



Binder-free cobalt phosphate one-dimensional nanograsses as ultrahigh-performance cathode material for hybrid supercapacitor applications



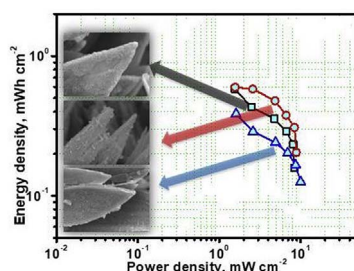
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HIGHLIGHTS

- Binder-free cobalt phosphate cathode for hybrid supercapacitor.
- Stable structure and good electrochemical interaction confirmed via morphology.
- Uniform and direct growth enhances the electrochemical performance.
- The OH⁻ ions more favor for large energy storage than NO₃⁻ ions.
- Ex-situ analysis confirms the influence of morphology on cyclic stability.

GRAPHICAL ABSTRACT



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ABSTRACT

One-dimensional (1D) nanostructure exhibits excellent electrochemical performance because of their physico-chemical properties like fast electron transfer, good rate capability, and cyclic stability. In the present study, Co₃(PO₄)₂ 1D nanograsses are grown on Ni foam using a simple and eco-friendly hydrothermal technique with different reaction times. The open space with uniform nanograsses displays a high areal capacitance, rate capability, energy density, and cyclic stability due to the nanostructure enhancing fast ion and material interactions. Ex-situ microscope images confirm the dependence of structural stability on the reaction time, and the nanograsses promoted ion interaction through material. Further, the reproducibility of the electrochemical performance confirms the binder-free Co₃(PO₄)₂ 1D nanograsses to be a suitable high-performance cathode material for application to hybrid supercapacitor. Finally, the assembled hybrid supercapacitor exhibits a high energy density (26.66 Wh kg⁻¹ at 750 W kg⁻¹) and longer lifetimes (80% retained capacitance after 6000 cycles). Our results suggest that the Co₃(PO₄)₂ 1D nanograsse design have a great promise for application to hybrid supercapacitor.

1. Introduction

Recently, hybrid supercapacitor have become essential for the rapid growth of modern society. Fundamental improvements in charge storage chemistry and electrode materials have been supporting the development of high-performance hybrid supercapacitor. Growing demands for energy have prompted research into advanced electrode materials for hybrid supercapacitor. A wide range of electrode materials

have been studied based on their charge storage mechanisms, such as electric double layer or non-faradaic reaction (EDL; carbon allotropes), pseudocapacitive or surface fast Faradaic reactions or multiple redox reactions within a potential range (PS; MnO₂, RuO₂, Mn₃O₄), and battery-type or prominent redox reactions at a given potential (NiO, Co₃S₄, CoFe₂O₄, Co₃O₄). The battery-type materials afford a higher specific capacitance and energy density than either EDL or PS via a dynamic redox reaction. Nevertheless, these materials tend to deteriorate with

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time and have a low rate capability [1,2]. To overcome this shortfall, there is a need for a novel design based on the development of nanostructures formed on a highly conductive electrode material.

Nanostructures with unconventional morphologies (flowers, rods, tubes, flakes, sheets), were studied with the aim of applying them as electrode materials. As a result, they were found to display a good energy storage performance. Among the various nanostructures, one-dimensional (1D) types have been studied for application to energy storage, given their unique physico-chemical properties, and low-resistance transport path for electrons and ions [3]. Yin et al. reviewed one-dimensional nanostructured conducting polymers for application to energy storage and conversion, given their low resistance and fast charge mobility, high mechanical strength, reduced ion or charge transportation, and exceptional electrochemical performance [4]. It was found that 1D carbon-nanofiber-based amorphous vanadium produced the best specific capacitance of 739 F g^{-1} at 0.5 A g^{-1} and exhibited an 80.3% retained capacitance after 1500 cycles [5]. The NiO nanotubes with nanosheets exhibited a specific capacitance of 919 F g^{-1} at 1 A g^{-1} and retained 94.7% of their initial capacitance after 2000 cycles. This proved that a 1D nanostructure with nanosheets enhanced the electrochemical performance through a synergistic effect, tubular morphology, and reduced diffusion path length for the ions [6]. A coaxial silver/MoO₂ nanowire was adapted by a two-step process, involving spray coating and electrodeposition. The binder-free electrode delivered a maximum specific capacitance of 500 F g^{-1} at 0.25 A g^{-1} [7]. The conductive material and binder-free CuS nanorods exhibited a specific capacitance of 378 mF cm^{-2} and excellent lifetimes, maintaining 90.2% of their initial capacitance after 2000 cycles as a result of their unique structural, electrical, and electrochemical properties [8]. Wei et al. reported on 1D porous materials for applications such as supercapacitors and batteries. The 1D porous materials boosted the capacity and increased the lifetime and rate capability due to its smaller crystal size, larger surface area, reduction in the diffusion path length, interconnected network, and empty space which prevents volume increase/shrinkage [9]. Nevertheless, only a very cursory attempt was made to prepare binder-free 1D nanograsses for energy storage.

