Tailor-Made Inorganic Nanopeapods: Structural Design of Linear Noble Metal Nanoparticle Chains

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Linear noble-metal nanoparticle (NP) chains have been demonstrated both theoretically and experimentally to be promising candidates for applications in one-dimensional nano-optical devices (e.g. plasmonic waveguides, plasmonic printing).[1–4] The ability of metal NP chains to transport electromagnetic energy below the diffraction limit has major advantages for scaling down the size of optical devices and components to the nanometer scale. Precise control of particle size, shape and separation in metal NP chains is an important issue for constructing nano-optical devices. Conventional electron-beam lithographic techniques and scanning-probe manipulation have enabled excellent control over the size and position of metal NPs but are time-consuming and costly.[2,5] Self-assembly routes enable metal NPs to be incorporated into preformed grooves but can control neither the separation between NPs nor their densities.[6] Other approaches to the fabrication of metal NP chains, including wet-chemistry etching[7] and exploitation of the Rayleigh instability of metal nanowires (NWs),[8] suffer from low throughput and limited controllability. Herein, we show a facile and controllable route to the fabrication of linear noble-metal NP chains, in which the size and separation of optically interesting NPs can be controlled easily.

Fabrication of Pt@CoAl2O4 inorganic nanopeapods is schematically illustrated in Figure 1a. First, Co/Pt ML NWs were electrodeposited into the nanoporous AAO template by pulsed potential electrodeposition. As-prepared Co/Pt ML NWs with alternately distributed Co and Pt segments served as the precursors and the backbones for subsequent generation of Pt@CoAl2O4 inorganic nanopeapods (Pt nanoparticle chains encapsulated in CoAl2O4 nanoshells) by template-based pulsed electrodeposition and high-temperature solid-state reaction. The separation between Pt nanoparticles (Dc-c) is proportional to the pulse duration for Co electrodeposition, tc-o, and can be changed at will. c) Metal nanoparticle chains fabricated on the basis of the Rayleigh instability of metal nanowires.[9]

Figure 1. Fabrication of peapod nanostructures. a,b) Fabrication of Pt@CoAl2O4 inorganic nanopeapods (Pt nanoparticle chains encapsulated in CoAl2O4 nanoshells) by template-based pulsed electrodeposition and high-temperature solid-state reaction. The separation between Pt nanoparticles (Dc-c) is proportional to the pulse duration for Co electrodeposition, tc-o, and can be changed at will. c) Metal nanoparticle chains fabricated on the basis of the Rayleigh instability of metal nanowires.[9]
external volume diffusion, respectively. The invariable constants are fixed to values equal to \(\sqrt{2 \times 2\pi}, 1.43 \times 2\pi, \) and \(2.06 \times 2\pi\) for surface diffusion, internal volume diffusion, and external volume diffusion, respectively. The invariable separation between NPs reduces the degree of freedom in most practical applications, especially in plasmonic applications. In contrast, in our approach the aspect ratio and the separation of metal NPs can easily be tailored without major limitations by virtue of the generic controllability of the diameter of nanopores of the alumina membrane used and of the length of metal segments by adjusting the pulse durations in electrodeposition. For an alumina template with a given resolution transmission electron microscopy (HRTEM) investigations reveal clearly that the present inorganic peapod nanostructures consist of highly crystalline metallic Pt peas and CoAl2O4 pods (Figure 2b). Energy dispersive X-ray (EDX) elemental analyses also confirmed that the pea part is composed of Pt as a major component and of Co, Al, and O as minor components stemming from the pod shell surrounding the peas (Figure 2c); the pod part of the structure contains Co, Al, and O as major components (Figure 2d). The small amount of Pt detected from the pod could be attributed to inelastic electron scattering by the pea. The atomic ratio of Co to Al was 1:2.3, close to that of stoichiometric CoAl2O4. The tubular nature of CoAl2O4 was further confirmed by a radial elemental linescan along the pod and elemental mapping analyses (see Figure S3 in the Supporting Information).

Figure 3 demonstrates that the size (\(D_p\)) and the separation (\(D_c\)) of Pt peas can be readily controlled using AAO membranes with different pore diameters and by adjusting the pulse durations for Pt and Co electrodepositions, \(\tau_{Pt}\) and \(\tau_{Co}\). A Pt@CoAl2O4 inorganic peapod prepared using a H2C2O4-anodized AAO membrane (Sample S1) is shown in Figure 3a. The Co/Pt ML NW precursor was electrodeposited with pulse durations \(\tau_{Pt} = 25s, \tau_{Co} = 6s\). In this specific inorganic nanoneapod, the diameter of Pt peas is 25.6 ± 1.6 nm, and the separation is 29.0 ± 2.9 nm. The inorganic nanoneapods presented in Figure 3b–d were prepared using H2SO4-anodized AAO membranes, but with different deposition pulse durations for Pt and Co: \(\tau_{Pt} = 18s, \tau_{Co} = 8s\) for Figure 3b (Sample S2), \(\tau_{Pt} = 18s, \tau_{Co} = 10s\) for Figure 3c (Sample S3), and \(\tau_{Pt} = 15s, \tau_{Co} = 12s\) for Figure 3d (Sample S4). It is clear that the sizes (\(D_p\)) of the Pt peas are typically smaller than those prepared from H2C2O4-anodized AAO membranes. Moreover, the separations (\(D_c\)) of Pt peas are roughly proportional to the Co pulse durations,

\[
D_p = \frac{1.43 \times 2\pi}{\tau_{Pt}}, \quad D_c = \frac{1.43 \times 2\pi}{\tau_{Co}}
\]

