Electronic Supplementary Information

Enhancing the Plasmonic Circular Dichroism by Entrapping Chiral Molecules at the Core-Shell Interface of Rod-Shaped Au@Ag Nanocrystals

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METHODS

Preparation of the core-shell nanocrystals. The Au nanorod solution was prepared according to the method described previously. The solution was centrifuged twice (9200 rpm, 10 min) and redispersed in a CTAB aqueous solution. The concentration of Au^0 was adjusted to 0.1 mM, and the final concentration of CTAB was 10 mM.

For the preparation of Au@Ag NCs shown in Figure 1, 3 mL of the Au nanorod solution was mixed with L- or D-Cys solution (6 μL, 10 mM), and the solution was incubated at 30 °C for 30 min. Then a calculated amount of $AgNO_3$ solution (10 mM) and the same volume of AA solution (0.1 M) were added. After mixing, the solution was put into a 70 °C water bath for 30 min.

To prepare the Au@Au NCs shown in Figure 3, 3 mL of the Au nanorod solution was mixed with L- or D-Cys solution (6 μL, 10 mM). After 30 min of incubation at 30 °C, $AgNO_3$ (6 μL, 10 mM), $HAuCl_4$ (12.6 μL, 23.8 mM), and AA (4.8 μL, 0.1 M) were added one-by-one. The solution was mixed and put into a 70 °C water bath for 30 min.

To prepare the cuboid Au@Ag NCs shown in Figure 3, the same preparation method as that for NCs in Figure 1 was used except that no Cys solution was added and the reaction duration should be extended to 5 h. After the reaction, the solution was centrifuged and the the supernatant was replaced with the same volume of 10 mM CTAB solution. Finally, L- or D-Cys solution (6 μL, 10 mM) was added and incubated in a 70 °C water bath for 30 min.

To prepare the arrow-like Au@Ag NCs shown in Figure 3, 3 mL of the Au nanorod solution was mixed with $AgNO_3$ (45 μL, 10 mM), $HAuCl_4$ (6.3 μL, 23.8 mM), and AA (45 μL, 0.1 M). The solution was first put into a 30 °C water bath for 4 h (to transform the Au nanorods into arrow shapes), and then move to a 70 °C water bath for 30 min (for the overgrowth of Ag on the arrow-like templates). The subsequent Cys modification was the same as that described for the Au@Ag cuboids.

Characterizations. Transmission-electron microscopy (TEM) images were captured on a Tecnai G2 20 S-TWIN TEM with an accelerating voltage of 200 kV. CD spectra were obtained on JASCO J810 CD spectrometer, and extinction spectra were acquired from a Cary 50 UV-vis-NIR spectrophotometer. Raman spectra were obtained in the solution phase using a Renishaw InVia Raman microscope with a 785 nm laser (100 mW). The exposure time was 60 s.

CD spectra were obtained on a JASCO J810 CD spectrometer with a scanning rate of 500 nm/min and a bandwidth of 5 nm. The corresponding extinction spectra are acquired on the same spectrometer, or on a Cary 50 UV-vis-NIR spectrophotometer for better signal-noise ratio. In both the measurement of CD and extinction, a 1-cm cuvette was used.

Numerical calculations. Finite-element method (FEM) calculations were performed in the Wave Optics module in COMSOL Multiphysics 5.0.The gold nanorod was modeled as a cylinder (height = 47 nm, diameter = 19 nm) capped with two semi-ellipsoid (long axis = 19 nm, short axis = 11 nm). The Ag shell was modeled as shown in Figure S3, with a height of 62 nm and a width of 29 nm. The refractive index of the medium was set to be 1.33, and the dielectric function of Au and Ag were adopted from Johnson and Christy.
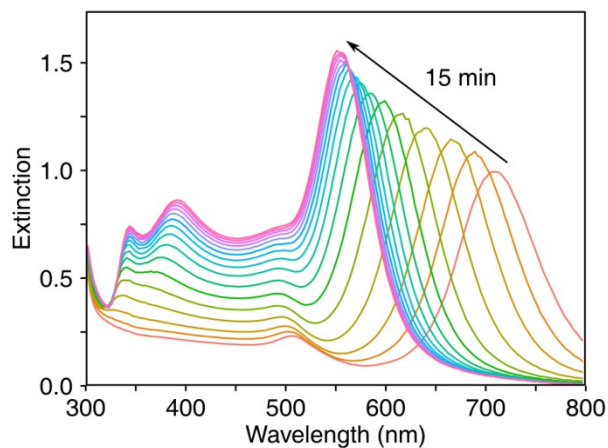
Figure S1. Extinction spectra evolution during the growth of Au@Ag in the presence of 20 µM L-Cys.

