Nickel-Cobalt Sulfide Nonwoven Cloth with Ultra-High Areal Capacitance for Flexible Supercapacitors

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***Abstract*—Supercapacitors represent a promising energy storage technology for flexible, miniaturized, and wearable electronic devices in the future. At present, to achieve high mechanical flexibility, many available flexible supercapacitors are constructed into thin electronic devices. However, the thin thickness of the whole supercapacitor electrode will greatly limit the mass loading of active materials and lower the energy density, which as a result, substantially hindering the application of supercapacitors for wearable electronic devices. Herein, we report a magnetic field induced fabrication of three-dimensional nonwoven cloth consists of cross-linked ultra-long NiCo sulfide nanowires as a high-performance supercapacitor cathode. Due to the stress release by slippage between the cross-linked nanowires under external force, the NiCo sulfide nonwoven cloth electrode with the thickness up to 0.5 mm can achieve ultra-high flexibility, even foldability and arbitrarily deformable properties. Most importantly, the thick three-dimensional architecture enables the high mass loading of active materials, which is crucial for high energy density flexible supercapacitors. The NiCo sulfide nonwoven cloth electrode demonstrates an ultra-high areal capacitance over 4.91 F cm^{-2}, with negligible capacitance decay after 10000 cycles, outperforming most of reported flexible supercapacitors and revealing its great potential for practical application in wearable electronic device.**

Keywords— flexible supercapacitor, NiCo sulfide, conductive network, wearable electronic devices

I. INTRODUCTION

The growing demands for flexible, miniaturized and wearable electronic devices require flexible and high-performance energy sources [1, 2]. Flexible supercapacitors are very promising due to their high power density, long cycle life, and safety; but their capacitance, especially the specific area capacitance, should be further improved to meet the growing energy supply demand and miniaturization requirement of various electronic devices in the future [3, 4]. To this end, tremendous efforts have been devoted to increasing the specific area capacitance to promote the practical application of flexible supercapacitors in wearable electronic devices. According to previous studies, developing high-performance electrode materials and increasing the number of reactive sites per area are two effective strategies to improve the specific area capacitance [5-8]. Based on these strategies, a series of flexible supercapacitor were fabricated successfully, including graphene and carbon nanotube-based [9-12], conducting polymer based [13， 14] and transition metal compound-based flexible supercapacitors [15, 16]. However, to achieve high flexibility, many available flexible supercapacitors are constructed into thin devices to ensure reliable contact between active materials and current collector and avoid the shedding of active materials when bending or twisting the supercapacitor [17, 18]. As a result, the thin thickness of the whole electrode will greatly limit the mass loading of active materials and lower the specific area capacitance, which substantially hindering the practical application of supercapacitors for wearable electronic devices.

Herein, we report a magnetic field induced fabrication of three-dimensional NiCo nonwoven cloth consisting of cross-linked ultra-long NiCo nanowires-based conductive network as highly flexible current collector, following with an in-situ sulfurization process to load electrochemically active NiCo sulfide (Ni-Co-S) on the nanowire surface. The Ni-Co-S was employed as active materials because of the the merit of good electrical conductivity [19], and the in-situ sulfurization process is believed to facilitate strong interfacial bonding between active materials and current collector, which improves the flexibility of the whole electrode. To our knowledge, benefiting from stress release by slippage between the cross-linked nanowires under external forces and the strong contact between the active Ni-Co-S and NiCo nonwoven cloth current collector, the NiCo sulfide nonwoven cloth (NSNC) electrode can achieve ultra-high flexibility, even foldability and arbitrarily deformable properties. Most importantly, the thick three-dimensional architecture enables fast electron charge, ion transport and high mass loading, which is crucial for high-specific-capacitance flexible supercapacitors. As a result, the NSNC electrode demonstrates an ultra-high specific areal capacitance around 4.91 F cm^{-2}, with only slightly capacitance decay after even 10000 cycles, outperforming most of reported flexible supercapacitors and revealing its great potential for practical application in wearable electronic devices.

II. EXPERIMENTAL

A. *Synthesis of nickel cobalt non-woven cloth and fabrication of NSNC.*

The Ni-Co nanowire conductive framework was fabricated by an electroless deposition method with the assistance of magnetic field. Firstly, a 30 mL solution containing 0.225 M $Na_3C_6H_5O_7$ (sodium citrate), 0.225 M $NiCl_2$, 0.075 M $CoCl_2$ and 0.20 mM H_2PtCl_6, and another 30 mL solution containing 3 vol% of hydrazine hydrate were prepared, respectively. Then, the pH of both above solution were adjusted to 12.5 with potassium hydroxide. After that, these two solutions were mixed together and heated to 60 °C for 1 hour with a piece of magnet placing above the solution. Then remove the magnet and cool down the sample. The in-situ formation of Ni-Co-S on the surface of NiCo nonwoven cloth was fabricated by a hydrothermal process. Typically, a piece of NiCo nonwoven cloth with 1 cm^2 surface area was immersed into an autoclave containing 15 mL deionized water, 15 mL ethanol and 6.8 mg thiourea (CH_4N_2S). Then, the autoclave was sealed for hydrothermal reaction at 150 °C for 5 h. After the autoclave was cooled down, the samples were rinsed with ethanol and de-ionized water for several times.