The atomic ratio of Co to Al was 1:2.3, close to that of stoichiometric CoAl2O4. The tubular nature of CoAl2O4 was further confirmed by a radial elemental linescan along the pod and elemental mapping analyses (see Figure S3 in the Supporting Information).
Statistical analyses demonstrate that pea size \((D_p)\) and separation \((D_{c-c})\) variations in all these samples are less than 10 and 15\%, respectively, (see Figures S4 and S5 and Table S1 in the Supporting Information), indicating good controllability.

In addition to Pt@CoAl₂O₄ inorganic nanopeapods with regular pea separations, periodically modulated peapod nanostructures can also be realized by applying different pulse waveforms during the electrodeposition. Figure 4a shows a TEM image of one inorganic nanopeapod prepared by successively applying double pulses: \(\tau_{Pt} = 18\) s, \(\tau_{Co} = 6\) s and \(\tau_{Pt}' = 18\) s, \(\tau_{Co}' = 15\) s. Two metal Pt NPs form a set of metal peas with a well-defined distance between the two NPs. These sets are embedded in a CoAl₂O₄ nanoshell with a regular separation. Figure 4b is another example showing a peapod nanostructure with gradually increasing separations between Pt peas (from left to right). The scale bars are 200 nm.

Figure 4. Structural engineering of Pt@CoAl₂O₄ inorganic nanopeapods. a) Inorganic nanopeapods with periodically distributed Pt nanoparticle pairs. b) Inorganic nanopeapods with gradually increasing separations between Pt peas (from left to right). The scale bars are 200 nm. c) Conceptual illustration of diameter-modulated inorganic nanopeapods prepared with diameter-modulated AAO membranes.

To gain insight into the formation mechanism of Pt@CoAl₂O₄ inorganic nanopeapods, we performed a series of control experiments by annealing the as-prepared Co/Pt ML NWs/AAO composites at different conditions. The morphology of the resulting nanostructures was found to be sensitive to the atmosphere and the annealing temperature (Figure 5).

When the sample was annealed in air below 500 °C, intermetallic alloying between Co and Pt occurred preferentially to form continuous CoPt alloy NWs (Figure 5b). When the sample was annealed at 600 °C, CoAl₂O₄ nanoshells started to emerge as the result of a solid-state reaction between metallic Co and the alumina pore walls. The resulting nanostructures were characterized as continuous CoAl₂O₄ pods containing randomly distributed Pt peas (Figure 5c). The size of Pt peas appeared to be non-uniform. The formation of hollow nanotubes of ternary compounds starting from a solid nanowire (ZnO) covered by an amorphous shell of Al₂O₃ has been reported recently and was attributed to the nanoscale Kirkendall effect. An analogous mechanism appears to operate in the present case of Co surrounded by Al₂O₃. We assume that two interfacial reactions take place competitively at the early stage of annealing: 1) the reaction between Co and Al₂O₃ at the interface of Co segments and the pore walls of alumina, 2) the intermetallic alloying at the interface of Co and Pt segments. As the reaction proceeds, however, de-alloying of the CoPt alloy takes place to form the thermodynamically more stable CoAl₂O₄ phase (i.e., at 600 °C), resulting in randomly distributed Pt NPs within tubular CoAl₂O₄ nanoshells. In other words, the early-stage reactions are mostly driven by kinetics, while the later stage is determined by thermodynamics. We believe that the net diffusion of Co metals into the pore walls of alumina results in the hollow CoAl₂O₄ nanoshells (pods). When the sample was directly heated to 700 °C, structurally well-defined Pt@
CoAl2O4 peapod nanostructures without any randomly distributed Pt NPs formed exclusively (Figure 5d). This result indicates that, under these annealing conditions (i.e., in air at 700°C), the formation of CoAl2O4 nanoshells by the diffusion of Co metal into the Al2O3 lattice is kinetically and thermodynamically more favorable than the intermetallic alloying between Co and Pt.

To check any possible contribution of oxygen in air to the formation of Pt@CoAl2O4 nanopeapods, as-prepared Co/Pt ML NWs/AAO composite was annealed at 700°C under argon atmosphere. We obtained Pt@CoAl2O4 peapod nanostructures even in this oxygen-deficient atmosphere. However, the size and the distribution of Pt peas were non-uniform, similar to the case of annealing in air at 600°C (Figure S6). This control experiment discloses that the annealing atmosphere has less impact on the formation of inorganic peapod nanostructures than the AAO membrane, but the oxygen atmosphere can effectively hinder the alloying process and accelerate the formation of CoAl2O4.

