Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Shape Auxiliary Approach for Carboxylate-Functionalized Gold Nanocrystals

Daeha Seo, Choong Il Yoo, Bong Hyun Chung, Im Sik Chung* and Hyunjoon Song*

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea, and BioNanotechnology Research Center, Korea Research Institute of Bioscience and Biotechnology (KRIBB), Daejeon 305-333, Korea

E-mail: hsong@kaist.ac.kr, cis123@kribb.re.kr

Experimental Section

Chemicals. Tetrachloroaurate trihydrate ($HAuCl_4.3H_2O$, 99.9+%, Aldrich), silver nitrate ($AgNO_3$, 99+%, Aldrich), 1,5-pentanediol (PD, 96%, Aldrich), 2-(dimethylamino)ethanol (DMAE, 99.0%, TCI), poly(acrylic acid) (PAA, 35 wt% solution in water, M_w = 100,000, Aldrich), and poly(2-hydroxyethyl methacrylate) (PHEMA, M_w = 20,000, Scienctific Polymer Products) were used without further purification. Poly(dimethylaminoethyl methacrylate) (PDMAEMA, 18.45% solution in toluene, Scientific Polymer Products) was used after solvent evaporation.

Synthesis of gold particles in the presence of PAA (reaction A). A PD solution of $AgNO_3$ (0.15 mM, 5.0 mM) was added to boiling PD (5.0 mL). Then PAA (3.0 mL, 1.0 M) and $HAuCl_4$ (3.0 mL, 0.050 M) PD solutions were periodically added every 30 s over 7.5 min, and the mixture was refluxed for additional 1 h. The particles were precipitated by centrifugation, and were thoroughly washed with ethanol in a precipitation/dispersion cycle.

Synthesis of gold octahedrons in the presence of PAA and DMAE (reaction B). A PD solution of $AgNO_3$ (0.15 mM, 5.0 mM) was added to boiling PD (5.0 mL). Then PD solutions of PAA (1.5 mL, 2.0 M), DMAE (1.5 mL, 2.0 M), and $HAuCl_4$ (3.0 mL, 0.050 M) were periodically added every 30 s over 7.5 min, and the mixture was refluxed for additional 1 h. The particles were precipitated by centrifugation, and were thoroughly washed with ethanol in a precipitation/dispersion cycle.

Synthesis of gold octahedrons in the presence of PDMAEMA (reaction C). A PD solution of PDMAEMA (0.10 mL, 0.15 M) was added to boiling PD (5.0 mL). Immediately, a PD solution of $HAuCl_4$ (0.2 mL, 0.05 M) was added to the reaction

mixture. The resulting mixture was refluxed for 1 h. The particles were precipitated by centrifugation, and were thoroughly washed with ethanol in a precipitation/dispersion cycle.

Synthesis of gold cubes and cuboctahedrons in the presence of PDMAEMA. A PD solution of $AgNO_3$ (0.15 mL) was added to boiling PD (5.0 mL). Then PDMAEMA (3.0 mL, 0.15 M) and $HAuCl_4$ (3.0 mL, 0.050 M) PD solutions were periodically added every 30 s over 7.5 min, and the mixture was refluxed for additional 1 h. The particles were precipitated by centrifugation, and were thoroughly washed with ethanol in a precipitation/dispersion cycle. The $AgNO_3$ concentrations used in the reactions were 10 mM (Ag/Au molar ratio = 1/100) for cubes and 5.0 mM (Ag/Au = 1/200) for cuboctahedrons.

Synthesis of gold polygons for pH-induced assembly. A PD solution of $AgNO_3$ (0.15 mL, 0.020 M) was added to boiling PD (31 mL). Then PDMAEMA (3.0 mL, 0.15 M) and $HAuCl_4$ (3.0 mL, 0.050 M) PD solutions were periodically added every 30 s over 7.5 min, and the mixture was refluxed for additional 1 h. The particles were precipitated by centrifugation, and were thoroughly washed with ethanol in a precipitation/dispersion cycle. The particles were finally dispersed in ethanol (30 mL).

pH-induced assembly/disassembly experiments. The gold polygons in ethanol (2.0 mL) were precipitated by centrifugation, and dispersed in NaOH solution in water (2 mL, pH 12) in a quartz cell mounted on a UV-Vis spectrophotometer. The solution was titrated either by HCl solution (0.25 M) or by NaOH solution (0.25 M) in order to set pH 2 and 12 of the particle dispersion, respectively. The extinction properties were measured by the UV-Vis spectrophotometer along repetitive acid and base titrations.

