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# Synthesis and characterization of flower-like $\beta$ -Ni(OH)<sub>2</sub> nanoarchitectures

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#### Abstract

Flower-like Ni(OH)<sub>2</sub> nanoarchitectures have been synthesized through a one-step mild hydrothermal reaction with the aid of ethylenediamine in NiCl<sub>2</sub> aqueous solution. The flower with the size of several micrometers in diameter is composed of the ultra-thin nanosheets of several nanometers in thickness. It was found the ethylenediamine is vital to the formation of the flower-like nanoarchitectures. The influence of the concentration of the ethylenediamine and the reaction temperature on the formation of the flowers was analyzed and the formation mechanism of the flowers was proposed. Such flower-like  $\beta$ -Ni(OH)<sub>2</sub> nanoarchitectures will find potential applications in the fields, such as electrode, or will be used as a starting material to produce NiO, which is widely used in the magnetic, catalysts, sensor and electrochromic devices.

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Keywords: Ni(OH)2; Nanoarchitectures; Hydrothermal synthesis; Nanosheet

# 1. Introduction

Nickel-based secondary alkaline batteries have been extensively used in industry and daily life [1,2]. The fabrication of  $\beta$ -Ni(OH)<sub>2</sub> with high electric conductivity and high proton diffusion ability is essential and a great challenge in order to improve the performance of these batteries. It has been reported that the nanostructured nickel electrodes with high specific surface area will speed proton diffusion, and thus have an improved electrochemical performance [3].

The  $\beta$ -Ni(OH)<sub>2</sub> with different shapes has been fabricated, such as tubes [4] and rods [5] by template synthesis, nanoribbon by hydrothermal treating [6], stacks of pancakes by a chemical method [7], hollow spheres by a simple solution chemistry method [8], and sheet-like geometry by the hydrothermal method [9–11]. The growth of flower-like  $\beta$ -Ni(OH)<sub>2</sub> nanostructures from the alkali solution of nickel dimethylglyoximate [12], from the

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hydrothermal hydrolysis of the nickel(II) complex solution of macrocycle polyamine [13] or from a water-in-oil reverse micelle/microemulsion system [14] also has been reported. But one-step simple fabrication of flower-like  $\beta$ -Ni(OH)<sub>2</sub> active material with high surface area remains a considerable challenge. To optimize the functional properties of the nanostructures for electrochemical applications, self-assembly method has been indispensable. At present, considerable efforts, such as wet chemical routes, solid liquid-phase arc-discharge, electrochemical method and vapor-phase evaporation, have been dedicated to the design of various nanoarchitectures [15–21], which undergo the special dynamics processes with different formation mechanisms, such as, Ostwald ripening [17,18], Kirkendall effect [19], and self-assembly of nanoscale blocks through hydrophobic interactions [20] or "oriented attachment" [21]. However, the full knowledge and precise control of the self-assemble process are still difficult.

In this paper, we report the one-step simple hydrothermal synthesis of flower-like  $\beta$ -Ni(OH)<sub>2</sub> nanoarchitecture with the aid of ethylenediamine in NiCl<sub>2</sub> aqueous solution.

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# 2. Experimental

### 2.1. Preparation of the sample

All chemicals were purchased and used without further purification. In a typical preparation of the  $\beta$ -Ni(OH)<sub>2</sub> nanoarchitectures, 0.5 g of NiCl<sub>2</sub> · 2H<sub>2</sub>O was dissolved in 30 mL of deionized water. Then 1.0 mL of ethylenediamine (en) was added drop by drop under constant stirring until the solution became blue and homogeneous. For easy morphology observations, the Si substrates were put directly inside the reaction container. Then the mixture was kept in oven in an ordinary glass jar at 90 °C for 12 h. Finally, the products and substrates were washed with deionized water several times to remove any residuals and then dried at 75 °C for 1 h.

# 2.2. Analyses of the sample

X-ray diffraction (XRD) was performed on the Philips X'Pert using Cu $K\alpha$  line. The morphology and microstructure were examined using field emission scanning electron microscopy (FESEM, Sirion 200) and transmission electron microscopy (TEM H-800 and HRTEM JEOL-2010). The nitrogen adsorption–desorption isotherm was measured on an Omnisorp 100CX.

