Supporting Information

Anti-Galvanic Reduction of Silver Ion on Gold and Its Role in Anisotropic Growth of Gold Nanomaterials

Hosuk Kang,[†,§] Bong-Geun Kim,[‡,§] Hyon Bin Na,[‡,*] and Seongpil Hwang[†,*]

[†]Department of Advanced Material Chemistry, Korea University, Sejong 339-700, Republic of Korea

[‡]Department of Chemical Engineering, Myongji University, Yongin 449-728, Republic of Korea

*Corresponding Authors

*E-mail: hyonbin@mju.ac.kr, sphwang@korea.ac.kr

[§]These authors contributed equally to this work.

Contents

Synthesis of anisotropic gold nanoparticles by controlling Ag deposition

Anisotropic Au nanoparticles were synthesized by seed-mediated growth using BSPP-stabilized AuNC seeds and modified growth solutions. To synthesize Au nanoparticles of various shapes, Ag^+ ion was differently introduced for each experiment.

Synthesis of Au nanorods without silver ion (b): A mixture of 0.5 ml of 10 mM $HAuCl_4$, 10 ml of 0.1 M CTAB, and 0.3 ml of DI water was prepared in a glass vial. After short-term incubation the color of mixture was changed to orange finally. At this point, 0.08 ml of 0.1 M ascorbic acid was added, and the mixture became transparent. Then, 24 μl of 2 μM BSPP-capped AuNC solution was added to the growth solution and further incubated for 3 h at 30 °C.

Synthesis of multiple twinned Au stars with fairly developed tips using Ag^+-treated seed (c): For the first time, 24 μl of 2 μM BSPP-capped AuNC solution was mixed with 0.1 ml of 10 mM $AgNO_3$ followed by the incubation at RT for 1 hr. The growth solution was separately prepared by mixing following reagents in the order listed and then gentle mixing; 0.5 ml of 10 mM $HAuCl_4$, 10 ml of 0.1 M CTAB, 0.2 ml of DI water, and 0.08 ml of 0.1 M ascorbic acid. Then, the growth solution was mixed with pretreated seed and resulting solution was incubated for 3 h at 30 °C.

Synthesis of twinned polyhedron Au nanoparticles using Ag^+-treated seed (d): For the first time, 24 μl of 2 μM BSPP-capped AuNC solution was mixed with 0.01 ml of 10 mM $AgNO_3$ and 0.09 ml of DI water followed by the incubation at RT for 1 hr. The growth solution was separately prepared by mixing following reagents in the order listed and then gentle mixing; 0.5 ml of 10 mM $HAuCl_4$, 10 ml of 0.1 M CTAB, 0.2 ml

of 0.5 M of H_2SO_4, and 0.08 ml of 0.1 M ascorbic acid. Then, the growth solution was mixed with pretreated seed and resulting solution incubated for 3 h at 30 °C.

Synthesis of Au nanorods with the assistance of silver ion (e): A mixture of 0.5 ml of 10 mM $HAuCl_4$, 0.02 ml of 10 mM $AgNO_3$, 10 ml of 0.1 M CTAB, and 0.08 ml of DI water was prepared in a glass vial. After short-term incubation the color of mixture changed to orange finally. At this point, 0.2 ml of 0.5 M H_2SO_4 and 0.08 ml of 0.1 M ascorbic acid were added, and the growth solution became transparent. Then, 24 μl of 2 μM BSPP-capped AuNC solution was added to the growth solution and the mixture was further incubated for 3 h at 30 °C.

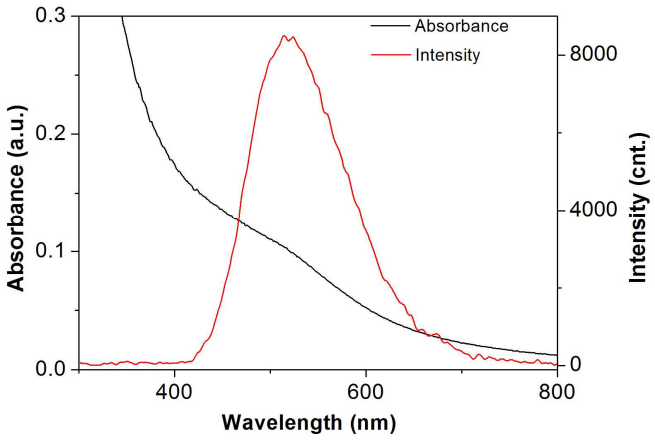

Figure S1. Absorbance and fluorescent spectra of Au nanocrystals (AuNCs)

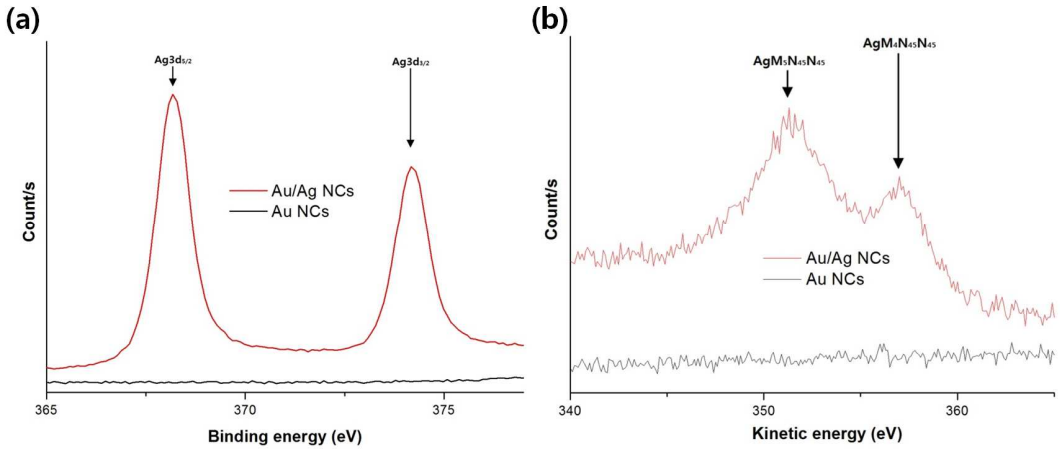

Figure S2. X-ray photoelectron spectroscopy (XPS) spectra of (a) Ag3d and (b) Ag MNN for AuNCs and 8 mM Ag-treated Au nanocrystals (Au/AgNCs).

