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Direct growth of vanadium nitride nanosheets on carbon nanotube fibers as novel negative electrodes for high-energy-density wearable fiber-shaped asymmetric supercapacitors

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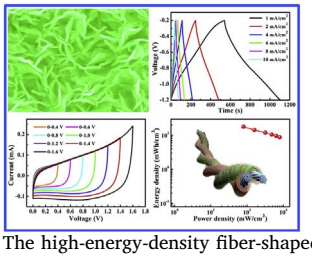
HIGHLIGHTS

- We directly grew VN nanosheets on carbon nanotube fibers as advanced electrodes.
- The VN electrode possessed a high specific capacitance of 188 F/cm^3.
- The as-assembled device possesses a maximum operating voltage of 1.6 V.
- The device showed a capacitance of 50 F/cm^3 and energy density of 17.78 mWh cm^{-3}.
- The device retained 91% of its capacitance after bending 90° for 3000 times.

GRAPHICAL ABSTRACT



The high-energy-density fiber-shaped asymmetric supercapacitor adopting vanadium nitride nanosheets as the negative electrode is successful assembled.

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ABSTRACT

Significant efforts have been recently devoted to constructing high-performance fiber-shaped asymmetric supercapacitors. However, it is still a paramount challenge to develop high-energy-density fiber-shaped asymmetric supercapacitors for practical applications in portable and wearable electronics. This work reports a simple and efficient method to directly grow vanadium nitride nanosheets on carbon nanotube fibers as advanced negative electrodes with a high specific capacitance of 188 F/cm^3 (564 mF/cm^2). Taking advantage of their attractive structure, we successfully fabricated a fiber-shaped asymmetric supercapacitor device with a maximum operating voltage of 1.6 V by assembling the vanadium nitride/carbon nanotube fiber negative electrode with the Zinc-Nickel-Cobalt ternary oxides nanowire arrays positive electrode. Due to the excellent synergistic effects between positive and negative electrodes, a remarkable specific capacitance of 50 F/cm^3 (150 mF/cm^2) and an outstanding energy density of 17.78 mWh/cm^3 (53.33 μWh/cm^2) for our fiber-shaped asymmetric supercapacitor can be achieved. Furthermore, the as-assembled fiber-shaped asymmetric supercapacitor device has excellent mechanical flexibility in that 91% of the capacitance retained after bending 90° for 3000 times. Thus, this work exploits a pathway to construct high-energy-density fiber-shaped asymmetric supercapacitor for next-generation portable and wearable electronics.

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1. Introduction

As a novel type of energy storage device for portable and wearable electronics [1–12], flexible supercapacitors (SCs) have attracted tremendous attention owing to high power density, excellent cycle stability, splendid flexibility and environmentally friendly [13–19]. Comparing with two-dimensional flexible SCs, fiber-shaped supercapacitors (FSCs) possess light weight, tiny volume and prominent weavability [14,15,20–32]. However, low energy density impedes their practical applications. Therefore, it is urgently desired to develop high-energy-density FSCs.

According to the equation $E = 1/2\ CV^2$, it is clearly concluded that enhancing capacitance (C) or expanding voltage (V) are two approaches to improve the energy density (E). Thus, developing fiber-shaped asymmetric supercapacitors (FASCs) is a feasible strategy for the practical application of portable and wearable electronics, which can achieve higher voltage through employing two materials with different potential windows. Now that high operating voltage can be acquired by the asymmetric configuration, enhancing capacitance is another significant issue. Despite positive electrode materials have been sufficiently studied, which can achieve adequately high capacitance, the capacitance of negative electrode materials still require further improvement. Negative electrode materials are mainly divided into carbon-based materials and metallic oxides. Carbon-based materials store charges by electric double-layer capacitor mechanism. They often possess high electrical conductivity but low capacitance. Metallic oxides such as Fe and Mo oxides are pseudocapacitive material with high theoretical capacitance, but their deficient electrical conductivity hinder the charge transmission and limit their practical capacitance. Therefore, developing high-capacitance negative electrode materials is very essential.

