Rapid Communication

Ni(OH)$_2$@Co(OH)$_2$ hollow nanohexagons: Controllable synthesis, facet-selected competitive growth and capacitance property

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Abstract
Hollow nanohexagons with a core–shell structure have been synthesized from a mixture of Ni and Co hydroxide by a mild wet chemical approach. Ni(OH)$_2$@Co(OH)$_2$ nanohexagons with controllable sizes of about 200 nm, morphology and structure are obtained. Comprehensive microstructure analysis reveals that the Ni(OH)$_2$ and Co(OH)$_2$ components are single-crystalline. The surfaces of the nanohexagons are smooth and their inner facets can be controlled to be parallel to the outer facets or rotated by 30°. A growth mechanism depending on the N$_2$H$_4$/C$_2$H$_5$OH content and reaction temperature has been proposed to explain the different structures. The parallel inner facets tend to form with higher amounts of N$_2$H$_4$ while the rotated ones tend to form at higher temperature. The specific capacitance of the hollow nanohexagon is about 369 F/g, which can be remained as high as 96.4% after 2500 cycles at current density of 1 A/g.

Introduction
A hollow nanohexagon is an universal fastener with six sides cut in a hexagonal shape, since it seems to be the easiest shape to grasp [1]. With its high torque resistance and small volume, these hexagons can be uniformly spaced on a planar surface and used in conjunction with a matching bolt to assemble mechanical mixtures. Many different nanostructures, such as nanoplates, nanotubes, nanorings, nanopillars and nanohelices [2-11], have been recognized, but the hollow nanohexagon is still a challenge. Great efforts have been made towards hollow nanohexagons. However, ideal hollow nanohexagons have never been reported. Similar nanostructures, such as such as nanosheets [12], nanoflake [9,13,14], and hollow nanostructures [15], [16-23] have widely been synthesized. It is...
necessary to produce uniform hexagonal structure with controllable size. Moreover, in the fields of electronics and semiconducting industries, it is also very important for the hollow hexagons to have unique electric and/or magnetic properties.

The challenge should be dealt with suitable materials and reaction conditions. Metal oxides or hydroxides with hexagonal crystal structure are potential candidates. Ferromagnetic transition elements, such as Fe, Co, and Ni, have been widely used for magnetic and spintron applications. Their hydroxides, such as β-Ni(OH)₂, Co(OH)₂ crystalline with hexagonal brucite structure (space group P₃m1) have nearly identical lattice parameters and chemical properties [13, 24-27], which makes them good candidates for hollow nanohexagons. Although composite Ni-Co hydroxides with diverse morphologies and self-assembled hierarchical structures, including flower-like nanosheets, [12] microspheres assembled from two-wheeled units, [24] porous nanoflake composite film, [13] and core-shell nanocolumns of Ni(OH)₂@Co(OH)₂, [14] etc. have been synthesized, hollow nanohexagons have never been reported. Here we describe a mild wet chemical synthesis of Ni(OH)₂@Co(OH)₂ hollow nanohexagons utilizing the difference in growth and/or dissolve speed for specific facets of Ni(OH)₂. The growth mechanism is proposed, and the electricity properties of the constructed nanohexagons have also been investigated.

**Experimental methods**

In a typical synthesis, CoCl₂·6H₂O and NiCl₂·6H₂O with a molar ratio of 9:1 were dissolved in de-ionized water. N₂H₄·H₂O (80 wt%, 0.1-0.5 ml) was added to the solution as reducing agent. During the reaction, the pH value of the solution was kept at 13 by adding NaOH. The solution was stirred for 5 min at room temperature and then heated at 120-180 °C for 6 h in a sealed Teflon-lined autoclave. The autoclave was then cooled to room temperature in air. The product was collected by centrifugation and washed several times with de-ionized water and ethanol with further centrifugation.

The overall crystallinity and phase purity of the as-synthesized samples were analyzed by X-ray powder diffraction on a Rigaku Dmax 2200 X-ray diffractometer using Cu Kα incident radiation. The morphologies and chemical compositions of the products were characterized by a Hitachi S-4800 scanning electron microscope (SEM) and a Carl Zeiss Ultra SEM equipped with an Oxford X-max energy-dispersive spectrometer (EDS). The crystal structure and elemental distribution are analyzed on an FEI Titan transmission electron microscope (TEM, 300 kV) equipped with a Gatan 6800 scanning electron microscope (SEM) and a Carl Zeiss electron microscope (TEM). The inserted TEM images show the crystal structure model of the hollow nanohexagon of the corresponding TEM images.

