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Three dimensional CoMoO₄ nanosheets on Nickel foam for high performance supercapacitors

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Abstract. Here we proposed novel CoMoO₄ nanosheets on nickel foam that used as a superior electrode for supercapacitors, with an excellent pseudocapacitive performance. The CoMoO₄ nanosheets based electrode provide high values of specific capacitance of 1.12 F/cm² corresponding to the current densities of 4 mA/cm². It exhibited good cycling life that the specific capacitance maintained with no decrease during 3000 cycles. Our work can be applied in mass applications of high-capacitance energy-storage supercapacitors.

1. Introduction

With the development of flexible electronic devices in recent years, supercapacitors have become the most attractive energy storage devices because of the rapid charging capability, high power density, and long working life. [1-9] However, there are still some limitations. For example, the capacity of supercapacitors is too low compares with traditional batteries, which confines its application in flexibility and integrated electronic devices severely. As a result, we should focus on constructing an all-solid-state supercapacitor as well as increasing the capacity.

Normally, supercapacitors can be divided into double-layer capacitors and Faraday tantalum capacitors according to the charge storage mechanism. [10-13] Tantalum capacitors are known for their excellent reliability, robustness, and parametric stability. In recent years, more and more researchers began to study the materials used in electrode, including the composition, structure, distribution, etc. [6, 10] Among the materials, NiCo₂O₄ and ZnCo₂O₄ are the most popular supercapacitor electrode materials due to their superior conductivity, large surface area and highly reactive oxidation state. [7, 14-17] Although these metal oxide-based supercapacitors exhibited relatively high capacity, the performance still needs to be improved to meet for practical application requirements.



In this paper, a novel CoMoO₄ nanosheets on nickel foam that used as electrodes of supercapacitors was reported. The unique design for supercapacitors enables superior pseudocapacitive performance, exhibiting high specific capacitance of 1.12 F/cm² corresponding to the current densities of 4 mA/cm². Moreover, this CoMoO₄ nanosheets based electrode presented excellent cycling stability that the specific capacitance showed no decrement after 3000 cycles.

2. Experiments

2.1. Materials Synthesis

All the chemicals used in this experiment were purchased from Sinopharm Chemical Reagent Co. Ltd. First, a piece of nickel foam was prepared. Then the nickel foam was loaded into the process chamber of hydrothermal, followed by the annealing process to grow CoMoO₄ nanosheets on electrode layer.

2.2. Materials Characterization

The crystal structures of as-prepared nanowires were examined by the X-ray diffraction (XRD; Cu target, K α , $\lambda=0.15406$ nm) with a Bruker D8 Advance X-ray diffractometer. The morphology and element analysis of the samples were characterized by scanning electron microscopy (SEM; FEI NanoSEM650), transmission electron microscopy (TEM; FEI Tecnai G2 F20). The electrochemical properties were carried out with a Chenhua CHI 760D electrochemical workstation [7, 18].

3. Results and discussion

To evaluate the morphology and element details of the as-prepared samples, SEM, TEM and XRD were evaluated, as shown in figure 1. Figure 1a-c displayed the SEM images of the nanosheets after three steps of fabrication procedures. Figure 1d presented the transmission electron microscopy (TEM) image of the nanosheet and figure 1e showed the high-resolution TEM (HRTEM) image of the samples. It is obvious that the clearly resolved lattice fringes of about 0.34 nm was in good agreement with the (002) plane of cubic structured CoMoO₄. Figure 1f shows the X-ray diffraction (XRD) analysis result. Peaks at $2\theta = 13.21, 23.33, 26.5, 32.9, 40.22$ and 54.44 degrees in the patterns of CoMoO₄ were well consistent with the (001), (021), (002), (022), (003) and (-440) planes of the cubic CoMoO₄ phase (JCPDS No. 21-0868). [19-22] All of the results above indicate that CoMoO₄ nanosheets were formed on nickel foam to be used as novel electrodes of supercapacitors.

