

Large-Scale Aqueous Synthesis and Growth Mechanism of Single-Crystalline Metal Nanoscrolls at Room Temperature: The Case of Nickel

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Here we report a simple and versatile one-pot route for the large-scale synthesis of single-crystalline Ni nanoscrolls at room temperature. The procedure is very simple, and only two chemicals (NiCl₂ and commercial Mn powder) were used throughout the entire synthetic process. Through a systematic investigation on the morphologies of the products collected from different growth stages, direct evidence of the evolution process, from a flat sheet to the formation of one-sided and two-sided nanoscrolls, is presented. Further, the disassociation of the as-synthesized nanoscrolls induced by the converged transmission electron microscope (TEM) electron-beam irradiation confirms the scroll-type structures. A corresponding growth mechanism of Ni nanoscrolls is proposed. In addition, we have successfully extended this simple method to synthesize La metal nanoscrolls. We believe that this method offers an attractive and simple way for the large-scale synthesis of other metal nanoscrolls.

Introduction

Since the discovery of carbon nanotubes (CNTs), considerable interest has been directed toward associated inorganic tubular nanostructures because of their unique electronic, optical, and mechanical properties, as well as their potential applications in electronics, chemical sensing, electron field emission, and batteries.^{1–6} There is a novel type of tubular nanostructure called a nanoscroll (NS),⁷ an interesting form that ideally consists of a single sheet rolling up into a tubelike nanostructure, with open-ended tips, and is seamless in structure, whose properties are suggested to be different from those of a nanotube.^{8–11} Considering carbon nanoscrolls (CNSs) as an example, it has been theoretically and experimentally reported that their electronic, optical, and stability properties are distinct from those of CNTs.^{8–10} In addition, their interlayer spaces are readily available for intercalation of other

molecules/particles, with capacities that can be easily tailored by changing the interlayer distance through the scrolling/unscrolling of a scrolled structure,^{12–14} by comparison, those in multiwalled CNTs cannot. This key feature, with a fully accessible surface, high surface/volume ratio, and adjustable interlayer distance is, therefore, crucial for viewing nanoscrolls as promising materials for many applications, such as hydrogen/energy storage, catalysis, sensors, supercapacitors, and nanoactuators.^{12–16}

To date, methods for the synthesis of scroll-type structures (e.g., C,^{7,10,17} TiO₂,¹⁸ PbO₂,¹⁹ SrAl₂O₄,²⁰ H₂K₂Nb₆O₁₇,²¹ K_{0.8}H_{3.2}Nb₆O₁₇,²² H₄Nb₆O₁₇,²³ SiGe,²⁴ Ti_{0.91}O₂,²⁵

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MnO₂²⁵ and Ca₂Nb₃O₁₀²⁵) have mainly focused on high-temperature processes,^{18–21} intercalation/exfoliation,^{7,10,17,22,23} and the strain-induced bending of layered systems.²⁴ Recently, relatively mild chemical precipitation conditions were adapted for the synthesis of scroll-like structures of NiS,²⁶ Cu(OH)₂,²⁷ and Te.²⁸ However, most methods reported so far remain limited in scope, due mainly to the formation of compounds and nonmetallic materials and/or to the very small amount of product synthesized (difficult to be scaled up). In addition, most structures obtained so far either have relative large diameters (up to several hundred nanometers), have low aspect ratios, or are not uniform in size, which to some extent limits not only the studies of their properties but also their practical applications to many fields. Therefore, the exploration of simple, cost-effective, environmentally benign methods for the large-scale synthesis of a wider variety of scroll-like nanostructures, with great uniformity, purity, and high length/diameter aspect ratios, remains a challenge.

On the other hand, one-dimensional (1D) metal nanostructures have been extensively studied over the past decade because of their interesting catalytic, electronic, magnetic, optical, chemical, and mechanical properties.^{29–31} In general, the intrinsic properties of a metal nanostructure can be tailored by controlling its size, shape, and crystallinity.³² To date, a large variety of 1D metal nanostructures with different morphologies (e.g., wires, tubes, and rods) have been synthesized and applied in many fields.^{29–31} However, to the best of our knowledge, single-crystal metal nanoscrolls have rarely been reported.

