



A room temperature solution-phase method to synthesize β -Ni(OH)₂ nanoneedles

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ABSTRACT

A simple room temperature solution-phase method has been employed to synthesize β -Ni(OH)₂ nanoneedles in the presence of a suitable cationic surfactant cetyltrimethylammonium bromide for the first time. The chemical composition and morphology of the as-prepared β -Ni(OH)₂ nanoneedles were characterized by X-ray powder diffraction and transmission electron microscopy. The effect of surfactant and NH₄OH on the morphology and size of β -Ni(OH)₂ nanoparticles was discussed in detail. The growth mechanism of the as-synthesized nanoneedles was discussed based on the experimental results. The results indicate that the binding between CTAB and β -Ni(OH)₂ crystal nuclei inhibits crystal growth randomly and favors needle-like single crystal growth with their preferred facets.

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1. Introduction

Ni(OH)₂ is a very important cathode material in Ni-based alkaline rechargeable batteries that are the most widely used in many applications [1]. The previous studies reported that Ni(OH)₂ with hexagonal layered structure has two polymorphs with α - and β -form [2]. The hexagonal brucite-type structure β -Ni(OH)₂ has Ni(OH)₂ layers stacking along the *c*-axis with an interlayer distance of 4.6 Å. It is well known that the β -Ni(OH)₂ is often used as the active material in positive electrodes due to its stability in strong alkaline electrolyte and excellent reversibility when charged to β -NiOOH [3]. It has been reported that the crystal structure, size and the morphology of Ni(OH)₂ have significant influence on its overall performance [4,5]. In addition, recent work also indicated that the nanostructured Ni(OH)₂ could significantly improve the capacity of the positive electrode [6]. Therefore, considerable attention has been focused on the synthesis of Ni(OH)₂ nanostructures with well-controlled morphology and size. Until now, several methods have been employed to prepare Ni(OH)₂ nanostructures with various morphologies, including nanorod [7], nanowire [8], nanotube [9], nanoribbon [10], and nanosheet [11,12]. However, a hydrothermal condition was usually required to form Ni(OH)₂ in these methods. Herein, we report on the synthesis of β -Ni(OH)₂ nanoneedles by a simple room temperature solution-phase method in the presence of surfactant hexadecyl trimethyl ammonium bromide (CTAB) for the first time.

2. Experimental procedure

All of the chemical reagents used in the experiments were of analytical grade as received without further purification. In a typical Ni(OH)₂ nanoparticle synthesis, 0.95 g NiCl₂·6H₂O was dissolved in 30 ml of 4.5 mM CTAB solution. Then 30 ml of 0.25 M NH₄OH solution was added dropwise into the NiCl₂ solution, finally 6 ml of 0.5 M NaOH solution was added dropwise into the above solution, under constant stirring. The green precipitates were collected and washed with distilled water, and then dried in a vacuum oven at 80 °C for 12 h.

The powder XRD analysis was performed using a Rigaku (Japan) Dmax X-ray diffractometer with graphite monochromatized Cu K α radiation ($\lambda = 0.154178$ nm), employing a scanning rate of 0.02°s^{-1} in the 2θ range from 10 to 90° . Transmission electron microscopy (TEM) images were taken with a HITACHI H-700 transmission electron microscope, using an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1a shows a typical XRD pattern of Ni(OH)₂ nanoparticles obtained in the presence of surfactant CTAB (4.5 mM) with NH₄OH concentration of 0.25 M. All the diffraction peaks can be indexed to hexagonal cell of brucite-type β -Ni(OH)₂ with lattice constants $a = 3.127$ and $c = 4.606$ Å (JCPDS No: 14-0117). The XRD pattern also demonstrates that the (001) peak has a stronger intensity than the other peaks, indicating that the (001) plane maybe is a preferential growth direction. One also can find a weak shoulder peak of the (001) plane. This weak shoulder peak at about 23° in 2θ angle can be indexed to (20 $\bar{1}$) plane of α -Ni(OH)₂ (JCPDF No. 41-1424), indicating that there are a few α -Ni(OH)₂ in the samples. Fig. 1b and c shows the typical TEM images of β -Ni(OH)₂ nanoparticles. These images show that a large quantity of needle-shaped nanoparticles with a narrow size distribution was achieved. The average diameter is about

