

Regulated Oxidation of Nickel in Multisegmented Nickel–Platinum Nanowires: An Entry to Wavy Nanopeapods**

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Oxidation of solid metal nanoobjects is a versatile approach to generating hollow metal oxide nanostructures.^[1] The mechanism for the solid-to-hollow conversions has been attributed to the Kirkendall effect, which describes an unbalanced interdiffusion of a thermal diffusion couple.^[2,3] When a metal nanoobject is exposed to oxygen at elevated temperatures, the outward diffusion of the metal cations is much faster than the inward diffusion of the oxygen anions through the oxide layer. As a result, a flux of vacancies is injected into the interior and gradually accumulates into a single void.^[4] The hollow metal oxide nanostructures formed in most cases are symmetric with a uniform wall thickness.

The oxidation behavior of some metal elements is exceptional. For example, the complete oxidation of Ni nanoparticles in air resulted in hollow NiO nanospheres with an off-centered cavity.^[1e,5] Similarly, irregular nanotubes with a fluctuant wall thickness were obtained by oxidizing Ni nanowires at high temperatures.^[1f,6a] It is verified that the sufficient mobility of vacancies in Ni induces the localization of limited void nuclei at random positions, which disequilibrate the following outward mass transfer of unconsumed Ni cores. The difficulty in forming homogeneous hollow NiO nanostructures hints that the rapid self-diffusion of injected vacancies in the Ni cores is a rather uncontrolled process. To date, it is very difficult only by oxidation to convert solid Ni nanoobjects into hollow NiO nanostructures of high uniformity.^[5,6] However, morphological regularity is of extreme importance for the reliable and reproducible applications of NiO nanostructures in fields ranging from resistive switching memory to sensors.^[7]

Herein, we report a novel route to fabricate highly uniform wavy Pt/NiO hollow nanopeapods by regulating the oxidation of Ni in predesigned multisegmented Ni/Pt nanowires. It is revealed that the Ni/Pt interface is an efficient platform for manipulating the oxidation behavior of Ni that intrinsically presents a random manner. Moreover, this

interface-tailored low-temperature oxidation strategy can be employed as a unique but general entry to novel wavy metal/oxide nanopeapods relative to the approaches existent for nanopeapod construction.^[8]

The multisegmented Ni/Pt nanowires with tailored parameters were prepared in a three-electrode electrochemical cell by pulsed electrodeposition using porous anodic aluminum oxide membranes as templates (see the Supporting Information).^[8a,9] After the removal of the alumina templates by alkaline etching, dispersed straight nanowires with a smooth surface were obtained (Figure 1a). A magnified SEM view (Figure 1b) displays that the nanowires consist of

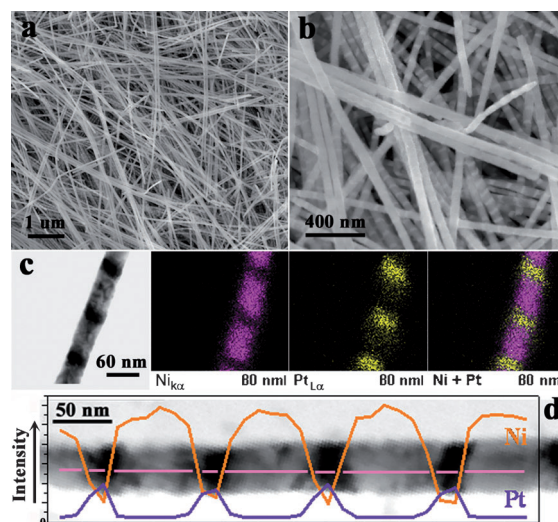


Figure 1. SEM images of electrodeposited multisegmented Ni/Pt nanowires after template removal: a) overview, and b) magnified view. c) STEM image and corresponding EDX element mappings of Ni, Pt, and Ni + Pt for one multisegmented Ni/Pt nanowire. d) STEM image of one multisegmented Ni/Pt nanowire and corresponding Ni and Pt intensity profiles along its growth direction by EDX line scanning.

periodically stacked segments with different contrasts, which is indicative of a heterogeneous multisegmented structure. From a typical STEM image of a single nanowire and corresponding energy-dispersive X-ray (EDX) spectroscopic element mappings of Ni and Pt (Figure 1c), it is concluded that the as-prepared nanowires have a top-to-bottom uniform diameter of approximately 50 nm with alternating lengths of 60 and 30 nm for the Ni and Pt segments, respectively. However, the result of the EDX line scanning shown in Figure 1d reveals the existence of trace Ni in each Pt segment. The valley-like intensity profile of Ni therein (Figure S2 in the Supporting Information) indicates that the Pt segments are

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enclosed by an ultrathin film composed of Ni or Ni-related compounds.

