A flexible spiral-type supercapacitor based on ZnCo$_2$O$_4$ nanorod electrodes

Hao Wu,$^{a,b}$ Zheng Lou,*$^b$ Hong Yang$^a$ and Guozhen Shen$^{a,b}$

Fiber electrochemical capacitors show advantages such as light weight and flexibility, and may also be easily integrated or woven into various electronic devices with low cost and high efficiency. In this work, we report the preparation of ZnCo$_2$O$_4$ nanorods on a Ni wire as the fiber electrodes, using a simple and rapid single-step hydrothermal process. The electrochemical properties of the free-standing supercapacitors were analyzed using a two electrode system. The supercapacitor achieved a specific capacitance of 10.9 F g$^{-1}$. An energy density of 76 mWh kg$^{-1}$ and a power density of up to 1.9 W kg$^{-1}$ were also obtained for the fiber supercapacitors. The flexible supercapacitor exhibited remarkable electrochemical stability when subjected to bending at various angles, illustrating the promise for use as electrodes for wearable energy storage.

1. Introduction

The increasing demand for portable and flexible electronics such as roll-up displays, photovoltaic cells, and wearable devices have initiated intensive efforts to explore flexible, lightweight and environmentally friendly energy storage devices.$^{1-5}$ As a new class of energy storage devices, flexible supercapacitors (SCs) have attracted much attention as a promising energy source for wearable electronics due to their remarkable advantages such as high power density and relatively large energy density, fast charge/discharge capability, light weight, excellent reliability and flexibility. Despite the significant advances achieved in electrode materials for SCs,$^6$–$^{11}$ the practical applications of supercapacitors were still seriously hindered due to the relatively poor performance of the electrode materials, such as low specific capacitance in carbon based materials, poor cycling stability in transition metal oxides, and very high cost of RuO$_2$ based materials. Therefore, more effort is still desired to further improve the electrochemical performance of electrode materials in order to build better SCs with both high power and energy densities. It has been proven to be an effective strategy to utilise nanostructure engineering, including nanoparticles, hollow nano-architectures and one-dimensional (1D) nanostructures to contribute greatly to the optimization of electrode properties with higher capacity/capacitance because of the increased active surface areas, short ion transport pathways and so on.$^7$–$^{12}$–$^{16}$

ZnCo$_2$O$_4$ has been considered as an attractive candidate for substitution of the conventional graphite anode in supercapacitors due to its superiorities such as improved reversibility, enhanced cycling stability, and good environmental benignity.$^{17-20}$ The ZnCo$_2$O$_4$ with a spinel structure, where the Zn$^{2+}$ occupies the tetrahedral sites and the Co$^{3+}$ occupies the octahedral sites, has been widely investigated as a high-performance material for supercapacitors.$^{17,21,22}$ In recent years, ZnCo$_2$O$_4$ as electrode materials for supercapacitors has begun to attract attention for its low cost and excellent electrochemical performance.$^{23-26}$ For example, Hope-Weeks’s group synthesized the ZnCo$_2$O$_4$ nanocrystal and tested its supercapacitor properties. However, the tedious preparation process and the low specific capacitance (700 F g$^{-1}$ at 5 mV s$^{-1}$) made it difficult to meet the demands of practical application.$^{15}$

Liu and co-workers recently fabricated a one dimensional ZnCo$_2$O$_4$ nanorods/nickel foam integrated electrode; although it exhibited good electrochemical performance at low current densities, its specific capacitance (1400 F g$^{-1}$ at 1 A g$^{-1}$) and cycling stability (only 1000 cycles at 6 A g$^{-1}$ were given) were still unsatisfactory.$^{21}$ Gang’s group has prepared highly porous ZnCo$_2$O$_4$ nanotubes, which shows a remarkable cycling ability of 689 F g$^{-1}$ at 10 A g$^{-1}$ after 3000 cycles together with an excellent rate capability of 588 F g$^{-1}$ at 60 A g$^{-1}$ (84% capacity retention).$^{22}$ From the above, we can conclude that ZnCo$_2$O$_4$ could be considered as attractive materials.

