In situ growth of Ni(OH)$_2$ nanoflakes on Ni foam as binder-free electrode for electrochemical pseudocapacitor

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Abstract. In this work, a facile one-step hydrothermal method has been adopted to prepare Ni(OH)$_2$ directly deposited on Ni foam in ultrapure water. The phase structure and morphology composition of the in-situ grown Ni(OH)$_2$/Ni foam (NF) were analyzed using an X-ray diffractometer (XRD) and scanning electron microscope with energy dispersive spectroscopy (SEM-EDS). The results indicate that Ni(OH)$_2$ nanoflakes uniformly in-situ grown on Ni foam construct a hierarchical structure, which in favour of full infiltration with electrolyte, and also beneficial to the reliable stability of the Ni(OH)$_2$/NF electrode. While being employed as an integrated binder-free electrode for electrochemical pseudocapacitor, the Ni(OH)$_2$/NF shows a high specific capacitance of 1470.8 F/g at 2.5 A/g in 2 M KOH. This work demonstrates a highly-simple and cost-effect approach for designing binder-free electrodes for high-performance electrochemical pseudocapacitor.

1. Introduction
As the rapid consumption of fossil fuels and the increasing seriousness of environmental pollution, and to seek renewable clean energy and the effective utilization of energy is imminent [1]. Energy storage, an intermediate step to the versatile, clean, and efficient use of energy, has received more and more attention and research interest in the world. Supercapacitors (SCs), as the most promising electrochemical energy storage components, possess the merits of high power density, fast charging-discharging, long service life, good cycle stability and environment friendly [2-3]. On the basis of working mechanism, SCs can be classified into two types: one is electric double layer capacitors (EDLCs) which store charge through the electric double layer formed between the electrode and the electrolyte, and the other is electrochemical pseudocapacitors which store charge by reversible Faraday reaction. Generally, the Faradaic pseudocapacitors have a higher capacity than EDLCs [4-5]. However, it remains a huge challenge to develop pseudocapacitor electrode materials with desirable electrochemical performance.

As a typical electrode material, Ni(OH)$_2$ has drawn wide attention because of its high theoretical capacitance value, low cost and environmentally friendly [6]. Diversified preparation methods have been adopted to prepare Ni(OH)$_2$ including chemical bath method [7], electrodeposition [8] and hydrothermal synthesis [9]. In these methods, Ni(OH)$_2$ materials were usually synthesized requiring nickel salts and binders or conductors to fabricate electrodes. The usage of extra additives always causes residual impurities and then leads to the decrease of electrochemical performance. Besides, the
use of nickel salts usually results in a weakening of the bonding force between Ni(OH)₂ material and the collector, which affects the electrochemical stability [10]. Very recently, Kaidong Xia [11] et al have fabricated Ni(OH)₂ flakes-Ni foam as binder-free electrode using an in situ electrochemical corrosion method in pure distilled water under hydrothermal condition. But the facile synthesis of Ni(OH)₂ nanoflakes by one-step hydrothermal method and their application to SCs have not been investigated.

In this paper, we have developed the facile one-step hydrothermal method to prepare Ni(OH)₂ directly deposited on Ni foam in ultrapure water without any other nickel sources and additives. The results revealed that the as-prepared Ni(OH)₂ nanoflakes uniformly in-situ grown on Ni foam construct a hierarchical structure. Moreover, the electrochemical measurements showed that the integrated Ni(OH)₂/NF binder-free electrode exhibited a high specific capacitance of 1470.8 F/g at 2.5 A/g in 2 M KOH electrolyte.

2. Experimental

Figure 1 reveals the synthesis procedure of the binder-free Ni(OH)₂/NF electrode. In a typical hydrothermal experiment, firstly, Ni foam (size 1 × 2 cm²) was ultrasonically cleaned with ethoanol, 1 M dilute hydrochloric acid and deionized water for 15 min, respectively. And then, the Ni foam was transferred into a Telfon-lined autoclave with ultrapure water. The temperature was maintained at 180°C for 8 h. After the experiment, the as-prepared sample was dried at 60°C for 12 h.

![Figure 1 Schematic diagram of synthesis process for in-situ Ni(OH)₂ nanoflakes.](image)

The crystalline structure of Ni(OH)₂/NF was characterized by X-ray diffraction (XRD, Bruker D8 Focus) using Cu Kα radiation (λ = 1.5406 Å) at 20 mA and 40 kV. The surface morphologies and chemical compositions of the Ni(OH)₂/NF sample were characterized using scanning electron microscopy (SEM, FEI QUANTA 200F) with energy disperse spectroscopy (EDS).

