Enhanced Electrochemical Performance of Cooper Sulfides Coated Electrochemical Modified Carbon Cloth and Its Application in Flexible Supercapacitors

Xin He¹,a, Xiling Mao¹,b, Wenyao Yang²,c, Yujiu Zhou¹,d, Weicen Liu¹,e, Yajie Yang¹,f, Jianhua Xu¹,*

¹School of Optoelectronic science and technology, State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China (UESTC), Chengdu, P. R. China,
²Engineering Research Center of New Energy Storage Devices and Applications, Chongqing University of Arts and Sciences, Chongqing 402160, P. R.China;

*Corresponding author e-mail: jianhuaxu8023@126.com, azjt80655839@163.com,
bxlmao2014@163.com, cyang0220@163.com, d18782941993@163.com,
e13378707788@163.com, fyajieyang215@163.com

Abstract. All high-performance flexible electrochemical energy storage devices such as supercapacitors (SCs) and lithium ion batteries (LIBs) are highly desirable as a result of the ever-increasing demands for stretchable electronics. In this work, an effective two-step strategy contain surface and structural modulation and hydrothermal method is developed to grow cooper sulfides onto a highly active surface with pores and numerous functional oxygenic groups. Arising from rough surface and increased active sites, the as-prepared activated loosen cooper sulfides coated electrochemical modified carbon cloths (CuS@ECC) electrode not only achieves a large capacitance (410 F cm⁻² at 1 mA cm⁻²) and fast kinetics but also shows excellent cycling durability (maintain 95% initial capacitance after 3000 cycles). This dual modification strategy may throw light on the rational design of new generation advanced composited electrodes for high-performance flexible supercapacitors.

1. Introduction
The portable foldable and bendable electronics like stretchable screen [1], smart bracelet [2] and wearable medical equipment had been quite developed for the breakthrough of the flexible electronic materials as light emitting diode, sensor and electronic components. [3] Due to the limited performance of existing power sources, there're still urge needs for stable and reliable energy providing. [2] Among most energy storage devices, supercapacitors exhibit high charging/discharging rate, long cyclic life and high safety but low energy density. [4] With these interesting features, the supercapacitors had been applied in various situation especially for high power demand, maintenance-free and frequently charging/discharging condition. But the relatively lower energy density limits the application. To extend the application of supercapacitors and achieve the miniaturization of whole
electronic devices, higher energy density is perpetual pursued. As a result, the supercapacitor electrode material with excellent flexibility and high specific capacitance had attracted many scholars' attention. Flexible electrodes could be constructed by free-standing material directly or coating pseudocapacitance material on stretchable substrates like conductive commercial carbon cloths (CC) or insulating fibers. [5,6,7,8] By the mechanism of energy storage process, the electrode material could be divided into electrochemical double layer capacitance (EDLC) material with dominating electrostatic process and pseudocapacitance material with prime faradic process. [9] The pseudocapacitance material as metallic oxides and sulfides possess higher specific capacitance than EDLC materials and good reversibility than battery materials for the faradic thermodynamics process and capacitive kinetic property. [10] Among the metallic sulfides, cooper sulfides had been applied in pseudocapacitance supercapacitors [11,12] and lithium ion batteries [13] for the abundant cooper resource, high specific capacitance and good conductivity.

Herein, electrochemical modified CC(ECC) based flexible supercapacitor electrodes were synthesized by electrochemical modify process and hydrothermal method. The ECC provide a rough and functional surface, which facile the CuS deposition and strengthen the connection of these components. Simultaneously, the in-situ formation of functional oxygen groups onto its surface during the electrochemical activation can also provide abundant active sites yielding pseudocapacitance. The CuS nanoparticle on the surface also offer extra capacitance stem from the pseudocapacitance. High area specific capacitance (410 mF cm$^{-2}$ under the current density of 1 mA cm$^{-2}$) and capacitance retention (95% after 3000 cycles) were obtained.

2. Experiment

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2.1. Materials

The commercial carbon cloth (WS1002) were purchased from CeTech, Co., Ltd, the cooper acetate monohydrate (Cu (CH$_3$COO)$_2$H$_2$O), Thiourea (CH$_4$N$_2$S), ethanol, sulfuric acid (98% H$_2$SO$_4$), acetone, and other reagents were analytical reagent grade and all the chemicals were used after purchasing without further purification or treatment. All the experiments were performed under ambient conditions.

