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Cobalt phosphide nanowire arrays grown on carbon cloth as novel electrode material for supercapacitors

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ABSTRACT

It is very important to exploit new electrode materials to enhance supercapacitor performances. In this study, the mesoporous cobalt phosphide (CoP) nanowire arrays on carbon cloth have been fabricated by low-temperature phosphidation of hydrothermally obtained Co precursor. The CoP electrode shows a remarkable areal capacitance of 1.89 F/cm^2 at current densities of 3 mA/cm^2. Furthermore, the electrode exhibits excellent cycling stability (~3% loss after the repetitive 4000 cycles at 18 mA/cm^2) and Coulombic efficiency (~97.6% after 4000 cycles).

1. Introduction

Due to the high power density, fast charging-discharging rate and long cycle life, Supercapacitors have been considered as promising electrochemical energy storage devices [1–5]. Supercapacitors are attracting extensive attention to meet future life demand for electric/hybrid vehicles, consumer electronics, and backup energy systems [6]. As is known to all, the properties of supercapacitors greatly depend on the characteristics of electrode materials. Until now, electrode materials for the supercapacitors are made mainly from carbonaceous materials, transition metal oxides/hydroxides and conducting polymers [7–9]. Transition metal oxides/hydroxides can provide higher specific capacitance and energy density due to their reversible and rapid redox reactions [5,8]. However, the electrochemical performances are still far below the expectation as a result of its relatively poor conductivity.

In this regard, an increasing number of researchers try hard to exploit new-style electrode materials to improve the electrochemical performances of supercapacitor. Transition metal phosphides have attracted extensive interest as promising supercapacitors materials in virtue of their fascinating characteristics such as metalloid properties, superior electrical conductivity and high specific capacitances [10–17]. Wang et al. have developed a simple strategy to synthesize Co_2P nanorods and nanoflowers electrode materials, and Co_2P nanoflowers delivered higher capacitance of 416 F g^{-1} than nanorods with 284 F g^{-1} at a current density of 1 A g^{-1} for supercapacitors [17]. However, the electrodes have been fabricated by the use of polymer binder and conductive additives that can cause “dead” volume, thus limit the capacitance and rate capability. The electrode materials directly grown on conductive substrates, such as Ni foam, carbon cloth and so on, can effectively address the above problems, improving the electrochemical performances of electrode materials. For instance, Chen et al. fabricated Ni_2P nanosheets array on Ni foam that displayed a remarkable specific capacitance of 2141 F/g^{-1} at 50 mV/s [10]. Therefore, it is thus of great interest to the rational design and fabrication of metal phosphides electrode materials with excellent electrochemical performances for supercapacitor applications.

Herein, we report the synthesis of the mesoporous CoP nanowire arrays on carbon cloth and the corresponding electrochemical properties are investigated. The CoP electrode exhibit high areal capacitance (1.89 F/cm^2 at current densities of 3 mA/cm^2) and excellent cycling stability (~3% loss after the repetitive 4000 cycles at 18 mA/cm^2).

2. Experiment section

2.1. Preparation of CoP nanowire arrays

All the reagents here were analytical grade (purchased from Sinopharm) and used without further purification. Prior to the synthesis, a piece of carbon cloth was cleaned by sonication sequentially in acetone, water and ethanol for 20 min each. In a typical procedure, 2 mmol of $Co(NO_3)_2{\cdot}6H_2O$, 10 mmol of $CO(NH_2)_2$ and 5 mmol of NH_4F were dissolved in 50 mL of water. Then the homogeneous solution and the cleaned carbon cloth was transferred into a Teflon-lined stainless autoclave and heated at 120 °C for 5 h. After it was cooled down to

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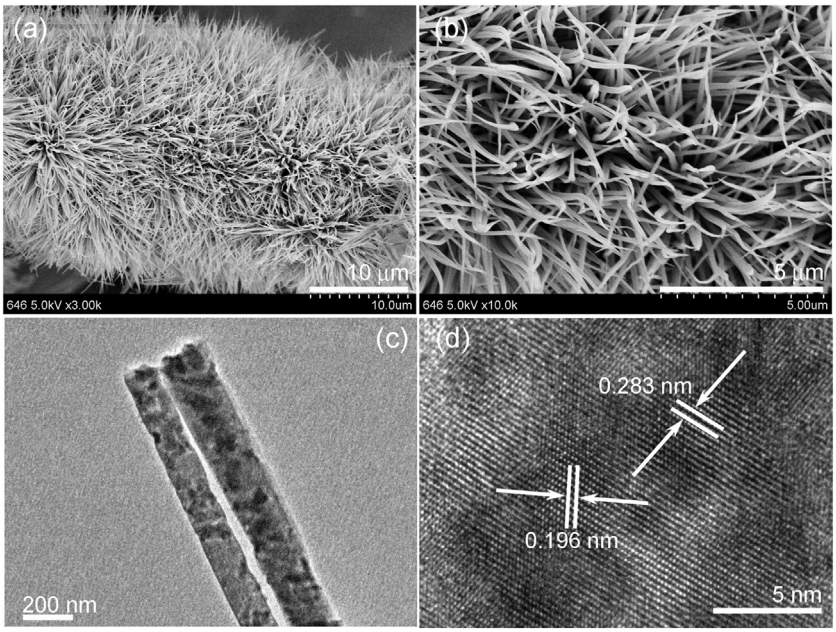