In the absence of Cys, the growth of Ag shell needs more than 4 h. The reaction was faster in the presence of cysteine because cysteine molecules that are free in solution can form complexes with Ag^+. Without cysteine, the mixture of 10 mM CTAB and 0.2 mM Ag^+ produces insoluable Ag-Br complexes, rendering the solution cloudy. After the addition of 20 µM Cys, the solution becomes clear, which suggests Cys and Ag^+ can form soluble complexes. The increase of solubility makes Ag^+ much more accessible to the Au surface, hence accelerated reduction rate.
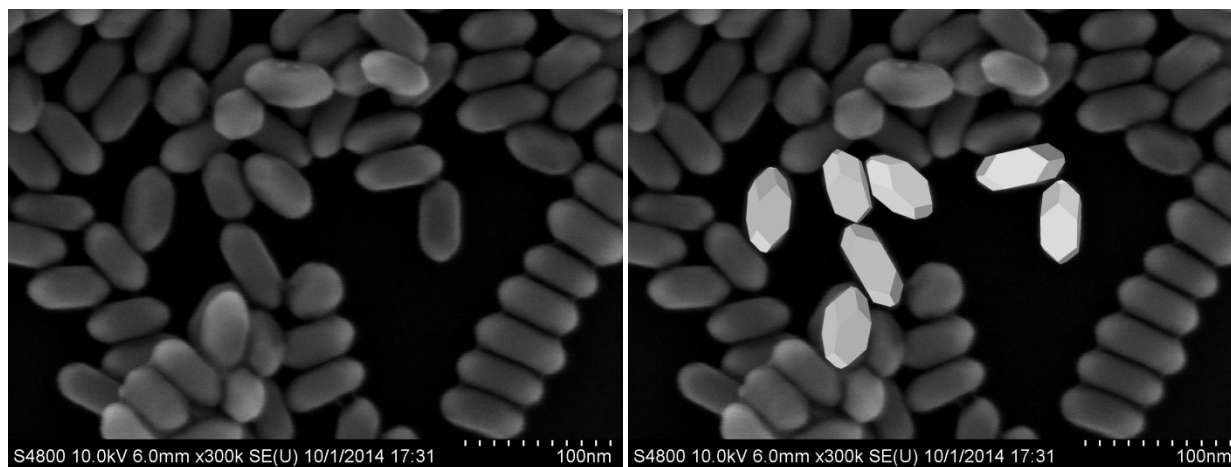
Figure S2. SEM image of the Au@Ag nanocrystals (Ag/Au ratio is 1.5). Models shown in the left image are determined from the image on the right.
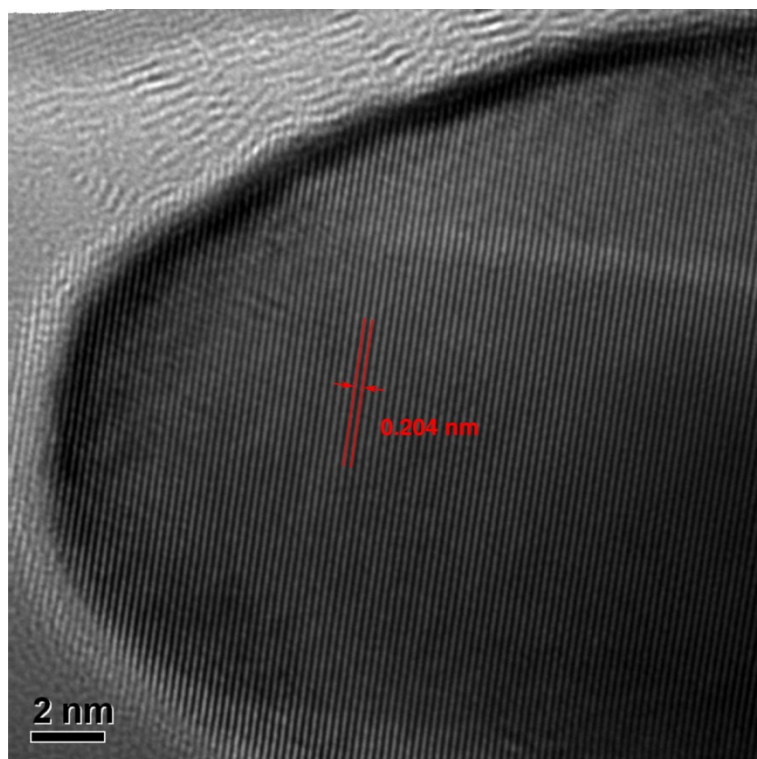
Figure S3. High-resolution TEM image of a Au@Ag nanocrystal. The Ag/Au ratio is 1.5.

