



One-step synthesis of sodium carboxymethyl cellulose-derived carbon aerogel/nickel oxide composites for energy storage



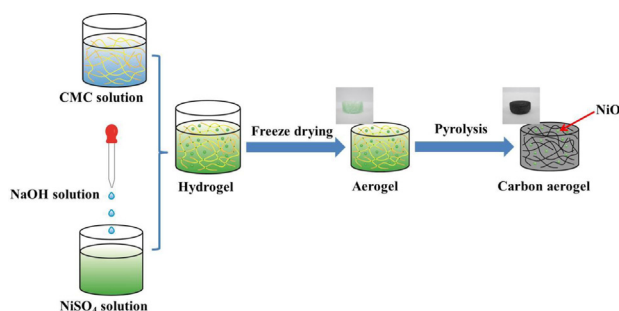
Miao Yu, Yingying Han, Jian Li, Lijuan Wang*

College of Material Science and Engineering, Northeast Forestry University, Harbin, PR China
Research Center of Wood Intelligent Science, Northeast Forestry University, Harbin, PR China

HIGHLIGHTS

- CA was prepared from pyrolysis of CMC aerogels cross-linked by NiSO₄.
- Introduction of NiO to CA could improve the supercapacitive behavior of composites.
- CA-1.0 with a surface area of 175.05 m²/g showed 81.67 mAh/g in a KOH electrolyte.
- The CA-1.0 electrode shows excellent electrochemical stability after 5000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate a facile and low-cost one-step method for the fabrication of porous carbon aerogel (CA)/NiO composites by pyrolysis of sodium carboxymethyl cellulose aerogels via a sol-gel and freeze-drying process. The structure and morphology of CA/NiO composites are characterized by scanning electron microscopy, X-ray diffraction and a nitrogen adsorption method. The magnetic properties are characterized using a vibrating sample magnetometer. The resultant CA/NiO composites possess an interconnected three-dimensional structure, high specific surface area of up to 175.05 m²/g and saturation magnetization of 3.14 emu/g. The CA/NiO composites present excellent electrochemical performance for supercapacitors, which exhibit a specific capacity of up to 81.67 mAh/g at a current density of 0.5 A/g in a 6 M KOH electrolyte solution. In addition, the CA-1.0 electrode shows excellent electrochemical cycling stability after 5000 charge/discharge cycles, with 94.5% capacity retention. The present study highlights new opportunities for CA/NiO composites to achieve advanced supercapacitor devices for energy storage and conversion.

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1. Introduction

In recent years, energy demands have increased due to the depletion of fossil energies, global economic expansion and climate change [1–3]. As a result, it is essential to develop alternative energy conversion and storage devices with the advantages of high

efficiency, environmental friendliness and reutilization. Lithium ion batteries and supercapacitors are two common energy systems with excellent properties of high capacity, and fast charging/discharging rates [4,5]. As one kind of promising energy storage device, supercapacitors are drawing increasing interest due to their distinct advantages, such as environmental friendliness, safety, low maintenance cost, long cycle life, high power density and short charge/discharge time compared with traditional lithium batteries and electrostatic capacitors [6–9]. Supercapacitors have strong potential in the fields of hybrid electric vehicles, digital

* Corresponding author at: College of Material Science and Engineering, Northeast Forestry University, Harbin, PR China.

E-mail address: donglinwj@163.com (L. Wang).

telecommunication systems, pulse laser devices and other energy storage systems [1,3,10].

Supercapacitors can usually be classified as either electrical double-layer capacitors (EDLCs) or pseudocapacitors, on the basis of their charge storage mechanism. For EDLCs, carbon-based materials are commonly used and the energy storage arises from electrostatic accumulation of ionic charges at the electrode/electrolyte interface due to their high porosity, which possess high power density and long cycle life, but low electrochemical capacitance [1,2,11]. The capacitances of pseudocapacitors derive from faradaic redox reactions of transition metal oxides, which could offer much higher electrochemical capacitance than carbonaceous materials. For energy storage applications, several kinds of transition metal oxides, such as NiO, MnO₂, Co₃O₄, MoO₃ and V₂O₅, have been investigated for pseudocapacitive components in carbon-based electrode materials [2,12–15]. Among them, NiO is one of the most promising electroactive materials for pseudocapacitors because of its high natural abundance, low cost, environmental friendliness and high theoretical capacitance [3]. However, NiO suffer from defects, including low electrical conductivity and poor cycling stability [16]. This has inspired attempts to develop porous carbon/NiO composites to combine the advantages of both EDLCs and pseudocapacitors, which will contribute to enhanced electrochemical performances for supercapacitors. Thus, such hybrids will have wide application prospects in a variety of energy storage and conversion systems [3].

Carbon aerogels (CAs) are a promising type of carbon material for supercapacitors due to their merits, such as high porosity, large surface area [17], low density, corrosion resistance and high electrical conductivity [18]. Traditionally, CAs are usually prepared by carbonization of organic aerogels, such as resorcinol/formaldehyde aerogels [19], cresol/formaldehyde aerogels [20] and phenol/formaldehyde aerogels [21]. However, these kinds of CAs show some disadvantages for supercapacitor applications, such as high costs, toxic precursors and complicated synthesis processes, which dramatically hinder their mass production and commercialization.

