Monitoring of Galvanic Replacement Reaction between Silver Nanowires and H AuCl 4 by In Situ Transmission X-ray Microscopy

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ABSTRACT: Galvanic replacement reaction between silver nanowires and an aqueous solution of H AuCl 4 has been successfully monitored in real time by using in situ transmission X-ray microscopy (TXM) in combination with a flow cell reactor. The in situ observations clearly show the morphological evolution of the solid silver nanowires to hollow gold nanotubes in the course of the reaction. Careful analysis of the images reveals that the galvanic replacement reaction on the silver nanowires involves multiple steps: (i) local initiation of pitting process; (ii) anisotropic etching of the silver nanowires and uniform deposition of the resulting gold atoms on the surfaces of the nanowires; and (iii) reconstruction of the nanotube walls via an Ostwald ripening process. The in situ TXM represents a promising approach for studying dynamic processes involved in the growth and chemical transformation of nanomaterials in solutions, in particular for nanostructures with dimensions larger than 50 nm.

KEYWORDS: Transmission X-ray microscopy, in situ TXM, liquid TXM, flow cell TXM, galvanic replacement reaction mechanism, silver nanowires

G alvanic replacement reactions between solid metal nanoparticles with oxidizing metal precursors represent a versatile strategy for synthesizing hollow metal nanostructures with tailored properties that are difficult (or even impossible) to achieve from their solid counterparts.1 For example, reactions of silver nanocubes with aqueous solutions of H AuCl 4 enable the synthesis of hollow nanoboxes with seamless walls and nanocages/nanoframes with porous walls that exhibit absorption bands tunable in the range of both visible and near-infrared (NIR) regions2,3 and have been used in biological imaging,4 medical therapy,5,6 drug delivery,7 catalysis,8 imaging with computed tomography (CT) technique. The flow cell TXM technique can overcome the limitations of in situ TEM for successfully observing the real-time morphological evolution of silver nanowires in the course of a galvanic replacement reaction with an aqueous solution of H AuCl 4 at room temperature.

A transmission X-ray microscope system works similarly to a conventional optical microscope. Figure 1 gives the schematic configuration of a typical transmission X-ray microscope that consists of a condenser lens, a beam stop, a pinhole, an objective lens (i.e., Fresnel zone plate), and a charge-coupled device (CCD) detector. The diffraction limited resolutions (R) is determined by 0.61λ/NA, where λ is the X-ray wavelength and NA is the numerical aperture of the objective lens.14 With current lens fabrication technology, the beams to pass through the loaded solution for imaging. The small reaction chamber makes it difficult to load silver nanowires with diameters larger than 100 nm into the cell. Herein, we report the use of in situ transmission X-ray microscopy (TXM) in combination with a flow cell for real-time monitoring the reaction between silver nanowires and H AuCl 4. The use of a flow cell allows us to trigger the reaction by delivering a H AuCl 4 solution into the cell when the TXM is ready for imaging. The large penetration length of hard X-rays in solution makes it possible to use reaction chambers as thick as hundreds of micrometers that allow easy manipulation of nanoparticles as well as potential in situ three-dimensional (3D) imaging with computed tomography (CT) technique. The flow cell TXM technique can overcome the limitations of in situ TEM for successfully observing the real-time morphological evolution of silver nanowires in the course of a galvanic replacement reaction with an aqueous solution of H AuCl 4 at room temperature.

Received: July 25, 2011
Revised: August 17, 2011
Published: September 06, 2011
achievable NA is in the range of several mrad with a multi-keV hard X-ray radiation, leading to spatial resolution of 10–15 nm but extended depth of focus of tens of micrometers.\textsuperscript{14,15} Although this resolution scale is lower than that of electron microscopy techniques,\textsuperscript{13,16} the TXM approach offers several unique advantages for in situ studies with solution-phase reactions:

1. The entire system can be operated in ambient environment due to the strong penetration of hard X-ray in air and solvents, leading to the compatibility with solution-phase reactions.
(2) The TXM has the capability to control image contrast of different elements by tuning X-ray energy. For instance, individual elemental compositions can be mapped by using their characteristic absorption edges, and furthermore the X-ray absorption near-edge structure (XANES) spectra can be used to map the chemical states of individual elements.

