



High performance supercapacitors based on three-dimensional ultralight flexible manganese oxide nanosheets/carbon foam composites



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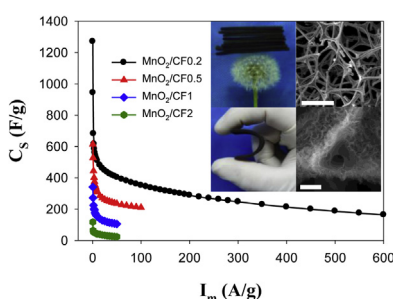
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HIGHLIGHTS

- Ultralight and flexible MnO₂/carbon foam (MnO₂/CF) composites are synthesized.
- Flexible carbon foam with low density is obtained by carbonizing melamine resin foam.
- MnO₂ nanosheets with a few nanometers thickness are grown on high-porous carbon foam.
- The porous MnO₂/CF can be fabricated into supercapacitor electrode without any binder.
- Supercapacitor from MnO₂/CF shows high specific capacitance and high energy density.

GRAPHICAL ABSTRACT



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ABSTRACT

The syntheses and capacitance performances of ultralight and flexible MnO₂/carbon foam (MnO₂/CF) hybrids are systematically studied. Flexible carbon foam with a low mass density of 6.2 mg cm⁻³ and high porosity of 99.66% is simply obtained by carbonization of commercially available and low-cost melamine resin foam. With the high porous carbon foam as framework, ultrathin MnO₂ nanosheets are grown through *in situ* redox reaction between KMnO₄ and carbon foam. The three-dimensional (3D) MnO₂/CF networks exhibit highly ordered hierarchical pore structure. Attributed to the good flexibility and ultralight weight, the MnO₂/CF nanomaterials can be directly fabricated into supercapacitor electrodes without any binder and conductive agents. Moreover, the pseudocapacitance of the MnO₂ nanosheets is enhanced by the fast ion diffusion in the three-dimensional porous architecture and by the conductive carbon foam skeleton as well as good contact of carbon/oxide interfaces. Supercapacitor based on the MnO₂/CF composite with 3.4% weight percent of MnO₂ shows a high specific capacitance of 1270.5 F g⁻¹ (92.7% of the theoretical specific capacitance of MnO₂) and high energy density of 86.2 Wh kg⁻¹. The excellent capacitance performance of the present 3D ultralight and flexible nanomaterials make them promising candidates as electrode materials for supercapacitors.

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1. Introduction

In recent years, a significant amount of effort has been devoted to exploring flexible and ultralight energy storage materials to meet the fast growing fashion of portable electronic devices, such as roll-up displays, electronic paper, wearable devices, mobile phones, and computers. Supercapacitors, also called electrochemical capacitors, characteristic of high power and reasonably high energy densities, currently fill the gap between batteries and conventional solid state and electrolytic capacitors [1–4]. Supercapacitors have become a versatile solution to various emerging energy applications, especially when high power delivery or uptake is needed. Supercapacitors can store energy either by ion adsorption (electrochemical double layer capacitors, EDLCs) or by fast surface redox reactions (pseudocapacitors) in nature [5]. EDLCs mainly use various carbon nanomaterials as electrode materials. EDLCs often display relatively low specific capacitance (Cs) and energy densities but high power densities [6]. In contrast, pseudocapacitors which store energy via redox reactions of electroactive materials, like conducting polymers and transition metal oxides/hydroxides, possess opposite properties [7].

In order to explore electrode materials with both high energy densities and power densities, much work has been done on integrating active materials on 3D self-supported substrates [8–16], especially on light and flexible carbon skeletons including reduced graphene oxide gel/foam, carbon foam/paper/cloth, carbon nanotube arrays/film, etc [17–23]. These composites have many advantages when used as supercapacitor electrode materials. First, with these materials, no binder is needed for constructing supercapacitor electrodes, which simplify the electrode preparing process. The usually used binders which often raise the electrode resistance and lead to low power density are indispensable during electrode preparing. Therefore, supercapacitors based on binder-free electrode materials usually show relatively higher power densities and better rate capacitance performance [24,25]. Second, 3D carbon substrates can not only avoid the aggregation of capacitance-active materials but also facilitate the electron transfer during charge/discharge process which ensures full use of the active materials [26,27]. Moreover, Due to the large porosity (>90%) and high conductivity of the ultralight carbon materials, the 3D porous structures are very beneficial for electrolyte diffusion and electron transfer. Therefore, supercapacitors based on these flexible and lightweight carbon materials always show excellent rate capacitance performance and stability. Previous studies showed that by depositing active materials like MnO_2 on the ultralight carbon materials, the specific capacitance and energy density of the hybrids can be greatly improved, which makes them promising candidates for flexible, ultralight energy storage materials [8,23].

