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Advanced electrochemical energy storage supercapacitors based on the flexible carbon fiber fabric-coated with uniform coral-like MnO_2 structured electrodes

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HIGHLIGHTS

- Novel coral-structured MnO_2 on carbon fiber fabric (CFF) was first time fabricated.
- Solid-state highly flexible CFF/MnO_2 based supercapacitor device is fabricated.
- The device exhibits an outstanding specific capacitance of 467 F/g.
- The device displays outstanding capacitance retention of 99.7% after 5000 cycles.
- Coulombic efficiency close to 100% is achieved for device with high energy density.

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ABSTRACT

The novel and efficient electrode materials have been developed for supercapacitor applications based on carbon fiber fabric/MnO_2 hybrid materials, in which MnO_2 was uniformly coated on the surface of carbon fiber fabric (CFF). A green hybrothermal method was used to functionalize CFF with coral-like MnO_2 nanostructures to improve the pseudocapacitance properties of the hybrid composites. These CFF/MnO_2 composites are used as excellent flexible electrodes for high-performance electrochemical supercapacitors applications. The morphological, structural and crystalline properties of composites were analysed by using various techniques such as FE-SEM, XRD, XPS, and Raman spectroscopy, respectively. The electrochemical performance was examined by cyclic voltammetry (CV), galvanostatic charge-discharge tests and electrochemical impedance spectroscopy (EIS). In a three-electrode system, the CV tests reveal the superior specific capacitance of 467 F/g at a current density of 1 A/g with capacitance retention of 99.7% and the columbic efficiency remains as high as 99.3% after 5000 cycles, demonstrating an outstanding electrochemical cyclic stability. In addition, high-performance device fabricated with CFF/MnO_2 demonstrated excellent energy density of 20 W h/kg at a power density of 0.175 kW h/kg. These novel electrode materials could be potential candidate for applications in practical and large-scale energy storage systems.

1. Introduction

Recently, the development of novel energy conversion and storage systems have been received a great research interest in nanoscience and nanotechnology as alternative energy sources to achieve a clean and sustainable world due to the limitation of fuels and environmental issues [1–4]. In this regard, electrochemical energy technologies such as rechargeable batteries, fuel cells, solar cells and supercapacitors have been recognised as the most important part of various energy storage technologies [5–10]. Among many technologies in energy storage systems, the electrochemical supercapacitors are safe and efficient devices that possess high energy density, powder density, excellent specific capacitance, long charge-discharge cycle life with highest reversibility, cell design flexibility, environmental and chemical stability, which enables them to find potential applications in the portable electronics, electric vehicles, large scale energy storage grids, etc. [11–14].

In general, electrochemical supercapacitors can be divided into electric double layer capacitors (EDLC) and pseudocapacitors according to the materials and electrochemical charge-discharge

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mechanism. Energy storage capacity of the double layer capacitors is limited and in order to increase the electrochemical properties (e.g. specific capacitance, power density) of electric double layer capacitors, large specific surface-area electrode needs to be used, such as nanostructured carbon materials (graphene, nanotubes, etc.) [15–17]. On other hand, the psedocapacitors shows faradic electrochemical reactions at the surface of electroactive nanomaterials have mainly used nanostructured metal oxides with the combination of carbon materials, which leads to increase of energy storage and specific capacitance of hybrid materials through the redox reactions between an inorganic and the organic components in the composite system [18–20].

Nanostructured carbon-based electrode materials are commonly used for the electrochemical applications due to low cost, thermal, chemical and environmental stability, and good electrical property with facile electron transport pathways for protons and electrons, and good reversible redox reactions [21,22]. However, their reversible redox processes, energy density, specific capacitance and cycle life stability are poor. To overcome these major challenges and drawbacks, the electrochemical properties of these materials can be improved by the combining them with nanostructured metal oxides. Among different metal oxides, manganese oxide (MnO_2) has been recognized as one of promising inorganic materials due to its easy synthesis process, low cost and excellent electrochemical properties [23]. Thus, this cutting edge research is most important topic and it is necessary to develop alternative low cost and novel electrode materials as next generation of supercapacitors that can charge and discharge in less time while delivering enhanced power density. The cost-effective and poor electrochemical properties (specific capacitance, high energy density and cycle life) of hybrid devices can be overcome by designing an electrode with flexible carbon fiber fabric (CFF) and MnO_2 that contribute an electrochemical behavior during charge and discharge.

