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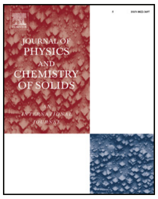

Facile synthesis of porous $FeCo_2O_4$ nanowire arrays on flexible carbon cloth with superior lithium storage properties

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ABSTRACT

In this work, one-dimensional (1D) needle-like porous $FeCo_2O_4$ nanowire arrays on flexible carbon cloth (CC) are successfully fabricated by a facile synthesis route and investigated as anode material for lithium ion batteries (LIBs). X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray photoelectron spectroscopy (XPS) have been applied to characterize the materials. The 1D $FeCo_2O_4$ nanowires provide a large surface area and enough space to accommodate volume changes. Besides, taking advantages of good conductivity from the CC substrate and the synergistic effect between Co and Fe ions, the integrated $FeCo_2O_4$ nanowire arrays/CC electrodes exhibits prominent lithium-storage performance with high reversible capacity of about 2101 mAh g^{-1} at 100 mA g^{-1} and outstanding capacity retention of 97.1% from 2 to 200 cycles, and retains high rate capacity of 876 mAh g^{-1} at 2 A g^{-1}. Even cycled at higher current density of 1 A g^{-1}, $FeCo_2O_4$ nanowire arrays/CC electrode still maintains stable reversible capacity of 1013.8 mAh g^{-1} after 350 cycles, corresponding to 78.3% of the second discharge capacity. Therefore, $FeCo_2O_4$ nanowire arrays/CC could be considered to be a promising candidate as anode material for flexible Li-ion batteries and future stretchable/bendable electronic devices.

1. Introduction

As the problem of energy depletion and environmental pollution has become increasingly serious, developing high-performance energy storage devices and energy-saving conversion technology has inspired the interest of global researcher [1–8]. Lithium-ion batteries (LIBs) as a renewable energy have been employed as dominant power source for large-scale application in electronic devices and hybrid electric vehicles [9–13]. However, commercial graphite can no longer meet the needs of today's society for high energy density, long-life energy storage devices due to the low theoretical capacity (372 mAh g^{-1}). Spinel Co_3O_4 as a typical transition-metal oxide has been regarded as one of the most promising anode materials for graphite substitute because of its large theoretical capacity (890 mAh g^{-1}) and excellent cycling performance [14–17]. However, the toxicity and high cost of cobalt element restrict the practical application of Co_3O_4 in LIBs.

It is advisable to replace Co in part with other environmentally friendly and inexpensive elements while maintaining its electrochemical properties. Such as, $MnCo_2O_4$ [18,19], $CuCo_2O_4$ [20], $ZnCo_2O_4$ [21], $FeCo_2O_4$ [22,23], $NiCo_2O_4$ [24,25], have become a research hotspot because of the complementarity and synergy of two element during the Li^+ charge/discharge process, which exhibits better mechanical stability and electronic conductivity than Co_3O_4. In special, $FeCo_2O_4$ is highly expected because of its cheapness and environmental friendliness of ferrum element and rich redox reactions [23,26,27]. Nevertheless, $FeCo_2O_4$ usually delivers poor capacity retention due to the low conductivity, large volume variations and severe particle aggregation during the Li^+ ions insertion and extraction processes, which hinder its practical application. Therefore, designing a high-efficiency and robust architecture to enhance the electrochemical properties of $FeCo_2O_4$ anode is of great importance.

Herein, 1D needle-like porous $FeCo_2O_4$ nanowire arrays on flexible carbon cloth (CC) were successfully synthesized via a facile hydrothermal reaction followed by annealing treatment. As-obtained composite with hierarchical structure has the following merits. Firstly, CC was used as current collector and conductive substrate for directly growing active materials, providing the composite with outstanding physical properties such as good tensile strength, high electronic conductivity and good flexibility [28]. Secondly, coupling of the cobalt ions and ferrum ions within $FeCo_2O_4$ necessarily takes advantages of synergetic effect and rich redox reactions of two metal species, leading to excellent electrochemical properties [23]. Thirdly, the 1D needle-like

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porous nanowires exhibit prominent lithium-storage performance due to its large surface area and short Li-ion diffusion length, as well as enough space to accommodate volume changes [29]. Therefore, as-prepared 1D $FeCo_2O_4$ nanowire arrays on CC exhibit superior electrochemical performance as anode materials for LIBs.

