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# One-pot methanol-mediated solvothermal synthesis of 3D porous Co-doped α-$Ni(OH)_2$/RGO nanosheets as a high-performance pseudo-capacitance electrode

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## ABSTRACT

An environment-friendly and cost-effective route has been explored to prepare three-dimensional (3D) porous Co-doped α-$Ni(OH)_2$ nanosheets vertically arranged on reduced graphene oxide (RGO) by one-pot methanol-mediated solvothermal synthesis. This process avoids the addition of any precipitating agent and oxidizing agent. Herein, methanol acts as solvent, structure-directing agent and it also can be oxidized to release $OH^-$. In addition, Co doping is considered to be an effective approach to improve the electronic conductivity and electrochemical performance for energy conversion. Thus, experiments using different doping amounts of Co are performed. The different feed molar ratios of $Co^{2+}$ to $Ni^{2+}$ are simply controlled, and the ultrathin Co-doped α-$Ni(OH)_2$/RGO nanosheets ($Co^{2+}$:$Ni^{2+}$ = 0.5:1) display the best capacitive property. The synthesized Co-doped α-$Ni(OH)_2$/RGO nanosheet electrode exhibits the highest specific capacitance of 2322 F $g^{-1}$ at current density of 1 A $g^{-1}$, outstanding rate performance of 1933 F $g^{-1}$ at 20 A $g^{-1}$, and excellent lifetime cycle with 87.9% retention level after 1000 cycles at 10 A $g^{-1}$. Moreover, an asymmetric supercapacitor is successfully manufactured with the Co-doped α-$Ni(OH)_2$/RGO as a positive electrode and activated carbon as a negative electrode. The hybrid device delivers a maximum energy density of 38.9 Wh $kg^{-1}$ and a maximum power density of 8000 W $kg^{-1}$. Our supercapacitor exhibits a remarkable cycle stability along with 88.2% specific capacitance retained over 2000 cycles at 5 A $g^{-1}$. These results may provide useful insights for fabricating high-performance electrode materials for energy storage applications.

## 1. Introduction

Supercapacitors, as novel and efficient energy alternatives, have received considerable attention because of the increasing consumption of conventional energy resources and resultant environmental deterioration [1]. These supercapacitors possess higher power density than batteries and higher energy density than conventional dielectric capacitors [2]. Thus, supercapacitors fall between the conventional energy storage systems and bridge the gap between these systems. However, the low energy density of supercapacitors hinders their practical application. To improve the unsatisfactory energy density of a supercapacitor, an electrode material with large specific capacitance ($C$) should be developed, and its working voltage ($V$) should be maximized according to the following equation, $E = 1/2\ CV^2$ [3], while high power delivery and long cycle life are maintained. Using organic electrolytes is an important approach to extend the cell voltage. However, these electrolytes usually suffer from high cost, poor ionic conductivity, and high hazardousness, compared with aqueous media. These characteristics could lead to security issues and inferior power density [4]. Thus, designing appropriate electrode materials with high specific capacitance is a better solution to improve energy density in aqueous electrolyte. Nickel hydroxide with two polymorphs (i.e., α and β) has been indicated to be the most promising electrode material because of its high theoretical capacitance, cost effectiveness, environment-friendliness, and distinct layered structure [5]. α-$Ni(OH)_2$ has attracted more attention than β-$Ni(OH)_2$, because the former has larger interlayer space rendering preferable capacitance and delivering more electrons in the redox reaction [6] However, poor electrical conductivity is the major

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bottleneck to impact rate capability and cycle life. This characteristic limits the application of high-capacity α-$Ni(OH)_2$ electrodes as a p-type semiconductor [7]. Furthermore, the aggregation of α-$Ni(OH)_2$ during preparation is another drawback which decreases the specific surface area of the active material [8]. Thus, this study is performed to increase the transfer of electrons and effectively prevent the restacking of the α-$Ni(OH)_2$ sheets.

Numerous studies have focused on improving the efficiency of electron transport by doping heterogeneous metal ions (e.g. $Al^{3+}$, $Y^{3+}$ and $Zn^{2+}$), surface modification, and the synthesis of hydroxide hybrids with various highly conductive materials [9,10]. Among these methods, introducing hetero element metal ions into the α-$Ni(OH)_2$ electrode can effectively enhance electronic conductivity because this process avoids the restriction of interfaces between α-$Ni(OH)_2$ and the introduced conducting materials. Co-doped α-$Ni(OH)_2$ can be synthesized given the similar ion sizes between two metal elements and compatibility of lattice structure [11]. Introducing Co into the structure increases free holes in the valence band, enhances the active site density via two-step reversible redox reactions, and reduces resistivity [12,13]. This process is advantageous for charge exchange and electrochemical properties. Meanwhile, doping Co to α-$Ni(OH)_2$ can considerably promote the electrochemical activity because of the synergistic effects of CoNi composite materials.