**Results and discussion**

The as-synthesized material was first identified as Ni-Co hydroxide by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). As shown in Figure 1(a), the X-ray diffraction pattern of the typical products exhibited a typical pattern similar to that of Co(OH)₂ and β-Ni(OH)₂. Small-size effects were shown by the broadened peak widths. By using the Scherer formula, \( d = 0.9 \lambda / (\beta \cos \theta) \), where \( \lambda \) is the X-ray wavelength (0.15406 nm), \( \theta \) is the Bragg diffraction angle, and \( \beta \) is the peak width at half-maximum, the (101) peak in Figure 1(a) gives a characteristic size of about 25 ± 8 nm.

Figure 1(b-e) demonstrate that the Ni-Co hydroxides synthesized hollow nanohexagons were very uniform. It is interesting to point out that two kinds of hollow nanohexagons can be obtained under different conditions. As shown in Figure 1(b) and (c), the inner facets of the hollow nanohexagons synthesized with 0.4 ml N₂H₄·H₂O at 120 °C.
are found to be parallel with the outer facets. Scanning electron microscopy (SEM, Figure 1(b)) and transmission electron microscopy (TEM, Figure 1(c)) images indicate that the products have a typical hexagonal structure with uniform size ~200 nm and morphology. The diameters of the nanohexagons depend on the quantity of reducing agent and reaction temperature. The diameters of the nanohexagons change from 193 ± 19 nm with 0.1 ml N$_2$H$_4$ \cdot H$_2$O to (263 ± 10) nm with 0.5 ml N$_2$H$_4$ \cdot H$_2$O. For the products synthesized with 0.4 ml N$_2$H$_4$ \cdot H$_2$O at 120 °C, the walls exhibit ideal hexagonal structure with wall thickness measured to be 26 ± 6 nm, which matches with the characteristic size calculated from XRD results.

Investigations indicate that the morphology of the nanohexagons can also be controlled by adjusting the amount of N$_2$H$_4$ \cdot H$_2$O during the reaction. Figure 51 shows the SEM images of the products synthesized with reducing agent varied from 0.1 ml to 0.5 ml at 120 °C. With the increase of the reducing agent, the products change from pure hexagonal nanodiscs (0.1 ml) via a mixture of nanodiscs and nanohexagons (0.2-0.3 ml) and to pure nanohexagons (≥ 0.4 ml). Further increase of the reducing agent amount will break the nanohexagons. The morphology evolution of the nanostructures via the amount of the reducing agent is also studied by measuring the wall thickness of the nanohexagons averaging from over 100 randomly picked nanostructures. As shown in Figure 51(f), the wall thickness of the nanohexagons decreases from 42 ± 5 nm to 24 ± 3 nm with the increase of the reducing agent from 0.3 ml to 0.5 ml. EDS analysis reveals that Co: Ni ratio in the product decreases linearly from 9:1 to about 1:5 with 0.1 ml N$_2$H$_4$ \cdot H$_2$O as the reaction temperature is increased from 120 °C to 180 °C. Excess addition of N$_2$H$_4$ \cdot H$_2$O will even decrease the yield.

TEM image (Figure 1(e)) and the corresponding diffraction pattern of the nanohexagon synthesized at 180 °C also confirms the single-crystalline nature of the products. Following the analysis in Figure 1(c), the surface of the Ni-Co hydroxide nanohexagons are terminated by hexagonal [100] planes as before. The inner facets of the nanohexagons are found to be terminated by [110] planes. The crystallographic structure of the nanohexagon is illustrated in the inset of Figure 1(e).

