General Assembly Method for Linear Metal Nanoparticle Chains Embedded in Nanotubes

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ABSTRACT

We demonstrate a flexible assembly method for producing linear metal nanoparticle chains embedded in nanotubes. The chain formation is based on the Rayleigh instability after annealing metal nanowires confined in nanotubes. Beginning with metal nanowires from arbitrary synthesis methods, atomic layer deposition (ALD) was applied to coat the wires first with a sacrificial layer then with a shell layer. Subsequently, the sacrificial layer was removed leading to confined wires in nanotubes with a free volume. Finally, embedded nanoparticle chains were produced inducing the Rayleigh instability by annealing the confined nanowires. This method is quite general not only for different metals but also for different shell materials. We are able to tune the particle spacing and diameter, the shape of the nanochains, the tube diameter and the shell thickness by ALD significantly.

The organization of nanoparticles into ordered functional structures in one, two, and three dimensions has received much attention due to their intriguing collective properties and potential applications.1–4 There are various available assembly routes such as electron beam lithography,5,6 dipole-directed assembly,7,8 template,9–11 and applying external magnetic or electric fields.12,13 However, these avenues are mainly suitable for organization of nanoparticles on a substrate or in a liquid solution. Only few methods have been developed for the assembly of metal nanoparticles into nanochains embedded in nanotubes.14,15 Keating et al. reported the fabrication of metal nanoparticle chains embedded in SiO2 nanotubes by selectively etching striped metal nanowires prepared by electrodeposition. This approach provides excellent control over particle size, placement, identity, and spacing.15 However, these parameters completely depend on the electrodeposition process, and the SiO2 coating is performed by a sol–gel method. A sacrificial metal is always necessary, which adds difficulty to the electroplating process and limits the range of available metals. It is not suitable for scaling up. On the other hand, assembly of metal nanoparticles into linear chains based on the Rayleigh instability by thermal annealing of metal nanowires has recently received an increasing interest, but these nanochains are mainly organized on a substrate surface.16–21 The Rayleigh instability was also used to fabricate Si nanoparticles embedded in SiO2.22 In that case the temperature is so high that the original SiO2 coating also changed its shape into an undulating cylinder. In a previous publication, we reported a flexible approach to the preparation of Cu nanoparticle chains encapsulated in nanotubes by the reduction of coated CuO nanowires.23 However, this approach is limited to few metal oxides, which can be reduced with H2. In this work, we present a more general assembly method for the synthesis of various metal nanoparticle chains embedded in nanotubes with tunable particle sizes and spacings. The chains are obtained based on the Rayleigh instability by annealing metal nanowires confined in nanotubes. Atomic layer deposition (ALD), a versatile coating technique with precise thickness control and excellent uniformity and conformability,24–27 is applied to coat the wires producing the nanotubes. The critical issue is to create sufficient free space in the nanotubes containing metal wires for the Rayleigh instability to occur during subsequent annealing. This is accomplished in our approach by removing a sacrificial layer also deposited by ALD. The particle size, shape, and spacing of nanochains do not depend on the specific preparation process of metal nanowires and can be controlled. This assembly method is applicable for a wide range of metals and tube materials.

A schematic for fabricating embedded metal nanochains (such as Au and Cu) is illustrated in Figure 1. Two different routes are applied for unaligned and aligned nanochains, respectively. The first approach starts with metal nanowires (Figure 1a). The wires are coated first with a sacrificial layer (such as Al2O3 and polyimide) and then with a shell layer of different materials (such as TiO2, Al2O3, and SiO2) by ALD. Then the sacrificial layer is etched away. Subsequent
annealing at a sufficiently high temperature produces nanochains based on the Rayleigh instability effect. It should be emphasized that this route is applicable for the conversion of metal nanowires from arbitrary synthesis approaches to embedded nanochains. The second one is suitable for aligned nanochains (Figure 1b). At first, shell and sacrificial layers are deposited onto the pore walls of anodic alumina templates by ALD. Subsequently, metal nanowires are grown inside the pores by electrodeposition. Aligned nanochains can be obtained by annealing after removal of the sacrificial layers and templates simultaneously. This route is potentially suitable for any metal of interest, which can be electrodeposited. For both routes, the shell thicknesses and the free space corresponding to the initial sacrificial layers can be easily controlled by the number of ALD cycles. In addition, it should be mentioned that both routes are applicable to prepare not only nanochains of a single metal, but also composite nanochains by annealing multisegment alloy nanowires confined in nanotubes surrounded by sufficient free volume created by etching away the sacrificial layers.

