



Manganese dioxide/biocarbon composites with superior performance in supercapacitors



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ARTICLE INFO

Article history:

Received 13 December 2016

Received in revised form 9 March 2017

Accepted 12 March 2017

Available online 14 March 2017

Keywords:

Biomass-carbon
KOH-activated
MnO₂ nanosheets
MnO₂ composites
Supercapacitors

ABSTRACT

In this paper, MnO₂/allium-giganteum-like biocarbon (KWB) composites (KWBM) have been prepared by a simple method. First, the biocarbon was derived from sugarcane bagasse by one-step carbonization and activation method, and then, MnO₂ nanosheets anchored on the surface of biocarbon and the KWBM was obtained. The analysis results demonstrated that chemical composition and microstructure of KWBM were closely related to the mass ratio of KMnO₄/KWB, and which further impacted electrochemical performance of KWBM profoundly. Especially, the KWBM-4 (the mass ratio of KMnO₄/KWB is 2) exhibited a highest specific capacitance of 402 F g⁻¹ at a current density of 1 A g⁻¹ in three-electrode system. The asymmetric two-electrode system with outstanding energy density was assembled by employing the KWBM-4 as the positive electrode and the KWB as the negative electrode. The two-electrode system displays a high energy density of 25.9 Wh kg⁻¹ at a power density of 750 W kg⁻¹ within a potential range of 0–1.5 V. Furthermore, the system exhibited high cycle stability with only 5.8% loss of its initial capacitance after 2000 cycles.

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1. Introduction

Supercapacitors, is one of the most promising energy storage devices with fast charge-discharge rates, superior power density and long cycle lifetime compared to the other chemical energy storage devices [1,2]. According to the energy storage mechanism, supercapacitors are classified as electrical double-layer capacitors (EDLC) and pseudocapacitors. The EDLC is based on charge separation at the electrode/electrolyte interface, whereas the latter is based on redox reaction occurring within the active materials [3–5]. Currently, carbon materials are often used for EDLC due to their high electrical conductivity and fast energy storage-releasing, while the transition metal oxides often used for pseudocapacitors because of multiple oxidation states at the charge-discharge process [6,7].

Among the multifarious transform metal oxides, MnO₂ is one of the most promising electrode materials for low cost, high theoretical capacity and environmental friendly supercapacitors devices [8]. However, the performances of single-phased MnO₂ are still insufficient to meet growing demands in supercapacitors due to its intrinsic properties, such as low conductivity and poor mechanical stability [9,10]. To solve these problems, one-dimensional (1D) nanostructure MnO₂ (such as

nanosheets MnO₂) has been found to be good candidate for its low density and excellent permeation [11,12]. Nevertheless, 1D MnO₂ still does not achieve the desired electrochemical performance due to its electrochemical dissolution during cycling [13]. Therefore, development of new type MnO₂ materials to meet the desired electrochemical performance is urgently desirable.

To respond the above requirement, carbon materials have been selected as a component for preparing MnO₂-based composites to effectively improve electrochemical performance [14]. At present, many kinds of carbon materials, such as activated carbon (AC) [15], graphene [16] and carbon nanotube [17] are often used as the carbon content in MnO₂-based composites because their high surface area, excellent electronic conductivity, unique internal structure and superior thermal stability [18]. However, most of methods for prepare of the above carbon materials often require complicated preparation conditions or special facilities, leading to the high cost [19]. For example, as a rising star of graphene, it is often obtained by reduction of graphene oxide (rGO), and graphene oxide (GO) often obtained from natural graphite by Hummers method [20]. The method is a complex process, and contains four steps: preoxidation, further oxidation, decomposition of excessive oxidant and removed metal ions [21]. Therefore, one preponderant method of preparation of carbon materials is direct pyrolysis of carbon precursors, such as pyrolysis of biomass or biowaste [22]. This method has been noticed by many researchers, and many biocarbon derived from

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biomass such as corncobs [23], cocoons [24] and watermelon rind [25] have been prepared. All the biocarbon materials described above present high specific surface area and abundant pore structure. Therefore, the biocarbon materials are very suitable for preparation of MnO₂-based composites.

Hence, in this work, we report an efficient method for preparation of MnO₂/biocarbon composites (KWBM) as the electrode materials for supercapacitors. The biocarbon (KWB) was obtained by direct pyrolysis of sugarcane bagasse, and then the KWBM was obtained by redox reaction between KMnO₄ and KWB under different mass ratios of KMnO₄/KWB. We found that the chemical component and specific surface area of KWBM had a profound effect on electrochemical performance of KWBM. In addition, an asymmetric two-electrode system was fabricated by employing KWBM-4 and KWB as positive and negative electrode, respectively. We also found that the asymmetric system possessed the high energy density and high cycle stability.

2. Experimental

2.1. Materials

Sugarcane bagasse was crushed by family-use grinder before use. The other reagents, such as ethanol, potassium hydroxide (KOH), hydrochloric acid (HCl) and potassium permanganate (KMnO₄), all were purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and of analytical grade, were used without further purification.

