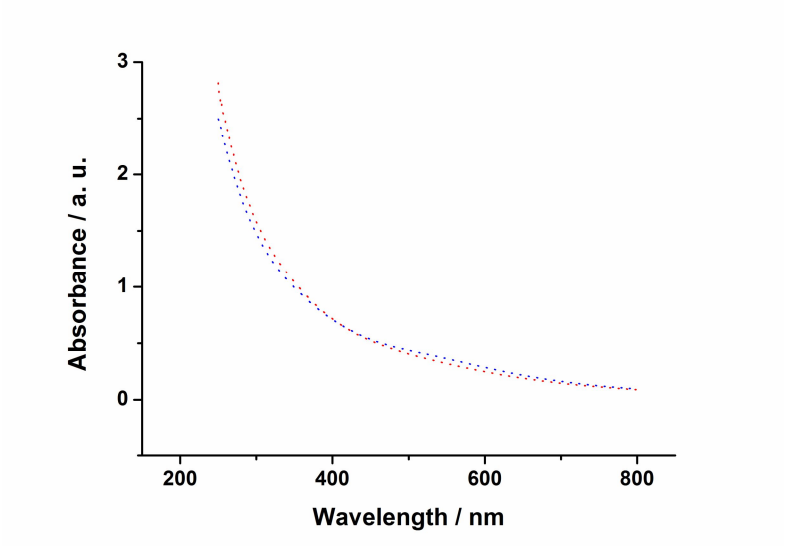

Fig. S1 The UV-vis spectra of 1.9 nm-diameter Pen-AuNPs. The red and blue dotted curves indicate the spectra of D- and L-Pen-AuNPs, respectively.

