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SUPPORTING INFORMATION

DNA Induced Intense Plasmonic Circular Dichroism of Highly Purified Gold Nanobipyramids

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Experiment section

Materials and Characterization

Tetrachloroauric acid ($HAuCl_4$), acetonitrile and dry ether were bought from Sinopharm. Silver nitrate, sodium borohydride, ascorbic acid, sodium citrate, 1-bromohexadecane, triethylamine and sodium dodecyl sulfate (SDS) were purchased from Alfa Aesar. Cetyltriethylammonium bromide (CTEAB) was synthesized according to the below method. Thiolated or non-thiolated DNA of HPLC grade was obtained from Invitrogen. All of the chemicals were used as received without further purification.

DNA sequence:

Sequence A: 5' AAG AAT TTA TAA GCA GAA-A10-SH 3'

Sequence B: Complementary DNA of sequence A with the sticky end:

5' TTT TTT TTT T TTC TGC TTA TAA ATT CTT GCG C 3'

Scanning electron microscopy (SEM) observation was carried out on a Hitachi S4800 SEM at 10.0 kV. UV−Vis absorption spectra were recorded on a Hitachi U-3010 spectrometer. CD spectra were collected on a Jasco J-810 spectrometer with temperature control accessory (using a quartz cuvette of 10 mm optical length). Density gradient centrifugation was performed on Hitachi CP80MX. Dynamic light scattering (DLS) measurement was performed with Zetasizer Nano ZS.

Synthesis of CTEAB: CTEAB surfactant was synthesized according to a previous literature.[1, 2] In a typical synthesis procedure, 0.1 mol 1-bromohexadecane and 0.1 mol triethylamine were refluxed in 100 mL acetonitrile for 24 h. The obtained two-phase product was firstly rotary-evaporated to remove the remained solvent and then freeze dried to generate a solid product. The dried solid was recrystallized with dry ether 3 times to remove all of the impurities. The final product was freeze dried for further use.

Synthesis of Au nanobipyramids (NBPs): The Au NBPs were synthesized by the previously reported two-step seed-mediated growth method.[3] First, of all, a seed solution was prepared in an aqueous solution of 0.25 mM sodium citrate by reduction of 10 mL of 0.125 mM $HAuCl_4$ with 0.15 mL 10 mM freshly prepared sodium borohydride. The obtained citrate-stabilized Au nanoparticle seeds were kept at 21 °C for 2 h before further use. Subsequently, different amount of seed solution was added to a growth solution containing 0.1 M CTEAB, 0.4 mM $HAuCl_4$, 0.06 mM ascorbic acid, and 0.06 mM silver nitrate. The reaction solution was kept at 21 °C for 24 h and then the resulting solution of Au NBPs was centrifuged to remove the excess CTEAB and redispersed in pure Milli-Q water.

Density gradient centrifugation: The separation of Au NBPs was conducted according to a density gradient centrifugation method. It included the following two steps.

1. Density Gradient Preparation: A five-layer step gradient was made using 50%, 60%, 70%, 80%, and 90% concentration (by volume) ethylene glycol of 10 mM CTEAB solutions. A density gradient was acquired by adding the layers to the centrifugation tube in a way of the gradually decreased density (lower ethylene glycol concentration). First, 1.5 mL of the 90% concentration solution was added to the bottom of the tube as the first layer. Then 1.5 mL of the 80% concentration solution was slowly added above on the first layer. The subsequent three layers

were added following the same procedure, and then a density gradient was obtained along the longitudinal direction of the centrifuge tube.

2. Au NBP Separation: Typically, 7.5 mL of as-synthesized Au NBP solution was centrifuged and redispersed in 0.5 mL 10 mM CTEAB solution. Then, 0.25 mL of the redispersed Au NBP solution was added on top of the density gradient prepared prior to centrifugation. After centrifugated at 8000 rpm for 20 min, micropipettors were used to manually extract the layered solutions. The extracted fractions were then centrifuged and redispersed in pure water for further modification and characterization.