The oxidation of the multisegmented Ni/Pt nanowires was performed at 350 °C for 1 h in air. As shown in Figure 2a,b,

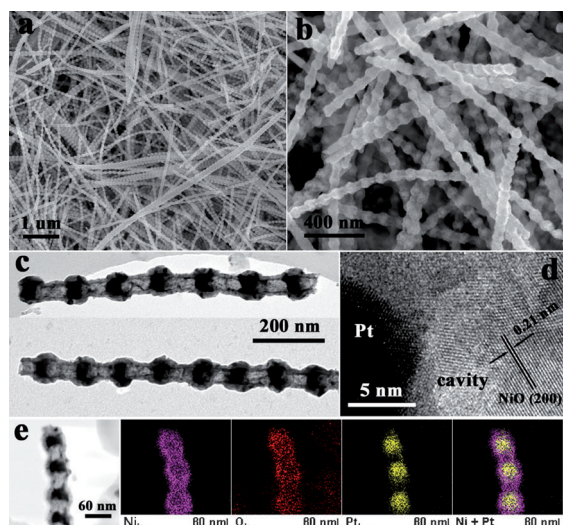


Figure 2. SEM images of the multisegmented Ni/Pt nanowires after annealing at 350 °C for 1 h in air: a) overview, and b) magnified view. c) Low- and d) high-resolution TEM images of the oxidized multisegmented Ni/Pt nanowires, representing a wavy nanopeapod structure. e) STEM image of a nanopeapod and corresponding EDX element mappings of Ni, O, Pt, and Ni + Pt, which reveal that equally spaced Pt nanopeas are embedded in hollow NiO nanopeapods.

the oxidized nanowires present a periodically wavy structure, in which the embossed sections are always of high contrast. TEM investigations (Figure 2c,d) in combination with EDX element mappings (Figure 2e) and selected-area X-ray diffraction (SAED) analysis (Figure S3) confirm that the Pt segments were nonreactive under the current conditions, while the Ni segments were completely oxidized to NiO with rock-salt (NaCl) structure. The oxidized nanowires represent several noticeable structural features. First, each Ni segment was converted into a polycrystalline NiO tubular structure with a uniform wall thickness of around 10 nm. Next, the Pt segments were also enclosed by a NiO thin shell, which connects adjacent hollow sections and integrates all the NiO into an uninterrupted nanotube. Finally, a string of Pt nanoparticles are encapsulated by the NiO nanotubes, representing an ideal nanopeapod structure. The space between neighboring Pt nanopeas is identical and consistent with the initial 60 nm length of the Ni segments. In addition, all the nanopeapods are wavy with periodical junction-like embossments at positions of the Pt segments. When the oxidation temperature was increased from 350 to 450, 550, and 650 °C with the same duration of 1 h, the morphology of the resultant nanopeapods was barely influenced (Figure S4).

For comparison, we also investigated the oxidation of pure Ni nanowires with a diameter of around 50 nm prepared by the template-assisted electrodeposition (Figure S5a). From the images shown in Figure S5b–e, it was verified that these nanowires are polycrystalline in nature, which is also the case for the Ni segments in the multisegmented Ni/Pt nanowires.

