**Abstract:** It is vital to improve the electrochemical performance of negative materials for energy storage devices. The synergistic effect between the composites can improve the total performance. In this work, we prepare α-Fe₂O₃@MnO₂ on carbon cloth through hydrothermal strategies and subsequent electrochemical deposition. The α-Fe₂O₃@MnO₂ hybrid structure benefits electron transfer efficiency and avoids the rapid decay of capacitance caused by volume expansion. The specific capacitance of the as-obtained product is 615 mF cm⁻² at 2 mA cm⁻². Moreover, a flexible supercapacitor presents an energy density of 0.102 mWh cm⁻³ at 4.2 W cm⁻². Bending tests of the device at different angles show excellent mechanical flexibility.

**Keywords:** α-Fe₂O₃@MnO₂; electrode materials; electrochemical performance; flexibility

1. Introduction

Supercapacitors (SCs) have attracted much attention from researchers as an innovative type of energy storage device [1–4]. Compared with traditional capacitors, SCs show the advantages of superior cycle stability, outstanding power density and fast charging/discharging [5–7]. Recently, electronic devices have progressively high requirements for long-term endurance. However, SCs is severely limited with low energy density [8–10]. According to the present research results, one of the most valid ways to settle this issue is to increase the specific capacity of electrode [11]. Therefore, designing electrodes with high specific capacitance is the primary task to broaden the application range of SCs. Currently, the research on positive and negative materials is unevenly developed and research on negative electrodes is relatively little, which makes it difficult to increase the energy density of SCs. Commonly used negative materials are carbon (AC, CNTs and rGO), transition metal oxides (such as Fe₃O₄, α-Fe₂O₃, MoO₃ and Mn₃O₄) and a small amount of metal nitride [12–17]. Among them, α-Fe₂O₃ is considered to have the highest potential and is the most widely used anode material, because of its high redox activity, large theoretical specific capacitance and environmental protection [18]. Nonetheless, the weak conductivity of α-Fe₂O₃ electrodes leads low practical specific capacitance and poor electrochemical stability [19,20]. Manganese dioxide (MnO₂) has gained extensive attention in the construction of supercapacitors due to its high oxidation activity [21]. At present, preparing nanocomposite materials utilizing the synergistic effect of two materials not only promotes redox reactions, but also enhance device energy density [22]. Co₃O₄@MnO₂, SnO₂@MnO₂, ZnO@MnO₂, CuO@MnO₂ and α-Fe₂O₃@MnO₂ nanostructures were compounded to achieve both excellent cyclic stability and high capacitance [23–26].

Seol et al. prepared two types of SCs (EDLC and PC) using activated carbon and graphene/Mn₃O₄ nanocomposite. The performance degradation of EDLC was negligible...
When utilized as negative material for SCs, with high oxidative activity, the synthesis of ordered nanostructures will help to construct Ag/AgCl as the reference electrode and Pt foil as the counter one, with deposition at X-ray photoelectron spectrometer (XPS, Amsterdam, Holland). The morphology and microstructure of the sample is characterized by scanning electron microscope (SEM, Gemini). The crystal structure and the elemental compositions of the products were investigated by an X-ray diffractometer (XRD, Shimadzu-7000, Kyoto, Japan, CuKa, 40 kV) and X-ray photoelectron spectrometer (XPS, Amsterdam, Holland.). The morphology and microstructure of the sample is characterized by scanning electron microscope (SEM, Gemini 300-71-31, Berlin, Germany).

The results under different angles bending tests demonstrated that the device possesses excellent mechanical flexibility.

Herein, we synthesized α-Fe₂O₃ nanorods structures through a hydrothermal route. Then, a MnO₂ film is coated on α-Fe₂O₃ surface by subsequent electrochemical deposition. When utilized as negative material for SCs, α-Fe₂O₃@MnO₂ electrode shows a specific capacitance of 615 mF cm⁻² at 2 mA cm⁻². After 10,000 cycles, it maintains 92.3% of the initial capacitance. Finally, a flexible supercapacitor possesses the maximum energy density is 0.102 mWh cm⁻³ at 4.2 W cm⁻². The results under different angles bending tests demonstrated that the device possesses excellent mechanical flexibility.

