Construction of fusiform \( \text{Co}_3\text{O}_4 \) for supercapacitors

Changwei Lai\# and Weiwei Kang\#*

1 Anyang Institute of Technology, Anyang, P.R. China.
2 School of Chemistry and Chemical Engineering, Southeast University, PR China
\# The authors contributed equally to this work

Abstract

A novel fusiform \( \text{Co}_3\text{O}_4 \) has been successfully synthesized by a solvothermal method. The fusiform structure can be synergistically determined by various characterization methods (such as XRD, XPS, SEM and TEM). Owing to the special morphology of fusiform \( \text{Co}_3\text{O}_4 \), it achieves specific capacitances of 544.3 F g\(^{-1}\) at the current densities of 0.5 A g\(^{-1}\) in a three-electrode system, exhibiting excellent cycling stability with a specific capacitance retention of 81.9% after 2000 cycles at a current density of 20 A g\(^{-1}\).

Introduction

Supercapacitors (SCs) have drawn great extensive attention in the past few decades because they have an ultrafast charge and discharge rate, good reliability, high power density and long cycling performance [1-3]. SCs can be generally classified into three types based on their energy storage mechanism: electrical double-layer capacitors (EDLCs) [4], pseudocapacitors [5] and hybrid supercapacitors [6,7]. Pseudocapacitors are governed by fast and reversible Faradaic redox reactions at the effective near-surfaces of the electrode materials. Transition metal oxides (TMOs) are recognized as ideal pseudocapacitive materials due to the enhanced capacitance and higher energy density than those of EDLCs [8,9]. Among the TMOs, \( \text{RuO}_2 \) has been considered as the most promising Faradaic pseudocapacitive materials [10,11]. However, \( \text{RuO}_2 \) is restricted in practical application because of its low porosity, toxic nature, and high cost. In view of the facts, \( \text{Co}_3\text{O}_4 \) attracts extensive interest for pseudocapacitor electrode materials due to its extremely high theoretical capacitance of 3560 F g\(^{-1}\), high redox activity, good electrochemical performance, high natural abundance, low cost, and environmental friendliness [12,13]. Up to now, many available methodologies have been developed to achieve various special \( \text{Co}_3\text{O}_4 \) nanostructures for supercapacitors [14-16].

Herein, we have prepared the fusiform \( \text{Co}_3\text{O}_4 \) for pseudocapacitors electrode materials, and further study the electrochemical properties of the fusiform \( \text{Co}_3\text{O}_4 \) in a three electrode configuration.

Experimental

Preparation of the fusiform \( \text{Co}_3\text{O}_4 \)

4.8 mmol of Co(NO\(_3\))\(_2\)·6H\(_2\)O and 0.8 mL of deionized water were dissolved in 30 mL of methanol under magnetic stirring, then 1.5 g of sodium dodecylbenzenesulfonate (SDBS) was added into the reaction solution, and the mixture was sonicated for 1 h to form a blue colloidal suspension. The resulting mixture was transferred into 40 mL Teflon-lined stainless steel autoclave liners and maintained at 200°C for 4 h. After cooling to room temperature naturally, the precipitates were filtered and washed with deionized water, then dried under vacuum oven at 60°C for 12 h. Finally, the samples were sintered in a muffle furnace in air to obtain the \( \text{Co}_3\text{O}_4 \) at 350°C for 2 h.

Characterization

The structures of products was analyzed by X-ray diffraction (XRD) on a D8-Discover diffractometer (Bruker, Germany) with Cu Ka radiation (\( \lambda = 0.154 \) nm). Detailed elemental analysis was carried out with an ESCALAB-250 X-ray photoelectron spectroscopy (XPS) (ThermoFisher Scientific, USA). Thermogravimetric analysis (TGA) was carried out on a SDT-Q600 instrument. The morphology of materials was identified by scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, Philips Tecnai-12).

