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In-situ growth of MnO_2 nanorods forest on carbon textile as efficient electrode material for supercapacitors

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ABSTRACT

Nowadays, the design and fabrication of high-performance and low-cost electrode materials for energy storage and conversion systems are highly desired. The nanostructured materials are interesting for energy-related applications due to the large surface area, enormous active sites which ensure the complete utilization of active material. In this paper, we report a three-dimensional (3D) MnO_2 nanorod forest network on carbon textile (MnO_2–NRF@CT) with the hierarchical porous structure as a binder-free electrode material for supercapacitor. MnO_2–NRF is directly grown on carbon textile surface by a simple one-step hydrothermal method. The carbon textile greatly improved the graphitization degree in MnO_2–NRF composite. Typically, MnO_2–NRF@CT sample indicates a partially graphitic structure having a low-intensity ratio of Raman D to G band (I_D/I_G = 0.68), which significantly increases the electrical conductivity and enhanced the performance of the supercapacitor. Consequently, the MnO_2–NRF@CT porous architecture as supercapacitor electrode exhibits outstanding electrochemical performance (961 F g^{-1} at 1 mA cm^{-2} in 1 mol/L Na_2SO_4 electrolyte). The MnO_2–NRF@CT shows good capacitance retention by achieving 92% of its initial capacitance after 5000 cycles. The long life and good stability highlighted its great potential for future supercapacitor applications.

1. Introduction

Energy is always an important issue for human beings. The ever-increasing population and economic development, raised the depletion of fossil fuels, resulting in massive emissions of greenhouse gases, climate changes, which create environmental problems [1,2]. These facts inspired the researcher for the development of new technological aspects of clean and sustainable energy sources. Solar, wind and water splitting are the novel types of power sources having low exhaust emissions, and promising candidates for stationary and transportation uses [3,4]. But unfortunately, these energy systems are often constrained by time and environmental conditions (e.g., the wind and solar) or geography (e.g., water). Therefore, energy storage systems, like supercapacitors (SCs) also known as electrochemical capacitors and batteries are needed to ensure continuous and balance power supply [5]. SCs have received intensive research attention from last decade owing to high power density and rapid charging/discharging process and can fulfil the gap between fuel cells and rechargeable batteries [6,7]. SCs typically shows superior power density, safe operation and lifecycle. These favorable characteristics are beneficial for practical applications of supercapacitors in the future. However, their energy density needs to improve to compete the batteries. Currently, SCs energy densities are lower than that of conventional batteries [8,9], therefore the enhancement of its energy density is a challenging task. Recently flexible energy storage devices attract great research attention due to the incorporation of foldable electronic equipment's, e.g., mobile phones, displays, computers, etc. [10,11]. Flexible solid-state SCs are particularly promising for achieving a compact, lightweight and reliable energy storage applications [12,13]. The electrode material is the fundamental component of SCs and mostly dictates its ultimate performance [14]. Numerous kinds of substrates have been employed as a current collector to rouse the electrochemical properties of supercapacitors such as graphene [15], nickel foam [16], carbon papers and carbon textiles. Among them, CT is regarded as the best choice due to

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its flexibility, soft and excellent mechanical strength for direct growth of a positive material on it [17]. Usually, the active materials are coated or deposited on CT substrates and then used as an electrode for supercapacitor, which comprises of polymer-binders and conductive agent mixed with positive materials [18,19]. In such situation, a part of electroactive sites of the positive material cannot contact with electrolyte due to use of conductive agents and binders. Therefore, the polymer-binder will decrease the inner diffusion of electrolyte ions into the electrode material and limits the supercapacitors performance. It is important to fabricate rational designs of electrodes for supercapacitor. Recently, directly grown nanostructured materials on conducting substrates without any binder, known as binder-free electrodes become an attractive technique among researchers [20]. Directly grown nanomaterials have some unique benefits, such as better electronic conductivity and more electroactive sites. Therefore, CT is chosen for the direct growth of active material for the fabrication of flexible electrodes of SCs [21].

Carbon, conducting polymers, transition metal oxides (TMOs) and transition metal dichalcogenides (TMCs) for Faradic redox supercapacitors show substantially higher specific capacitance as compared to carbon-based supercapacitors [22]. TMOs and conducting polymers are classically employed as electroactive positive materials for pseudocapacitors [15,23]. One successful model is the application of RuO_2 in the armed field due to its high specific capacitance of > 600 F/g. However, toxicity issues and the higher cost of RuO_2 limit its common application [24]. Therefore, incredible efforts have been made to develop inexpensive and environment-friendly alternatives, such as MnO_2, Fe_3O_4, Co_3O_4, NiO [25–28].