Functionalization of the Au NBPs with DNA: 0.7 mL purified Au NBPs were first mixed with 0.3 mL water and 74 μL 100 μM DNA of sequence A. A mixture of 155 μL 0.1 % SDS and 155 μL 0.1 M buffer solution of sodium phosphate (pH = 7.4) was added to the solution of Au NBPs and DNA, and incubated for 24 h. Subsequently, 8 aliquots of 32.5 μL 1 M sodium chloride were added into the mixture solution at 4 h intervals between each addition. The DNA modified Au NBPs were centrifuged twice to remove the excessive DNA and redispersed in the buffer solution containing 0.01% SDS, 250 mM sodium chloride, and 0.01 M sodium phosphate (pH = 7.4) for the following CD characterization.

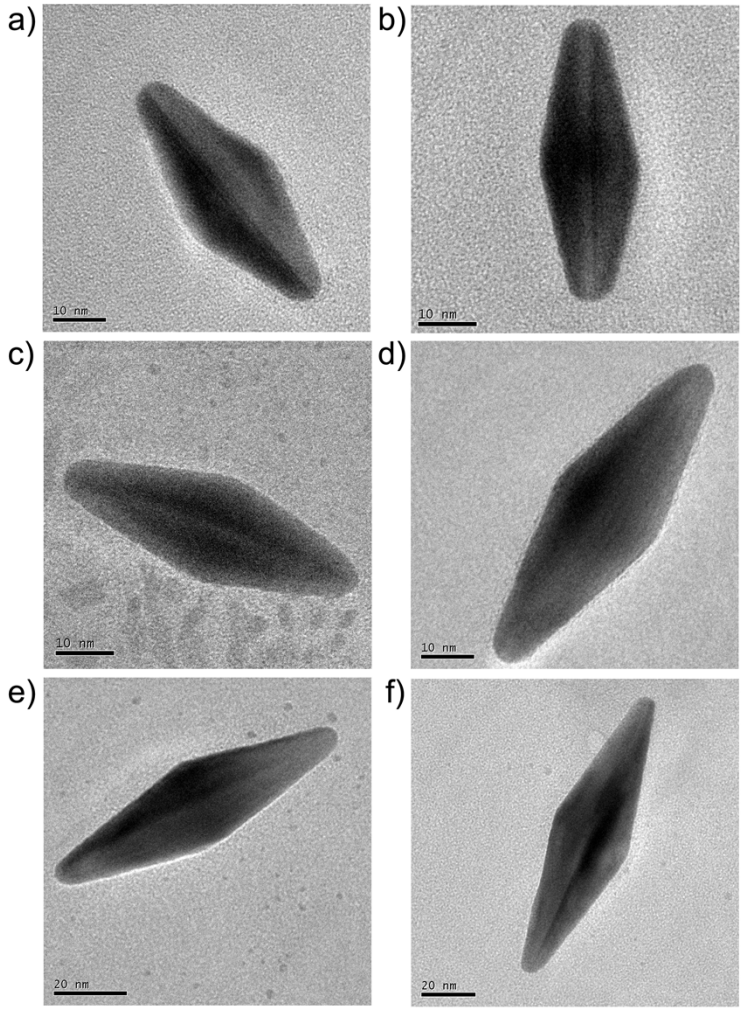

Fig. S1 TEM images of Au NBPs with different aspect ratios.

Table S1. Geometrical and optical data of different Au NBPs from a) to f) in Fig. S7.

	a	b	c	d	e	f
LSPR peak position (nm)	692	724	750	789	821	862
Aspect Ratio	2.44	2.75	2.84	3.09	3.49	3.65
Tip Angle (°)	34.2	27.2	25.8	24.3	23.6	22.5