Electrochemical measurements

In the three-electrode system, the CV tests of individual electrodes were carried out in the potential range of -0.2 to 0.6 V vs. saturated calomel reference electrode (SCE) by varying the scan rate from 2 to 100 mV s\(^{-1}\). GCD was performed at different current densities varying from 0.5 to 40 A g\(^{-1}\). The specific capacitance (\( C, \text{F g}^{-1} \)) of the electrode was calculated by using the following equations: 

\[
C = \frac{I \Delta t}{m \Delta V},
\]

where \( C \) is the specific capacitance (F g\(^{-1}\)), \( I \) is the discharge current (A), \( \Delta t \) is the total discharge time (s), \( m \) is the mass (g) of the active material in the electrode and \( \Delta V \) is the potential range in the discharge process (V), respectively.

Results and discussion

Characterization of the structure

The crystalline structure of \( \text{Co}_3\text{O}_4 \) was confirmed by X-ray diffraction (XRD). Figure 1a shows the XRD patterns of \( \text{Co}_3\text{O}_4 \), exhibiting diffraction peaks attribute to the (111), (220), (311), (222),...
(400), (422), (511) and (440) planes of the cubic Co$_3$O$_4$ phase (JCPDS 42-1467), respectively. These features suggest that the as-prepared materials are crystallized well. To further determine the Co$_3$O$_4$ structure, the Co 2p XPS spectrum indicates that two main peaks at 781.1 and 796.1 eV, corresponding to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ with a spin-orbit splitting of 15.0 eV as shown in the figure 1b [17]. And it can further verify the formation of Co$_3$O$_4$ by the two prominent shake-up satellite peaks (denoted as "Sat.") for Co$^{2+}$, which is consistent with the observation from XRD. In the low and high-magnification SEM images (Figure 1c), the fusiform Co$_3$O$_4$ shows average short diameter of 10-12 µm and the both ends in a range of 20-25 µm. Moreover, the transmission electron morphology (TEM) image can further confirm the fusiform morphology (Figure 1d).

Figure 1. (a) XRD pattern, (b) Co 2p XPS spectrum, (c) Low and high-magnification (inset) SEM images, (d) TEM image of the fusiform Co$_3$O$_4$

Figure 2. The electrochemical properties of Co$_3$O$_4$: (a) CV curves at different scan rates, (b) Galvanostatic charge-discharge curves at different current densities, (c) The specific capacitance at various current densities, (d) Cycling performance at a current density of 20 A g$^{-1}$ (the inset shows the Nyquist plots)
Construction of fusiform Co$_3$O$_4$ for supercapacitors


Electrochemical properties

The electrochemical properties of the fusiform Co$_3$O$_4$ were systematically studied by cyclic voltammmograms (CV) and galvanostatic charge-discharge (CD) in three electrode configuration. In figure 2a, the CV of Co$_3$O$_4$ shows the obvious pseudocapacitance features in 6 M KOH solution. The redox peaks in CV curves can be ascribed to the conversions between different cobalt oxidation states, according to the follow sequential reactions [18,19]:

\[
\begin{align*}
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow 3\text{CoOOH} + e^- \quad (1) \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (2)
\end{align*}
\]

Figure 2b shows the CD curves of the fusiform Co$_3$O$_4$ at different current densities from 0.5 to 40 A g$^{-1}$. A higher specific capacitance value of 544.3 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$ was achieved (Figure 2c). Moreover, the long-term stability of Co$_3$O$_4$ was carried out using the charge-discharge cycling test at a high current density of 20 A g$^{-1}$. After 2000 cycles, it retains 81.9 % of its initial capacitance (Figure 2d). From the EIS spectra of the fusiform Co$_3$O$_4$ (inset), the electrochemical resistance (Rs) and charge transfer resistance (Rct) are respectively determined as around 0.53 Ω and 0.62 Ω, demonstrating the electrical conductivity and ion transfer of the as-prepared materials (Figure 3).

Conclusion

In summary, we demonstrate a novel fusiform Co$_3$O$_4$, exhibiting an excellent pseudocapacitive performance. It is believed that this study may open up a new research strategy for Co$_3$O$_4$, as it has potential promises for pseudocapacitors electrode materials.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 21304018, 51404098, 51174077).

References


Copyright: ©2018 Lai C. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.