As indicated in the XRD patterns, the hollow nanohexagons consist of Ni(OH)$_2$ and Co(OH)$_2$ with the same space group (P31m) and almost identical lattice parameter (Lattice Difference ≤ 0.006 nm). [28,29] Normal high resolution TEM and selected area diffraction (Figure S3) have difficulty to distinguish them. Then EFTEM analysis was conducted to reveal the elemental distribution within a nanohexagon, following our previous work on BCN nanotube. [30] Both kinds of nanohexagons are investigated, as shown in Figure 2. Figure 2(a) shows a bright-field TEM image with elemental mapping of the nanohexagons synthesized with 0.4 ml N$_2$H$_4$ \cdot H$_2$O at 120 °C. The elemental mappings of nickel, cobalt and oxygen are rendered with different colors. The green color in the shell of the nanohexagon represents cobalt, the red color in the inner layer represents nickel and the blue color throughout the entire nanohexagon represents oxygen. The results indicate that the Ni-Co hydroxides form a core-shell structure with a Ni (OH)$_2$ core and a Co(OH)$_2$ shell.

The relatively larger lattice parameter of Co(OH)$_2$ (a = 0.3186 nm, c = 0.4653 nm) compared with that of Ni (OH)$_2$ (a = 0.3127 nm, c = 0.4606 nm) may be responsible for the formation of core-shell structure, similar to FePt nanoparticles with a compressed core and expanded shell [15,31]. Despite of the different inner facets, the elemental mapping of the nanohexagon synthesized with 0.4 ml N$_2$H$_4$ \cdot H$_2$O at 120 °C is Ni(OH)$_2$@Co(OH)$_2$ reveals a similar structure. As demonstrated in Figure 2(b), the nanohexagons all have Ni(OH)$_2$ cores and Co(OH)$_2$ shells, so the structure can be described as Ni(OH)$_2$@Co(OH)$_2$. The only difference is that the wall of the nanohexagon with inner hexagon rotated 30° with respect to the outer one becomes thicker to meet the rotation requirement between them. However, the smallest distance in the rotated nanohexagon can be as small as that of the parallel one.

Based on the above characterization, a possible growth mechanism for the evolution from Co$_9$SiNi$_{11}$O$_{33}$ (OH)$_2$ nanoplates to facet-selective competitive growth and capacitance property, Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.01.006.
hollow nanohexagons with the variation of the amount of reducing agent or reaction temperature may be proposed. Both internal crystal factors and external factors, such as the additives [32], reaction time [5,33] and reaction temperature [34-36] should be considered.

The formation of core-shell Ni(OH)$_2$@Co(OH)$_2$ nanohexagons can be divided into three steps: (I) formation of Co(OH)$_2$/Ni(OH)$_2$ nuclei, (II) formation of Co$_{0.9}$Ni$_{0.1}$(OH)$_2$ nanoplates and (III) formation of Ni(OH)$_2$@Co(OH)$_2$ nanohexagons. The reaction process in steps II and III can be described as the following equations:

\[
\begin{align*}
0.9\text{CoCl}_2 &- 6\text{H}_2\text{O} + 0.1\text{NiCl}_2 - 6\text{H}_2\text{O} + 2\text{NaOH} = \text{Co}_{0.9}\text{Ni}_{0.1}\text{(OH)}_2 + 12\text{H}_2\text{O} + 2\text{NaCl} \quad (1) \\
\text{Co}_{0.9}\text{Ni}_{0.1}(\text{OH})_2 + 0.5\text{xNiH}_2 &\text{O} - \text{H}_2\text{O} = \text{Co} + 0.1\text{Ni}(\text{OH})_2[@(0.9-x)] \text{Co(OH)}_2 + 0.5\text{xNi}_2\text{O}_3 + 2.5\text{xH}_2\text{O} \quad (0 \leq x \leq 0.9) \\
\end{align*}
\]

\(x\) is the fraction of Co ions in the precursors.

In formation step II, the Co-Ni hydroxide nanoplate tends to grow along the [001] zone axis to form hexagonal structure. In step III, facet-selective reaction begins from the center of the hexagonal nanoplate to form the hollow nanohexagon. The formation of the nanohexagons is schematically illustrated in Figure 3.

In the current synthesis system, N$_2$H$_4$+H$_2$O acts as a strong reducing agent. Co/Ni hydroxide tends to be reacted first, as expressed by Eq. (1). Since Co/Ni hydroxide has a hexagonal brucite structure (Figure 3(a)), it can form thermodynamically stable hexagonal thin sheets built an n intrinsic lamellar structure, as shown in Figure 3(b). Unlike the reported synthesis of Ni(OH)$_2$ and Co(OH)$_2$ nanoplates, [14] in which Co ions were added after the formation of Ni(OH)$_2$, mixed Ni ions and Co ions were added before the introduction of any other reactant in our case. SEM and TEM investigations indicate that the reaction occurs when the temperature exceeds 120°C. In this step, hexagonal Co$_{0.9}$Ni$_{0.1}$(OH)$_2$ nanoplates with a homogeneous distribution of Ni and Co were formed.

