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Original Research Paper

# Synthesis of periodically stacked 2D composite of α-Ni$(OH)_2$ monolayer and reduced graphene oxide as electrode material for high performance supercapacitor

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In this work, we report a facile approach for the synthesis of a periodically stacked 2D composite of α-Ni$(OH)_2$ monolayer and reduced graphene oxide (rGO) single layer as electrode material for application in supercapacitors. The self-assembly of ordered nanostructure was spontaneously driven by the electrostatic attraction between positively charged α-Ni$(OH)_2$ monolayers and negatively charged graphene oxide (GO) single layers. The produced intermediate was reduced in $H_2$ atmosphere to obtain target composite. The periodic 2D nanostructure provided the fast transfer channel for electrolyte ions between layers and minimized the diffusion process of electrolyte ions. The key for the composite is that the alternately intercalated rGO in the multilayered composite greatly reduced the internal resistance originating from α-Ni$(OH)_2$. Consequently, the composite presented high electrochemical performance for the supercapacitor application.

## 1. Introduction

The increasing demand for energy and growing concern about global warming/air pollution have stimulated tremendous research effort on energy storage/conversion devices with advanced characteristics such as high-power, low cost, and environment-friendly. Supercapacitors are considered promising candidates for such devices due to their much higher power density output and faster charging process than batteries [1–6]. There are two general categories of supercapacitors: (1) electrical double layer capacitors (EDLCs) based on the quick adsorption/desorption of ions at the interface of carbon-based electrode materials; (2) redox capacitors depending on the faradaic reactions of electrode materials including metal hydroxide, oxide and polymers. Of the two categories of supercapacitors, the latter is more interesting and also frustrating due to its significant advantages such as much higher energy density and its disadvantages such as lower power density. Lots of challenges are still remained in redox capacitors, especially for their electrode materials.

Multilayer-structured Ni$(OH)_2$ as an electrode material for redox capacitors is particularly attractive due to its much higher theoretical specific capacitance than other materials. There have been numerous works focusing on building various nanostructures to eliminate the inherent disadvantages of Ni$(OH)_2$ [6–9]. The major disadvantage of Ni$(OH)_2$ is its low electric conductivity close to insulator [10], which results in the poor high-rate capability as well as the low power output of supercapacitors. To solve this issue, a popular strategy is to compound Ni$(OH)_2$ with electrically conductive carbon-based materials to improve its conductivity [11–16]. Among various carbon-based materials, two-dimensional graphene possessing excellent conductivity has been considered an ideal material for achieving this aim [5,17,18]. It was reported that graphene-compounded Ni$(OH)_2$ presented enhanced electrochemical performance because of the improved electron transfer originating from graphene.

The most heavily employed route for fabricating Ni$(OH)_2$/-graphene composite utilizes in-situ reaction of nickel salt in the suspension of graphene or GO, forming product with random distribution of individual components as shown in Fig. 1a. The randomly distributed graphene is capable of lowing the contact resistance between Ni$(OH)_2$ and current collector. However, it does not help solving the inherent issue of Ni$(OH)_2$: high internal resistance originating from its multilayered structure. As a result, the improvement of electrochemical performance contributed by graphene is quite limited, especially the high rate performance. Based on the electrochemical mechanism of redox capacitors, we designed a structure as shown in Fig. 1b for the Ni$(OH)_2$/graphene

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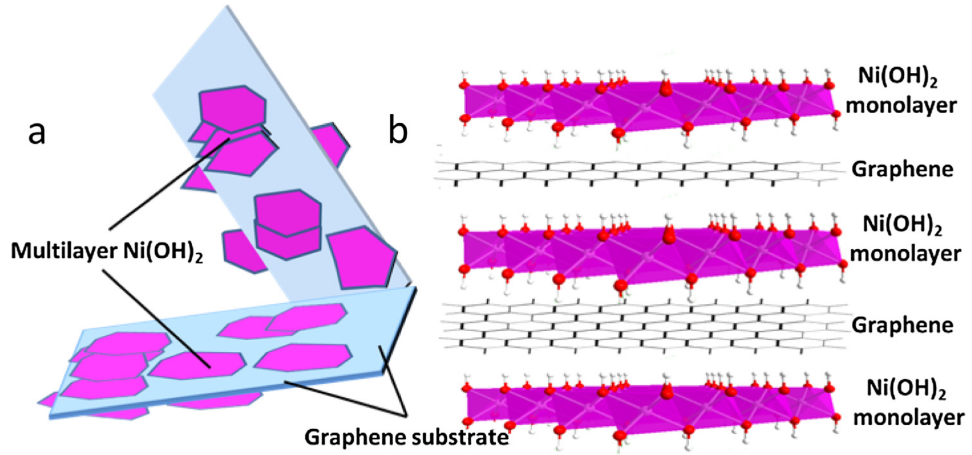

**Fig. 1.** Schematic illustration for the randomly assembled composite of $Ni(OH)_2$ and graphene (a) and the periodically stacked 2D composite of graphene single atomic layers and $Ni(OH)_2$ monolayers (b).

composite according to the structure characteristics of $Ni(OH)_2$ and graphene. The composite presents microstructure with periodically stacked graphene single atomic layers and $Ni(OH)_2$ monolayers extracted from their multilayered parent. This ordered structure would be an ideal structural solution to greatly reduce the internal resistance of $Ni(OH)_2$ because of the homogeneous and intimate contact between graphene and $Ni(OH)_2$.

