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MnO_2 nanograsses on porous carbon cloth for flexible solid-state asymmetric supercapacitors with high energy density

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ABSTRACT

Flexible solid-state supercapacitors (SCs) have shown great potential in portable electronics. However, the development of MnO_2-based electrodes for flexible SCs is hampered by the low energy density, especially on the whole electrode basis, as a result of the small mass loading and poor utilization of MnO_2. Here high mass loading of 4.5 mg/cm^2 and large capacitance of 464 F/g (2088 mF/cm^2) for MnO_2 nanograsses were achieved by taking use of porous carbon cloth (TCC) which has large specific surface area. Benefiting from the full utilization of MnO_2, high energy density of 841 μWh/cm^2 and robust cyclic stability (96% capacitance retention after 20000 cycles) are achieved by assembling an efficient asymmetric supercapacitor (ASC) with 2 V operating voltage. These results open up new paths for developing high-performance electrode materials and applying for advanced energy storage devices.

1. Introduction

The recent boom in multifunctional, portable and wearable electronics highlights the need for high-performance, lightweight and flexible power sources [1,2]. SCs store energy through rapid and reversible ion adsorption/desorption at the surface of high-surface-area carbons [3,4], and therefore activated carbon [5], ordered mesoporous carbon [6,7] and hierarchical porous carbon [8,9] are widely investigated. By virtue of high power density, quick charge-discharge capability, long cyclic life and good safety, flexible solid-state SCs have attracted intensive attention [3,10]. Although, a large variety of flexible electrodes based on graphene [11–14], nanotubes [15–17], polymers [18] have been explored in the past few years, the development of low-cost electrode materials with high areal energy to fulfill the demand of electricity consumption remains a critical challenge.

Energy density can be enhanced by adopting ASC, which mostly consists of a pseudocapacitive electrode and an electric double-layer capacitive electrode. By coupling their complementary potential window, the operating voltage of the ASC can be extended, hence significantly improving the energy density. Among various transition metal oxides (NiO [19], VO_X [20,21], CoO [22], Fe_2O_3 [23], $NiCo_2O_4$ [24,25], and MnO_2 [26–28]), MnO_2, is regarded as the most promising materials for pseudocapacitors due to their large theoretical specific capacitance (1370 F/g), low cost and natural abundance [29–32]. However, the development of MnO_2-based electrodes for flexible SCs is still at the early stage and is hampered by the inferior mechanical flexibility and poor electric conductivity (10^{-5}–10^{-6} S/cm) which makes it difficult to reach their theoretical capacity. An effective strategy is to combine with flexible conductive substrates such as graphene [33,34], metal substrates [35–37], carbon nanofibers [38–40] and so on. Since one of charge storage mechanisms involves protons and cations adsorption/desorption at the surface of electrodes, to date, most reported MnO_2-based electrodes shown good pseudocapacitance only has a small mass loading of MnO_2 (< 1 mg/cm^2) [24,29,41]. In addition, the specific capacitance of MnO_2 decreases significantly with the increase of mass loading and thus, leading to low energy density especially on the whole electrode basis because of the reduced electrical conductivity, decreased active surface area and poor utilization of MnO_2 [24,35,42]. Therefore, it is challenging to fabricate MnO_2-based nanocomposites with excellent flexibility, high capacitance at a large mass loading of active materials and improved cyclic stability.

Porous carbon supports with large specific surface area, good conductivity would be promising, as a large number of pores can provide active sites for the uniform growth of MnO_2, and thus permitting high mass loading and full utilization of MnO_2, as well as fast electronic/ionic transfer. Besides mass density, the crystal structure, morphology and ion conductivity of MnO_2 affect its electrochemical capacity. Previous studies have established that birnessite MnO_2 with a lamellar structure exhibits excellent electronic and ionic

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conductivity, as well as mechanical and chemical stability [43]. Further decreasing the crystallinity and partial size of MnO_2 can also facilitate the faradaic reactions, ensuring its high utilization [44,45]. Hence, the pursuit of novel MnO_2-based materials possessing high energy densities for flexible ASCs should not cease.

In the present study, well-organized ultrathin MnO_2 nanograsses were in-suit grown on TCC by a simple wet-chemical method, which was used as a binder-free electrode. TCC with large specific surface area is demonstrated to be not only an ideal mechanical and conductive support for full utilization of MnO_2, but additional active materials for charge storage. The porous structure of TCC can provide active sites for the uniform growth of MnO_2, and thus leading to high capacitance of 464 F/g (2088 mF/cm^2) for MnO_2 at a high mass density of 4.5 mg/cm^2. A flexible solid-state ASC with the 2 V operating voltage was assembled by applying MnO_2 nanograsses/porous carbon cloth (MnO_2/TCC) and TCC as positive and negative electrodes, respectively. High energy density of 841 μWh/cm^2 was achieved at power density of 2 mW/cm^2. Also, the flexible ASC was stable up to 20000 cycles, indicating a good cycling stability of MnO_2/TCC. These results all indicate that the environmental friendly and low-cost approach may be promising for developing high-performance electrode materials and applying for advanced energy storage devices.

2. Experimental

2.1. Preparation of TCC

TCC was synthesized by high-temperature treatment of CC [46] Briefly, commercial CC (Shanghai Hesen Electric Co. Ltd., China, HCCP330) was heated to 1000 °C for 1 h with a rate of 5 °C/min in industry nitrogen. The areal loading of TCC is about 15.2 mg/cm^2.