B. *Fabricaation of activated carborn@NiCo nonwoven cloth (ACNC)*

Activated carbon powder, acetylene black and PVDF (8:1:1 in mass ratio) were mixed together and stirred in NMP solution to form a uniform slurry. Subsequently, the as prepared slurry was screen printed on NiCo nonwoven cloth via a scraper with consistent height of 20 μm.

C. *Materials characterizations and electrochemical measurements:*

Scanning electron microscopy (FE-SEM, SAPPHIRE SUPRA 55) was used to characterize the morphology and microstructure of samples. The X-ray diffraction was conducted on a Bruker DS RINT2000/PC, Germany, at a diffraction angle ranging from 25° to 80°. The electrochemical measurements were carried out on a VMP3 working station (Bio-Logic). In the half cell test, NSNC and ACNC were employed as the working electrode directly, a Pt sheet and a saturated calomel electrode (SCE) was used as counter and reference electrode, respectively. In the full cell test, NSNC acts as cathode and ACNC acts as anode and a 1 M potassium hydroxide solution was employed as electrolyte. Cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) were used to evaluate the electrochemical performance. The potential window ranges from -0.1 to 0.5 V (vs SCE) for the cathode and -0.8 to 0 V (vs SCE) for the anode, and thus 0 to 1.6 V for the asymmetric NSNC//ACNC cell. The specific capacitance was calculated by following equations:

$$C_a = \frac{\int i(V)dV}{S \cdot v \cdot \Delta V} \tag{1}$$

$$E = \frac{C_a \Delta V^2}{2} \tag{2}$$

$$P = \frac{E}{t} \tag{3}$$

where C_a is specific area capacitance of electrodes (F cm^{-2}), ΔV is the voltage range (V), S is the geometric area of the electrode (cm^2), E is the energy density (Wh cm^{-2}), P is the power density(W cm^{-2}) and Δt is the discharge time (s).

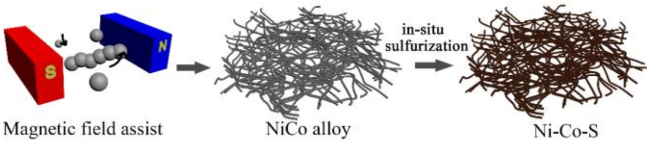

Figure. 1 (a) Schematic illustration of the fabrication process of NSNC electrode.

III. RESULTS AND DISCUSSION

The strategy for the fabrication of NSNC is illustrated in Fig.1. The three dimensional NiCo nanowire nonwoven cloth was first synthesized by a magnetic-assist chemical deposit process. Then the NiCo was in-situ transformed into Ni-Co-S on the nanowire surface in a thiourea solution, through a typical hydrothermal process. To ensure that the in-situ transformation of Ni-Co-S can only occur on the surface of nanowires without destroying the integrity of the three-dimensional nonwoven network, the concentration of thiourea was controlled to be very low and the temperature and reaction time were also controlled. (see details in experimental section).

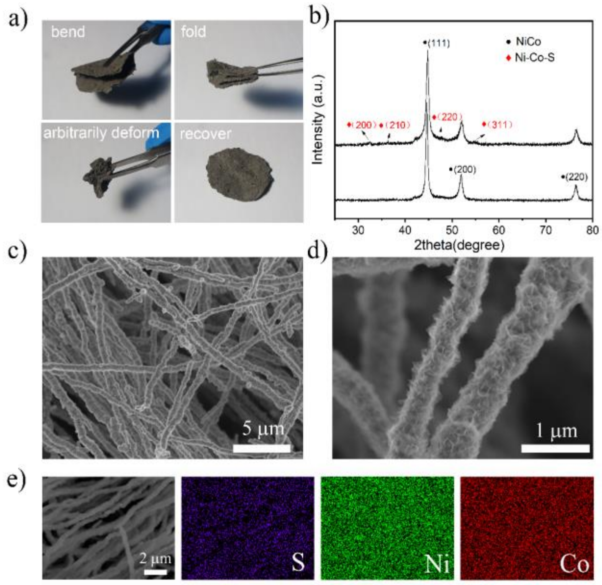

Figure. 2 (a) Physical images of NSNC electrode (b) XRD patterns of NSNC and NiCo nanowire nonwoven cloth (c-d) SEM images of NSNC （e） EDX mapping images of NSNC.

