Supporting Information

Quantitatively In-situ Imaging Silver Nanowire Hollowing Kinetics

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1. Analysis based on Fick's laws

Concentration distribution of Ag. For simplification, we assume that the core and the shell are perfect cylinder of pure Ag and perfect hollow cylinder of pure Ag_2O, respectively, and that they are in good contact with each other. Fick's laws can provide a simple model for the concentration distribution of Ag in the shell. From Fick's second law in cylindrical coordinates we can obtain

$$\frac{\partial C}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}(r\frac{\partial C}{\partial r}) \tag{1}$$

where C is the concentration of Ag, r is the distance from the center of the nanowire and D is the diffusion coefficient of Ag in Ag_2O; the symmetry of cylinder is considered and the longitudinal mass transport is ignored. For a steady-state system (i.e. $\partial C/\partial t = 0$), after applying the boundary conditions $C_{Ag}(r_i) = C_i$ and $C_{Ag}(r_o) = 0$ (subscripts i and o stand for the inner and outer surfaces of the shell, respectively), we can obtain the concentration distribution of Ag

$$C_{Ag}(r) = C_{Ag}(r_o) - \left[C_{Ag}(r_o) - C_{Ag}(r_i)\right]\frac{\ln(r_o/r)}{\ln(r_o/r_i)}$$

$$= \frac{C_i}{\ln(r_o/r_i)}(\ln r_o - \ln r) \qquad (r_i \leq r \leq r_o) \tag{2}$$

Estimating the diffusion coefficient of Ag in Ag_2O. From Fick's first law the diffusion flux J can be written as

$$J(r) = -D\frac{\partial C_{Ag}(r)}{\partial r} = D\frac{C_i}{r \cdot \ln(r_o/r_i)} \tag{3}$$

Meanwhile, from the definition of J we can write

$$J(r_i) = -\frac{d\left(\pi r_c^2 L\right)}{V_m \cdot (2\pi r_i L)dt} = -\frac{r_c}{V_m \cdot r_i} \cdot \frac{dr_c}{dt}. \tag{4}$$

Here, $V_m = 1/C_i$ is the molar volume of Ag, subscript c stands for the core, and L is the length of the Ag nanowire segment. At the inner interface of the shell ($r = r_i$), from equation (3) and (4) we have

$$D\frac{1}{\ln\left(r_o / r_i\right)} = -r_c \frac{dr_c}{dt} \tag{5}$$

Both sides of equation (5) are integrated over time t when estimating the diffusion coefficient D in order to reduce error. By defining $F(t) \equiv \frac{1}{2} r_c^2(t_0) - \frac{1}{2} r_c^2(t)$ and

$G(t) \equiv \int_{t_0}^{t} \frac{dt}{\ln\left[r_o(t)/r_i(t)\right]}$, where t_0 is the selected initial time of the integration, we are

able to relate the diffusion coefficient D to two time-dependent quantities, $F(t)$ and

$G(t)$, both of which can be easily calculated from the measured geometrical parameters:

$$D = \frac{F(t)}{G(t)} \tag{6}$$

2. X-ray absorption by the nanowires

Main factor affecting the X-ray absorption. The contrast of the transmission x-ray microscopy (TXM) images results from the absorption of the x-ray beam by the material, which can be describe by this equation

$$(I_0 - I_t) \cdot S = I_0 \cdot \iint_S \left(1 - e^{-\mu l}\right) dS \qquad (7)$$

where I_0 and I_t are incident intensity and transmitted intensity of the x-ray beam, respectively. The surface integral area S is in the plane perpendicular to the x-ray propagation, l is the thickness along the x-ray propagation direction, and

$$\mu = n\sigma = \rho N_A \sigma / A \qquad (8)$$

where n is the atomic number density, ρ is the mass density, N_A is the Avogadro number, A is the atomic mass number, and σ is the absorption cross section. μ_O is less than one hundred thousandth of μ_{Ag} at 12 keV (the energy at which the TXM images of Ag nanowires are recorded),[1] so the absorption by O atoms is negligible. Meanwhile, the influence of valence change from Ag to Ag_2O is also negligible since this energy is far away from the L edge (3.5-3.8 eV) and the K edge (25.5 eV). When the influences by the O atoms and the valence change can be ignored, the absorption is determined by the distribution of Ag atoms.

