

Supporting Information

Monitoring of Galvanic Replacement Reaction
between Silver Nanowires and HAuCl_4 by In-Situ
Transmission X-Ray Microscopy

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Experimental Procedure

Synthesis of Ag nanowires. Silver nanowires were synthesized through the modified polyol process reported elsewhere.¹ In a typical synthesis, 5 mL of ethylene glycol (J. T. Baker) was added to a 100-mL three-neck round flask, which was partially immersed in an oil bath set at 160 °C. Heating was then continued under air for 1.5 hrs. Meanwhile, ethylene glycol solutions of 0.10 M AgNO₃ (Aldrich) and 0.15 M poly(vinyl pyrrolidone) (PVP, $M_w \approx 55000$, Aldrich, the concentration was calculated in terms of the repeating unit) were prepared. To 10 mL of PVP solution were added 22 μ L of 100 mM NaCl (Fisher) solution and 200 μ L of 0.5 mM tris(acetylacetonato)iron(III) (Fe(acac)₃, Aldrich) solution, resulting in final concentrations of 0.06 mM and 2.2 μ M for NaCl and Fe(acac)₃, respectively. In the next step, 3 mL of each solution (i.e., AgNO₃ and PVP with additives) were simultaneously injected into the hot ethylene glycol with a syringe pump (KDS-200, KD Scientific Inc., Holliston, MA) at a rate of 45 mL/h. The reaction was maintained at 160 °C for additional 1.5 hrs. Magnetic stirring of 240 rpm was applied throughout the entire synthesis.

Assembly of flow cell reactor with Ag nanowires. Two thick stainless steel disks were manufactured to open windows as shown in Figure S1. Each disk was used to hold a Si₃N₄ membrane with a thickness of 100 nm by bonding them together with glue. In order to allow reaction solution to be injected into and discharged from the cell, two Teflon tubes were attached to one steel disk through two holes. On the other hand, an aliquot of 0.1 mL dispersion of the as-synthesized Ag nanowires was transferred to a microcentrifuge tube and diluted with 1.4 mL ethanol. The diluted dispersion was then centrifuged at 6000 rpm for 10 min. The supernatant was discarded and the solid precipitate was then re-dispersed with 1 mL ethanol. The new dispersion was then centrifuged at 6000 rpm for 10 min. After the supernatant was discarded, the solid precipitate was then re-dispersed with 5 mL ethanol. A drop of the dispersion was cast on the surface of one Si₃N₄ membrane that was fixed on a steel disk. Evaporating ethanol in a fume hood at room temperature deposited Ag nanowires on the Si₃N₄ membrane. A flow cell reactor was then assembled according to the images shown in Figure S1.

Alignment and focusing adjustment of the transmission x-ray microscope. With structure similar to a conventional optical microscope, the TXM was aligned in a similar fashion by sequentially bringing each optical element into the optical axis defined by the x-ray beam source and the

center of the detector. Once the system was well-aligned, the flow cell reactor would be placed on the sample stage. A visible light microscope (off the x-ray beam path) was first used to select areas of interest, but it could not have sufficient resolution to identify individual nanowires of interest. The x-ray beam (with energy of 12 keV) was then used to search within these areas and identify nanowires for detailed study. Because this experiment was dose-sensitive, this search process was performed at lower resolution and with beam shuttered between exposures. After particular nanowires were identified, a close neighbor was used to focus the sample to avoid unnecessary radiation exposure to the region of interest. The nanowire was then exposed to acquire time sequence images shown in Figures 2-4.

In situ monitoring of the morphological evolution of the Ag nanowires. In order to trigger and maintain the continuous galvanic replacement reaction between the Ag nanowires attached to the Si_3N_4 membrane and the aqueous solution of HAuCl_4 (Aldrich) at room temperature, a HAuCl_4 solution with concentration of 1 mM was injected into the flow cell with a syringe pump at a rate of 0.01 mL/s. Right before the HAuCl_4 was in the flow cell, the x-ray beam shutter was open to shine the Ag nanowires and their images were continuously recorded at a time interval of 2 s. Each image was processed by dividing a background image acquired without sample and linearized by taking a natural log function. The display grey scale was adjusted to the overall absorption density window throughout the time-lapsed image sequence to maximize the contrast while providing relative perception of material density change.

