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$Ti_3C_2T_x$-foam as free-standing electrode for supercapacitor with improved electrochemical performance

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ABSTRACT

To prevent restacking of the $Ti_3C_2T_x$ layers, the $Ti_3C_2T_x$-foam has been successfully synthesized through thermal treatment of $Ti_3C_2T_x$-film with the hydrazine monohydrate. The interconnected porous structure of $Ti_3C_2T_x$-foam could effectively reduce the restacking of the $Ti_3C_2T_x$ sheets and shorten the diffusion path of ions and accelerate the intercalation/de-intercalation of ions. The $Ti_3C_2T_x$-foam-80 used as free-standing electrode achieves a high areal capacitance of 271.2 mF/cm^2 (122.7 F/g) at a scan rate of 5 mV/s in 1 M KOH electrolyte. It also exhibited a high capability rate of 65.5% from 5 mV/s to 100 mV/s and good cycle life with 88.7% retention of its initial after 10,000 cycles at a scan rate of 50 mV/s.

1. Introduction

With the increased urgent demand of energy storage devices for environment-friendly high-power energy sources, supercapacitors (SCs) have been attracting more and more attention of researchers [1–4] on account of their significant advantages of high power density, superior cycle-life and high rate charge and discharge [5–8]. Because of above advantages, SCs make up many markets ranging from electronics to transportation and stationary applications [9–11]. According to the charge storage mechanisms of the SCs, they can be divided into two types: electric double-layer capacitors, in which charge is stored via electrosorption of ions on electrode materials; and pseudocapacitors, in which the capacitance is owing to surface redox reactions [12–14]. However, the energy density of SCs is still not high enough for their extensive practical application [15], so improvement of the performance of SCs is a severe challenge for researchers.

MXenes, are a novel large family of 2D early transition metal carbides and nitrides, with have a general formula of $M_{n+1}X_nT_x$, where n = 1, 2 or 3, where M represents is an early transition metal, X represents is carbon and/or nitrogen, T is a surface functionality [16–19]. They were generally synthesized by the extraction selective etching of the “A” element layers from the ternary carbides MAX phase using hydrofluoric (HF) aqueous solution [12,20]' a solution of dissolved lithium fluoride (LiF) in and hydrochloric acid (HCl) [21,22], and ammonium bifluoride (NH_4HF_2) aqueous solution [23]. Up to now, MXenes have been demonstrated as promising electrode materials for energy storage devices that contains lithium ion batteries [24–26], lithium ion capacitors [27], SCs [13,22,28], and electrochemical hydrogen storage [29]. However, similar to other 2D materials, the performance of MXenes is still limited owing to their restacking or aggregating, which hinder the ionic transport from the electrolyte into the electrode. In recent years, many efforts have been made to improve their electrochemical performance [30]. The most used strategy is introducing layer spacers, such as carbon materials, polymers, metal ions and transition metal oxides, which prevent the stacking by increasing the interlayer spacing.

On the other hand, integration of 2D materials into 3D macroscopic structures could provide effective accesses for ionic and electronic transport in electrode materials, thus producing high-performances. In fact, 3D macroscopic structures of graphene have been investigated, which offer the enhanced performance in energy storage [31–34]. Therefore, MXenes could also overcome their restacking or aggregating through integration of 2D structures into 3D macroscopic structures. For example, Zhao et al. have processed 2D MXene flakes into hollow spheres and 3D architectures by a template method [35]. Lukatskaya et al. designed highly accessible macroporous MXene hydrogel electrode with improved ion accessibility to electrochemically redox active sites, which achieves excellent rate performance [36]. Li et al. demonstrated that novel $Ti_3C_2T_x$ aerogel exhibits a large specific surface area and high areal capacitance [37]. However, these 3D architectures

