

Supporting Information for:

Capping Agent Replacement Induced Self-organization of Ultrathin Nanowires: A New and General Approach for Fabricating Large Surface Area Nanoporous Films with Controllable Thickness and Ligament Size

By Rui Liu, Jing-fu Liu, Su-juan Yu, and Gui-bin Jiang*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China and Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China.

Fax: (+86) 10-6284-9192

E-mail: jfliu@rcees.ac.cn

Chemicals:

TX-114 was purchased from Sigma-Aldrich. HAuCl_4 , H_2PtCl_6 , RuCl_3 , RhCl_3 , $\text{Pd}(\text{NO}_3)_2$, NaCl , KBr and KI were supplied by Sinopharm Chemical Reagent Company (Beijing, China) and potassium borohydride (KBH_4) Jingke Chemical Institute (Tianjing, China). All the chemicals were analytical grade or above, and Milli-Q water (Millipore) was used throughout the experiments.

Experimental

NPF Fabrication

Ultrathin nanowires (NWs) of Au, Pd, Pt, Ru and Rh were synthesized according to our previous developed method. In brief, 0.05 mmol HAuCl₄, Pd (NO₃)₂, H₂PtCl₆, RuCl₃ and RhCl₃ were placed in 50 ml conical flask. After stirring in ice bath for 30 min, 3 mL (for HAuCl₄), 1 mL (for Pd(NO₃)₂) or 2 mL (for H₂PtCl₆, RuCl₃ and RhCl₃) 0.1 M KBH₄ solution were injected into the flasks to make a 50 ml solution, and stirring for another 20 s. Proper amount of NaCl solution was added to the as-synthesized NW dispersion/ solution to reach a total Cl⁻ concentration no less than 6 mM for Pd, Rh and Ru, 10 mM for Pt and then transferred into the substrates (silicon wafer, glass slide or ITO glass slide) containing flat-bottomed container. The container was kept undisturbed at 4 °C for 12 h to let NWs deposit onto the silicon surface.

For the fabrication of hybrid film, the synthesized Au (2 mL), Pd (21 mL) and Pt (1 mL) NWs dispersion were mixed together, reach a final Cl⁻ concentration of 6 mM and ready for sedimentation.

To scavenging TX-114 from Au NWs dispersion, as well as fabricating reduced Graphene Oxide (rGO) doped Au NPF, 20 μL 0.2 mg/ mL rGO dispersion (prepared by a modified Hummers method, which was described in *Y. X. Xu, H. Bai, G. W. Lu, C. Li, G. Q. Shi, J. Am. Chem. Soc.* 2008, **130**, 5856.) was added into 2 mL Au NWs dispersion.

Effect of halide ion

2 mM extra Cl⁻, Br⁻ or I⁻ were added into Au NWs, their effect on Au NWs sedimentation process was studied by recording their time-dependent UV-Vis spectra, and their effect on film morphology was studied by HRSEM.

Characterization

Optical characterization was carried out by UV/Vis spectroscopy with a Beckerman nucleic acid/protein analyzer (Du 800, Beckman Coulter, Beckman, USA). SEM images were obtained with S-4800 or S-3000 scan electron microscope operated at 5 KV (Hitachi, Japan). TEM images were obtained with an H-7500 transmission electron microscope (Hitachi, Japan), and HRTEM images were obtained from a JEM-2100F field emission transmission

electron microscope (JEOL, Japan). The specimen for TEM/HRTEM was prepared by ultrasonically removing the Au NPF from the silicon wafer and dipped on amorphous carbon film-coated copper grid sample holders. Pore size analysis was conducted on a Quadrasorb SI surface area analyzer and pore size analyzer (Quantachrome Instruments). XRD analysis of the samples was performed with an X'pert PRO instrument (PANalytical), using Cu K α radiation ($\lambda=0.15418$ nm). XPS analysis was conducted on ESCALab220I-XL. Raman spectra was recorded on a Renishaw InVia plus Raman microscope, 785 nm (diode) lasers as the excited source, The laser power was maintained at 5 mW and the acquisition time was 10 s.

Results and Discussion

The addition of extra Cl⁻, Br⁻ or I⁻ significantly accelerate the sedimentation process, c.a. most of Au NWs deposited in less than 6 hour. The addition of 2 mM Cl⁻ only result in a fast replacement of TX-114 and fast sedimentation (the slope corresponding to the sedimentation stage increased from 0.195 to 0.776, Fig S5, S6). However, in the case of add Br⁻/I⁻, the peak near 500 nm (transverse mode SPR) is much more strong than Cl⁻, while the absorbance in the NIR region (longitudinal mode SPR) decrease faster than in the case of Cl⁻, both of which can be attributed to the strong chemical etch effect of Br⁻/I⁻ which cut Au NWs into short nanorod even nanoparticle, as well as the fast removal of TX-114 induced Au NWs fusion.