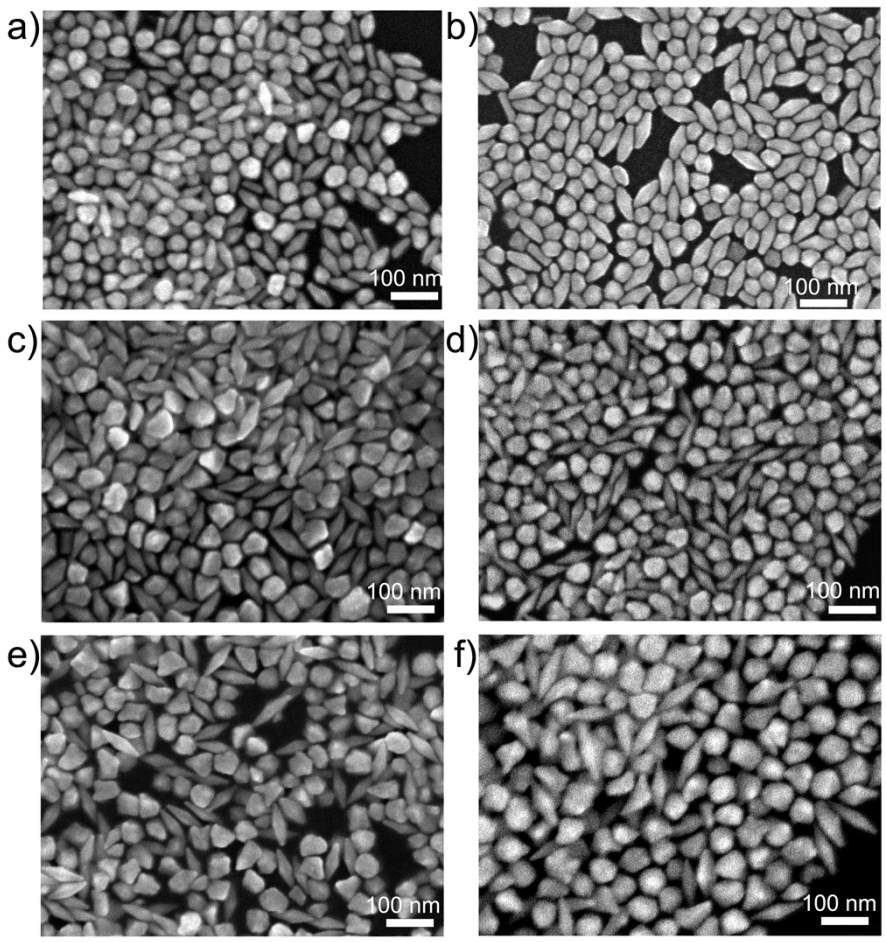

Fig. S2 SEM images of as-synthesized products with different LSPR characteristics. a) to f) correspond to the curve a) to f) in Fig. 1. The yield of Au NBPs in the products is decreased as red shift of LSPR peaks.

