

Supporting Information

Hierarchical Hybrid Nanostructures: Controlled Assembly of Polymer-Encapsulated Gold Nanoparticles via a Rayleigh-Instability-Driven Transformation under Cylindrical Confinement

Hao-Wen Ko, Chun-Wei Chang, Mu-Huan Chi, Chien-Wei Chu, Ming-Hsiang Cheng, Zhi-Xuan Fang,
Ke-Hsuan Luo, and Jiun-Tai Chen*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30010

EXPERIMENTAL SECTION

Materials

Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99 %) was purchased from Sigma Aldrich. Sodium citrate (dihydrate, granular) was purchased from J. T. Baker. Thiol-terminated polystyrene (PS-SH) with weight-average molecular weights (M_w) of 5.8 (PDI=1.10) and 53 (PDI=1.06) kg/mol were obtained from Polymer Source. Tetrahydrofuran (THF) was obtained from Macron. Toluene was obtained from Echo Chemical. *N*-methyl-2-pyrrolidone (NMP) was purchased from Mallinckrodt.

Sodium hydroxide (NaOH) was purchased from Tedia. AAO templates (average pore diameter ~230 nm, thickness ~60 μm) were purchased from Whatman.

Synthesis of Au Nanoparticles (AuNPs)

AuNPs with uniform sizes were synthesized using a citrate reduction method.^{1, 2} First, a 20 mL (0.88 mM) HAuCl_4 solution in a beaker with a magnetic stirrer was heated by a hot plate until boiled. Subsequently, a 2.4 mL (1 wt %) sodium citrate solution was quickly added in the boiling HAuCl_4 solution with simultaneous stirring. After the color of the solution turned brilliant red, the synthesized AuNPs were collected. The AuNPs solutions were used as starting solutions for the ligand-exchange process to prepare PS-encapsulated AuNPs.

Synthesis of PS-Encapsulated AuNPs

PS-encapsulated AuNPs were synthesized using a ligand-exchange method.^{3, 4} First, a 3 mL solution containing 3 mg PS-SH in THF was added to a 12 mL solution of AuNPs. After the mixtures were sonicated for 1 h and incubated for 24 h, a reddish-violet precipitate was obtained. The precipitate was then separated and rinsed via centrifugation (12000 rpm, 10 min) for several times. Finally, the PS-encapsulated AuNPs were redispersed in organic solvents and used as starting solutions for the preparation of hierarchical hybrid nanostructures.

Preparation of AAO Templates

AAO templates with average pore sizes of ~60 nm were prepared using a two-step anodization method.⁵ First, an aluminum foil (99.9997%) was cleaned by ultrasonication in isopropyl alcohol (IPA) for 10 min. The foil was then electropolished at 20 V in a mixed solution of ethanol/perchloric acid (80:20) at 4

°C for 2 min. After the foil was rinsed by deionized (DI) water, it was anodized at 40 V in 0.3 M oxalic acid solution at 16 °C for 1 h. Subsequently, the foil was etched in a mixed solution of phosphoric acid (H_3PO_4) (6 wt %) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) (1.8 wt %) for 1 h to remove the aluminum oxide layer. The second anodization process was conducted at 40 V in 0.3 M oxalic acid solution at 16 °C for 2 h. To control the pore sizes, a pore-widening process was performed in phosphoric acid (5 wt %) at 30 °C and the pore diameter of the AAO template is ~60 nm.

Fabrication of Hybrid Nanotubes Containing Au@PS NPs

To fabricate hybrid nanotubes, an Au@PS NPs solution (5 wt %) in NMP was first prepared. An AAO template was then immersed in the solution for 10 s, followed by a wiping process using Kimwipes to remove the residual solution on the surface of the AAO templates. The residual solvents of the sample were dried completely using a vacuum pump. Finally, the AAO template was removed selectively by 5 wt % NaOH(aq) to release the hybrid nanotubes containing Au@PS NPs.

Fabrication of Hybrid Nanospheres Containing Au@PS NPs

To fabricate hybrid nanospheres, an AAO template was first immersed in an Au@PS NPs solution (5 wt %) in NMP. After the surfaces of the AAO template were wiped by Kimiwipes, the sample was immersed in deionized (DI) water and the surfaces of the AAO template were wiped again. The residual solvents of the sample were dried completely using a vacuum pump. Finally, the AAO template was removed selectively by 5 wt % NaOH(aq) to release the hybrid nanospheres containing Au@PS NPs.