Characterization. Scanning electron microscopy (SEM) images were obtained using

a Philips XL30S FEG operated at 10 kV. X-ray photoelectron spectroscopy (XPS) studies were carried out using a VG ESCA2000 with a Mg Kα source. FT-IR data were collected on a BRUKER EQUINOX55 spectrometer. Samples were prepared by a few drops of the colloidal solutions on a silicon wafer (P-100) followed by drying in air. The UV-Vis spectra were collected on a Jasco V530 UV-Vis spectrophotometer using the colloidal solutions in water.

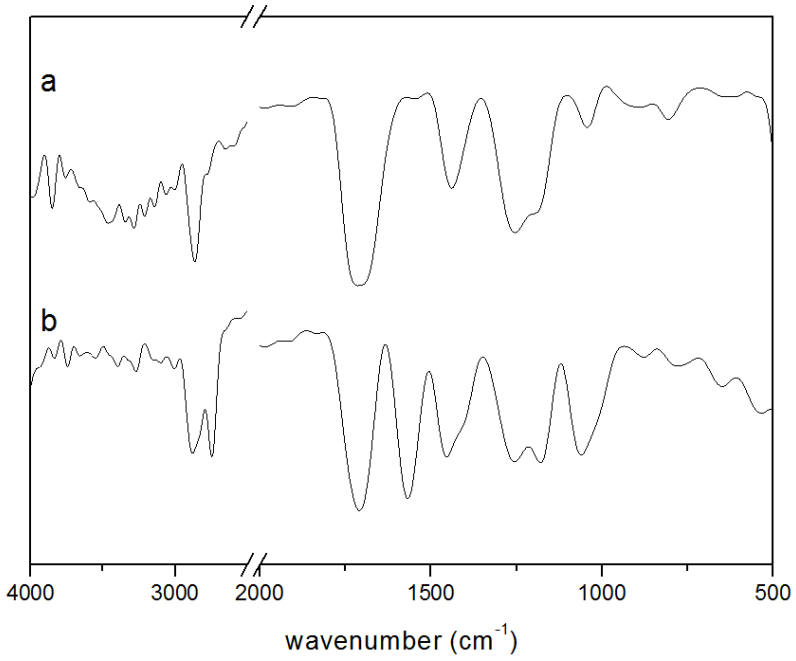

Fig. S1 FTIR spectra of (a) pure PAA and (b) the product of the reaction with PAA and DMAE within 10 min.

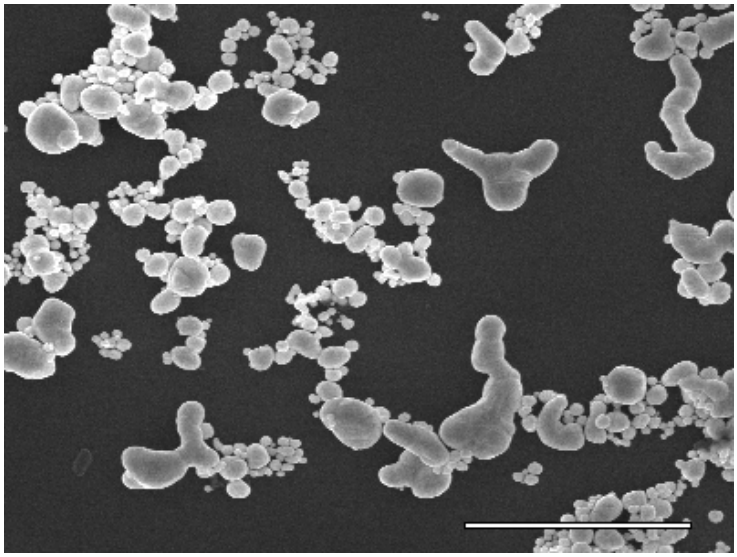

Fig. S2 SEM image of the gold residue produced in the presence of PHEMA. The bar represents 2 μm.

