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A Simple Synthesis of Two-Dimensional Ultrathin Nickel Cobaltite Nanosheets for Electrochemical Lithium Storage

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ABSTRACT

We report a simple microwave-assisted method to fabricate high-quality two-dimensional (2D) ultrathin $NiCo_2O_4$ nanosheets with a geometrically graphene-like architecture. The unique large-area nanostructures represent an ultrahigh surface atomic ratio with almost all active elements exposed outside for surface-dependent electrochemical reaction processes. Experimental results reveal that the as-synthesized ultrathin $NiCo_2O_4$ nanosheets show excellent electrochemical performances for lithium storage application. The ultrathin $NiCo_2O_4$ nanosheets could deliver a high first discharge capacity (1287.1 mAh g^{-1}) with initial Coulombic efficiency of 80.0% at 200 mA g^{-1} current density. The reversible lithium storage capacity still retains at 804.8 mAh g^{-1} in the 100th cycle, suggesting a good cycling stability. The excellent electrochemical properties of the as-synthesized $NiCo_2O_4$ nanosheets could be ascribed to the unique ultrathin 2D architecture, which could offer large exposed active surface with more lithium-insertion channels and significantly reduce lithium ion diffusion distance. The cost-efficient synthesis and excellent lithium storage properties make the 2D $NiCo_2O_4$ nanosheets as a promising anode material for high-performance lithium ion batteries.

1. Introduction

As one of the promising energy storage and conversion devices, rechargeable lithium ion batteries have spurred intense research to resolve the ever-increasing energy and environmental issues due to their efficient high energy density [1–5]. Despite its successful application in portable electronic devices, the rechargeable lithium ion batteries are also urgently being developed for powering the ever-emerging vehicles, such as hybrid and all-electric vehicles [6–8]. This urgent demand brings about intensive research in developing advanced electrode materials. It has been reported that an array of metal salts with multiple-electron redox centres, typically including metal oxides and fluorides, could exhibit highly reversible reactivity toward lithium by a conversion mechanism [9]. During the conversion reactions, the active metal salt are generally reduced to ultrafine metallic clusters embedded into the resultant lithium salt phase upon lithiation and then reversibly restored to the initial state after delithiation [8,10–12]. Consequently, these materials can deliver much higher specific capacities than present commercial insertion electrodes, such as graphite anode. Considerable efforts are being devoted to fabricating optimum metal salt electrode materials for substantial improvements in the electrochemical properties [13].

Among various available conversion-type anode materials, single-phase multicomponent or mixed transition-metal oxides have been regarded as the extremely prospective substitutes for their better electrochemical performance owing to their possible synergetic effects resulting from the complex active chemical compositions [14–16]. Very recently, $NiCo_2O_4$ anode materials have received much attention because of the high theoretical specific capacity of 890 mAh g^{-1} for lithium ion batteries [17,18]. Yao et al. fabricated the hollow $NiCo_2O_4$ nanospheres via template-assisted synthesis and obtained superior electrochemical performances for lithium ion batteries [19]. Porous $NiCo_2O_4$ microflowers were synthesized through a traditional solvothermal method followed by heat-treatment and shown excellent cycling stability for lithium storage [20]. It is a common strategy to construct nanostructures for application in electrode materials [21,22]. However, the most present $NiCo_2O_4$ nanomaterials lack the ability to guarantee favourable reaction kinetics for the efficient mass transport and charge transfer processes due to the existing resistance toward lithium ion and electron between the surface and inner of active materials in principle. It could be anticipated that the surface-dominated 2D nanostructure should be the most ideal architectures to avoid the above-mentioned issues [23,24]. The overall performances of transition-metal oxide anodes can be

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significantly enhanced by improving the surface electrochemical reactivity [25,26]. So it is greatly to be wished for researchers to rationally design and fabricate 2D $NiCo_2O_4$ nanomaterials for the concern about their possible application as advanced anode materials for next-generation lithium ion batteries.

The $NiCo_2O_4$ nanosheet-based hybrid structures have been widely investigated as electrode materials for supercapacitors, in which favourable reaction kinetics and maximum active material utilization are achievable for ultrafast energy storage [27–30]. However, there is little report about synthesis of freestanding 2D $NiCo_2O_4$ nanostructures for electrochemical lithium storage applications. It is believable that 2D $NiCo_2O_4$ nanostructures could maximize electron transport and ion diffusion and eliminate the obstructed ion diffusion process in some other nanomaterials and the bulk counterparts [31–33]. Additionally, the large volume variation of $NiCo_2O_4$ electrode materials could also be alleviated in the 2D nanostructures with enough free interspace [23,34]. More importantly, the facile and cost-efficient fabrication of 2D $NiCo_2O_4$ architecture at large scale is also of great interest. Recently, the ever-increasing synthesis has been reported about the 2D $NiCo_2O_4$ nanostructures supported by various growth substrates, such as flexible carbon fabric [35,36], carbon nanofiber [37,38], carbon nanotubes [39], and halloysite nanotubes [30]. To the best of our knowledge, the synthesis of freestanding 2D $NiCo_2O_4$ nanostructures being independent of any growth substrates has been rarely reported to date. In this work, we first present a simple and cost-efficient strategy to fabricate high-quality ultrathin 2D $NiCo_2O_4$ nanosheets through a novel microwave-assisted liquid-phase growth method followed by heat-treatment. The electrochemical behaviours of ultrathin $NiCo_2O_4$ nanosheets as anode materials for lithium ion batteries are investigated through galvanostatic charge-discharge test and cyclic voltammogram (CV) measurement. The preliminary results show that the ultrathin $NiCo_2O_4$ nanosheets could exhibit a high electrochemical activity toward lithium ion.

