



Regular Article

High electrochemical performance of hybrid cobalt oxyhydroxide/nickel foam graphene

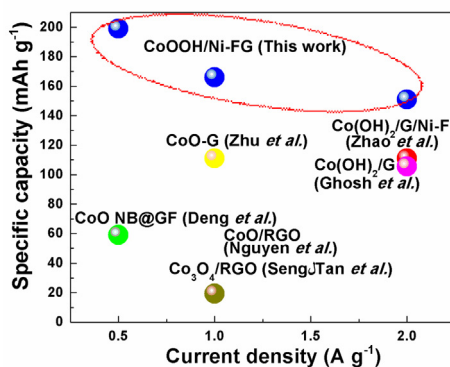
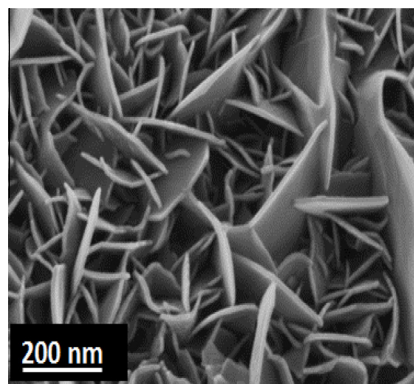


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GRAPHICAL ABSTRACT

A mesoporous nanosheets of cobalt oxyhydroxide (CoOOH) synthesized on nickel foam graphene (Ni-FG) substrate exhibited the specific capacity of 199 mA h g⁻¹ at a current density of 0.5 A g⁻¹.



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ABSTRACT

In this study, we report the in-situ hydrothermal synthesis of mesoporous nanosheets of cobalt oxyhydroxide (CoOOH) on nickel foam graphene (Ni-FG) substrate, obtained via atmospheric pressure chemical vapour deposition (AP-CVD). The produced composite were closely interlinked with Ni-FG, which enhances the synergistic effect between graphene and the metal hydroxide, CoOOH. It is motivating that the synthesized CoOOH on the Ni-FG substrate showed a homogenous coating of well-ordered intersected nanosheets with porous structure. The electrochemical properties of the material as electrode showed a maximum specific capacity of 199 mA h g⁻¹ with a capacity retention of 98% after 1000 cycling in a three electrode measurements.

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1. Introduction

Recently, research on electrode materials for supercapacitor applications has become one of the most important research topics

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in energy storage materials. Supercapacitor has received much attention due to its advantages of long cycle life, moderate specific energy density ($\sim 10 \text{ Wh kg}^{-1}$), high power density ($>10 \text{ kW kg}^{-1}$) and short charging time [1–3]. These characteristics meet the increasing demand for power tools, hybrid electric vehicles and time-dependent electric power systems for portable electronics [4]. In the supercapacitor, the electrode material plays a significant role in the electrochemical capacitive performance. In the last decades, different types of electrode materials have been used in supercapacitor including carbonaceous materials, transitional metal hydroxides/oxide and conducting polymers [1,2,5,6]. Amongst these transitional metals, hydroxides/oxides have received much attention for high-performance due to their high specific capacitances, low costs, low toxicity, great flexibility in structure and morphology [7–14].

In addition, the cobalt oxyhydroxide is an improved charge storage material due to its morphology control nature of micrometer/nanometer scale and reasonably lower material costs [15,16]. However cobalt oxyhydroxide practical capacitance is less than 200 F g^{-1} due to its low conductivity [17]. To improve the ionic transportation and electrical conductivity, various metal nanostructures and composites combined with carbon materials such as activated carbon, conducting polymers and graphene, with high surface area and high conductivity have been studied [18–22]. Among these materials, a porous and light-weight, graphene foam material (i.e. 3D structured graphene from nickel foam templates) has been studied extensively as an ideal matrix for the growth of metal nanostructures because of its high conductivity [23–26]. Different kinds of nanostructured metal hydroxides/oxides have been deposited on graphene foam (GF) electrodes for supercapacitor applications [27,28]. For instance, Zhu et al. [9] considered Cobalt oxide (CoO) nanorods cluster on three-dimensional graphene (CoO-3DG) through a facile hydrothermal method followed by heat treatment which improved electrochemical capacitive performance, Dong et al. also produced 3D graphene/ Co_3O_4 nanowire composites which demonstrated remarkable performance in supercapacitor [29], Zhao et al. synthesized $\text{Co}(\text{OH})_2$ /graphene/Ni foam nano electrodes with high cycling stability for supercapacitor [30], Shim et al. also reported 3D CO_3O_4 /graphene/nickel foam with enhanced electrochemical performance for supercapacitor [31] and Deng et al. [32] synthesized CoO composited with 3D GF through a combination of hydrothermal method and thermal treatment which exhibited a high specific capacitance, excellent rate capability, and cycling stability as electrode material.