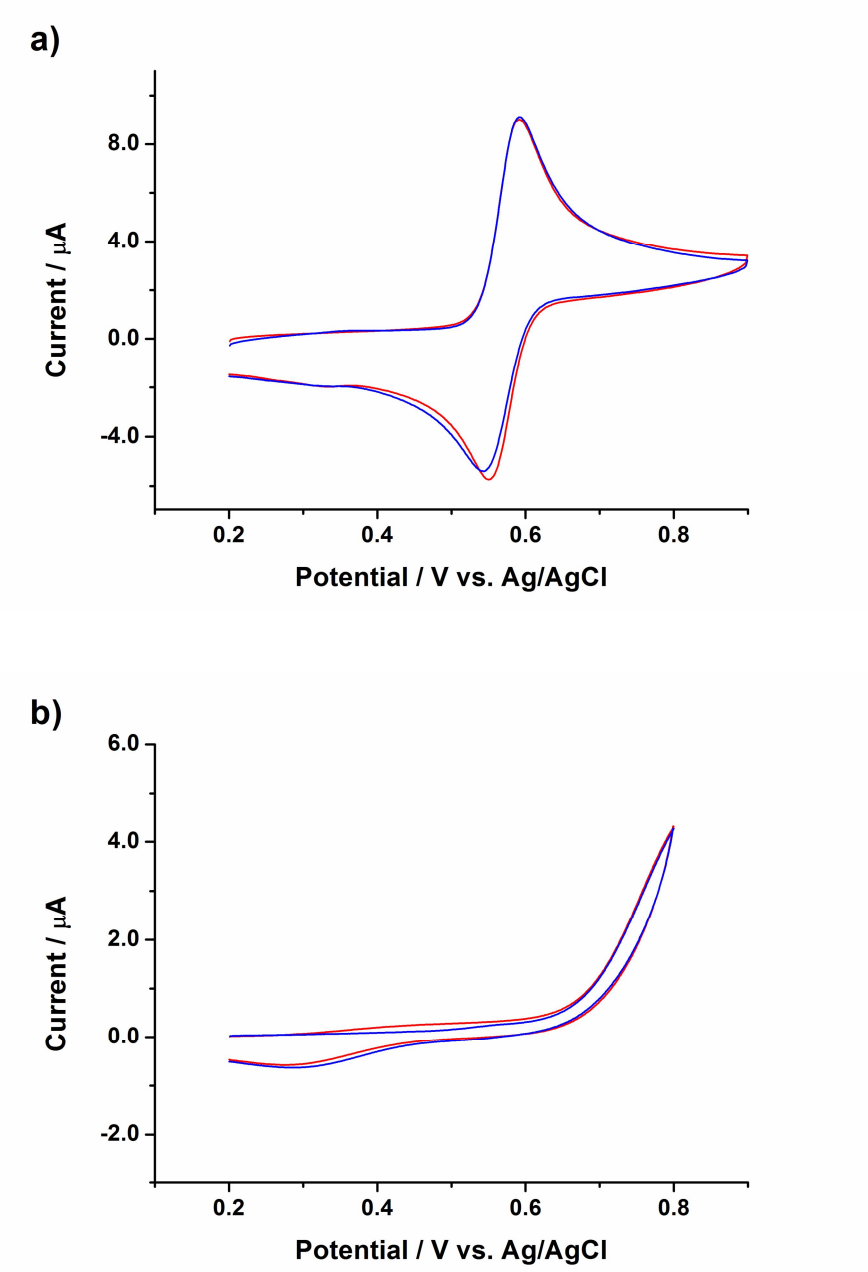

Fig. S2 Cyclic voltammograms for DOPA on a) bare gold and b) BDT-modified gold electrodes in 0.25 M H_2SO_4 (pH 0.6). The scan rate was 50 mV/s. The electrode area was 2.01 mm^2. The red and blue curves indicate the voltammograms for D- and L-DOPA, respectively.

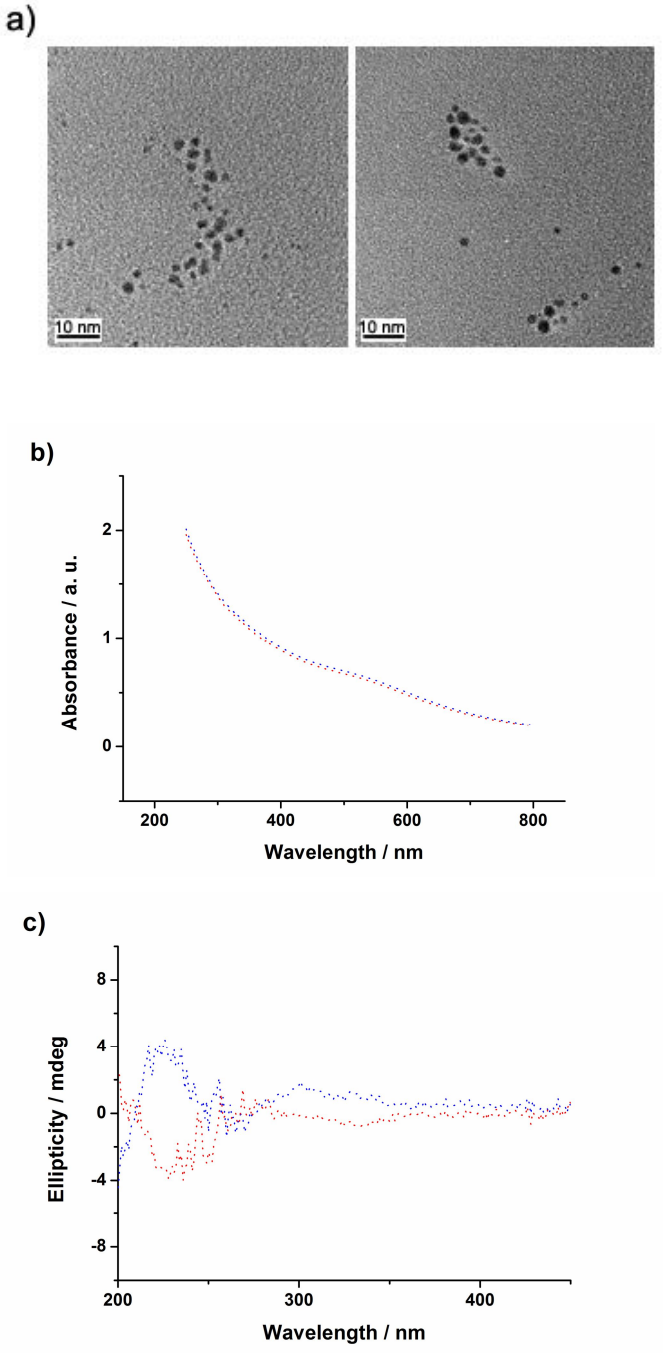

Fig. S3 Characterization of 3.1-nm-diameter Pen-AuNPs. a) TEM images of D-Pen AuNPs (left) and L-Pen AuNPs (right). b) UV-vis and c) CD spectra of D-Pen AuNPs (red dotted line) and L-Pen AuNPs (blue dotted line).