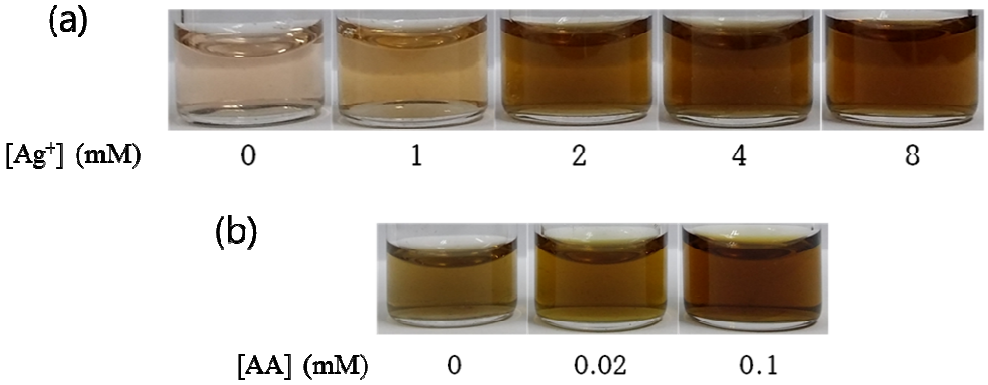

Figure S3. Photographic images of (a) AuNCs treated with different concentration of $AgNO_3$ and (b) AuNCs treated with fixed concentration of $AgNO_3$ (8 mM) and different concentration of ascorbic acid. NC dispersions were incubated with $AgNO_3$ in the dark for 1 h and 5 min, respectively.

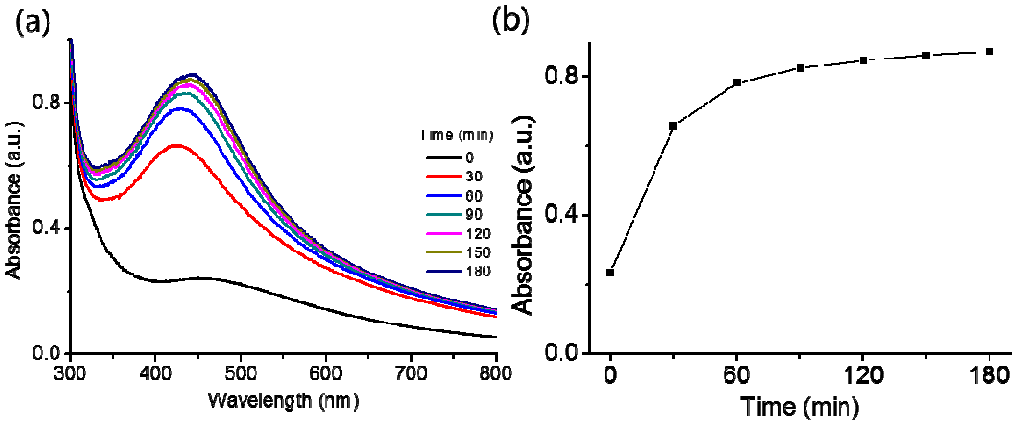

Figure S4. (a) Evolution of absorbance spectra of AuNCs in the presence of $AgNO_3$ (8 mM). (b) Absorbance at 427 nm as a function of time.

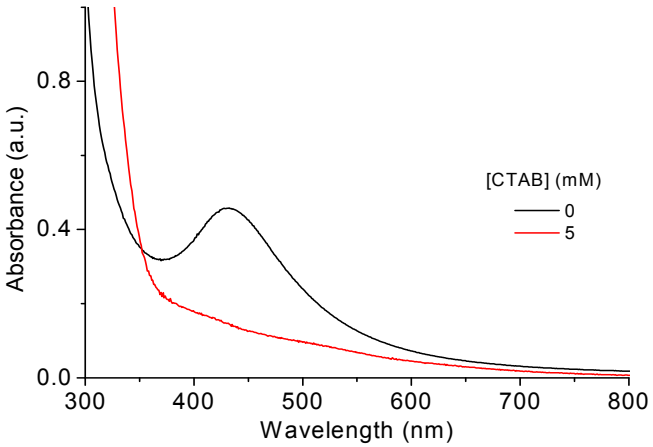

Figure S5. Absorbance spectra of AuNC dispersions after 5 min of the addition of $AgNO_3$ (1 mM) and ascorbic acid (0.1 mM) in absence and presence of CTAB (5 mM).

Binding energy (eV)	
Ag $3d_{5/2}$	368.18
Ag $3d_{3/2}$	374.18
Auger parameter (AP, eV)	
AP-$3d_{5/2}$, $M_4N_{45}N_{45}$	725.18
AP-$3d_{5/2}$, $M_5N_{45}N_{45}$	719.48

Table S1. XPS Ag 3d fitting parameters and Auger parameters of Ag/Au NCs