The stripes are all in the same direction, indicating that the nanocrystal is single crystalline. 0.204 nm corresponds to the separation of {100} facets.

Table S1 Statistics of the Au@Ag NC geometry.

Ag/Au	Length	Width	Average aspect ratio
0	57.9 ± 4.9	18.9 ± 1.6	3.1 ± 0.3
0.5	58.8 ± 4.5	21.9 ± 1.6	2.7 ± 0.2
1.0	59.7 ± 5.7	25.8 ± 2.0	2.3 ± 0.2
1.5	59.7 ± 5.0	30.5 ± 2.2	2.0 ± 0.2
2.0	61.1 ± 5.3	36.4 ± 2.3	1.7 ± 0.1

Note: at least 150 NCs are counted.

As the Ag shell becomes thicker, two new LSPR modes at higher frequencies emerged. FEM calculation was used to identify the nature of the two modes. **Figure S4a** shows the extinction spectrum for Ag/Au ratio of 1.72. The calculated spectrum agrees well with the measured spectrum. Along with the longitudinal dipole mode, there are two main peaks and a weak peak in the range of 300-400 nm. The nature of the extinction peaks is readily elucidated from the surface charge distribution patterns as shown in **Figure S4b**.

a

b

338 nm: 367 nm: 388 nm:
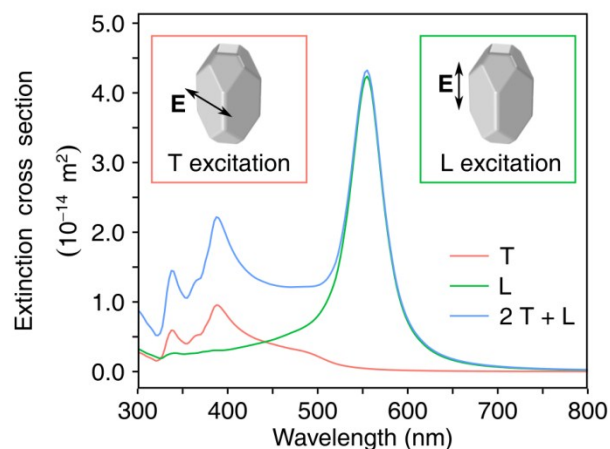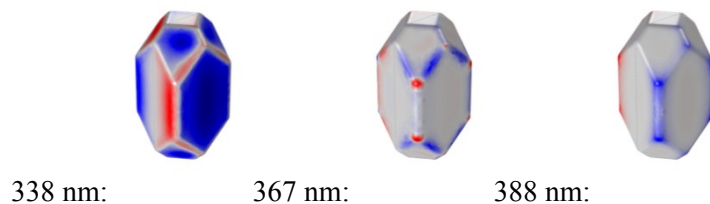
Figure S4. (a) Calculated extinction spectra of Au@Ag and (b) the surface charge distribution on the NCs at different wavelength. Blue and red colors correspond to negative and positive charges, respectively. The Ag/Au ratio is 1.72.

The peak at the shortest wavelength (338 nm) is a multipole mode.

The weak peak at 367 nm is also a multipole mode, but the surface charges are concentrated on the edges and corners. This peak disappears in the measured spectrum because of peak broadening due to the nonuniformity of the nanocrystals.