In this work, we report, a simple and versatile one-pot route for the large-scale synthesis of Ni nanoscrolls. This gives evidence of metal nanoscrolls formed in aqueous solution, under ambient temperature and pressure, without the aid of external forces such as heating, ultrasonication, and/or selective etching (strain-induced bending of layered systems), as reported by others.^{20,22,24} The as-synthesized Ni nanoscrolls are single crystals and quite uniform in size, a few tens of nanometers in diameter and several tens of micrometers or more in length. Through a systematic investigation of the growth process, direct evidence is presented of the bending and rolling-up evolution process, from a flat sheet to the formation of one-sided (that is, rolled in one direction) and two-sided (that is, rolled, from each end, in opposite directions) nanoscrolls. The proposed growth mechanism may shed light on the study of the formation processes of other inorganic nanoscrolls.

Experimental Section

Materials. Nickel(II) chloride hexahydrate (NiCl₂·6H₂O) and manganese powder (–325 mesh, ≥99%) were purchased from Sigma-Aldrich and used as received. Doubly distilled deionized (DI) water was used for all preparations in the synthesis of Ni nanoscrolls.

Nanostructure Synthesis. In a typical synthesis, an aqueous NiCl₂ (175 mL, 2 M) solution was quickly added in a 250 mL beaker which contained 16.6 g of commercially available sacrificial Mn powder. Ni²⁺ is reduced according to the following reaction:



where the atomic concentration of Ni was greater than that of Mn to ensure that Mn atoms could be completely oxidized into Mn²⁺, precipitating only Ni nanoscrolls. After the completion of the reaction, the product was washed several times with DI water, collected by filtration, and dried in an oven at 40 °C under Ar atmosphere.

Nanostructure Characterization. The morphologies and structures of the products were characterized by a field emission scanning electron microscope (FESEM, Hitachi S-5200), operating at 5 kV, a transmission electron microscope (TEM, Philips CM10), operating at an accelerating voltage of 100 kV (a spot size diameter of 3.5 μm and a beam current of 6.8 × 10^{–9} nA), and a high-resolution transmission electron microscope (HRTEM, JEOL 2100F), operating at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was carried out using a Hitachi S-4800 FESEM operating at 15 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Discover diffractometer operating at 40 kV and 40 mA, with Cu Kα radiation (λ = 0.154 nm). For scanning electron microscopy (SEM) observations, small amounts of samples were directly mounted on the conductive carbon tape, thus the original morphology of the nanostructures can be directly observed. For TEM observations, specimens were prepared by dispersing the samples in methanol by ultrasonication and deposited onto carbon-coated copper grids by drop-casting. For the time-dependent morphology evolution study, a drop of dispersion taken from different reaction stages was placed on a carbon-coated copper grid, followed by solvent evaporation under ambient conditions.

Results and Discussion

In a typical synthesis, based on the galvanic replacement reaction, we used commercially available Mn powders, rather than any presynthesized nanostructures or bulk materials, as the sacrificial metal to reduce the desired metal salt precursor (in our case, NiCl₂) at room temperature, without adding either surfactant or catalyst. The inset in Figure 1a (also see the Supporting Information, Figure S1) demonstrates the success of our one-pot, large-scale synthesis of 18 g of Ni nanoscrolls. The product that precipitated out of the solution is attracted by a small cuboid magnet, indicating the intrinsic magnetic property of the as-synthesized nickel sample. The entire Ni product lies just beneath the original solution surface (Supporting Information, Figure S1a), which implies how effective this method is, in that for any given amount of Ni product, a much smaller amount of solution is needed compared to the other methods. The low-magnification SEM images (Figure 1a and Figure S2a,b in the Supporting Information)