MnO_2 is considered as an alternative electrode material for pseudocapacitors and widely studied owing to its high specific capacitance in aqueous electrolytes, and offer many technological features such as natural abundance, low cost, environmental friendliness and wide potential window [29,30]. As with other electroactive transition metal oxides, manganese oxide stores electrical charge by simultaneous injection of electrons and charge-compensating cations into the solid and are, therefore, potentially useful for charge storage applications such as cathodes in secondary lithium batteries, electrochromic devices, and recently electrochemical supercapacitors in aqueous electrolytes [31]. Charge storage properties of transition metal oxides are closely related to electrical conductivity in the solid phase and ionic transport within the pores. In this regard, layered manganese oxides possessing bicontinuous networks of solid and pore are attractive candidates for application as active electrode materials [32]. However, the low electrical conductivity of MnO_2 hinders its practical applications. MnO_2–based electrodes materials reported in the literature are mostly in powder form and thus need binders and conductive agents for the fabrication of electrodes, which limits their performance up to few thousand cycles [33], therefore we emphasized to enhance the conductivity by directly growing it on highly conductive carbon textile substrate [24].

In this study, we purposed in-situ 3D MnO_2 nanorod forest network on carbon textile (MnO_2–NRF@CT) with the hierarchical porous structure as a binder-free electrode material for supercapacitor. CT substrate shows good performance for relatively high mass loading of MnO_2 without any mechanical peeling or pressing process. The MnO_2 shows a strong binding with carbon textile substrates, which is useful for stable cycling performance. The as-prepared electrode exhibits an outstanding specific capacitance of 961 F g^{-1} at a current density of 1 mA cm^{-2} and 92% capacitance retention after 5000 charge/discharge cycles in 1 mol/L sodium sulphate (Na_2SO_4) neutral aqueous electrolyte, which could be possibly useful for upcoming large-scale stationary energy storage applications.

2. Experimental section

2.1. Chemicals and materials

Flexible carbon textile with a thickness of 0.20 mm was purchased from Shanghai LCMT (Lishuo Composite Material Technology) Company. Potassium permanganate ($KMnO_4$), sodium hydroxide (NaOH), and nitric acid (HNO_3) were purchased from Beijing Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals in this article were of analytical grade.

2.2. Hydrothermal synthesis of MnO_2–NRF @ CT

Carbon textile (CT) was employed as a substrate and α-MnO_2 nanorods forest was grown on CT by the simple hydrothermal method. CT was soaked into a 0.3 mol/L HNO_3 solution for 4 h (h) to eliminate solvable contaminations, washed with acetone and DI-water respectively. Dried CT substrate was placed along the wall side of a Teflon-lined autoclave. In a typical synthesis of MnO_2–NRF@CT, 0.0022 mol/L of $KMnO_4$, 0.0015 mol/L of NaOH were dissolved in 25 mL DI-water with continuous magnetic stirring for 15 min at room temperature. The reaction solution was finally moved into a 35 mL capacity Teflon-lined stainless steel autoclave. The sealed autoclave was hydrothermally reacted in an oven at 140 °C for 24 h. The as-prepared samples were washed 5–7 times with DI-water and then dried at 90 °C for 12 h.

The MnO_2 powder left in Teflon was washed, dried at 90 °C for 6 h and kept for comparative studies. A schematic representation of the growth mechanism of the MnO_2–NRF@CT is shown in Fig. 1(a). Digital photographs of pristine CT and annelid MnO_2–NRF@CT are demonstrated in Fig. 1(b), respectively. The dark purple colour of CT confirms the successful homogeneous growth of MnO_2.

2.3. Characterization

The structural properties of the samples were characterized by X-ray diffractometer (X'Pert MPD-XRD). The surface morphology of the as-prepared products was studied by field emission scanning electron microscopy (FESEM, ZEISS SUPRA™ 55), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED JEM 2010) and energy dispersive spectroscopy (EDS, OXFORD 55-XMX). X-ray photoelectron spectroscopy (XPS) was obtained using an AXIS ULTRA^{DLD} (Kratos) equipped with Al Kα source. Multipoint Brunauer–Emmette–Teller (BET) was carried out to calculate the product's specific surface area. Barrett–Joy-ner–Halenda (BJH) method was used to measure the pore size distribution. Fourier transform infrared spectroscopy (FTIR) was recorded on a Thermo Fisher Nicolet 6700 spectrometer. Raman spectra were recorded on a Raman spectrometer (Yvon HR 800, Horiba Jobin, 532 nm laser), to examine the structural properties of the as-synthesized MnO_2 nanorods forest on carbon textile.

2.4. Electrochemical measurements

The electrochemical test was accomplished via electrochemical analyzer, CHI 660D workstation in Na_2SO_4 (1 mol/L) electrolyte, by 3-electrode system. Whereas, MnO_2–NRF@CT (1 × 1 cm^2) as the working electrode, silver/silver chloride (Ag/AgCl) as the reference electrode and a platinum foil as the counter electrode. The mass loading of MnO_2–NRF on the surface of carbon textile is about 1.6 mg/cm^2, carefully calculated the weight difference before and after hydrothermal treatment. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency loop from 0.01 to 10^5 Hz, with a perturbation amplitude of 5 mV under the open circuit potential.