Fig. 1. (a, b) SEM images, (c) TEM image and (d) HRTEM image of mesoporous CoP nanowires.

room temperature, the carbon cloth was washed with water thoroughly and dried. To prepare CoP, the Co precursor/carbon cloth and NaH_2PO_2 were put at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the furnace. Subsequently, the samples were heated at 300 °C for 2 h under Ar atmosphere [18].

2.2. Materials characterization and electrochemical measurements

As-synthesized products were characterized with a D/max-2550 PC X-ray diffractometer (XRD; Rigaku, Cu-Kα radiation), a scanning electron microscopy (SEM; S-4800), a transmission electron microscopy (TEM; JEM-2100F) equipped with an energy dispersive X-ray spectrometer (EDX), X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG ESCA-LAB surface analysis system. The mass of electrode materials was weighed on an XS analytical balance (Mettler Toledo; δ = 0.01 mg). All the electrochemical measurements were performed on an Autolab (PGSTAT302N potentiostat). The electrochemical studies of individual electrodes were performed in a three-electrode mode in a 6 M KOH solution. The reference electrode and counter electrode were SCE and platinum, respectively.

3. Results and discussion

The mesoporous CoP nanowire arrays were grown on carbon cloth by low-temperature phosphidation of hydrothermally obtained Co precursor [18]. Carbon cloth is woven by carbon fibers with high flexibility, high conductivity (Fig. 1, Supporting Information), which can be chosen as optimal current collector for fast and effective electrolyte ion transport [19]. Importantly, the electrode materials directly grow on carbon cloth can avoid the use of polymer binder and conductive additive in traditional slurry derived electrode, improving the utilization rate of electrode materials. The morphologies and microstructures of the mesoporous CoP nanowire arrays have been investigated by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1a and b show SEM images of the CoP nanowire arrays with lengths of 3–8 μm grown radially on carbon fibers. Importantly, compared with Co precursor nanowires (Fig. S2a), the morphology and structure have no change after low-temperature phosphidation treatment. Fig. 1c presents the typical TEM image of the mesoporous CoP nanowires, from which the mesoporous structure with a rough surface was observed clearly. The Co precursor nanowires (Fig. S2b), however, are solid with a smooth surface. A high-resolution transmission electron microscopy (HRTEM) image of CoP nanowires shown in Fig. 1d reveals lattice fringes of 0.196 and 0.283 nm, which can be assigned to {112} and {011} planes of CoP, respectively. The elemental mappings demonstrate that Co and P elements are uniformly distributed on the fiber, which also suggests the even deposition of CoP on the fiber (Fig. 2).

The as-synthesized CoP nanowires were characterized by X-ray diffraction (XRD) to identify its crystallographic structure as shown in Fig. 3a. All the diffraction peaks can be indexed to the orthorhombic CoP (JCPDS No. 29-0497), suggesting successful conversion of Co precursor into CoP. Besides, the peaks at around 26° and 43° were also observed, coming from the carbon cloth substrate. Energy dispersive X-

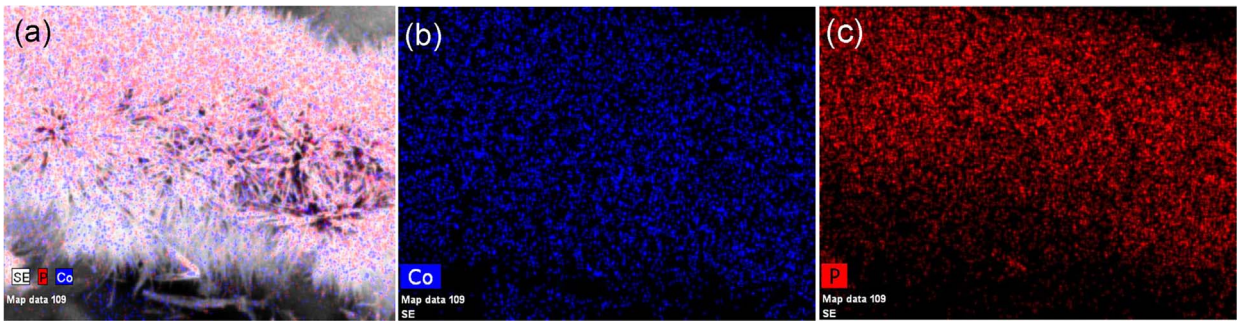

Fig. 2. Elemental distribution maps for (a) Co and P, (b) Co, (c) P.