2. Experimental Section

Material Preparation

The α-Fe₂O₃ sample was synthesized via a hydrothermal method. In total, 0.808 g Fe(NO₃)₃·9H₂O, 0.2841 g Na₂SO₄ and 0.5 g PVP were dissolved into 45 mL deionized water. Then, a clean carbon cloth (2.5 × 2.5 cm²) and the above mixed solution was transferred into an 80 mL autoclave and kept 110 °C for 9 h. Finally, the as-prepared electrode was measured through an electrochemical workstation (Shanghai Chenhua). Electrochemical performance methods include cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The as-synthesized materials were used as the working electrode, Pt foil as the counter electrode and Ag/AgCl as the reference electrode.

3. Results and Discussion

Figure 1 presents the growth process of α-Fe₂O₃@MnO₂ products on carbon cloth. Firstly, α-Fe₂O₃ nanorods are obtained via a facile hydrothermal approach. Afterwards, a
layer of MnO₂ film is deposited by subsequent electrochemical deposition on the nanorod-shaped α-Fe₂O₃ surface.

Figure 1. Synthesis schematic of the products.

First, the crystal structure of the obtained product is studied by XRD. Figure 2a shows the XRD patterns of α-Fe₂O₃ and α-Fe₂O₃@MnO₂ composites. A typical peak of the carbon cloth can be clearly observed. The peaks at 2θ values of 33.4°, 35.8°, 49.7°, 54.4°, 64.3° and 72.4° can be indexed to (104), (110), (024), (116), (300) and (1010) planes of α-Fe₂O₃ phases, respectively (PDF No. 84-0308). Those at 28.7°, 37.6°, 41.1°, 47.2° and 72.6° match well with (310), (121), (420), (510) and (631) planes of MnO₂ (PDF No. 72-1982). The shape and sharpness of the diffraction peaks in figure reveal that the products possess high crystallinity.

Figure 2. Structural characterization using (a) XRD patterns and (b–d) XPS spectra.
Then, XPS is used to investigate the $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ materials surface element composition. In Fe 2p spectra, the characteristic peaks of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ at 711.2 eV and 724.8 eV, respectively (Figure 2b). Additionally, two shake-up satellite peaks (Sat.) at 716 eV and 732.9 eV are determined. This indicates that Fe$^{3+}$ exists in composite product [29]. Figure 2c depicts the two main peaks of O 1s spectra located at 529.9 eV and 532 eV [30]. Binding energies at 529.9 eV, labeled as O$_1$, denote metal oxygen [31]. Another O$_2$ peak located at 532 eV is due to some degree of hydrolysis on the product surface [32]. For Mn 2p spectra (Figure 2d), four peaks at 642.2 eV, 645.8 eV, 653.9 eV and 658.1 eV are from Mn 2p$_{3/2}$, Sat., Mn 2p$_{1/2}$ and Sat., respectively [33].

Figure 3a indicates that $\alpha$-$\text{Fe}_2\text{O}_3$ shows a short rod-like structure. In addition, it can be found that many nanorods homogeneously grown on carbon cloth with uniform size and shape, and the cross-section of nanorods is rough. The high magnification image (Figure 3b) shows the as-synthesized products average length is 100 nm. Figure 3c presents a thin MnO$_2$ film covers $\alpha$-$\text{Fe}_2\text{O}_3$, and still maintains the shape of nanorods. From Figure 3d, the cross-section of $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ nanorods becomes smooth.

Next, we analyzed several as-obtained electrode electrochemical performances by CV, GCD and EIS. Figure 4a shows CV curves of $\alpha$-$\text{Fe}_2\text{O}_3$, MnO$_2$ and $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ materials. Evidently, $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ delivers a large CV area in $-1$–$0$ V, reflecting its good energy storage effect in this range. At 8 mA cm$^{-2}$ (Figure 4b), the GCD curves obvious that $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ product with long discharge times, which can be correlative to the synergistic effect between $\alpha$-$\text{Fe}_2\text{O}_3$ and MnO$_2$ materials. Figure 4c presents CV curves of $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ from 5 to 40 mV s$^{-1}$. The shape of CV curves almost the same as the scan rate increased, indicating excellent reversibility of electrode. In Figure 4d, the GCD curves of $\alpha$-$\text{Fe}_2\text{O}_3$@MnO$_2$ materials are measured from 2 to 10 mA cm$^{-2}$. Areal capacitance ($C_a$) is obtained by GCD, and the equation is shown below:

$$C_a = \frac{1}{V} \int V dt / V$$ (1)
The capacitance of the positive NiCo$_2$S$_4$ is also studied by the same methods. Figure 4g presents the CV curves of NiCo$_2$S$_4$ sample. Fe$_2$O$_3$ and MnO$_2$ products present only 71.4% and 75% of the initial capacitance. This phenomenon is due to the MnO$_2$ film covering the Fe$_2$O$_3$ nanorods, which can help alleviate the volume expansion during long cycle measurements. Similarly, the positive NiCo$_2$S$_4$ is only reduced by 7.7% after 10,000 cycles, while α-Fe$_2$O$_3$@MnO$_2$ is only reduced by 7.7% after 10,000 cycles, while α-Fe$_2$O$_3$ and MnO$_2$ electrodes Rs value is 5.1 Ω, 4.1 Ω and 3.3 Ω, respectively. According to above analysis, α-Fe$_2$O$_3$@MnO$_2$ shows the largest slope and smallest Rs, so the conductivity of composite material is better than α-Fe$_2$O$_3$ and MnO$_2$.

At the end, the cyclic stability is investigated at 4 mA cm$^{-2}$. Figure 4f indicates that the capacitance of α-Fe$_2$O$_3$@MnO$_2$ is only reduced by 7.7% after 10,000 cycles, while α-Fe$_2$O$_3$ and MnO$_2$ products present only 71.4% and 75% of the initial capacitance. This phenomenon is due to the MnO$_2$ film covering the α-Fe$_2$O$_3$ nanorods, which can help alleviate the volume expansion during long cycle measurements. Similarly, the positive NiCo$_2$S$_4$ is also studied by the same methods. Figure 4g presents the CV curves of NiCo$_2$S$_4$.

In Equation (1), I is current density, $\int Vdt$ stands for the integral area of discharge curve and V is the constant discharge voltage range (V). The α-Fe$_2$O$_3$@MnO$_2$ electrode delivers 615 mF cm$^{-2}$ specific capacitance at 2 mA cm$^{-2}$. EIS is a significant factor in assessing the electrochemical kinetics of products. The sample is tested over a frequency range of 0.01 Hz to 100 kHz (Figure 4e). In the low frequency region, the slope of the straight line shows the ion diffusion resistance. Among the three samples, α-Fe$_2$O$_3$@MnO$_2$ sample presents the largest slope, which expresses fast diffusion of ions in electrolyte [34]. The intersection with the real axis represents the equivalent resistance (Rs) [35]. Figure 4f indicates that the cyclic stability is investigated at 4 mA cm$^{-2}$. Figure 4f shows that the positive NiCo$_2$S$_4$ is also studied by the same methods. Figure 4g presents the CV curves of NiCo$_2$S$_4$.
sample. Redox peaks and shapes, confirming its pseudocapacitive material. Five symmetrical GCD curves shows an obvious platform (Figure 4h), which indicates their Faradaic redox behavior [36]. At 2 mA cm$^{-2}$, the specific capacitance is 720.8 mF cm$^{-2}$. Nyquist plots of NiCo$_2$S$_4$ products are shown in Figure 4i; the value of $R_s$ is 0.9 Ω.

To further explore the α-Fe$_2$O$_3$@MnO$_2$ electrodes for practical applications, a flexible supercapacitor is assembled. From Figure 5a, the voltage windows of α-Fe$_2$O$_3$@MnO$_2$ and NiCo$_2$S$_4$ are $-1$–$0$ V and $0$–$0.6$ V, respectively. Figure 5b shows CV curves from 1.1 V to 1.5 V with a sweep rate of 100 mV s$^{-1}$, demonstrating the device can maintain operate stably within 1.5 V. It can be seen that with the decrease of voltage, the area becomes small. Figure 5c depicts all CV curves at different scan rates keep similar shapes, revealing outstanding rate performance of device. GCD curves from 1 to 8 mA cm$^{-2}$ possess the same charging and discharging time (Figure 5d). The specific capacitance of the device at 1 mA cm$^{-2}$ is 37.8 mF cm$^{-2}$ and it still delivers 15.6 mF cm$^{-2}$ at 8 mA cm$^{-2}$. The equivalent resistance value of the device is 1.9 Ω, as shown in Figure 5e.

