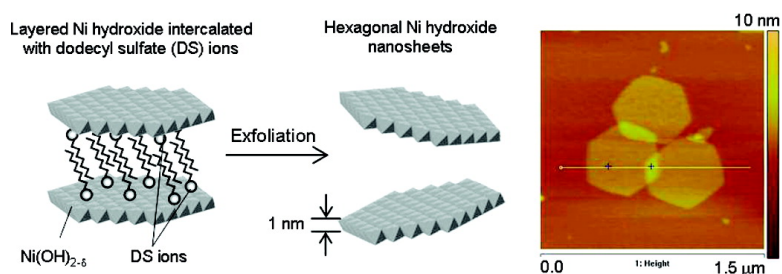


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Synthesis of Hexagonal Nickel Hydroxide Nanosheets by Exfoliation of Layered Nickel Hydroxide Intercalated with Dodecyl Sulfate Ions

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Exfoliation of layered compounds has attracted much attention as a promising method for preparing nanosheets with a homogeneous thickness of around 1 nm.^{1–4} Nanosheets can be viewed as a new class of inorganic macromolecules. Their thickness is in the molecular range, while their lateral size ranges from several hundred nanometers to several micrometers. Thus, nanosheets have properties of both the bulk material and molecules. In addition, nanosheets have a geometric advantage over other types of nanomaterials because highly oriented films can be easily grown by layer-by-layer (LBL) and Langmuir–Blodgett (LB) techniques.⁵ It is also possible to fabricate superlattice-like films using various nanosheets as building blocks⁶ and then various nanodevices, such as electrical and optical devices, through the combination of nanosheets.⁷ One of the issues in using nanosheets as building blocks is control of the lateral shape of the nanosheets. In general, it is difficult to achieve uniformity of lateral shape in nanosheets. The combination of different nanosheet shapes results in large gaps in the nanosheet-assembled film, which deteriorates the quality and properties of the films. If the shape is a regular hexagon or square, a gap-free homogeneous film can be prepared by LBL and LB techniques. Although hexagonal nanosheets prepared by the hydrothermal method have been reported, nanosheets with homogeneous thickness have not been obtained.⁸

In this Communication, we show for the first time that hexagonal nickel hydroxide nanosheets with homogeneous thickness can be prepared by exfoliation of layered nickel hydroxides intercalated with dodecyl sulfate (DS) ions. Nickel hydroxide has attracted increasing attention owing to its applications in alkaline rechargeable batteries, and the electrochemical properties of nickel hydroxide are directly affected by its morphology and size. The present nickel hydroxide nanosheets will be utilized not only in new nanodevices such as nanocells but also to study the fundamentals of electrochemical reactions.

Layered nickel hydroxides intercalated with DS were synthesized by precipitation of an aqueous solution of divalent nickel and sodium dodecyl sulfate (SDS) through hexamethylenetetramine (HMT) hydrolysis as follows. Three types of aqueous solutions (0.5 M Ni(NO₃)₂·6H₂O, 0.25 M SDS, and 1 M HMT solutions) were prepared, and then the divalent nickel (4 mL), SDS (40 mL), and HMT (12 mL) solution were mixed in a 200 cm³ Teflon vessel with deionized Milli-Q water (44 mL). The mixed solution was heated at 120 °C for 24 h under airtight conditions. After the reaction, the precipitates obtained were centrifuged, washed with distilled water and ethanol, and dried at room temperature. The precipitates (50 mg) were mixed with formamide (50 mL) to exfoliate the host layers, and the resulting suspensions were heated for several days at 40 °C without agitation. Subsequently, the suspensions were centrifuged (2000 rpm), and the supernatants were used as the nanosheet solutions.