Structure Analysis and Characterization

The hybrid nanostructures were characterized by a JEOL JSM-7401F model scanning electron microscope (SEM) at an acceleration voltage of 5 kV and a JEOL JEM-2100 model transmission electron microscope (TEM) at an acceleration voltage of 200 kV. For the SEM measurements, the samples were dried completely using a vacuum pump and coated with platinum of 4 nm. For the TEM measurements, the samples were also dried completely using a vacuum pump and placed on copper grids. The absorption spectra (ranged from 350 to 800 nm) were recorded by a Hitachi U4100 model ultraviolet–visible spectroscope. For the Au@PS NPs solutions in NMP, NMP was used as a reference spectrum; for the hybrid nanostructures dispersed in 5 wt % NaOH(aq), 5 wt % NaOH(aq) was used as a reference spectrum.

SUPPORTING RESULTS

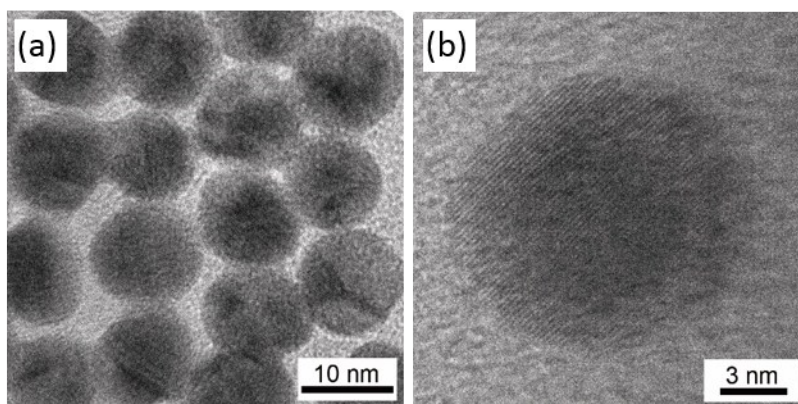


Figure S1. TEM images of (a) many Au@citrate NPs and (b) a single Au@citrate NP.

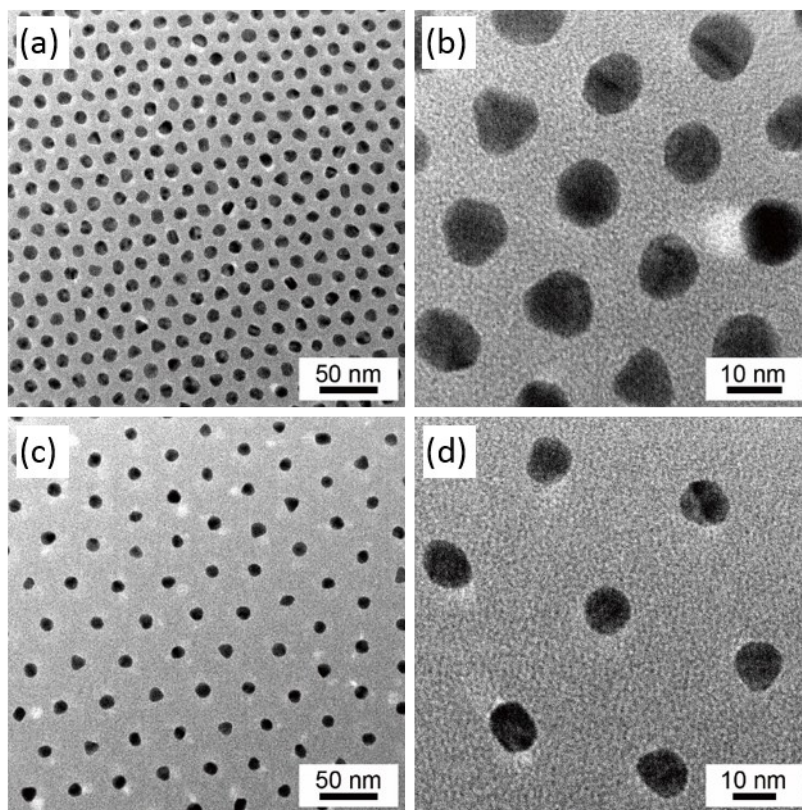


Figure S2. TEM images of Au@PS NP monolayers: (a and b) Au@PS_{5.8k} NP monolayers at lower and higher magnifications and (c and d) Au@PS_{53k} NP monolayers at lower and higher magnifications.