2. Experimental section

Materials Synthesis: All the chemicals in this work were of analytical grade and directly used after purchase without further purification. $FeCo_2O_4$ nanowires grown on CC was prepared as following. In a typical procedure, 1 mmol of $Fe(NO_3)_3 \cdot 9H_2O$, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 4 mmol of NH_4F and 10 mmol of urea were dissolved in 35 mL deionized water under violent stirring for 20 min at room temperature. A piece of carbon cloth (1 × 8 cm) was immersed with concentrated HNO_3 solution for 2 h, and then cleaned with acetone, ethanol and deionized water for 10 min each. The solution was transferred into a 40 mL Teflon-lined autoclave and the cleaned CC substrate was immersed into the solution. The autoclave was sealed and maintained at 120 °C for 6 h. After the autoclave cooling to room temperature naturally, as-obtained precursor was taken out, washed with ethanol and distilled water for several times, and dried at 70 °C for 2 h. Finally, the precursor was put in a quartz tube and annealed at 400 °C in air for 2 h to obtain $FeCo_2O_4$ nanowires supported on the CC. The mass loading of the $FeCo_2O_4$ sample is calculated to be about 1.6 mg cm^{-2}.

Structural Characterization: X-ray diffraction (XRD, Rigaku D/max 2500) with Cu K $_a$ radiation was used to characterize the crystal structure of as-synthesized $FeCo_2O_4$ nanowire arrays/CC. The scan electron microscopy (SEM) images of the samples were observed on FEI Helios Nanolab 600i, transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were characterized by FEI Tecnai G2 F20. Inductive coupled plasma atomic emission spectrometry (ICP-AES) was utilized to confirm the surface chemical compositions of samples. The valence states of metal ions in the products were confirmed by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi).

Electrochemical measurements: The electrochemical properties of $FeCo_2O_4$ nanowire arrays/CC anode were tested by a CR2025 coin cells assembled in an argon-filled glove box. A small piece of the $FeCo_2O_4$ nanowire arrays/CC (1 cm × 1 cm) is directly used as the working electrode and lithium metal as the counter and reference electrode. The electrolyte is 1 M $LiPF_6$ solution in a mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate with a volume ratio of 1:1:1. Electrochemical workstation (CHI660E, Chenhua Instrument Company, China) was used to obtain the cyclic voltammogram (CV) curve and electrochemical impedance spectroscopy (EIS) of $FeCo_2O_4$ nanowire arrays/CC anode. The galvanostatic discharge-charge tests were cycled at desired current densities with an electrochemical test instruments (LANHE, CT2001A).

3. Results and discussion

The synthesis process and the corresponding electrode architectures of the $FeCo_2O_4$ nanowire arrays on CC is illustrated in Fig. 1. Typically, the precursor nanowires were radially coated on the CC substrate via facile hydrothermal reaction at 120 °C for 6 h, as shown in Fig. S1. Subsequently, the $FeCo_2O_4$ nanowire arrays on CC were obtained by annealing of the precursor at 400 °C in air for 2 h. The crystallographic structure of as-obtained $FeCo_2O_4$ nanowire arrays grown on CC is first characterized by X-ray diffraction (XRD) pattern, as shown in Fig. 2a. All of the diffraction peaks excluding the peak at 25.8° is assigned to the CC substrate can be matched with spinel $FeCo_2O_4$ (JCPDS card no. 71-0816), which is consistent with previous reports [30,31]. The diffraction peaks at 19.1°, 31.4°, 36.9°, 44.9°, 59.5° and 65.4° could be ascribed to the (111), (220), (311), (400), (511) and (440) lattice planes of the $FeCo_2O_4$ phase.