The peak at 388 nm is a dipole mode, with the surface charges concentrated on the edges and corners. It is referred to as a corner dipole mode.
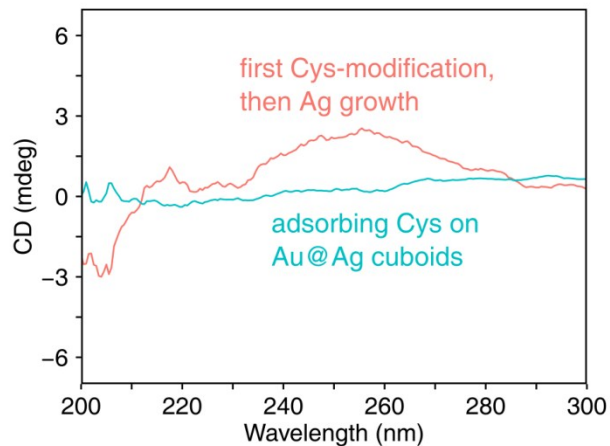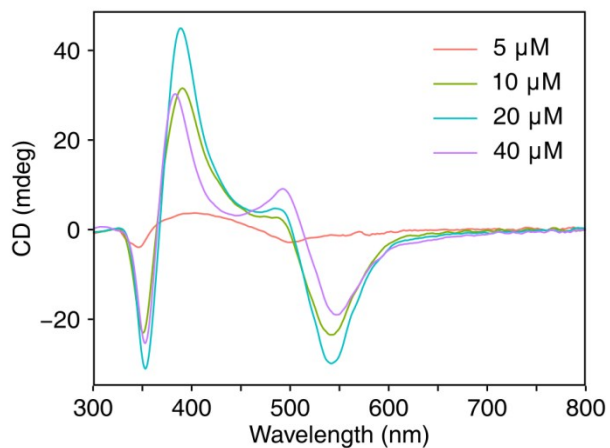
Figure S5. CD spectra under 300 nm.

Figure S6. CD spectra of the Au@Ag NCs prepared with different concentrations of L-Cys.
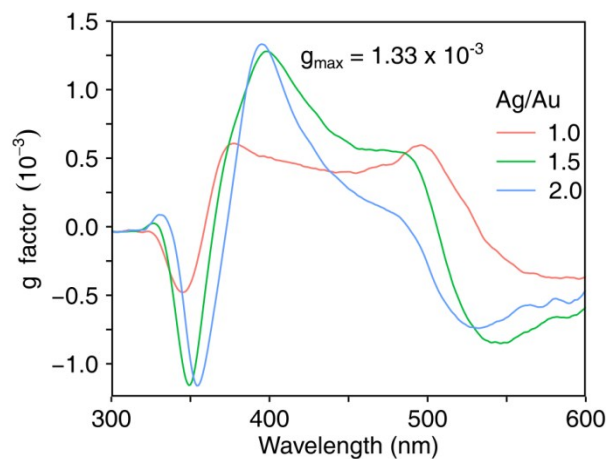

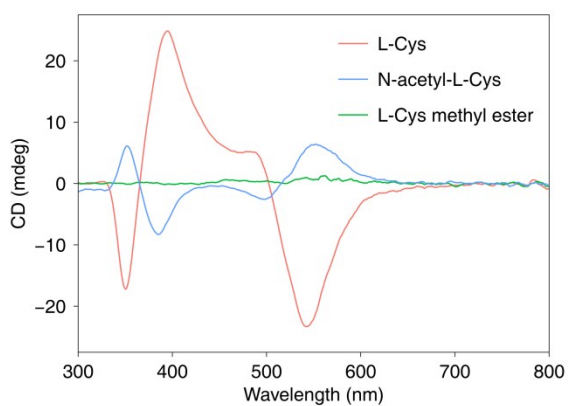**Figure S7.** Anisotropic factor spectra of the Au@Ag NCs.