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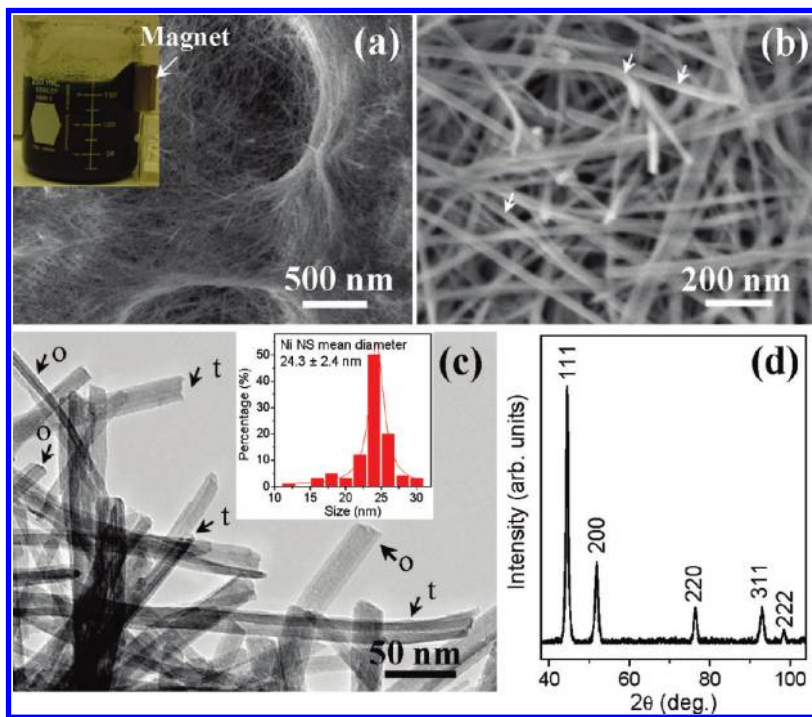


Figure 1. (a,b) SEM images, (c) TEM image and diameter distribution (inset), and (d) powder XRD patterns of as-synthesized Ni nanoscrolls; the arrows in parts b and c point out the typical scroll-like structures.

show that the as-synthesized Ni product is composed of numerous nanowire-like structures, with uniform diameters and substantial lengths of up to several tens of micrometers. These nanowire-like structures knit together to form a bird nestlike architecture. The high-magnification SEM image (Figure 1b) indicates that the diameters of the wirelike structures are in the range of 20–30 nm. In addition, a close observation reveals that some of the wirelike structures actually look more like two-sided nanoscrolls (arrows in Figure 1b). To further investigate the Ni nanostructure, we performed a transmission electron microscopy (TEM) study. Figure 1c shows a representative TEM image of the tips of Ni nanostructures with a mean diameter of 24.3 ± 2.4 nm (inset of Figure 1c). The thickness-projected mass contrast of each wirelike structure shows the real scroll-like structure with obviously open-ended tips; some are one-sided nanoscrolls (indicated by arrows o), and the others are two-sided (indicated by arrows t). In order to see more detailed structures, including the scroll bodies, rather than only their tips, the sample was sonicated in methanol for 3 h to obtain a better sample dispersion, before putting one drop of solution onto the TEM grid. The obvious tubelike nanostructures with asymmetric mass contrasts (Supporting Information, Figure S2c), as well as the appearance of the sheetlike structures at the edges of the structures further confirm the scroll-like structures of the Ni products. The EDX spectrum (Supporting Information, Figure S2d) confirms the purity of the Ni nanoscrolls. The powder X-ray diffraction (XRD) pattern (Figure 1d) matches well with the Ni face-centered cubic (fcc) structure (JCPDS, 04-0850). The peaks located at 44.53, 51.88, 76.43, 93.02, and 98.46 can be assigned to the

(111), (200), (220), (311), and (222) planes of Ni, respectively, which reveals the high crystallinity of the Ni nanoscrolls.

To date, some studies have reported on the formation of inorganic micro- or nanoscrolls from layered or artificial lamellar structures.^{20,22,24} However, direct evidence of the bending and rolling-up processes in aqueous solution for the self-assembled metal nanoscroll formation (including one-sided and two-sided nanoscrolls with extremely high length/diameter aspect ratios) has never been reported. In order to obtain a complete view of the nanoscroll formation process and its growth mechanism, we conducted a morphological evolution study, using SEM and TEM techniques, during a time-dependent reaction experiment at room temperature.

