



Targeted synthesis of novel hierarchical sandwiched NiO/C arrays as high-efficiency lithium ion batteries anode



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HIGHLIGHTS

- Novel 2D sandwich-like NiO/C arrays on Ti foil are synthesized for the first time.
- Sandwiched structure possesses large specific surface area.
- The porous structure facilitates ion transfer and Li-ion absorption.
- The interspace between each nanoparticles buffers volume expansion.
- The sandwiched composite exhibits excellent electrochemical performance.

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ABSTRACT

In this contribution, the novel 2D sandwich-like NiO/C arrays on Ti foil are successfully designed and fabricated for the first time via simple and controllable hydrothermal process. In this strategy, we use green glucose as carbon source and ultrathin Ni(OH)₂ nanosheet arrays as precursor for NiO nanoparticles and sacrificial templates for coupled graphitized carbon layers. This advanced sandwiched composite can not only provide large surface area for numerous active sites and continuous contact between active materials and electrolyte, but also protect the active nanoparticles from aggregation, pulverization and peeling off from conductive substrates. Furthermore, the porous structure derived from lots of substances loss under high-temperature calcinations can effectively buffer possible volume expansion and facilitate ion transfer. In this article, sandwiched NiO/C arrays, utilized as anode for LIBs, demonstrated high specific capacity (~1458 mAh g⁻¹ at 500 mA g⁻¹) and excellent rate performance and cyclability (~95.7% retention after 300 cycles).

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1. Introduction

In the last decades, the ever-growing demand for large scale energy storage including fast charging electronics and electric vehicles has triggered significant research efforts on high-energy and power-density lithium-ion batteries (LIBs) [1–3]. LIBs are regarded as an ideal power source among the various available electrical energy storage mediums due to its high energy densities, long cycle life, environmental friendliness and safety [4,5]. However, power and energy densities of current generation LIBs are limited by electrode materials. Therefore, it is of great significance to exploit the enhanced electrode materials for its important impact on

battery capacity, stability, safety and cost [6,7]. When compared with conventional carbon-based materials, transition metal oxides (M_xO_y, where M = Fe, Co, Ni, Mn) have been proposed as one of the most promising anode materials based on their higher theoretical capacities and the conversion reaction, different from the classical insertion/de-insertion or Li-alloying processes [8]. The electrochemical conversion mechanism of M_xO_y with Li⁺ is commonly considered as [9–11]: M_xO_y + 2yLi⁺ + 2ye⁻ → yLi₂O + xM. Among transition metal oxides, nickel oxide (NiO) has attracted a great deal of research interests owing to their numerous promising applications, such as catalyst [12], gas sensors [13] and magnetic materials [14]. Meanwhile, they are widely used as anodes for LIBs [15–17]. It has been reported that NiO is highly favoured as attractive anode material for its low potential vs. Li/Li⁺, low cost, low toxicity and superior safety compared with other transition metal oxides [18]. Furthermore, it possesses high theoretic capacity of 717 mAh/g and

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high volumetric energy density (almost 5.8 times over graphite) [18,19]. Unfortunately, the poor electrical and ionic conductivity of NiO usually depresses its electrochemical performances, especially at high rates [20,21]. Moreover, the sluggish kinetics of the conversion reaction as well as the big volume expansion of NiO anode (95.69%) can exactly restrict the development of NiO due to large sized electrode materials [10,22].

To circumvent these shortcomings, the major approaches towards remission of these encountered issues are to reduce the size of active materials to nanoscale, design and fabricate carbon-coated materials or mix the active materials with high conductive materials and dope with foreign atoms [23,24]. In the previous researches, many nanostructured NiO have been reported, including nanocone [25], nanotubes [16], nanofilm [26] and nanowires [27]. As for the nanoscale materials, they can not only shorten both the electron and Li⁺ fast diffusion pathways, but also increase electrode/electrolyte surface contact, so as to enhance the cyclic stability and high-rate capacity [8,28,29]. Nevertheless, there comes the biggest bottleneck problem for nanoscale materials that they would easily get aggregated and further introduce more structural defects, resulting in poor cycling performance. Moreover, addition of excess carbon black or conducting polymer can limit the LIBs' cyclability. Thus, to synthesize sophisticated nanomaterials, particularly with designed and fabricated unique structural details, is always being desperately needed. Among all the designed electrode materials, direct growth of two-dimensional (2D) nanostructures with activity of Li storage on conducting substrates like Ti foil and Ni foam seems a feasible solution to balance among electrolyte diffusion, Li⁺ exchange between electrolyte and active materials, and charge transfer [30–32].

