In situ fabrication of mesoporous NiO@Graphite paper electrode with multilayered nanosheet wall structures for high-performance supercapacitors

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Abstract. A mesoporous NiO@graphite paper with multilayered nanosheet wall structures (M-NiO@GP) was synthesized through a facile and low-cost hydrothermal reaction and thermal annealing process. The as-prepared M-NiO@GP electrode presents high specific capacitance (2.57 F cm$^{-2}$), exhibits superior cyclic stability (92.3% capacitance retention after 10000 charge–discharge cycles) and brilliant rate capability (about 56.0% capacitance retention when the current density increased 20 times). Such high-performance capacitive behavior is attributed to the wall structure of NiO with the multilayer nanosheets, which could shorten the ion transfer distance. Meanwhile, the high specific surface area and mesoporous structure of the electrode could serve as an efficient path for OH$^-$ transfer and diffusion. The improved electrical conductivity of the electrode enabled stable and efficient electron transports and consequently improved the overall electrochemical performance of supercapacitors. Therefore, the demonstrated high conductive M-NiO@GP electrode is a promising candidate for practical supercapacitor applications.

1. Introduction

With increasing global energy demands and consumptions, energy crisis and environmental pollutions have attracted more and more attention[1]. A great deal of efforts have been spent on developing renewable and environmental energies such as wind and solar energy in an economical way, but efficient energy storage and conversion systems are also required for these intermittent renewable energies[2]. Among these energy storage and conversion systems, supercapacitors (SCs) are promising energy storage devices attributed to superior power density, rapid charge-discharge rate and excellent long-term cycling life[3].

The key to improving the electrochemical performance of SCs lies in the performance improvement of electrode materials[4]. Based on the energy storage mechanism, electrode materials usually divide into three different types: double-layer capacitor (EDLCs)[5], pseudocapacitor materials [6] and battery-type materials[7]. Among these electrode materials, battery-type materials with high specific surface area and appropriate aperture distribution have been widely investigated as positive electrode materials for supercapacitors in virtue of their large specific capacities, environmental benignity, superior cycling stability and excellent power density[8]. Comparing to other battery-type electrodes, NiO electrode has been investigated as a promising electrode material for energy storages device, on account of its high theoretical specific capacitance, economic property and environmental friendly[9]. However, the NiO electrodes with low electrical conductivity limit electrode from reaching good rate performance and
high specific capacitance and consequently restrict their practical application in supercapacitors. With regard to the electrochemical properties of NiO electrode, considering that the specific capacitance of electrode intensively depended on the high specific surface area and low internal resistance, many researchers have spent a large number of efforts on how to increase the specific surface area and decrease the internal resistance of NiO electrode. For instance, an effective way is directly generating NiO nanostructure electroactive materials on a highly conductive substrate to avoid using the binder, which increased the internal resistance of the electrode, diminished the charge transfer rate and consequently leading to inferior electrochemical performance[10]. After directly growing the NiO nanostructure on the highly conductive substrate, the electrical conductivity of the electrode is improved. Nevertheless, the specific surface area of the electrode materials has been affected to some extents, which limits ion exchange between the electrolyte and the surface of the electrode and results in inferior electrochemical properties[11]. Therefore, it is necessary to develop suitable NiO electrode materials to overcome these defects.

In this work, we introduce a facile and economic method for growing mesoporous NiO with multilayered nanosheets wall architecture on the high conductive graphite paper (M-NiO@GP) through a hydrothermal process and thermal annealing process. The as-prepared electrode exhibited a high specific surface capacitance (2.57 F cm⁻²), brilliant rate capability (56.0% capacitance retention while the current density increased 20 times) and outstanding cyclic stability (92.3% retention after 10000 repeating charge-discharge tests). The unique M-NiO@GP structure could enhance the electrochemical performance of electrode due to its large specific surface area with mesoporous structure and good internal resistance, which could supply more electroactive sites for redox reaction, promote OH⁻ efficiently transports between the electrolyte and the electrode and increase charge transfer efficiency. These results demonstrate that the M-NiO@GP is a promising candidate for energy storage device.

