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The design and fabrication of $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites as high-performance anodes for Li-ion batteries

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ABSTRACT

The $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites were rationally designed and prepared by a two-step hydrothermal synthesis and subsequent annealing treatment. The one-dimensional (1D) Co_3O_4 nanowire arrays directly grew on Ni foam, whereas the 1D $\text{Co}_3\text{V}_2\text{O}_8$ nanowires adhered to parts of Co_3O_4 nanowires. Most of the hybrid nanowires were inlaid with each other, forming a 3D hybrid nanowires network. As a result, the discharge capacity of $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites could reach 1201.8 mAh/g after 100 cycles at 100 mA/g. After 600 cycles at 1 A/g, the discharge capacity was maintained at 828.1 mAh/g. Moreover, even though the charge/discharge rates were increased to 10 A/g, it rendered reversible capacity of 491.2 mAh/g. The superior electrochemical properties of nanocomposites were probably ascribed to their unique 3D architecture and the synergistic effects of two active materials. Therefore, such $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites could potentially be used as anode materials for high-performance Li-ion batteries.

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1. Introduction

As one of the most important electrochemical storage devices, Li-ion batteries (LIBs) have been rapidly evolving in different applications, ranging from new generation of portable electronic devices to electric vehicles [1]. However, current commercialized graphite anode has the low theoretical capacity that hinders their further applications in LIBs [2,3]. This promotes intensive researches for alternative anode materials with high capacity and long cycling lifetime. Due to the much higher theoretical capacities over the commercially used graphite, transition metal oxides (TMOs) have been regarded as promising candidates as alternative anode materials for LIBs [4,5]. In particular, cobalt oxide (Co_3O_4) has been well regarded as distinguished anode due to their high capacity, good chemical/thermal stability, and low cost for synthesis [6–8]. However, their practical application is largely restrained by the low electrical conductivity, poor cycle stability and large volume expansion during the charge/discharge process.

To address this problem, the first approach is to grow the active materials directly on conductive collectors, which can enhance their electronic conductivity and structure stability, leading to im-

proved electrochemical performance [9,10]. Especially, the Ni foam has porous architecture with large surface area, good electronic conductivity and structure stability, which can be an ideal deposition substrate [11,12]. The second approach is to design binary metal oxides to improve electrochemical performances in view of their improved redox activity and electrical conductivity than that of single metal oxides [13–16]. Among them, binary metal $\text{Co}_3\text{V}_2\text{O}_8$ based materials have been intensively studied as electrode materials for supercapacitors [17] and catalysis [18]. As a novel anode for LIBs, $\text{Co}_3\text{V}_2\text{O}_8$ shows superior electrochemical activities, which may have potential application in LIBs [19]. Recently, much attention has been paid to a judicious design of nanostructured electrode materials and smart hybridization of two materials in synergy [20–26]. Such an electrode system has demonstrated enhanced electrochemical performances using rational design of nanocomposites in structure and component [27,28]. In particular, three-dimensional (3D) nanostructured electrodes are more attractive because they can take full advantages of different nanostructures and components, while offering good physical isolate with less aggregation during battery cycling to achieve superior electrochemical performances [29–31]. For instance, Kong et al. fabricated 3D $\text{Co}_3\text{O}_4/\text{MnO}_2$ hierarchical nanoneedle arrays by a facile two-step hydrothermal, which presented improved electrochemical properties for LIBs compared to the single Co_3O_4 nanowires arrays [32]. Zheng synthesized $\text{Co}_3\text{O}_4/\text{Fe}_2\text{O}_3$ branched nanowire heterostructure via a two-step hydrothermal reaction to enhance

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the electrochemical performance [33]. Wu fabricated $\text{Co}_3\text{O}_4/\text{NiO}/\text{C}$ nanowire arrays, which showed a high capacity (1053 mAh/g) and good rate capability [34]. To date, different nanostructured single Co_3O_4 and $\text{Co}_3\text{V}_2\text{O}_8$ have been synthesized and applied for LIBs [35–39]. Nevertheless, few studies have been performed concerning electrochemical performance of their 3D integrated electrodes on porous substrates by rationally combining merits of Co_3O_4 and $\text{Co}_3\text{V}_2\text{O}_8$.

In this study, we designed and fabricated $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites by a two-step hydrothermal synthesis and subsequent annealing treatment. It showed unique 3D architectures consisted of a large number of interlaced hybrid nanowires, in which the 1D Co_3O_4 nanowire arrays directly grew on Ni foam, and 1D $\text{Co}_3\text{V}_2\text{O}_8$ nanowires inlaid and adhered to parts of Co_3O_4 nanowires. This electrode exhibited outstanding electrochemical performance in terms of the high reversible capacity, outstanding long-life cycling stabilities and impressive high-rate capability. The improved lithium storage performance could be attributed to the 3D hybrid nanowires architecture and synergetic effects between Co_3O_4 and $\text{Co}_3\text{V}_2\text{O}_8$ component. The proposed nanocomposites could be potentially used as anode materials for LIBs.

2. Experimental

2.1. Synthesis of $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites

Synthesis of $\text{Co}_3\text{O}_4/\text{Ni}$ nanocomposites. The $\text{Co}_3\text{O}_4/\text{Ni}$ nanocomposites were prepared by a routine hydrothermal synthesis method. In a typical synthesis, 0.93 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 160 mL deionized water, followed by addition of 0.96 g of $\text{CO}(\text{NH}_2)_2$ and 0.24 g NH_4F with continuous stirring. The mixture was transferred into a 200 mL Teflon-lined autoclave, with insertion a piece of clean Ni foam, and hydrothermally treated in an oven at 100 °C for 5 h. The obtained Ni substrate with pink precipitates was washed with deionized water, and further heated in air at 350 °C for 2 h for subsequent processing.