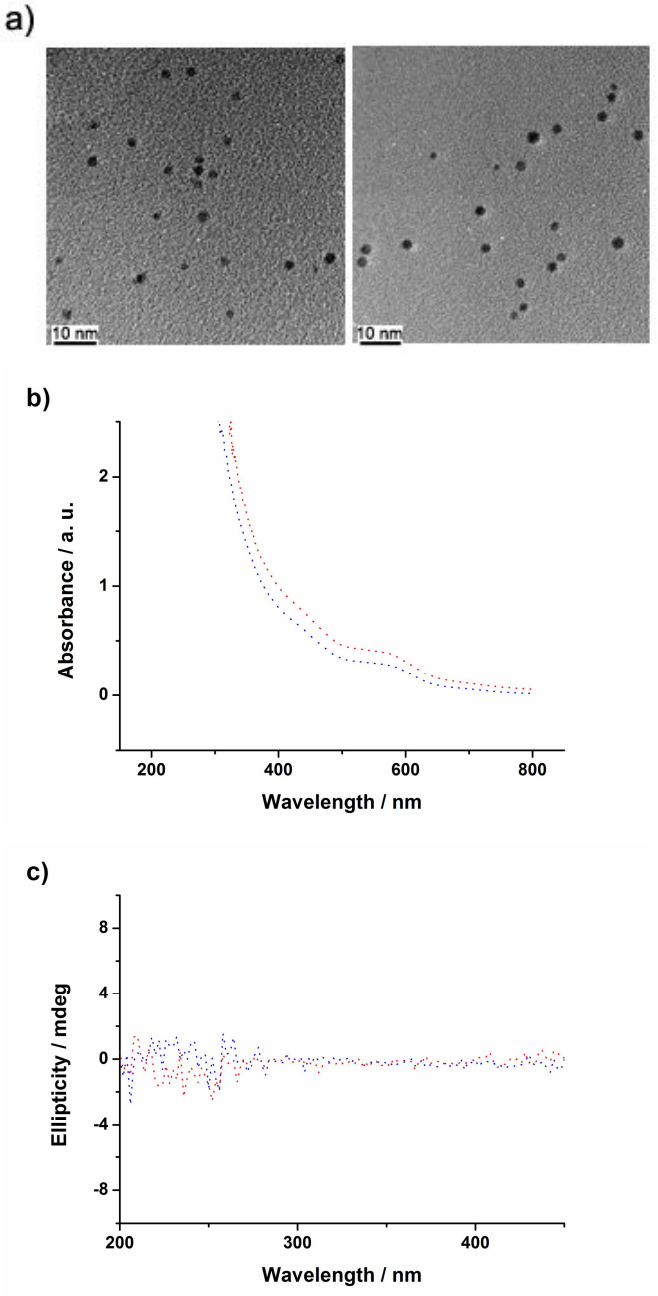

Fig. S4 Characterization of 4.0-nm-diameter Pen-AuNPs. a) TEM images of D-Pen AuNPs (left) and L-Pen AuNPs (right). b) UV-vis and c) CD spectra of D-Pen AuNPs (red dotted line) and L-Pen AuNPs (blue dotted line).

