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# Porous NiO/graphene hybrid film as anode for lithium ion batteries

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ABSTRACT

Porous NiO/graphene hybrid film is prepared by a combination of chemical bath deposition and a graphene spin-coating. The material is characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The film has a porous structure, and it is covered by graphene sheets. The electrochemical performance as anode materials for lithium ion batteries is investigated by galvanostatic charge–discharge cycle and cyclic voltammetry. The hybrid film that contains 8 wt% of graphene exhibits an initial charge capacity of 885 mA h $g^{-1}$ and an initial coulombic efficiency of 85%, and its cycling performance is enhanced significantly compared with that of bare NiO film. It is believed that the porous structure and the covering of graphene play important roles in the electrochemical performance.



## 1. Introduction

Among the transition-metal oxides for lithium ion batteries, NiO has received a considerable attention due to its high theoretical capacity, easy preparation and low cost [1–6]. However, the low conductivity of NiO limits its actual capacity and rate capability. Meanwhile, the pulverization of NiO occurred during the reactions leads to fast capacity fade. Preparing porous materials with large specific surface area is an effective way to overcome these drawbacks. A lot of porous NiO materials, such as fibers [7], microspheres [8], microtubes [9], nanosheets [10] and nanofilms [11] are fabricated, and they deliver high initial charge capacities ranged from 600 to 800 mA h $g^{-1}$. Graphene, an ideal matrix, can not only alleviate pulverization due to its high mechanical flexibility but also improve the electrode conductivity. Several NiO nanoparticles or nanosheets have been synthesized, and incorporated with graphene by means of precipitation [12–14], hydrothermal treatment [15–17], ultrasonic treatment [18], thermal decomposition [19], and so on. They show enhanced capacities, cyclabilities, and rate capabilities than those of bare NiO. However, these enhancements are attributed to the high mass percentage of graphene in the composites (20–77%). The high content of graphene not only brings a low initial coulombic efficiency below 65%, but also reduces the specific volume capacity and increases the cost. Therefore, designing NiO/graphene hybrid with large specific surface area, high conductivity, stable structure and low graphene content is very critical.

Herein, a porous NiO/graphene hybrid film with low content of graphene is developed, in which NiO shows array structure composed of interconnected aligned nanoflakes. This array structure can enlarge the contact area between active material and electrolyte, and optimize the charge transport. Graphene covers on the top, and it has the ability to improve the conductivity and stabilize the structure. As a result, the NiO/graphene hybrid film has exhibited enhanced performance.

## 2. Experimental

The precursor film was deposited on a nickel substrate by a chemical bath deposition method as reported in our previous work [5]. Commercial graphene (Nanjing XFNANO Materials Tech Co., Ltd.) was ultrasonically dispersed in distilled water (1 mg $mL^{-1}$). Different volumes of dispersion (50, 100, 150 and 200 μL) were absorbed by a microliter syringe and spin-coated on the precursor film. The film was finally heat treated at 350 °C for 1 h under flowing argon. The mass percentage of graphene in the hybrid film was analyzed by a simultaneous thermal analyzer (Netzsch, STA 449 F3) with the accuracy of 0.1 μg.

The materials were characterized by means of X-ray diffraction (XRD, Bruker D8 advance; Cu Kα radiation), scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL JEM-2100F).

Test cells were assembled in an argon-filled glove box. The hybrid film was used as the working electrode, pure lithium foil as the courter electrode, and Celgard 2400 membrane as the separator. The cells were cycled on a battery analyzer (MTI BST8-3) using

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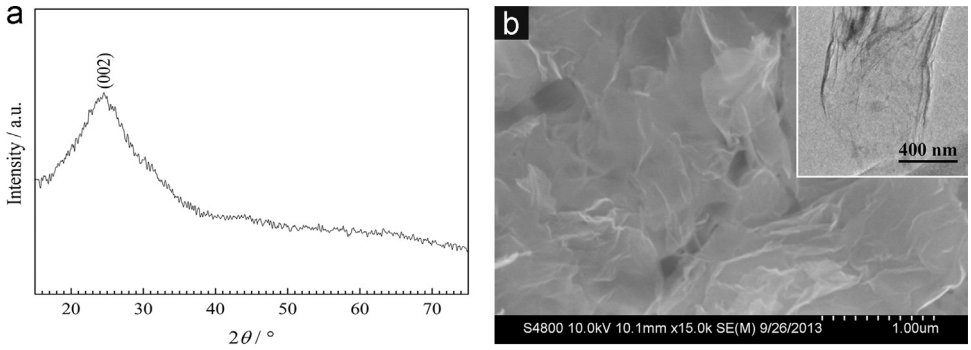