Among the battery-type nanostructured materials, only a very few studies have addressed the use of transition metal phosphates for energy-storage applications using a 1D nanostructure. In general, non-metal PO₄³⁻ oxyacid anions are better than oxides, hydroxides, sulfides, and phosphites, given their good conductivity, chemical stability, non-toxicity, and low cost [10]. Li et al. prepared nickel-cobalt phosphate 2D nanosheets using a one-step hydrothermal method, producing nanosheets with a specific capacitance of 1132 F g^{-1} . Similarly, the assembled device had a very high energy density of 35.8 Wh kg^{-1} [11]. Novel flower-like Ni₃(PO₄)₂ and Fe₃(PO₄)₂·8H₂O were prepared by a co-precipitation method. The prepared electrodes had high specific capacitances of 1464 F g^{-1} and 200 F g^{-1} at 0.5 A g^{-1} for the flower-like Ni₃(PO₄)₂ and Fe₃(PO₄)₂·8H₂O, respectively. Subsequently, an assembled asymmetric supercapacitor exhibited a high specific capacitance of 94 F g^{-1} with an energy density of 32.6 Wh kg^{-1} [12]. The cobalt phosphate 3D hierarchical morphology was synthesized using a co-precipitation method. It had a high specific capacitance of 350 F g^{-1} at 1 A g^{-1} , and a lifetime in excess of 1000 charge/discharge cycles [13]. Zhang et al. synthesized Ni_xCo_{3-x}(PO₄)₂ hollow shells using a microemulsion-template hydrothermal method. The Ni_xCo_{3-x}(PO₄)₂ hollow shells performed well in electrocatalytic and supercapacitor applications. They offered a high specific capacitance (940 F g^{-1} at 1 A g^{-1}) and a long cycle life (retaining 85% of their initial specific capacitance after 1000 cycles) [14]. Xi et al. prepared amorphous/crystalline cobalt phosphate ultrathin nanowire, and found that it exhibited a high specific capacitance (1174 F g^{-1}) [15]. Given the above, to the best of our knowledge, very few reports have been published addressing the application of 1D transition metal phosphates to hybrid supercapacitor applications, as well as binder- and conductive-agent-

free battery-type 1D nanostructures. The binder- and conductive-agent-free electrodes feature a high electrochemical utilization of active material and thus reduce the “dead weight”. These prompted us to prepare binder-free battery-type cobalt phosphate 1D nanograsses for application to high-performance hybrid supercapacitor. The cobalt phosphate has a high theoretical capacitance and undergoes multiple redox reactions [15]. Accordingly, it is thought that binder-free cobalt phosphate 1D nanograsses would exhibit a high level of electrochemical performance [16,17].

In the present study, we successfully synthesized cobalt phosphate 1D nanograsses with different reaction times (6, 12, and 18 h) and developed appropriate reaction conditions based on their physical and electrochemical performance. The uniform binder-free 1D nanograsses enhance the ion accessibility, reduce the ion diffusion path and make the electron transport faster, leading to a higher level of performance. The Co-12h exhibited a higher capacitance, less loss of areal capacitance, and a significantly longer lifetime. Ex-situ field-emission scanning electron microscope images revealed that the Co-12h contributed to large charge/discharge cycles and excellent ion interaction with the materials. Furthermore, a hybrid supercapacitor or hybrid supercapacitor device was assembled with a configuration consisting of activated carbon//cobalt phosphate, and was found to deliver a high specific capacitance, excellent energy density, and a longer lifetime [16]. These results indicate that cobalt phosphate 1D nanograsses could be used as potential cathode candidates in the development of hybrid supercapacitor in the near future.

2. Experimental

2.1. Sample preparation

The starting precursors Co(NO₃)₂·6H₂O and NH₃H₂PO₄ were purchased from Sigma-Aldrich and were used without any further purification. The nickel foam thickness (1.6 mm), size (300 × 300 mm), porosity (95%) was purchased from Sigma-Aldrich and was cleaned using the following procedure. Nickel foam was cleaned with 3M HCl solution under ultrasonication for 15 min. Again, the nickel foam was cleaned with DI water and acetone several times and dried in vacuum oven for 12 h. A simple hydrothermal method was adopted to prepare uniform Co₃(PO₄)₂ 1D nanograsses on nickel foam, given their low cost, uniform particle size, and limited aggregation. The binder-free electrode enhances the cycling and mechanical stability [17]. The precursors were mixed at a mole ratio of 3:2 and then dissolved in 50 mL deionized water while stirring. After mixing, the transparent solution was then transferred to a Teflon-lined autoclave. The cleaned nickel foam (2 cm × 4 cm) was immersed in the above solution, as shown in Fig. 1a. The hydrothermal setup was placed in a programmed oven at 180 °C for 12 h. After cooling to room temperature, the nickel foam was cleaned in deionized water and ethanol with sonication. Finally, the sample was dried in a vacuum at 80 °C for 12 h. This sample was designated Co-12h. A similar procedure was performed to prepare the samples with reaction times of 6 h (Co-6h) and 18 h (Co-18h). The photographic images (Fig. S1a, b) of Nickel foam clearly proves that hydrothermal reaction does not alter the structure. This confirms the structural stability of nickel foam. After reaction, the entire nickel foam becomes navy color due to the uniform growth of Co-12h.

2.2. Characterization techniques

A Bruker D8 Advance Cu Kα radiation X-ray diffraction (XRD) instrument was used to examine the phase purity and crystallinity of the samples. The size and morphological features of the samples were analyzed using FESEM (JEOL-7001F) and TEM (JEOL JEM-2010). Furthermore, the electronic states of the elements were analyzed using X-ray photoelectron spectroscopy (XPS, VG Scientifics ESCALAB250). Nitrogen adsorption-desorption isotherms were measured at 77 K using

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