When oxidation was carried out at 350 °C for 1 h in air, the Ni nanowires were only partially oxidized, forming a Ni/NiO core-shell structure enclosing several irregular interior voids (Figure S6a). Reactions at 450 and 550 °C for the same duration were still insufficient for the thorough conversion of Ni to NiO though the interior voids were obviously enlarged (Figure S6b,c). Complete oxidation of the Ni nanowires was only achieved subsequent to annealing at 650 °C for 1 h, accompanied by the formation of rugged NiO nanotubes with a non-uniform wall thickness (Figure S6d). The above observations are generally in agreement with previous reports.^[1f,6a]

When the Ni nanowires are exposed to the air, a skinny NiO layer is instantly generated at the surface by reaction with adsorbed oxygen. Then, the direct contact between Ni and O₂ is blocked. Nevertheless, oxygen adsorbed on the oxide surface can induce the tunneling of electrons from Ni through the barrier. As a result, an electric field in the oxide layer is established, which will facilitate the outward diffusion of Ni²⁺ ions through the initially formed NiO layer. At low temperatures, this field-assisted diffusion is a dominating mechanism for the formation of oxide shells.^[10] However, when the thickness of the NiO layer exceeds a threshold, such a driving force becomes invalid because of the significantly reduced electric field. For the Ni nanowires, a limited value of 10–12 nm was detected during the oxidation process at a temperature of 350 °C (Figure S6a).^[6a] This is also the reason why the oxidation of the residual Ni nanowires is strongly reduced or even impossible once a NiO shell with a thickness of approximately 10 nm was grown under this condition.

To achieve the complete oxidation of the Ni nanowires, a temperature up to 450 °C must be employed to enhance the thermally dominant diffusion of the inner Ni ions in addition to the field-assisted process. Increasing the temperature to 550 and 650 °C does not alter the mechanism derived from the nanoscale Kirkendall effect, but further favors the reaction kinetics.^[6a] For metal nanowires such as Cu, injected vacancies aggregate uniformly at the Cu/Cu₂O interface to form multiple interfacial voids. The homogeneous void distribution is expected to ensure a symmetric outward mass transfer of the residual Cu until completely hollow Cu₂O nanotubes are generated.^[14] In contrast, only several localized voids with large sizes are observed for the partially oxidized Ni nanowires (Figure S6a,b). This phenomenon has been ascribed to the comparable diffusion coefficient of vacancies in Ni relative to that of Ni in NiO.^[15] Vacancies with sufficient mobility can migrate over a long distance and coalesce into segmented voids prior to the complete transport of Ni through the NiO layer. Afterward, oxidation of the nanowires only broadens the regions in which the solid Ni is present. Since the positions where the segmented voids initially settle down are uncontrolled, rugged NiO nanotubes with a non-uniform wall thickness are normally produced.

As evidenced in Figure 2, the multisegmented Ni/Pt nanowires, however, were oxidized to the periodic hollow nanopeapods with a uniform wall thickness. Moreover, such a complete conversion was realized only at a rather low temperature of 350 °C for the period of 1 h. From a simple structural consideration, the multisegmented Ni/Pt nanowires seem like discrete Ni nanorods (50 × 60 nm) derived from the

Ni nanowires periodically inserted by isometric Pt segments (30 nm). However, since all the introduced Ni/Pt interfaces are closed, the overall Ni surface exposed to the air is unchanged. In addition, it was found that the oxidation of Ni nanoparticles with a smaller size of 26 nm could not produce any uniform and completely hollow NiO nanostructures even at 400 °C for up to 4 h.^[5] Therefore, the size-dependent oxidation behavior of Ni cannot be regarded as a major factor responsible for the formation of the wavy nanopeapods.

For understanding the evolution mechanism of the wavy nanopeapods, oxidation of the multisegmented Ni/Pt nanowires was also performed at 350 °C for only 10 min. Figure 3a,b exhibits typical TEM images of the intermediates

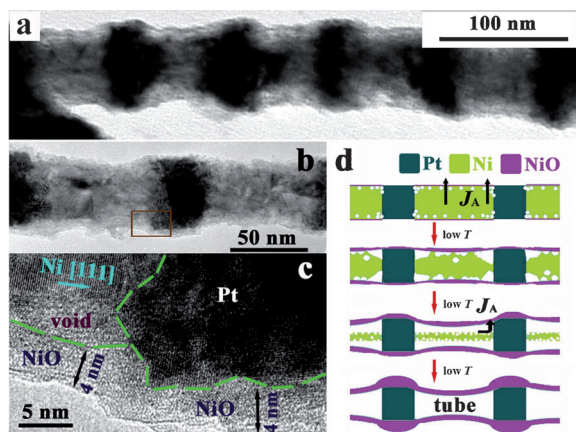


Figure 3. TEM images of the multisegmented Ni/Pt nanowires after annealing at 350 °C for 10 min in air: a,b) overview, and c) HRTEM observation on the marked area in (b). d) Scheme for the formation of the nanopeapods from the multisegmented Ni/Pt nanowires with alternating lengths of 60 and 30 nm for the Ni and Pt segments, respectively.

