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Vertically cross-linked and porous $CoNi_2S_4$ nanosheets-decorated SiC nanowires with exceptional capacitive performance as a free-standing electrode for asymmetric supercapacitors

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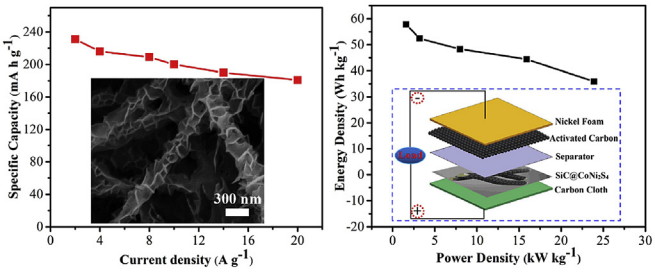
HIGHLIGHTS

- SiC NWs@$CoNi_2S_4$ NSs on CC electrode material was prepared via hydrothermal technology.
- The integrated hybrid electrode delivers extraordinary electrochemical characteristics.
- An asymmetric supercapacitor based on SiC NWs@$CoNi_2S_4$ NSs on CC was successfully assembled.
- The device exhibits high power and energy density, and long-term cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a simple, low-cost and mild hydrothermal technology of growing vertically cross-linked ternary nickel cobalt sulfides nanosheets ($CoNi_2S_4$ NSs) with porous characteristics on SiC nanowires (SiC NWs) supporters with outstanding resistances to oxidation and corrosion, good conductivity and large specific surface area deposited directly on carbon cloth (CC) is successfully developed, forming a new family of free-standing advanced hybrid electrode for asymmetric supercapacitors (ASCs). Such integrated electrode (SiC NWs@$CoNi_2S_4$ NSs) manifests intriguing electrochemical characteristics such as high specific capacity (231.1 mA h g^{-1} at 2 A g^{-1}) and rate capability due to the synergistic effect of SiC NWs and $CoNi_2S_4$ NSs with unique morphology. Additionally, an asymmetric supercapacitor is also assembled via using this special hybrid architectures as positive electrode and activated carbon (AC) on Ni foam (NF) as negative electrode, and it can yield a high energy density of 57.8 W h kg^{-1} with a power density of 1.6 kW kg^{-1} and long cycling lifespan. This study constitutes an emerging attractive strategy to reasonably design and fabricate novel SiC NWs-based nanostructured electrodes with enhanced capacity, which holds great potential to be the candidate of electrode materials for environmentally benign as well as high-performance energy storage devices.

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1. Introduction

Lately, supercapacitors (SCs), also called electrochemical capacitors, have attracted intense attention as one of the most promising energy-storage systems owing to their desirable merits such as high power density, rapid charge/discharge process, superlong cycle life as well as noticeable reliability [1,2]. With features complementary to conventional capacitors and rechargeable batteries, the SCs as power sources hold great promise for fast bursts of energy and high power applications including hybrid electric vehicles, heavy transport and aerospace industry [3,4]. Principally, the electrochemical double-layer capacitors related to ion adsorption have low energy/power density and thus hard to satisfy the ever-growing demand for peak-power assistance in heavy equipments [5]. Therefore, more and more research efforts were concentrated on potential electrode materials with desired specific capacity and energy density [6,7].