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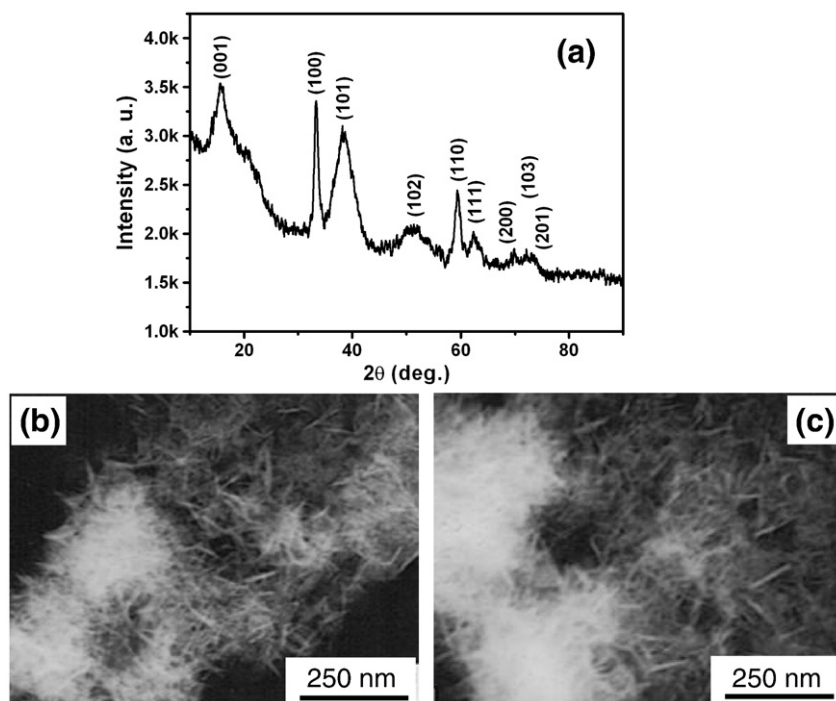


Fig. 1. (a) XRD pattern, (b) and (c) TEM images of the β -Ni(OH)₂ nanoneedles obtained by precipitation of NiCl₂ aqueous solution with NH₄OH (0.25 M) and NaOH (0.5 M) alkaline solution in the presence of surfactant CTAB (4.5 mM) at room temperature.

9 nm and the length is up to about 200 nm of the as-prepared β -Ni(OH)₂ nanoneedles.

The experiments were conducted to investigate the influence of NH₄OH concentration on the phase, morphology and size of Ni(OH)₂ nanoparticles. Fig. 2a shows the typical XRD pattern of Ni(OH)₂ nanoparticles obtained with NH₄OH concentration of 2.5 M, while keeping other experimental conditions constant. All the diffraction peaks can be indexed to a hexagonal cell of brucite-type β -Ni(OH)₂

(JCPDS No: 14-0117). Again, at about 23° in 2θ angle a weak shoulder peak coming from α -Ni(OH)₂ was observed. Fig. 2b and c shows the typical TEM images of the as-prepared β -Ni(OH)₂ nanoparticles, clearly indicating that a large quantity of needle-like β -Ni(OH)₂ nanoparticles was obtained. The average diameter of the needle-like β -Ni(OH)₂ nanoparticles is about 20 nm, which is larger than that of the β -Ni(OH)₂ nanoneedles prepared with lower NH₄OH concentration (0.25 M) as presented in Fig. 1b and c.

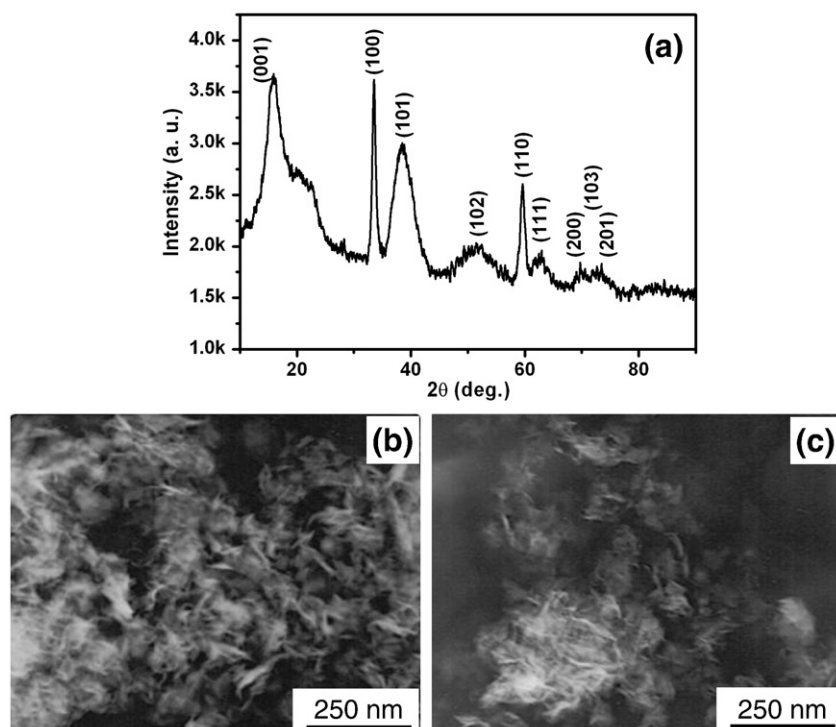


Fig. 2. (a) XRD pattern, (b) and (c) TEM images of the β -Ni(OH)₂ nanoneedles obtained with NH₄OH (2.5 M), keeping other experimental conditions constant.