Evaluation of the possibility for the formation of AgCl during the reaction. The image field shown in this work (Figure S4, left) is $21 \mu\text{m} \times 21 \mu\text{m}$ with an area of $4.41 \times 10^{-4} \text{ mm}^2$. In this area, there are three Ag nanowires with different dimensions: one has a diameter of 80 nm and a length of $7 \mu\text{m}$; one has a diameter of 90 nm and a length of $3 \mu\text{m}$; one has a diameter of 160 nm and a length of $13 \mu\text{m}$. The overall volume of these three nanowires is $\sim 3.15 \times 10^{-13} \text{ cm}^3$. By considering that the density and atomic weight of silver are $10.8 \text{ g}\cdot\text{cm}^{-3}$ and $108 \text{ g}\cdot\text{mol}^{-1}$, respectively, the molar amount of silver atoms in this image field is about $3.15 \times 10^{-14} \text{ mol}$. We assume that other areas on the window membrane are covered with the same density of Ag nanowires, the total amount of silver atoms on the window membrane with an area of $2 \text{ mm} \times 2 \text{ mm}$ (i.e., 4 mm^2) is $(3.15 \times 10^{-14} \text{ mol}) \times (4 \text{ mm}^2 / 4.41 \times 10^{-4} \text{ mm}^2) = 2.9 \times 10^{-10} \text{ mol}$. As shown

in the in-situ results, the silver nanowires are completely dissolved within 30 s. During this period, a volume of 0.30 mL (i.e., $0.01 \text{ mL/s} \times 30 \text{ s}$) solution flows through the reactor. As a result, the maximum concentration of Ag^+ ions in the reactor is $(2.9 \times 10^{-10} \text{ mol}) / (0.30 \times 10^{-3} \text{ L}) = 9.7 \times 10^{-7} \text{ mol/L}$. According to the stoichiometric relationship in eq. (1), the maximum concentration of Cl^- ions is $(4/3)[\text{Ag}^+] = 1.3 \times 10^{-6} \text{ mol/L}$. The product of the maximum concentrations of Ag^+ and Cl^- ions is $(9.7 \times 10^{-7}) \times (1.3 \times 10^{-6}) = 1.3 \times 10^{-12}$, that is more than 100 times lower than the solubility product constant (i.e., 1.77×10^{-10}) of AgCl at 25 oC.² As a result, there is no AgCl solid formed in the course of the galvanic replacement reaction.

Reference

1. Wiley, B.; Sun, Y.; Xia, Y. "Polyol synthesis of silver nanostructures: control of product morphology with Fe(II) or Fe(III) species", *Langmuir* **2005**, *21*, 8077-8080.
2. *CRC Handbook of Chemistry and Physics*, 86th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2005, pp8-119.

Movie S1. Morphological evolution of three Ag nanowires in the course of galvanic replacement reaction observed in a flow cell reactor using in situ TXM. The acquiring time for each frame was 2 s that was intendedly shortened in this movie in order to more easily visualize the morphological variation of the nanowires. The time (t) spanned from -30 s to 208 s that was normalized by the time when the image of Figure 2A was recorded. Evolution of the solid Ag nanowires into hollow nanotubes was clearly observed when $t < 40 \text{ s}$. More and more Au nanoparticles were formed and condensed around the nanotubes as the in-situ monitoring is continued.