Figures 2a–d show representative SEM images of the product, as a function of reaction time for 2 h, 28 h, 1 day, and 5 days, respectively. It is clear that, after 2 h, the Mn particle surface becomes very rough (Figure 2a), decorated with various ridgelike structures. After 28 h, the ridge-like structures grow longer and wider to form relatively smooth Ni nanowalls/nanosheets (Figure 2b), up to a few hundreds of nanometers wide and several micrometers or more long but less than 20 nm thick. In addition, deep in the crevices of the Mn particle (an example is seen in the center of Figure 2b, indicated by arrows), many Ni nanosheets are also formed. After 1 day, the product exhibits a peculiar spongelike architecture (Figure 2c) which is entirely constructed of numerous nanosheets. These nanosheets, with greater sizes (width and length) but thinner thicknesses (several nanometers), exist everywhere, even deep inside the original spaces of sacrificial Mn particles. A typical flat sheet ~ 300 nm wide is shown in Figure 2c. All the nanosheets are interconnected to form network

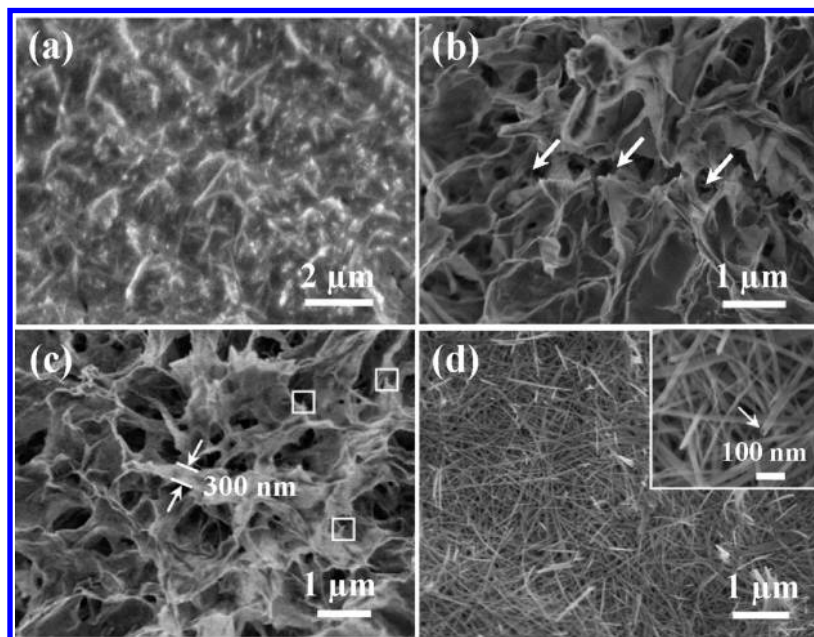


Figure 2. SEM investigation of the morphological evolution of Ni nanoscrolls, as a function of Mn particle immersion time in NiCl_2 solution for (a) 2 h, (b) 10 h, (c) 1 day, and (d) 5 days, respectively. The arrows in part b show the crevice of the Mn particle.

