Nanostructures

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Layered Cobalt Hydroxide Nanocones: Microwave-Assisted Synthesis, Exfoliation, and Structural Modification**

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Layered materials have drawn immense attention because of their distinctive properties and their wide range of practical and potential applications, such as anion/cation exchangers, selective separation membranes, catalysts, adsorbents, chemical or biosensors, solid-state nanoreactors, and molecular sieves.[1–5] It is generally believed that layered materials might be able to form tubular structures by a rolling mechanism. Various layered materials, such as carbon, boron nitride (BN), transition-metal halides, oxides, and chalcogenides, could roll up or fold up into tubular forms, for example nanotubes.[6–8] In particular, conical structures with hollow interiors, namely nanocones/nanohorns formed from carbon and boron nitride, have also been discovered.[9–12] Due to the conical feature, nanocones/nanohorns might have special electronic, mechanical, and field-emission properties. However, apart from carbon and boron nitride systems, there are few reports of conical structures originating from the rolling-up of layered materials. On the other hand, layered materials could be exfoliated/delaminated into unilamellar nanosheets by controlling layer-to-layer interaction through soft chemical procedures.[13–15] In particular, unilamellar nanosheets, typically about one nanometer in thickness and several tens of nanometers to several micrometers in lateral size, can curl or fold up into nanotubes/nanoscrolls.[16–18] Very recently, carbon nanotubes could be unzipped/exfoliated to fabricate graphene sheets and ribbons.[19–21] The question arises as to whether conical structures be formed by the rolling-up of layered materials other than carbon and boron nitride, and if they can be further unwrapped/exfoliated into unilamellar nanosheets. The answer will be very important in revealing the formation mechanism of nanocones/nanohorns as well as the energy balance between nanocones/nanohorns and nanosheets.

Layered cobalt hydroxide has received enormous attention in recent years on the basis of its unique catalytic, magnetic, and electrochemical properties.[22] It is well-known that layered cobalt hydroxides have two polymorphs: α- and β-$Co(OH)_2$. The α form consists of stacked layers intercalated with various anions (such as CO_3^{2-}, NO_3^-, Cl^-) and water molecules in the interlayer gallery, which thus has a larger interlayer spacing (> 0.70 nm) than that of β-$Co(OH)_2$ (0.46 nm) without guest species.[23,24] We have recently demonstrated hexagonal microplatelets of layered α- and β-cobalt hydroxides could be selectively synthesized by homogeneous precipitation using hexamethylenetetramine (HMT) as an alkaline reagent.[23] Herein, we present layered cobalt hydroxide nanocones intercalated with dodecyl sulfate (DS) ions that can be formed by a facile microwave-assisted method in which the surfactant sodium dodecyl sulfate (SDS) is used as a structure-directing agent. Furthermore, unilamellar cobalt hydroxide nanosheets can then be obtained by direct exfoliation of these nanocones in formamide. By using layered cobalt hydroxide nanocones as the precursor, cobalt oxyhydroxide (CoOOH) and cobalt oxide (Co_3O_4) nanocones can also be obtained by oxidation in alkaline solution and thermal decomposition, respectively. This feature offers a vast opportunity to rationally design related nanostructures based on layered hydroxides.

Figure 1a shows a typical scanning electron microscopy (SEM) image of as-prepared product obtained by using 3 mmol HMT and 5 mmol SDS at 100 °C for 1 h. A large

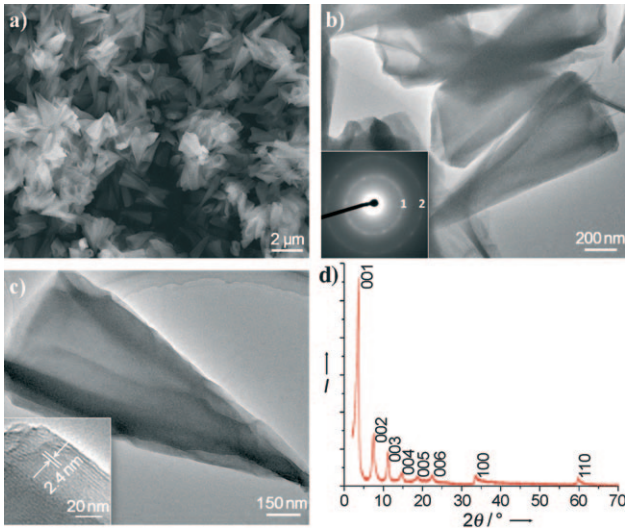

Figure 1. a) SEM and b) TEM images of layered cobalt hydroxide nanocones. The inset in (b) shows an SAED pattern taken on nanocones: 1) 100, 2) 110. c) TEM and (inset) HRTEM images of an individual nanocone. d) XRD pattern of layered cobalt hydroxide nanocones intercalated with DS ions.

