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In-situ growth of cobalt oxide nanoflakes from cobalt nanosheet on nickel foam for battery-type supercapacitors with high specific capacity

Shuying Kong [a], Fan Yang [b], Kui Cheng [a,*], Tian Ouyang [a], Ke Ye [a], Guiling Wang [a], Dianxue Cao [a,*]

[a] Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

[b] College of Science, Northeast Agricultural University, Harbin 150030, China

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ABSTRACT

Ni foam supported Co_3O_4 nanoflakes is prepared for battery-type supercapacitor application through a simple three-step route. In briefly, Co metals are first deposited on Ni foam with a nanosheet morphology. The CoC_2O_4 protrudes out from the surface of Co through an in-situ reaction with $H_2C_2O_4$ to form dendritic-like nanowires morphology. Finally, Co_3O_4 are obtained through thermal decomposition of the CoC_2O_4 precursor and the dendritic-like nanowires morphology is melting and transforming into a nanoflakes morphology. The unique architectures morphology with porosity and interconnected channels has great advantages since it can effectively increases the contact surface area with electrolyte, which could significantly not only enhances surface area but also the ion/electron diffusion. Electrochemical tests show that Co_3O_4 nanoflakes exhibit a high specific capacity up to 576.8 C g^{-1} at a current density of 1 A g^{-1} and remain 283.7 C g^{-1} capacity at a high current density of 50 A g^{-1}, as well as 82% capacitance retained after 5000 cycles. These above results demonstrate the great potential of Co_3O_4 nanoflakes in the development of battery-type supercapacitors.

1. Introduction

The ever worth environment issue and the decreasing availability of fossil fuels have caused an ever increasing demand for exploring green, high-efficiency, and renewable energy storage system (EES) [1,2]. Among these EES, Li-ion battery and supercapacitor have been drawn a range of interests and considered as promising power sources for electric vehicles (EVs) and efficient energy storage devices to integrate the electricity generated from intermittent energy source (such as wind or solar) into the electrical power grid. Different with Li-ion battery stores energy through the intercalation/de-intercalation of Li^+ within the bulk materials result in a significantly high energy density but limited power density and cycling performance, supercapacitor can provides higher power density and excellent cycle life but lower energy density because of the charge storage occurs at the interface between the electrode materials and electrolyte [3–5]. In general, supercapacitors could be divided into the electric double layer capacitor (EDLC) [6] and pseudo-capacitor (PC) [7]. Compared with EDLC, the capacitance of pseudo-capacitor arises from reversible and fast *Faradic* redox reactions that can provide high energy density. Therefore, many efforts have been endeavored to prepare various redox-active transition-metal oxides, such as nickel or cobalt based oxides or hydroxides [8–13], as the electrode materials for PC. However, based on the fundamental definition of capacitance [14], the PC represents the materials equipped with electrochemical signature, i.e., a linear response of the charge accumulated with applied potential increasing, and a quasi-rectangular CV [15]. Hence, in this situation, various reported literature about transition metal oxide/hydroxides with *Faradic* behavior have be considered as a battery-type capacitor material [16–20].

Recently, Co_3O_4, as a typical battery-type electrode material, has been concerned attribute to its high theoretical capacity, outstanding reversible redox behavior, and good corrosion stability [21,22]. However, along with other battery-types capacitor materials, Co_3O_4 has suffered with the issues of poor rate capability and cycle stability. In order to improve the energy density of battery-type capacitor materials at high rates, it is critical to enhance the ion and electron transfer rate, and thus to ensure plenty electro-active materials occur the *Faradic* redox reaction. Nowadays, nanostructures (nanowire, nanoflake, nanotube etc.) have been demonstrated to be unique in promoting the mass transport, ion diffusion and electron transport, thus boosting the electrochemical performance [23,24]. Particularly, this nanostructure directly growth on the substrate usually exhibited much larger capacity than that of nano-powders based materials. In this condition, every nanostructure direct contact with the substrate and thus can make sure that all nanostructures participate in the redox reaction, which increases the utilization of active materials and avoids the "dead zoom" caused by adding ancillary materials (conductive carbon and binder). The open architecture also promote the electrolyte sufficiently contacts

* Corresponding authors.
E-mail addresses: chengkui@hrbeu.edu.cn (K. Cheng), caodianxue@hrbeu.edu.cn (D. Cao).