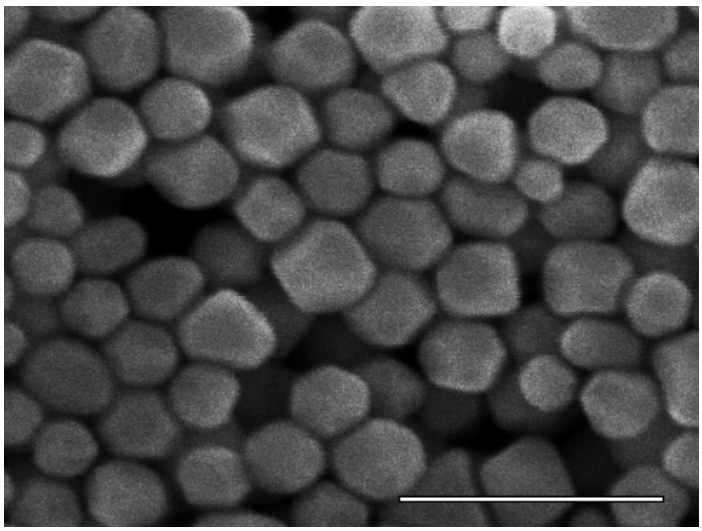

Fig. S3 SEM image of gold cuboctahedrons synthesized in the presence of PDMAEMA. The bar represents 200 nm.

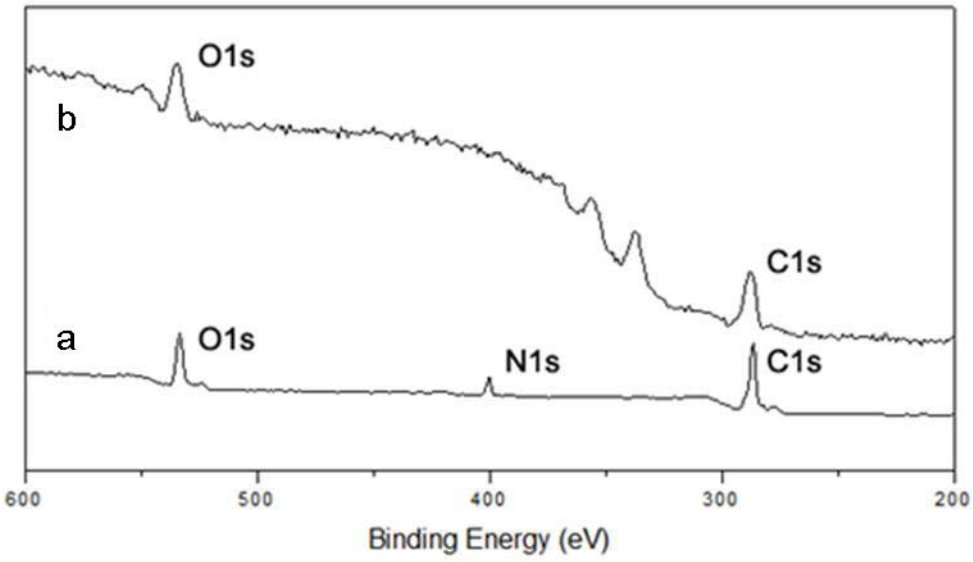

Fig. S4 XPS survey scan of (a) free PDMAEMA and (b) the gold nanoparticles synthesized in the presence of PDMAEMA.