(3) The large working distance (e.g., over 2 cm in the system reported in this work) and open system design enable easy integration of reaction vessels and easy access to the reaction vessels to manipulate complicated reaction conditions.

In this work, a flow cell (Figure S1, Supporting Information) is placed in the X-ray beam path of the TXM system to study the galvanic replacement reaction between Ag nanowires and an aqueous solution of HAuCl₄:

\[
3\text{Ag} + \text{AuCl}_4^- \rightarrow 3\text{Ag}^{\text{III}} + \text{Au} + 4\text{Cl}^-
\]

Figure 3. Magnified TXM images of the thin nanowires highlighted in box I, Figure 2B, before and after they reacted with HAuCl₄ for different times. Similar to those in Figure 2, the black arrows highlight the positions at which the nanowire was fragmented, while the blue arrows highlight the positions at which the openings were sealed to form a hollow nanotube. The scale bar applies to all images.
the cell, respectively. In a typical experiment, the Ag nanowires synthesized through the well-established polyol process\textsuperscript{17} are first centrifuged and redispersed in ethanol to achieve a dispersion solution with appropriate concentration. Placing a drop of the solution on the surface of one Si$_3$N$_4$ membrane followed by drying in air at room temperature results in the deposition of the Ag nanowires on the surface of the membrane. The van der Waals forces between the nanowires and the Si$_3$N$_4$ membrane are strong enough to prevent the nanowires from moving during reaction, enabling the in situ monitoring of morphological variation of single nanowires as the galvanic reaction proceeds. In the next step, the flow cell with Ag nanowires is assembled, as shown in Figure S1, Supporting Information, and then placed in the TXM system. The imaging process was initiated immediately before an aqueous HAuCl$_4$ solution with a concentration of 1 mM is continuously injected into the flow cell by a syringe pump to trigger the galvanic replacement reaction, and the nanowires in the imaging field are continuously monitored in real time.

Figure 2 compares the images of the Ag nanowires and the corresponding products obtained at different reaction times. The two wires at the top left region of Figure 2A are thin with diameters of 80–90 nm and short with lengths of 3–7 μm. In contrast, the wire at the bottom right region is thick with...
diameter of \( \sim 160 \) nm and long with length of \( \sim 13 \) \( \mu \)m. This bimodal distribution of the Ag nanowires is consistent with their scanning electron microscopy (SEM) images shown in Figure S2, Supporting Information. Most of the as-synthesized Ag nanowires exhibit diameters in the narrow range of \( 70 - 90 \) nm, while a very small fraction (\(<1\)%) of the nanowires exhibit larger diameters in the range of \( 100 - 200 \) nm. The images in Figure 2 clearly show the morphological evolution of solid Ag nanowires into hollow nanotubes (Figure 2A versus 2D) as the reaction proceeds. At the beginning of the reaction (e.g., \( 12 \) s as shown in Figure 2B), the replacement reaction initiates only at some spots (such as those highlighted with arrows) that have surface energy higher than other surface areas of the nanowires, leading to the formation of pits at these spots. The reaction continues to etch the Ag nanowires from these pits and simultaneously deposit Au on the surfaces of the nanowires because the newly formed surfaces of the pits have an even higher surface energy and thus higher reactivity. When the reaction lasts long enough, the Ag nanowires are completely dissolved to leave tubes of Au (or Ag–Ag alloy due to the possible alloying of Au with the underneath silver nanowires) (Figure 2D). As shown in Figure S3, Supporting Information, the tubes detach from the window membrane into the waste solution after reaction, leading to a difficulty for further chemical analysis of the resulting tubes with techniques like energy dispersive X-ray scattering (EDS). However, the deposited material should be Au according to eq 1 and the previous ex-situ studies on the galvanic replacement reactions.\(^3\) As highlighted by the arrows, the surface morphologies near the initially formed pits (as highlighted by the arrows in Figure 2B) are slightly different depending on the diameters of the Ag nanowires.