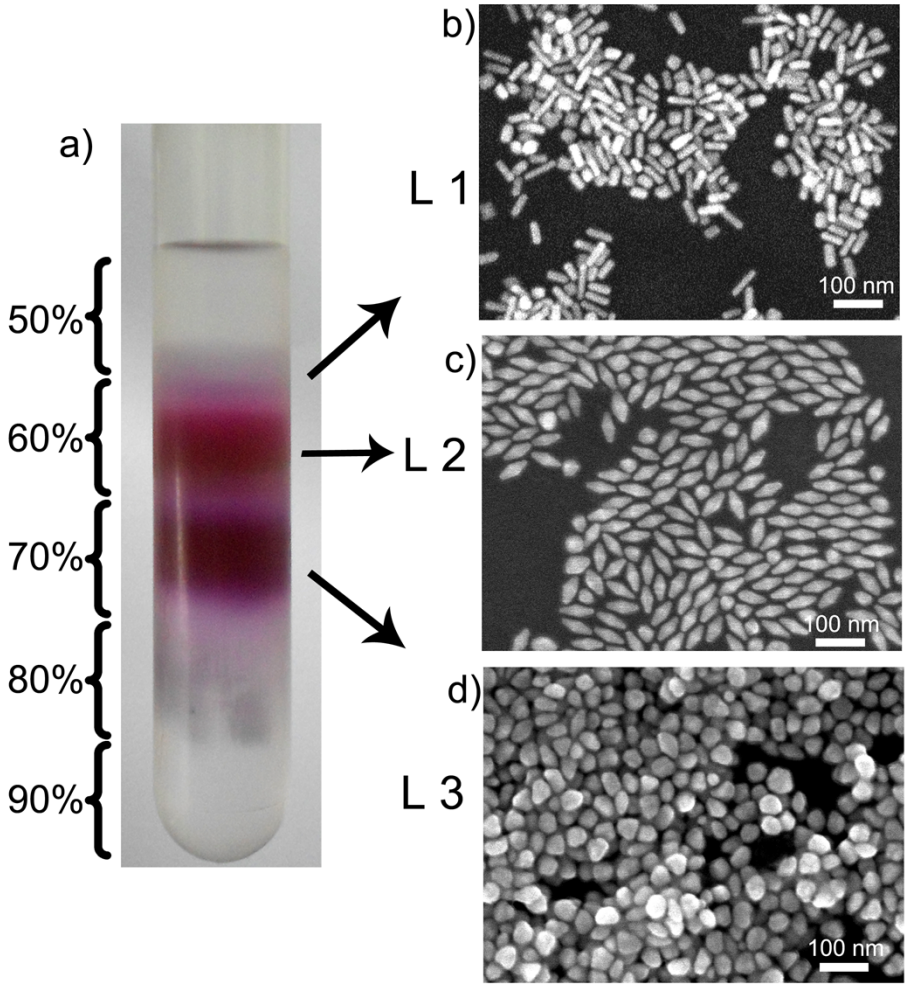

Fig. S3 SEM images for the products at different layers in the tube after density gradient centrifugation: b) Layer 1 mainly includes Au NRs; c) Layer 2 is mostly consisted of Au NBPs with the yield of higher than 90 %; d) Layer 3 is mainly composed of spherical Au NPs.

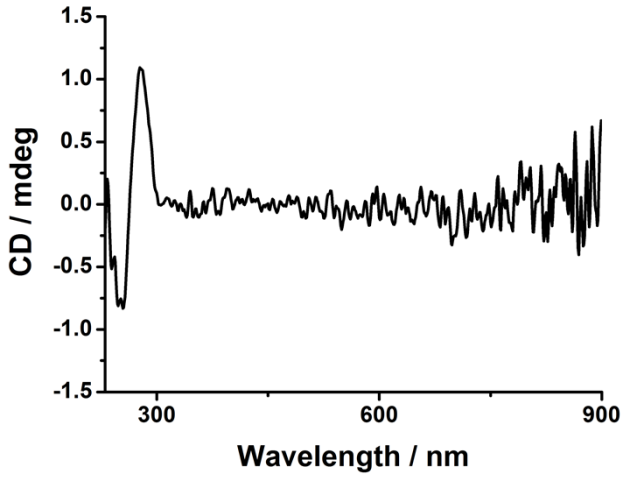

Fig. S4 CD spectra of cDNA with the concentration of 25 nM.