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quantity of conical nanostructures was found in the product. A typical transmission electron microscopy (TEM) image (Figure 1b) also clearly shows that as-prepared nanocones possess conical structures with hollow interiors. These nanocones have an average bottom diameter of about 400 nm, tip diameter of about 20 nm, and length of up to 2 μm. The wall thickness ranges from a few to several tens of nanometers. The inset in Figure 1b shows the SAED pattern taken on a few nanocones, which can be indexed to in-plane or [001] zone-axis diffraction of hexagonal cobalt hydroxide with a lattice constant of $a = 0.31$ nm. Figure 1c depicts a typical TEM image of an individual nanocone. A high-resolution transmission electron microscopy (HRTEM) image (inset) shows the layered structure; the interlayer spacing is measured at about 2.4 nm. The layered structure was also confirmed by X-ray powder diffraction (XRD). A basal reflection series (Figure 1d) corresponds to an interlayer distance of 2.4 nm. Taking into account the green color of the product, the nanocones may be identified as DS^--intercalated α-type cobalt hydroxide.[23] The chemical composition of as-prepared products is estimated to be $\{Co(OH)_{1.75}DS_{0.25}{\cdot}0.4\,H_2O\}$ based on thermogravimetric and differential thermal analysis (Supporting Information, Figure S1).

The morphology and size of the products strongly depend on the synthetic parameters, such as reaction time, temperature, and surfactant. Figure 2a shows a typical SEM image of as-prepared product obtained at 100 °C for 10 min. Apart from a few nanocones, a large quantity of lamellar structures with rolled-up or curled edges can be clearly observed. When the reaction time was prolonged to 30 min, the product was mainly composed of nanocones (Figure 2b), indicating that the lamellar structures gradually curled into nanocones with longer reaction time. The inset in Figure 2b is a higher-magnification SEM image of an individual nanocone, which evidently exhibits the curling and folding up of an individual lamella onto itself to form a nanocone. The reaction temperature also influences the morphology of final products. When the reaction temperature was reduced to 60 °C, only lamellar structures are obtained (Supporting Information, Figure S2), whilst the product mainly consisted of nanocones at temperatures higher than 80 °C (Figure 2c). In particular, surfactant SDS seems to play a crucial role in the formation of layered cobalt hydroxide nanocones. A SEM image (Figure 2d) shows the as-prepared product synthesized at 100 °C for 1 h without SDS surfactant. Hexagonal platelets with average lateral size of about 5 μm and thickness of several tens of nanometers were produced, and they are identified as β-$Co(OH)_2$ without intercalating any anionic species on the basis of the XRD result (Supporting Information, Figure S3). Based on the experimental results, we assume that DS^--intercalated lamellar structures with few layers are firstly formed, and then tend to curl up at the edge, producing a conical angle (θ, ca. 10 to 60°) rather than a tubular structure owing to their morphological features and relatively lower energy barrier.[25] The lamellar structures gradually roll up along the conical angle, which may further grow and finally form nanocones under suitable conditions (Supporting Information, Figure S4).

By dispersing the layered cobalt hydroxide nanocones in formamide, a translucent green colloidal suspension was formed. Figure 3a shows a typical photograph of the colloidal suspension. Clear Tyndall light scattering was discerned for the suspension, indicating the presence of abundant exfoliated nanosheets dispersed in formamide. The UV/Vis absorption spectrum of the colloidal suspension is shown in Figure 3b. In the visible region, a broad absorption band

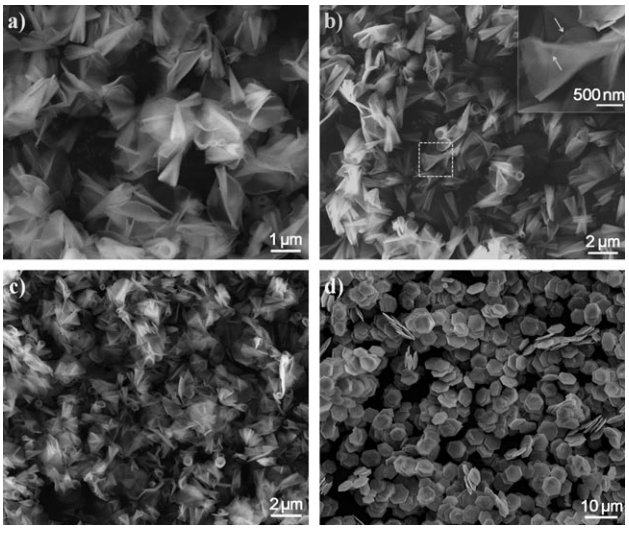

Figure 2. SEM images of as-prepared products synthesized at different reaction times and temperatures. a) 100 °C, 10 min; b) 100 °C, 30 min; c) 80 °C, 1 h. The inset in (b) is a high-magnification SEM image obtained from the area marked by a quadrangle. d) SEM image of as-prepared product obtained in the absence of surfactants at 100 °C for 1 h.