2. Experimental

2.1. Materials synthesis

All chemical reagents used in the present synthetic procedure were of analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.. To synthesize the $NiCo_2O_4$ nanosheets, 10 mmol of $Co(NO_3)_2 \bullet 6H_2O$, 5 mmol of $Ni(NO_3)_2 \bullet 6H_2O$, and 60 mmol urea were added into a mixture solution of ethanol glycol/water (7:1 v/v, 240 mL) under vigorous stirring until being dissolved completely. The mainly synthetic stage was carried out in a microwave reactor (SINEO MAS-II, Sineo Microwave Chemistry Technology Co., Ltd, Shanghai China). The irradiation power was set at 700 W. After microwave treatment for 30 minutes, a great amount of puffy blue colloid precipitates come out. Then the reaction system was cooled naturally to room temperature. The resultant green product was obtained by centrifugation and dried in oven overnight at 80 °C. After heat treatment at 350 °C for 2 h in air, the final $NiCo_2O_4$ nanosheets were obtained.

2.2. Structure characterization

The X-ray diffraction (XRD) technology was first employed to determine the crystal structures and crystalline phase of the as-synthesized samples on a XRD machine (XRD, Bruker D8) with Cu Kα (λ = 0.15418 nm) radiation. The microstructure and morphology were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20, 200 kV). The element composition was investigated by X-ray photoelectron sperctra (XPS, PHI Quanteral II, Japan). The nitrogen adsorption isotherms were collected on a N_2 adsorption apparatus (NOVA4200e, Quantachrome Instruments, USA).

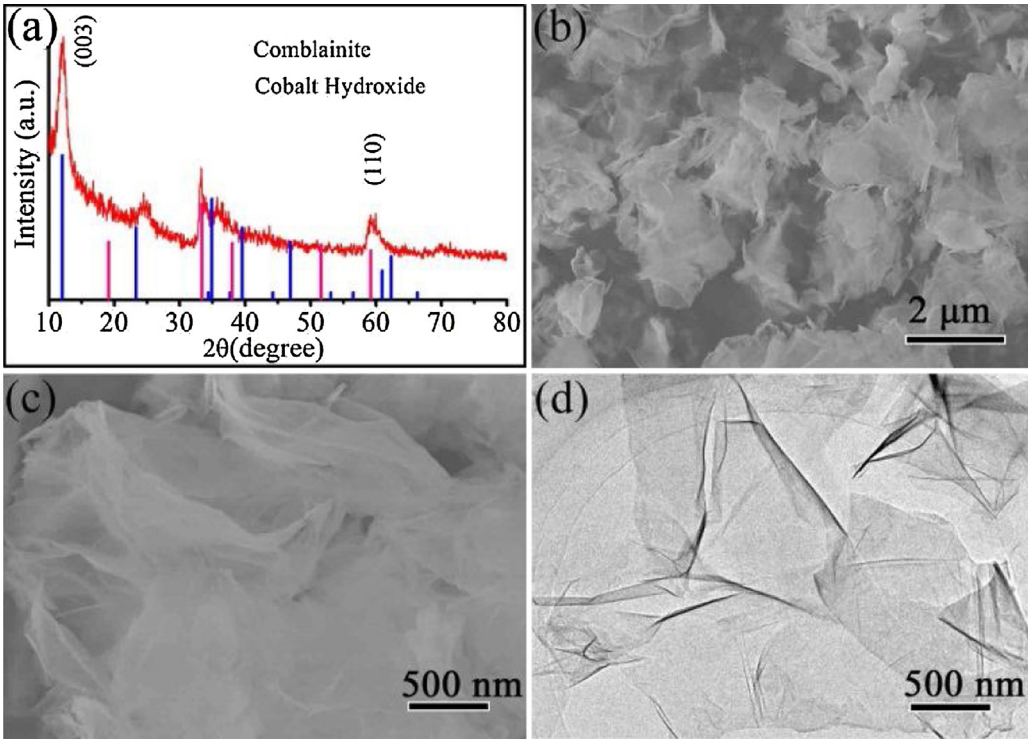

Fig. 1. Morphology and microstructure characterizations of the NiCo-based precursor nanosheets: (a) XRD pattern, (b) and (c) typical low-magnification and magnified FESEM images, and (d) TEM image.