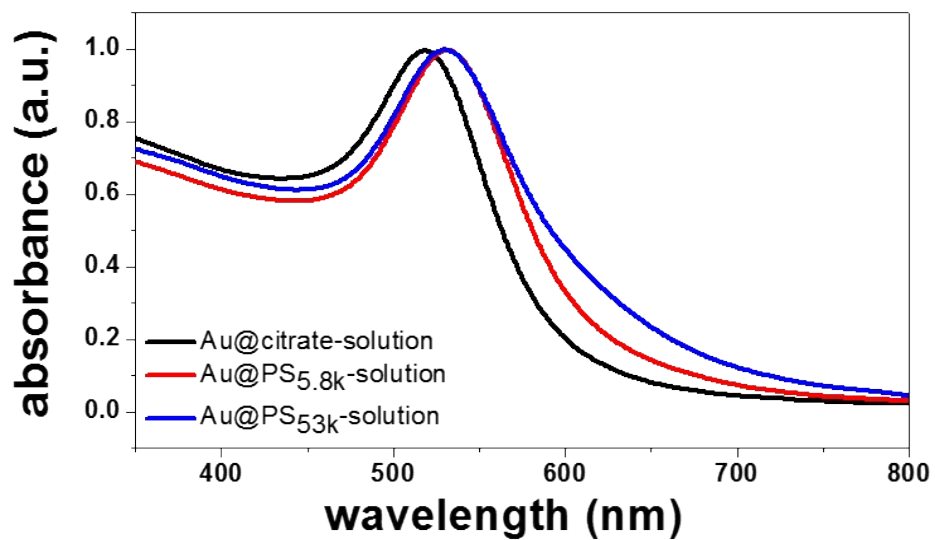


Figure S3. UV-Vis spectra of Au@citrate NPs and Au@PS NPs solutions.

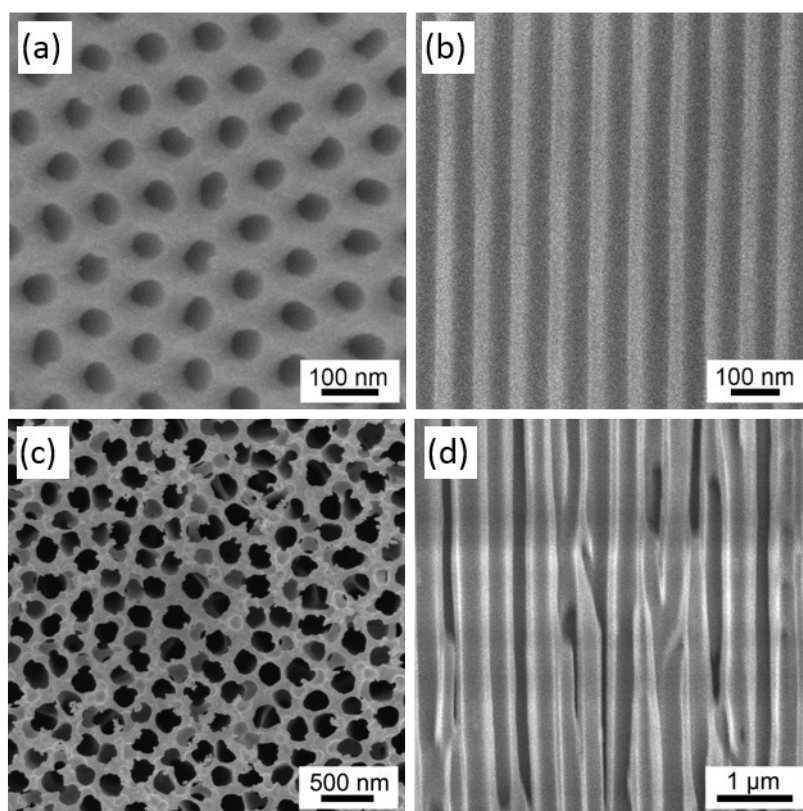


Figure S4. (a and b) Top-view and cross-sectional SEM images of AAO templates with average pore sizes of ~ 60 nm; (c and d) top-view and cross-sectional SEM images of AAO templates with average pore sizes of ~ 230 nm.