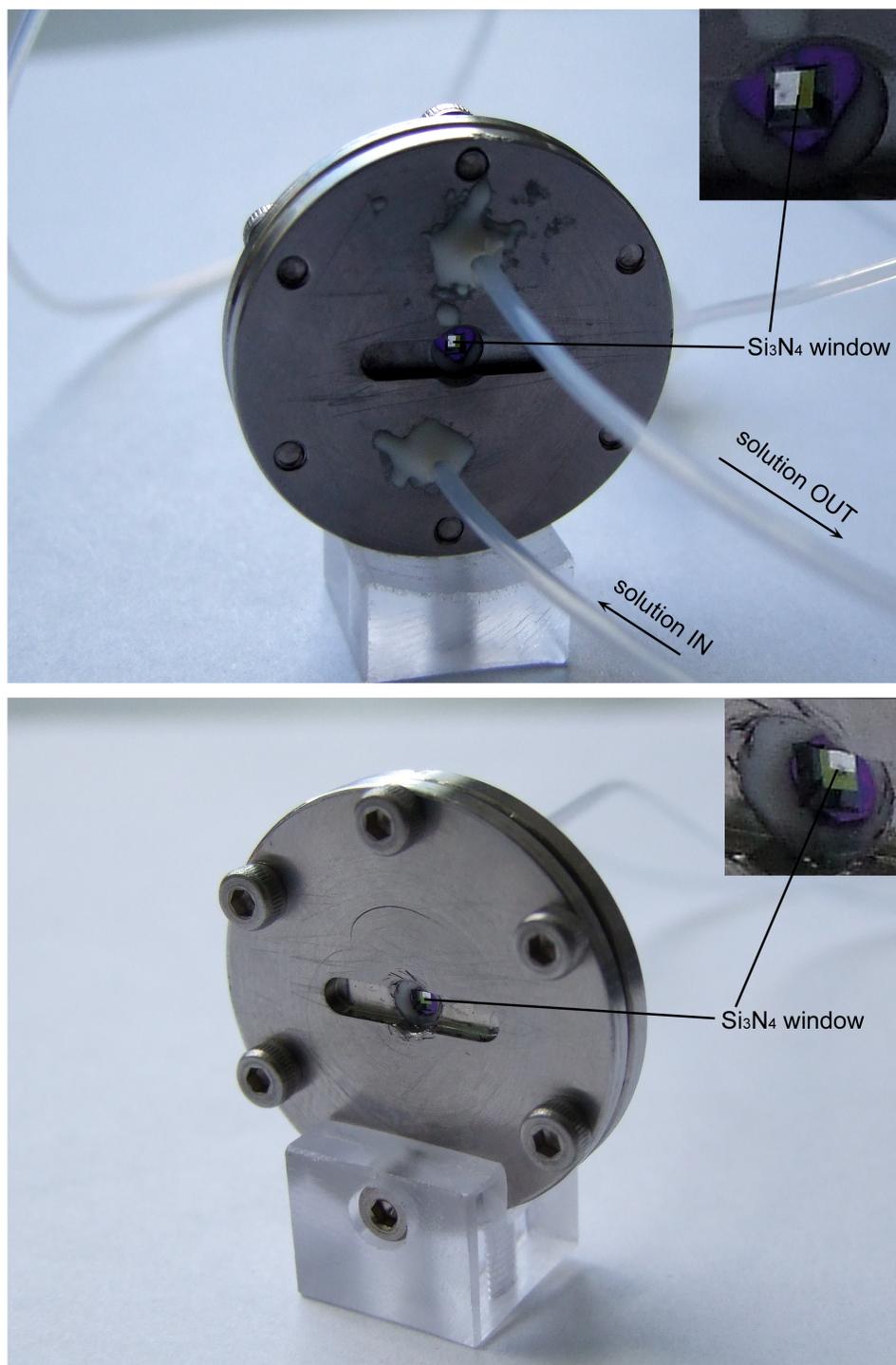


Figure S1. Photographs of the flow cell reactor.

