



# Ni(OH)<sub>2</sub> nanoflakes electrodeposited on Ni foam-supported vertically oriented graphene nanosheets for application in asymmetric supercapacitors

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## ABSTRACT

Binderless Ni(OH)<sub>2</sub> nanoflakes grown on Ni foam (NF)-supported vertically oriented graphene nanosheets (V-GNs) has been fabricated as a positive electrode material for asymmetric supercapacitor (ASC), coupled with activated carbon (AC) as a counter electrode material. The introduction of V-GNs leads to dense growth of nanocrystalline β-Ni(OH)<sub>2</sub> that is confirmed by X-ray diffraction, transmission electron microscopic and scanning electron microscopic analyses. The electrochemical performances of the Ni(OH)<sub>2</sub>/GNs/NF electrode are characterized by cyclic voltammetry and charge–discharge tests, which exhibit high specific capacitance of 2215 F g<sup>-1</sup> at a scan current density of 2.3 A g<sup>-1</sup>, enhanced cycling stability and high rate capability. The Ni(OH)<sub>2</sub>/GNs/NF-AC-based ASC can achieve a cell voltage of 1.4 V and a specific energy density of 11.11 Wh kg<sup>-1</sup> at 0.5 mA cm<sup>-2</sup> with a nearly 100% coulombic efficiency at room temperature.

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## 1. Introduction

Supercapacitors are energy storage devices that bridge function for the power/energy gap between conventional capacitors and batteries, having high power density, short charging time, and long cycling life and shelf life [1,2]. The currently commercial supercapacitors are symmetric electric double layer capacitors (EDLCs) based on high surface area carbon materials in the two electrodes in aqueous or organic electrolytes. EDLCs can achieve high specific capacitance (above 100 F g<sup>-1</sup>) and fast response time (~1 s), but the storage energy in the range of 2–10 Wh kg<sup>-1</sup> is not sufficient for applications where both high energy storage capacity and fast charge-discharge ability are important including plug-in electric vehicles [3,4]. Asymmetric supercapacitor (ASC), also known as asymmetric hybrid energy storage cell [5,6], consisting of electrochemical active materials in a positive electrode different from that of in a negative electrode, are being developed since the first report in 1999 of the exceeded 10 Wh kg<sup>-1</sup> found in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-activated carbon (AC) [4]. Pseudocapacitive metal oxides have been studied as the positive electrode in the past and the greater energy density than that of EDLCs is achieved, but relatively low cycling stability and poor conductivity often result in low performance of ASC [7].

Ni(OH)<sub>2</sub> is an attractive pseudocapacitive material in view of its high theoretical specific capacitance, well-defined redox transitions, and low cost [8–11]. However, poor conductivity of block Ni(OH)<sub>2</sub> always limits fast electron transfer required for a high power density. To overcome this shortcoming, conventional method introduces carbon black, graphite, or metal powders as conductive additives into the Ni(OH)<sub>2</sub> electrode. However, the additive carbon always encounters fast oxidation in the electrochemical window of some pseudocapacitive materials, such as Ni(OH)<sub>2</sub> at potential of 0.45–0.5 V vs SHE (standard hydrogen electrode) in KOH electrolyte [12]. It is known that hexagonal Ni(OH)<sub>2</sub> has two most common forms of polymorphs: α and β, both showing a promising electrode material for the supercapacitors [13,14]. The α-form Ni(OH)<sub>2</sub> with large interlayer spacing has been accepted to exhibit superior electrochemical properties compared to the β-form [15]. Yang et al. electrodeposited α-Ni(OH)<sub>2</sub> with desirable 3D and porous structure on a Ni foam (NF) as electrode material, and an ultrahigh capacitance (3152 F g<sup>-1</sup> at a current density of 4 A g<sup>-1</sup>) was obtained [10]. Tang et al. produced α-Ni(OH)<sub>2</sub> nanostructure on the NF by a chemical bath deposition process. The electrode exhibited a high specific capacitance of 2820 F g<sup>-1</sup> [16]. However, α-Ni(OH)<sub>2</sub> is a metastable phase and would transform to β-Ni(OH)<sub>2</sub> during charge-discharge process, especially at relatively low discharge current densities, which leads to significant capacitance decay and thereby unstable performance of the supercapacitors [8,15]. In addition, the flaking

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off of  $\text{Ni}(\text{OH})_2$  during cycles has been proved to be another reason of low cycling stability [10,16]. Therefore, an effective synthesis methodology and new strategies are required for  $\text{Ni}(\text{OH})_2$ -based electrodes to develop high performance of supercapacitors with enhanced lifetime.