For example, the replacement reaction at the pits formed on the thin nanowires (highlighted by the black arrow in box I, Figure 2B) tends to break the nanowires into segments (highlighted by the black arrows in Figure 2C and D). Figure 3 shows a series of images of the thin nanowires that have been obtained at a time interval of \( 2 \) s to track their morphological evolution in details. At the very early stage of the reaction (e.g., \( 6 \) s), a number of tiny bright spots correlated to material loss (highlighted by the black arrows) start to appear on the surface of the left thinner nanowire (with a diameter of \( \sim 80 \) nm), indicating the initiation of pitting process. The pits increase in their dimensions and eventually break the nanowire into segments as the reaction proceeds (highlighted by the black arrows in the image obtained at \( 20 \) s). During the period of reaction, more pits are also formed on the surface of the nanowire to induce the similar fragmentation (Figure S4, Supporting Information). As a result, the product derived from this thin Ag nanowire exhibits a quasi-linear assembly of very short hollow tube segments and clusters of nanoparticles (e.g., the image obtained at \( 30 \) s). In contrast, another Ag nanowire on the right side has been converted into a continuous hollow nanotube, although this nanowire exhibits nonuniform diameters along its longitudinal axis. Its tip had a diameter of \( \sim 80 \) nm that is similar to the diameter of the nanowire on the left side, and its stem has a slightly larger diameter of \( \sim 90 \) nm. As highlighted by the blue arrows, the replacement reaction also initiates with the formation of pits at both the end and the stem, and the complete reaction results in the formation of a continuous nanotube with a closed end. The difference of the two nanowires shown in the image obtained at \( 30 \) s indicates that the lateral dimension (i.e., diameter) and the surface geometry/crystalline orientation of a Ag nanowire play important roles in determining the morphological evolution of the Ag nanowire in the course of the galvanic reaction of eq 1. In spite of the low solubility of AgCl,\(^14\) no AgCl solids are observed during the reaction because the concentrations of Ag\(^+\) and Cl\(^-\) ions released from the reaction of a small number of Ag nanowires with HAuCl\(_4\) are low enough to prevent the precipitation of AgCl (see Supporting Information for details). When the reaction time is too long (e.g., \( >32 \) s), additional Au nanoparticles are deposited on the outside surfaces of the hollow nanotubes (Figure S3 and Movie S1, Supporting Information) due to the reduction of HAuCl\(_4\) by reducing species that are generated from the high-dose X-ray irradiation of water.\(^19\)

As pointed out previously, increasing the diameter of Ag nanowires is beneficial to the formation of nanotubes with continuous walls. Figure 4 shows a series of images of the thick Ag nanowire with a diameter of \( \sim 160 \) nm (highlighted in box II, Figure 2B) in the course of the replacement reaction, clearly showing the transformation of the solid nanowire into a continuous nanotube. Similar to the thin nanowires shown in Figure 3, the reaction also initiates the formation of pits at some spots on the surface of the nanowire (as highlighted by the blue arrows). Continuous reaction etches out the thick Ag nanowire along its longitudinal axis and deposits a Au layer on the surface of the nanowire, eventually resulting in the formation of a hollow nanotube at \( 38 \) s. Apparently, the hollowing process of the thick nanowire takes a longer time than the thin wires because more silver has to be etched during the reaction. The holes formed at the pits remain open until the Ag nanowire had been completely dissolved (as highlighted by the blue arrows in the image obtained at \( 34 \) s). Further reaction leads to an Ostwald ripening process that can reconstruct the morphology of the nanotube to smooth its
surface with a decrease in surface energy. As a result, the holes are sealed to form a continuous nanotube (as highlighted by the blue arrows in the image obtained at 38 s) because no additional Ag⁺ ions will be released inside the nanotube to diffuse out.