Herein, by flexible coaxial fiber assembly of hierarchical ZnCo$_2$O$_4$ nanorod arrays/Ni wire electrodes, we designed a

$^a$The Key Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, and Shanghai Municipal Education Committee Key Laboratory of Molecular Imaging Probes and Sensors, Shanghai Normal University, Shanghai 200234, China.

$^b$State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China.

E-mail: zlou@semi.ac.cn, gzshen@semi.ac.cn
new class of flexible all-solid-state planar-integrated fiber supercapacitors (FSC), allowing us to obtain good electrochemical capacitance performance, with a high specific capacitance of 10.9 F g\(^{-1}\) at a scan rate of 10 mV s\(^{-1}\), an energy density of 76 mWh kg\(^{-1}\) and a power density of up to 1.9 W kg\(^{-1}\). To our knowledge, this is the first time that ZnCo\(_2\)O\(_4\) nanorod arrays have been grown on a Ni wire substrate and directly used as electrode materials for supercapacitors.

## 2. Experimental

### 2.1. Synthesis of materials

Hydrochloric acid (HCl), ethanol and acetone were procured from Merck (India) Ltd. Potassium hydroxide (KOH; FW = 56.11), urea [CO(NH\(_2\)]\(_2\); MW = 60.06), cobalt nitrate hexahydrate (Co(NO\(_3\)]\(_2\)-6H\(_2\)O; FW = 291.04), ammonium fluoride (NH\(_4\)F; FW = 37.04) and zinc nitrate hexahydrate- (Zn(NO\(_3\)]\(_2\)-6H\(_2\)O; FW = 297.47) were procured from Alfa Aesar A Johnson Matthey company. Polyvinylalcohol (PVA; MW = 70 000−100 000) was procured from Himedia Laboratories Pvt. Ltd. Moreover, double distilled water was used for all the experiments.

**Synthesis of the ZnCo\(_2\)O\(_4\) nanorods on a Ni wire.** Prior to deposition, commercial Ni wires were cleaned by sonication sequentially in acetone, 1 M HCl solution, deionized water and ethanol for 15 min. After being dried, the Ni wire was transferred into a Teflon-lined stainless autoclave. In a typical synthesis of ZnCo\(_2\)O\(_4\) nanorods, 1 mmol Zn(NO\(_3\)]\(_2\)-6H\(_2\)O, 2 mmol Co(NO\(_3\)]\(_2\)-6H\(_2\)O, 6 mmol CO(NH\(_2\)]\(_2\) and 5 mmol of NH\(_4\)F were dissolved in 30 mL deionized water by constant stirring, and the mixture was stirred to form a pink solution in the 50 mL Teflon-lined stainless autoclave. Then, the pre-treated Ni wires were put in the above autoclave, heated to 120 °C, and kept at that temperature for 6 h. After the autoclave had cooled down to room temperature, the product was collected, washed, vacuum-dried, and then thermally treated at 350 °C for 3 h at a rate of 5 °C min\(^{-1}\) to obtain ZnCo\(_2\)O\(_4\) nanorods.

The PVA/KOH polymer electrolyte was prepared as follows: in a typical process, 3 g PVA was dissolved in 25 mL DI water with stirring at 98 °C for 1 h. Then, 3 g KOH was dissolved in 5 mL DI water. Finally, the above two solutions were mixed together at 60 °C under vigorous stirring until the solution became clear.

### 2.2. Characterization

The synthesized products were characterized with an X-ray diffractometer (XRD; X’Pert PRO, PANalytical B.V., the Netherlands) with radiation from a Cu target (\(\text{K}_{\alpha}, \lambda = 0.15406 \text{ nm}\)). The morphologies of the samples were characterized using electron microscopy (SEM; NANOSEM 650-6700F, 15 kV) and transmission electron microscopy (HRTEM; JEOLJEM-2010HT).

### 2.3. Electrochemical characterization

CV were examined at the scan rates of 0.01−1000 V s\(^{-1}\) and EIS were recorded in the frequency range of 0.01−100 kHz with a 5 mV ac amplitude at a CHI760D electrochemical workstation.