2. Experimental section

2.1. Materials
Nickel nitrate (Ni(NO₃)₂·6H₂O, ≥98.0%), polyethylene glycol (PEG 200, AR) and Ammonium fluoride (NH₄F, ≥98.0%) were obtained from Chengdu Kelong Chemical Reagent Factory. Ammonium molybdate ((NH₄)₂MoO₄, ≥98.5%), nitric acid (HNO₃, ≥99.0%) and ethyl alcohol (C₂H₅OH, ≥99.7%) were purchased from Aladdin Ltd. (Shanghai, China). All analytical grade reagents were used as received without further purification. Graphite paper was supplied by Qingdao Dongkai Graphite Co., Ltd and was pre-treated by HNO₃ at room temperature, and then cleaned by sonication ordinally in distilled water and ethyl alcohol three times each to eliminate the impurities on the surface of graphite paper.

2.2. Sample preparation
In a typical synthesis procedure, Ni(NO₃)₂·6H₂O (1.163 g), NH₄F (0.296g) and (NH₄)₂MoO₄ (0.196 g) were successfully dispersed in deionized water (DI water, 60 mL). After vigorous stirring for 15 min, 1 mL PEG 200 was introduced into the solution and sonication for 15 min. Then, the obtained solution and a piece of GP (2×4 cm, after further purification) were transferred into a 100 mL Teflon-lined autoclave. The reaction equipment was kept at 120 °C for 12 h to grow NiO nanosheets on GP. After cooling to room temperature, the solid sample was washed thoroughly with DI water three times and subsequently dried in the vacuum oven for 10 h at 50 °C. Annealing the above solid sample at 350 °C for 2 h with a ramp rate of 2 °C min⁻¹ in air atmosphere obtained the final product named M-NiO@GP. The sample was fabricated by a similar procedure without PEG 200 in the solution named NiO@GP. The mass loadings of M-NiO@GP and NiO@GP were estimated to be 3.17 mg cm⁻² and 3.09 mg cm⁻², respectively.
2.3. Characterization

The micromorphologies of samples were observed by the field-emission scanning electron microscopy system (Inspect F, FEI Co., US). The X-ray diffraction (XRD) patterns of samples were tested by Philips X’pert X-ray diffractometer. The specific surface area and pore size distributions of samples were investigated by Brunauer-Emmett-Teller (BET) methods. The mass loading of electroactive materials was determined by electronic balance (Sartorius BT-25S, 0.01 mg accuracy).

2.4. Electrochemical measurements

All electrochemical performances were recorded in a standard three-electrode system using an electrochemical workstation (CHI660D, Chenhua, China). The samples were used as working electrode, platinum mesh and the saturated calomel electrode was used as the counter electrode and reference electrode, respectively. The long-term cycling test was carried on a CT2001A rapid sampling battery testing system (LAND, China).

3. Results and discussion

![Figure 1](image)

Figure 1(a) displays XRD patterns of the GP, NiO@GP and M-NiO@GP. The (002) and (004) planes of Graphite-2H (JCPDS No. 41-1487) were found in the XRD patterns of three samples matching the peaks located at 26.4° and 54.5°, which are corresponding to the GP. The observed three peaks located at 37.3°, 43.3° and 62.9° correspond to (111), (200) and (220) planes of NiO (JCPDS No. 47-1049)[12]. Figure 1(b) displays SEM image of the pure GP. As shown in the SEM images of the as-synthesised NiO@GP (figure 1(c) and 1(d)), it is clear that mass production is nanosheets architecture with approximately 10 μm in diameter and 60 nm in thickness. Figure 1(e) is a typical SEM image of M-NiO@GP, in which M-NiO of uniform combination microstructure with about 60 nm thickness can be observed. The high-magnification SEM image in figure 1(f) demonstrates that the wall structure of M-NiO is made up of 5-7 layers of nanosheets. Given the unique nanostructure of M-NiO@GP, the electrochemical performance may be enhanced.
From the N$_2$ adsorption-desorption isotherms of NiO@GP and M-NiO@GP (figure 2(a)), it is obvious that the two isotherms are IV isotherm, suggesting that NiO@GP and M-NiO@GP are mesoporous structure, which could work as OH- pathways for rapid ion transfer-diffusion[13]. As shown in the pore size distributions of NiO@GP and M-NiO@GP samples (figures 2(b) and 2(c)), a large number of pores are converged in 2-20 nm, further confirming mesoporous structures of samples. The calculated specific surface area of M-NiO@GP is 56.92 m$^2$ g$^{-1}$, which is larger than that of NiO@GP (31.22 m$^2$ g$^{-1}$), implying more active area of M-NiO@GP could service for redox reaction and consequently increases the electrochemical performance of M-NiO@GP.