Synthesis of $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites. The Ni foam substrate covered by Co_3O_4 nanowires was then used as the “substrate” to guide the growth of $\text{Co}_3\text{V}_2\text{O}_8$ nanowires in the hydrothermal reaction. Next step was to dissolve 1.6 g $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$ and 1.55 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 160 mL deionized water, then took the homogeneous solution into a 200 mL Teflon-lined stainless steel autoclave with insertion of the obtained $\text{Co}_3\text{O}_4/\text{Ni}$ samples at 150 °C for 6 h growth. The formation mechanism of $\text{Co}_3\text{V}_2\text{O}_8$ was: $2\text{Na}_3\text{VO}_4 + 3\text{CoCl}_2 \rightarrow \text{Co}_3\text{V}_2\text{O}_8 + 6\text{NaCl}$. After that, the samples were dried at 200 °C for 12 h under vacuum to obtain the $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites.

2.2. Characterization of electrode materials

The structure of the obtained products was examined with X-ray diffraction (XRD; Rigaku Co., D/MAX 2400 diffractometer with Cu $K\alpha$ radiation, $\lambda = 0.15418$ nm). The morphology and structure were characterized by scanning electron microscopy (SEM; JEOL, JSM-6701F) and transmission electron microscopy (TEM; JEOL, JEM-2010) with energy dispersive spectrometer (EDS). Inductively coupled plasma (ICP-AES, IRIS Intrepid II XSP) was carried out to measure the element component of samples.

2.3. Electrochemical measurements

The electrochemical performances were tested using CR-2032 coin-type cells. The $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites were directly used as the working electrode. The mass loading of the active materials was around 1–1.5 mg/cm². All cells were assembly in an argon-filled glove box with a Li foil as the counter electrode, a Celgard 2300 membrane as the separator and a mixture of 1 M LiPF_6 in ethylene carbonate and dimethyl carbonate (1:1, by volume) as the electrolyte, and the amount of electrolyte was about 70–80 μL . Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured by the electrochemical workstation (CHI660C, Shanghai China). The charge–discharge cycling was performed by the lithium-ion battery cycler (LAND CT2001A, Wuhan China) at different current rates.

3. Results and discussion

3.1. Synthesis and structure characterization

The XRD patterns in Fig. 1(a) show the overall crystal structure and phase purity of the two as-obtained products: pristine $\text{Co}_3\text{O}_4/\text{Ni}$ and $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites. All the diffraction peaks for the two samples fitted well with standard XRD patterns of Co_3O_4 (JCPDF: 65-3103) and $\text{Co}_3\text{V}_2\text{O}_8$ (JCPDF: 16-0675) phases. The diffraction peaks at 31.4°, 36.9°, 59.6°, and 65.5° were correlated to the 220, 311, 511, and 440 reflections of Co_3O_4 , respectively; whereas the diffraction peaks at 15.1°, 35.7°, 57.6° and 63.2° were associated with the 110, 311, 511 and 440 reflections of $\text{Co}_3\text{V}_2\text{O}_8$, respectively. No additional peaks from possible impurities were observed, indicating that the composites were made of Co_3O_4 and $\text{Co}_3\text{V}_2\text{O}_8$ with high purity. In addition, EDS microanalysis of $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8$ samples scratched from the Ni foam showed that products consisted of Co, V and O elements (Fig. 1(b)), which further confirmed that the nanocomposites were mainly made of

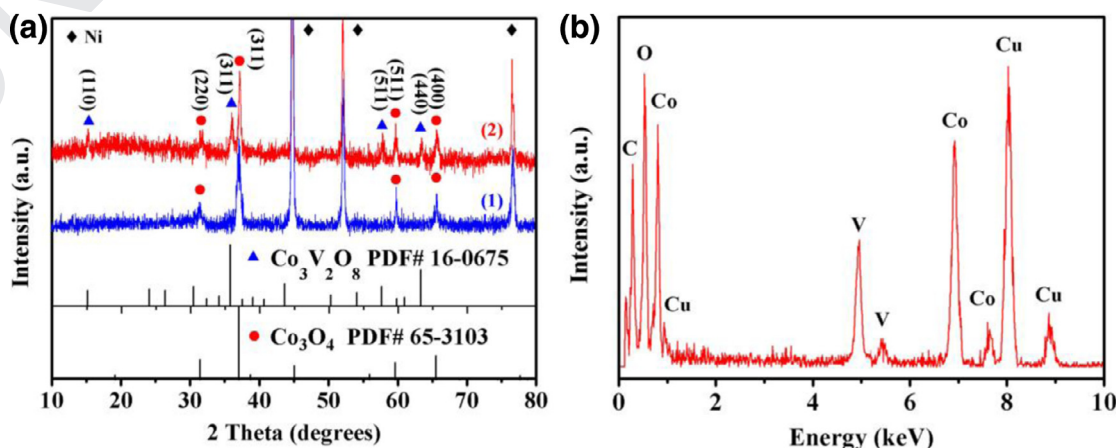


Fig. 1. (a) XRD patterns of (1) $\text{Co}_3\text{O}_4/\text{Ni}$ and (2) $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8/\text{Ni}$ nanocomposites. (b) EDS spectra of $\text{Co}_3\text{O}_4/\text{Co}_3\text{V}_2\text{O}_8$ samples scratched from the Ni foam.

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