Incorporation of highly electrical conductive materials into metal oxide/hydroxide [16,17], synthesis of binary metal hydroxide [18,19], and forming spinel nickel cobaltite ( $\text{NiCo}_2\text{O}_4$ ) [20] have been reported to possess higher electrochemical activity than the corresponding single oxide/hydroxide. In addition, using carbon materials as support for growth of nanostructured active materials is one of the strategies to increase performance of ASC [4,9,21–26]. Recently, Gong et al. grew nanoflake  $\alpha$ - $\text{Ni}(\text{OH})_2$  on NF-supported carbon nanotube (CNT) by a chemical bath deposition [16]. They demonstrated an improved specific capacitance and high areal mass loading of  $\text{Ni}(\text{OH})_2$  due to the introduction of CNT. Wei et al. employed a fast, facile, and cost-effective microwave heating method to produce flowerlike  $\alpha$ - $\text{Ni}(\text{OH})_2$  on graphene sheets for applications in a high-voltage (0–1.6 V) ASC [23]. Single-crystalline  $\beta$ - $\text{Ni}(\text{OH})_2$  directly grown on NF-supported graphene-based materials was found a high cycling stability reported by Wang et al., and the high specific capacitance and rate capability was related to the high-quality graphene sheets with low oxidation [9]. However, results from Yang et al. exhibited that functional groups such as hydroxyl, epoxy, carboxyl and carbonyl groups at the basal planes and edges of graphene oxide provided sites for growth of  $\alpha$ - $\text{Ni}(\text{OH})_2$  and therefore a good electrochemical stability [27]. Very recently, Zhang et al. reported a reduced graphene oxide (RGO) and  $\text{Ni}(\text{OH})_2$  composite synthesized by electrophoretic deposition [28]. An advanced pseudocapacitance performances was obtained due to the synergetic effect of the RGO and  $\text{Ni}(\text{OH})_2$ . In our previous work,  $\alpha$ - $\text{Ni}(\text{OH})_2$  was electrodeposited on NF-supported horizontally oriented graphene [21]. The graphene film was found to be crucial to enhance the stability of the  $\alpha$ - $\text{Ni}(\text{OH})_2$ . Comparatively, vertically oriented graphene nanosheets (V-GNs) are a class of networks of ‘graphitic’ platelets, also referred to as carbon nanowalls or nanoflakes, having lateral and vertical dimensions of 0.1 to tens of micrometers for an individual GN nanosheet and a thickness of only a few nanometers (even less than 1 nm) [29]. Compared with conventional horizontally oriented graphene, the rising interest in the application of V-GNs initially stems from their unique orientation, exposed sharp edges, non-stacking morphology, and huge surface-to-volume ratio [30]. The earliest report on the excellent filtering performance of V-GNs as electrode was made by Miller et al. in an EDLC [31]. Zhao et al. have obtained 1–7 layers of V-GNs that exhibited  $1.49 \times 10^4$  F of capacitance [32]. Recently, Zheng et al. used V-GNs as support for growth of  $\text{Co}(\text{OH})_2$  and an enhancement of cycling stability of the electrode was found [24].

In present work, we use NF-supported V-GNs as a substrate for electrodeposition of  $\text{Ni}(\text{OH})_2$ . To evaluate the capacitive performance of the composite electrode in a full-size supercapacitor system, investigation is carried out using a  $\text{Ni}(\text{OH})_2/\text{GNs}/\text{NF}$ -based anode and an AC-based cathode in 6 M KOH aqueous electrolyte, as illustrated in Fig. 1. The introduction of V-GNs exhibits an enhanced specific capacitance, large voltage window of  $\text{Ni}(\text{OH})_2/\text{GNs}/\text{NF}$ -AC-based supercapacitor with high energy densities, and longer cycling stability. To the best of our knowledge, it is the first report on nanoflake  $\beta$ - $\text{Ni}(\text{OH})_2$  electrodepositing on V-GNs and has good electrochemical performance.