The addition of extra halide ions also changed the morphology of fabricated NPFs (Fig S7), unlike the uniform surface and small ligament size in the presence of Cl⁻, the addition of Br⁻ or I⁻ result in large pore size/ligament size. So a good balance between TX-114 capping induced stabilization/TX-114 removal induced destabilization is the key point of acquiring hierarchical NPF with uniform surface and small ligament size.

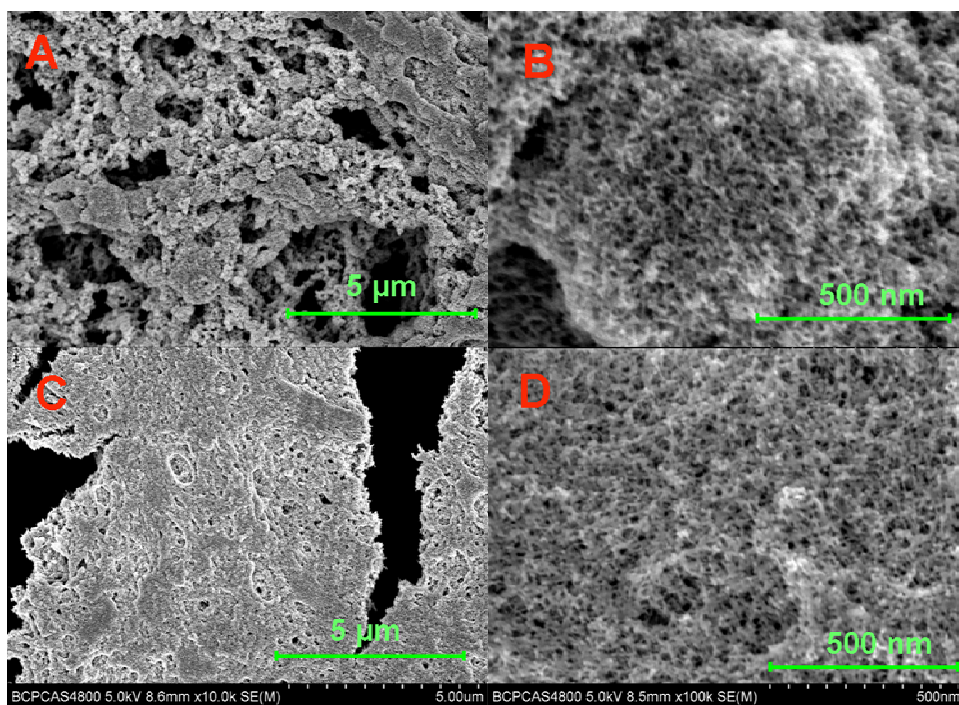


Figure S1. (A) and (C) Low-magnification SEM images of Au NPFs prepared by deposition of Au NWs dispersion (1 cm in depth) at 25 °C and 4 °C. (B) and (D) are their corresponding high-magnification SEM images.