**Fig. 1.** (a) XRD pattern of graphene, and (b) SEM and TEM (top right) images of graphene.

**Table 1**
Comparison of the hybrid films with different mass percentage of graphene.

| Dispersion volume (μL) | Graphene content (wt%) | Initial coulombic efficiency (%) |
|---|---|---|
| 0 | 0 | 72.8 |
| 50 | 5.2 | 79.6 |
| 100 | 8.0 | 85.0 |
| 150 | 10.1 | 81.8 |
| 200 | 11.3 | 77.6 |

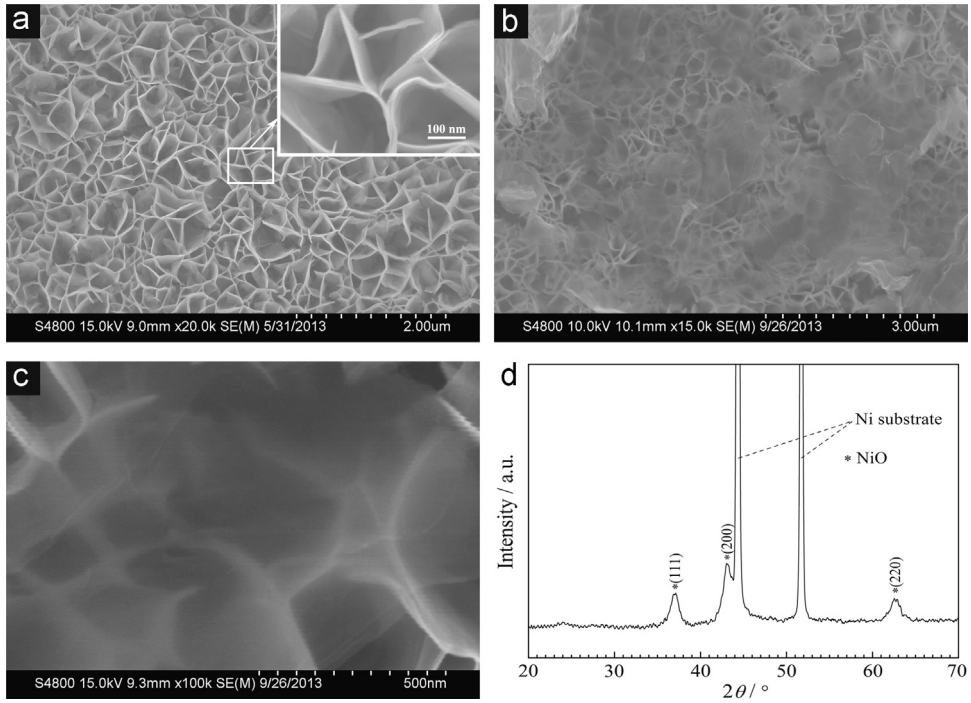


**Fig. 2.** SEM images of (a) the porous NiO film and (b, c) the porous NiO/graphene hybrid film. XRD pattern of (d) NiO/graphene hybrid film.

different current densities between 0.02 and 3 V. Cyclic voltammetry (CV) analysis was performed on an electrochemical workstation (CHI 604D) using a scan rate of 0.1 mV $s^{-1}$ between 0 and 3 V.

## 3. Results and discussion

Fig. 1a is the XRD pattern of commercial graphene. The broad peak around 24° corresponds to the (002) plane of graphene. Fig. 1b shows the SEM and TEM (top right) images of graphene sheets, and both of them show a rippled and crumpled feature.

The hybrid films prepared from different volumes of graphene dispersion are compared in Table 1. The film prepared using 100 μL dispersion has the graphene content of 8 wt%, and it has the highest initial coulombic efficiency of 85%. Therefore, this sample was investigated further.

The morphology changes after the coating of 100 μL dispersion can be seen in Fig. 2. Bare NiO film (Fig. 2a) is porous, constructed by many interconnected aligned nanosheets that are hundreds of