![Graphs](image)

Figure 5. (a) CV curves of the α-Fe$_2$O$_3$@MnO$_2$ and NiCo$_2$S$_4$ electrode at 40 mV s$^{-1}$. (b) CV curves in different potential windows at 50 mV s$^{-1}$. (c) CV curves. (d) GCD curves. (e) EIS. (f) CV curves at different bending angles. (g) Cycling performance at 2 mA cm$^{-2}$. (h) Ragone plot.

At present, electronic devices are developing towards wearable, which puts forward higher requirements for the mechanical flexibility of supercapacitors [37]. We twisted the device and then examined it by cyclic voltammetry (Figure 5f). While device is folded at 15°, 45°, 90° and 135°, the shape sustains virtually unchanged, demonstrating its superior
mechanical stability. Figure 5g illustrates that the device maintains 88.9% capacitance retention after 6000 cycles. Figure 5h is the Ragone diagram of $\alpha$-Fe$_2$O$_3$@MnO$_2$/NiCo$_2$S$_4$. The capacitor values of energy density ($E$) and power density ($P$) can be derived based on the Equations (2) and (3):

$$E = \frac{1}{2} \times C_a \times V^2$$  

(2)

$$P = \frac{3600 \times E}{\Delta t}$$  

(3)

where $C_a$ stands for the areal capacitance of the capacitor, $V$ represent the discharge voltage and $\Delta t$ is the discharge time. At 1 mA cm$^{-2}$, the energy density of device is 0.102 mWh cm$^{-3}$ at 4.2 W cm$^{-2}$. This is better than some previously reported materials [38–41] (Table 1).

Table 1. Electrochemical performance of various devices.

| Supercapacitor                          | Capacitance | Energy Density (mWh cm$^{-3}$) | Power Density (W cm$^{-2}$) | Capacitance Retention | Ref.         |
|-----------------------------------------|-------------|--------------------------------|-----------------------------|-----------------------|-------------|
| PEDOT-PSS/δ-MnO$_2$                     | 2.4 F cm$^{-3}$ | 0.018                          | 0.018                       | 88%                   | [38]        |
| Fe$_2$O$_3$NTs@PPy//MnO$_2$             | 0.0594      | 1                              | 87.5%                       | [39]                  |
| ZnO@MnO$_2$                             | 26 mF cm$^{-2}$ | 0.04                           | 2.44                        | 87.1%                 | [40]        |
| Fe$_2$O$_3$/Ni/Yarns                    | 0.67 F cm$^{-3}$ | 0.086                          | 3.87                        | 87.1%                 | [41]        |
| $\alpha$-Fe$_2$O$_3$@MnO$_2$//NiCo$_2$S$_4$ | 37.8 mF cm$^{-2}$ | 0.102                          | 4.2                         | 88.9%                 | this work   |

$\alpha$-Fe$_2$O$_3$@MnO$_2$ delivers excellent performance, which can be explained by the following reasons: (a) Nanostructure uniformly covered on the carbon cloth, which provides outstanding electrical conductivity and flexibility; (b) With $\alpha$-Fe$_2$O$_3$ as a strong mechanical support and MnO$_2$ as an outer layer, this structure not only protects the morphological structure, but also provides many active sites; (c) The composite utilizes the synergistic effect of $\alpha$-Fe$_2$O$_3$ and MnO$_2$, so that electrode processes high capacitance and low resistance.

4. Conclusions

In this manuscript, $\alpha$-Fe$_2$O$_3$@MnO$_2$ nanorods are synthesized through a hydrothermal route and subsequent electrochemical deposition. By combining two oxides of $\alpha$-Fe$_2$O$_3$ and MnO$_2$, it is favorable to accelerate the electron transport and the oxidation reaction. The synergistic effect between two materials improves electrochemical performance for negative electrode. MnO$_2$ film, after electrodeposition, affects the performance of the electrode material, and the full use of the active area of the film increases, which increases the capacitance of the electrode material. XPS results show that the material processes abundant redox valence states. $\alpha$-Fe$_2$O$_3$@MnO$_2$ sample presents high specific capacitance and excellent cycling stability. Furthermore, the as-assembled capacitors still show outstanding electrochemical performance and mechanical stability. Therefore, it provides an alternative method for constructing supercapacitor negative materials with higher specific capacitance.

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