The results obtained from the in situ TXM observations clearly show the morphological evolution of single Ag nanowires in the course of the galvanic replacement reaction between the nanowires and aqueous solution of HAuCl₄ at room temperature. Figure 5 summarizes the pathways for hollowing the Ag nanowires with different diameters. Contacting HAuCl₄ with Ag nanowires initiates the galvanic reaction between them at some specific spots rather than uniformly over the whole surfaces of the nanowires because these spots usually exhibit higher surface energy originating from crystalline defects such as steps, dislocations, etc. Once the reaction starts, pits with irregular shapes and surfaces are then formed at these spots. The pitting process locally etches the Ag nanowires, while the resulting Au atoms are uniformly deposited on the intact surfaces of the nanowires to form Au sheaths. Continuous reaction etches out more Ag from the surfaces of the pits and deposits more Au on the outside surfaces of the nanowires, leading to the formation of hollow tubes. Depending on the diameter of the Ag nanowires, the relative etching rates along the longitudinal and transverse directions are different. As shown in Figure 5A, the reaction etches thin nanowires along their transverse direction faster than along their longitudinal direction when the diameters of nanowires are less than 80 nm, leading to fragmentation of the nanowires. In contrast, the reaction etches thick nanowires (with diameters larger than 90 nm) with a preference along their longitudinal axes, resulting in the formation of nanotubes with continuous walls (Figure 5B). On the other hand, if the reaction initiates the formation of pits at the end of a nanowire, then continuous reaction tends to etch the nanowire along its longitudinal axis regardless of its diameter (Figure 5A). During this process, the reaction occurs similar to the electrochemistry in a battery (inset, Figure 5). Ag atoms on the surfaces of the pits are oxidized to release Ag⁺ ions that can diffuse out through the openings of the pits, while the leftover electrons diffuse to the surfaces of the nanowires to reduce AuCl₄⁻ ions into Au atoms that are directly deposited on the surfaces to thicken the Au sheaths. Once the Ag nanowires are completely dissolved, the replacement reaction stops. In the next step, an Ostwald ripening starts to reconstruct the walls of the Au nanotubes to seal the holes, leading to the formation of continuous nanotubes (Figure 5B). It is worthy to note that most of the poly(vinyl pyrrolidone) (PVP) molecules adsorbed on the surfaces of the Ag nanowires are removed during the washing/centrifuge processes. The residual PVP molecules do not influence the galvanic replacement reaction between the Ag nanowires and HAuCl₄, and eventually they are desorbed from the surfaces of the nanotubes.

In conclusion, we have observed the morphological evolution of Ag nanowires involved in the galvanic reaction between nanowires and a HAuCl₄ solution in real-time by combining TXM imaging with a flow cell reactor. The in situ results clearly reveal the multiple-step process associated with the chemical transformation of solid Ag nanowires into hollow Au (or Au–Ag alloy) nanotubes at room temperature: (i) local initiation of the reaction at certain spots with high surface energy; (ii) formation of pits at these spots; (iii) dissolution of the Ag nanowires through these pits and deposition of Au sheaths outside of the nanowires; and (iv) reconstruction of the nanotubes via an Ostwald ripening process. The information provides a better understanding of galvanic replacement reactions on the nanometer scale and helps us to better control the synthesis of hollow nanostructures with tailored properties. Although the spatial resolution of TXM imaging is ∼25 nm (with pixel size of ∼10 nm) in this study, it can be potentially improved when advanced lithographic techniques are available for fabricating zone plates (objective lenses) with better performance. The energy of incident X-rays can be finely tuned to achieve spatially mapped XANES and electron energy loss spectroscopy that offer the capability to study the dynamic evolution of elemental and chemical composition of the samples. Many other detectors are possibly integrated to the TXM system for simultaneously monitoring variations of crystalline structures by X-ray diffraction, local chemical states by X-ray Raman and fluorescence, etc.

As a result, in situ TXM is complementary to in situ TEM and is promising to study the growth and transformation of nanomaterials in solutions.

**ASSOCIATED CONTENT**

*Supporting Information.* Experimental procedures, Figures S1–S4 with corresponding figure captions, and Movie S1 caption. This material is available free of charge via the Internet at http://pubs.acs.org.

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**ACKNOWLEDGMENT**

Use of the Center for Nanoscale Materials, Advanced Photon Source, and Electron Microscopy Center for Materials Research at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357. Help from Drs. Wenge Yang and Yang Ren is appreciated.

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