### 2.4. Calculation

The specific capacitances can be calculated from the CV curve by using the equation:

\[
C = \frac{Q}{V} = \frac{I}{S} \quad (1)
\]

\[
C_v = \frac{C}{m} \quad (2)
\]

where \(C\) is the capacitance, \(Q\) is the charge accumulated in the capacitors, \(V\) is the potential in the CV curve, \(I\) is the current in the CV curve, and \(S\) is the scan rate.\(^{29}\) The energy density and power density of the device were obtained from the equations:\(^{30}\)

\[
E = C \times \Delta V^2 / 7200 \quad (3)
\]

\[
P = E \times 3600 / \Delta t \quad (4)
\]

where \(E\) is the energy density (in Wh g\(^{-1}\)), \(P\) is the power density (in W g\(^{-1}\)) and \(\Delta t\) is the total discharge time (in seconds).

## 3. Results and discussion

The fabrication of the fiber solid-state SC is shown in Fig. 1. First, one commercial Ni wire sample, serving as an anode, was wound around a steel rod and then pulled out, resulting in the formation of a spiral-type electrode (Fig. 1 step 1, 2). ZnCo\(_2\)O\(_4\) nanorods grown on the Ni wire were synthesized by the hydrothermal method (Fig. 1 step 3), and the spiral-type electrode was then coated with a layer of PVA/KOH gel electrolyte (Fig. 1 step 4). The gel electrolyte acted as a separator not only uniformly coated on the anode and cathode wires surface but also on supporting materials to make the fiber device...
50 nm. The microstructures of the ZnCo$_2$O$_4$ nanorods were grown on the Ni wires substrate with a diameter of about 50 nm, which agrees well with the SEM images. One-dimensional nanorods could greatly contribute the higher capacity/capacitance because of the increased active surface areas and short ion transport pathway. Fig. 2e demonstrates the HRTEM image of a single porous ZnCo$_2$O$_4$ nanorod.

The ZnCo$_2$O$_4$ nanorods were grown on Ni wires via a conventional hydrothermal method. Fig. 2a–c shows the scanning electron microscopy (SEM) images of the products with 5 mmol NH$_4$F. It can be seen that the ZnCo$_2$O$_4$ nanorods were uniformly grown on a Ni wire, as shown in Fig. 2a. Fig. 2b and c depict the SEM image of the pure ZnCo$_2$O$_4$ nanorods grown on the Ni wires substrate with a diameter of about 50 nm. The microstructures of the ZnCo$_2$O$_4$ nanorods were also investigated by using transmission electron microscopy (TEM). Fig. 2d shows a low-magnification TEM image of single ZnCo$_2$O$_4$ nanorods. From the image we can see that the ZnCo$_2$O$_4$ nanorods have a porous structure with a diameter of about 50 nm, which agrees well with the SEM images. One-dimensional nanorods could greatly contribute the higher capacity/capacitance because of the increased active surface areas and short ion transport pathway. Fig. 2e demonstrates the HRTEM image of a single porous ZnCo$_2$O$_4$ nanorod.

The clearly resolved lattice fringes show that the d-spacing of 0.24 and 0.28 nm marked in the pattern could be indexed to the (311) and (220) crystal planes of the ZnCo$_2$O$_4$ phase, which further confirmed the formation of crystalline ZnCo$_2$O$_4$ nanorods and agreed well with the result of X-ray diffraction (XRD) data. The phase and composition of the nanorods were investigated by peeling off the nickel wires. As shown in Fig. 2f, the XRD pattern of the precursor is well consistent with previous reports. It is obvious that all of the observed peaks' position are in good agreement with the ZnCo$_2$O$_4$ structure of the standard card of JCPDS card no. 23-1390.

