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Self-assembled 3D cobalt phosphate octahydrate architecture for supercapacitor electrodes

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ABSTRACT

Hierarchical 3D cobalt phosphate octahydrate ($Co_3(PO_4)_2 \cdot 8H_2O$) architecture with flower-like morphologies assembled from 2D microsheets are successfully synthesized at room temperature by a green precipitate process without adding any surfactant. The as-prepared architecture with an interconnecting 2D microsheets structure provide large nanoscale pore channels for ion transport, exhibits remarkable pseudocapacitive activities including good specific capacitance (350 F/g at 1 A/g), rate capability (227 F/g at 10 A/g), and excellent cycling stability (capacitance increase to retention 102% after 1000 cycles).

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1. Introduction

Supercapacitors (SCs), a new kind of clean energy storage device, are considered to be a viable approach for meeting the increasing demand of green energy storage and conversion [1,2]. Generally, the SCs can be divided into the electrical double-layer capacitors (EDLCs) and the pseudocapacitors. Because pseudocapacitors have higher specific capacitance than EDLCs due to their fast and reversible redox reaction, there recently has been considerable interest in using pseudocapacitive materials [3]. However, the low capacitance value and power density have hindered their practical application. One of the potential solutions for improving the capacitor performances is to prepare the hierarchical 3D structure, because the short diffusion distance and large specific surface area can enhance the electron transport and the contact between active material and electrolyte [4,5].

Recently, several works concerned with hierarchical structure with excellent capacitor performances have been reported, and many methods have been developed to fabricate the hierarchical structure, including hydrothermal reaction [6,7], electrodeposition-heat-treatment [8], template method [9,10] etc. However, these methods are fraught with many problems including high temperature, high energy consumption, time-consuming and low yield. Thus, the development of a facile, low-cost and large-scale yield method for fabricating hierarchical structure is still a challenge. Moreover, there are few reports about the synthesis of hierarchical 3D cobalt phosphate octahydrate ($Co_3(PO_4)_2 \cdot 8H_2O$) architecture.

Herein, we present a facile, environmentally friendly approach to large-scale hierarchical 3D $Co_3(PO_4)_2 \cdot 8H_2O$ architecture by a green precipitate process at room temperature (Fig. S1). This method engages the following advantages: (i) low energy consumption, the reaction is carried out at room temperature; (ii) non-toxic reagents, the phosphorous salts and cobalt acetate are used to provide PO_4^{3-} and Co^{2+} for the precursors, respectively. H_2O is used as the solvent without adding any surfactants or templates; (iii) time-saving, only 1 h is needed. As an electrode material, the as-prepared $Co_3(PO_4)_2 \cdot 8H_2O$ architecture assembled by many interconnecting 2D microsheets exhibits good specific capacitance, rate capability and cycling stability.

2. Experimental

Aqueous solution of cobalt acetate ($Co(CH_3COO)_2$) and disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4) and trisodium phosphate (Na_3PO_4) were prepared as stock solutions in advance. A total of 10 mL of 0.15 M stock solution of phosphorous salts was added dropwise to 10 mL of 0.08 M Co ($CH_3COO)_2$ aqueous solution under vigorous stirring. After stirring for 1 h, the precipitates were harvested by centrifugation, followed by washing several times with water and ethanol. Finally, the precipitates were dried in an oven. The products prepared by Na_2HPO_4, NaH_2PO_4 and Na_3PO_4 were named as P1, P2 and P3, respectively.

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The crystalline phase was examined by X-ray diffraction (XRD) using a Rigaku D/Max-2550 diffractometer with Cu_{Ka} radiation. The microstructure of products was characterized by SEM (Nova Nano-SEM450, 20 kV), TEM (Tecnai G2 F20 S-Twin, 200 kV) and N_2 adsorption–desorption measurement (ASAP2020). CV, chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI 660D electrochemical working station (CH Instruments, Inc., Shanghai) using a KCl-saturated Ag/AgCl electrode, a platinum wire, and the $Co_3(PO_4)_2 \cdot 8H_2O$ based electrode as the reference, counter, and working electrodes, respectively. The working electrode were made from mixing $Co_3(PO_4)_2 \cdot 8H_2O$, acetylene black and poly-vinylidene fluoride with a mass ratio of 80:10:10 to obtain a slurry, then the slurry was coated on nickel foam, after drying under vacuum at 100 °C for 12 h, the nickel foam was pressed to be a thin foil at a pressure of 5 MPa. The supporting electrolyte was 3.0 M KOH aqueous solution.

3. Results and discussion

The structures of the as-prepared products were first characterized by SEM. Fig. 1a and b shows typical SEM images of the as-prepared products by simply reacting $Co(CH_3COO)_2$ with Na_2HPO_4 and NaH_2PO_4, respectively. It can be clearly seen that 3D architecture with flower-like morphologies assembled from interconnecting 2D microsheets are obtained, and the average size is about 5–12 μm. The N_2 adsorption–desorption isotherms (Fig. S2) indicate the presence of mesopores, which is favorable for electrolyte penetration and contributes to high capacitance. However, when Na_3PO_4 as precursor added into this system, a large amount of irregular and agglomerate particles were obtained (Fig. 1c). Their energy-dispersed spectrum (EDS, Fig. S3) indicate the existence of Co, P and O elements. The crystalline nature of them was further examined by XRD analysis (Fig. 1d), powder XRD of P1 and P2 confirm that $Co_3(PO_4)_2 \cdot 8H_2O$ nanocrystallites have been obtained under our experimental conditions, which can be indexed to be in agreement with $Co_3(PO_4)_2 \cdot 8H_2O$ (JCPDS file no. 41-0375), indicating the facile precipitate process for

synthesizing $Co_3(PO_4)_2 \cdot 8H_2O$ architecture can have good crystallinity using inexpensive metal salts as precursors at room temperature. However, a large and broad peak of P3 is found, indicating the presence of amorphous phase.