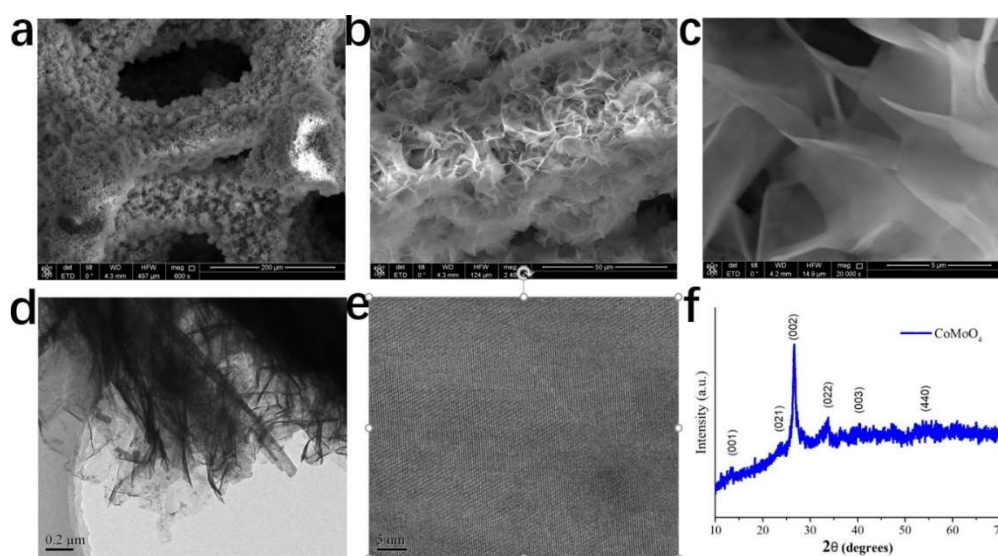


Figure 1. (a-c) SEM images after the three steps of fabrication procedures; (d) TEM image of the nanowires; (e) corresponding HRTEM image nanowires; (f) XRD patterns of the obtained nanowires.

To further evaluate the performance of the CoMoO₄ nanosheets based electrode, electrochemical tests were carried out in a three-electrode electrochemical cell with 2 M KOH electrolyte, as shown in figure 2. Figure 2a presented the cyclic voltammogram (CV) curves of CoMoO₄ nanosheets electrode measured at the scan rate of 5 - 50 mV/s in the voltage window of -0.2~0.4 V vs. From the closed CV curves, we can learn apparent redox peaks caused by Faradic capacitive behavior, indicating superior faradic capacitive behavior. This kind of CoMoO₄ nanosheets was introduced to establish hierarchical structures, increase the specific surface areas greatly and add more active materials, thus increasing the area specific capacitance.

Galvanostatic charge-discharge (CD) measurements under different current densities (4 mA/ cm², 6 mA/ cm² and 10 mA/ cm²) were also carried out in the potential window from -0.2 to 0.4 V versus saturated calomel electrode (SCE). The GCD curves showed good symmetry, indicating an excellent capacitor performance. Figure 2c showed the relationship between specific capacitances and current densities. According to the discharge curves of GCD test, we can calculate the specific capacitances of CoMoO₄ nanosheets electrode were 1120 mF/ cm², 868 mF/ cm² and 618 mF/ cm² at the current densities of 4 mA/ cm², 6 mA/ cm² and 10 mA/ cm². And the corresponding faradic reactions involved during the charge-discharge process could be described by the following equations: [5, 23-26]

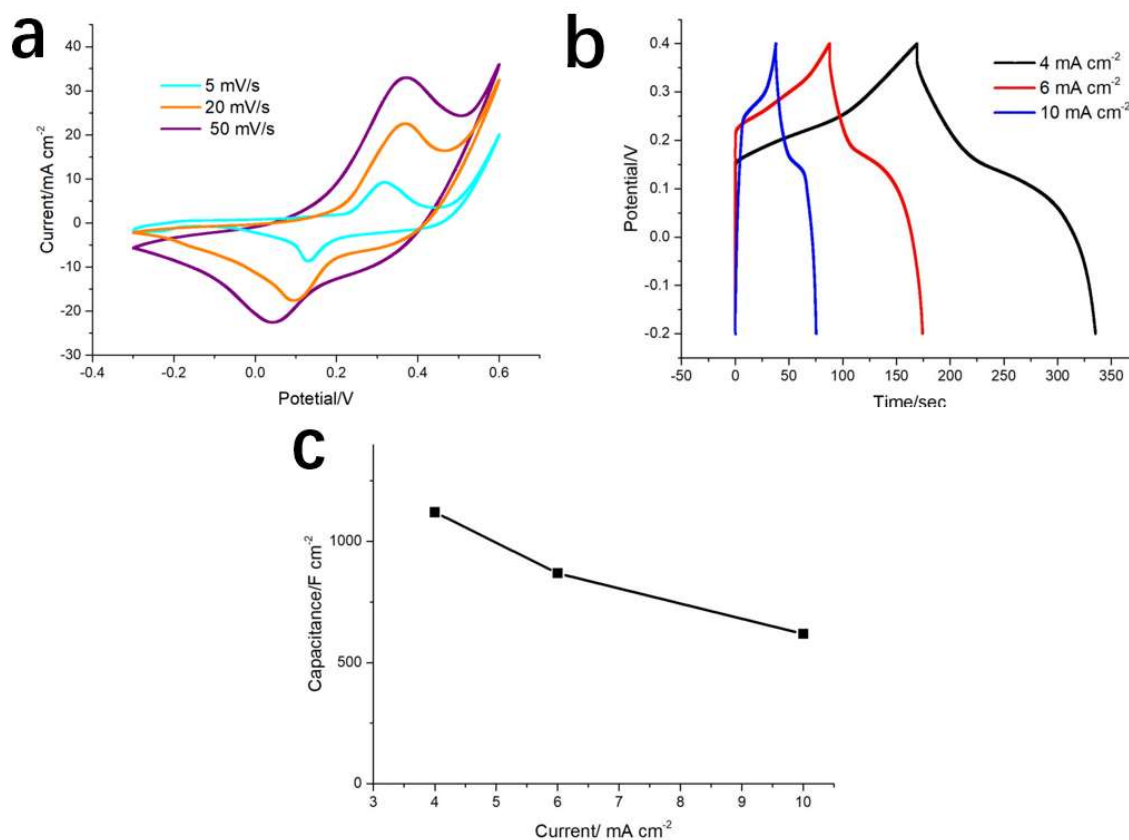
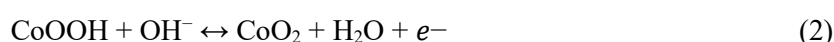