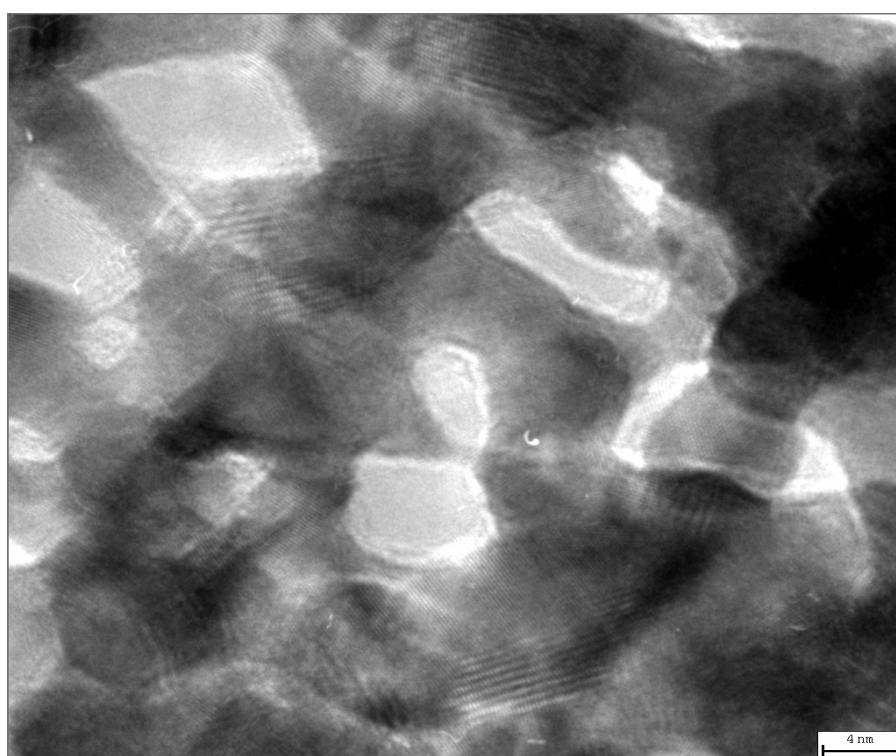
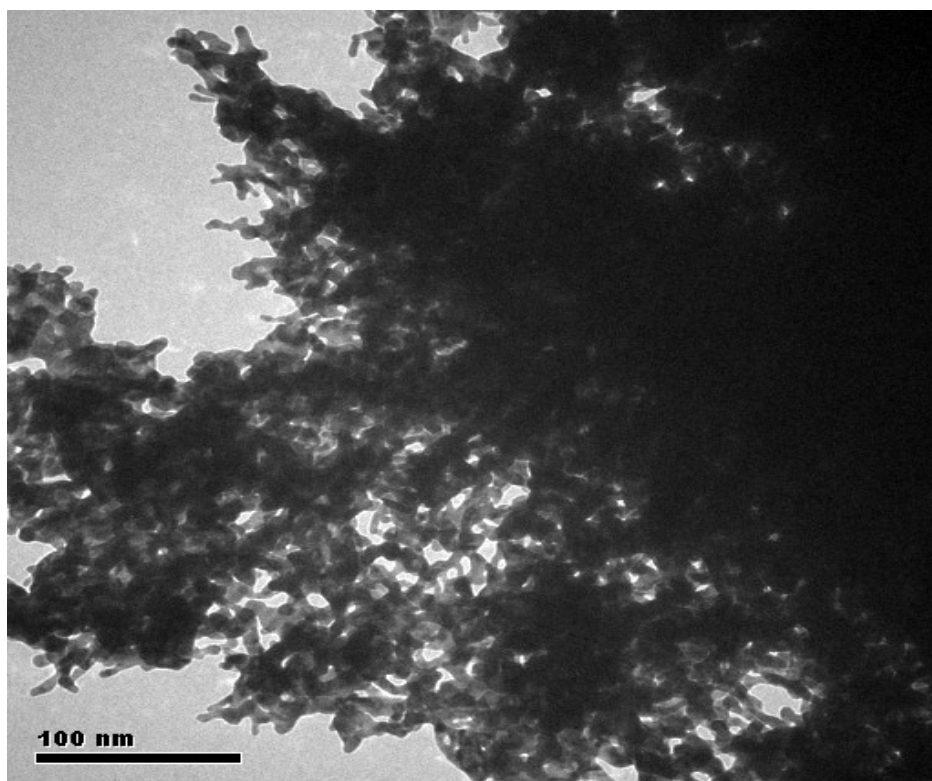


Figure S2. TEM and HRTEM images of the as-synthesized Au NPFs.

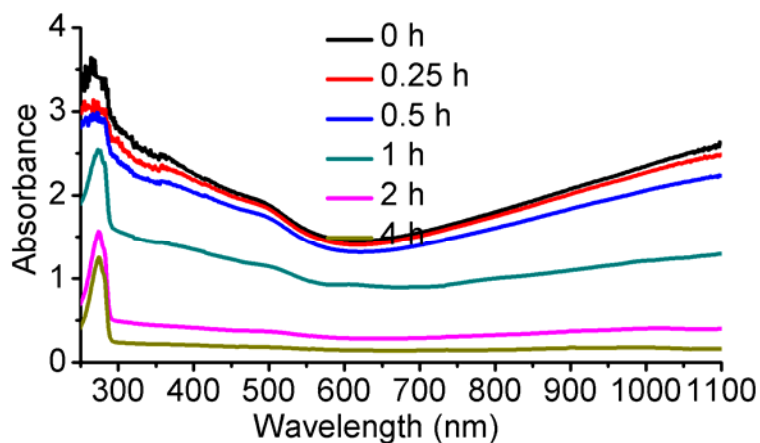


Figure S3. Time-dependent UV/Vis spectra of the deposition solution at 25 °C. Deposition time (from upper to lower): 0, 0.25, 0.5, 1, 2, 4 hour.