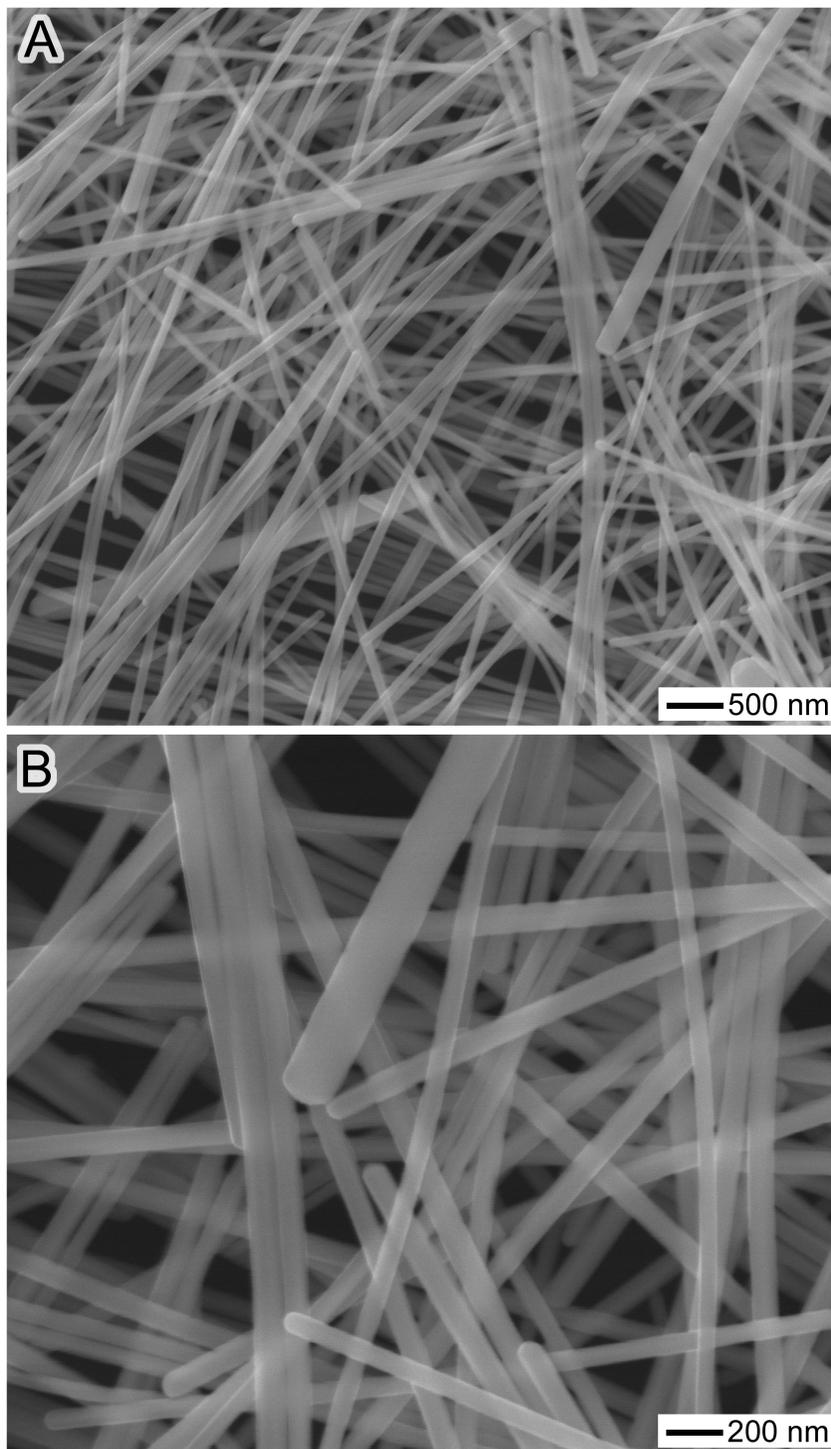


Figure S2. Scanning electron microscopy (SEM) images of the as-synthesized Ag nanowires. Most of them exhibit diameters in the narrow range of 70~90 nm while a very small fraction (<1%) exhibit larger diameters in the range of 100~200 nm.