Among various carbon-based materials, CFF was chosen in this study because it is one of the most widely used current collectors for energy storage devices due to its one-dimensional structure, high corrosion resistance, high electrical conductivity, low cost and easy fabrication process. The coral-like structured MnO_2 were directly vertically grown on surface of an horizontal 1D structured CFF collectors, enabling one-step fabrication process of supercapacitor electrodes without using any binders or conductive additives. For supercapacitor application, in particular, such unique structures endows the active electrode hybrid materials with a high proportion of surface atoms and active sites on the exposed surfaces and sufficient contact with the electrolyte, short ion and electron diffusion path, benefiting fast charge transfer and electrochemical reactions which proceed at room temperature without requiring any special equipment. These advantages render it an industrially feasible and promising strategy for large-scale production of high-performance energy storage materials. Also, to the best of our knowledge, the reports in the literature on coral-like MnO_2/CFF hybrid solid-state flexible devices as the efficient electrodes with versatile electrochemical properties for the high-performance electrochemical supercapacitor applications are scarce.

In this work, after consideration of the problems described above, highly flexible and warp-proof CFF well covered with uniform coral-like MnO_2 structures have been successfully fabricated for the first time through the green hydrothermal process at different reaction conditions and investigated CFF/MnO_2 flexible electrodes for their morphological, structural and electrochemical properties by using FE-SEM, XRD, XPS, Raman, cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy, respectively. Flexible CFF present in the composite system act as an ideal template as it can enable to gradually grow MnO_2 coral-structures on the outer surface of the carbon fabric, as well as current collector of the device. The fabricated CFF/MnO_2 hybrid flexible solid-state electrodes without binder and any additives possessed outstanding electrochemical supercapacitive properties. This device shows an outstanding specific capacitance of 467 F/g in an environmentally friendly 1 M Na_2SO_4 aqueous electrolyte and superb cycle performance to maintain almost 100% of the initial capacitance after 5000 cycles, indicating excellent electrochemical cycle stability, which can be ascribed to the unique structure of the electrode for fast ion diffusion. They also show an excellent energy density of 20 W h/kg, low charge transfer resistance and faster charge/discharge rates. The formation mechanism of the coral-like MnO_2 nanostructures on the surface of carbon fiber fabric is also presented. In addition, the green process and novel electrode materials reported in this study can be simpler and more economical. These unique structured novel electrodes are alternative and promising materials for development of next-generation electrochemical energy storage systems, such as advanced supercapacitors and batteries.

2. Experimental

2.1. Fabrication of CFF/MnO_2 composite electrodes

A commercially available carbon fiber fabric (CFF) (GDL-CT, FuelCellsEtc, USA) was used as supporting material for coating with MnO_2 nanostructures through a hydrothermal method. Prior to the synthesis, polymer sizing on the surface of carbon fabric was removed by heating the fabric at 450 °C for 15 min in argon atmosphere. After the removal of sizing, carbon fabric was cut to a size of 3.0×3.0 cm and placed standing inside the liner of a Teflon-lined autoclave. In a typical synthesis procedure, 56.9 mg of potassium permanganate ($KMnO_4$) (Sigma-Aldrich) was dissolved in 60 mL of deionized water under constant magnetic stirring for 30 min, forming a 6 mM $KMnO_4$ solution. Then, the fully dissolved solution was transferred into an 80 mL capacity Teflon-lined stainless steel autoclave liner and the liner was sealed in a stainless steel autoclave. Finally, the reaction was kept at 175 °C for 4 h. After the autoclave was cooled down to room temperature, the sample was removed, washed with distilled water and ethanol several times, and dried at 60 °C for 10 h under vacuum. To investigate the effect of the reaction time on the growth process of MnO_2 structures on the surface of carbon fiber fabric, similar procedures were also conducted under the hydrothermal process at 175 °C for 1 and 7 h.

2.2. Characterization

The morphology of CFF and CFF/MnO_2 hybrids were investigated by the field emission scanning electron microscopy (FE-SEM, JEOL6701) without coating of gold or platinum before FE-SEM analysis. X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation (GBC MMA diffractometer). The surface composition of the samples was examined by X-ray photo electron microscopy (XPS, Thermo-Scientific 2000) using monochromated Mg Kα radiation. Raman spectroscopy of the samples was recorded using a Invia Raman spectrophotometer (Renishaw plc, UK).

2.3. Electrochemical property measurements using three-electrode and two-electrode systems

Electrochemical property measurements of cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were conducted with a potentiostat on an electrochemical workstation (CH1, 660 E, Shangai Chenhua) at room temperature within a voltage window of 0–1.0 V at various