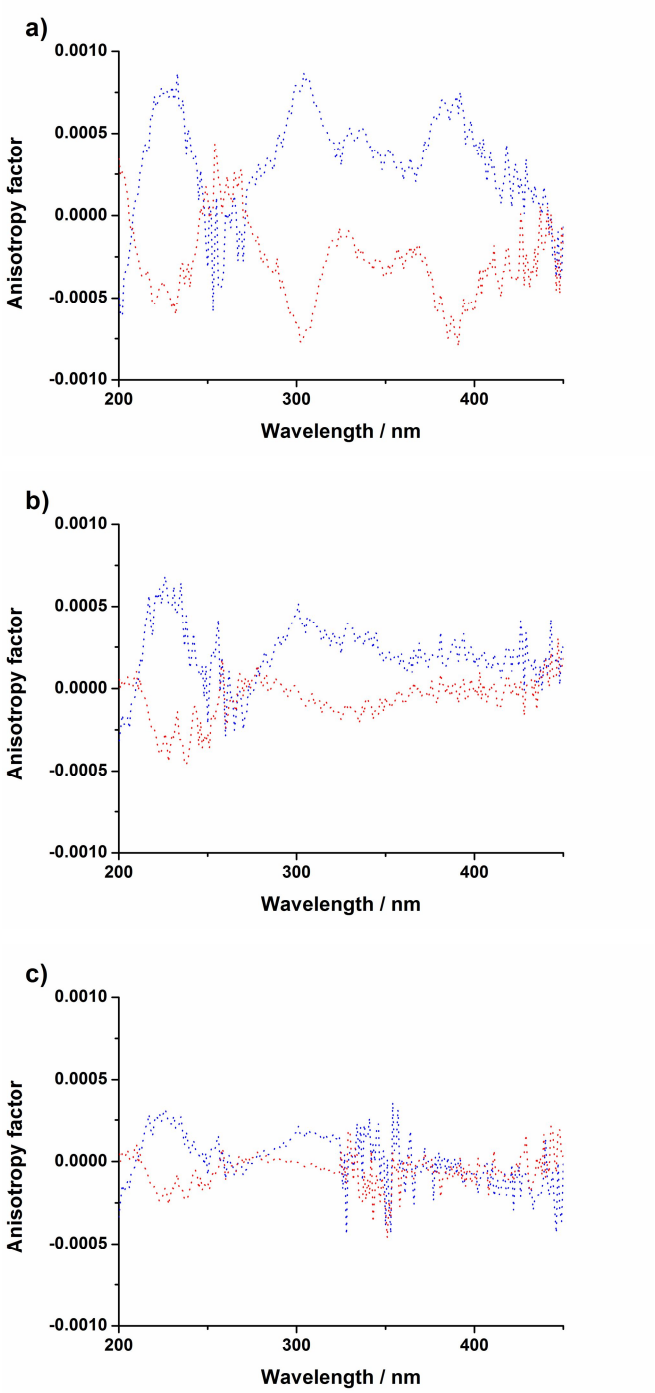

Fig. S5 Anisotropy factors (g-factors) for (a) 1.9-, (b) 3.1-, and (c) 4.0-nm-diameter Pen-AuNPs. $g=\triangle\varepsilon/\varepsilon \fallingdotseq \theta/(33*A)$, where ε is the extinction coefficient, A is the absorbance, and θ is the ellipticity.

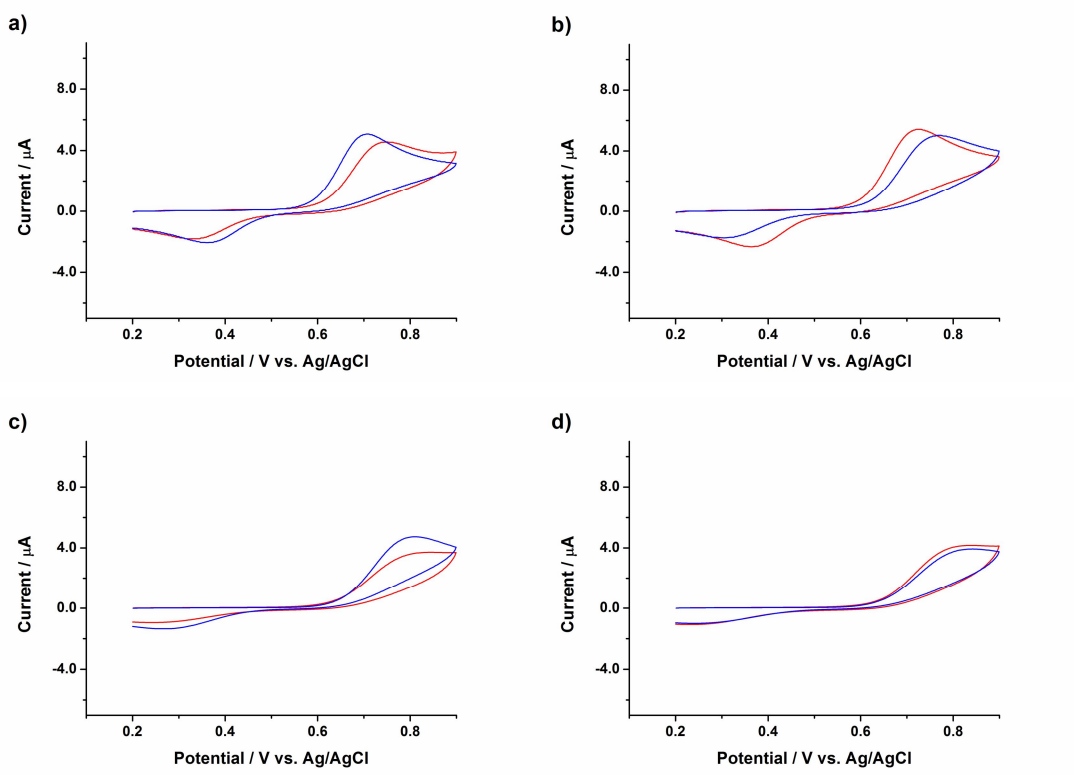

Fig. S6 Cyclic voltammograms for enantioselective recognition of DOPA using Pen-AuNPs of various sizes in 0.25 M H_2SO_4 (pH 0.6). The scan rate was 50 mV/s. The electrode area was 2.01 mm^2. a) 3.1-nm-diameter D-Pen AuNPs, b) 3.1-nm-diameter L-Pen-AuNPs, c) 4.0-nm-diameter D-Pen AuNPs, and d) 4.0-nm-diameter L-Pen-AuNP-immobilized gold electrodes. The red and blue curves indicate the voltammograms for D- and L-DOPA, respectively.