However, the preparation of ultralight carbon materials is usually time-consuming and complicated. There are mainly two ways to fabricate the ultralight carbon support materials. One is that graphene/carbon nanotube hydrogels are first prepared through hydrothermal self-assembly of graphene or carbon nanotube. The hydrogels are then dried via freeze drying/lyophilization to get aerogels [17,18]. In another way, graphene layers or carbon nanotube array/sponge can be directly grown on various substrates through chemical vapor deposition, followed by removing substrates [8,28]. Both methods not only take time and need critical preparation conditions, but also produce only small-scale output. Therefore, it is still an urgent and important issue to explore facile methods to prepare flexible and ultralight energy storage materials with large-scale production and low cost.

In this paper, ultralight and flexible carbon foam (CF) with low density of 6.2 mg cm^{-3} was simply synthesized through carbonizing commercial melamine resin foam (MRF) with low cost and

large-scale production. This novel carbon foam is quite different from other resin-derived 3D porous carbon foams/monoliths/aerogels in the preparation, porous structure, density and flexibility. Traditionally, carbon foams/monoliths/aerogels were prepared by carbonizing blends of phenolic resins and templates like silica spheres, Zeolite Y, polystyrene spheres and block copolymers [29–31]. The removable, expensive polymer latex, silica, or other colloidal particles are energy-consuming and uneconomic, and the synthesis procedure is complicated and time-consuming [32]. What is more, the output and the processability of these carbon materials are largely limited. In this study, a type of large-scale producible and flexible carbon foam can be easily obtained from direct carbonization of low-cost melamine foam. The density of the carbon foam is comparable to other ultralight aerogel/foam/sponge-like materials, like graphene foam/aerogels and CNT sponges [28,33–38]. Meanwhile, the prepared carbon foam can serve as an excellent 3D porous framework to fabricate ultralight supercapacitor electrode due to its low density and high flexibility. To the best of our knowledge, this is the first report of 3D supercapacitor fabricated from melamine resin-derived composite. Here, MnO_2 nanosheets/CF composites were prepared by *in situ* reaction between KMnO_4 and carbon and functioned as ultralight and flexible supercapacitor electrode materials for the first time. The electrochemical studies indicated that the as-prepared coaxial composites showed excellent capacitance performance. The highest specific capacitance of MnO_2 could reach 1270.5 F g^{-1} which is 92.7% of its theoretical specific capacitance (1370 F g^{-1}) [39]. Moreover, the supercapacitor fabricated with the present 3D network materials exhibited high energy density of 86.2 Wh kg^{-1} , high power density of 160.0 kW kg^{-1} and also high stability. Overall, this research provides a simple and efficient method for preparing MnO_2 /CF composites from the low-cost and large-scale available melamine resin foam. With the advantages of easy fabrication, low cost, lightweight, high flexibility and excellent capacitance performance, the fabricated 3D porous MnO_2 /CF hybrids represent a class of promising electrode materials for supercapacitors.

2. Experimental

All the reagents used in the experiments were analytical grade and were used without further purification.

2.1. Preparation of carbon foam

Carbon foam was prepared by carbonizing melamine resin foam (MRF, supplied by Puyang Green Univerish Chemical Co., Ltd.) under Ar flow of 100 mL min^{-1} . MRF was cut into pieces with size of $0.5 \text{ cm} \times 3.5 \text{ cm} \times 25 \text{ cm}$ before carbonization. The carbonization process is as follows: the temperature was first raised from room temperature to $300 \text{ }^\circ\text{C}$ at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ and kept for 5 min; in the next step, the temperature was further raised to $400 \text{ }^\circ\text{C}$ at a rate of $1 \text{ }^\circ\text{C min}^{-1}$ and kept for 5 min; finally, the temperature was raised to $1000 \text{ }^\circ\text{C}$ at a rate of $3 \text{ }^\circ\text{C min}^{-1}$ and kept for 1 h.

2.2. Fabrication of MnO_2 /carbon foam composites (MnO_2 /CF)

After carbonization, carbon foam retained one eighth of the size of the pre-carbonization MRF. We found that in order to improve the hydrophilicity of the prepared carbon foam, it should be soaked in ethanol first and then washed with abundant deionized water to remove ethanol, otherwise, it can hardly infiltrated by KMnO_4 aqueous solution. 55 mg of the pre-treated carbon foam was immersed in a 200 mL KMnO_4 aqueous solution in a glass bottle. The bottle was then put into a water bath at $60 \text{ }^\circ\text{C}$ until the purple

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