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Highly flexible and large areal/volumetric capacitances for asymmetric supercapacitor based on $ZnCo_2O_4$ nanorods arrays and polypyrrole on carbon cloth as binder-free electrodes

Xinming Wu *, Lian Meng, Qiguan Wang, Wenzhi Zhang, Yan Wang

School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an 710032, PR China

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ABSTRACT

Flexible asymmetric supercapacitor (FAS), as a promising candidate for wearable or flexible electronic devices, draws great attention since it exhibits the flexibility and enhanced areal/volumetric capacitances comparing with the symmetrical Faraday capacitors. Herein, we grow unique $ZnCo_2O_4$ nanorods arrays on carbon cloth ($ZnCo_2O_4$-CF) by a simple hydrothermal method, and the electrode exhibits a remarkable areal (volumetric) capacitance of 5.18 F cm^{-2} (167.5 F cm^{-3}) at 5 mA cm^{-2} and exceptional capacitance retention of 92.8% after 3000 cycles. A FAS was fabricated using $ZnCo_2O_4$-CF as the positive and PPy-CC (deposition of Polypyrrole on carbon cloth) as negative electrodes, respectively. Especially, the asymmetric electrodes help the device to exhibit a wide potential window of 1.6 V and a high areal (volumetric) capacitance of 1.8 F cm^{-2} (148 F cm^{-3}). As a result, the FAS shows a maximum energy of 2.3 mW h cm^{-2} (18.9 mW h cm^{-3}) at a power density of 7.82 mW cm^{-2} (82.2 mW cm^{-3}) and a good stability after 5000 cycles at a current density of 5.0 A cm^{-2}. Furthermore, the FAS shows good flexibility and can withstand bending at different angles while keeping electrochemical performance constant.

1. Introduction

As an important electrochemical energy storage device, supercapacitors have high reliability, power density and longer cycle life compared with ordinary batteries, which are expected to be widely used in new energy storage devices [1]. With the demand of wearable electronic devices, bendable supercapacitors as the energy supply unit for flexible electronic devices have received extensive attention such as flexible memory devices and wearable health monitoring devices [2]. However, previous studies have shown that a single symmetric electrode material has a lower potential window and a poorer areal (volumetric) capacitance [3]. Therefore, further efforts are still needed to overcome these shortages from the respects of exploration and preparation strategy of electrode materials. As is know to all, Nanostructures including one dimensional electrode materials have high specific surface area, which is advantageous for increasing the contact area of the electrolyte, thus improving the electrochemical performance of the electrode material [5–6]. Among many nano-electrode materials, AB_2O_4 type ternary oxides, especially $ZnCo_2O_4$, has attracted great attention due to their large theoretical capacitance, extensive sources, easy preparation, and controllable structure [4,7]. At the same time, as an important conductive polymer, polypyrrole (PPy) is a promising pseudocapacitive electrode material due to it low cost, environmental friendliness and ease of fabrication for large-scale flexible devices. Hence, reasonable assembly $ZnCo_2O_4$ and PPy electrodes on flexible substrate are expected to fabricate high performance flexible supercapacitors.

In this work, we grow unique $ZnCo_2O_4$ nanorods arrays on carbon cloth ($ZnCo_2O_4$-CF) by a simple hydrothermal method for the first time, and the electrode shows a remarkable areal (volumetric) capacitance of 5.18 F cm^{-2} (167.5 F cm^{-3}) and exceptional capacitance retention of 92.8% after 3000 cycles. At the same time, the $ZnCo_2O_4$-CC was used to design as cathode electrode while PPy was grown on CC (PPy-CC) as anode to improve the asymmetric device performance. As a result, the FAS ($ZnCo_2O_4$-CC//PPy-CC) exhibit a wide potential window of 1.6 V, a high areal (volumetric) capacitance of 1.8 F cm^{-2} (148 F cm^{-3}) and good flexibility.

2. Results and discussions

In order to fabricate nanostructure of $ZnCo_2O_4$ with high specific surface area, the use of simple hydrothermal method is an effective strategy. The preparation process of FAS is shown in Fig. 1. Fig. 1(a) is a SEM image of a typical carbon cloth. It can be seen

* Corresponding author.
E-mail address: Aimar_wu@aliyun.com (X. Wu).