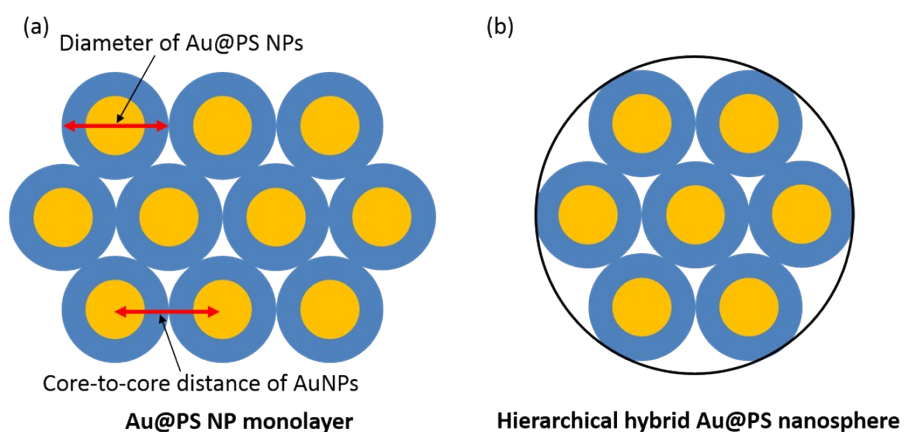


Figure S5. Graphical illustrations of a Au@PS_k NP monolayer and a hierarchical hybrid Au@PS nanosphere.

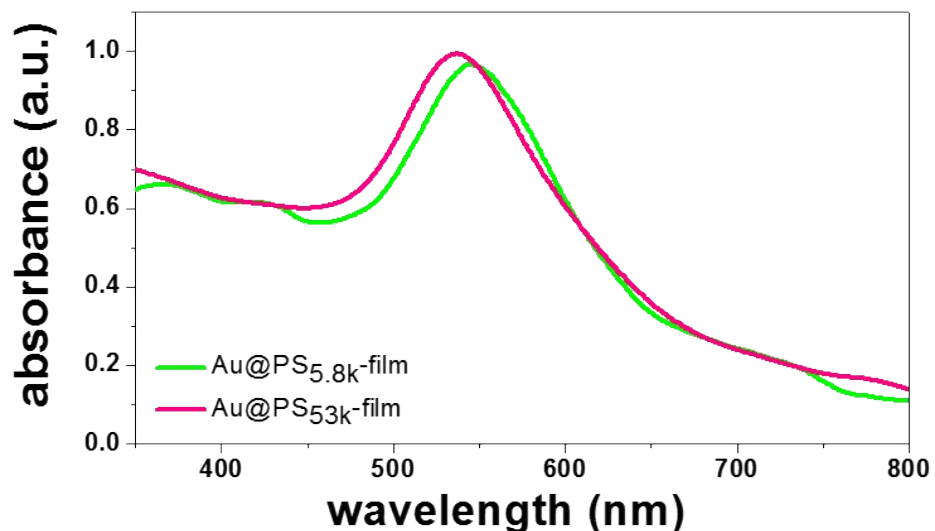


Figure S6. UV-Vis spectra of Au@PS_{5.8k} NP monolayers and Au@PS_{53k} NP monolayers.

Table S1. Average numbers of AuNPs and sizes of hierarchical hybrid Au@PS nanospheres.

Hierarchical hybrid Au@PS nanospheres	Au@PS _{5.8k} / 230 nm AAO	Au@PS _{53k} / 230 nm AAO	Au@PS _{5.8k} / 60 nm AAO	Au@PS _{53k} / 60 nm AAO
Average diameter (nm)	124.5	146.2	49.7	49.7
Average size (nm ³)	8079350	13083095	513970	513970
Average number of AuNPs	214.5	54.8	13.6	2.2

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