Gold nanowires used for unaligned nanochains were prepared by electrodeposition within the pores of anodic alumina templates. Then nanowires were released by a 4 M NaOH aqueous solution at 45 °C for 6 h. For aligned Au and Cu nanochains, electrodeposition was performed after ALD of shell and sacrificial layers. ALD was carried out in a commercial hot-wall flow-type ALD reactor (SUNALE™ R75, Picosun, Finland) utilizing N₂ as a precursor carrier and purge gas at a pressure of 2 Torr. Deposition of Al₂O₃ was performed with Al(CH₃)₃ (TMA) and deionized H₂O as precursors at a growth rate of 1.0 Å per cycle and 150 °C. The pulse and purge times for both precursors were 0.1 and 4 s, respectively. Titanium tetraisopropyl oxide (TIP) and H₂O were used as precursors for TiO₂ coating. Deposition was performed at a growth rate of 0.25 Å per cycle and 150 °C. Pulse and purge times for TIP were 1 and 2 s, respectively. Both times for H₂O were 2 s. Deposition of SiO₂ was carried out according to reference. Polyimide was deposited with ethylenediamine (EDA) and 1,2,3,5-benzene-tetracarboxylic anhydride (PMDA) as precursors at a growth rate of 2 Å per cycle and 160 °C. Both pulse and purge times for EDA were 2 s, for PMDA 3 and 5 s, respectively. During deposition, TMA, EDA, and H₂O were kept at room temperature. TIP and PMDA were kept at 60 and 150 °C, respectively.

In this study, Au nanowires (Figure 2a) prepared by electrodeposition within the pores of alumina templates (~40 nm in pore diameter, the Al₂O₃ matrix was etched away after electrodeposition) are applied as an example for the first route. Figure 2b shows the Au nanowires coated by Al₂O₃ (20 nm) and then TiO₂ (10 nm). The Au wires exhibit a brighter contrast than the outer Al₂O₃ and TiO₂ layers. It should be noted that the wires are always located at the center of the composite nanowires revealing the conformal thickness of ALD coatings. The perfectly smooth surfaces can be clearly seen showing one advantage of ALD. Ideally, the surface roughness of the coated nanowires depends on that of the initial Au nanowires. After the sacrificial Al₂O₃ is removed, Au nanowires usually lean on the inside of the TiO₂ nanotubes, clearly revealing the formation of free volume (Figure 2c,d). Figure 2e shows the nanochains obtained by annealing the Au nanowires in TiO₂ nanotubes with free volume. It can be observed that the Au nanowires undergo morphological changes to decay into nanoparticles with clear spacings while the shells maintain the tubular structures. Bright spots observed in the nanotubes indicate regions of Au particles. These nanoparticles mainly exhibit a nearly spherical shape with a diameter close to the inner diameters (~80 nm) of the TiO₂ nanotubes (Figure 2e). Some nanorods are also observed, resulting from the contact between wires before coating or bundles of two or more wires formed during the removal of alumina templates. Figure 2f shows the nanochains obtained by annealing Au nanowires
in TiO$_2$ nanotubes with less free volume obtained by a decreased thickness of sacrificial Al$_2$O$_3$ layers (5 nm). As can be seen considerably different morphologies are induced; the Au nanowires fragmented to form long nanorods instead of spherical nanoparticles. Their diameters are strictly limited by the inner diameters of the nanotubes. The above results indicate that the particle shapes and spacings of the chains can be controlled by changing the thickness of the initial sacrificial layers, which can be easily achieved by adjusting the number of ALD cycles. Au nanowires coated directly with TiO$_2$ (10 nm thick) without a sacrificial Al$_2$O$_3$ layer were also annealed for further investigation of the effect of missing free volume inside the nanotubes. The Au nanowires do not undergo any fragmentation, well maintaining initial one-dimensional morphologies (not shown). Apparently, the free volume created by the removal of a sacrificial layer is crucial for the nanowires to decay into nanoparticles during annealing.

For oxidation-resistant metals, a polymer film such as polyimide deposited by ALD can be used as a sacrificial layer instead of Al$_2$O$_3$. This is advantageous for directly removing the sacrificial layer when the coated nanowires are annealed in air saving a separate removal process. The removal of the sacrificial material and fragmentation of wires can therefore be performed within one step. Then a complete gas phase process is available for the chain formation. Figure 3a shows Au nanowires coated first by polyamide (15 nm) and then with Al$_2$O$_3$ (10 nm). The Au wires are also located just in the center of the composite nanowires with a brighter contrast than the Al$_2$O$_3$ coating layers. The nanochains produced by annealing the coated wires are presented in Figure 3b. It can be observed that the wires fragment into rodlike particles with a larger diameter but a shorter length compared to the Au nanorods embedded in TiO$_2$ tubes initially with 5 nm thick Al$_2$O$_3$ (Figure 2f). The Al$_2$O$_3$ shells show much more transparent properties because of the smaller atomic number of Al compared to Ti. We want to emphasize that this avenue is feasible for nanochain fabrication of various oxidation-resistant metals embedded in nanotubes of a wide range of oxides. This allows us to avoid the stability issues of shell materials against NaOH or H$_3$PO$_4$ aqueous solutions when Al$_2$O$_3$ is used as a sacrificial layer.