The detailed structure of $Co_3(PO_4)_2 \cdot 8H_2O$ was investigated by TEM, as shown in Fig. 2a and b, which further indicate that the 3D architecture are assembled from several interconnecting 2D microsheets. The HRTEM images and their corresponding diffraction patterns suggest high degree of crystallization of the $Co_3(PO_4)_2 \cdot 8H_2O$ (Fig. 2c, d), which is consistent with XRD results. TEM image of P3 (Fig. 3e) reveals the agglomerate particles are composed of numerous nanosheets. Based on the above results, we speculate that pH values of reaction system play an important role in controlling the morphology and structure of the as-prepared products. When $Co(CH_3COO)_2$ and Na_3PO_4 were used as precursors, the CH_3COO^- might adsorb preferentially with the Co^{2+} of $Co_3(PO_4)_2 \cdot 8H_2O$ planes, which can effectively enhance stability and reduce their growth rates, thus, nanosheets were obtained. When Na_3PO_4 was replaced by Na_2HPO_4 or NaH_2PO_4, the decreasing of pH values may facilitate the generation of CH_3COOH, which may weaken the ability of selective adsorption on planes and results in the products transformed into microstructure. Moreover, when H_3PO_4 (pH = 1.64) was added, no products were obtained, indicating the pH has an optimal value.

In order to estimate the electrochemical performance of the $Co_3(PO_4)_2 \cdot 8H_2O$ materials, CV was measured. Fig. 3a shows the CV curves of P1, P2 and P3 recorded at 50 mV/s. All the CV curves exhibit remarkable redox peaks and their shape is distinguished from the rectangular shape of conventional EDLCs, indicating their pseudocapacitive properties. Fig. S4 shows the CV curves of P1, P2 and P3 at different scan rates. It is noted that the total peak current density increases obviously with increasing the scan rates, demonstrating the good rate property and excellent capacitance behavior. Also, the oxidation and reduction peaks shift toward higher and lower potentials, respectively, with a large potential separation.

Fig. 3b compares the CP curves of the $Co_3(PO_4)_2 \cdot 8H_2O$ materials at 1 A/g. As can be seen, a distinct potential plateaus is obtained for the three comparison samples and the calculated specific capacitance of
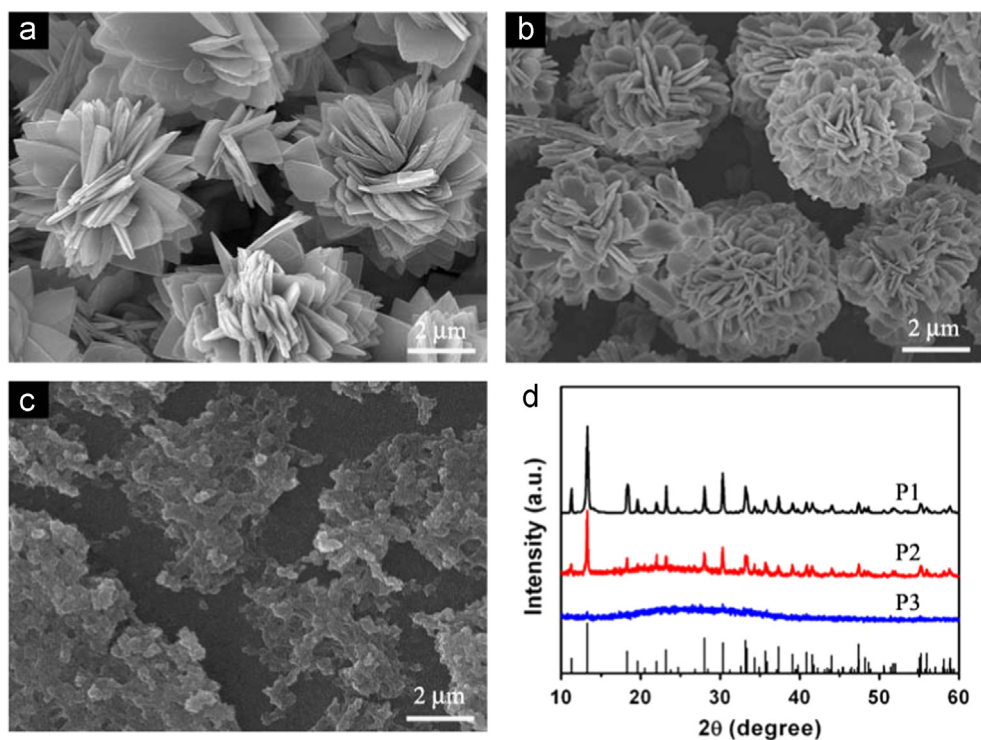

Fig. 1. SEM images (a) P1, (b) P2, (c) P3 and XRD patterns (d) of the as-prepared products.