



Research paper

In situ fabrication of nickel based oxide on nitrogen-doped graphene for high electrochemical performance supercapacitors



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ABSTRACT

In this article, we synthesize Ni(OH)₂ homogeneous grown on nitrogen-doped graphene (Ni(OH)₂/NG), subsequently, small and uniform nickel oxide nanoparticle (NiO/NG) is also successfully obtained through tube furnace calcination method. The high specific capacitance of the NiO/NG electrode can reach to 1314.1 F/g at a charge and discharge current density of 2 A/g, meanwhile the specific capacitance of Ni(OH)₂/NG electrode is also 1350 F/g. The capacitance of NiO/NG can remain 93.7% of the maximum value after 1000 cycles, while the Ni(OH)₂/NG electrode losses 16.9% of the initial capacitance after 1000 cycles. It can be attributed to nickel hydroxide instability during charge–discharge cycles.

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1. Introduction

Intense research on alternative energy sources for energy storage and transformation has been imminent because of the increasing demand for energy and growing attention about environmental degradation [1,2]. Supercapacitors, as an energy storage device, exhibit high power capability, long cycle lifetime and fast charge and discharge rates have been applied in various fields [3,4].

Advance electrode materials for capacitors are vital to elevate electrochemical properties of supercapacitors. Recently, several transition metal hydroxides (Co(OH)₂ [5], Ni(OH)₂ [6]), metal sulfides (CoS [7], NiS [8]), metal oxides (MnO₂ [9], Co₃O₄ [10], NiO [11]) and conductive polymeric materials (polyaniline [12], polythiophene [13], polypyrrole [14]) have been used as electrochemical pseudocapacitors materials, which can enhance the capacitive performance. Among these transition metal materials and conductive polymeric materials, Ni-related electrode materials exhibit many promising characters, such as environmental compatibility, good redox reversibility, long cycle life and high theoretical specific capacitance, so they have very strong competition as electrode materials for supercapacitors [15]. Recently, many well preformed NiO and NiOH compounds have been successfully synthesized. For example, the reported coral-like NiO nanobars could exhibit 1085 F g⁻¹ at 1 A g⁻¹ [16]. Huang et al. reported that the NiO nanosheets deposited on the nickel foams can achieve 674.2 F g⁻¹ at 1 A g⁻¹ [17]. The mesoporous NiO nanoflake arrays could deliver 400 F g⁻¹ at 2 A g⁻¹ [18], as proven by the Tong group. Du et al.

reported nano-NiO flower-like microspheres with a specific capacitance of 762 F g⁻¹ at 1 A g⁻¹ [19]. Nevertheless, it still exits a difficulty to obtain higher specific surface area for nickel oxides-based pseudocapacitors due to its large particle size and serious agglomeration, which led to low electrical conductivity. In order to solve this problem, there is one attempt to grow high conductive materials on graphene nanoflakes. Because graphene nanoflakes not only possess specific properties such as carrier feature, excellent quality of electricity, but also have large surface area of metal oxide dispersed evenly. In order to further increase the active point on the surface of graphene, more and more researches have been implemented to synthesize surface modified graphene [20]. Nitrogen-doped on the graphene surface can induce a charge polarization due to the electronegativity differences between nitrogen and carbon atoms [21,22]. More importantly, nitrogen inserts into the sp² hybridized honeycomb lattice of graphene layers, which can dramatically increase the electrical conductivity and can offer strong anchoring sites for metal nanoparticles [23,24]. Chen et al. reported that the NiO nanosheets deposited on nitrogen-doped graphene can achieve 342 F g⁻¹ at 5 mV s⁻¹ [25]. Wang et al. reported NiO/NG which showed a high specific capacitance of 1225 F g⁻¹ at 2 A g⁻¹ [26].

In this work, we demonstrate a simple method and situ grown processes to synthesis small size Ni(OH)₂/NG and NiO/NG composites. The obtained two materials are used as a hybrid electrode for supercapacitor application, and their electrochemical properties are compared. The NiO/NG electrode has a higher specific capacitance and good cycle stability than Ni(OH)₂/NG electrode, which indicates that NiO/NG hybrid is a perfectly desirable material for supercapacitor applications.

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2. Experimental section

2.1. Materials

Natural flake graphite with a particle size of 150 nm was derived from Qingdao Guyu graphite Co., Ltd. NaOH, Hexamethylenetetramine ($C_6H_{12}N_4$) and Nickel(II)nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were obtained from Sinopharm Chemical Reagent Co., Ltd., China, and all reagents were employed without further purified. N,N-dimethylformamide (DMF) was also received from Sinopharm Chemical Reagent Co., Ltd., China. All solutions were using deionized water in the process of the whole experiment.

2.2. Synthesis of NG

Graphene oxide (GO) was synthesized by an improved Hummers method as reported in our previous work [27]. After removal of remaining metal ion and acid, the GO was dissolved in deionized water by ultrasonic processing for 45 min. $C_6H_{12}N_4$ was slowly added to the GO dispersion continuously stirring for 30 min, after that, the mixed solution was settled by ultrasonic processing for 30 min. To the best of my knowledge, the GO sheets bear negative charged position ($-COOH$, $-OH$) on both sides of the sheet, which has possibility adapting to positive charged ammonium ions. Therefore, with the help of electrostatic interaction, the negative charged GO could package the positive changed nitrogen, resulting in nitrogen functionalization of GO. Then the mixed solution was put into a 100 mL capacity Teflon lined stainless steel autoclaves at 180 °C for hydrothermal reaction 10 h.