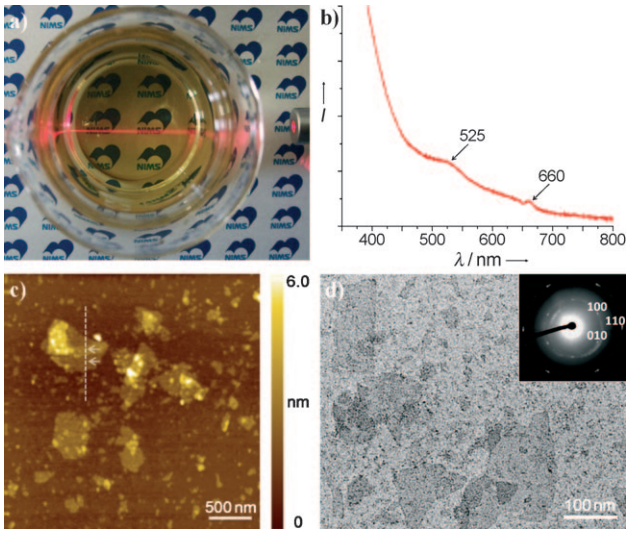

Figure 3. a) Photograph of a colloidal suspension of the exfoliated cobalt hydroxide nanosheets. The suspension is side-illuminated to demonstrate the Tyndall scattering effect. b) UV/Vis absorption spectra of colloidal suspension of the exfoliated nanosheets. c) Tapping-mode AFM image of the exfoliated nanosheets deposited on a silicon substrate. Arrows indicate a height of 1.0 nm. d) TEM image of the exfoliated cobalt hydroxide nanosheets. Inset: SAED pattern taken from an individual nanosheet.

centered at about 525 nm is observed, which is the typical $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transition of Co^{2+} octahedrally coordinated by weak-field ligands.[26] Furthermore, weak peak at around 660 nm corresponding to the absorption features of Co^{2+} with a tetrahedral coordination geometry can also be detected.[24] The UV/Vis results can be regarded as the evidence for the maintenance of octahedral and tetrahedral coordination of cobalt ions in the exfoliated nanosheets, indicating that the α-type host layer architecture of cobalt hydroxide was retained during the exfoliation process. A tapping-mode atomic force microscope (AFM) image (Figure 3c) shows sheet-like objects with lateral dimensions of several hundred nanometers. These nanosheets are irregular in shape, suggesting breakage or fracture of the nanocones during the delamination process. The thickness of the nanosheets was measured to be about 1.0 nm, which is very similar to that previous observed for layered double hydroxide (LDH) nanosheets (ca. 0.8 nm).[13a] The slightly larger value might be due to either the DS adsorption or the tetrahedral coordination on each side of the hydroxide plane.[24] A typical TEM image (Figure 3d) indicates very faint but homogeneous contrast of the nanosheets, reflecting their ultrathin and uniform thickness. The inset shows a typical SAED pattern taken from an individual nanosheet, and is compatible with the in-plane hexagonal unit cell ($a = 0.31$ nm).

More interestingly, layered cobalt hydroxide nanocones could be transformed into other related structures (such as CoOOH and Co_3O_4) that retain their original morphological features, which would endow their potential application in various fields. The layered cobalt hydroxide nanocones can be gradually oxidized into CoOOH in alkaline medium (Supporting Information, Figure S5). After treatment in alkaline solution, the color of the product turns from green to dark brown, which also indicates the transformation of hydroxide into oxyhydroxide.[27] Figure 4a depicts a typical SEM image of as-prepared CoOOH, which reveals that the initial conical structure was maintained. A TEM image reveals the CoOOH nanocones with hollow interiors (Figure 4b). The average bottom diameter of the CoOOH nanocones is smaller than that of the layered cobalt hydroxide nanocones, which is caused by the removal of DS ions and the resultant decrease in interlayer spacing. The inset shows an SAED pattern taken from a mass of the nanocones, which can be indexed as the CoOOH structure. Figure 4c shows a typical HRTEM image of a selected area of an individual CoOOH nanocone. The interlayer spacing is measured to be 0.44 nm, which agrees well with the separation between (003) lattice planes of CoOOH.

Co_3O_4 could also be obtained by calcination of layered cobalt hydroxide nanocones (Supporting Information, Figure S1). The product was composed of many pores, but still maintained the original conical framework (Figure 4d) through pyrolysis and dehydration. The upper inset shows the SAED pattern, revealing the satisfactory crystallinity of Co_3O_4 nanocones. The lattice spacings in the HRTEM observation for Co_3O_4 nanocones shown in lower inset of Figure 4d are measured to be about 0.29 and 0.24 nm, which are consistent with the values of the {220} and {311} lattice planes of spinel Co_3O_4, respectively.