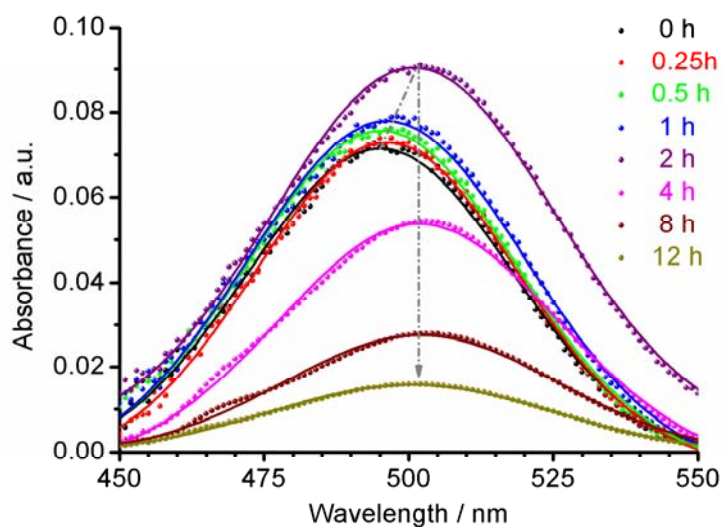


Figure S4. Baseline subtracted UV/Vis spectra of the deposition solution (dotted line) and their corresponding gauss fitting (solid line).

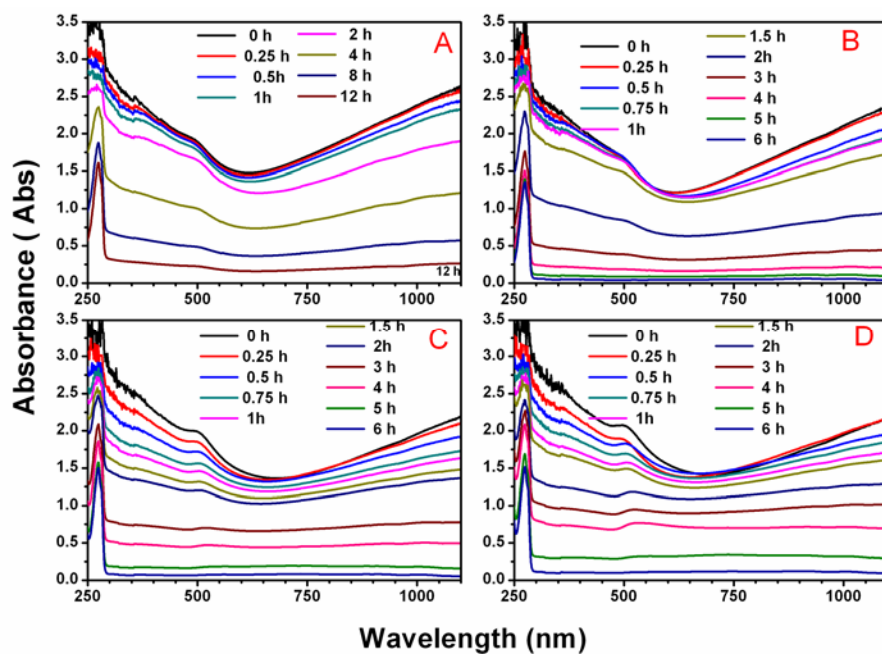


Figure S5. Time-dependent UV/Vis spectra of the deposition solution at 4 °C without (A) and with 2 mM extra Cl^- (B), Br^- (C), and I^- (D).