Calculating the X-ray absorption from measured geometrical parameters. For simplification, we assume that the core and the shell are perfect cylinder of pure Ag and perfect hollow cylinder of pure Ag_2O, respectively, and they are concentric. By considering the geometrical relationship and using the measured geometrical parameters, l can be expressed by r, and the x-ray absorption can be calculated from equation (8).

The influence of the oxidation on the x-ray absorption. The final volume of the nanowires is approximately 1.57 times of the original volume after complete oxidation. Assuming the expansion due to the oxidation is isotropic, after oxidation we have

$$l' = kl, \ S' = k^2 S, \ \mu' = \frac{\mu}{k^3} \tag{9}$$

here $k^3 = 1.57$. From equation (7) to (9) we can obtain the change of the x-ray absorption after oxidation

$$\Delta I_{oxidation} = I_0 \cdot \iint_S [k^2 \left(1 - e^{-\frac{1}{k^2}\mu l} \right) - \left(1 - e^{-\mu l} \right)] dS \tag{10}$$

Use Taylor series, we write the equation as

$$\Delta I_{oxidation} = I_0 \cdot \iint_S \left\{ \left[\mu l - \frac{1}{2k^2}(\mu l)^2 + \frac{1}{6k^4}(\mu l)^3 - \dots \right] - \left[\mu l - \frac{1}{2}(\mu l)^2 + \frac{1}{6}(\mu l)^3 - \dots \right] \right\} dS$$

$$= I_0 \cdot \iint_S \left[\frac{1}{2}\left(1 - \frac{1}{k^2} \right)(\mu l)^2 - \frac{1}{6}\left(1 - \frac{1}{k^4} \right)(\mu l)^3 + \dots \right] dS \tag{11}$$

here $k = 1.16$, and $\mu_{Ag} = 777$ cm^{-1} at 12 keV;[1] since the l is typically less than 500 nm in our experiment, the sum of the terms in the square brackets is positive and smaller than 2.0×10^{-4}, which means the oxidation will result in a subtle increase in the absorption.

The influence of the diffusion on the x-ray absorption. Consider the case that an infinitesimal particle (with thickness l_3) in the nanowire moves from one point (with thickness l_1) to another (with thickness l_2, $l_1 > l_2$), the change of the x-ray absorption is

$$\Delta I_{diffusion} = I_0 \cdot \iint_S \left[(1 - e^{-\mu l_1}) + (1 - e^{-\mu l_2} \cdot e^{-\mu l_3}) \right] dS - I_0 \cdot \iint_S \left[(1 - e^{-\mu l_1} \cdot e^{-\mu l_3}) + (1 - e^{-\mu l_2}) \right] dS$$

$$= I_0 \cdot \iint_S \left[(e^{-\mu l_2} - e^{-\mu l_1}) \cdot (1 - e^{-\mu l_3}) \right] dS > 0 \tag{12}$$

During the hollowing process the Ag atoms always diffuse from high concentration to low concentration and move towards places of smaller thickness. Therefore the x-ray absorption increases as the Ag atoms diffuse.

Extracting the x-ray absorption from grayscale. First, each TXM image is normalized by dividing the pixel grayscale values by the average pixel value of the background area. After normalization the average pixel value of the background is approximately 1. The absorption by the nanowire segment is then calculated by subtracting the normalized pixel value from 1 and integrating all the results over the segment of interest.

Reference:

1. Mcmaster, W. H.; Del Grande, N. K.; Mallett, J. H.; Hubbell, J. H. Compilation of X-Ray Cross Sections, *Lawrence Livermore National Laboratory Report* UCRL-50174 Section II Revision I **1969**, 16-17 & 94-95.