Figure 3(a) shows the CV curves of NiO@GP and M-NiO@GP electrodes at 2 mV s$^{-1}$; (b) GCD curves at a current density of 2 A cm$^{-2}$; (c) rate performance of NiO@GP; (d) CV curves of M-NiO@GP electrode from 1 to 20 mV s$^{-1}$; (e) GCD curves of M-NiO@GP electrode at various current densities and (f) rate performance of M-NiO@GP.

Figure 3(a) shows the CV curves of NiO@GP and M-NiO@GP electrodes at 2 mV s$^{-1}$ with a potential range from 0 to 0.6 V. The M-NiO@GP electrode possesses larger integral area than that of NiO@GP, indicating the better electrochemical performance of M-NiO@GP. It is apparent from the GCD curves of two samples (figure 3(b)) that M-NiO@GP owns specific capacitance (2.57 F cm$^{-2}$), which is double that of NiO@GP (1.27 F cm$^{-2}$), further demonstrating M-NiO@GP has the optimal specific capacitance. From the rate performance of NiO@GP (figure 3(c)), the specific capacitance of NiO@GP maintains only 26.8% retention of its initial capacitance. As shown in figure 3(d), the CV curves of M-NiO@GP
possess a pair of redox peaks, suggesting good electrochemical reversibility[14]. Figure 3(e) exhibits the GCD curves of the M-NiO@GP electrode at different current densities. The calculated specific capacitances of M-NiO@GP are 2.57, 2.23, 1.96, 1.72 and 1.44 F cm\(^{-2}\) at a current density of 2, 4, 10, 20 and 40 mA cm\(^{-2}\), respectively. As displayed in figure 3(f), the specific capacitance still retained about 56.0\% retention of that of initial when the current density increased 20 times, demonstrating excellent rate performance of M-NiO@GP, which may attribute to high specific surface area and appropriate aperture distributions.

Figure 4 (a) The Nyquist plots of NiO@GP and M-NiO@GP electrodes; (b) long-term testing of M-NiO@GP electrodes at a current density of 10 mA cm\(^{-2}\) and (c) The Nyquist plots of M-NiO@GP electrodes before and after cyclic tests.

To evaluate the electrical conductivity of NiO@GP and M-NiO@GP electrodes, the electrochemical impedance spectroscopy (EIS) plots of two samples are depicted in figure 4(a). As displayed in figure 4(a), the M-NiO@GP electrode exhibits smaller semicircular shape and steeper vertical straight line than NiO@GP, indicating efficient charge transfer of M-NiO@GP electrode and leading to better electrochemical performances[15]. The long-term stability test of M-NiO@GP electrode was accomplished with repeating 10000 GCD cycles at 10 mA cm\(^{-2}\) to access the application probably of supercapacitors (figure 4(b)). The sample still maintains 92.3\% capacitance retention, implying brilliant cycling stability of the M-NiO@GP electrode. In order to understand the excellent electrochemical performance of the M-NiO@GP electrode, the EIS measurement was also performed after the cyclic test. In the Nyquist plots of the before and after cyclic tests (figure 4(c)), the semicircular shape slightly increased and the vertical straight line maintained almost the same slope, suggesting remarkable stability of the sample and further demonstrates the excellent electrochemical performance of the sample.

4. Conclusions
In summary, multilayer NiO covered on the GP has been successfully synthesized by a facile and economic method. The M-NiO@GP electrode exhibits high specific area capacitance (2.57 F cm\(^{-2}\)), brilliant rate performance (56.0 \% capacitance retention) and excellent cycling stability (92.3\% after 10000 cycles). The enhancement electrochemical performance could be attributed to a large specific surface area with appropriate aperture distributions and prominent electrical conductivity of the M-NiO@GP with unique structures. This M-NiO@GP electrode material is a promising candidate for energy storage devices.

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