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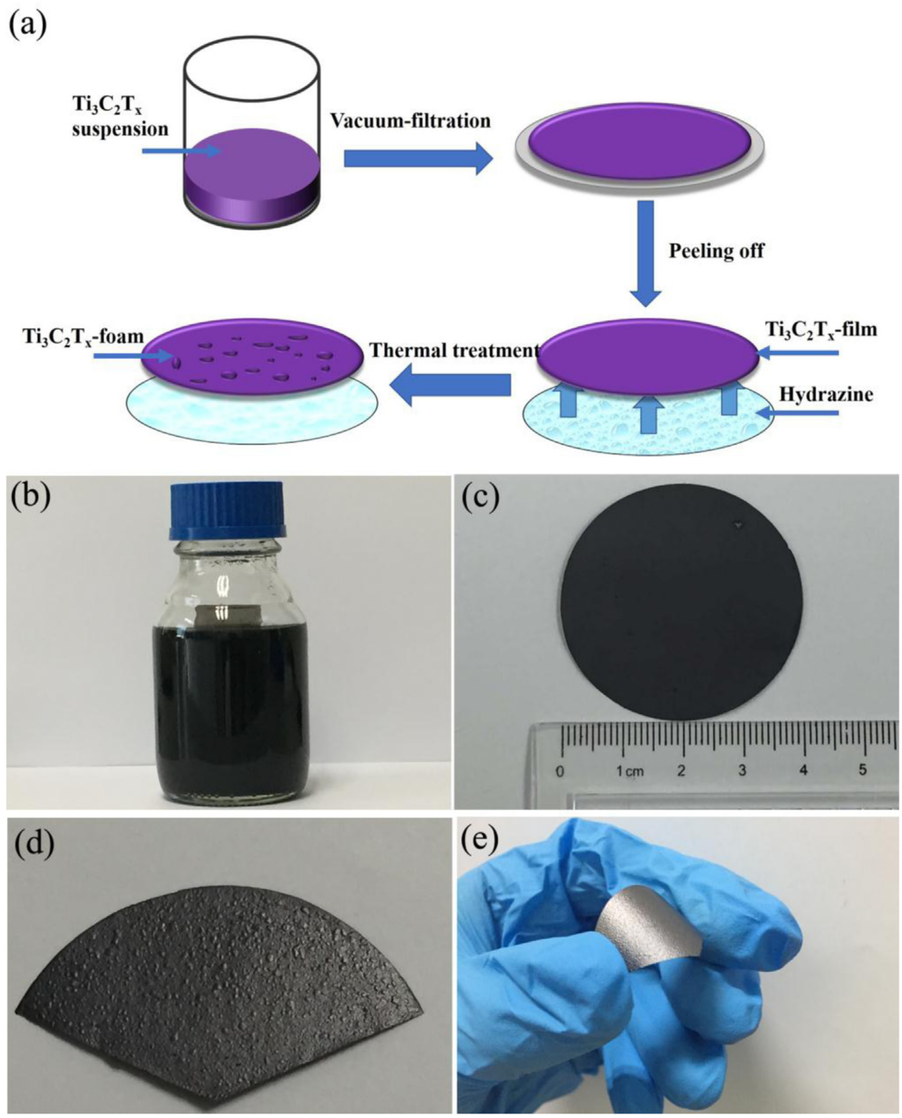

Fig. 1. (a) Schematic illustration of the thermal treatment process to prepare $Ti_3C_2T_x$-foam. Photograph of the (b) $Ti_3C_2T_x$ suspension used for vacuum filtering, (c)$Ti_3C_2T_x$-film, (d) $Ti_3C_2T_x$-foam-80, (f) $Ti_3C_2T_x$-foam showing its flexibility.

of MXenes were prepared using templates or the processes were complicated. Herein, we delicately design a simple method without any templates to prepare $Ti_3C_2T_x$-foam. The 3D porous morphology of $Ti_3C_2T_x$-foam could effectively prevent the restacking of the $Ti_3C_2T_x$ sheets and shorten the diffusion path of ions. Thus, the $Ti_3C_2T_x$-foam electrode shows improved electrochemical performance with high areal capacitance, good rate performance, and stable cycle life.

2. Experimental section

2.1. Synthesis of $Ti_3C_2T_x$ -film

The $Ti_3C_2T_x$ was successfully synthesized by selectively etching Al out of Ti_3AlC_2 powder. Firstly, 1.56 g LiF was dissolved in 20 mL 12 M HCl with stirring. One gram of Ti_3AlC_2 was slowly added to the above solution at room temperature. To avoid overheating, it must be slow during the process of adding the Ti_3AlC_2. The etching process of reaction mixture was held at 35 °C for 48 h under stirring. After 48 h, the obtained mixture was washed by three times of 1 M HCl aqueous solution, three times of 1 M LiCl aqueous solution, and several times of deionized water. Until pH of the supernatant was approximately 6, the suspension was collected. During washing process, the above solution or deionized water was added and hand-shaked for about 5 min before centrifugation at 8000 rpm for 5 min. The colloidal suspension of $Ti_3C_2T_x$ was decanted and collected for further investigation. Finally, the resulted suspension was vacuum-filtered through a polypropylene membrane to form a free-standing $Ti_3C_2T_x$-film. The thickness of $Ti_3C_2T_x$-film was tailored by controlling the concentration and volume of the colloidal suspension.

2.2. Synthesis of $Ti_3C_2T_x$-foam

To prepare $Ti_3C_2T_x$-foam, the hydrazine monohydrate was added into the autoclave, then a free-standing $Ti_3C_2T_x$-film was put into the autoclave. Then, the autoclave was putted in oven and heated at 90 °C for 10 h (at the rate of 2.3 °C/min) to obtain the $Ti_3C_2T_x$-foam. The obtained $Ti_3C_2T_x$-foams were labelled as $Ti_3C_2T_x$-foam-40 and $Ti_3C_2T_x$-foam-80, which were according to addition of 40 μL and 80 μL hydrazine monohydrate during thermal treatment, respectively.

For comparison, $Ti_3C_2T_x$-film was treated by similar method except that 80 μL of H_2O, sodium hydrogen sulfite (1.44 M), or ascorbic acid (VC) (0.85 M) was added respectively instead of hydrazine monohydrate.