Previous reports indicated that a higher density of imperfections, such as surface roughness, [35] planar defects, [36] and a high surface tension, [38] exist near the center of the nanoplates. The imperfections reduce the dissolution energy of the nanocrystals, and thus a higher dissolution rate is possible in the center of the nanoplates (Figure 3(c)). With the addition of reducing agent, the nanoplate begins to dissolve from the center according to Eq. (2). Then nanoscale holes will form near the center of the nanoplates, as shown in Figure 3(c). The nanoscale holes will connect to form a big hole. With prolonged reaction time, the hole becomes gradually larger and finally results in the formation of the nanohexagon. The observed hexagonal holes in the products reveals that the facet-selected growth dominates.

As expressed in Eq. (2), Co$^{2+}$ is more easily to grow from the hydroxide than Ni$^{2+}$. During the reaction, the Co$_{0.9}$Ni$_{0.1}$(OH)$_2$ precursor was reduced to metallic Co and a Ni(OH)$_2$ core formed in the center. With the reaction proceed, the content of Ni$^{2+}$ in the precursor decreased. In the end the Ni$^{2+}$ in the precursor was exhausted and Co(OH)$_2$ shell was formed. Such element distribution has been confirmed by EFTEM analysis.

Previous reports [28] indicated that the bonds between certain ions and [110] facets of a hexagonal Fe$_2$O$_3$ would be strengthened at increased temperature. In our case, when the reaction temperature was increased from 120°C to 180°C, the bond between the ions and [110] facets of Ni(OH)$_2$ is more strengthened than that between the ions and [100] facets at the stabilization period, which result in the formation of hexagon terminated with six equivalent [100] facets. It should also be noted that in this case, the stress resulting from the lattice difference of Ni(OH)$_2$ and Co(OH)$_2$ may be minimized in the Ni(OH)$_2$@Co(OH)$_2$ hollow nanohexagons. As shown in Figure 3(d), the stress observed from the contrast in the HRTEM image of the nanohexagons is relaxed.

The electrochemistry of the Ni(OH)$_2$@Co(OH)$_2$ nanohexagons has also been investigated. As shown in Figure 4, cyclic voltammetry (CV) and chronopotentiometry (CP) experiments were performed. The working electrode was prepared by mixing Ni(OH)$_2$@Co(OH)$_2$ hollow nanohexagons...
(synthesized with 0.4 ml N2H4∙H2O at 120 °C), carbon black and polytetrafluoroethylene in a weight ratio of 7:2:1 and pressing the mixture into a nickel foam. As shown in Figure 4(a), the cyclic voltammogram consist of two pairs of redox couples. The CV curves have changed in different scanning rates. The reduction peaks P1 (−0.02 V) and P2 (+0.229 V) and oxidation peaks P3 (+0.053 V) and P4 (+0.319 V) vs Ag/AgCl can be distinguished out. The shape of the CV curve in Figure 4(a) is quite different to that of a double layer capacitor, which indicates that the capacitance characteristics of these two pairs of redox couples are governed by Faradaic reactions [39]. In anodic process, Co2+ shift to Co3+ and Co4+ step by step, and in cathodic process, the Co4+ shifts to Co2+. The redox peaks, P1 and P3, can be attributed to the valence state changes between Co2+ and Co3+, which can be described by the following equation:

\[ \text{Co(OH)}_2 + \text{OH}^- \rightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \]  

Another couple of redox peaks, P2 and P4 in Figure 4 can be attributed to the changes between Co3+ and Co4+, which can be described as:

\[ \text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \]  

In our nanostructure, the Ni(OH)₂ shell should also be considered in the redox reaction, [38], [39] which can be described as

\[ \text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \]  