formed at this stage. The outer surface at the Ni/Pt interface became slightly rippled accompanied with the formation of a thin NiO layer. Large voids have already been generated, which exclusively locate at the Ni/Pt/NiO three-phase interface. For some Ni segments, voids developed at each end are approaching and start to fuse into a penetrating one. The HRTEM image shown in Figure 3c demonstrates that a continuous NiO sheath with a thickness of approximately 4 nm encloses the junctions of the intermediates. In contrast, oxidation of the pure Ni nanowires on the same conditions did not produce any visible voids at the NiO/Ni interface under our TEM observations (Figure S6e).

When the multisegmented Ni/Pt nanowires are annealed at elevated temperatures, high thermal stress will be generated in the vicinity of the Ni/Pt interface because of the different thermal expansion coefficients of Ni and Pt. As a result, the diffusion of Ni ions near the Ni/Pt interface is accelerated.^[11] Furthermore, a very thin NiPt phase mixture might exist at the interface (see the Supporting Information); thus, the oxidation of Ni therein can be further enhanced. Therefore, a rapid nucleation of initial voids is achieved along the external edges of the Ni/Pt interface. With the oxidation proceeding, these voids will further enlarge by self-evolution

and also by gradually swallowing vacancies or tiny voids formed in the regions off the Ni/Pt interface for lowering the overall surface free energy of the system.^[5] During TEM observations, nanowires with variations of the Ni and Pt segment lengths were occasionally encountered, as summarized in Figure S7. For the Ni segments with shorter lengths, formation of a continuous gap around the Ni/NiO interface is more time-efficient. The morphologies of these intermediates (Figure S7a,b) clearly support that the growth of the NiO shell is accompanied by a synchronous radial shrinkage of the Ni core. Therefore, it can be suggested that the presence of the Ni/Pt interface initiates the homogeneous void distribution at the Ni/NiO interface of each Ni segment, and thus determines the final development of tubular NiO sections with a uniform wall thickness.

Nevertheless, since the outward diffusion of Ni at 350 °C is subject to the field-assisted mechanism, it is necessary to further clarify the driving force for the continuous mass transfer of the Ni core once the electric field becomes invalid owing to the thickening of the NiO shell. As shown in Figure 2, the segmented Ni with a diameter of 50 nm only forms tubular NiO sections with a wall thickness as low as 10 nm. Such a “slimming” transformation is unexpected from a stoichiometric point of view. It is known that noble metals such as Pt have excellent adsorption properties for gas.^[12] Hence, a monolayer of oxygen is expected to adhere on the surface of the Pt segments along with the Ni when the multisegmented nanowires are exposed to air. It is assumed that the oxygen layer tightly adsorbed on the segmented Pt also induces the tunneling of electrons from adjacent Ni atoms. The subsequently established electric field will assist the migration of Ni ions to the Pt surface by formation of a preliminary NiO film. It seems that this process occurs even at room temperature, which explains why a skinny NiO shell was detected on the Pt segment surface for the pristine multilayered Ni/Pt nanowires (Figure S2).

The above finding indicates that the outward flow of Ni ions near the Ni/Pt interfaces will split owing to the presence of the Pt segments. Loading of partial NiO on the Pt platforms indeed reduces the thickness of the NiO shell in the Ni areas close to the interface. These thinner sites can provide rapid paths for the outward diffusion of Ni based on the field-driven mechanism. Especially when the thickness of the overall oxide shell reaches the limited value of 10 nm, these fragile positions turn into the only diffusion exits for the interior Ni core. For the current multisegmented nanowires with a Ni segment length of 60 nm, the frequency of the Ni/Pt interfaces are sufficient to migrate the residual Ni to the segmented Pt surface before an inevitable blockage finally happens for these paths due to the same thickening effect. As a result, completely hollow NiO tubular sections with a uniformly thin wall can be generated at a temperature lower than those required for the thermally dominant diffusion. Note that the loading of NiO on each Pt segment is accomplished by two diffusion flows from its adjoining Ni units. Such a deposition manner possibly causes the growth of a thicker NiO shell enclosing the segmented Pt. Based on the above description, the evolution of the nanopeapods from the multisegmented Ni/Pt nanowires is schematically illustrated in Figure 3d.