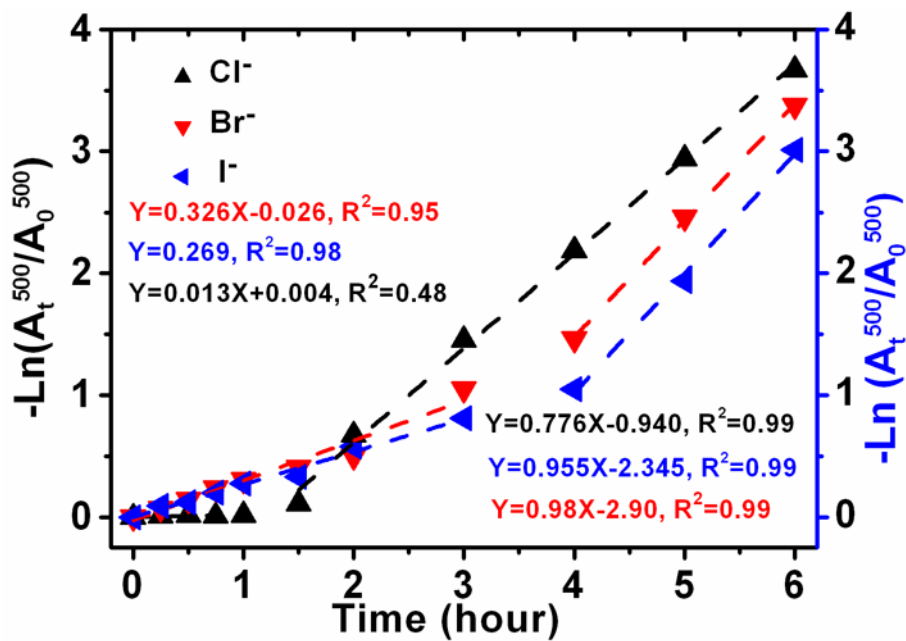


Fig. S6. Plot of $-\text{Ln}(A_t^{500}/A_0^{500})$ to sedimentation time (dots) and their linear fitting (dotted lines).

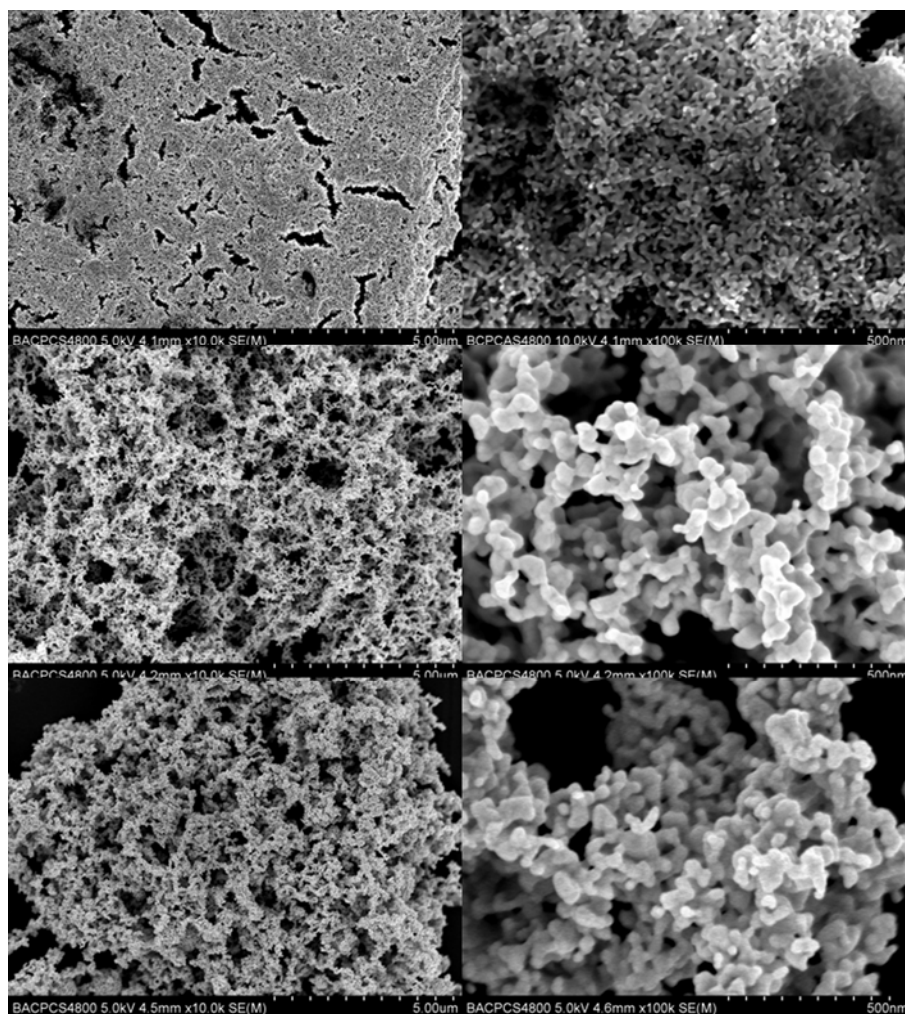


Figure S7. Low-magnification SEM images of Au NPFs prepared by deposition of Au NWs dispersion in the presence of 2 mM extra Cl⁻ (upper), Br⁻ (middle), and I⁻ (lower).