Figure 1 shows the X-ray diffraction (XRD) pattern for a nanosheet precursor. Several (00*n*) reflections were observed. The

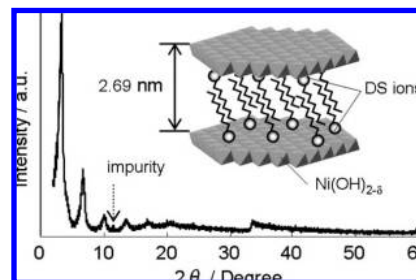


Figure 1. XRD pattern and structural model of layered nickel hydroxide intercalated with dodecyl sulfate (DS) ions.

basal spacing calculated from the reflection angle was 2.69 nm. The very weak peak around 12° was attributed to the layered nickel hydroxide intercalated with carbonate ions, which was generated by the hydrolysis reaction of HMT over a long time. When the reaction time was decreased, the impurity peak was not observed, but the morphology of the precursor became inhomogeneous. On the basis of the results of X-ray fluorescence, thermal gravimetry/differential thermal analysis, anion chromatography, and elemental analysis, the chemical composition of the precursor obtained was estimated to be Ni(OH)_{1.65}(DS)_{0.33}(NO₃)_{0.02}·0.7H₂O. However, the estimated chemical composition has an error margin because the present precursor contains an impurity phase. The structural model of the present precursor is shown in Figure 1.

The nickel hydroxide nanosheet was prepared by exfoliation of the above precursor in a formamide solution. The concentration of Ni in the nanosheet solution was 4.6×10^{-4} M. The nanosheet solution obtained was deposited on a mica substrate by spin-coating to prepare samples for atomic force microscopy (AFM) analysis. Figure 2a shows typical AFM images of the nanosheets. The thickness of the nanosheets was measured to be 1.1 nm. In general, the thickness observed by AFM is larger than that estimated from crystallographic data because of absorption of water and DS ions and other systematic factors in the AFM measurements. However, it is clear from measurements of many sheets that they represent unilamellar sheets (Figure 2b). This indicates that the precursor with layered structure was exfoliated by the exfoliation process. Figure 2c shows the size distribution data of hexagonal nanosheets. The average size was 585 nm, and the yield of the hexagonal sheet was around 55–65%, indicating that formation of hexagonal nanosheets with monolayer thickness is dominant in this method. Figure 2d shows a typical transmission electron microscopy (TEM) image and selected area electron diffraction (SAED) pattern of hexagonal nickel hydroxide nanosheets. The SAED pattern displayed hexagonally arranged spots, although they tended to change into arcs or rings during the observation. The lattice constant measured from the SAED pattern was $a = 0.31$ nm, which is approximately the same value as the in-plane structural parameter of layered Ni(OH)₂ ($a = 0.313$ nm). This indicates that the atomic

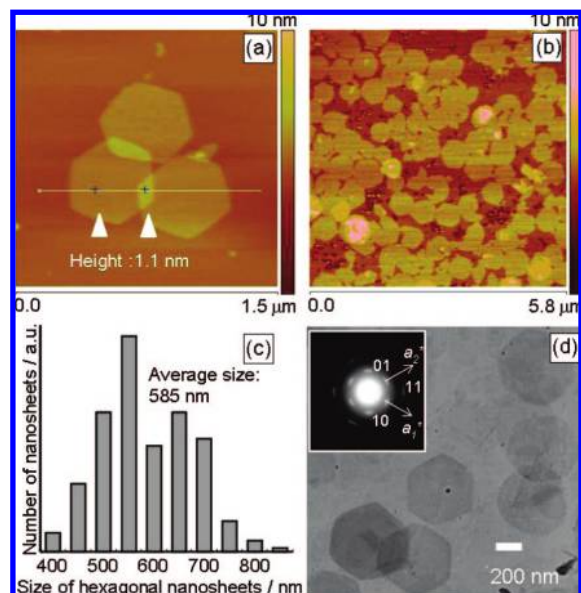


Figure 2. (a,b) AFM images (narrow and wide area), (c) size distribution data, and (d) TEM image with SAED pattern of hexagonal nickel hydroxide nanosheets.