As show in Fig. 2a, the nanowire nonwoven cloth can be well maintained after the hydrothermal process. Notably, this novel NSNC electrode can achieve ultra-high flexibility, even foldability and arbitrarily deformable properties. The formation of NiCo alloy nanowires and Ni-Co-S after hydrothermal process can be further confirmed by X-ray diffraction patterns (Fig. 2b). For pure NiCo alloy nanowire nonwoven cloth, the diffraction peaks at 44.7°，52.0° and 76.5° can be index to (111), (200), (220) plan. For NSNC, three new peaks indexed to Ni-Co-S can be observed, which further confirmed the formation of NiCo sulfide on the surface. The typical FE-SEM images of the NSNC are shown in Fig. 2c and 2d, in which NiCo exhibits a nanowire shaped structure with Ni-Co-S nanosheets uniformly grow on the surface. This nanowire structure is believed to offer large surface area and accelerate the electron and mass transport. Additionally, the energy-dispersive spectroscopy (EDS) mapping images indicated the uniform distribution of Ni, Co and S elements.

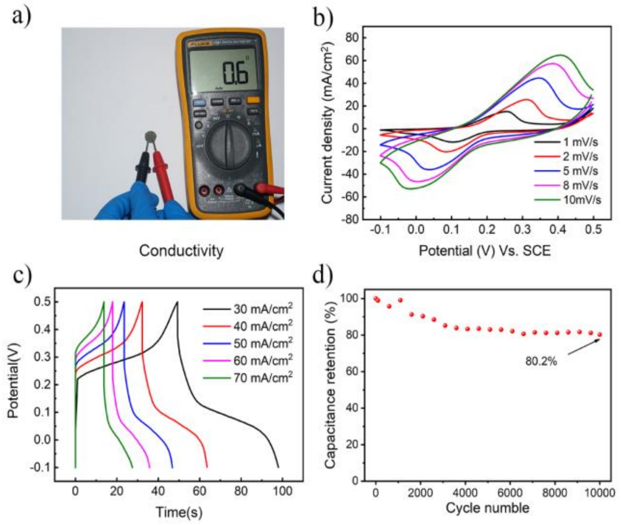

Figure. 3 (a) Conductivity of NSNC. (b) CV testing results of NSNC electrode (c) GCD curves of NSNC electrode (d) Cycling stability of NSNC electrode.

Before going to the electrochemical testings, we evaluated the conductivity of NSNC electrode. As shown in Fig. 3a, the NSNC electrode shows a very low ohmic resistance of 0.6 Ω, indicating fast electron transfer in such three dimensional nonwoven cloth structure. Then, the electrochemical properties of NSNC as cathode was investigated in half cell measurement with 1 M KOH electrolyte. Figure 3b shows the CV curves with different scan rates, which shows a typical Ni-Co-S redox peaks and agrees with previous report. [20] The probably reaction mechanism of these redox peaks may as following equation: [20, 21]

$$CoS + OH^- \rightleftharpoons CoSOH^- + e^-$$

$$CoSOH^- + OH^- \rightleftharpoons CoSO + H_2O + e^-$$

$$NiS + OH^- \rightleftharpoons NiSOH + e^-$$

The galvanostatic charge/discharge curves of the NSNC were carried out at different current densities (30-70 mA cm^{-2}). As shown in Fig. 3c, the GCD curves at different current densities are almost symmetric, which indicates the high efficiency of the reaction and the highly reversibility of such redox reactions. According to the above results, the specific areal capacitance was calculated to be 4.91 F cm^{-2} at 1mV s^{-1}, which is far higher than most of the flexible electrodes in previous reports. Notably, the NSNC also shows a distinguished cyclic stability at scan rate of 10mV s^{-1} and keep 80.2% of initial capacitance even after 10000 cycles (Fig.2d).

Activated carbon was widely used as anode materials in commercial supercapacitors due to its excellent cycling stability compared to conducting organic polymer and iron based anode materials. Thus, we introduced activated carbon on the surface of NiCo nonwoven cloth to fabricate a reliable ACNC anode electrode. CV and GCD technologies were carried out to evaluate the electrochemical performance of ACNC. In Fig. 4a, the quasi-rectangular shape indicates typical double layer capacitors behavior. The capacitance of the ACNC electrode is calculated up to 2.53 F cm^{-2} at 1 mV s^{-1}. In addition, the capacitance can be retained at about 61.6% when the scan rate range from 1 mV s^{-1} to 10 mV s^{-1} according to the CV curves. The GCD curves are almost symmetric, which is a typical shape of carbon materials (Fig. 4b). All these electrochemical performances indicate that the ACNC electrode could serve as an reliable anode to assemble with NSNC electrode.