# 3. Results and discussion

# 3.1. Characterization of flower-like $\beta$ -Ni(OH)<sub>2</sub> nanoarchitectures

Fig. 1 shows the XRD pattern of the products on Si substrate. All the diffraction peaks can be indexed as  $\beta$ -Ni(OH)<sub>2</sub> phase with cell constants of a = 3.125 and c = 4.660, which are consistent with the standard values (JCPDS card 74-2075). No diffraction peaks corresponding to other phases are observed. According to Scherrer's formula, the length of the crystalline domain along the



Fig. 1. XRD pattern of nickel hydroxide prepared at 90  $^{\circ}$ C for 12 h and that from the JCPDS card 74-2075.

*c*-axis ( $L_{001}$ ) is evaluated at 0.465 nm and that along the (110) direction ( $L_{110}$ ) equals 0.27 nm.

Fig. 2 shows the FESEM images of the products on Si substrate. One can see that the as-prepared sample consists of a large quantity of fairly uniform particles with the average size of about 2  $\mu$ m in diameter (Fig. 2a). The highmagnification FESEM images (Fig. 2b–d) reveal that all the  $\beta$ -Ni(OH)<sub>2</sub> particles have flower-like morphology. The flower is composed of many nanosheets with thickness of several nanometers, and some small nanosheets random situate in the center of the flower and some large nanosheets surround these small ones. The nanosheets grow perpendicularly to the surface of Si substrate and intersect with each other.

Fig. 3 shows the TEM images of the flowers from Si substrate. Si substrate was used only for easy morphology observations. In fact, flower-like nanoarchitectures were also formed on other substrates. One can see that the thickness of the nanosheet gradually changes from edge to center being thick in center (Fig. 3a). The lattice fringes can be clearly seen in the HRTEM image of the tip zone of a single nanosheet with the electron beam parallel to the surface of the nanosheet (Fig. 3b). The spacing between the neighboring fringes is about 0.46 nm, belonging to the (0001) crystal planes of  $\beta$ -Ni(OH)<sub>2</sub>, which is in good agreement with the XRD results. The average thickness of a single nanosheet was found to be about 2.81 nm. The brim of the nanosheet is of good transparency to the electron beam (Fig. 3c), and the corresponding HRTEM image (Fig. 3d) shows that the fringe spacing is about 0.27 nm, corresponding to the  $(0 \ 1 \ \overline{1} \ 0)$  crystal planes of  $\beta$ -Ni(OH)<sub>2</sub>, which is in accordance with XRD results.



Fig. 2. FESEM images of the Ni(OH)<sub>2</sub> flowers prepared at 90  $^{\circ}$ C for 12h at different magnifications.



Fig. 3. Morphologies of the Ni(OH)<sub>2</sub> flowers prepared at 90 °C for 12 h: (a) TEM image of an individual flower, (b) HRTEM image of the tip region of a nanosheet with the electron beam parallel to the surface of a nanosheet, (c) a single nanosheet and corresponding SAED and (d) corresponding HRTEM image of a nanosheet with the electron beam perpendicular to the surface of the nanosheet.

The selected area electron diffraction (SAED) pattern shown in the inset in Fig. 3c also reveals the hexagonal structure of the  $\beta$ -Ni(OH)<sub>2</sub>. The results indicate that the nanosheet grows within the (0001) plane and some of the nanosheets observed in Fig. 2 are ultra-thin and easily assemble up.

It was found that the concentration of the ethylenediamine and reaction temperature both affect the formation of the flower-like  $\beta$ -Ni(OH)<sub>2</sub>. When the concentration of the ethylenediamine is higher than 2 mL, no  $\beta$ -Ni(OH)<sub>2</sub> was formed except Ni film. It is worth noting that the Ni film only formed on the silicon substrate, and nothing was formed when used Cu, Ni, Au, stainless steel, glass and  $ZrO_2$  substrates. The origin of these phenomena is not clear right now. It might be due to the activation of Si substrate by ethylenediamine. When the reaction temperature increased to  $120 \,^{\circ}$ C (in autoclave), the size of the  $\beta$ -Ni(OH)<sub>2</sub> flower increases to about 5 µm in diameter, and the number of nanosheet composed of the flower increases (see Fig. 4a and b). When the concentration of ethylenediamine was reduced to 0.5 mL, no size change of the  $\beta$ -Ni(OH)<sub>2</sub> flower was observed, but the nanosheet composed of the flower decreased (Fig. 4c), and when the concentration of ethylenediamine was further decreased to 0.2 mL, no flower except very large nanosheet was formed (see Fig. 4d). These results indicated that high reaction temperature and high ethylenediamine concentration can speed the nucleation and growth of  $\beta$ -Ni(OH)<sub>2</sub> flower. It was found



Fig. 4. FESEM images of the Ni(OH)<sub>2</sub> prepared at 120 °C with (a and b) 1.0 mL, (c) 0.5 mL and (d) 0.2 mL ethylenediamine in a Teflon-lined autoclave for 6 h.