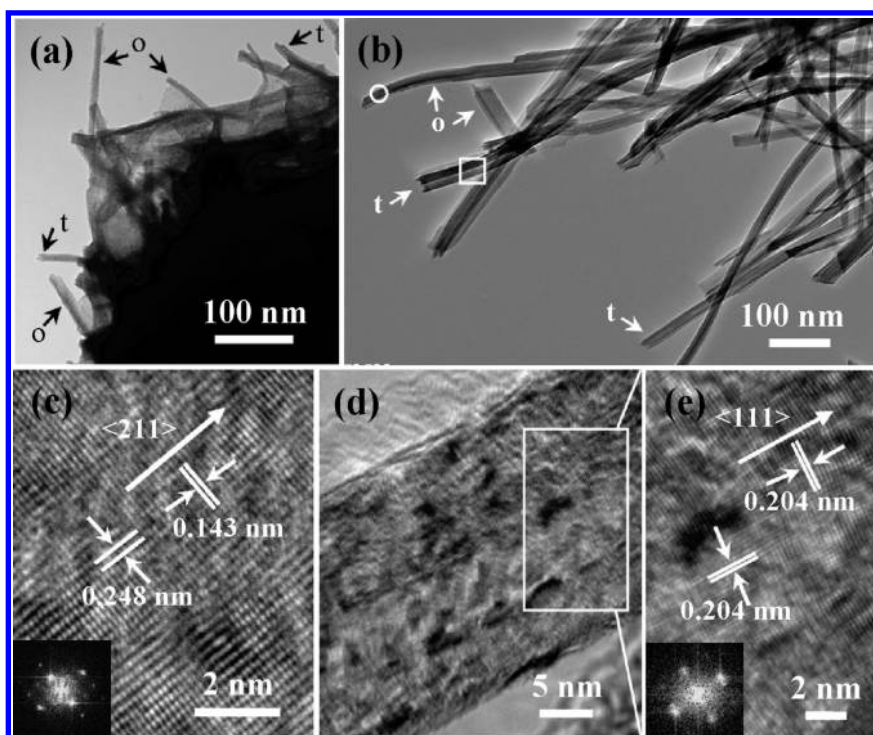


Figure 3. TEM investigation of the morphological evolution of Ni nanoscrolls as a function of reaction time for (a) 1 day and (b) 5 days, respectively; o and t represent one- and two-sided nanoscrolls, respectively. HRTEM images of (c) a one-sided nanoscroll and (d,e) a two-sided nanoscroll, circled and squared in part b, respectively; insets are the corresponding FFT patterns.

structures. In addition, at the extruding parts of the surface, some needlelike structures are formed (squares in Figure 2c); this may well be the initial formation of the scroll-like structure. After 5 days, uniform wirelike structures were formed (Figure 2d). The high-magnification SEM image (inset of Figure 2d) reveals the tubular structure of Ni wires, with diameters in the range of 20–30 nm.

In order to obtain more detailed information of the real growth process of the Ni nanoscrolls, a more detailed

systematic TEM investigation on time-dependent structural formation was carried out (Figure S3 in the Supporting Information). The results are consistent with those under SEM investigation. Specifically, after 1 day, many rudimentary nanoscrolls were formed (Figure 3a). Most of the structures are of half sheets bonded/connected with others, with the other half scrolls freely dangling on the surfaces (arrow o); some of the others are two-sided nanoscrolls (arrow t) with freely dangling tips. After

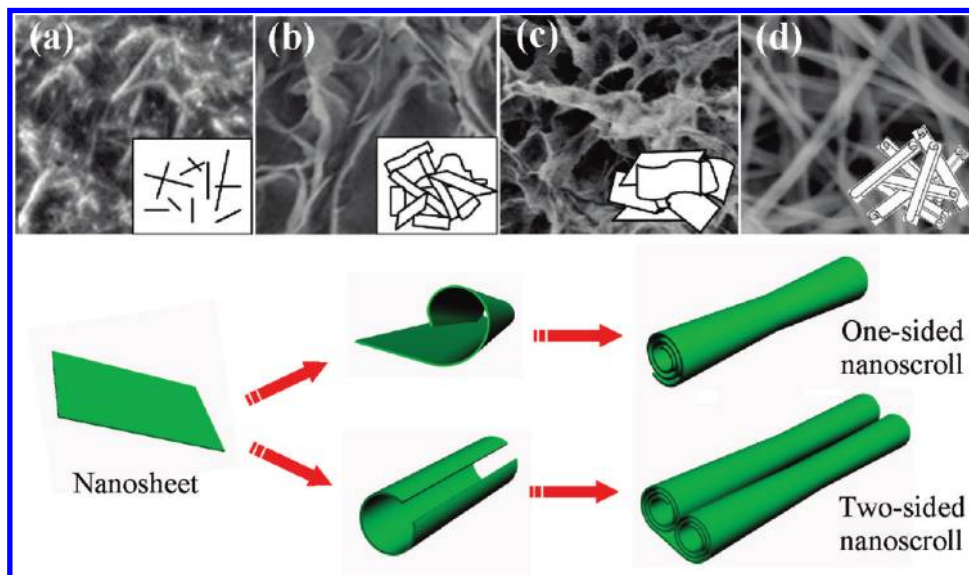


Figure 4. Schematic illustration of the formation and shape evolution of Ni nanoscrolls.