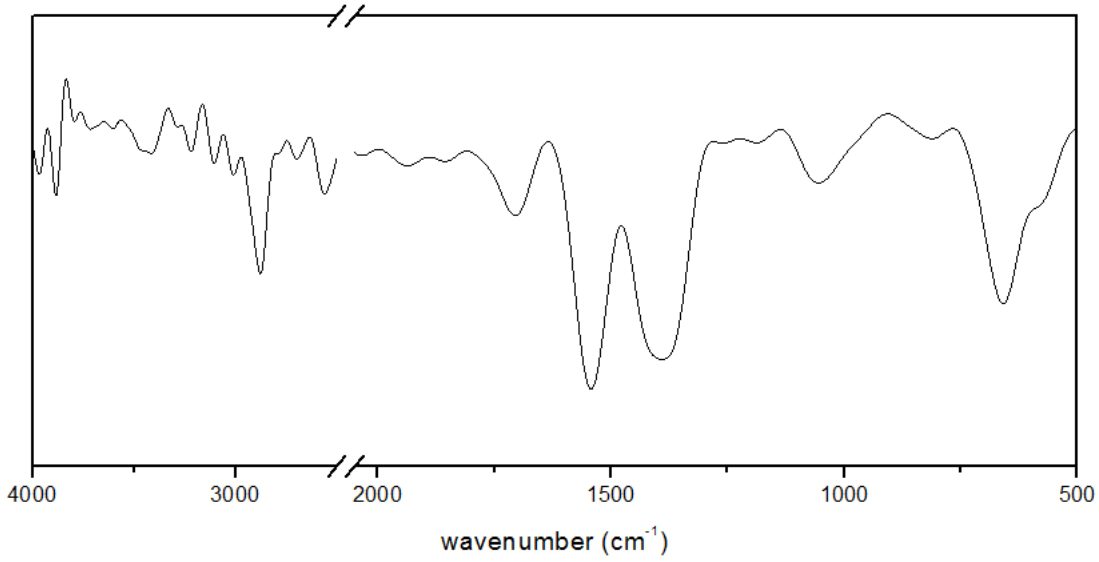

Fig. S5 FTIR spectrum of gold nanocrystals synthesized by the reaction with PAA and DMAE after NaOH treatment.

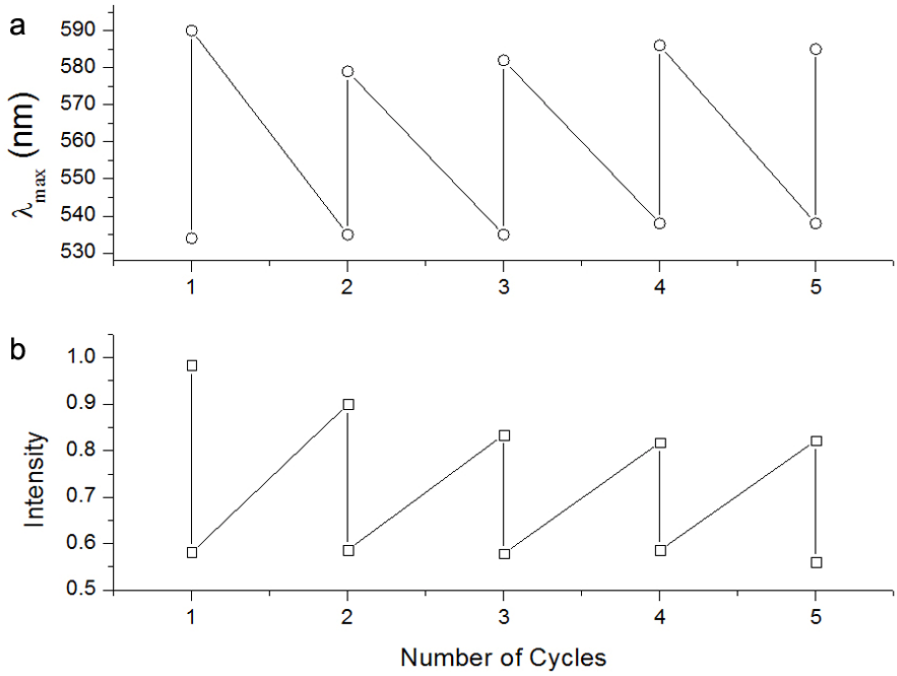

Fig. S6 Cyclic changes of (a) the maximum position and (b) intensity in the extinction peak of gold nanocrystals during pH-dependent assembly/disassembly.