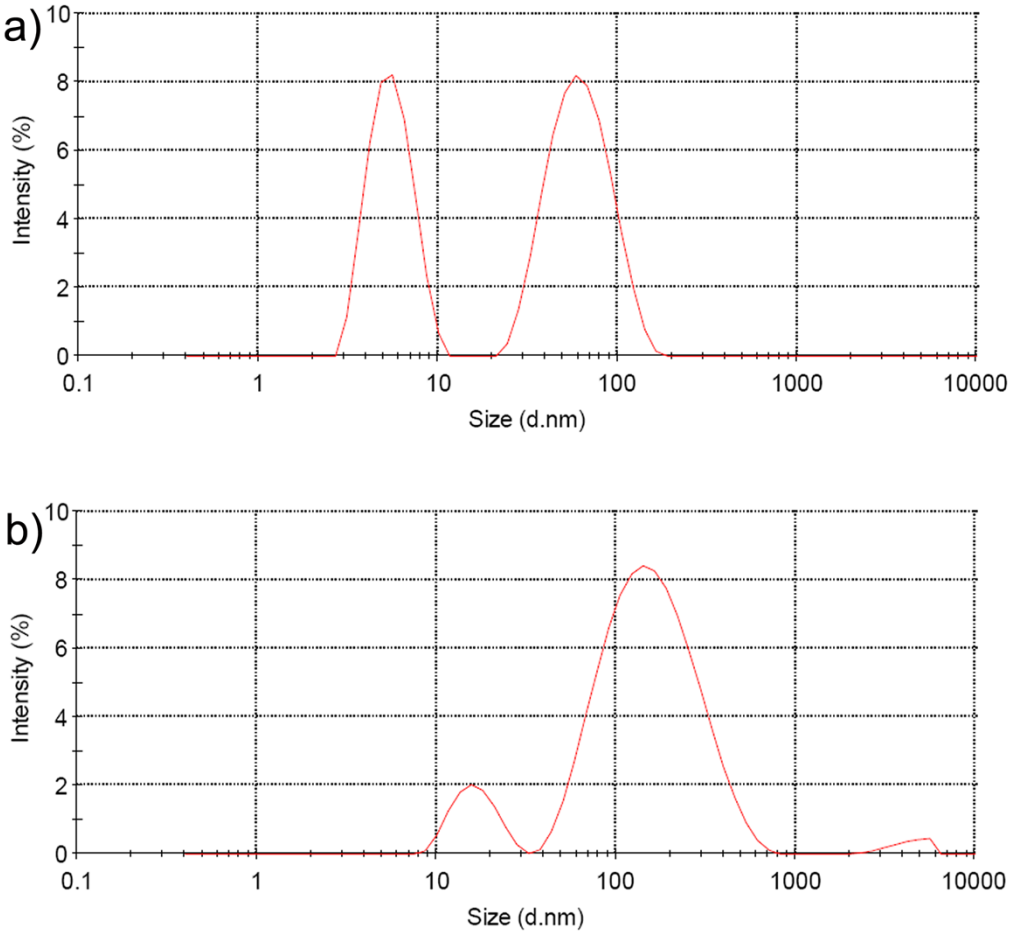

Fig. S5 DLS measurement of the DS-DNA modified Au NBPs at a) 60 °C and b) 20 °C. Analogously to the previous reports,[4] the DLS peaks are shifted from 65 nm to 178 nm and 4357 nm, respectively, indicating that the assembly of DNA modified Au NBPs is occurred at the temperature of 20 °C. Note that the peak below 20 nm originates from the rotational diffusion of Au NBPs, which should be omitted from the size distribution analysis.[5]

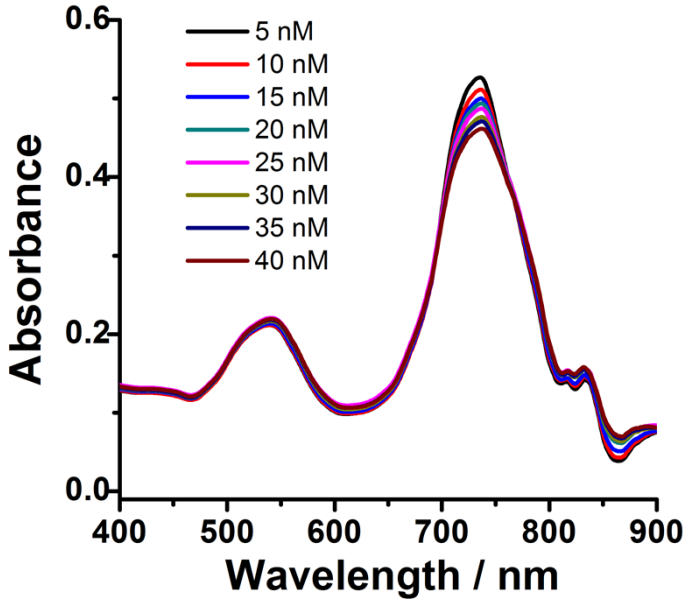

Fig. S6 UV-Vis spectra of Au NBP assemblies at 20 °C with varying concentration of cDNA (from 5 nM to 40 nM).

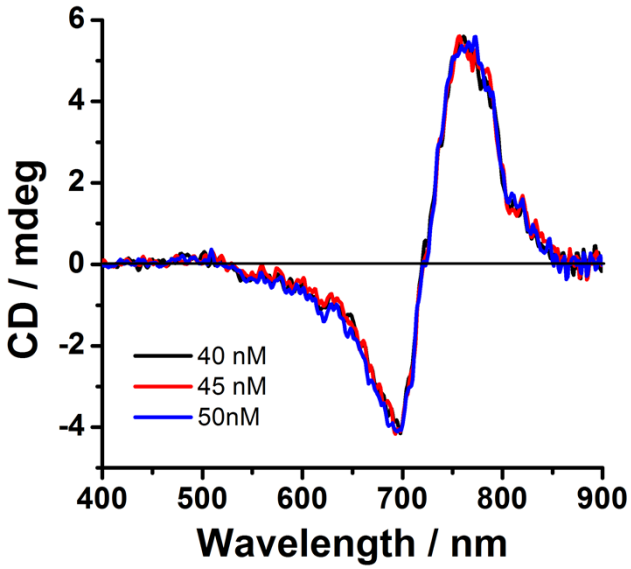

Fig. S7 CD spectra of Au NBP assemblies at 20 °C with varying concentration of cDNA from 40 nM to 50 nM.

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