5 days, uniform Ni nanoscroll structures, one-sided (arrow o) and two-sided (arrow t), were entirely formed (Figure 3b and Figure S4 in the Supporting Information). Assuming that a one-sided nanoscroll, 20–30 nm in diameter, evolved from a flat nanosheet (~ 300 nm wide, in Figure 2c), we will recognize that a nanoscroll normally consists of several (up to a few tens) layered rolls. The different mass contrasts in each nanoscroll, especially the tips, clearly present its composition of a certain number of layered rolls (Supporting Information, Figure S4b–d). A high-resolution TEM image (Figure 3c) of a one-sided nanoscroll (circle, in Figure 3b), with visible lattice fringes, and the corresponding fast Fourier transformation (FFT, inset of Figure 3c) further confirm the single crystalline form of the nanoscrolls. The fringes perpendicular to the scrolling axis are evenly separated by 0.143 nm, matching the (211) planes of the fcc crystalline Ni, which indicates that the scroll axis is along the $\langle 211 \rangle$ direction. The fringes parallel to the scrolling axis, with 0.248 nm interplanar separation, correspond to the (110) planes. Figure 3d shows the HRTEM image recorded from a two-sided nanoscroll (square, in Figure 3b), and a magnified HRTEM image of its center (connecting the two rolls) is shown in Figure 3e, where the same lattice features (0.204 nm, $\langle 111 \rangle$ direction), parallel and perpendicular to the scrolling axis, demonstrate that the two-sided nanoscroll actually forms from one single crystalline 2D nanosheet.

On the basis of the above results, we propose a mechanism for the formation of Ni nanoscroll structures (Figure 4). First, the initial replacement reaction between Mn and Ni^{2+} proceeds rapidly, due to the large difference in their redox potentials, Mn^{2+}/Mn (-1.18 V) and Ni^{2+}/Ni (-0.257 V). This promotes the random formation of Ni nuclei and ridgelike structures standing on the Mn particle surfaces (Figure 2a,b). In the second stage, those structures act as seeds for further Ni precipitation, forming much longer and wider but thinner (due to the reorganization

of Ni atoms on the further sacrifice of Mn atoms) nanowalls connecting to form network structures and, finally, a spongelike architecture. Note that the formation of Ni nuclei and ridgelike structures standing on the Mn particle surfaces may act as the diffusion barrier for more Ni^{2+} getting into the core, which slows down the replacement reaction with the inner Mn. In addition, as the reaction proceeds, the concentration of the Ni^{2+} decreases, which also slows down the replacement reaction, providing the time for the crystallization of the Ni nanowalls. Meanwhile, at the edges, some nanosheets with free sides (not bonded to others), have begun to roll up to form rudimentary nanoscrolls (the squares in Figure 2c and Figure 3a). We attribute this rolling mainly to a kinetically, rather than thermally, driven process because the rolling was conducted at room temperature. The exact formation mechanism of the scroll nanostructure is still under investigation. However, on the basis of our investigation, several key factors that initiate the rolling process are proposed: (1) a structural stress originating from Ni atomic reorganization of the nanosheet during the reaction process, as well as the influence by the connection with the other nanosheets;²⁰ (2) the greater buoyancy of the Ni nanosheets than of the Ni nanosheet–Mn particle composite results in the flaking off of the nanosheets, providing the driving force for the rolling processes; (3) its unique layered structure (Figure 3c), oriented with large lattice spaces which are the preferred rolling axes;²⁷ and (4) the asymmetry of the nanosheet caused by the organization of intrinsic magnetic Ni atoms and also by the electronic structures and polar properties of the ions in solution.^{22,27,33} Once the Mn atoms have been totally consumed (i.e., without the sustentaculum of Mn particles), those spongelike architectures constructed of numerous nanosheets will no longer be stable in the solution. They will tend to separate into small parts. The

