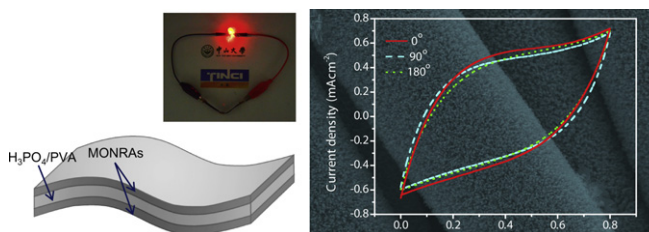Short communication

Manganese dioxide nanorod arrays on carbon fabric for flexible solid-state supercapacitors

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HIGHLIGHTS

- Controllable growth of MnO_2 nanorods on 3D conductive carbon cloth.
- The MnO_2 nanorods achieved a high specific capacitance of $678\,F\,g^{-1}$ at $0.3\,A\,g^{-1}$.
- A flexible and solid-state supercapacitor based on MnO_2 has been demonstrated.
- The fabricated device exhibited good electrochemical performance.

GRAPHICAL ABSTRACT

ABSTRACT

We reported the synthesis of large-area manganese oxide nanorods (MONRAs) on carbon fabric and their implementation as flexible supercapacitors. Electrochemical measurements demonstrated that MONRAs exhibited a high capacitance ($678\,F\,g^{-1}$ at a current density of $0.3\,A\,g^{-1}$) with high flexibility and excellent cycle performance (less than 3% capacitance loss after 10,000 cycles). Furthermore, the fabricated solid-state devices based on these MONRAs electrodes exhibited good electrochemical performance and could power a red LED well for about 5 min after charging at $0.5\,mA\,cm^{-2}$ for 30 s, with an energy utilization efficiency of about 80%. These findings show that MONRAs are a kind of very promising electrode material for flexible supercapacitors.

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1. Introduction

Increasing power and energy demands for next-generation portable and flexible electronics such as roll-up displays, photovoltaic cells, and wearable devices have inspired intensive efforts to explore flexible, lightweight and environmentally friendly energy storage devices [1–4]. Supercapacitors, also known as electrochemical capacitors, have received considerable attention as novel flexible energy storage devices, due to their unique power and energy densities [5–9]. On the basis of the different charge storage mechanisms, supercapacitors are classified into electrical double-layer capacitors (EDLCs) [10–12] and pseudocapacitors [13–17]. Compared to EDLCs, pseudocapacitors based on metal oxides or conducting polymers are more attractive because they can provide much higher capacitance and energy density through Faradic reaction [13–17]. Among various pseudocapacitive

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materials, manganese dioxide (MnO_2) has been considered to be the most attractive candidate in terms of its superior capacitor performance, low cost, environmentally friendly nature, and natural abundance. However, due to its poor electric conductivity (10^{-5}–10^{-6} S cm^{-1}), the theoretical capacitance (1370 F g^{-1}) has not been achieved [18–23]. One dimensional (1D) nanoarrays hold great attention as electrode materials because they can provide high interfacial area, short ion diffusion path and fast electrical pathways. The direct growth of nanoarrays on conductive substrates can facilitate the diffusion of active species and transport of electrons, and hence may further broaden their applications in energy storage device [24–26]. In this regard, considerable efforts have been paid to the preparation of 1D MnO_2 nanoarrays, and significant advance has been achieved [18,20,21,27,28]. However, facile synthesis of large-area 1D MnO_2 on conductive substrates is still a challenge. On the other hand, the investigation of flexible integrated supercapacitors based on pristine MnO_2 is very limited.

We have recently demonstrated that the synthesis of large-area manganese oxide nanorod arrays on F-doped SnO_2 coated glass (FTO) and Ti substrates through a simple electrodeposition method [18]. In this paper, we reported the growth of large-area manganese oxide nanorods (MONRAs) and nanowires (MONWs) on carbon fabric by expanding this method and their implementation as flexible supercapacitors. Carbon fabric was here chosen as the substrate mainly due to its cost-effectiveness, high conductivity, and excellent chemical stability. On the other hand, the flexible nature of carbon fabric is also preferable for designing a flexible device. Electrochemical measurements showed that MONRAs electrode exhibits an excellent specific capacitance as high as 678 F g^{-1} at a current density of 0.3 A g^{-1}. In addition, MONRAs electrode showed excellent long-term cycle stability. Furthermore, a demo of solid-state supercapacitor with high flexibility and good electrochemical capacitor performance was assembled. The tandem devices could power a red LED well for about 5 min after charging at 0.5 mA cm^{-2} for 30 s, with an energy utilization efficiency of about 80%.