The electrochemical properties of the ZnCo$_2$O$_4$ nanorods on a Ni wire electrode were first measured in a three-electrode cell using a 3 M KOH electrolyte; a platinum electrode and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. Fig. 3a shows the representative cyclic voltammetry (CV) curves recorded at different scan rates ranging from 10 to 100 mV s$^{-1}$, and one pair of redox peaks can be clearly seen. All of the curves show obvious pseudocapacitance features with a pair of well-defined redox peaks within 0–0.45 V (vs. SEC). The pair of peaks is mainly associated with the Faradaic redox reaction related to M–OH/M–O–OH, where M refers to Ni or Co. Accompanying the increase in the scan rate, the peak currents were also increased, suggesting that the one-dimensional porous nanorods were beneficial to fast redox reactions, furthermore no redox peaks can be observed in the pure nickel wire at 10 mV s$^{-1}$. To further evaluate the potential application of the ZnCo$_2$O$_4$ as electrodes for electrochemical supercapacitors, galvanostatic charge–discharge measurements were carried out between 0 and 0.45 V (vs. SEC) at various currents ranging from 0.8 to 3.0 mA, as shown in Fig. 3b. The voltage plateaus during the charge/discharge process were consistent with the CV results and the nonlinear characteristics further verified the pseudocapacitance behavior. The electrochemical reaction of ZnCo$_2$O$_4$ with the electrolyte can be written as follows:

$$\text{ZnCo}_2\text{O}_4 + \text{OH}^- \rightarrow \text{ZnCo}_2\text{O}_4/\text{OH} + \text{ZnCo}_2\text{O}_4\text{–OH}$$

Here, ZnCo$_2$O$_4$/OH represents the electric double layer formed by the hydroxyl ion, and ZnCo$_2$O$_4$–OH represents the product formed by the cathode reaction involving the hydroxyl ion.

Fig. 4a shows a galvanostatic charging–discharging test which was conducted in a stable potential window between...
0 and 1 V at various current densities ranging from 0.5 to 2 mA. We can observe that the charge/discharge behavior has a good symmetry, indicating that the charge/discharge straight line was provided with excellent coulomb efficiency.\(^{36}\) Fig. 4b illustrates the charge/discharge behavior of the FSC devices at a current of 0.5 mA. A relatively small voltage drop (0.15 V) is shown in Fig. 4b, indicating excellent SC performance of the as-designed FSC. From Fig. 4c, we can judge that the FSC devices are operated by scan rates ranging from 10 to 200 mV s\(^{-1}\). From the plot, it can be observed that the curves of the two electrode systems are obviously different from those of the above three-electrode systems (Fig. 3a), which mainly represent the absence of redox peaks. Briefly, supercapacitors can be classified into two categories: the non-Faradaic electrical double-layer capacitor and the Faradaic redox pseudocapacitor. These two mechanisms can work separately or together, depending on the active electrode materials used in the capacitors. For our two-electrode system, it clearly reveals that the feature of electrical double-layer capacitor occupied a more dominant position than that of the typical pseudocapacitor. Besides, no obvious redox peaks are observed in the present work, indicating that the current supercapacitors are charged and discharged at a pseudoconstant rate.\(^ {37,38}\) Thus, we can draw the conclusion that two-electrode devices are primarily nonfaradaic within their corresponding voltage window.\(^ {37}\)

Actually, this common phenomenon is observed in many symmetric supercapacitors reported previously.\(^ {26}\) We calculated the capacity of the flexible device at different scan rates, ranging from 10 to 100 mV s\(^{-1}\) and the corresponding result is depicted in Fig. 4d. From the curve, the largest capacitance could be obtained to be about 10.90 F g\(^{-1}\) at a scan rate of 10 mV s\(^{-1}\), and the specific capacitance was calculated to range from 4.85 F g\(^{-1}\) at 100 mV s\(^{-1}\) to 10.90 F g\(^{-1}\) at 10 mV s\(^{-1}\), which was higher than that of ZnCo\(_2\)O\(_4@\)carbon fibers (0.4 mF at 100 mV s\(^{-1}\) to 0.85 mF at 30 mV s\(^{-1}\))\(^ {26}\) and revealed that one-dimensional ZnCo\(_2\)O\(_4\) nanorods could greatly contribute to the optimization of electrode properties with higher capacity/capacitance. The cycling performance of the FSC at a progressively increased current was carried out as shown in Fig. 4e. After 800 times of continuous cycling at varied current, the current returned to 1 mA and was revealed to be 97.9% of the initial capacitance at 1 mA. It could then be recovered and maintained for another 200 cycles, which was much higher than previously reported values.\(^ {21,30}\) Fig. 4f shows cyclic stability, we can find that the capacitance was maintained at 92% of its original value at 2 mA after 3500 charge/discharge cycles, revealing its excellent cycling stability, which can be attributed to the mechanical stability of the active materials and good contact between the electrode and current collector origin of the direct growth of ZnCo\(_2\)O\(_4\) nanostructures on the Ni wire substrate. Above that, it makes it possible to consider it as an attractive candidate in supercapacitors due to its superior qualities such as improved reversible capacities, and enhanced cycling stability.