2.2. The synthesis of electrodes

Fig. 1 shows a schematic illustration of the synthesized procedure of the CuS@ECC composite electrode. Firstly, the ECC were obtained by an electrochemical activation method. Before activation,
a piece of carbon cloth (1*3 cm, mass per unit area 11.3 mg cm$^{-2}$) was cleaned by ethanol, acetone, and deionized water in turn. The electrochemical activation was carried out in a standard three electrode cell in an acid of and 1M H$_2$SO$_4$ aqueous solution with platinum wire as counter electrode and Ag/AgCl electrode as reference electrode under a 50 times Cyclic voltammetry from 0V to 3 V by the scan rate of 10mV s$^{-1}$, neglecting the water splitting. ECC were washed with deionized water after activation process. Then, the CuS nanoparticles were synthesized on ECC by hydrothermal method. 5mmol Cu(CH$_3$COO)$_2$H$_2$O and 5mmol CH$_3$N$_2$S was dissolved in 60 ml deionized water to form a green solution. And then, transferred into a 100 ml Teflon-lined stainless-steel reactor with a piece of cleaned 1*3 cm$^2$ ECC substrate and a piece of cleaned 1*3 cm$^2$ CC substrate (both ultrasonic in ethanol and distilled water before using) as a contrast. The sealed reactor was then heated to 120 °C and kept for 12 h to form CuS nanoparticles. Finally, all these obtained samples were washed by deionized water and then airing in 60 °C to remove the retained solvent.

2.3. Characterization and electrochemical measurements
The morphology and microstructure of the electrodes were characterized by scanning electron microscopy (SEM, HITACHI S4800), X-Ray Diffraction (XRD, PANalytical B.V. X'Pert Powder). The CuS@ECC served as the working electrodes directly. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to characterize the electrochemical characteristics of the electrodes. The CV curves were measured under different scan rates of 2–100 mV s$^{-1}$ between -0.2 and 0.8 V. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 k Hz to 0.1 Hz at an open circuit potential with an ac perturbation of 5 mV. All electrochemical measurements were carried out in a three-electrode system (CHI660D electrochemical workstation, Chenhua, Shanghai) with 1 M H$_2$SO$_4$ aqueous solution as electrolyte. A platinum plate and an Ag/AgCl electrode were used as the counter and reference electrode, respectively.

Specific capacitance ($C_{sp}$) derived from GCD test was calculated from equation1 as follows:

$$C_{sp} = \frac{I t}{(\Delta V A)}$$

Where $C_{sp}$ (Fcm$^{-2}$), I (A), t (s), $\Delta V$ (V) and A(cm$^2$) are the specific capacitance, the discharge current, the discharge time, the total potential window and the area of the active material, respectively.

3. Results and discussion

![Figure 2. Morphology characterization of the and CuS@ECC and CuS@CC. (a) (b) SEM images of CuS@ECC. (c) (d) SEM images of CuS@CC.](image_url)
As Figure 1 shows, the copper sulfides were synthesized by hydrothermal method. Compared to the aggregate morphology of CC based CuS, homogeneous cus nanoparticles were grown on the surface of ECC, which resulted in more active sites interactive to the electrolyte ions (Figure 2). The difference between the two samples might be attribute to the rough and porous electrochemical modified surface. During the electrochemical oxidation and activation, the surface of the CC had been etched and activated by the oxidation and produce lot of pores and oxygen-containing functional groups. The nucleation process of CuS core occurred in the pores of ECC surface, and then the growing CuS core won’t stick to each other by the limitation of carbon matrix as the CC based CuS nanoparticles. Consequently, osteoporosis and uniform CuS were obtained after hydrothermal reaction upon the surface of ECC. The carbon cloth acting as both the flexible current collector and reaction matrix. Besides, the pores and functional groups afford mechanical bindings and electrostatic force, which acting as anchor for decreasing the contact resistance and enhancing the adhesive force.

References are cited in the text just by square brackets [1]. Two or more references at a time may be put in one set of brackets [3, 4]. The references are to be numbered in the order in which they are cited in the text and are to be listed at the end of the contribution under heading references, see our example below.

![Figure 3. Structural characterization of CC, ECC and CuS@ECC. (a) FT-IR spectra of the CC, ECC samples. (b)XRD patterns of CuS@ECC and ECC samples.](image)

To reveal the functional groups of the surface introduced by the electrochemical modify process, the FTIR measurement were taken and the curves were presented in Figure 3(a). Compared to the untreated CC sample, there appear peaks in 1588.54,1711.11 and 3350.16 cm\(^{-1}\) of ECC electrode. The band at 1711 cm \(^{-1}\) can be assigned to the C=O stretching vibration from ketones, aldehydes or carboxyl groups, which band is predominantly due to carboxylic acid groups. The band at about 3350 cm\(^{-1}\) can be assigned to the O–H stretching mode of hydroxyl functional groups. This band in the region of 1600 cm \(^{-1}\) (at 1588 cm \(^{-1}\)) is assigned to an aromatic ring stretching mode or a highly conjugated hydrogen bonded C=O, analogous to the structure of acetylacetone. \cite{14} The results of FTIR study show that the oxidation of CC increases the amount of surface oxygen complexes that present initially.

The crystal phase of ECC and CuS@ECC were indicated in the XRD curves. XRD patterns (Figure 3(b)) of the as-prepared CuS@ECC show that the diffraction peaks all match well with the standard peaks of hexagonal CuS. The peak appear at 26.8 degree could be attributed to the (002) crystal face.
of carbon cloth, which accord with the ECC sample. The result of XRD curves demonstrate that the covellite phase CuS had been successfully coated on the surface of ECC by hydrothermal process.

