NiO/Ni$_x$Co$_{3-x}$O$_4$ porous ultrathin nanosheet/nanowire composite structures as high-performance supercapacitor electrodes

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Introduction

Supercapacitors as promising energy storage devices have attracted a lot of attention in recent years because they have higher power density and cycle performance than lithium ion batteries. They are being integrated into microelectronics, textiles and electric vehicles, transforming our lifestyle. Large-scale energy storage is helping to improve the intermittency problems with renewable energy sources such as solar, wind and wave.

Capacitive positive electrode materials made of nanosheet-shaped transition-metal compounds, such as metal oxides/hydroxides and layered double hydroxides (LDH), without additives, have been demonstrated to hold great potential for advanced supercapacitors. This kind of electrode without any binders or conductive agents can effectively cut down the "dead surface" in conventional slurry-derived electrodes, facilitate more efficient charge and mass transportation, and simplify the electrode-preparation process. Moreover, compared to traditional bulky materials, the 2D nanosheet-shaped transition metal compounds aid in shortening the transport distance of the ions because of their large aspect ratio and can further improve the utilization of the active materials.

Among these metal oxides and hydroxides materials, NiO and Ni(OH)$_2$ (ref. 9) have attracted a lot of attention due to their high theoretical capacitance, excellent chemical stability, low cost and low toxicity. However, the comparatively poor electrical conductivity of NiO (0.01–0.32 S m$^{-1}$) or Ni(OH)$_2$ is the major defect as the electrode material. Thus, cobalt ions can be introduced into NiO or Ni(OH)$_2$, which can improve the conductivity of electrode materials because Co$^{2+}$ can be oxidized to conductive CoOOH (12.8 S cm$^{-1}$) during the redox reaction process. The addition of cobalt ions is also helpful to raise the oxygen overpotential helpful with widening potential window. What's more, the slow kinetics of faradaic reactions of NiCo-based materials is another factor that limits their electrochemical performance. It is desirable to develop NiCo-based electrodes with large ion accessible surface area. Previous studies have primarily been focused on development of NiCo-based nanomaterials with controlled morphology and enhanced surface area, such as nanosheets, nanowires, nanoflowers and nanorods. However, the simple and convenient methods to prepare large scale composite porous nanostructures are rarely reported, while it is valuable for practical applications.

In this paper, we report a simple process for large-scale fabrication of self-standing composite film electrodes composed of cobalt doped nickel oxide NiO/Ni$_x$Co$_{3-x}$O$_4$ porous ultrathin nanosheet/porous nanowire composite structure for functional devices.
supercapacitors. The flexible Ni-foam plays a dual role both as the current collector and the substrate of the architecture materials. Owing to this unique nanosheet/nanowire composite structure, the one annealed in air at 300 °C displays the best electrochemical behavior, which can achieve a specific capacitance of 270 mF cm⁻² at 5 mA cm⁻² after 10 000 cycles and maintain the excellent cycling stability of the electrode that remains about 89% of the max capacitance after 20 000 cycles at the current density of 5 mA cm⁻².

**Experimental section**

**Synthesis of the NiO/NiₓCo₃₋ₓO₄ porous nanowires/porous nanosheet composite structure on nickel foam**

A piece of nickel foam, 1 cm × 1.5 cm, was respectively cleaned by acetone, absolute ethanol and deionized water in an ultrasound bath. For a typical run, Ni(NO₃)₂·6H₂O (4.2 mmol), Co(NO₃)₂·6H₂O (1.4 mmol) (Ni/Co molar ratio 3 : 1), and HMT (5.6 mmol) were dissolved into distilled water (100 mL) at room temperature, and the solution was then transferred into a Teflon-lined stainless steel autoclave (200 mL). The Ni-foam substrate was then immersed into the solution and kept in an electric oven at 120 °C for 24 h. The autoclave was then removed from the oven and cooled to room temperature. The precursor was washed thoroughly with water and ethanol, and finally dried at 80 °C in air for 12 h, yielding the precursor nanohybrids on the Ni-foam. Subsequently, the NiO/NiₓCo₃₋ₓO₄ porous nanosheet/nanowire composite structure were obtained through heat treatment at different temperature (250 °C, 300 °C and 350 °C) for 2 h at a heating rate of 1 °C min⁻¹ in air. The weight of samples was measured before preparation and after annealing and the mass loading of active materials was about 0.33 mg cm⁻² if the corrosion effect of solution on Ni foams is neglected.