## 2. Experimental

### 2.1. Synthesis of carbon nanomaterials

All chemicals were analytical grade and used as received. NF was used as a current collector and also a substrate for growth of

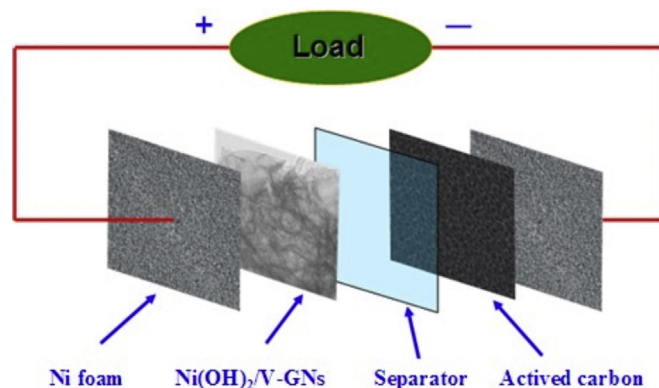


Fig. 1. Illustration of  $\text{Ni}(\text{OH})_2/\text{GNs}/\text{NF}$ -AC for ASC.

V-GNs by plasma-enhanced chemical vapor deposition (PECVD). Before putting into the PECVD reaction chamber, it was chemically cleaned with dilute hydrochloric acid, acetone, and deionized water, respectively. After that, NF was heated for 40 min in Ar atmosphere up to 800 °C. Then  $\text{CH}_4$  was immediately introduced into the chamber with a ratio of  $\text{CH}_4/\text{Ar} = 1/4$  (the flow rate is 20 and 80 sccm) at a total pressure of 4 torr, while a 200 W RF plasma was used to ignite the reaction for 10 min.

### 2.2. Electrodeposition of $\text{Ni}(\text{OH})_2$

To prepare  $\text{Ni}(\text{OH})_2$ , the electrodeposition was conducted on the as-prepared GNs/NF and NF as well, with a conventional electrolytic cell of three electrodes consisting of a saturated calomel electrode (SCE) as reference electrode, a platinum plate as counter electrode and the GNs/NF (2.0 cm  $\times$  2.0 cm) as working electrode. The electrolyte was an aqueous solution of 0.1 M  $\text{Ni}(\text{NO}_3)_2$ . The electrodeposition experiments were all carried out at a constant current until a deposition charge quantity was 0.72 C, and the reaction temperature was 45 °C. After deposition, the as-prepared electrodes were washed with water for several times.

### 2.3. Characterization

The mass of the deposited  $\text{Ni}(\text{OH})_2$  was measured to be about 0.43 mg from the mass difference before and after electrochemical deposition by means of a micro-balance (Sartorius BT125D) with an accuracy of 0.01 mg. The crystal structure of the  $\text{Ni}(\text{OH})_2$  was examined by a Rigaku wide-angle X-ray diffractometer using  $\text{Cu K}\alpha$  radiation source at a wavelength of 0.1541 nm and selected area electron diffraction (SAED) pattern operated by transmission electron microscopy (TEM) (Hitachi H-8100). TEM operated at 160 kV and high resolution (HR) TEM (JOEL TEM-2010) operated at 200 kV were used to investigate the microstructure of the composite. The surface morphology and microstructure were also examined by scanning electron microscope (SEM) (JOEL JSM-6700F). Raman spectra measurement was conducted on a T64000 (Horiba) spectrometer, with a 514.5 nm  $\text{Ar}^+$  laser excitation, a laser power of 0.107 W and an accumulation time of 30 s. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo ESCALAB 250 spectrometer with an Al K $\alpha$  radiation source to analyze the chemical bonding state and composition of the samples. Electrochemical measurements were carried out via a computer-controlled potentiostat (CHI760D or PARSTAT2273) with a three-electrode cell containing a 1 M KOH solution, a SCE as reference electrode and a Pt foil as counter electrode.

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