In addition to high specific capacitance, rapid transfer of electrons, and superior cycling stability properties, the effective specific surface area of electrode materials is advantageous to acquire an ideal supercapacitor [14,15]. As a new allotrope of carbon, RGO has been regarded as the appropriate support matrix for α-$Ni(OH)_2$ because of its large surface area, superior electrical conductivity, outstanding mechanical properties, and distinctive chemical stability [16,17]. Graphene-based materials have been recorded to boost electrochemical performances when used as an ideal substrate for growth of electroactive material in electronic equipment, energy storage and electrocatalysts [18,19]. Partial area of α-$Ni(OH)_2$ electrode material is not utilized because of the poor connection with the current collector resulting from low electronic conductivity. The presence of sheet-like RGO improves the utilization rate of pseudocapacitive electrode materials, remarkably contributing to the electrochemical performance. Moreover, RGO can prevent the α-$Ni(OH)_2$ flakes from agglomeration and restacking as well as promote the conductivity of the hybrid electrodes. These characteristics result in a dramatic enhancement in capacitive performance.

In recent years, various methods have been reported to synthesize the $Ni(OH)_2$ such as microwave-assisted heat treatment method [20], chemical precipitation [21], and chemical bath deposition [22]. Common additional alkali sources such as hexamine, ammonia urea and hexamethylenetetramine were used in most of these methods. In this paper, we reported a facile methanol-mediated solvothermal reaction to fabricate 3D porous Co-doped α-$Ni(OH)_2$ nanosheets perpendicular to the surface of the RGO when combined with chemical doping and RGO as structural support. The one-step synthesis route did not require expensive equipment and other alkali source, which dramatically cut down the cost and improved the synthetic efficiency. Organic solvents such as tert-butanol, ethylene glycol have attracted a great deal of attention as a directing agent for synthesis of nanomaterials [23,24]. Herein, the use of methanol helped to control the rate of crystal growth by slowly releasing $OH^-$ and promoted the slow formation of thinner and larger nanosheets. The RGO in the composite served a dual function, that is, as the template for the uniform size distributions of Co-doped α-$Ni(OH)_2$ nanosheets and as the electron transport channel. In the meantime, the α-$Ni(OH)_2$ constituents of Co-doped α-$Ni(OH)_2$ nanosheets guaranteed the enhancement of capacitive properties, because Co doping facilitated the charge transfer efficiency and high rate discharge performance. Electrochemical measurements showed that the composite exhibited an outstanding pseudocapacitive performance of 2322 F $g^{-1}$ at 1 A $g^{-1}$ and 1933 F $g^{-1}$ at 20 A $g^{-1}$ (83.2% capacitance retention from 1 A $g^{-1}$ to 20 A $g^{-1}$) and an excellent retention level (87.9% retention after 1000 cycles). Furthermore, a hybrid device was successfully fabricated and its electrochemical performance was investigated.

## 2. Experimental

### 2.1. Synthesis of 3D porous Co-doped α-$Ni(OH)_2$/RGO nanosheet electrode materials

Graphite oxide (GO) was obtained from natural graphite using a modified Hummers method previously described elsewhere [25]. The Co-doped α-$Ni(OH)_2$/RGO nanosheets were fabricated by employing one-pot methanol-mediated solvothermal synthesis. Typically, 20 mg of GO was added into 20 mL of methanol and ultrasonicated for 1 h to form a uniform dispersion. Then, a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in the dispersion, and the resultant mixed solution was ultrasonicated for 0.5 h. The homogeneous solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 12 h to allow the formation of Co-doped α-$Ni(OH)_2$/RGO (CNG) nanosheets. The resulting samples were washed several times with deionized water and dried at 80 °C for 12 h in a vacuum oven to remove the adsorbed solvents. Samples with different $Co^{2+}$ feeding molar ratios to $Ni^{2+}$, namely, 0.25:1, 0.33:1, 0.5:1, 1:1, and 2:1, were fabricated using the abovementioned process. The corresponding samples were designated as CNG 0.25:1, CNG 0.33:1, CNG 0.5:1, CNG 1:1, and CNG 2:1. These composites were investigated to determine the optimum capacitance performance. For comparison, Co-doped α-$Ni(OH)_2$ and α-$Ni(OH)_2$/RGO materials were prepared similarly, except for the absence of RGO or without Co doping contents. GO in 20 mL of methanol was transferred into a Teflon-lined autoclave for solvothermal treatment at 180 °C for 12 h to obtain RGO.

### 2.2. Characterization

The morphologies were characterized by scanning electron microscopy (SEM, FEI Nova 450 Nano) and transmission electron microscopy (TEM, Tecnai $G^2$ F30). X-ray diffraction (XRD) patterns equipped with Cu Kα radiation (0.15406 nm) to analyze the structure information of the samples was operated at a scan rate of 5° $min^{-1}$ in a scanning scope of 5°–90°. X-ray photoelectron spectroscopy (XPS) was conducted by an ESCALAB 250 X-ray photo electron spectrometer (ThermoFisher) with Al Kα X-ray source ($h\upsilon = 1486.6$ eV). Brunauer-Emmett-Teller (BET) was measured by $N_2$ adsorption-desorption isotherms from a Autosorb-iQ-C instrument. Raman spectroscopy was performed to investigate the vibrational modes of the samples using a 532 nm laser beam on a inVia Raman spectrometer.

### 2.3. Preparation of electrodes and electrochemical measurement

The working electrodes were fabricated as follows. Briefly, 80 wt % as-prepared materials, 10 wt% acetylene black, and 10 wt% polytetrafluoroethylene were ultrasonically dispersed in a small amount of anhydrous ethanol. The resulting homogeneous solution was put into an oven and dried at 80 °C for a certain time. Then, the resulting mud-like material with a few drops of anhydrous ethanol was rolled into a thin slice using a test tube. The slice was then