**Characterizations**

The structure and morphology of obtained samples were examined by field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM) (JEOL JEM-2100F with an acceleration voltage of 200 kV). Powder X-ray diffraction (XRD) (Cu K, = 1.5406 Å) was obtained on a Rigaku Ultima IV X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) (AXIS ULTRA DLD, Kratos, Japan) was performed to analyze the surface chemical composition and valance states of the samples. Thermogravimetric analysis (TGA) (Pyris 1 TGA) was carried out with a temperature ramp of 10 °C min⁻¹. Raman spectrum (laser excitation λexc = 532 nm) was utilized to investigate the crystallographic texture. To determine the bulk composition of the whole samples, the ICP atomic emission spectrometer (ICP-AES) was employed in the experiment (shown in the ESI, Table S1†).

**Electrochemical measurements**

The electrochemical measurements of the NiO/NiₓCo₃₋ₓO₄ nanosheet/nanowire composite structure were carried out through a three-electrode cell in a 1 M KOH aqueous electrolyte, with the platinum plate electrode and Hg/HgO electrode as the counter and reference electrode. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) tests and galvanostatic charge–discharge measurements were performed on CHI760B Electrochemical Workstation. The electrochemical capacitance was calculated as the following equation:

$$C = \frac{I \Delta t}{A \Delta V},$$

where C (mF cm⁻²) is the electrochemical capacitance of the electrode, I (A) represents the current density, t (s) is the discharging time, ΔV (V) is the discharging potential range, and A (cm²) is the area of the active material in the electrode.

**Results and discussion**

The typical XRD pattern of the NiO/NiₓCo₃₋ₓO₄ porous nanowire/porous ultrathin nanosheet composite structure annealed at 300 °C is shown in Fig. 1. For the NiO, the five peaks

![Fig. 1](image-url)
The XRD patterns of samples annealed at 250 °C and 350 °C are similar to the pattern of the sample annealed at 300 °C, which indicates that the precursors start to transform to NiO and Ni_{x}Co_{3-x}O_{4} at 250 °C.

In order to further substantiate the NiO/Ni_{x}Co_{3-x}O_{4} formation, the TGA/DTG measurements were used to evaluate the functional relationship between the mass change and the temperature. Fig. 1b shows the TGA curves of the as-prepared precursor measured from room temperature to 900 °C. The initial weight losses accompanied by an endothermic reaction below 150 °C was assigned to the loss of adsorbed water and the evaporation of intercalated water molecules. On further increasing the temperature, the major weight loss (20–22%) occurred in between 220–340 °C, which may be due to the decomposition reaction of nickel cobalt hydroxide precursor and the crystallization of NiO/Ni_{x}Co_{3-x}O_{4}. To further substantiate the TGA results, DTG analyses is also given in Fig. 1b. The observed endothermic peaks below 150 °C is due to the removal of adsorbed water molecules in the structural water of nickel cobalt hydroxide precursor. Similarly, the formation of NiO/Ni_{x}Co_{3-x}O_{4} porous nanowire/porous ultrathin nanosheet composite structure by the decomposition of hydroxide is confirmed through the obtained endothermic peak at 285 °C. In addition, a weight loss of about 6 wt% in the temperature range between 340 °C and 470 °C arises in the TGA curve with a step existing at about 350 °C in the DTG curve, which is attributed to the reaction between O2 and hydrocarbons remained on surface of the sample.

The surface chemical composition and atomic valence states of the composite nanostructures can be further analyzed by XPS. Fig. 2a presents the full XPS spectrum of the NiO/Ni_{x}Co_{3-x}O_{4} porous nanosheet/nanowire composite structure annealed at 300 °C. The XPS analysis of NiO/Ni_{x}Co_{3-x}O_{4} porous structure shows that the atomic percentages on the sample surface of Ni, Co and O are 25.81%, 5.00% and 43.35%, indicating that Ni is enriched on the surface of the composite structure. The high resolution Ni 2p and Co 2p XPS peaks are shown in Fig. 2b and c. In Ni 2p spectra for the sample annealed at 250 °C, two sets of broad signals corresponding to Ni 2p3/2 (855.1 eV) and Ni 2p1/2 (872.6 eV) are observed, which demonstrates that the elemental Ni is in a range of typical Ni^{2+} or Ni^{3+} bound to oxygen. The intense satellite peaks indicate that the majority of nickel elements in the crystal lattice are Ni^{2+} cations. The sample annealed at 300 °C has the more proportion of the Ni^{2+} than other samples which annealed at 250 °C and 350 °C.
The electronegativity difference between Ni and O facilitates the adsorption of O on the Ni nanowires, which is consistent with the Raman spectra (Fig. S1a). The peaks at 187, 534 and 647 cm⁻¹ correspond to the characteristic peaks for F₂g, F₂g and A₁g stretching modes of the 2D NiCo₂O₄ nanowires. These peaks are assigned to the typical D (disordered carbon) and G (sp²-carbon) bands and indicate the good graphitization degree of carbon remained in the materials with small particle sizes. The D/I G value of 1.0 is generally typical of amorphous carbon and the decay of satellite peaks also demonstrates this result. 