2. Experimental

2.1. Synthesis of MONRAs and MONWs

All reagents used were of analytical grade and were used directly without any purification. Standard MnO_2 and Mn_3O_4 were purchased from Alfa Aesar. Both MONRAs and MONWs were fabricated by a template-free electrodeposition method in a simple three-electrode glass cell. Carbon fabric was used as working electrode. A Pt wire and a saturated calomel electrode (SCE) that connected to the cell with a double salt bridge were used as counter electrode and reference electrode, respectively. Anodic electrodeposition of MONRAs was performed at a constant current of 0.4 mA cm^{-2} in a solution containing 0.01 M manganese acetate ($MnAc_2$) and 0.02 M ammonium acetate (NH_4Ac). Anodic electrodeposition of MONWs was carried out at a constant current of 0.4 mA cm^{-2} in a solution containing 0.05 M $MnAc_2$ and 0.02 M NH_4Ac. The temperature of both reactions was kept at 70 °C.

2.2. Fabrication of solid-state device

The solid-state device was fabricated with two pieces of MONRA electrodes. A separator (NKK TF45, 40 μm) was placed between the two electrodes, and polyvinyl alcohol (PVA)–H_3PO_4 gel was used as a solid electrolyte. PVA–H_3PO_4 electrolyte was simply made as follows: 2 g H_3PO_4 was mixed with 20 mL deionized water and then 2 g PVA powder was added. The whole mixture was heated up steadily to 85 °C under vigorously stirring until the solution became clear. Then the solution was kept at 85 °C without stirring. Two pieces of carbon fabric with MONRAs were immersed in PVA–H_3PO_4 gel for 3 min with the bare carbon fabric part above the gel. Then they were took out and assembled together with a separator (NKK TF45, 40 μm) placed between them, leaving aside the bare carbon fabric part as the electrode. After the PVA–H_3PO_4 gel was solidified at room temperature, the solid-state device was prepared.

2.3. Characterization

The morphology, microstructure, and compositions of the products were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), X-ray diffractometry (XRD, D8 ADVANCE), transmission electron microscopy (TEM, JEM2010-HR), laser Micro-Raman Spectrometry (Renishaw inVia), photoelectron Spectroscopy (XPS, ESCALab250). Inductively coupled plasma atomic emission spectroscopy (ICP, SPECTRO) was used to analyze the loading of manganese oxide on carbon fabric. The mass loading of MONRAs and MONWs is about 0.31 mg cm^{-2} and 0.42 mg cm^{-2}. The electrochemical properties of the products were investigated with cyclic voltammetry (CV), charge−discharge measurements and electrochemical impedance spectroscopy by employing a CHI 660D electrochemical workstation (Chenhua, Shanghai).

3. Results and discussion

Fig. 1(a) shows the optical image of the samples prepared by electrodeposition. A uniform gray film was formed on the surface of carbon fabric when the electrodeposition was carried out with a current density of 0.4 mA cm^{-2} in a solution containing 0.05 M $MnAc_2$ and 0.02 M NH_4Ac (rectangle in Fig. 1(a)). The structure of the as-prepared MONWs and MONRAs was characterized by the SEM technique, as shown in Fig. 1(b)–(f). Fig. 1(b) and (c) clearly demonstrates that the well-established structure of MONWs was grown on carbon fibers. These nanowires have a diameter of 60–90 nm and length of up to several micrometers. Additionally, these nanowires interlace together to form a three-dimensional network. By contrast, a dark film consisting of a large number of uniform nanorods was obtained when the concentration of $MnAc_2$ decreased to 0.01 M (dot rectangle in Fig. 1(a) and (d)). From Fig. 1(e)–(f), we can see that free-standing and dense nanorods of 50–100 nm in diameter and 2.5 μm in length were grown uniformly on each carbon fiber. The result above indicates that the morphology of product can be readily controlled by simply varying the concentration of $MnAc_2$ in electrodeposition process.

X-ray diffraction (XRD) patterns were collected from the nanowires and nanorods to study the crystal structure (Fig. S1a). To avoid that the peaks would be covered by the strong peak of carbon fabric, the prepared product were peeled off from the carbon fabric before the test. Some peaks are observed for MONRAs and MONWs. The peaks located at 18.1°, 36.7°, 37.5° and 60.3° in MONRAs can be indexed to tetragonal MnO_2 (JCPDS # 44-0141), while all the peaks in MONWs can be well assigned to the tetragonal Mn_3O_4 (JCPDS # 24-0734). In order to further analyze the chemical compositions, Raman spectra of MONRAs and MONWs were conducted and the standard MnO_2 and Mn_3O_4 samples were also examined in the same conditions. From Fig. 2(a), only one sharp peak at 644 cm^{-1} is observed for MONRAs, which is attributed to (Mn−O) symmetric stretching vibrations of MnO_6 octahedron in MnO_2·compounds [29,30]. Besides one sharp peak at 660 cm^{-1}, there are still three weak peaks at 316, 375 and 552 cm^{-1} in MONWs. All these peaks are in consistent with the stretching vibrations of Mn_3O_4 [29,30]. Thus, the Raman results indicate that MnO_2 is dominant in MONRAs while Mn_3O_4 is dominant in MONWs, which is in agreement