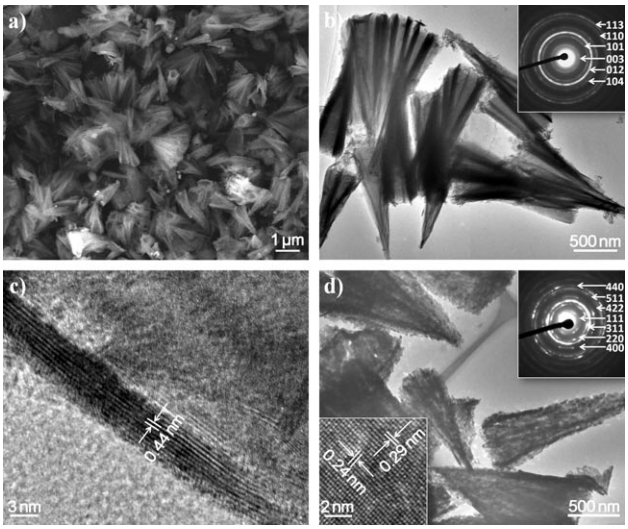

Figure 4. a) SEM, b) TEM, and c) HRTEM images of CoOOH nanocones obtained by reacting layered cobalt hydroxide nanocones in a 0.5 M NaOH solution for 6 h. The inset in (b) shows an SAED pattern taken on nanocones. d) TEM image of Co_3O_4 nanocones obtained by calcination of layered cobalt hydroxide nanocones in air at 700 °C for 2 h. The upper right and lower left insets in (d) are an SAED pattern and an HRTEM image of Co_3O_4 nanocones, respectively.

In summary, we have developed a simple and reliable synthetic strategy for production of layered cobalt hydroxide nanocones by using HMT as an alkaline reagent and SDS as both a surfactant and structure-directing agent. The results demonstrate that conical structures with hollow interiors might form through a rolling process of lamellar hydroxide. Unilamellar cobalt hydroxide nanosheets can be obtained by direct exfoliation of layered cobalt hydroxide nanocones in formamide. Furthermore, layered cobalt hydroxide nanocones can be transformed into CoOOH and Co_3O_4 nanocones by oxidation in alkaline solution and thermal decomposition, respectively. The synthetic strategy presented herein may provide an effective route to synthesize and rationally design other inorganic nanocones and nanosheets, which would be helpful in understanding the energy equilibrium between folding-up and unwrapping of layered structures. These conical structures with hollow interiors can also be expected to bring new opportunities for further fundamental research, and also for technological applications in catalysts, solid-state sensors, and as anode materials in lithium-ion rechargeable batteries.

Experimental Section

In a typical procedure, $CoCl_2{\cdot}6H_2O$ (1 mmol), HMT (3 mmol), and SDS (5 mmol) were charged into a Teflon-lined autoclave of 100 cm^3 capacity. The autoclave was filled with Milli-Q water up to 80% of the total volume, then sealed and microwave-heated at 100 °C for 1 h under magnetic stirring. After the reaction finished, the green precipitate was filtered, washed with water and ethanol, and finally dried at 60 °C for 5 h. The resulting product (30 mg) was mixed with formamide (50 cm^3) in a conical beaker, which was tightly capped after purging with nitrogen gas. Then, the mixture was agitated in a mechanical shaker at 120 rpm for 24 h, yielding a translucent green

colloidal suspension. To remove possible unexfoliated nanocones, the suspension was further treated by centrifugation at 4000 rpm for 20 min. To obtain the CoOOH nanocones, 50 mg corresponding green product was dispersed in NaOH solution (0.5 M, 100 cm^3) under magnetic stirring for 6 h in an ambient environment. Layered cobalt hydroxide nanocones were also annealed in air at 700 °C for 2 h to prepare Co_3O_4 nanocones.

XRD data were collected by a Rigaku RINT-2000 diffractometer with monochromatic $Cu_{K\alpha}$ radiation ($\lambda = 0.15405$ nm). The morphology of the synthesized products was examined using a JEOL JSM-6700F field-emission scanning SEM. TEM was performed on a JEOL JEM-3100F energy-filtering (Omega type) transmission microscope. UV/Vis absorption spectra were recorded using a Hitachi U-4100 spectrophotometer. Thermogravimetric–differential thermal analysis measurements (TG-DTA) were carried out using a Rigaku TGA-8120 instrument in a temperature range of 25–900 °C at a heating rate of 1 °C min^{-1}.

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