Aligned Au nanochains were prepared as a representative example for the second fabrication approach. Au nanowires confined in SiO$_2$ nanotubes with free volume (Figure 4a) were obtained by electrodeposition in the pores of alumina templates with ∼200 nm pore diameters, which were deposited first with SiO$_2$ (12 nm) and then Al$_2$O$_3$ (25 nm) into the inner walls of the pores before electrodeposition. The Al$_2$O$_3$ layers and templates were removed after electrodeposition. The Au nanowires have a large diameter of about 125 nm, requiring a higher annealing temperature or a longer heating time for the wires to transform into chains. For example, these wires only underwent a slight diameter perturbation even if heated at 700 °C for 5 h (Figure S1 in Supporting Information), and thus were much more stable than Au wires with a diameter of 40 nm (Figure 2). The observed diameter-dependent thermal stability of the wires is consistent with previous results in the literature.$^{18-20}$ Therefore, a heating temperature of 800 °C was selected. We can see that well-aligned Au nanochains of nanorods were produced after annealing at this temperature for 1 h (Figure 4b,c). The diameters of these nanorods are also controlled by the inner diameters (∼175 nm) of the confining SiO$_2$ nanotubes. Importantly, it should be noted that the nanochain parameters can also be controlled by modifying the thickness of the Al$_2$O$_3$ layers like in the first approach, correspondingly tuning the diameter of the Au wires via electrodeposition. For example, when the thickness of Al$_2$O$_3$ layers is increased to 50 nm, the confined Au nanowires with

**Figure 2.** Synthesis of Au nanochains embedded in TiO$_2$ nanotubes. SEM images: (a) Au nanowires; (b) Au nanowires coated first by Al$_2$O$_3$ (20 nm) and then TiO$_2$ (10 nm); (c,d) confined Au nanowires with surrounding free volume after removing Al$_2$O$_3$; (e) Au nanochains produced by annealing Au nanowires confined in 10 nm thick TiO$_2$ shells after removing the 20 nm thick Al$_2$O$_3$; (f) Au nanochains produced by annealing Au nanowires confined in 20 nm thick TiO$_2$ shells after removing the 5 nm thick Al$_2$O$_3$. Annealing was performed at 550 °C for 5 h in air.

**Figure 3.** Synthesis of Au nanochains embedded in Al$_2$O$_3$ nanotubes. (a) SEM image of Au nanowires coated first by polyamide (15 nm) and then Al$_2$O$_3$ (10 nm). (b) SEM image of Au nanochains embedded in Al$_2$O$_3$ nanotubes by directly annealing the coated nanowires at 600 °C for 5 h in air.
a diameter of 75 nm mainly decayed into nearly spherical nanoparticles with a larger spacing after annealing, as shown in Figure 4d,e. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were used to investigate the crystal structures of the starting Au nanowires and the obtained nanoparticle chains. It is revealed that the Au nanowires and the formed nanoparticles are single-crystalline (Figures S2 and S3 in Supporting Information).

To demonstrate that this approach is general not only for embedded nanochains of different metals but also for different shell materials, aligned Cu nanochains embedded in TiO2 nanotubes were fabricated. Figure 4f shows copper nanowires confined in TiO2 nanotubes obtained using the same approach. The thicknesses of TiO2 and sacrificial Al2O3 layers are 30 and 20 nm, respectively. The Cu nanowires have a diameter of about 100 nm. Since the thermal stability of TiO2 is not comparable with SiO2, a lower annealing temperature of 650 °C was applied. At this temperature, a long annealing time of 20 h is necessary for the complete fragmentation of the wires because of the large diameters. For example, the copper nanowires decayed into long sections or produced undulated wires after annealing at 650 °C for 5 h (Figure S4 in Supporting Information). After annealing for 20 h, these copper nanowires decayed into chains of nanorods as well (Figure 4g) like the Au nanowires confined in SiO2 (Figure 4b,c). It is obvious that aligned nanochains embedded in nanotubes with tunable outer diameters can be conveniently fabricated by depositing an Al2O3 layer before deposition of the shell layers to reduce the pore diameters.