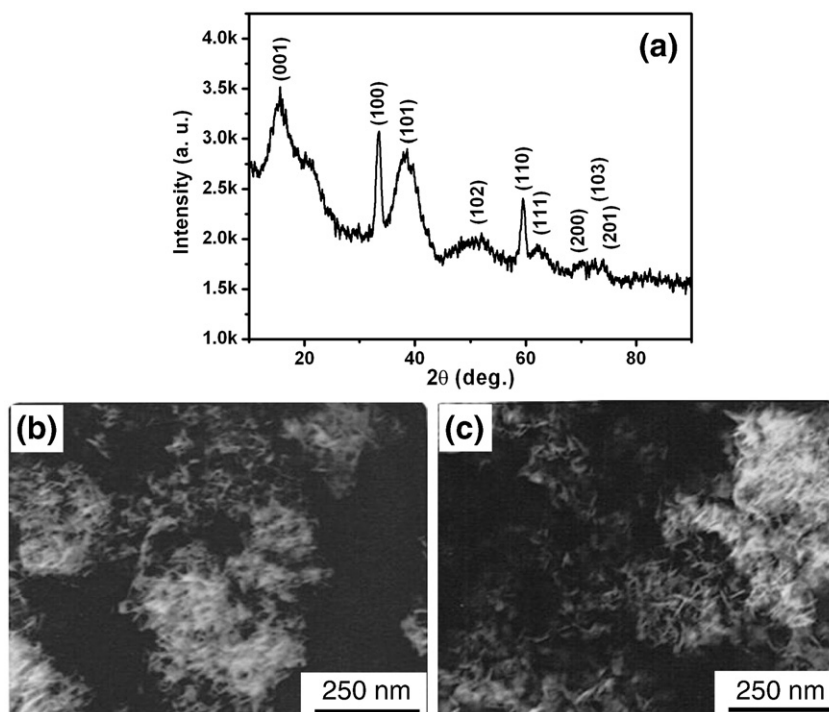


Fig. 3. (a) XRD pattern, (b) and (c) TEM images of the β -Ni(OH)₂ nanoneedles obtained with NH₄OH (12.5 M), keeping other experimental conditions constant.

In order to further understand the influence of NH₄OH concentration on morphology and size of Ni(OH)₂ nanoparticles, the experiments were conducted with higher NH₄OH concentration of 12.5 M. Fig. 3a shows the typical XRD pattern of the as-prepared Ni(OH)₂ nanoparticles with NH₄OH concentration of 12.5 M. Again, all the diffraction peaks can be indexed to hexagonal cell of brucite-type β -Ni(OH)₂ (JCPDS No: 14-0117). However, at about 23° in 2 θ angle a weak shoulder peak coming from α -Ni(OH)₂ was also observed. The TEM images shown in Fig. 3b and c indicate that the as-prepared β -Ni(OH)₂ nanostructures are also composed of nanoneedles with smaller average diameter and shorter length, compared with samples prepared with lower NH₄OH concentrations (0.25 and 2.5 M) as shown in panels b and c of Figs. 1 and 2. Thus, the experiments clearly indicate that the concentration of NH₄OH has a obvious effect on the size of β -Ni(OH)₂ nanoparticles.

It is well known that the pH value of a solution has a great effect on the nucleation and growth of the crystals. When the experiments were carried out at low NH₄OH concentration (0.25 M), the OH[−] concentration in the solution is relatively low, resulting a low nucleation rate of β -Ni(OH)₂ nanoparticles that is beneficial to the fixation of CTAB molecules on

the β -Ni(OH)₂ nanoparticles. The nanoparticles fixed by CTAB molecules coalesce with adjacent ones by decreasing their surface energy to form nanoneedles with longer length as shown in Fig. 1b and c. With the increase of NH₄OH concentration to 2.5 M, although the OH[−] concentration is not high, there are some extra OH[−] that can insert into (001) planes of β -Ni(OH)₂, resulting in the enlargement of (001) plane distance and thus increase in diameter of β -Ni(OH)₂ nanoneedles as seen in Fig. 2b and c. However, when NH₄OH concentration further increases to 12.5 M, the OH[−] concentration is high, leading to a high nucleation rate of nanoparticles. A high nucleation rate of β -Ni(OH)₂ will decrease the diameter and length of nanoneedles as presented in Fig. 3b and c. Similar results were observed in the growth of β -Ni(OH)₂ nanorods [13].