Carbon nanotube fibers (CNTFs) are identified as the most potential current collector for high-performance FASCs due to their high electrical conductivity, light weight, excellent flexibility, large specific surface area and outstanding mechanical properties [14,15,32–34]. To improve the electrochemical performance of fibrous electrodes, researchers have devoted great efforts to growing nano-structured active materials on them [35–42]. Among high-performance negative materials for asymmetric SCs, vanadium nitride (VN) has attracted great attention owing to its good electrical conductivity ($\sigma_{bulk} = 1.67 \times 10^6$/Ωm), large potential window, fast reversible Faradic redox reactions and high specific capacitance (1340 F/g) [14,32,43–47]. Xiao et al. fabricated freestanding mesoporous VN nanowires by a simply vacuum-filtering method, which displayed a specific capacitance of 178 mF/cm^3 at a current density of 1.1 mA/cm^3 [44], but the vacuum-filtering method make VN cling to the substrate and only have small effective surface area contacting to the electrolyte. Wang et al. achieved a specific capacitance of 98.5 F/g for the urchin-like VN negative electrode at a current density of 0.5 A/g [45], but large contact resistance by polymer binders limits its performance. Lu et al. fabricated porous VN nanowires on a carbon cloth with a specific capacitance of 298.5 F/g [47], but low surface area touching with electrolyte also caused by the flat nanostructure led to insufficient capacitance. Although certain progress has been achieved, there is still a capacitance gap of VN between the theoretical value and experimental value. To solve this problem, a plausible approach is to directly grow three-dimensional nanostructured VN on the fibrous electrode, which has large effective surface area and decreased contacting resistance.

In this paper, a novel type of VN nanosheets (NSs) on CNTF was synthesized through a solvothermal process and a subsequent annealing treatment and used as the negative electrode. By adopting Zn-Ni-Co ternary oxides (ZNCO) nanowire arrays (NWAs) as the positive electrode to combine with the VN NSs/CNTF, we have successfully fabricated a high-performance flexible FASC with a maximum operating voltage of 1.6 V. The as-prepared FASC device possesses a high specific capacitance of 50 F/cm^3 (150 mF/cm^2) and an outstanding energy density of 17.78 mWh/cm^3 (53.33 μWh/cm^2). After bending 3000 times, 91% of capacitance retention can be obtained, indicating excellent flexibility.

2. Experimental section

2.1. Synthesis of VN NSs on CNTFs

The VN NSs on the CNTFs were synthesized by a two-step method containing a simple solvothermal process and a subsequent annealing treatment. First of all, the CNTFs were treated in O_2 plasma at a power of 150 W for 30 min. In a classic process, 0.3 mL vanadium oxytriisopropoxide (VOT) was dissolved in 45 mL of isopropanol alcohol (IPA) under stirring. Then the solution and the pre-treated CNTFs were transferred into a 50-mL Teflon-lined stainless steel autoclave. After that, the autoclave was sealed and maintained at 200 °C for 10 h. When the autoclave naturally cooled down to room temperature, the resultant CNTFs coated by VO_x NSs were taken out, rinsed in ethanol and then dried at 60 °C overnight under vacuum. At last, the hybrid fibers were annealed in ammonia at 600 °C for 2 h to obtain the VN NSs.

2.2. Fabrication and assembling of the FASCs

The FASCs were assembled by employing the ZNCO/CNTF as the positive electrode and the VN/CNTF as the negative electrode with KOH/poly(vinyl alcohol) (PVA) gel electrolyte. First, the KOH/PVA gel electrolyte was manufactured. In a typical process, 11.2 g KOH and 10 g PVA were mixed in 100 mL of deionized water at 95 °C for 2 h under vigorous stirring. After the mixture turned clear, both ZNCO/CNTF and VN/CNTF electrodes were immersed into KOH/PVA gel electrolyte for 5 min and dried at 60 °C for 1 h. Repeat this process one time. At last, the two electrodes were twisted together and dried overnight until the KOH/PVA gel electrolyte was solidified completely to obtain the assembled FASCs.

2.3. Materials and characterizations

All the chemical reagents are purchased from commercial sources and used without further purification.

Morphologies of the samples were characterized using a scanning electron microscope (SEM) (Hitachi S-4800, 5 kV) and the microstructure and high-resolution transmission electron microscope (TEM) images were gained via an FEI Tecnai G2 20 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. A Rigaku D/MAX2500 V X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5418 Å) was used to obtain the X-ray diffraction patterns of samples. X-ray photoelectron spectroscopy (XPS) on an ESCALab MKII X-ray photoelectron spectrometer with non-monochromatized Mg Kα X-rays as the excitation source was utilized to analyze the chemical composition and oxidation states of samples.

Electrochemical measurements were performed using an electrochemical workstation (CHI 760E, Chenhua). Electrochemical properties of the as-prepared electrodes were measured by a three-electrode system in 3 M KOH aqueous electrolyte. The electrode materials, the Pt wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. The electrochemical impedance spectroscopy (EIS) measurements were carried out with a voltage amplitude of 5 mV at open-circuit potential at frequencies from 10^{-2} Hz–10^5 Hz. The performance of the all-solid-state FASC device was tested in a two-electrode system.

3. Results and discussion

The all-solid-state FASC device was fabricated in a twisting configuration, which is schematically exhibited in Fig. 1. First, CNTFs were applied as the substrate and current collector. Then VO_x NSs (VN NSs