The naturally cooled sample was washed with deionized water until the solution neutral and transparent. In the end, the functionalization NG was successful obtained.

2.3. Synthesis of $Ni(OH)_2/NG$

The $Ni(OH)_2/NG$ composites were prepared by solvothermal method. In our experiment, 50 mg of GO, 1.164 g of $Ni(NO_3)_2 \cdot 6H_2O$, 1.0587 g of hexamethylenetetramine (HMT) and 5 mL of DMF were added into 50 mL of deionized water with vigorous stirring until the solution blending homogeneous. Then slowly heated the suspension liquid to 80 °C. The pH of the mixture was adjusted to 8.5 by adding the $C_6H_{12}N_4$ solution drop by drop. The solution was kept at 80 °C with magnetic stirring for 10 h. In this process, $C_6H_{12}N_4$ slowly released $-OH$, which made nickel hydroxide in situ formed and well-distributed in N-doped graphene.

2.4. Synthesis of NiO/NG

NiO/NG samples were obtained by heating the prepared $Ni(OH)_2/NG$ composites at 400 °C for about 2 h in the tube furnace. The pure NiO nanoparticles were obtained by the same two-step methods without adding graphene. In ICP test, NiO concentration was 82.6%.

2.5. Preparation of working electrode

All the electrochemical measurements were performed on Autolab (CHI660D) with a three electrode system. They are working electrode, platinum plate counter electrode and saturated calomel electrode (SCE) as reference electrodes at room temperature, respectively. The working electrodes were made up by active materials (NiO/NG , $Ni(OH)_2/NG$ or NiO) at 80 wt%, vinylidene fluoride (PVDF) at 10 wt% and acetylene black at 10 wt% [28], the mixture was then stirred to form a homogeneous solution, and was deposited on the surface of nickel foam overnight. The nickel foam

was then dried at 60 °C in a vacuum drying oven for 48 h. The loads with the active material in the electrode was pressed at 15 MPa. The electrochemical representations of the active materials were tested by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) to investigate the electrochemical performance in 6.0 M KOH solution. The average capacitance of the electrode was calculated from the GCD curves using the following equation:

$$C_s = I\Delta t / (m\Delta V)$$

where C_s is the specific capacitance ($F g^{-1}$) of the electrodes, I is the charge and discharge current (A), Δt is the discharging time (s), m is the mass of the electroactive material of the electrode (g), and ΔV is the discharging potential drop (V), respectively.

2.6. Characterization of the supports

The structures of the prepared compounds were performed by Powder X-ray diffraction (XRD) on a Bruker D8 Advance equipped with Cu-KR radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning speed of $7^\circ/\text{min}$ in the 2θ range from 5° to 100° . The FTIR spectroscopy was tested on a Nicolet NEXUS470 in the range from 400 cm^{-1} to 4000 cm^{-1} . Raman spectra was recorded at room temperature and AU10 exhibited on a 532 nm laser source with a Renishaw (In Via) spectrometer. The morphology and the size of the compounds were exhibited by the transmission electron microscopy (TEM) at 120 kV which the model was JEOL-JEM-2010 (Japan). For the electrochemical performance characterization, all the electrochemical measurements were tested with a three electrode system using AutolabCHI660D (ChenHua Instruments, Shanghai, China) at room temperature.

3. Results and discussion

3.1. XRD analysis of NG, $Ni(OH)_2/NG$ and NiO/NG

The phase information of samples was characterized by XRD. The XRD patterns of prepared NiO/NG , NG and $Ni(OH)_2/NG$ are shown in Fig. 1. The XRD patterns of NG have an obvious broad peak at $2\theta = 13.478$, which corresponds to the (0 0 2) crystal plane of graphene. And the interplanar spacing (0.89 nm) of NG is broader than common graphene ($2\theta = 9.20^\circ$, 0.34 nm), because of the presence of oxygen-containing groups or the nitrogen atom doped [29]. The characteristic diffraction peaks of $Ni(OH)_2$ is

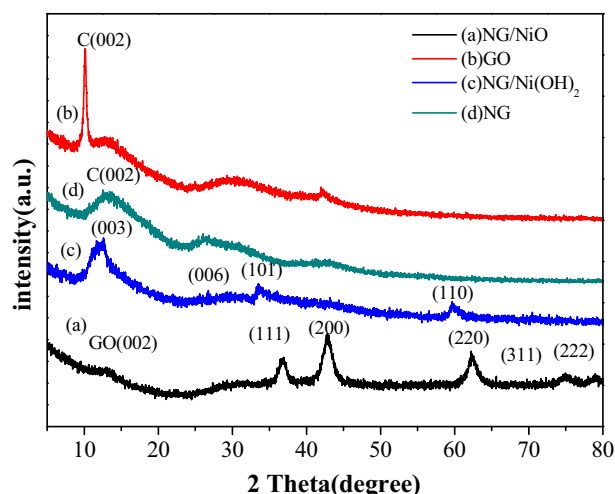


Fig. 1. XRD patterns of (a) NiO/NG , (b) NG, and (c) $Ni(OH)_2/NG$.

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