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Ultrasound assisted formation of Mn_2SnO_4 nanocube as electrodes for high performance symmetrical hybrid supercapacitors

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ABSTRACT

In this work, we have synthesized Mn_2SnO_4 material with nanocube morphology from $MnSn(OH)_6$ intermediate via a simple one-pot sonochemical synthesis. The structural and morphological studies of the material were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The Mn_2SnO_4 nanocubes were used as the active electrode material for supercapacitor applications. It delivered a maximum specific capacitance of 298 F g^{-1} at a current density of 1 mA cm^{-2}. The Mn_2SnO_4 nanocubes showed excellent cycle stability with capacitance retention of 89% over 5000 cycles and desirable rate capability retain 223 F g^{-1} at a current density of 15 mA cm^{-2} in a three electrode system. Further, these materials were applied to the symmetric supercapacitor device, and it exhibited high specific capacitance (144 F g^{-1} at 3 mA cm^{-2}), good cycle stability (75% capacitance retention after 1000 cycles), high energy density (30.4 Wh kg^{-1}) and power density (7.9 kW kg^{-1} at 26.4 Wh kg^{-1}) in a potential range of 2 V in 1 M Na_2SO_4 aqueous electrolyte. These results suggest that Mn_2SnO_4 nanocubes show suitable electrode material for high-performance supercapacitor applications.

1. Introduction

In recent years, electrochemical energy storage devices have attracted great attention due to the increasing demands for sustainable and renewable power sources in the current electronic industry. Many attempts have been assigned to growing flexible, thin light-weight and environmental friendly energy storage devices like batteries and supercapacitors [1,2]. Supercapacitors are promising candidates for the next-generation energy storage devices because of its higher energy density compared to conventional capacitors as well as higher power density compared to secondary batteries [3]. Indeed, a lot of research has been done in the development of high performance supercapacitor due to their high power density, fast charge–discharge cycles and long cycle life [4,5]. Therefore, it has been used for various applications such as hybrid electric vehicles, transportable electronic devices and smart electricity grid devices [6]. Based on the charge storage mechanism, supercapacitors can be classified into two categories: (i) electrochemical double layer capacitors (EDLC's), (ii) pseudocapacitor. In EDLC's, carbon based materials (for instance, activated carbon fibers, carbon nanotubes, graphene etc.) were used as electrode materials [7–9], in which the energy was stored in charge accumulation at the electrode–electrolyte interface [10]. In pseudocapacitor, conducting polymers (polyaniline, polypyrrole, polythiophene etc.) [11–13] and transition metal oxides/hydroxides (RuO_2, MnO_2, Co_3O_4, NiO etc.) were used as electrode materials [14–21], in which the energy was stored at the electrode–electrolyte interface in faradaic or reversible redox reactions [22]. Among these, transition metal oxides have significant attention due to their great structural flexibilities and different oxidation states of the metal oxides, which offer it greatly to promote their intrinsic electronic and catalytic properties [23,24]. Ruthenium oxide (RuO_2) is one of the most effective electrode materials for supercapacitors; it delivers a specific capacitance of 704 F g^{-1} [14]. The major drawback of this material was toxic in nature and high cost to minimize the commercial applications [25]. Therefore, the researchers have focused to develop the new electrode materials with non-toxic, low cost as well as to improve electrochemical performance of the supercapacitor device.

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Recently, binary metal oxides with spinel structure have received great interest due to their low cost, environmentally friendliness and high performance in many energy storage applications such as Li-ion batteries and supercapacitors [26]. They can increase the electrochemical performances synergistically in terms of reversible capacity, fast electrode kinetics, high structural stability, electrical conductivity and favorable electroactive surface/interface between the electrode and electrolyte [6,27]. It is also expected that binary metal oxides may provide more redox reactions originated from both metal oxide cations, as compared to the corresponding individual metal oxide. To date, various metal oxide stannate nanoparticles have shown excellent electrical, optical and magnetic properties and widely used in Li-ion batteries, antibacterial study, photocatalyst, solar cells and supercapacitors [28–32]. So far many research groups have been developed different metal oxide stannates such as Co_2SnO_4, Zn_2SnO_4, Ca_2SnO_4, Mn_2SnO_4 and Mg_2SnO_4 [32–36]. Among them, Mn_2SnO_4 shows a cubic spinel structure with space group Fd3m and these materials (Mn and Sn) are individually excellent electrochemical active materials with high capacitance for supercapacitors because of nontoxic, less expensive and natural abundance. In literature, Liang et al. reported that the uniform Mn_2SnO_4/Sn/carbon composite cubic particles with a porous structure as anode material through facile hydrothermal method and subsequent annealing process [35]. Conventionally, a solid-state reaction of SnO and Mn_2O_3 has been carried out at various temperatures ranging from 700 °C to 800 °C [37]. Single-crystalline Mn_2SnO_4 nanowires with ferromagnetic behavior have been prepared by chemical vapor deposition (CVD) at 900–1000 °C under oxygen flow [38]. Sonochemical synthesis is also a facile one-step approach used in the preparation of numerous materials such as metal alloys, zeolites, metal carbides/nitrides, metal oxides/sulfides, which can be operated in ambient conditions [39]. It causes an unusual chemical environment through an acoustic cavitation process (formation, growth and implosive collapse of bubbles). This can generate a concentrated hotspot with extremely high temperature (5000 K) and pressure (1000 atm), which is responsible for the hydrolysis and condensation of the precursor solution [40,41]. The several advantages of sonochemical methods are to provide high phase purity, control the size and morphology, reduce the agglomeration of as-prepared nanomaterials, and to form the uniform shape and narrow size distribution than any other conventional methods which can be used to fabricate different nanostructured materials [42].