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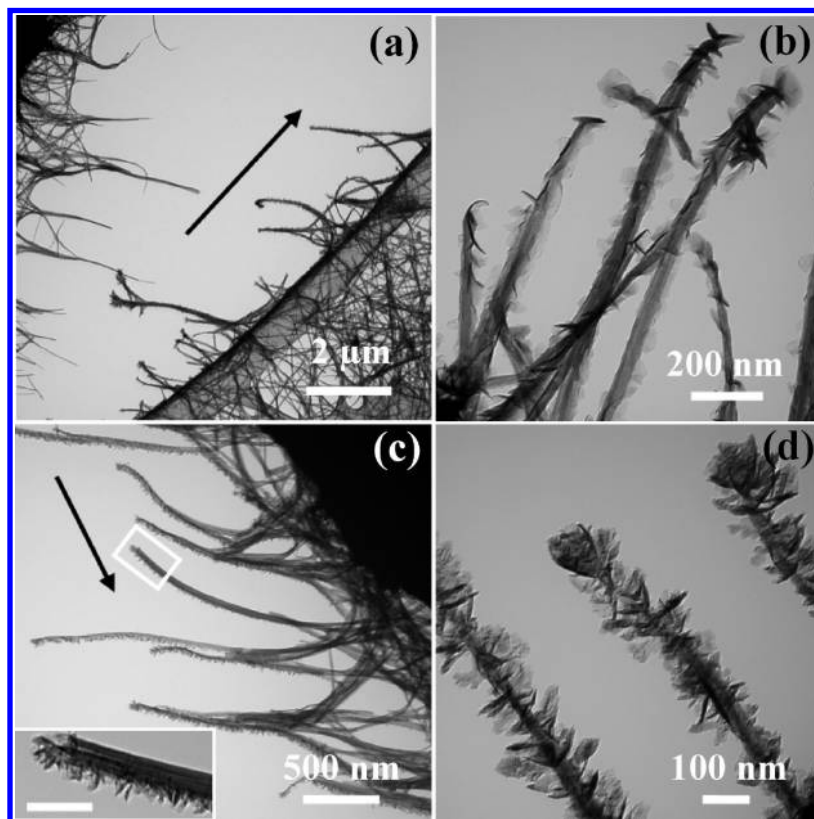


Figure 5. TEM images of the nanoscrolls decorated with flower-petallike nanosheets, formed by the illumination of a strong TEM electron beam, with a long-time exposure (a) and (b) and short-time exposures from one direction (c) and two directions (d), respectively. The inset, with a scale bar of 200 nm, shows the enlarged view of a two-sided nanoscroll (boxed in part c) affected by the strong beam illumination.

released nanosheets will continue their rolling process. Therefore, with the formation of the nanoscrolls, more and more nanosheets will be released and further form into nanoscrolls in an accelerating cascade. Finally, uniform nanoscrolls were formed and knitted into nestlike structures.

Interestingly, during TEM observation, we noticed that the Ni nanoscrolls are sensitive to a very strong converged electron beam, resulting in partial change of the structures and providing interesting features. This suggested that the use of intensive-electron-beam radiation can further demonstrate the Ni scroll-like structure. After converging the electron beam to a very high brightness and choosing the nanoscrolls dangling out of the lacy carbon film as the targets, we moved the sample slowly from side to side (as indicated by an arrow in Figure 5a). Interestingly, nanoscrolls that were exposed to the electron beam changed into flowerlike structures, with many petals growing from the scroll stem, while the nonexposed nanoscrolls remained in their original structures. An enlarged view of the damaged section (Figure 5b) shows that (1) the stems still maintain the scroll structures (one-sided and two-sided) and (2) the petals are a few tens of nanometers wide and a few nanometers thick, which is consistent with the thickness of the nanosheet before rolling up to form the nanoscrolls. This is quite reasonable, since, as a result of rolling, defects are generated within a structure to allow strain release, stabilizing the overall scroll structure.¹⁹ As a further demonstration, we

chose another area of the TEM sample and moved the sample very quickly, instead of slowly as previous, along one direction (arrow in Figure 5c). We found that the nanoscrolls bent away from the moving direction and only the side which first reached the electron beam was damaged, decorated with many petals similar to those that appeared previously. When the sample was moved back in the opposite direction, symmetrical flowerlike structures (Figure 5d) were formed. Thus, the disassociation of Ni structures under TEM electron beam irradiation further confirms that the as-synthesized Ni nanostructures are, indeed, nanoscroll structures.