Recently, cellulose has drawn significant interest because of its renewability and biocompatibility [22]. Cellulose is the most abundant biopolymer in nature, and is renewable, sustainable and environmentally friendly [23]. Cellulose aerogels can be prepared from cellulose by the process of gelation, solvent exchange and freeze drying [22], and subsequent pyrolysis treatment could obtain CAs.

Several works have reported the fabrication of cellulose-based CAs for energy storage applications. CAs were prepared by Zu et al. from nanocellulose, which show excellent electrochemical properties for supercapacitors [22]. Zhuo et al. reported hierarchical porous CAs obtained from cellulose aerogels, which show a promising application in the fields of supercapacitors and CO₂ capture [24]. However, an alkali-urea system is needed for dissolving cellulose, which is a complex and time-consuming process that hampers its application. Wang et al. reported CA microbead nanowhisker-like NiO composites, which underwent a long process, including inverse emulsion polymerization of resorcinol/formaldehyde, drying, carbonization, immersion and calcination [16]. This process is very complicated, high in cost and time consuming. To the best of our knowledge, there is no report of the preparation of CA/NiO composites based on cellulose as a carbon source. Sodium carboxymethyl cellulose (CMC) is a type of cellulose derivate from carboxymethylation of the hydroxyl group in cellulose molecules, which is non-toxic, biocompatible and water soluble [23,25]. Moreover, CMC can be cross-linked with metal ions, such as Ca²⁺, Mg²⁺, Al³⁺ and Fe³⁺, to enhance its properties due to the existence of carboxyl groups [23].

We herein demonstrate a facile one-step strategy for the preparation of CA/NiO composites by directly pyrolysis of CMC aerogels by a sol-gel process, followed by freeze-drying and the use of NiSO₄

as a cross-linking agent. The as-prepared CA/NiO composites exhibit an interconnected three-dimensional network structure and high specific surface area. When used as supercapacitor electrodes, the CA/NiO composites efficiently combine both the merits of carbon materials and transition metal oxides, which showed a high specific capacity (81.67 mAh/g at 0.5 A/g) and excellent long-term cycle performance (94.5% capacity retention after 5000 cycles). The present work provides an effective and facile method for sustainable fabrication of high-performance porous CA materials for advanced energy storage applications.

2. Experimental

2.1. Materials

Sodium carboxymethyl cellulose (CMC) was purchased from Anli LLC (Henan, China), D-(+)-gluconic acid-lactone (GDL) was supplied by Luoluo (Shanghai, China), nickel sulfate (NiSO₄) was procured from Bodi Chemical LLC (Tianjin, China), and sodium hydroxide (NaOH) was obtained from Tianli LLC (Tianjin, China), glycerol was provided by Yongda Chemical LLC (Tianjin, China), polytetrafluoroethylene (PTFE) was obtained from Chenghexiang (Shenzhen, China), acetylene black was bought from Tianyi LLC (Tianjin, China), and nickel foam was bought from Jiayisheng (Kunshan, China).

2.2. Preparation of CMC aerogels and CAs

Firstly, 2 g of CMC, 1 g of GDL and 0.25 g of glycerol were dissolved in 50 mL of deionized water. Then, the mixture underwent a magnetic stirring process for 30 min at room temperature until a transparent solution was obtained. NiSO₄ (0–1 g) was dissolved in deionized water and 0.5 mL of NaOH solution (0.01 mol/L) was added to this solution under stirring to obtain a homogeneous suspension. Subsequently, the suspension was mixed with the obtained CMC solution and stirred for 5 min to ensure homogeneity. The mixed gel solution was then poured into a cylindrical polystyrene tubule and kept for 3 days at room temperature for further gelation and the cross-linking reaction. Finally, the gel underwent freeze-drying at –50 °C for 60 h under vacuum conditions to obtain the CMC aerogels. The as-prepared CMC aerogels were carbonized at 800 °C in a tube furnace for 2 h at a heating rate of 5 °C/min under a N₂ atmosphere to obtain the CAs. The corresponding composite CA samples are denoted as CA – x, where x represents the addition amount of NiSO₄. The pure CAs are denoted simply as CA. The facile preparation process of the CA/NiO composites is shown in Scheme 1.

2.3. Characterization

The morphology of the samples was characterized by scanning electron microscopy (SEM, FEI, Sirion), and the samples were sputter-coated with a thin layer of gold before observation. Transmission electron microscope (TEM) observation of the samples was conducted using a JEM-2100 equipment. X-ray diffraction (XRD) (Rigaku, D/max 2200) with Cu K α radiation was utilized to analyze the crystal structure of the samples at a scanning speed of 5°/min in the range of 5–80°. X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD spectrometer) was used to measure the element composition of the samples. N₂ adsorption and desorption measurements were conducted on an N₂ adsorption analyzer (ASAP 2020) at –196 °C. The specific surface area was calculated using the Brunauer–Emmet–Teller method, and the Barrett–Joyner–Halenda method was employed to investigate the pore size distribution. Magnetic properties of the sample were explored on

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