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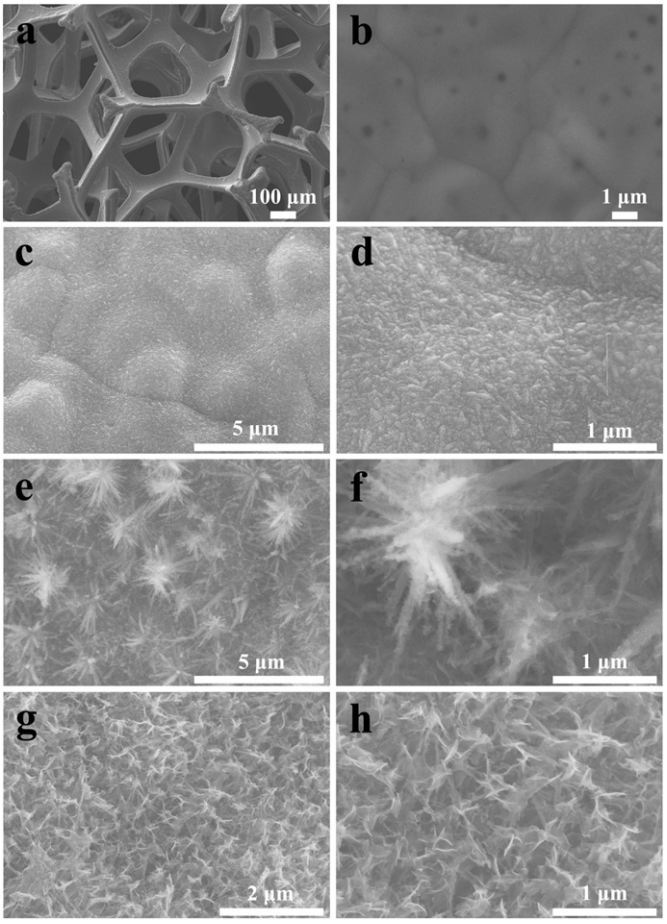

Fig. 1. Different resolution SEM images of bared Ni foam (a and b), Co (c and d), CoC_2O_4 (e and f) and Co_3O_4 (g and h), respectively.

with the inner region of the electrode, which could reduce the internal resistance and improve high-power performance [25,26]. More important, the three-dimensional (3D) structure could effectively mitigates the structural destruction caused by the phase transition during the discharge/charge process.

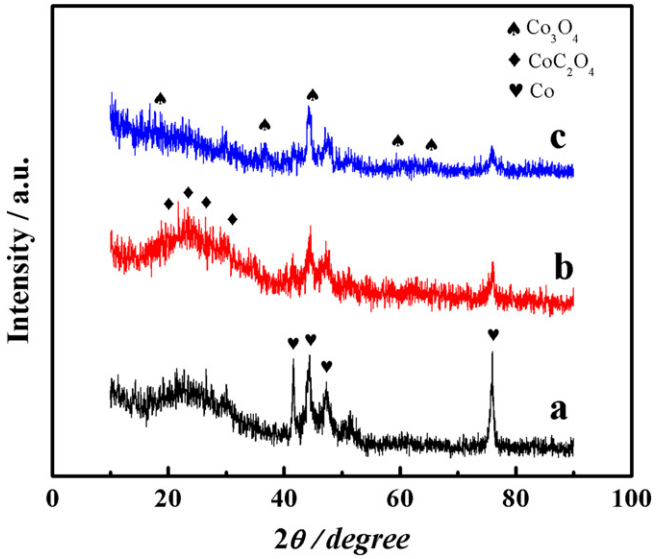

Fig. 2. XRD patterns of Co (a), CoC_2O_4 (b) and Co_3O_4 (c), respectively.