The electrochemical performance was the most pivotal properties that we concerned, and the GCD, CV and EIS measurement were taken. GCD curves collected from CC, CuS@CC and CuS@ECC electrodes at 1 mA cm\(^{-2}\) are shown in Figure 4(b). Among them, the CuS@ECC electrode delivered the longest charge/discharge time, again showing its remarkable electrochemical performance. The specific capacitance of the CC, CuS@CC and CuS@ECC samples are 10, 75, 410 mF cm\(^{-2}\) under the current density of 1 mA cm\(^{-2}\). The dramatically increased capacitance could be attributed to the homogeneous morphology and loosen and porous structure of CuS nanoparticles on the ECC surface, which shorten the path of electrolyte ions and facilitate the redox reaction. CV curves collected from CC, CuS@CC and CuS@ECC electrodes at 10 mV s\(^{-1}\) are shown in Figure 4(b). Two redox peaks were found in the CV curves and exhibit the reversible faradic energy storage process. Both the CC, CuS@CC and CuS@ECC electrodes yielded distinct capacitive current while the CC and CuS@CC electrodes had very small ones, revealing that the introduction of surface functional group and rough morphology upon electrochemical oxidation can significantly boost the capacitance of CuS.

![Graphs](image)

**Figure 4.** Electrochemical performance comparison of CC, CuS@CC and CuS@ECC samples. (a) GCD curves under 1mA cm\(^{-2}\). (b) CV curves at a scan rate of 10 mV s\(^{-1}\). (c) GCD curves under 0.5, 1, 2, 4, 5 mA cm\(^{-2}\) of CuS@ECC. (d) CV curves at a scan rate of 2, 5, 8, 10, 20, 50 mV s\(^{-1}\) of CuS@ECC.
The CV curves under different scan rates from 2 to 50 mV s\(^{-1}\) and GCD curves at different current densities from 0.5 to 5 mA cm\(^{-2}\) are presented in Figure 4 (c) and (d). In addition, the capacitance could retain 50% (200 mF cm\(^{-2}\)) when the current density increased to 5 mA cm\(^{-2}\), which indicates a good rate performance of CuS@ECC sample. The nearly rectangle shape of the CV curves exhibit a good reversibility of the electrochemical process of CuS@ECC. The position of peaks extended with the scan rates increased, which also confirm the faradic intrinsic mechanism. All these results persuasively demonstrate that the capacitive performance of the CuS@CC can be effectively promoted by this present one-step electrochemical modify method.

![Figure 5](image.png)

**Figure 5.** (a)Nyquist plot from EIS curves for different samples. (b) The cycling performance of these electrodes at a current density of 1 mA cm\(^{-2}\).

The AC impedance measurements could also represent the kinetics properties of these samples. The high frequency zone is combined with EDLC process and indicate the ESR of the electrodes. The semicircle in high frequency zone is related to the electron transfer process, and the line at the low frequency zone present the capacitive behavior of the electrodes. As the EIS curves exhibit (Figure 5(a)), the larger semicircle of the CuS@ECC electrode could resulted from the larger electron transfer resistance stem from redox reactions, which leading to a larger pseudocapacitance. The lower capacitance of CuS@CC might be attributed to the aggregating of the active materials, which means the redox reactions only occurred in the thin surface of CuS. And the lower angle of straight line to x-axis of CuS@ECC exhibit a better capacitance behavior than the others, which fit the result of GCD and CV curves. It could be demonstrated that the successful improvement of pseudocapacitance stem from the electrochemical activation method. Moreover, the CuS@ECC electrode exhibited excellent cycling stability with very little capacitance decrease (5%) after 3000 cycles, as shown in Figure 5(b), compared to 30% of CuS@CC. This might be attributed to the anchor effect of pores and functional groups on the ECC surface, which prevent CuS from peeling off the surface of the electrode. The electrochemical performance of CuS electrodes had been prominently enhanced by the strategy of electrochemical oxidation.

**4. Conclusion**

To conclude, we have demonstrated a facile strategy for construction of highly active porous CuS@ECC with the help of electrochemical etching and oxidation process. The capacitive properties of the CuS@CC have proven to be significantly boosted by producing porosity and functional oxygen groups. Taking the merits of the increased active sites, devised fast electron and ion diffusion rates, the as-obtained CuS@ECC electrode reaches large areal capacitance (400 mF cm\(^{-2}\) at 1 mA cm\(^{-2}\)) and good rate capability (≈50% capacitance retention at 5 mA cm\(^{-2}\)) as well as prominent cycling stability.
This work provides new opportunities for the rational design of hierarchical composited flexible metallic sulfides electrodes as efficient energy storage electrodes via precisely tailoring structure and surface.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC) (Grant Nos. 51477026 & 61471085 & 61774030), the National Science Funds for Creative Research Groups of China (Grant No. 61421002), Chongqing Postdoctoral Science Special Foundation (No. Xm2017051), Chongqing Engineering Research Center of New Energy Storage Devices and Applications (No. KF20170202, KF20180202) and the Scientific Research Project of Chongqing University of Arts and Sciences (No. R2016DQ11 and P 2016DQ14). work was financially supported by xxx fund.

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