By adjusting the pulse periods of electrodeposition, we also prepared multisegmented Ni/Pt nanowires with longer Ni segments (see the Supporting Information). The images in Figure 4a,b show the morphology of multisegmented Ni/Pt

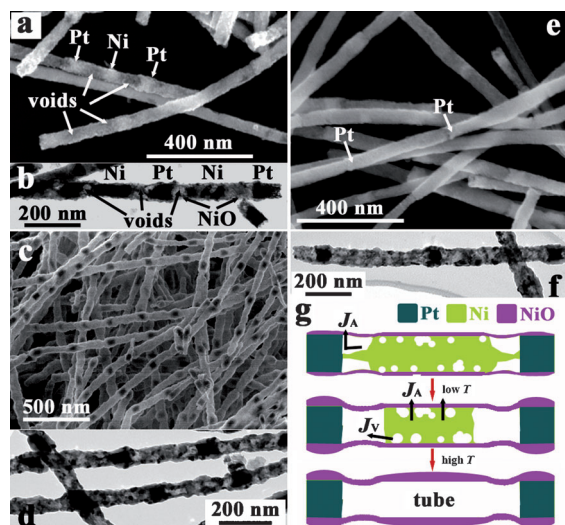


Figure 4. Images of multisegmented Ni/Pt nanowires with alternating 200 nm Ni and 50 nm Pt segments after annealing at 350 (a: SEM, b: TEM) and 450 °C (c: SEM, d: TEM) for 1 h in air. Images of multisegmented Ni/Pt nanowires with alternating 400 nm Ni and 50 nm Pt segments after annealing at 350 (e: SEM) and 450 °C (f: TEM) for 1 h in air. g) Scheme for the formation of nanopeapods from the multisegmented Ni/Pt nanowires with longer Ni segments.

nanowires with alternating 200 nm Ni and 50 nm Pt segments after annealing at 350 °C for 1 h in air. The reduction of the frequency of the Ni/Pt interfaces prevents the transformation of each Ni segment to a completely hollow NiO nanotube. Instead, segmented cavities are constantly localized at both sides of the Ni/Pt interface. A structure with alternating Pt and Ni nanopeas encapsulated by a slightly rippled NiO nanopod was thus produced. Hollow Pt/NiO nanopeapods were obtained when the oxidation was performed at 450 °C for 1 h (Figure 4c,d). Although this temperature in general can activate the thermal diffusion of Ni based on the Kirkendall effect, these segmented Ni nanowires present an accelerated oxidation rate as a result of the enhanced outward mass transfer at the early oxidation stage. When multisegmented Ni/Pt nanowires with alternating 400 nm Ni and 50 nm Pt segments were oxidized at 350 (Figure 4e) and 450 °C (Figure 4f), the interface-facilitated effect still takes effect. However, the nanopeapods formed at 450 °C only have wavy NiO sheaths with a uniform thickness in the areas near the Pt segments. The Ni fractions far away from the Ni/Pt interface were converted into rugged tubular NiO nanostructures, because the oxidation is out of control of the interface. The scheme in Figure 4g summarizes the development of nanopeapod structures by oxidation of multisegmented Ni/Pt nanowires with longer Ni segments.

In conclusion, we have investigated the oxidation of Ni in multisegmented Ni/Pt nanowires at low temperatures. It was revealed that the existence of the Ni/Pt interface effectively regulates the oxidation behavior of the Ni segments. By

designing the Ni/Pt nanowires with optimal parameters, we fabricated highly ordered wavy Pt/NiO nanopeapods at temperatures as low as 350 °C. The Pt/NiO nanopeapods may find important applications because of their interesting magnetic properties. The strategy developed herein is also expected as a general route for fabrication of other metal/oxide nanopeapods.

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