Figure S8. CD spectra of Au@Ag NCs grown from Au nanorods with modification of 20 µM L-Cys, *N*-acetyl-L-Cys, and L-Cys methyl ester.
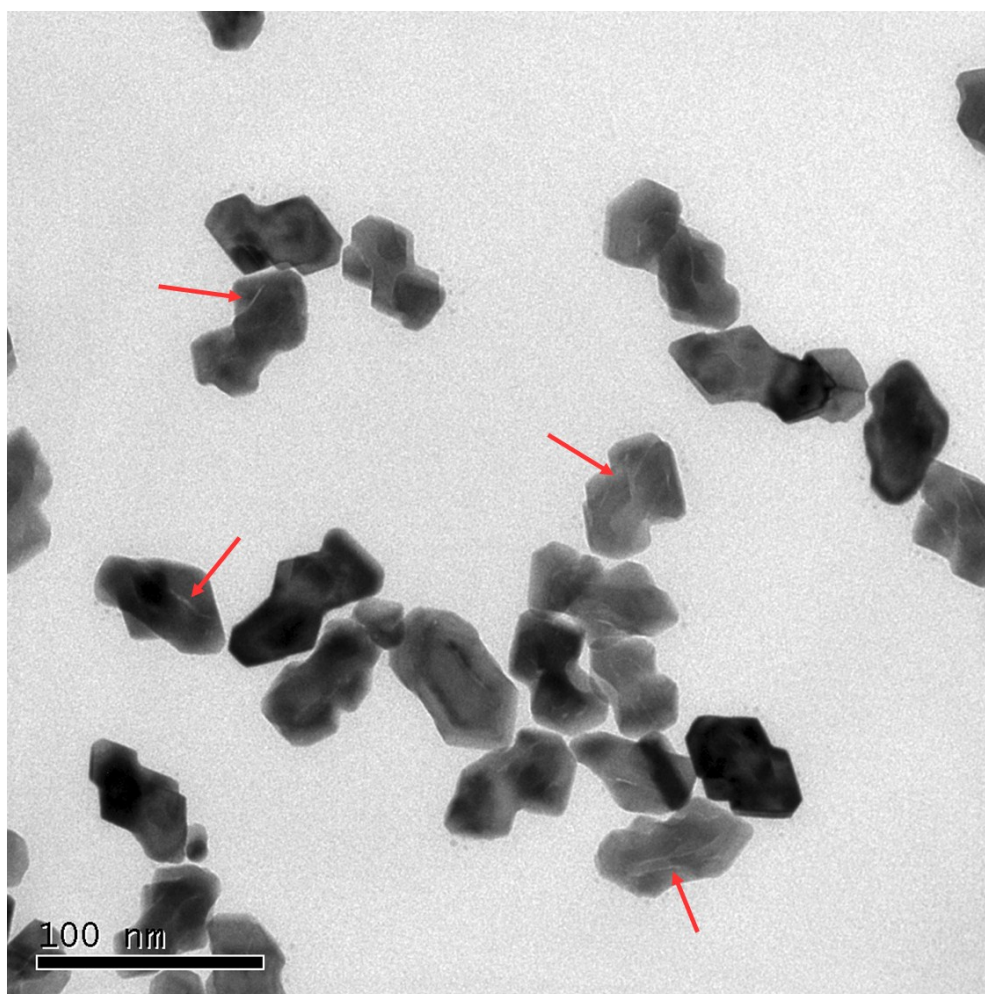