In this study, mesoporous nanosheets of cobalt oxyhydroxide (CoOOH) were synthesized on Ni foam graphene (Ni-FG) substrate by facile two-step processes, namely, hydrothermal reaction to produce CoAl-LDH nanosheets on Ni-FG which were converted to CoOOH nanosheets on Ni-FG by alkaline etching of the Al cations in CoAl-LDH using a NaOH solution. The CoOOH/Ni-FG electrode showed the specific capacity of 95 mA h g^{-1} at 10.0 A g^{-1} with 98% capacity retention after 1000 cycles.

2. Experimental details

2.1. Graphene growth on nickel foam using AP-CVD

A Ni foam graphene substrate was synthesized by growing graphene sheets on the polycrystalline Ni foam (3D scaffold template with a macroporous structure) using atmospheric pressure chemical vapour deposition (AP-CVD). Polycrystalline Ni foam (Ni-F) (3D scaffold template with a macroporous structure) with an areal density of 420 g m^{-2} and 1.6 mm in thickness, was used as a substrate for graphene growth. A piece of Ni-F ($2 \text{ cm} \times 3 \text{ cm}$) was treated with dilute hydrochloric acid, ethanol and distilled

water to clean the surface of the foam. A cleaned Ni-F was placed at a centre of a quartz tube for graphene growth and was annealed at $1000 \text{ }^\circ\text{C}$ under Ar and H_2 gases for 60 min and graphene was synthesized from a mixture of Ar: H_2 : CH_4 (300:200:10 sccm respectively) gases at a temperature of $1000 \text{ }^\circ\text{C}$ for 10 min. Immediately after 10 min, the CH_4 flow was stopped and samples were rapidly cooled down (under Ar and H_2 gases) by pushing the quartz tube to the cooler region of the furnace. At less than $80 \text{ }^\circ\text{C}$, Ni-F graphene was off loaded from AP-CVD quartz tube. A synthesized Ni foam graphene (Ni-FG) substrate was further used for growth of CoOOH nanosheets.

2.2. CoOOH growth on Ni foam graphene (Ni-FG) using hydrothermal method

CoOOH nanosheets supported on nickel foam graphene were deduced from in-situ hydrothermally prepared CoAl-LDH on Ni-FG substrate by alkaline etching in concentrated NaOH solution as reported in Ref. [33]. A solution (pink in colour) for hydrothermal reaction was prepared by adding $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol), Al ($\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2 mmol), NH_4F (8 mmol) and $\text{CO}(\text{NH}_2)_2$ (10 mmol) in 36 mL of deionized water and stirred for 10 min, as demonstrated in Fig. 1. Ni-FG substrate was immersed into the above solution and then carefully transferred into a sealed Teflon-lined stainless-steel autoclave and kept at a temperature of $100 \text{ }^\circ\text{C}$ for 24 h (Fig. 1). After cooling of the autoclave to room temperature, the obtained CoAl-LDH coated on Ni-FG was cleaned with deionized water. Then, the CoAl-LDH coated Ni-FG was immersed in 5 mol L^{-1} NaOH for 48 h and subsequently rinsed with deionized water, followed by ethanol for 5 min using ultrasonic bath, and dried at $60 \text{ }^\circ\text{C}$ for 6 h to obtain the final product CoOOH nanosheets (shown by micrograph image in the last step of Fig. 1) on Ni-FG substrate. The weight of the CoOOH film on Ni-FG substrate was measured by weighing the Ni-FG substrate before and after hydrothermal process, and a mass loading of $\sim 5 \text{ mg cm}^{-2}$ was obtained.

3. Materials characterizations

The as-prepared Ni-FG and CoOOH film on Ni-FG were characterized by X-ray diffraction (XRD) using a XPERT-PRO diffractometer (PANalytical BV, Netherlands) with theta/2 theta geometry, operating with a Co $K\alpha$ radiation source ($\lambda = 1.789 \text{ \AA}$). The XRD spectra were acquired at a scanning rate of 0.2 s^{-1} and 2θ range

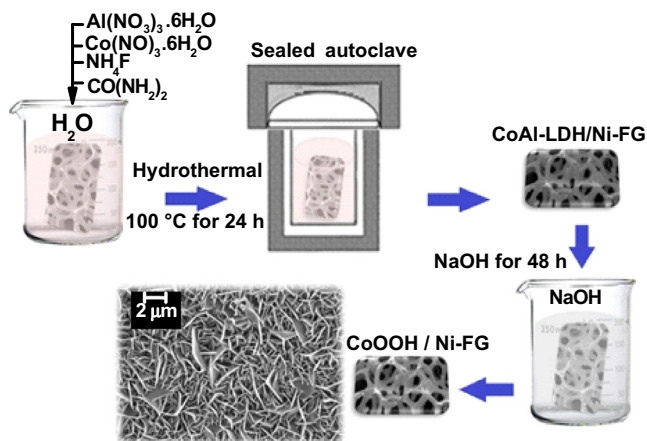


Fig. 1. A schematic view of the hydrothermal growth of CoAl-LDH on graphene synthesized on Ni foam and alkaline etching in concentrated NaOH solution which produces a mesoporous structure of CoOOH on Ni foam graphene.

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