The photographic images of the bent CC grown with $FeCo_2O_4$ nanowires shows its prominent flexibility that can be folded and flexed, which makes $FeCo_2O_4$ nanowire arrays/CC a potential candidate in flexible device, as shown in Fig. 2b. Scanning electron microscopy (SEM) technique is employed to confirm the morphology and detailed structure of $FeCo_2O_4$ nanowire arrays/CC products, as shown in Fig. 2c–f. It should be noted that the morphology and integration of $FeCo_2O_4$ nanowires is unchanged after annealing treatment of precursor nanowires. Fig. 2c–e shows the low-magnification SEM images, which clearly depicts that the entire CC are fully covered with uniform and dense $FeCo_2O_4$ nanowires. The high-magnification SEM image (Fig. 2f) clearly exhibits that these $FeCo_2O_4$ nanowires have an average diameter of ~100 nm and a mean length of ~5 μm. Moreover, a conical structure of $FeCo_2O_4$ nanowire can be also observed. It is anticipated that the $FeCo_2O_4$ nanowires have excellent capillary pathways and good electron transportation capability, which is beneficial to improve the electrochemical performance due to the rapid insertion and extraction of lithium ions in the redox process.

Fig. 3a and b shows the TEM images with different magnifications of an individual $FeCo_2O_4$ nanowire, indicating that the nanowires are mesoporous structure owing to the pyrolysis and dehydration during annealing treatment. And the diameter of $FeCo_2O_4$ nanowire gradually decreases from root to tip. The HRTEM image of $FeCo_2O_4$ nanowires, as shown in Fig. 3c, clearly exhibits that well-resolved lattice fringes with lattice spacing of approximately 0.46 nm correspond to the (111) facet of $FeCo_2O_4$. The selected area electron diffraction (SAED) pattern (inset in Fig. 3c) depicts several well-defined diffraction rings, corresponding to the (111), (220), (311), (400), (511), and (440) planes, which indicates the poly-crystalline nature of $FeCo_2O_4$ nanowires. The SAED analysis is also in good agreement with the XRD results. Fig. 3d displays the elemental maps of an individual $FeCo_2O_4$ nanowire, indicating that the nanowire consists of Co, Fe, and O elements. Besides, Co, Fe, and O are uniformly distributed in the whole $FeCo_2O_4$ nanowires. Fig. S2 depicts the energy-dispersive X-ray spectroscopy (EDX) of as-fabricated composite (inset is the atomic ratio of metal element investigated by inductive coupled plasma atomic emission spectrometry (ICP-AES)). It is clearly seen that the composite contains only Fe, Co, O elements consistent with the observation of elemental maps, and the atomic ratio of Co and Fe is in good agreement with its stoichiometry, which indicates that the formation of pure $FeCo_2O_4$ nanowires.

The oxidation states and surface chemical compositions of metal ions in the $FeCo_2O_4$ nanowires were investigated by X-ray photoelectron spectroscopy (XPS). Fig. 4 an exhibits the full survey scan spectrum, the sharp peaks at 286.2, 530.2, 714.3, 780.2 eV correspond to the characteristic peaks of C 1s, O 1s, Fe 2p and Co 2p, respectively, which indicates the purity of $FeCo_2O_4$ product. The deconvolution and fittings of peaks were conducted using Gaussian method on the basis of the Shirley background correction. Fig. 4b shows the Fe 2p spectra, in addition to two "shoulder" satellite peak at 716.7 eV and 731.9 eV, the fitting peaks located at binding energy of 711.8 and 723.5 eV can be attributed to pin-orbit peaks of the Fe $2p_{3/2}$ and Fe $2p_{1/2}$, indicating the appearance of Fe^{2+} [22]. Likewise, as shown in Fig. 4c, the fitting peaks locates at 779.9 and 794.9 eV are attributed to Co^{3+} with the satellite peak at 785.4 eV, whereas the fitting peaks at 781.1 and 796.5 eV are from Co^{2+} with the satellite peak at 803.7 eV [22,23]. Furthermore, the O 1s emission spectrum is well fitted to three fit peaks, the fitting peaks at binding energy of 530.2 eV can be ascribed to metal – oxygen bond, the other two peaks at 531.3 and 532.5 eV are attributed to the OH^- groups oxygen and surface bound water, respectively, as shown in Fig. 4d [26,32].

The electrochemical properties of $FeCo_2O_4$ nanowire arrays/CC electrode were first evaluated through cyclic voltammetry (CV) measurements to determine the charge and discharge reaction potentials using 1D porous $FeCo_2O_4$ nanowire arrays/CC as the anode materials for lithium ion batteries. Fig. 5a shows the CV curves of $FeCo_2O_4$ nanowire arrays/CC electrode in the first three cycles at 0.2 mV/s scan rate and within 0.01–3 V potential range. The cathodic peak at 0.01 V