



# Template synthesis and characterization of nanostructured hierarchical mesoporous ribbon-like NiO as high performance electrode material for supercapacitor



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## ABSTRACT

In this paper, nanostructured hierarchical mesoporous ribbon-like NiO was synthesized by a hard-template method combining the calcination process. Nickel sulfate hexahydrate, guanidine hydrochloride and mesoporous carbon were used as nickel precursors, precipitant of weak base and template, respectively. The resultant NiO samples were characterized by Raman spectroscopy, energy dispersive spectrometer, X-ray diffraction, N<sub>2</sub> adsorption and desorption, scanning electron microscopy and transmission electron microscopy. The electrochemical performances were evaluated by cyclic voltammetry (CV), cyclic chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) in 6M KOH solution. The typical hierarchical mesoporous ribbon-like NiO shows a good electrochemical performance: a high specific capacitance of 1260 Fg<sup>-1</sup> at 1 Ag<sup>-1</sup>, 748 Fg<sup>-1</sup> at high current density of 20 Ag<sup>-1</sup> and 95% capacity retention at a current density of 10 Ag<sup>-1</sup> in a testing range of 5000 cycles.

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## 1. Introduction

Industrialization is putting a severe burden on energy storage, intensive investigations have been done on hierarchical nanostructures for their potential advantages. NiO-based materials, as one of the most important p-type wide-band-gap transition metal oxide semiconductors, have been attracted increasing attention, due to its availability, environmental-friendly, high chemical/thermal stability, high theoretical capacitance and low cost [1]. In recent years, many research efforts have been devoted to fabricating the NiO for their promising potential in diverse applications, including adsorption in water treatment [2–4], catalysis [5], energy storage of supercapacitors [6–8] and lithium ion batteries [9,10]. For example, Zhang and co-workers reported the synthesis of NiO hollow spheres by a glycerin-assisted hydrothermal synthesis method used as sensing materials [11]. Hu et al. obtained NiO film using a two-step process through an electrochemical route and it was used as supercapacitor electrode [12]. Zaban and co-workers prepared the fluorine-doped tin oxide based NiO electrodes for the photoelectrochemical purpose [13].

The electrochemical performances of metal oxides are highly depended on their porosity and surface area. Usually, hierarchical structure possesses high porosity and large surface area, which can facilitate the diffusion of molecules and ions, so that enhance the performances of metal oxide. Sacrificial template synthesis is a straightforward, versatile and effective approach to tailor and fabricate hierarchical materials [14–17]. For example, Cao and co-workers prepared hierarchical structured NiO nanotube arrays with the help of ZnO nanorod template, it exhibits a high capacitance of 675 Fg<sup>-1</sup> at 2 Ag<sup>-1</sup> [18]. Yuan et al. developed a sacrificial template strategy to synthesize short NiO nanotubes which delivered a high specific capacitance of 903 Fg<sup>-1</sup> at 1 Ag<sup>-1</sup> [19]. However, it is still far away from the theoretical value (2573 Fg<sup>-1</sup>). In addition, Wang and co-workers found that the maintenance of the original belt-like morphology of NiO nanostructures after heat treatment posed great difficulties [20]. Therefore, it is of great necessary to find an interesting template to construct the nickel oxide with well-maintained fascinating morphology, suitable pore size and high specific surface area, all of them are beneficial for the NiO nanostructures to possess excellent performances in the application of supercapacitor.

In this work, a hard-template method is proposed to synthesize nanostructured hierarchical mesoporous ribbon-like NiO electrode material with well-maintained morphology, suitable pore size and high specific surface area. Guanidine hydrochloride was used as

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precipitant and the mesoporous carbon as a hard template to control the structure growth and pore size distribution. To the best of our knowledge, the use of mesoporous carbon as a hard template to synthesize NiO has not been reported before. The mechanism of Ni(OH)<sub>2</sub> growth and NiO synthesis were studied. The influence of templates on the characteristics and electrochemical properties of resultant NiO were also studied.

## 2. Experimental

### 2.1. Material preparation

Nickel sulfate hexahydrate (NiSO<sub>4</sub>·6H<sub>2</sub>O), sodium chloride (NaCl), guanidine hydrochloride (CH<sub>6</sub>N<sub>3</sub>Cl), anhydrous ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and active carbon were purchased from Sinopharm Chemical Reagent Co. Ltd. Polytetrafluoroethylene (60%) was purchased from Shanghai 3F New Materials Co. Ltd. Nickel gauze was obtained from the Shanghai Hongxiang Plant. All the chemicals and reagents were of analytical grade and were used without further purification. Mesoporous carbon was synthesized according to the procedures reported by Zhang and co-workers [21]. SiO<sub>2</sub> aerogels was synthesized according to Gan and co-workers reported previously [22].

Typically, 0.5257 g (2.0 mmol) of NiSO<sub>4</sub>·6H<sub>2</sub>O was dissolved into 80 mL deionized water under magnetic stirring. Then, 0.1169 g (2.0 mmol) of NaCl and 0.7642 g (8.0 mmol) CH<sub>6</sub>N<sub>3</sub>Cl were added to the above solution slowly at room temperature with another continuous stirring for 30 min. 60 mg of mesoporous carbon was placed into a container, and the Ni-containing, guanidine hydrochloride and NaCl mixed solution was added dropwisely into it under magnetic stirring, followed by a vacuuming process. Then the precursor/template was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 16 h. After the autoclave cooled down to room temperature, the product of Ni(OH)<sub>2</sub>/C was separated by filtration, washed with water and ethanol, dried at 100 °C for 12 h, and then calcinated at 450 °C for 4 h in air with a rising rate of 1 °Cmin<sup>-1</sup> to remove the template of mesoporous carbon and obtain the final product of NiO. In addition, activated carbon (removed by calcination in air) and SiO<sub>2</sub> aerogels (removed by NaOH etching) were also used as templates to prepare different NiO materials for comparison.