Fig. 5.  $N_2$  adsorption-desorption isotherm of the  $Ni(OH)_2$  flowers. The inset is a schematic illustration of the thickness calculation of the  $Ni(OH)_2$  nanosheets.

that when ethylenediamine was replaced by ammonia and CTAB, or water was replaced by alcohol and ethylene glycol, no  $\beta$ -Ni(OH)<sub>2</sub> flower was formed [9–11].

# 3.2. Specific surface area and thickness of nanosheet

The N<sub>2</sub> adsorption–desorption isotherms of the  $\beta$ -Ni(OH)<sub>2</sub> flowers at different relative pressures are shown in Fig. 5. It is found that the specific surface area of Ni(OH)<sub>2</sub> flowers is about 182 m<sup>2</sup>/g calculated by the Brunauer–Emmett–Teller (BET) method, which is higher than that of  $114 \text{ m}^2/\text{g}$  previously reported for nickel hydroxide power [22]. Specific surface area is defined as the accessible area of solid surface per unit mass of materials. Assuming the contact area between the nanosheets and side area of the nanosheets are very small and can be ignored comparing with the surface area of the nanosheets, in this case the specific surface area  $(S_0)$  can be described as  $S_0 = 2S/m$ , where S is the single surface area of nanosheets and m is the mass of the nanosheets, as shown in the inset in Fig. 5. From the relation  $m = \rho V = \rho Sd$ , here m is the mass of the sample,  $\rho$  the mass density and d the thickness of the nanosheet, we have  $S_0 = 2S/m = 2S/\rho Sd = 2/\rho d$ , and thus we get  $d = 2/(\rho S_0)$ . Using the data  $S_0 = 182 \text{ m}^2/\text{g}$  and  $\rho = 3.97 \text{ g/cm}^3$ , we finally get the average thickness of the nanosheet d = 2.76 nm, which almost equals the results obtained from TEM. This result also proved that this method can effectively solve the average thickness of the flexible and ultra-thin nanosheets, which is generally difficult to be observed directly from FESEM and TEM. It is worth noting that the flower-like  $\beta$ -Ni(OH)<sub>2</sub> has a tap density of about  $2.72 \text{ g/cm}^3$ , which is higher than the minimum requirement for commercial material (2.2 g/cm<sup>3</sup>), and thus the flower-like  $\beta$ -Ni(OH)<sub>2</sub> will be expected to be used as positive electrode material for rechargeable batteries.

### 3.3. Formation mechanism of $\beta$ -Ni(OH)<sub>2</sub> flower

To study the formation mechanism of the flower-like  $\beta$ -Ni(OH)<sub>2</sub> nanoarchitectures, some of the Si substrates were taken out at different reaction times. After reaction at 120 °C for 0.5 h, the nanosheets perpendicular to Si substrate were formed (see Fig. 6a). The number and the size of the nanosheets increase with time, and after reaction for 1.5 h, the  $\beta$ -Ni(OH)<sub>2</sub> flower was formed (see Fig. 6b). The observation of the morphology below the flower after reaction for 6 h, as shown in Fig. 4a, clearly indicates that the flower is formed on the dispersive nanosheets.

From above results, a formation mechanism of the flower-like nanoarchitectures can be proposed. It was reported that the ethylenediamine is known to be a very



Fig. 6. FESEM images of the layer of  $Ni(OH)_2$  nanosheets hydrothermal synthesis with solution 1 in a Teflon-lined autoclave at 120 °C for (a) 0.5 h, and (b) 1.5 h.