2.2. Preparation of MnO_2/TCC composites

MnO_2 nanograsses were grown on TCC with a simple wet-chemical method. A piece of TCC was immersed in 100 mL distilled water and 1 mmol $KMnO_4$ in 5 mL solution was added and dispersed with the assistance of ultrasonic method. Then the whole solution with TCC in it was treated at 85 °C for 1 or 6 hours to get MnO_2/TCC, and hence MnO_2 nanograsses in-suit grew on the surface of TCC. Finally, the sample was washed thoroughly with deionized water and then dried at 70 °C. The mass density of MnO_2 on the TCC was about 4.5 mg/cm^2 for 1 h sample and 6.6 mg/cm^2 for 6 h sample. The as-prepared composite was used for the positive electrode for ASCs. If there is no special mention, MnO_2/TCC in this work refers to 1 h sample. For comparison, commercial CC and TCC synthesized at 600 °C (TCC_{600}) were also chosen as the carbon support for growth of MnO_2 according to the same procedure. The prepared composites were denoted as MnO_2/CC and MnO_2/TCC_{600}, respectively. The specific capacitance of pure MnO_2 was obtained by excluding the contribution of the corresponding carbon substrate. To estimate the capacitance of the corresponding carbon substrate, MnO_2/TCC was treated by 2 M HCl at 90 °C to remove MnO_2 and then tested in 5 M LiCl with a three-electrode system.

2.3. Material characterization

Scanning electron microscope (SEM) images and energy-dispersive X-ray (EDX) mapping spectra were obtained with a SU-70 microscope. High-resolution TEM (HRTEM) was taken on Tecnai G2 F30 S-Twin at an acceleration voltage of 300 KV. An ESCALAB MARK II spherical analyzer using an aluminumanode (Al 1486.6 eV) X-ray source was used to collect the X-ray photoelectron spectra (XPS) data. X-ray

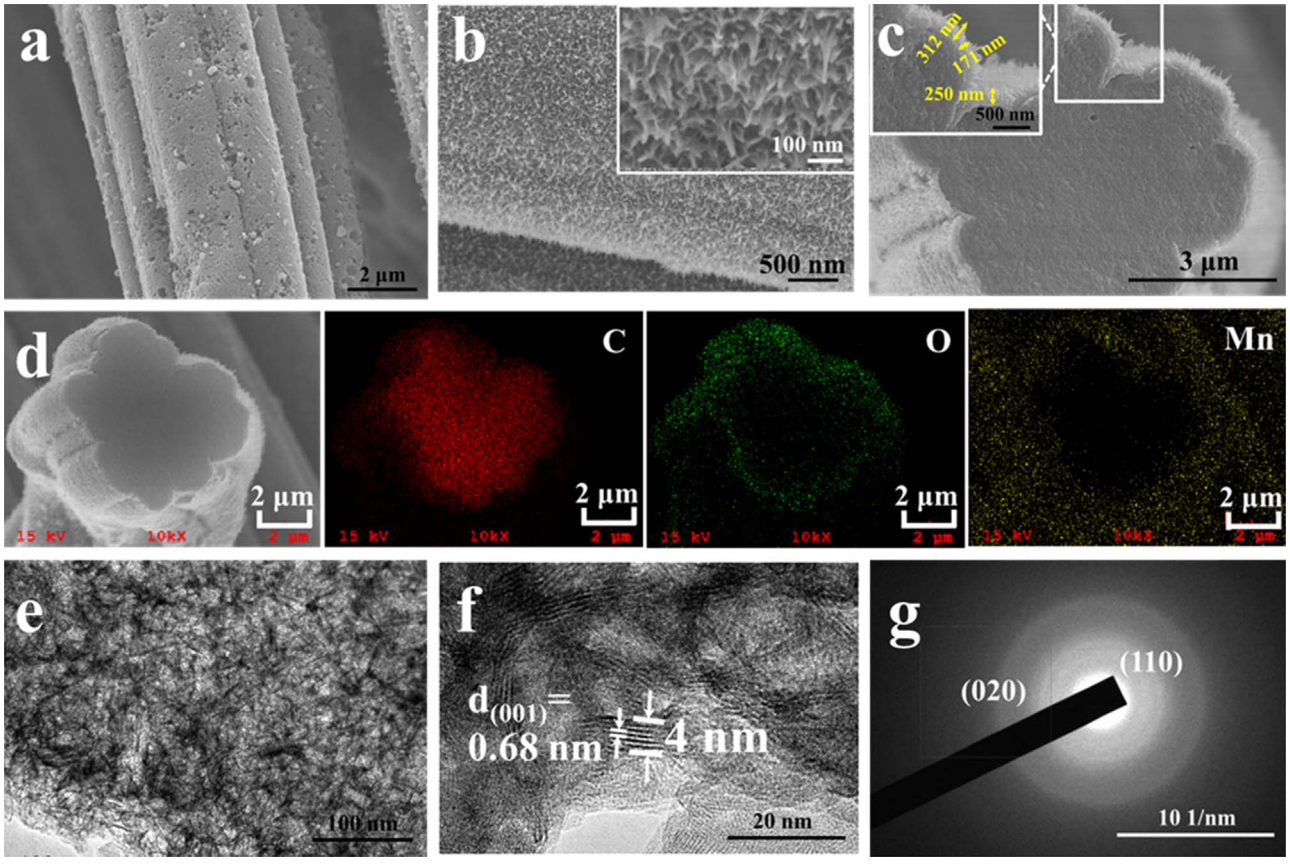

Fig. 1. (a) SEM image of TCC. (b) SEM image of MnO_2/TCC with a higher magnification of the surface in the inset. (c) SEM image of the hierarchical structure with a corresponding higher magnification of the MnO_2 nanosheets in the inset. (d) EDX analysis of MnO_2/TCC, implying a uniform MnO_2 layer growing on the surface of TCC. (e) and (f) HRTEM images of MnO_2 nanograsses. (g) Selected area electron diffraction pattern of MnO_2 nanograsses.