In recent years, rare earth metals have found application in many fields, such as metallurgy,³⁴ chemical engineering,³⁵ and hydrogen storage.^{36,37} However, few studies have been reported on their morphologies and structures, let alone their scroll-like structures at the nanoscale. To demonstrate the capability of this method to produce other metal nanoscroll structures uniformly and in large-scale, we chose the synthesis of La nanoscrolls, obtained via a replacement reaction between Mn and LaCl₃ solution, as an example. The morphological

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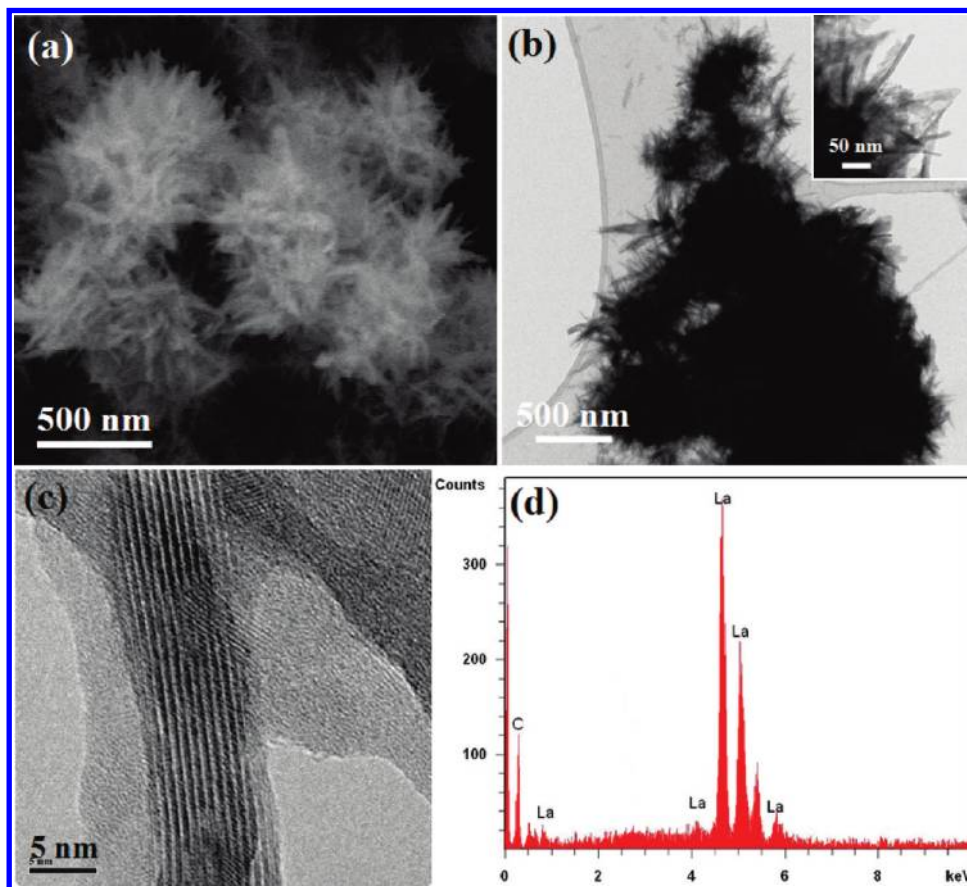


Figure 6. SEM and TEM images and a corresponding EDX spectrum of the as-synthesized La nanoscrolls. The carbon signal in the EDX spectrum came from the carbon tape substrate.

and purity characterizations, using SEM, TEM, and EDX, are shown in Figure 6. These La nanoscrolls are about 5 nm in diameter and several hundreds of nanometers in length with a high surface area. We believe that this tubelike structure may have great potential in many applications.

Conclusions

Uniform, novel, single-crystalline Ni nanoscrolls with high aspect ratios have been successfully synthesized, for the first time, on a large scale by a simple aqueous solution method, based on the Mn replacement reaction, without using any template or surfactant, at room temperature. Time-dependent observations, using SEM and TEM techniques, revealed the rolling-up process of the nanoscrolls. The disassociation induced by the converged bright TEM electron-beam further confirmed the scroll-type structures. The proposed growth mechanism may guide the

study on the formation process of other inorganic nanoscrolls. In addition, using this simple method, we successfully investigated the possibility of obtaining La metal nanoscrolls. Thus, we believe that this method offers an attractive and convenient way for the large-scale synthesis of other inorganic nanoscrolls.

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Supporting Information Available: Additional information for the large-scale synthesis and morphological evolution study of Ni nanoscrolls (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.