Movie 1. Morphological evolution of the Ag nanowires in the course of photon-induced oxidation observed in a flow cell reactor using in situ TXM. The acquiring time for each frame was 2 s. There are 20 frames displayed per second in this movie in order to more easily visualize the morphological variation of the nanowires. The time spanned from 0 min to 40 min that was normalized by the time when the image of Figure 1(b) was recorded. The Evolution of the solid Ag nanowires into hollow nanotubes was clearly observed.

Movie 2. Magnified TXM images of the Ag nanowires I highlighted by the red solid line box in Figure 1(b). The acquiring time and frame per second are the same as Movie 1. The hollowing process of the selected nanowire segment was clearly observed.

Movie 3. Magnified TXM images of the Ag nanowires II highlighted by the green dashed line box in Figure 1(b). The acquiring time and frame per second are the same as Movie 1. Both the hollowing process and the longitudinal diffusion of the core were clearly observed.
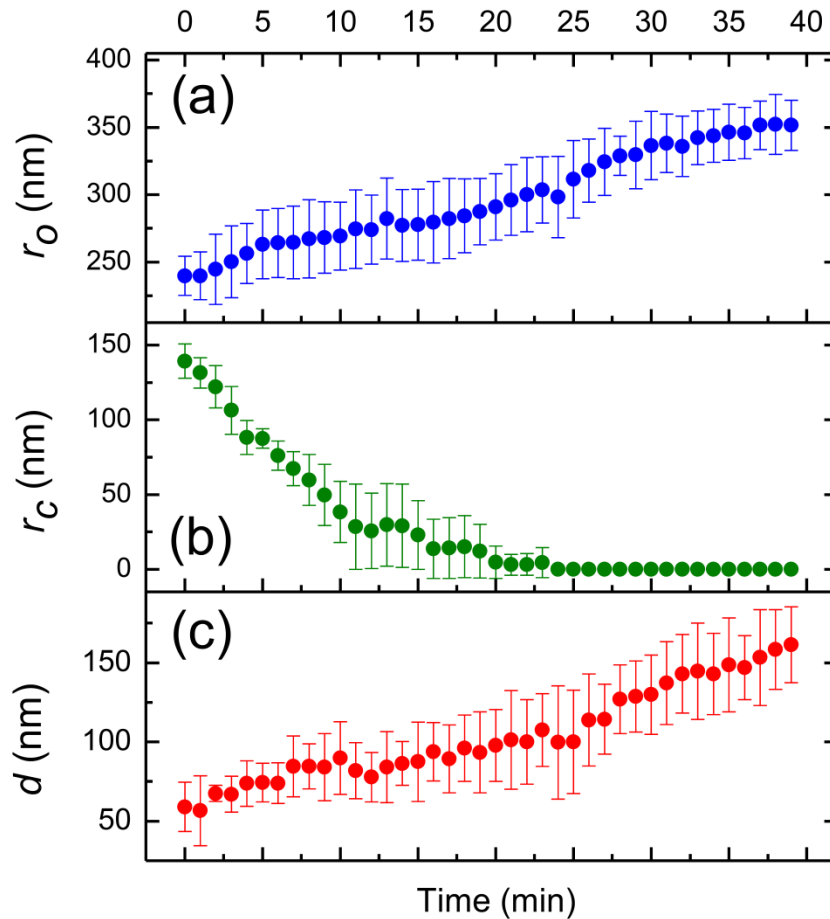
Figure S1. (a)-(c) The time dependence of the geometrical parameters r_o, r_c, and d of the silver nanowire II highlighted by the green dashed line box in Figure 1(b). The definition of r_o, r_c, and d is the same as that defined by the blue, red, and green markers in Figure 2(a). It is noticeable that the nanowire II is not uniform so the parameters here are the average values. The calculated x-ray absorption of the silver nanowire II shown in Figure 4(b) (red circles) is calculated based on the geometrical parameters shown in this figure.