Among the numerous available electrode materials for SCs, metal sulfides are deemed as a typical category because of their superior inherent properties and distinguished electrochemical characteristics [8–10]. Particularly, ternary nickel cobalt sulfides showed an outstanding electronic conductivity, at least two orders of magnitude higher than the oxide counterparts and much higher conductivity than those of the binary sulfides. Moreover, with both nickel and cobalt ions, the ternary sulfides can provide richer redox reactions than the corresponding single-component sulfides, leading to superior electrochemical activities [11,12]. However, they are always limited by poor rate capacity and cycling stability owing to their agglomeration in substrates and the structural degradation of the electrode arised from the volume change of the active materials during consecutive electrolyte ion insertion/extraction process [13,14]. To overcome the above shortcomings, carbon nanomaterials such as carbon nanotube or graphene with large surface area and excellent electrical conductivity are commonly selected as scaffolds to grow the nickel cobalt sulfides for fabricating active materials-framework nanocomposites electrode, which has been demonstrated to be effective in this respect [8,15,16]. Despite this, in the fabrication of the aforementioned hybrid electrodes, the addition of polymer binder and conductive additive inevitably increases the "dead" weight and blocks electron transfer, and the utilization of press machine may give rise to the damage of architectures of the sulfides, which significantly sacrifices overall energy storage capacity. Apparently, the fabrication process requires both various equipment and complicated operation. Therefore, it is greatly urgent and imperative to develop a simple route for making the sulfides homogeneously distribute on a sort of suitable skeleton materials toward additive-free hybrid electrodes for high-performance SCs. Recently, fruitful researches indicate that SiC NW, as a class of favorable functional semiconductor one-dimensional (1D) nanomaterial, possessing superior thermal and physicochemical stability, high mechanical strength, large specific surface area as well as excellent electrical conductivity [17–20], is an attractive candidate among different available supporters. Furthermore, Gu et al. [21] and Alper et al. [22] have prepared pure SiC NWs directly grown on CC or SiC films as self-supported electrode materials for SCs, exhibiting exceptional cycling stability, high areal capacitance, fascinating anticorrosion and antioxidation, and excellent flexible properties. On the basis of the superiorities described above, it is entirely reasonable to believe that the SiC NWs supporters can allow the sulfides deposited on their surfaces to evenly disperse and effectively avoid the collapse of the hybrid electrode structures. In addition, the vertically cross-linked sheets-like sulfides with porous structures possess sufficient open space and surface area, which offers efficient ions-transport pathways and numerous electroactive sites for fast reversible redox reaction, greatly enhancing the capacitive performance. Therefore, such a binder- and conductive-agent-free electrode made by directly decorating the sulfides ($CoNi_2S_4$) with particular architectures on the SiC NWs via a simple hydrothermal strategy can completely satisfy the critical requirements of brilliant SCs electrode materials. To the best of our knowledge, this novel $CoNi_2S_4$ NSs structure was rarely synthesized in the previous studies [23,24], moreover, preparation of the $CoNi_2S_4$ NSs heterojunction-modified SiC NWs hybrid electrodes for SCs also remains unreported until now.

Herein, for the first time, the porous and vertically cross-linked $CoNi_2S_4$ NSs with uniform distribution are successfully grown on the SiC NWs deposited on CC with robust adhesion through a simple, low-cost and mild hydrothermal strategy, which can directly serve as a new class of free-standing high-performance hybrid electrode for ASCs, wherein the SiC NWs skeleton and the $CoNi_2S_4$ NSs electroactive materials present a promising synergistic effect for capacitors. Benefiting from their perfect combination, the integrated electrode exhibits a high specific capacity of 231.1 mA h g^{-1} at 2 A g^{-1}, and prominent rate capability (197 mA h g^{-1} at 20 A g^{-1}) as well as cycling stability by retaining 93.2% of its original state after 4000 cycles. Moreover, the fabricated SiC NWs@$CoNi_2S_4$ NSs//AC hybrid device delivers high energy density and power density, and long cycling lifespan. Thus, the reasonable design would be expected as an ideal way to prepare advanced electrode for SC devices with remarkable energy/power density.

2. Experimental section

2.1. Chemicals and materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), hexamethylene-tetramine (HTM), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$), potassium hydroxide (KOH) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. N-methyl-2-pyrrolidinone (NMP) was supplied by Tianjin BASF Chemical Co., Ltd. All the chemical reagents were AR grade and used without further purification. Silicon powder (200 mesh) was obtained from Sinopharm Chemical Reagent Co., Ltd and graphite powder was offered by Qingdao Tianheda graphite Co., Ltd. In addition, activated carbon (YP–50F), conducting carbon black (Vulcan XC-72), polyvinylidenedifluoride (HSV900), commercial carbon cloth and nickel foam were procured from Kuraray, Cabot Corp., Arkema, Toray and Heze Tianyu Technology Development Co. Ltd., respectively.

2.2. Preparation of SiC NWs directly grown on CC

SiC NWs directly grown on the CC have been successfully synthesized by chemical vapor reaction (CVR). The milled analytically pure silicon and graphite powders (mixing molar ratio of 1: 1.5) were employed as the starting raw materials. CC was used as the substrate, $Ni(NO_3)_2$ (ethanol solutions of 0.01 mol L^{-1}) was used as the catalyst source. Initially, the substrate was immersed in the catalyst ethanol solutions for 10 min, and naturally dried in air. Second, a piece of carbon cloth, Si-graphite mixture powders and the substrate were orderly placed into a homemade graphite chamber, then the chamber was placed into a vacuum furnace. Before heating, the system was purged 2-3 times with high-purity argon (Ar) using a rotary vacuum pump to eliminate oxygen from the furnace chamber. Third, the temperature of the furnace was heated to 1250 °C from room temperature at a mean rate of 350–400 °C h^{-1} and maintained at peak temperature for 13–16 min. Finally, the power was switched off and the furnace was