The redox potentials between Ni2⁺ and Ni3⁺ are close to those between Co3+ and Co4⁺ (P2 and P4). Their coupling makes the P2 and P4 peaks in Figure 4(a) pronounced. Specific capacitance can be calculated from the CV curves in Figure 4(a) using the following formula:

\[ C_v = \frac{\int I \, dt}{m \Delta V} \]  

where \( I \) is the current density, \( dt \) is the time differential, \( m \) is the mass of electroactive material and \( \Delta V \) is the range of potential window. The average specific capacitance of the nanohexagons is calculated to be ~302 F/g at a scanning rate of 5 mV/s. At higher scanning rate, the average specific capacitance is found to decrease exponentially (Figure 4(c)), indicating incomplete charging at higher scanning rate. [40] Figure 4(b) demonstrates the chronopotentiometric behavior of the nanohexagons electrode between −0.1 V and +0.40 V at various current densities, as indicated, in 6 M KOH electrolyte. The shape of the CP curves mainly shows its capacitive characteristic, which corresponds with the CV curves.

The specific capacitance of the nanohexagons can also be obtained by chronopotentiometric experiment. It can be calculated by the following equation:

\[ C_p = \frac{I \Delta t}{m \Delta V} \]  

where \( I \) is the constant charge/discharge current, \( m \) is the mass of electroactive material, \( \Delta t \) is the total discharge time and \( \Delta V \) is the range of the potential window during discharge. Figure 4(b) depicts the chronopotentiometric spectra of the synthesized nanohexagons at current densities of 0.3 A/g, 0.5 A/g and 1 A/g. The corresponding specific capacitances are calculated to be 369 F/g,
The value of the specific capacitance at higher current density (1 A/g) is found to be significantly smaller than those at lower current densities (0.3 A/g and 0.5 A/g), indicating incomplete charging during the process. If you compare the specific capacitance (312 F/g) at current density of 1 A/g using chronopotentiometric measurement with that (302 F/g) obtained from CV measurement at scanning rate of 5 mV/s, you can found that they have similar values, indicating similar charging performance in these two experiments. Moreover, the similarity of the values at lower current densities (0.3 A/g and 0.5 A/g) indicate almost complete charging performance during these processes. Then the value measured at current density of 0.3 A/g using chronopotentiometric measurement can represent the specific capacitance of the synthesized hollow nanohexagons.

As the specific capacitance of the material is greatly influenced by its specific area [41,42], a BET (Brunauer–Emmett–Teller) measurement was taken to measure the specific surface area of the synthesized nanohexagons. The obtained specific surface area of 23.3 m²/g is found to be only little higher than the theoretical one (~21.2 m²/g) calculated from the observed geometry by SEM and TEM, revealing excellent smooth surfaces of the synthesized nanohexagons. Then the area specific capacitance (C²Α²/C) of Ni(OH)₂@Co(OH)₂ nanohexagons can be calculated to be ~15.8 F/m², which is comparable to the value of Ni(OH)₂ (16.9 F/m²) [43] and about three times of the value of Co(OH)₂ (~5.4 F/m²) [42]. The result indicates the synthesized Ni(OH)₂@Co(OH)₂ nanohexagons can keep high specific capacitance, which may be attributed to the synergy effect in the core@shell structure.

The cycling performance of supercapacitor using hollow nanohexagon was examined in 6M KOH electrolyte at current density of 1 A g⁻¹ and the result is depicted in Figure 4(c). It can be found that the nanohexagons exhibit extraordinary stability in KOH electrolyte solution. After 2500 cycles, the specific capacitance (~358 F/g) still remains over 95% of the maximum capacitance. The electrochemical impedance spectroscopy (EIS) analysis measurement was taken and corresponding Nyquist plot is shown in Figure 4(d). In the high frequency area, the intersection of the curve at real part Z’ indicates the bulk resistance of the electrochemical system, and the semicircle displays the charge-transfer process along the working electrode-electrolyte interface. The result indicates that the hollow nanohexagon has excellent charge transfer properties.
property compared with other Co(OH)$_2$ or Ni(OH)$_2$ nanostructures. The charge transfer resistance (1.48 Ω) of the synthesized Ni(OH)$_2$@Co(OH)$_2$ nanohexagons is only about 12% of the Ni-doped Co(OH)$_2$/ITO nanowires (12.8 Ω). [44] In low frequency area, the slope of the curve shows the Warburg impedance which represents the electrolyte diffusion in the electrode and proton diffusion in the nanohexagons. The slope of the straight line in the low frequency region is larger than that of the 45° straight line, indicating typical capacitor behavior [45].

Appendix. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jnanoen.2014.01.006.

References


Q2 Uncited references

[25], [26], [27], [37].

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