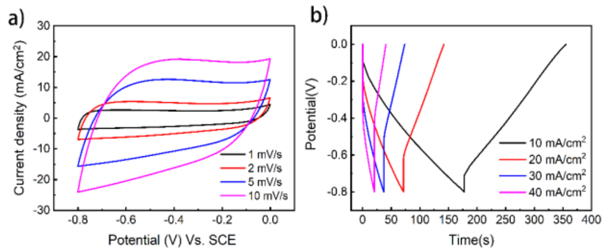

Figure. 4 Electrochemical characterization of ACNC electrode (a) CV curves and (b) charge–discharge curves.

The electrochemical performance of the assembled supercapacitor device was evaluated by CV and charge–discharge analytical technology. As shown in Fig. 5a, the asymmetric supercapacitor shows remarkable capacitive behavior contributing from Ni-Co-S and the activated carbon. The CV curves maintained the shape even at scan rates up to 20 mV s^{-1}, which indicates the good rate performance of the supercapacitor. The charge-discharge curves of the asymmetric supercapacitor are shown in Fig. 5b. The curves show a perfect quasi-triangular shape, indicating a high reversibility of the supercapacitor. [22-24] Furthermore, the device can shows a maximum energy density of 672 μWh cm^{-2} at the power density of 1.5 W cm^{-2} and 426 μWh cm^{-2} at 14.4 W cm^{-2}. Benefiting from the novel three-dimensional conductive architecture and strong adhesive force between NiCo nanowire and the in-situ formed Ni-Co-S nanosheets, this supercapacitor exhibits excellent cycling stability, remaining at 97.3% of its initial capacitance even after 5000 CV cycles (Fig 5c). Furthermore, a light-emitting diodes(LED) can be powered for more than 2 min by using two asymmetric supercapacitors in series (Fig 5d).

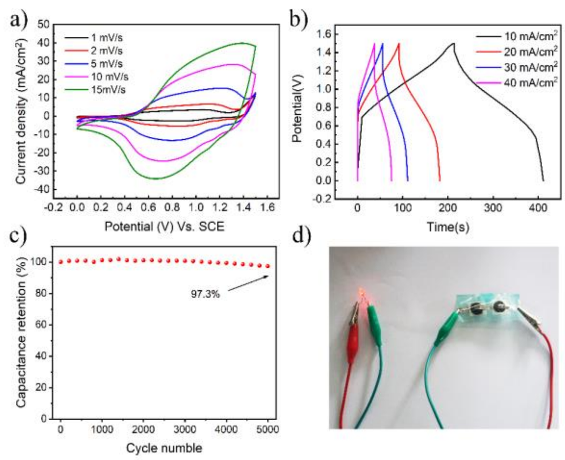

Figure. 5 (a) CV curves of NSNC//ACNC symmetric supercapacitor at different scan rates (b) GCD curves of NSNC//ACNC symmetric supercapacitor (c) Cycling stability of NSNC//ACNC symmetric supercapacitor (d) a photo of the symmetric supercapacitor powering LED.

The excellent electrochemical performance of NSNC can be attributed to following three aspects: 1) NiCo nonwoven cloth with three dimensional porous structure can offer large surface area for the exposed of active sites and provide an integrated conductive network for the fast transport of electrons; 2) the in-situ formation of Ni-Co-S with uniform nanosheet structure can offer more active sites and thus improve the capacitance; 3) the excellent flexibility and strong adhesive force between Ni-Co-S nanosheets and NiCo current collector promote the long-term cycling stability performance.

IV. Conclusion

In summary, a three-dimensional Ni-Co sulfide nanowire nonwoven cloth was fabricated successfully induced by magnetic field. To our knowledge, with the merit of high surface area porous structure, excellent electron conductivity, strong adhesive force between active Ni-Co-S nanosheets and NiCo current collector, and the controllable thickness of the electrode for large mass loading, our NSNC electrode exhibits superb high specific area capacitance up to 4.91 F cm^{-2} while maintaining excellent flexibility. The flexible supercapacitor assembled by activated carbon and Ni-Co-S also exhibits a high energy density of 672 μWh cm^{-2} and excellent cycle stability with only 2.3% capacitance degradation after 5000 cycles. In view of the highly flexibility and ultrahigh specific area capacitance, the three-dimensional porous NSNC electrode are believed to have huge potential in the application of flexible supercapacitors and wearable electronic devices.

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