According to the Rayleigh instability theory, the nanowires without confinement tend to decay into spherical particles. The diameter $D$ and wavelength $\lambda$ of these particles are determined by the radius $R$ of the starting wires, namely, $D = 3.78 R$ and $\lambda = 8.89 R$. In our study, the wires are confined in nanotubes. It can be reasonably inferred that if the inner diameter of the nanotubes is over 3.78 $R$, the wires will undergo fragmentation into spherical particles (Figure 5a) if neglecting the contact effect of the wires with the nanotube shells. In contrast, if the inner diameter is below 3.78 $R$, the nanotube shells will suppress the further diameter undulation when the undulated amplitude is equal to the inner diameter. Consequently, the fragmentation trend into spherical particles is prevented by the shells resulting in the formation of nanorods (Figure 5b). As for TiO2 nanotubes containing Au nanowires ($R = 20$ nm) with an initial Al2O3 layer of 20 nm thick, the inner diameter is 80 nm ($2h + 2R$), being close to 3.78 $R$ (75 nm). The wires indeed decay into nearly spherical particles (Figure 2e) with a wavelength of 180–270 nm. In contrast, with an initial Al2O3 layer of 5 nm, the inner diameter is 50 nm, much smaller than 3.78 $R$. Fragmentation of the wires leads to long nanorods with a wavelength of 230–310 nm (Figure 2f). Further, the diameter undulation of the wires coated by only TiO2 without voids is completely prevented by the shells, thus the wires maintain their continuous one-dimensional structure. Our experiment results clearly confirm the above inferences. The values for the wavelength might slightly vary if the process is optimized. In this work, we refrained from optimization, since every particular combination of materials would require a
for the chains of nanorods following the equation below
calculate the ratio of the spacing to the length of nanorods envisioned value.
and should be taken into consideration for a precise perturbation wavelength of the wires cannot be neglected between the wires and the surrounding shells) on the diameter This implies that the effect of confinement (the contact between the wires and the surrounding shells) depends on the original diameter (2R) of the starting wires and the thickness (h) of the initial sacrificial layers.

separate optimization, which is not the scope of the manuscript. However, it should be noted that there is a remarkable discrepancy between the predicted wavelength (8.89 R = 178 nm) and measured wavelengths, which even increase with the increasing confinement (reduced inner diameters). This implies that the effect of confinement (the contact between the wires and the surrounding shells) on the diameter perturbation wavelength of the wires cannot be neglected and should be taken into consideration for a precise envisioned value.

On the basis of the constant volume of the metal phase before and after the fragmentation of wires, we can basically calculate the ratio of the spacing to the length of nanorods for the chains of nanorods following the equation below

\[ \frac{S}{L} = \frac{h^2}{R^2} + 2h/R \]

where S is the spacing, L is the length of nanorods, and h is the thickness of the initial sacrificial layer (Figure 5b). It can be seen from this equation that the ratio quickly increases with the increasing thickness of sacrificial layer, thus the spacing increases and the length of nanorods reduces (with R being constant). This is consistent with the trend that, when the inner diameter increases, the aspect ratio of the nanorods reduces and eventually spherical particles are produced when the inner diameter is large enough, as confirmed above.

In conclusion, we have demonstrated two routes of a flexible assembly method for producing linear nanoparticle chains embedded in nanotubes by annealing metal nanowires confined in nanotubes based on the Rayleigh instability. Although the fragmentation did not lead to perfectly uniform particle dimensions in our preliminary experiment, an optimization of the preparation process can be envisioned to improve this feature. This method is quite general not only for different metals but also for different tube shell materials given the available wide range of materials which can be deposited by ALD. We are able to tune the particle spacing, diameter, and shape of the nanochains, and tube diameter and shell thickness by ALD significantly. This opens the possibility to prepare various embedded nanoparticle chains with tunable optical, electric, and magnetic properties.

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Supporting Information Available: Intermediate shapes of Au nanowires confined in SiO2 nanotubes after annealing at a lower temperature and of Cu nanowires confined in TiO2 nanotubes after annealing for a shorter annealing time. TEM and SAED analysis of the Au nanowires and nanoparticles of the formed nanochains confined in SiO2 nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

References

Figure 5. Schematic transformation mechanisms from nanowires to nanochains. (a) Wire confined in nanotubes with a sufficiently large inner diameter, \(2h_1 + 2R > 3.78 \, R\), decays into spherical nanoparticles by gradually increased diameter undulation. (b) Diameter undulation of wires confined in nanotubes without a sufficiently large inner diameter, \(2h_2 + 2R < 3.78 \, R\), is stopped by the tube shells when the undulated amplitude is equal to the inner diameter. A decay into nanorods occurs. Typical SEM images are also shown for both cases. The inner diameter \((2R + 2h)\) depends on the original diameter \((2R)\) of the starting wires and the thickness \(h\) of the initial sacrificial layers.