As discussed above, the AAO template serves as a reactant and plays an important role in the formation of CoAl2O4 nanoshells (pods) during the high-temperature annealing of Co/Pt ML NWs/AAO composite in air. It has been well-documented that the pore walls of anodic alumina consist of two main layers (a relatively pure inner oxide layer and an anion-contaminated outer oxide layer). The outer layer, the surface of which comes in contact with the Co/Pt ML NWs in the present study, is mainly characterized as amorphous aluminum oxide, containing anions from the electrolyte used in anodization (such as OH− from water, SO42− from H2SO4, CO32− from H2CO3, or PO43− from H3PO4). It is believed that Co at the surface of anodic alumina is partially oxidized to CoO by reacting with the oxygen released from the AAO template with subsequent solid-state diffusion of CoO into Al2O3 lattice to form CoAl2O4.[18] That is, the reactions shown in Equation (1) could occur.

\[ \text{Co} + \text{O} \rightarrow \text{CoO} \]
\[ \text{CoO} + \text{Al}_2\text{O}_3 \rightarrow \text{CoAl}_2\text{O}_4 \]  

(1)

In fact, a previous study showed that calcination of CoO/Al2O3 composite catalysts above 600°C appears to cause gradual diffusion of CoO into alumina, thus resulting in the formation of CoAl2O4.[19] Moreover, water has been found to facilitate migration of Co into alumina to form CoAl2O4 by increasing the interaction between Co and Al2O3.[18c, 20]

In summary, Pt@CoAl2O4 inorganic nanopeapods with designed separations between the Pt nanoparticles were synthesized. Combination of pulsed electrodeposition of multilayered metal nanowires into anodic aluminum oxide membranes and a subsequent solid-state reaction between metals and alumina provides a facile and controllable way for the realization of noble metal@oxide inorganic peapod nanostructures. The present synthetic approach could also easily be extended to the fabrication of other metal@oxide inorganic nanopeapods.

Experimental Section

Membrane preparation: The AAO membranes were prepared by a two-step process reported previously.[21] Briefly, high-purity aluminum sheets (99.999%) were first electropolished in a mixture of HClO4 and C2H5OH (1:3 v/v) for 4 min. The polished Al sheets were anodized in 0.3 m H2C2O4 at 40 V or 0.3 m H2SO4 at 25 V at 1°C. The first anodization was usually carried out for 20 h. Subsequently, the anodized Al sheets were put into an acid mixture (6 wt% H2PO4 and 1.8 wt%, CrO3) to completely remove the porous layer. Then, the second anodization was conducted for 16 h at the same conditions as the first anodization. Free-standing alumina membranes were obtained by a stepwise voltage reduction technique. The nominal pore diameters of as-prepared membranes were 45 ± 5 nm for H2C2O4 anodization and 30 nm for H2SO4 anodization.

Electrodeposition of Pt@multilayered nanowires: Before electrodeposition, a layer of gold was sputtered on one side of the AAO membrane to make the surface electrically conductive. The electrodeposition was carried out in a standard three-electrode electrochemical cell. Gold-coated AAO and a platinum mesh were used as working electrode and counter electrode, respectively, and a saturated calomel electrode (SCE) served as a reference. The electrolyte consisted of 0.3 m CoCl2·6H2O (Sigma), 0.01 m K2PtCl6 (Sigma), and 0.485 m H2BO3 (Aldrich), with >18 MΩ deionized water. The deposition potential was controlled to periodically switch between −0.3 V (vs. SCE) for Pt deposition and −1.0 V (vs. SCE) for Co deposition by a Princeton Applied Research potentiostat (PAR 263 A). The number of deposition cycles was typically in the range of 200–300.

Fabrication of Pt@CoAl2O4 nanopeapods: As-prepared Co/Pt ML NWs/AAO membrane composite was heated on a hot plate in air. The temperature of the hot plate was ramped to 700°C within 10 min and then was maintained for 1–5 h. Subsequently, the sample was cooled to room temperature. In the control experiments, Co/Pt ML NWs/AAO composites were annealed in air at different temperatures and annealed in argon atmosphere (100 mL min−1, high-purity Ar, 99.99%). In all experiments, the temperature was rapidly increased to a set value within 10 min.

Characterization of Pt@CoAl2O4 nanopeapods: The normal TEM characterization was performed with a JEOL JEM-1010 transmission electron microscope, and HRTEM and EDX examinations were carried out by using JEOL JEM-4010, Philips CM20FEG, and FEI TITAN 80–300 microscopes. For TEM investigations, the samples were immersed in 2 m NaOH solution at 45°C for several hours to completely remove alumina. The product was then washed with a large amount of deionized water and finally was dispersed in absolute ethanol. Subsequently, a drop of the suspension was placed on a carbon-coated copper grid for examination.

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