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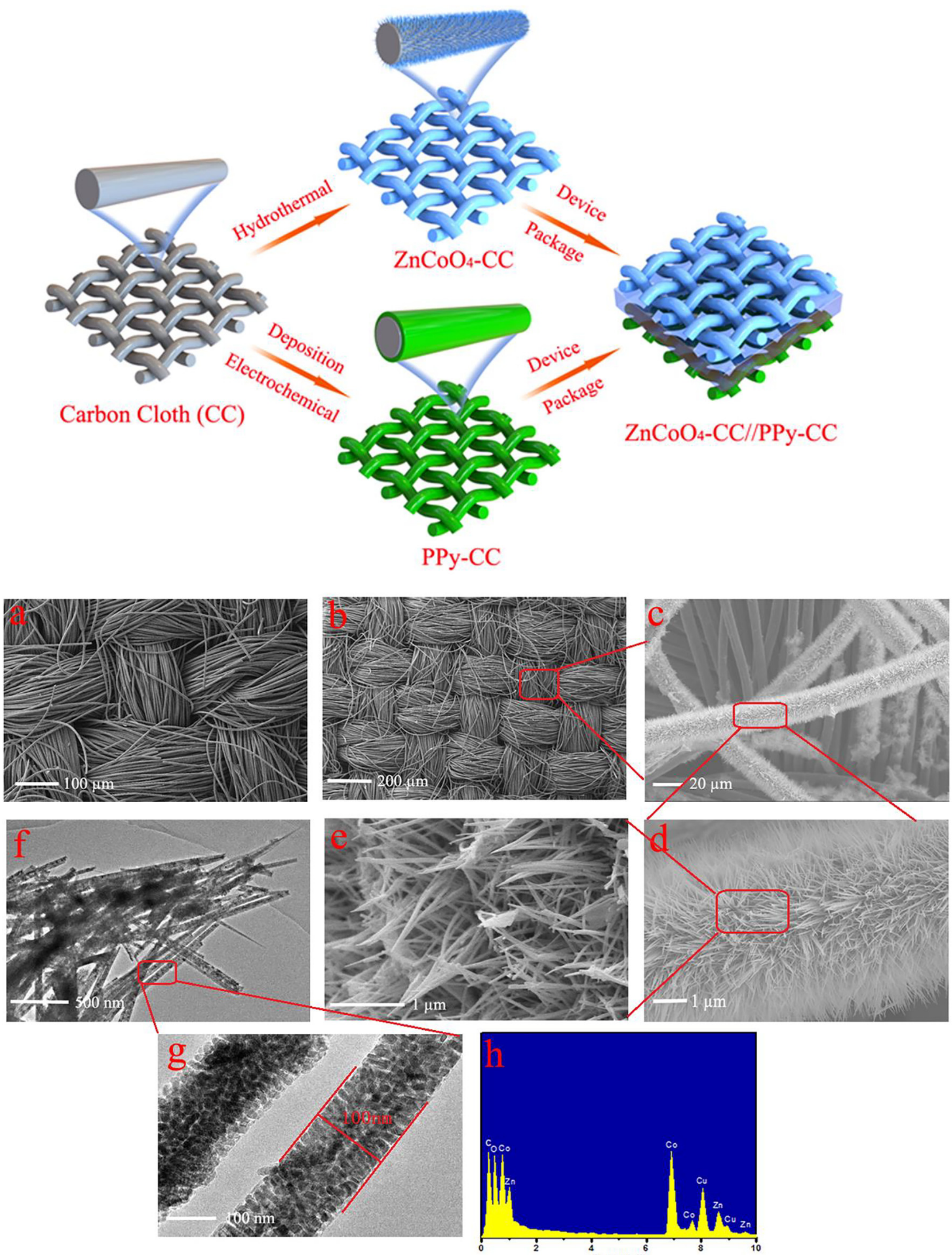

Fig. 1. Schematic illustration for the fabrication of FAS. SEM images of the carbon cloth (a) and $ZnCo_2O_4$-CC (b, c, d, e), TEM images of $ZnCo_2O_4$ nanorods (f, g) and EDX results of $ZnCo_2O_4$-CC (h).

from the Fig. 1(a) that the carbon cloth is woven from many single carbon fibers. After hydrothermal deposition of $ZnCo_2O_4$, the color of the carbon cloth changed from black to gray significantly (Fig. 1(b)), indicating that $ZnCo_2O_4$ has grown better on the surface of carbon cloth. Further observation of the $ZnCo_2O_4$-CC microstructure, the relevant SEM images are shown in Fig. 1(c, d, e). From these it can be seen that the single carbon fiber that forms carbon cloth grows a dense nanorods $ZnCo_2O_4$ with uniform distribution, thickness, length, and is oriented toward the fiber radial direction. Further observe the microstructure of nanobrush arrays, the high magnification TEM images of Fig. 1(f, g) are clearly exhibited that the $ZnCo_2O_4$ nanorods arrays has a diameter of 100 nm and a