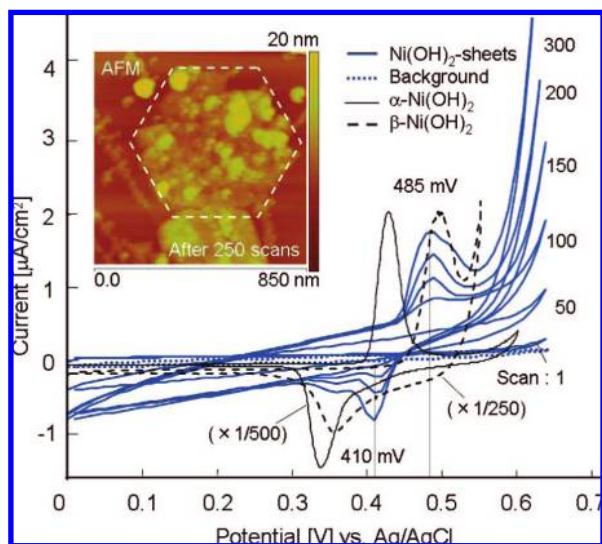


Figure 3. Cyclic voltammograms of nickel hydroxide nanosheets and AFM image of nickel hydroxide nanosheets after 250 scans. α - and β -Ni(OH)₂ were prepared by electrochemical co-precipitation.¹⁰

structure of the sheets is not destroyed during the exfoliation process. Some researchers have studied layered nickel hydroxide and nanosheets thereof, but the exfoliation and observation of mono-nickel nanosheets have not been reported.⁹ The present study is the first to directly identify the preparation of a mono-nickel nanosheet. Moreover, the shape of the nanosheets was hexagonal, as was that of the precursor. Although some nanosheets were irregular in shape, the hexagonal precursors could be made to retain their initial shapes and be exfoliated into hexagonal nanosheets.

Figure 3 shows the typical cyclic voltammograms (CVs) of nickel nanosheets recorded at a scan rate of 20 mV/s in a 0.1 M NaOH electrolyte. The electrode was prepared by immersing highly oriented pyrolytic graphite (HOPG) substrates into a nanosheet suspension for 15 min. After immersion, the substrates were washed with deionized water and dried at room temperature. Upon in-

creasing the scan number, clear oxidation (at 485 mV, E_O)/reduction (at 410 mV, E_R) current peaks were observed, which is similar to those for the reaction between β -Ni(OH)₂ and β -NiOOH.¹⁰ On the other hand, the difference between oxidation and reduction potentials ($\Delta E_p = E_O - E_R$) was 75 mV (good electrochemical reversibility), which is similar to that of the reaction between α -Ni(OH)₂ and γ -NiOOH.¹⁰ These electrochemical properties are presumably based on the two-dimensional structure of nickel hydroxide nanosheets.

As for the reactivity of the electrochemical reaction of nickel hydroxide, it has been reported that nickel hydroxide with a small crystalline size has higher reaction efficiency than that with large crystalline size.¹¹ In the case of nickel hydroxide nanosheets, the a -axial length (average length: 585 nm) is very large before electrochemical reaction. However, after 250 electrochemical cycles, the morphology of the nanosheet changed and the hexagonal shapes consisted of many small particles, as shown in the inset AFM image of Figure 3. This result agrees well with the CV data, showing that the oxidation/reduction current increased with increasing electrochemical cycling. In addition, the small particles were also observed at the step edge on HOPG substrate, indicating that dissolution and deposition of Ni ions occur during the electrochemical reaction. This process might bring about the structural change of the nanosheets.

In conclusion, 1-nm-thick hexagonal nickel hydroxide nanosheets were prepared by exfoliation of layered nickel hydroxides intercalated with DS ions, which exhibited charge–discharge properties in strong alkaline electrolyte. The electrochemically active nanosheets are expected to be used as building blocks for ultrathin film devices.

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Supporting Information Available: XRF, TG, FT-IR, and elementary analysis data of layered nickel hydroxide intercalated with dodecyl sulfate, size distribution data of hexagonal nanosheets, and UV/vis spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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