2.2. Preparation of KOH-activated biocarbon (KWB) derived from sugarcane bagasse

KWB was obtained by KOH activation method and the typical process as follows: first, sugarcane bagasse was cut into small pieces (opening size approximately 2 mm) and washed with distilled water for 8 h at 90 °C, and then dried at 80 °C for 24 h. Second, 1 g cleanly sugarcane bagasse and 0.6 g KOH were poured into 12 mL absolute ethanol with stirring and heated at 60 °C until all of the ethanol was evaporated, and then dried at 70 °C for 12 h. Third, the remnant mixture was pyrolyzed in a tubular furnace in N₂ atmosphere at 800 °C (heating rate is 10 °C min⁻¹) for 2 h. Finally, the obtained carbon material was washed by 1 M HCl solution and deionized water till the filtrate became neutral and collected after vacuum dry.

2.3. Preparation of MnO₂/KWB composites (KWBM)

The KWBM composites were prepared by directly reacting KMnO₄ with KWB. In a typical process, 0.05 g KMnO₄ dissolved in 100 mL deionized water, and then 0.1 g KWB (the mass ratio of KMnO₄/KWB is 0.5:1) added the above solution. Subsequently, the mixture was stirred under water bath at 70 °C until the color of solution changed from Modena to tawny. The products removed from solution and washed with deionized water for several times, and dried in vacuum at 80 °C for 12 h to obtain of the KWBM-1 composite. The other products were denoted as KWBM-2, KWBM-3 and KWBM-4 for the mass ratio of KMnO₄/KWB is 1:1, 1.5:1 and 2:1, respectively.

2.4. Structure characterization

The morphology of samples were observed by transmission electron microscopy (TEM, H-8110, Hitachi Co., Ltd. Tokyo, Japan) and scanning electron microscopy (SEM, S-4300, Hitachi Co., Ltd. Tokyo, Japan). Nitrogen adsorption-desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2020 apparatus. The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) equation. All samples were outgassed under vacuum at 80 °C overnight prior to measurement. The crystallographic structure of the samples was observed by X-ray diffraction (XRD, XRD-6000, Shimadzu Co., Ltd. Kyoto,

Japan) equipped with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) analysis was performed on the PHI Quantum 5000 equipped with an Al Kα radiation source.

2.5. Electrochemical test

The electrochemical tests were measured with an electrochemical workstation (CHI 660D, Shanghai Chenhua, China) in the two or three-electrode system in 1 M KOH electrolyte. For three-electrode system, saturated calomel electrolyte and platinum-wire electrode were used as reference and counter electrode, respectively. The test electrodes were first prepared by mixing the KWB and polytetrafluoroethylene (PTFE) at a mass ratio of 95:5, and mixing KWBM with carbon black (CB) and PTFE at a mass ratio of 80:15:5. After that, the mixing were grinding adequately to obtain a homogeneous paste, that was coated onto the Ni foam for current collector and dried under vacuum at 80 °C for 24 h, and then compressed at 10 MPa for 5 min. Cyclic voltammetry (CV), and galvanostatic charge/discharge (GCD) were conducted in a potential window from -0.8 to 0 V for KWB biocarbon, and 0 to 0.7 V for KWBM composites respectively. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 10⁵ to 10⁻² Hz at open circuit potential with as ac perturbation of 5 mV. The symmetric two-electrode system was assembled with two almost identical working electrodes (the active material was KWBM-4 composites sample, and the counter electrode was KWB biocarbon sample). The CV and GCD tests were run at different voltage windows.

The standard calomel reference electrode (SCE) based on GCD curves was evaluated according to the following equation (Eq. (1)):

$$C_m = \frac{I \times t}{\Delta V \times m} \quad (1)$$

where I is discharge current (A), t is the discharge time (s), ΔV is the voltage window (V), and m is the mass of active material on working electrode in three-electrode system, in two-electrode system is the total mass of active material on two working electrodes [26].

3. Results and discussion

3.1. Microstructural characterization

Fig. 1 illustrates the preparation process of KWB frameworks and KWBM composites. At first, the KWB was obtained by carbonized and activated sugarcane bagasse at one step (as shown in Fig. 1a) [3]. As shown in Fig. 1d and e, the sugarcane bagasse exhibited a typical bundle-microtube-like structure of the biological tissue. While after carbonization and activation, the special structure was destroyed and an allium-giganteum-like structure with high interconnected frameworks which is favorable for the ion diffusion and suitable for preparation of MnO₂-based composites [27], can be clearly found in the as-resulted KWB (as shown in Fig. 1f and g). Therefore, KWB was used as both scaffolds and reducing agents for MnO₂ growth in this study. MnO₂ nanosheets grew on the surface of KWB based on the self-limiting reaction (Re. (2)) between KMnO₄ and KWB in neutral aqueous solution [28,29].



The morphology and microstructure of the prepared KWBM composites are shown in Fig. 2. The surface and interconnected frameworks of KWBM were coated by MnO₂ nanosheets in all samples. Moreover, it is noteworthy that a little of uncoated KWB was observed in the red circle of Fig. 2a (KWBM-1) and b (KWBM-2). The uncoated KWB gradually decreased with the mass ratio of KMnO₄/KWB increased till, KWB was completely coated by MnO₂ nanosheets when the mass ratio of KMnO₄/KWB is 2 (as shown in Fig. 2d). In addition, the high resolution

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