Electrochemical tests were done at an electrochemical workstation (CHI660E). In the testing process, Ni(OH)₂/NF, Hg/HgO, and platinum foil were used as the working electrode, reference electrode, and counter electrode, respectively. The electrochemical performance of Ni(OH)₂/NF electrode was evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in 2 M KOH electrolyte at room temperature. The frequencies of EIS were set from 0.01 Hz to 100 KHz under the open circuit potential with 5 mV sinusoidal perturbation.
3. Results and Discussion

The XRD pattern of Ni(OH)$_2$/NF prepared at 180°C for 8 h is shown in Figure 2a. The results indicate that the Ni(OH)$_2$ exhibits a hexagonal β-Ni(OH)$_2$ crystal structure (JCPDS no.14-0117). Besides the three XRD peaks for the Ni foam, no other peaks are present. This confirms the purity of the product and suggests the in situ growth of β-Ni(OH)$_2$ on Ni foam. The morphologies of Ni(OH)$_2$ on Ni foam are investigated by SEM and the corresponding images were displayed in Figure 2b-e. It is clear that the as-prepared Ni(OH)$_2$ nanoflakes uniformly in-situ grown on Ni foam construct a hierarchical structure. The β-Ni(OH)$_2$ nanoflakes are of mean size of about 800 nm and a thickness of about 50 nm (Figure 2e).

Figure 2 XRD pattern (a) and SEM images of Ni(OH)$_2$/NF with different magnifications.

In order to study further of the chemical composition, EDS was adopted to measure chemical states of the surface elements and the mapping spectrum were showed in Figure 3a-d. As expected, the Ni(OH)$_2$ nanoflakes are uniformly grown on the NF surface and firmly attached to the NF. The EDS element mapping (Figure 3a, 3c-d) appears that the elements of Ni and O are homogeneously distributed on Ni(OH)$_2$ nanoflakes, which in accordance with the results from the XRD pattern and SEM images (Figure 2). Compared with the Ni foam where scraped off Ni(OH)$_2$ (Figure 3b-d, green arrow), the selected element distribution (Figure 3e, yellow square) confirms the in situ growth of Ni(OH)$_2$ on Ni foam.

Electrochemical properties of the as-prepared Ni(OH)$_2$/NF integrated electrode were investigated using a three-electrode system in 2 M KOH electrolyte. Figure 4a reveals the CV curves of the Ni(OH)$_2$/NF electrode at different scan rates from 5 mV/s to 25 mV/s in a potential window of 0-0.7V. The CV curves possess a pair of redox peaks, ascribing to the typical Faraday behavior [12-13]. Besides, the oxidation and reduction peaks demonstrate symmetric and remain the shapes unchanged with the increasing scan rates, indicating excellent reversible electrochemical performance and pseudo-capacitance. The GCD curves of the Ni(OH)$_2$/NF integrated electrode at potential window of 0-0.6 V with different current densities are presented in Figure 4b. As can be seen from the figure, corresponding to the redox reaction, all the GCD curves show the discharge potential platform. The
homologous Faraday redox reaction is as follows according to equation (1), and the mass specific capacitance of the Ni(OH)\(_2\)/NF electrode is calculated on the basis of equation (2) [14-15]:

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

(1)

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

(2)

As plotted in Figure 4c, the specific capacity was calculated to be 1470.83 F/g, 1366.67 F/g, 1333.33 F/g, and 1200.30 F/g under a current density of 2.5 A/g, 4 A/g, 5 A/g, and 10 A/g, respectively.

As illustrated in Figure 1, schematic diagram for charge transfer path of the in-situ Ni(OH)\(_2\) integrated electrode, the excellent electrochemical properties are attributed to the high capacitance of Ni(OH)\(_2\) and the unique hierarchical nanoflakes directly grown on Ni foam, which in favour of full infiltration with electrolyte, and also beneficial to the reliable stability of the Ni(OH)\(_2\)/NF electrode during the charge-discharge process. Furthermore, the electrochemical kinetic processes between electrode and electrolyte were evaluated and analyzed by EIS. As revealed in Figure 4d, the Nyquist plot of the Ni(OH)\(_2\)/NF electrode is consist of a semi-circular at high frequency region and an inclined straight line at low frequency region. The small resistance of Ni(OH)\(_2\)/NF electrode can be observed with \( R_s = 0.59 \, \Omega \). This further confirms the effect of in situ growth of Ni(OH)\(_2\) based binder-free electrode.

Figure 4 CV (a) and GCD (b) curves, areal capacitance (c), and Nyquist plot (d) of the Ni(OH)\(_2\)/NF electrode.

4. Conclusions
Ni(OH)\(_2\) nanoflakes were successfully prepared by a facile one-step hydrothermal method directly grown on Ni foam in ultrapure water without any other nickel sources and additives. Owing to the in situ growth of Ni(OH)\(_2\) nanoflakes construct a hierarchical structure, while being employed as binder-free electrode for electrochemical pseudocapacitor, the Ni(OH)\(_2\)/NF integrated electrode exhibits a high specific capacitance of 1470.8 F/g at 2.5 A/g in alkaline electrolyte.
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