Figure S9. TEM image of Au@Cys@Au nanocrystals. Red arrows indicate cavities inside the nanocrystals.
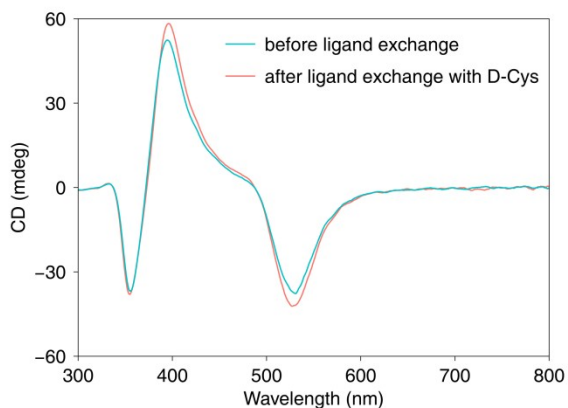
Figure S10. CD spectra of Au@Au NCs prepared with 20 µM L-Cys show little change after surface ligand exchange with 20 µM D-Cys.
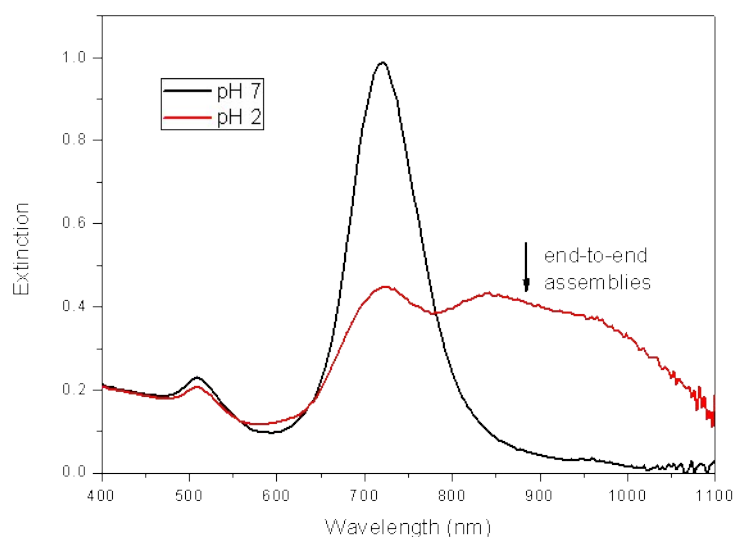

Figure S11. Extinction spectra of Cys-modified Au nanorods at pH 7 and pH 2. The concentration of CTAB and L-Cys is 10 mM and 20 uM, respectively. The red-shift of the longitudinal LSPR mode indicates the end-to-end assembly of the Au nanorods.

For more information of end-to-end assembly of Au nanorods, please refer to *J. Phys. Chem. Lett.* **2010**, 1, 1181-1185.
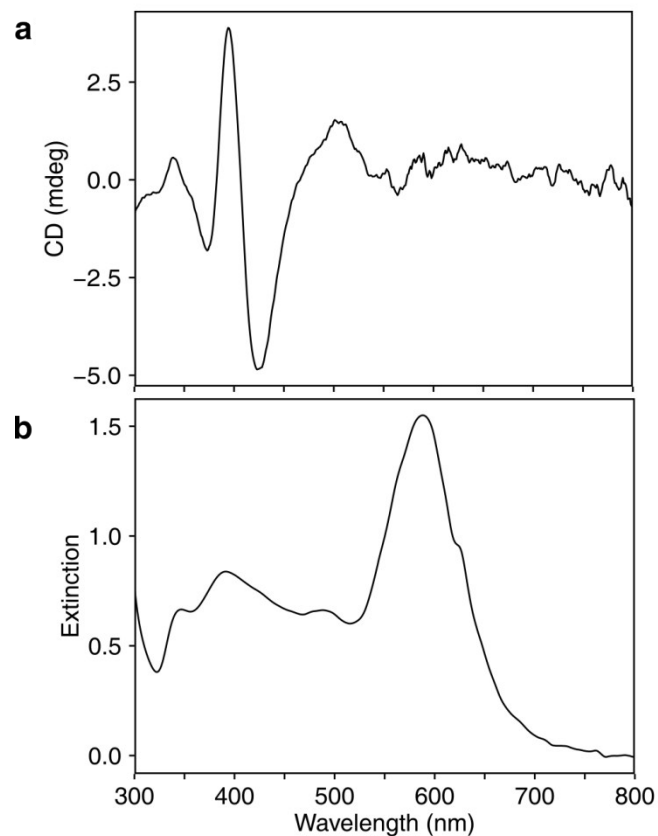
Figure S12. (a) CD and (b) extinction spectra of Au@Ag nanocrystals prepared by coating Ag on Au nanorods modified by L-Cys specifically on their sides.