The difficulty in building the proposed structure of composite is the lack of driving force for the ordered assembly of individual components. In this work, we proposed a facile approach utilizing the driving force originating from electrostatic attraction between $Ni(OH)_2$ monolayers and GO single layers to self-assemble the ordered nanostructure. The intercalated graphene between the single layers of $\alpha$-$Ni(OH)_2$ significantly lowered the internal resistance of $\alpha$-$Ni(OH)_2$, and also prevented the irreversibly restacking or agglomeration of $\alpha$-$Ni(OH)_2$, leading to the great promotion of electrochemical performance.

## 2. Experimental

### 2.1. Materials

Graphite powder, potassium permanganate ($KMnO_4$, ≥99.5%), sodium nitrate ($NaNO_3$, ≥99.0%), sulfuric acid ($H_2SO_4$, 95–98%), hydrochloric acid (HCl, 36–38%), and hydrogen peroxide ($H_2O_2$, ≥30%), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, ≥98.0%), formamide ($CH_3NO$, ≥99.5%) and morpholine ($C_4H_9NO$, ≥98.5%) were purchased from Aladdin. All materials were used without further treatment.

### 2.2. Synthesis of GO and rGO

Graphene oxide was synthesized according to a modified Hummers' method [19]. In a typical procedure, 0.5 g graphite and 0.5 g $NaNO_3$ were added into 23 mL $H_2SO_4$. The mixture was stirred in an ice bath, forming a suspension. Then, 3.0 g $KMnO_4$ was gradually added to this suspension under magnetic stirring. After that, the suspension was placed in ultrasonic bath and irradiated for 20 min at room temperature. Then, the suspension was diluted by 40 mL distilled water. Finally, 100 mL distilled water and 3 mL $H_2O_2$ were added to the suspension in order to reduce the residual permanganate to soluble manganese ions. During this process, the colour of the suspension was changed from dark brown to yellow. The product was collected through the sequent steps of vacuum filtration, washing with 250 mL HCl aqueous solution (36–38% HCl/distilled water = 1:10), and another washing with distilled water. The wet product was freeze-dried for 12 h to obtain dried GO. Its yield (the weight of GO divided by the weight of graphite powder) was ~84%. Part of GO was reduced in a tube furnace at 200 °C for 1 h under $Ar_2/H_2$ atmosphere to obtain rGO.

### 2.3. Synthesis of α-$Ni(OH)_2$ monolayers

$\alpha$-$Ni(OH)_2$ monolayers were synthesized by grinding a mixture of 0.5 g $Ni(NO_3)_2{\cdot}6H_2O$ and 1 mL morpholine in a mortar at room temperature. After grinding for 5 min, a sticky paste was formed. The paste was aged in a 50-mL beaker sealed by parafilm at room temperature for 4 h. Then, a transparent colloidal solution of $\alpha$-$Ni(OH)_2$ monolayers was formed by dispersing the aged paste in 50 mL formamide under ultrasonification for 5 min. In order to determine the yield, $\alpha$-$Ni(OH)_2$ was separated from another aged paste and washed by water with centrifugation, and dried at 80 °C in an oven. The calculated yield of $\alpha$-$Ni(OH)_2$ was ~86% based on the weight of dried $\alpha$-$Ni(OH)_2$.

### 2.4. Synthesis of α-$Ni(OH)_2$ monolayer/rGO composite

50 mg GO was dispersed in 200 mL distilled water by ultrasound, forming a transparent yellowish colloidal solution. Then, the GO colloidal solution was mixed with the 50-mL colloidal solution of $\alpha$-$Ni(OH)_2$ monolayer. Precipitate was produced immediately after mixing the two colloidal solutions. Product was collected by the sequent steps of filtrating suspension, washing with water, and freeze-drying. After drying, the product was reduced in a tube furnace at 200 °C for 1 h in $Ar_2/H_2$ atmosphere.

### 2.5. Characterization

The structure of samples was measured with a Shimadzu LabX XRD-6100 diffractometer using Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å). Thermogravimetric analyses on samples were conducted on a NETZSCH STA409PC thermal analyser using heating rate of 10 °C $min^{-1}$ from 18 to 1000 °C under air ambience. JEOL JEM-1400 transmission electron microscope (TEM) and Hitachi S-4800 cold-cathode field-emission scanning electron microscope (FE-SEM) were used to observe the morphology of samples. The element analysis on the samples were carried out with EDAX Genesis 400 X-ray microanalyzer attached on the Hitachi S-4800 FE-SEM. The outline and thickness of samples were measured by Bruker MultiMode 8 atomic force microscope (AFM) in tapping mode.

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