Herein, we devise and create a sandwich-like structure with NiO nanoparticles encapsulated by well-graphitized coupled carbon layers on Ti foil as high-efficiency LIBs anode. We use randomly dispersed Ni(OH)₂ nanosheets as sacrificial templates and green glucose as the carbon sources, respectively. Under the action of hydrogen-bonding, the glucose molecules are tightly absorbed onto the surface of the precursor. Then the polymer-coated precursor is calcinated in Ar atmosphere at 700 °C followed by annealing in air to obtain the sandwiched NiO/C array. This special nanoarchitecture, combined the direct growth of nanostructure active materials on conducting substrates with designed synthesis of sandwiched composite, possesses numerous outstanding advantages. Direct attachment to current collector like Ti foil can certainly improve the conductivity as well as separate active materials from each other, completely avoiding the aggregation and agglomeration between individual carbon sheets in normal electrodes [33–35]. As for the unique sandwiched structure, its 2D morphology helps to shorten pathway for fast Li⁺ and electron transfer and enlarge exposed surface for more lithium-exchange channels, leading to high electrical conductivity and cyclic stability. In addition, both top and bottom graphene layers tightly coated on the surface of functional materials can effectively prevent active nanoparticles from aggregation and peeling-off during long-time electrochemical reactions. More importantly, its porous structure derived from lots of substance loss under calcinations can not only effectively separate nanoparticles and buffer possible volume changes, but also accelerates more Li-ion absorption, bringing in higher specific capacity superior cyclic stability. Therefore, this unique nanoarchitecture obtained here demonstrates strikingly enhanced electrochemical performance.

2. Experimental

2.1. Materials

All chemicals or materials were utilized directly without any

further purification before use: ethylene glycol (Fisher Chemical, 99.99%), ammonium hydroxide (NH₃·H₂O, 28–30 wt%, J. T. Baker), nickel nitrate (Ni(NO₃)₂, 99.9%, Aldrich), sodium carbonate (Na₂CO₃, 99.9%, Aldrich), glucose (Cica-Reagent, Kanto Chemical) and Titanium Foil (0.127 mm (0.005 inch) thick, annealed, 99%, Alfa Aesar).

2.2. Preparation of Ni(OH)₂ nanosheet arrays on Ti foil

Prior to the synthesis, a Ti foil with size of 1*3 cm was rinsed with deionized water and pure ethanol subsequently or sonically cleaned by a mixture of deionized water, ethanol and acetone with volume ratio of 1:1:1 for 10 min. Afterwards, the Ti foil was tilted against the wall of autoclave at a certain angle, with the interested surface facing down. The Ni(OH)₂ nanosheet arrays were synthesized by a typical method. ethylene glycol (10 mL), concentrated NH₃·H₂O (12 mL), 1 M Na₂CO₃ aqueous solution (4 mL), and 1 M Ni(NO₃)₂ aqueous solution (4 mL) were mixed step-by-step under strong stirring with intervals of 2 min. After that, the precursor solution was stirred for another 10 min, and then the mixture changed into a dark blue solution. Subsequently, the mixed solution was transferred into the autoclave. The autoclave was then tightly sealed and left in an electric oven at 170 °C for 16 h. After the autoclave was cooled naturally to room temperature in air, the Ti foil was taken out and dried in vacuum oven at 60 °C for at least 3 h.

2.3. Preparation of sandwiched NiO/C arrays on Ti foil

Ti foil with Ni(OH)₂ nanosheet array covered was tightly tilted against the inner wall of a clean 45 ml Teflon liner. Then glucose aqueous solution (5 ml, 1 M) was mixed with additional D.I. water (25 ml) to form a homogeneous solution after 5 min ultrasonication. The above solution was introduced into the above-mentioned 45 ml Teflon-lined autoclave and sealed tightly. Then heated the liner in an electricoven at 180 °C for 4 h. After that, washed the Ti foil using D. I. water and ethanol, and dried the foil in air at 60 °C overnight to remove the residue water and ethanol. Afterwards, the dried samples were loaded into the tube furnace and calcined in Ar atmosphere at 700 °C for 200 min with a ramp of 1 °C/min. Finally the samples were annealed at 250 °C for 200 min in air to oxidize the previously formed Ni to NiO.

2.4. Carbon content of sandwiched NiO/C arrays on Ti foil

First, the composite was scraped off by a thin knife. The NiO/graphene composites (200 mg) were dissolved in concentrated hydrochloric acid (10 M) under vigorous stirring. Standing for almost 2 days, the final samples floated on the liquid level. Afterwards, the samples were washed using centrifugation with three cycles of deionized water and one cycle of ethanol, and then dried in air at 60 °C for 24 h to remove the residual water and ethanol. The carbon content of sandwiched NiO/graphene arrays was then calculated using the formula:

$$C\% = W(C)/W(NiO/C) \times 100\%$$

where W(C) and W (NiO/C) were the weight of carbon and NiO/graphene, respectively.

2.5. Material characterization

The synthesized materials are characterized on a transmission electron microscope (TEM, Philips, Tecnai, F30), field-emission scanning electron microscope (SEM, JSM-7800F, 5 kV) equipped with an energy dispersive spectrometer (EDS) analyser, X-ray

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