10 μM of PEG-OMe solution (0.1 mM) was added into 1 mL Au nanorod solution and incubated for 30 min to block the ends of Au nanorods. Subsequent procedures are the same as coating Ag on Cys-modified Au nanorods.
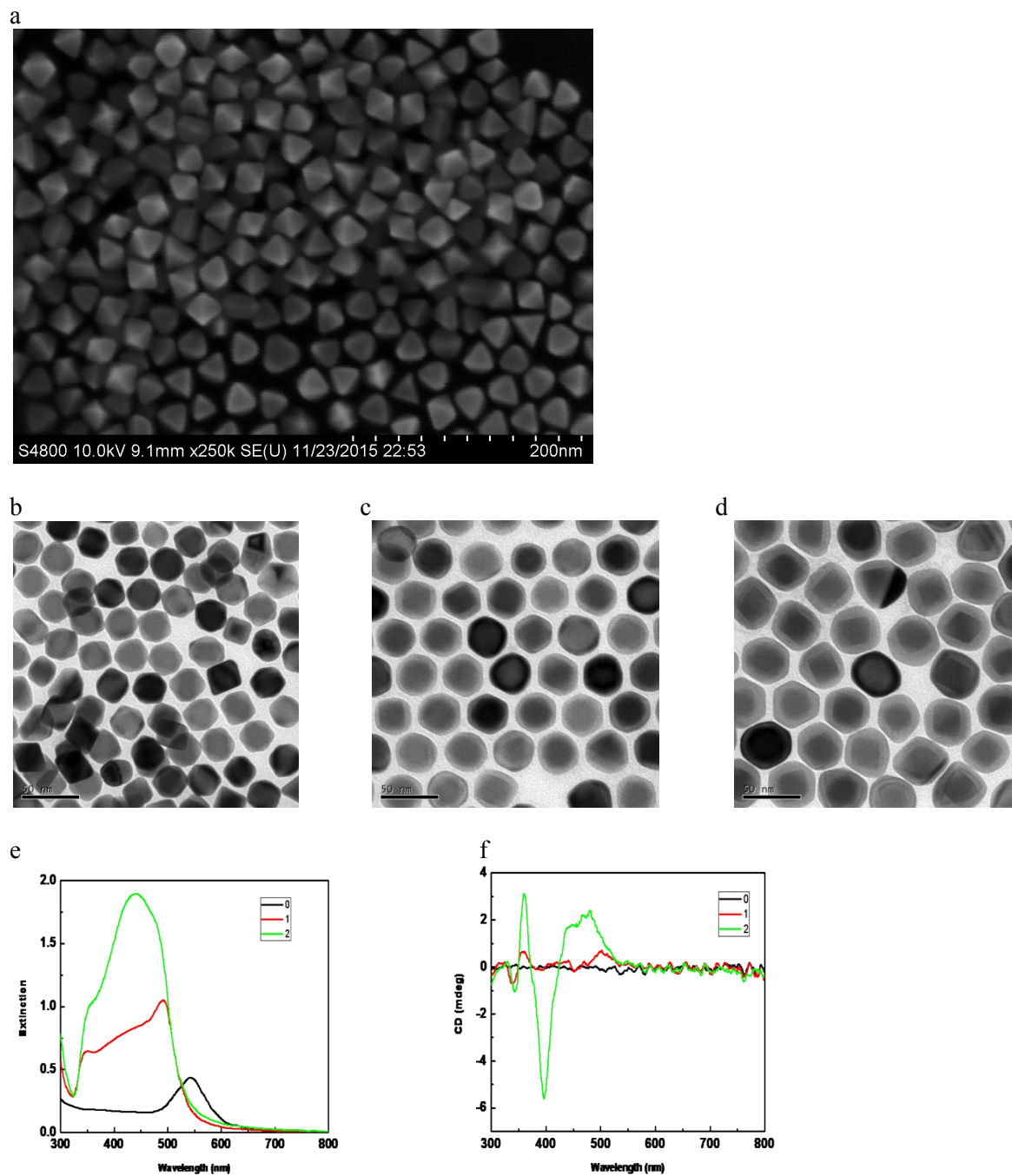
Figure S13. (a) SEM image of the Au octahedra. (b-d) TEM images of the Au octahedra (b), Au@Ag1 (c), and Au@Ag2 (d). (e) Extinction spectra of Au octahedra, Au@Ag1, and Au@Ag2. (f) Corresponding CD spectra.

Preparation method of Au octahedra is adopted from *J. Am. Chem. Soc.,* 2008, 130, 6949–6951.