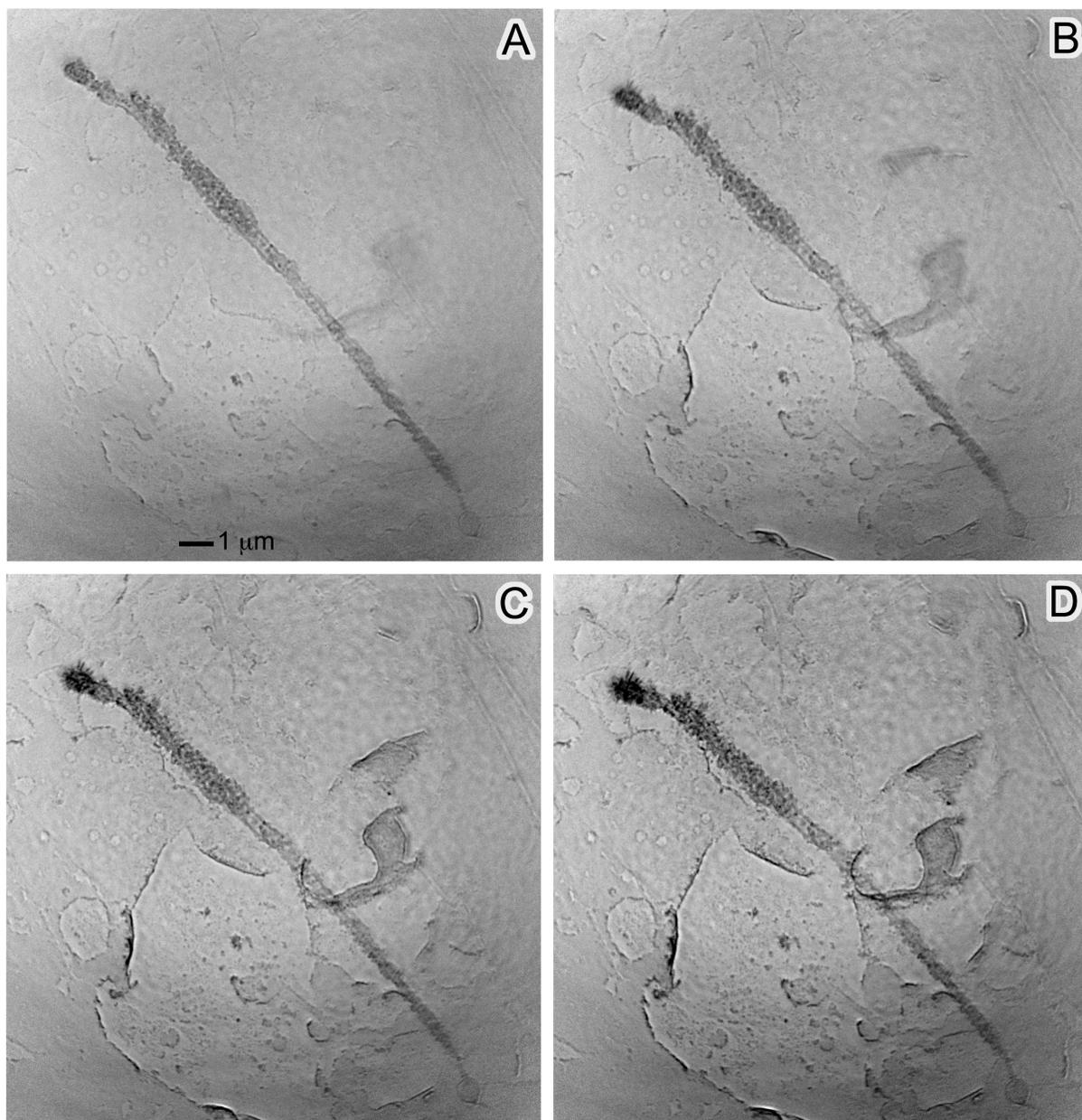


Figure S3. TXM images of the Ag nanowires (as shown in Figure 2A) after they reacted with HAuCl_4 at room temperature for different times: (A) 50 s, (B) 60 s, (C) 70 s, and (D) 80 s. The increased surface roughness and wall thickness of the nanotubes and the increased contrast of the background indicate the deposition of Au nanoparticles from the solution. More gold nanoparticles were formed at longer times. The scale bar in (A) also applies to (B-D).

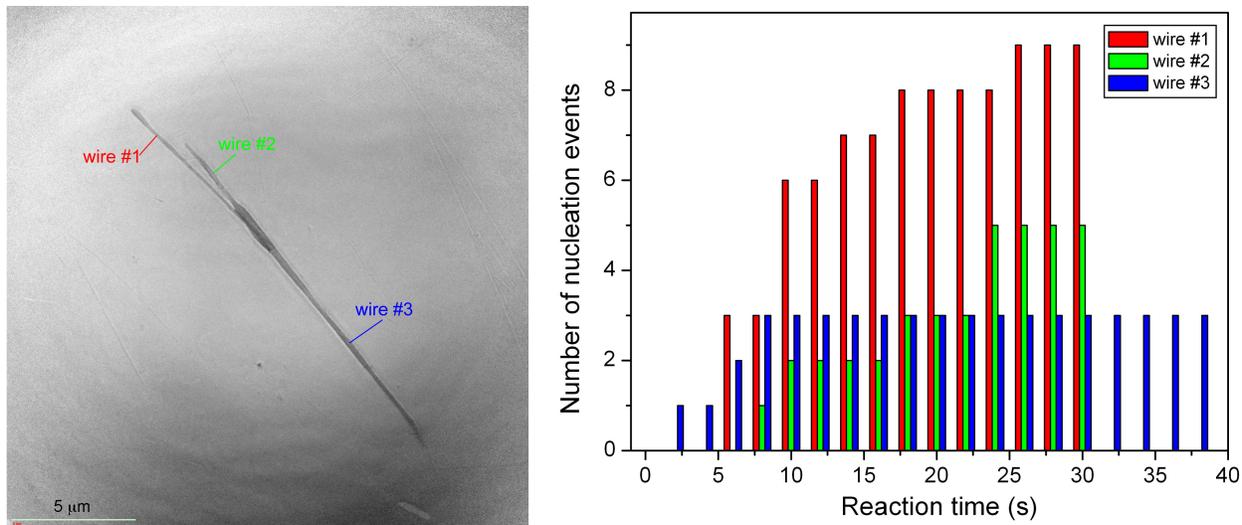


Figure S4. The number of nucleation events (i.e., the number of pits) as a function of reaction time for different nanowires as shown in the TEM image.