Figure 2. (a) CV and (b) galvanostatic charge-discharge curves of the CoMoO₄ nanosheets electrode; (c) the areal capacitances of the CoMoO₄ nanosheets electrode at varied galvanostatic CD current densities.

Figure 3 presented the AC impedance of CoMoO₄ nanosheets supercapacitor electrode and cycle stability of the symmetrical supercapacitor at the current density of 10 mA/ cm². From figure 3a we can conclude that the impedance of CoMoO₄ nanosheets supercapacitor electrode equals to a resistance less than 2 Ω. It is also a proof that CoMoO₄ nanosheets based supercapacitor is an ideal candidate as energy-storage device due to its high capacitance. Moreover, the cycling stability was also carried out under the current density of 10 mA/ cm², as shown in figure 3b. The capacitance of as-prepared device showed no decrement during 3000 times cycling, indicating an excellent long-life cycle.

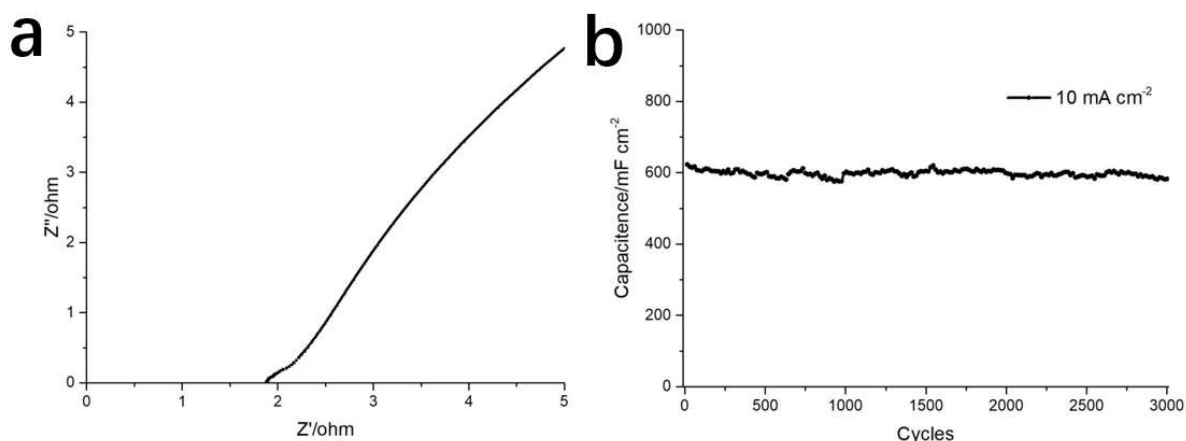


Figure 3. (a) AC impedance of the CoMoO₄ nanosheets supercapacitor electrode; (b) cycle stability of the symmetrical supercapacitor at the current density of 10 mA/ cm².

4. Conclusion

In summary, we developed a novel electrode material of CoMoO₄ nanosheets on nickel foam which could be used for supercapacitors. This kind of structure displayed remarkable pseudocapacitive performance, showing the specific capacitance of 1120, 868 and 618 mF/ cm² corresponding to the current densities of 4 mA/ cm², 6 mA/ cm² and 10 mA/ cm², respectively. The CoMoO₄ nanosheets based electrode exhibited good cycling stability that the specific capacitance showed no decrement after 3000 cycles.

Acknowledgments

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