### 2.2. Characterization of NiO materials

Raman spectra were acquired on a Renishaw inVia Reflex Raman Microprobe, under λ<sub>exc</sub> = 514 nm laser excitation to identify the NiO. Energy dispersive spectrometer (EDS) images were collected on an electron microscope, using a 200 kV accelerating voltage. The crystal structure of prepared NiO samples was studied by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with Cu Kα (λ = 0.15418 nm) radiation. The N<sub>2</sub> adsorption and desorption isotherms were measured by an automatic gas-adsorption apparatus (Micromeritics Tristar 3000) to estimate the porosity and surface area parameters. Brunauer–Emmett–Teller (BET) model and Barrett–Joyner–Halenda (BJH) method were used to calculate the specific surface areas and pore size distributions, respectively. The morphology of NiO<sub>2</sub> was observed by field emission scanning electron microscopy (FESEM, XL30, Philips) and transmission electron microscopic (TEM, JEOL2100 microscope).

### 2.3. Electrochemical measurements

The measurements of electrochemical performances using cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were conducted in a CHI 660D instrument with a typical three-electrode system.

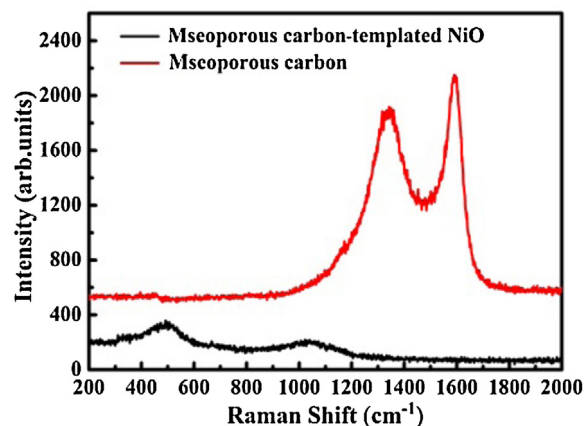


Fig. 1. Raman spectra of mesoporous carbon and mesoporous carbon-templated NiO.

An Ag/AgCl electrode was used as the reference electrode and nickel gauze as the counter electrode. The working electrode containing 2–3 mg active materials (as-prepared NiO) were prepared by mixing the as-prepared NiO, graphite, and polytetrafluoroethylene in a mass ratio of 8: 1: 1 in a required amount of ethanol, and dried slightly at 60 °C for 12 hours to form the paste. Then, the paste with a thickness of 1 mm, pressed by bead machine under 10 Mpa on Ni-gauze substrate and served as the working electrode which was soaked in 6 M KOH solution for 24 h to facilitate the electrolyte to completely diffuse into the pores of materials [23].

## 3. Results and discussion

Fig. 1 shows the Raman spectra of the mesoporous carbon and mesoporous carbon-templated NiO. The peaks locate at 1363 cm<sup>-1</sup> and 1597 cm<sup>-1</sup> assign to D-band and G-band which are caused by the E<sub>2g</sub> phonon of Csp<sup>2</sup> atoms [24]. For pure NiO, there are several peaks in the range of 200–2000 cm<sup>-1</sup>, which can be assigned to the stretches of the Ni–O bands. In detail, the peaks at 500 cm<sup>-1</sup> and 1090 cm<sup>-1</sup> could be attributed to the first-order longitudinal optical (LO) and 2LO phonon modes of NiO, respectively [25]. It is clear that no peaks from mesoporous carbon are observed in the NiO sample, indicating the completely removal of mesoporous carbon for the calcination in air at 450 °C for 4 h.

Energy dispersive spectrometry (EDS) analysis was performed to identify mesoporous carbon-templated NiO, as shown in Fig. 2. It is clearly observed that only the Ni and O elements signals and no signals from carbon are observed, it is further confirmed that mesoporous carbon is completely removed through the calcination process.

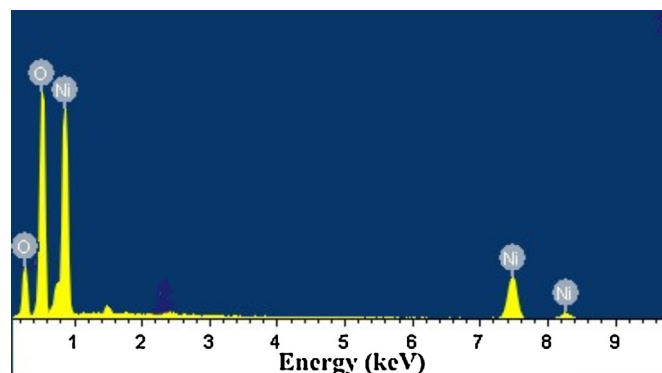


Fig. 2. Energy dispersive spectrometry of mesoporous carbon-templated NiO.

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