The electrolyte is the important key factor of the electrochemical capacitors, as the operating potential window, specific capacitance, power density are greatly determined by the choice of electrolytes. The suitable properties of an electrolytic system for supercapacitors are high ionic conductivity, wide potential window, and high electrochemical and thermal stability, low viscosity, low toxicity and low cost, etc. [43]. For instance, when the supercapacitors are worked in the organic electrolytes or ionic liquids, the operational potential window range can be extended up to 4.0 V [44,45]. But the main disadvantages of these electrolytes are poor conductivity, high viscosity, eco-unfriendly, high cost and poor power rates [46]. Aqueous electrolytes have several advantages, compared to the organic electrolytes. That is, they are cheaper, environmentally friendly and more conductive [46]. The most commonly used aqueous electrolytes were acidic (H_2SO_4) and basic (KOH). Unfortunately, the maximum voltage for H_2SO_4 or KOH electrolytes is often limited to only 0.8–1.0 V because of over potentials for hydrogen/oxygen evolution and water decomposition at ~1.23 V [47]. The limited potential window of aqueous electrolytes can be improved by different ways; (i) adjustment of the electrode masses, which allows the operating potential of the electrodes to be maintained within optimal potential window range and the evolution of either H_2 or O_2 to be avoided [48], (ii) tailoring the carbon properties for the positive and negative electrode, which enables even 2.0 V to be reached [46], (iii) another way that allows theoretical limits to be overcome by electrolytes with neutral pH were recognized as promising solutions for water-based supercapacitors operating with extended voltage [49].

In this work, we report one-pot sonochemical synthesis of Mn_2SnO_4 nanocubes as electrodes for symmetric supercapacitor device application operating with extended voltage window at 2.0 V using a neutral aqueous electrolyte. The structural, morphological and electrochemical properties of Mn_2SnO_4 nanocubes were investigated. Electrochemical performances of Mn_2SnO_4 nanocubes were studied by cyclic voltammetry (CV), galvanostatic charge-discharge technique and electrochemical impedance spectroscopy. The material showed excellent capacitive performance including high specific capacitance, rate capability, and desirable cycling stability, which can be a promising potential candidate for electrochemical energy storage applications.

2. Materials and methods

2.1. Materials

Manganese chloride hexahydrate ($MnCl_2$ $6H_2O$), tin (IV) chloride pentahydrate ($SnCl_2$. $5H_2O$), poly(vinylidene fluoride) (PVDF) were purchased from Sigma–Aldrich. Carbon black (Daejung Chemicals Ltd, South Korea), *N*-methyl-pyrrolidone (NMP), ethanol and sodium hydroxide were purchased from Daejung Chemicals Ltd, South Korea. All the chemicals used in this experiment were analytical grade and used without further purification. All the aqueous solutions used in these experiments were prepared with deionized (DI) water (18.2 MΩ cm, Elga DI water system).

2.2. Ultrasound assisted synthesis of Mn_2SnO_4

To synthesize Mn_2SnO_4 nanocubes through the ultrasound method in alkaline medium, at first, 30 mL of 0.06 M $MnCl_2 \cdot 6H_2O$ solution and 30 mL of 0.03 M $SnCl_4 \cdot 5H_2O$ solution were prepared separately using double distilled water. Then the two solutions were mixed together under magnetic stirring. Then, 20 mL of 2 M NaOH solution was added slowly in drops under stirring, the precipitates with light brown color were formed. After that, it was kept in a sonicator (with a frequency of 50–60 Hz and a power of 490 W) for 30 min. The obtained precipitates with dark brown color were centrifuged and washed using deionized water several times thoroughly, followed by ethanol and then dried at 60 °C for 12 h. The dried sample was calcinated at 550 °C under N_2 atmosphere for 2 h with a heating rate of 3 °C min^{-1} to obtain crystalline phase Mn_2SnO_4 nanocubes.

2.3. Characterization

The phase purity and crystal structure of the material was characterized by using the powder X-ray diffraction technique (XRD, Rigaku, Cu Ka radiation operating at 40 keV/40 mA). The morphologies of the material was studied by field emission scanning electron microscope (FE-SEM) using a JEOL JSM-5900 FESEM coupled with energy-dispersive X-ray spectroscopy (EDX). The surface elemental composition and chemical state of the sample was analyzed through XPS measurement using an ESCALAB 250 system (Thermo VG Scientific) with monochromatic excitation. The electrochemical measurements were carried out by Versastat 4 electrochemical workstation at room temperature.