[Electronic Supplementary Information]

Size-Controlled Gold Nano-Tetradecapods with Tunable Optical and Electromagnetic Properties

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Fig. S1 TEM images of (A) single-crystal Au nanospheres with a diameter of 10 nm used as seeds for the preparation of Au rhombic dodecahedra and (B) Au rhombic dodecahedra with an edge length of 25.5 nm used as seeds for the preparation of Au nano-tetradecapods.



Fig. S2 (A) HRTEM image of a branch part of the Au nano-tetradecapod and fast Fourier transform patterns acquired from the same colored boxes in the TEM image, and (B) lattice spacing measurements.



Fig. S3 TEM images of Au nanocrystals obtained with the standard procedure except the use of different volumes of DMF: (A) 0.6 mL, (B) 1.5 mL, (C) 3.0 mL, and (D) 4.8 mL, respectively.

Fig. S3 shows the Au nanocrystals prepared with different volumes of DMF in the reaction while the other reaction conditions were kept the same as the standard procedure. When the reactions were conducted with 0.6 mL and 1.5 mL of DMF, which were relatively small amounts (ca. 10% and 25 % v/v, respectively), Au rhombic dodecahedra with rounded edges were obtained. The overall sizes of the obtained Au rhombic dodecahedra were slightly increased compared to the seeds whereas the shape exhibited no significant changes, indicating that Au rhombic dodecahedral cores were grown evenly in all directions. Because the {110} faces of Au were not completely stabilized due to the relatively low concentration of DMF, Au rhombic dodecahedral seeds could grow in all directions, resulting in the formation of rounded rhombic dodecahedra. When the volume of DMF was raised to 3.0 mL (ca. 50 % v/v), Au rhombic dodecahedra with tiny branches were obtained. The branches formed preferentially on the vertices of the rhombic dodecahedral core, similar to a tetradecapod, though their size was quite small compared to those obtained under the standard procedure. When the volume of DMF was over 4.8 mL (ca. 80 % v/v), Au nano-tetradecapods similar to those prepared under the standard procedure were obtained. It seems that DMF can firmly stabilize the {110} facets of Au nanocrystals, and that most of the newly formed Au atoms were deposited on the vertices of the rhombic dodecahedral core. This led to the preferential growth on the vertices of the rhombic dodecahedral core, and the formation of Au nano-tetradecapods.



Fig. S4 TEM images of Au nanocrystals obtained with the standard procedure except for the use of different concentration of trisodium citrate: (A) 0 μ M, (B) 4.2 μ M, (C) 33.3 μ M, and (D) 83.3 μ M, respectively.

Fig. S4 shows TEM images of Au nanocrystals prepared by the standard procedure except that different concentrations of trisodium citrate were used. When the trisodium citrate was excluded from the reaction mixture, Au rhombic dodecahedra with sharp edges were obtained. Although protruding tips at the vertices were partially observed, the tips of the resultant nanocrystals were much smaller compared to the branches of the Au nano-tetradecapods prepared by the standard procedure, which suggests that branches could not be grown in the longitudinal direction without trisodium citrate. Meanwhile, when a relatively low concentration of trisodium citrate (4.2μ M, 1/3 of the standard procedure) was introduced to the reaction mixture, branches of the resultant Au nanocrystals were recognized at most of the standard procedure), Au nano-tetradecapods similar to the standard products were obtained. The average branch size was also close to that of the Au nano-tetradecapods obtained by the standard procedure. In the present reaction system, it is thus believed that trisodium citrate plays a critical role in the formation of Au nano-tetradecapods, especially for the longitudinal growth of branches. Once branches have been formed preferentially at the vertices, trisodium citrate

can be quickly adsorbed onto those branches and stabilize them, and then induce longitudinal branch growth.^[S1-S3] Since the protruded branches would have relatively higher surface energies than those of faces, trisodium citrate could be preferentially adsorbed onto those branches rather than on faces.^[S4-S6] However, when the concentration of trisodium citrate was increased beyond that of the standard procedure to 83.3 μ M, the branches were non-selectively grown not only on the vertices of the rhombic dodecahedral cores but also on their faces and edges. It is speculated that the reduction rate was accelerated as the concentration of trisodium citrate can act as not only a stabilizer but also a reducing agent,^[S7-S9] the concentration of Au atoms rapidly increased and thus Au nuclei were simultaneously generated around the core, leading to random formation of branches.



Fig. S5 The overall size and branch length of the Au nano-tetradecapods as a function of (A) the volume of $HAuCl_4$ solution and (B) the reaction temperature, respectively. Relatively broad size distributions are attributed to the random orientations of Au nano-tetradecapods, which can vary the viewing direction and the corresponding measured sizes.



— 50 nm

Fig. S6 TEM images of Au nanocrystals prepared using the standard procedure, but at different reaction temperatures: (A) 40 °C, (B) 60 °C, (C) 80 °C, and (D) 100 °C, respectively.



Fig. S7 Plots of the LSPR peak positions of obtained Au nanocrystals as a function of (A) the volume of HAuCl₄ solution and (B) the reaction temperature, respectively.



Fig. S8 A plot of the LSPR peak positions as a function of size ratio (black: Au nanotetradecapods obtained using different volumes of $HAuCl_4$ solution, blue: those obtained under different reaction temperatures, and green: Au nano-hexapods in ref.10), respectively.



Fig. S9 FDTD-simulation for calculating |E| distributions of Au spheres with a diameter of (A) 3.2, (B) 4.3, (C) 5.7, (D) 7.6 nm, and Au rhombic dodecahedron with an edge length of 25.5 nm, when it was (E) located at the monitor plane to cross its center, (F) tilted at 45-degrees, (G) observed at the other plane, and (H) tilted at 45-degrees. The *k* vector and *E* vector are perpendicular and parallel to the profile monitor, respectively.



Fig. S10 (A) Models of (from left) Au nano-tetradecapods with 3.2, 4.3, 5.7 and 7.6 nm branches, and a rhombic dodecahedron with an edge length of 25.5 nm, respectively (the same as those in Figure 4, but tilted 45-degrees), for FDTD simulation. (B-F) FDTD simulations of the electric field amplitude (|E|) distributions of the corresponding models above. Scale bars represent 20 nm. The *k* vector and *E* vector are perpendicular and parallel to the profile monitor, respectively.



Fig. S11 (A) Models of (from left) Au nano-tetradecapods with 3.2, 4.3, 5.7 and 7.6 nm branches, and a rhombic dodecahedron with an edge length of 25.5 nm, respectively (the same as those in Figure 4, but observed at the other plane), for FDTD simulation. (B-F) FDTD simulations of the electric field amplitude (|E|) distributions of the corresponding models above. (G) The 45-degree tilted models of those in (A) for FDTD simulation. (H-L) FDTD simulations of the electric field amplitude (|E|) distributions of the corresponding models above. Scale bars represent 20 nm. The *k* vector and *E* vector are perpendicular and parallel to the profile monitor, respectively.



Fig. S12 FDTD simulations of the electric field amplitude (|E|) distributions of the Au nanotetradecapods with different sized rhombic dodecahedral cores (in edge length) and branches (in parenthesis) (the same as those in Figure 5, but tilted at 45-degrees): (A) 15 nm (3.2 nm), (B) 25.5 nm (3.2 nm), (C) 45 nm (3.2 nm), (D) 15 nm (7.6 nm), (E) 25.5 nm (7.6 nm), and (F) 45 nm (7.6 nm), respectively. Scale bars represent 20 nm. The *k* vector and *E* vector are perpendicular and parallel to the profile monitor, respectively.

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