Many reports are available on the synthesis and supercapacitor properties of Co_3O_4 nanostructure on different substrates [27,28]. Huang et al. [29] described a chemical bath deposition synthesis of Co_3O_4 thin film on ITO substrate with a specific capacitance of 102.2 C g^{-1} at a constant current density of 0.2 A g^{-1}. Wu and co-author [30] fabricated Co_3O_4 porous nanowall via electrodeposition which showed a specific capacitance of 178.8C g^{-1} at 2 A g^{-1}. Cao et al. [31] reported the preparation of hierarchically porous Co_3O_4 film with a capacitance of 249.7C g^{-1} at a discharge current density of 2 A g^{-1}. Guduru's group [32] designed a facile and versatile precipitation by means of plasma spray technique approach for preparation Co_3O_4 nanostructures. Electrochemical performance showed a specific capacitance of 56.7C g^{-1} for a specific current rate of 2.75 A g^{-1}. Yuan et al. [33] illustrate the successful synthesis of Co_3O_4 porous nanoflake by liquid crystalline template, which exhibits a capacity of 243.7C g^{-1} at 2 A g^{-1}. Unfortunately, in all these cases the observed specific capacity is considerably below the theoretical value of Co_3O_4, especially at high rates.

In this work, an easily-controllable, facile and in-situ growth of Co_3O_4 nanoflakes has been proposed. Co is first electrodeposited on Ni foam and then in-situ reacted with $H_2C_2O_4$ solution to form CoC_2O_4 with a dendritic-like structure. The following thermal treatment makes the CoC_2O_4 precursor finally transform into mesoporous spinel Co_3O_4 nanoflakes. The unique 3D Co_3O_4 nanoflakes structure has brought large specific capacity and excellent electrochemical stability at high rates, suggesting the manageable and measurable approach would provide guidance for developing battery-type capacitor materials.

2. Experimental

2.1. Synthesis

The synthesis Co_3O_4 nanoflakes involve electrodeposition, in-situ chemical bath reaction and calcination. Co was electrodeposited on Ni foam with the electrolyte solutions consist of 0.25 mol L^{-1} $CoCl_2$ and 70 ml L^{-1} Tris(2-Hydroxyethyl)Amine. The deposition was performed by using a constant current density of −10 mA cm^{-2} for 30 min at room temperature. Then, the obtained samples were soaked in 0.3 mol L^{-1} $H_2C_2O_4$ solutions consist of 95% C_2H_5OH + 5% H_2O (volume ratio) for 3 h at 45 °C without stirring. After rinsed with deionized water, the samples were finally annealed at 300 °C for 1 h under air atmosphere.

2.2. Materials characterization

X-ray diffractometer (XRD, Rigaku TTR III) using a Cu Kα radiation was used to analysis the crystalline phase of as-prepared materials, Field emission scanning electron microscopy (FE-SEM, Hitachi SU8000) was employed to characterize the microstructure. The Transmission electron microscopy (TEM) and SAED patterns were obtained on a JEM-2010FEF.

2.3. Electrochemical measurements

The electrochemical measurements were conducted in a conventional three electrode electrochemical cell with the as-prepared Co_3O_4 nanoflakes as working electrodes, and a Pt auxiliary electrode and a Hg/HgO reference electrode. Cyclic voltammetry (CVs), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were carried out on an Autolab PGSTAT302 (Eco Chemie). EIS measurements were performed by applying an alternating voltage with 5 mV amplitude in a frequency scope from 0.01 Hz to 100 kHz at the open circuit potential. The test of cycle life was performed using a LAND battery program-control test system.