good complexing agent [23,24] and the amide is easy to absorb on the surface of Si substrate [25,26]. At first, NiCl<sub>2</sub> · 2H<sub>2</sub>O would combine with deionized water to get intermediate products such as hydrated nickel cation named  $[Ni(H_2O)_6]^{2+}$  in solution. The rate of replacement of bound water in nickel complexes can be greatly affected by ligands coordinated to the nickel. As the number of nitrogen coordinated to the nickel increases, the rate of exchange of water by amine increases, and the other intermediate product such as the trisethylenediamine complexes of nickel(II) named [Ni(en)<sub>3</sub>]<sup>2+</sup> was formed [27–29] and the whole mixed solution became blue. With increasing temperature, the complexes reacted with water to form nanosheets on Si substrate, and as the reaction continued, the nanosheets assembled to Ni(OH)<sub>2</sub> flowers, as shown schematically in Fig. 7. The chemical reactions can be described as follows:

$$Ni^{2+} + 6H_2O \rightarrow [Ni(H_2O)_6]^{2+},$$
 (1)

$$[Ni(H_2O)_6]^{2+} + 3en \rightarrow [Ni(en)_3]^{2+} + 6H_2O,$$
(2)

$$[Ni(en)_3]^{2+} + 3H_2O \rightarrow Ni(OH)_2 + 2[H_2NCH_2CH_2NH_3]^{2+} + en.$$
(3)

As is known, in hydrotalcite-like compounds, the alkaline layered hydroxide has a hexagonal close packing of hydroxyl ions, where each divalent metal ion (e.g.,  $M^{\alpha} = Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ni^{2+}$ ) is octahedron sharing their edges to form 2D brucite-like sheets which then stack upon one another to form a layered solid via various interlayer chemical interactions [30,31]. In general, under normal precipitation condition, such compounds easily present the thin sheet-like crystallite morphology with the sheet surface perpendicular to the *c*-axis of crystal. It is believed that the formation of the flower composed of many nanosheets depends not only on the type of the metal hydroxide but on the existence of ethylenediamine as well. During the reaction, the ethylenediamine not only acts as the complex regent but also plays a key role in the formation of the flower. Because of the ethylenediamine, the Ni(OH)<sub>2</sub> nanosheet becomes very flexible [29], and can be wrinkled and bent, which will help nanosheets connect with each other and leads the formation of flower. In the initial growth stage, the interfacial energy between the nuclei and Si substrate is minimum when the lowest energy plane of



Fig. 7. Schematic illustration of the formation mechanism of the Ni(OH)<sub>2</sub> flowers.

the nuclei faces parallel to the substrate surface, the  $Ni(OH)_2$  nuclei grow within their (001) plane parallel to the substrate, and thus the nuclei are randomly packed with an instantaneous process on the substrate. As the reaction continues, the secondary nucleation is much more preferential on the Ni(OH)<sub>2</sub> particle surface than on the substrate surface due to the fact that the nucleus/particle interfacial energy has a minimum value. In this case, the newly formed nucleus is attached onto the surface of the Ni(OH)<sub>2</sub> particles. Since the concentration of the nickel complexes is kept lower around the growing crystals near the substrate, the growth continues in the direction of the bulk solution. The subsequent nucleation grows preferentially on the surface of the already grown particles. In this case, there is no preferential growth direction until the growing crystals come into contact with each other. As a hydrotalcite-like compound, the Ni(OH)<sub>2</sub> can easily form a sheet-like particle [30,31]. Then the Ni(OH)<sub>2</sub> particles assemble and form flowers [32]. Such flower-like nanoarchitectures with high specific surface area will find potential applications in the fields, such as electrode, or can be used as a starting material to produce NiO used in magnetic, catalysts, sensor and electrochromic devices [33,34].

### 4. Conclusion

The flower-like  $\beta$ -Ni(OH)<sub>2</sub> nanoarchitectures have been synthesized by hydrothermal synthesis with the aid of ethylenediamine in NiCl<sub>2</sub> aqueous solution. The flower with the size of several micrometers is composed of many nanosheets. The nanosheet grows within the (0001) planes. The flowers have a specific surface area of about  $182 \text{ m}^2/\text{g}$ , and the average thickness of a single  $\beta$ -Ni(OH)<sub>2</sub> nanosheet is about 2.8 nm. It was found the ethylenediamine plays an important role in the formation Ni(OH)<sub>2</sub> nanoarchitecture, and no flower is formed when it is higher than 2 mL. It was considered that the nuclei/Si substrate and nucleus/ $\beta$ -Ni(OH)<sub>2</sub> particle interfacial energies are controlling factors in the formation of the nanosheets and assembling of the flowers. The flowers with high specific surface area are promising positive-electrode materials for alkaline rechargeable batteries or can be used as a starting material to produce NiO nanostructure that is widely used in the catalysts, sensor and electrochromic devices.

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