The high-magnification TEM images shown as Fig. S3 reveal that the diameter of nanowires is about 50–80 nm and the mesopores are also present both in the ultrathin nanosheets and nanowires with a size of 5 to 8 nm. This kind of ultrathin porous structure in the nanohybrids is very important, as it facilitates the fast mass transport of electrolytes within the electrodes for quick redox reaction. 

The surface oxyhydroxide or the substitution of oxygen atoms at the surface by hydroxyl groups. The atomic percentages of C remained on the simple surface. The high-magnification TEM images shown as Fig. S3 reveal that the diameter of nanowires is about 50–80 nm and the mesopores are also present both in the ultrathin nanosheets and nanowires with a size of 5 to 8 nm. This kind of ultrathin porous structure in the nanohybrids is very important, as it facilitates the fast mass transport of electrolytes within the electrodes for quick redox reaction. 

The high-magnification TEM images shown as Fig. 3c and d reveal that the diameter of nanowires is about 50–80 nm and the mesopores are also present both in the ultrathin nanosheets and nanowires with a size of 5 to 8 nm. This kind of ultrathin porous structure in the nanohybrids is very important, as it facilitates the fast mass transport of electrolytes within the electrodes for quick redox reaction. 

The high-magnification TEM images shown as Fig. S3 reveal that the diameter of nanowires is about 50–80 nm and the mesopores are also present both in the ultrathin nanosheets and nanowires with a size of 5 to 8 nm. This kind of ultrathin porous structure in the nanohybrids is very important, as it facilitates the fast mass transport of electrolytes within the electrodes for quick redox reaction.
a specific capacitance of 270 mF cm\(^{-2}\) (about 810 F g\(^{-1}\)) at 5 mA cm\(^{-2}\). Afterward, the capacitance retention was 88.89% of the max capacitance, indicating excellent long-term stability of the NiO/Ni\(_{x}\)Co\(_{3}\)-O\(_4\) composite electrode, which exceeds those of the previously reported Ni-based materials.\(^9\)\(^{42}\) By comparison, the samples annealed at 250 °C and 300 °C presented much higher capacitance than sample annealed at 350 °C. These results highly highlight the vital roles of the cobalt ions and the presence of hydrocarbons into electrochemical active electrode materials.

Fig. 4d shows the rate performance of the sample annealed at 300 °C. The specific capacitances obtained were 220, 216, 180, 160 and 120 mF cm\(^{-2}\) at current densities of 1, 2, 5, 10 and 20 mA cm\(^{-2}\) respectively, which shows up better rate performance than single NiO materials.\(^{35}\)\(^{44}\) Clearly, the specific surface capacitance gradually decreases with increasing current density. The specific capacitance decreases gradually with increasing current density, which can be attributed to the diffusion effect limiting the diffusion and migration of the electrolyte ions within the electrode at high electric current density because of the time constraint and only the outer active surface can be utilized for charge storage, resulting in low electrochemical utilization of the electroactive materials.\(^{45}\)\(^{47}\)

To further study the different electrochemical performance after annealing and the decay of the specific capacitance after cycling tests, EIS measurements were carried out at an open circuit potential in a frequency ranging from 0.1 Hz to 100 kHz. As shown in Fig. 5, in the high-frequency region the intersections on the Z'axis represent the equivalent series resistance of capacitors (R\(_s\)) including the internal resistance of electrode materials, the ohmic resistance of the electrolyte and contact resistance between electrodes and current collectors.\(^{35}\)\(^{48}\) Obviously, NiO/Ni\(_{x}\)Co\(_{3}\)-O\(_4\) nanohybrids at 300 °C annealing temperature has the smaller equivalent series resistance value than other NiO/Ni\(_{x}\)Co\(_{3}\)-O\(_4\) nanohybrids as shown in Fig. 5a, reflecting the optimum electronic and ionic conductivities of NiO with the presence of Ni\(_{x}\)Co\(_{3}\)-O\(_4\) at 300 °C annealing temperature. This result is consistent with good cycle performance results of NiO/Ni\(_{x}\)Co\(_{3}\)-O\(_4\) composites. As shown in Fig. 5b, the electrode has a higher R\(_s\) and worse electric conductivity after cycling tests, leading to decay of the electrochemical performance. The inset SEM image with cracks further indicates volumetric changes after cycles.
Conclusion

In summary, a facile and low cost synthesis approach was adopted to synthesize cobalt doped nickel oxide porous ultra-thin nanosheet/porous nanowire composite structure. Moreover, the as-prepared sample displays excellent electrochemical performance, the maximum specific capacitance of 270 mF cm\(^{-2}\) and capacitance retention of 88.9% after 20 000 cycles. Such a simple and cost-effective synthetic approach would open new doors for the development of a serial of high-quality NiCo-based materials, and offer promising applications for high-performance energy-storage devices.
Conflicts of interest

There are no conflicts of interest to declare.

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