Electrochemical impedance spectroscopy (EIS) and rate capability are two important parameters to determine the performances of SCs. Fig. 5a shows the energy density and power density (Ragone chart). The energy density varied from 42 to 76 mWh kg\(^{-1}\) with a power density ranging from 0.50 to 1.9 W kg\(^{-1}\). Our fabricated FSC also revealed an open circuit voltage of 0.4 V which can be maintained for 10.8 h after being
fully charged and can also have a low leakage current of 0.4 mA (Fig. 5b and c), indicating excellent energy storage performance. Fig. 5d and the inset show the Nyquist plots in frequencies ranging from 100 kHz to 0.01 Hz with an ac perturbation of 5 mV. In the high frequency region, the intercept of the semicircle with the real axis represents the equivalent series resistance (ESR) including the resistance of the electrolyte solution, the intrinsic resistance of the active material, and the contact resistance of the interface active material/current collector. The x-intercept of the Nyquist plots represents the ESR of two-electrode SC, and the charge transport resistance is 2.23 Ω,39 revealing that our electrodes have a very small resistance with good ion response. The reason may be that one-dimensional nanorods could shorten the ion transport pathway and decrease resistance.

The mechanical stability of the FSC under bending states is a key parameter for practical use. Compared with the planar device, the fiber device can be strong enough to bear the generated tensile force, and the performance of fiber supercapacitors is almost the same under different angles, which is very useful in practical applications.40 Thus the flexibility of our coaxial FSC was further enhanced. A schematic diagram in Fig. 6a shows the FSCs in different bending states. Fig. 6b shows the charge/discharge curves at a current of 1.5 mA under the different angles, which demonstrate that our device can maintain good fiber shape and have excellent flexibility. Fig. 6c demonstrates the CV curves of the FSC deformed from the straight state to the 90° status. Meanwhile the low performance degradation indicates the high stability of the as-fabricated coaxial FSC. Fig. 6d presents the photos of our coaxial FSC under the different bending states (30°, 45°, 60°, 90°), which demonstrated that our device has excellent flexibility. These results make it possible to design patterns for wearable devices applications.

4. Conclusions

We have successfully developed a spiral-type flexible fiber supercapacitor based on ZnCo2O4 nanorod electrodes as active materials on a Ni wire. The specific capacitances reached 10.9 F g−1 at a scan rate of 30 mV s−1, an energy density of 76 mWh kg−1 and a power density of up to 1.9 W kg−1. Outstanding cycling ability and excellent flexibility have also been achieved. The enhanced performance is attributed to the one-dimensional ZnCo2O4 nanorod structure, which increases active surface areas, shortens ion transport pathways and so on. In view of their excellent electrochemical performance and facile and cost-effective synthesis, these ZnCo2O4 nanostructures might hold great promise as advanced electrode materials for high-performance supercapacitors. Furthermore, by decreasing the diameter of the metal fiber, flexible fiber supercapacitors with smaller diameter and size are expected to be fabricated, which will make it possible to weave the fiber supercapacitor into design patterns for wearable electronic applications.

Acknowledgements

This work was supported by the National Natural Science Foundation (61377033).

Notes and references