Next, we investigated the influence of surfactant on the phase, morphology and size of Ni(OH)₂ nanoparticles. Fig. 4a shows the typical XRD pattern of Ni(OH)₂ nanoparticles prepared in the presence of 4.5 mM poly(vinyl pyrrolidone) (PVP, Mw $\approx$ 30 000, the concentration was calculated in terms of the repeating unit), while keeping the other experimental conditions constant. All the diffraction peaks of the XRD pattern can also be indexed to the hexagonal cell of brucite-type β -Ni(OH)₂ (JCPDS No: 14-0117). However, the

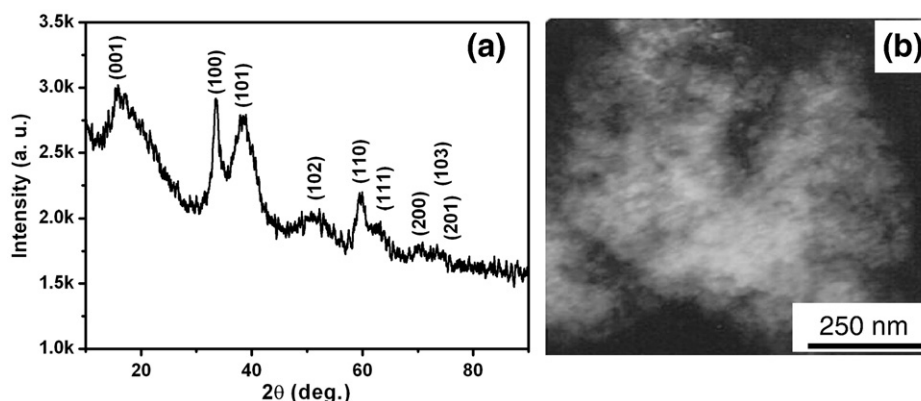


Fig. 4. (a) XRD pattern and (b) TEM images of the β -Ni(OH)₂ nanoparticles obtained by precipitation of NiCl₂ aqueous solution with NH₄OH (0.25 M) and NaOH (0.5 M) alkaline solution in the presence of PVP (Mw $\approx$ 30 000, the concentration was calculated in terms of the repeating unit) at room temperature.

TEM images as shown in Fig. 4b indicate that the spherical nanoparticles, instead of nanoneedles, were obtained in the presence of PVP. Thus, surfactant CTAB plays a key role for the formation of β -Ni(OH)₂ nanoneedles.

On the basis of the above experimental results and analysis, we propose a possible growth process of β -Ni(OH)₂ nanoneedles that may mainly comprise two processes: 1) formation of β -Ni(OH)₂ crystal nuclei and 2) subsequent crystal growth from these nuclei to form β -Ni(OH)₂ nanoneedles. In the first growth process, Ni²⁺ in NH₄OH aqueous solution first reacts with NH₃ to form a relatively stable complex, [Ni(NH₃)₆]²⁺, due to its strong affinity to Ni²⁺ at room temperature. Afterwards, the [Ni(NH₃)₆]²⁺ further reacts with OH⁻ mainly coming from NaOH to form β -Ni(OH)₂ crystal nuclei. During the crystal growth process, the formation of [Ni(NH₃)₆]²⁺ complex would sharply decreased the free Ni²⁺ concentration in the solution, resulting in a relatively low reaction rate of Ni²⁺ ions. A slow reaction rate causes the separation of nucleation and growth steps leading to the formation of the crystalline β -Ni(OH)₂ crystal nuclei firstly. In the second growth process, the newly formed β -Ni(OH)₂ crystal nuclei, which are fixed by CTAB molecules, coalesce with adjacent ones, decreasing their surface energy and enhancing needle-like nanoparticle production. The results indicate that the binding between CTAB and β -Ni(OH)₂ crystal nuclei inhibits crystal growth randomly and favors needle-like single crystal growth with their preferred facets. This can be confirmed by experimental results that the spherical β -Ni(OH)₂ nanoparticles, instead of nanoneedles, were formed in the presence of PVP as presented in TEM images of Fig. 4b.

4. Conclusion

In summary, crystalline β -Ni(OH)₂ nanoneedles were synthesized by a facile room temperature solution-phase route. Chemical composition,

morphology and size of the nanoneedles were characterized by XRD and TEM. The results indicate that the surfactant CTAB plays an important role for the formation of β -Ni(OH)₂ nanoneedles. A possible growth mechanism has been proposed to illustrate the growth of β -Ni(OH)₂ nanoneedles on the basis of experimental results and analysis.

Acknowledgments

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