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Enhanced supercapacitive performance of delaminated two-dimensional titanium carbide/carbon nanotube composites in alkaline electrolyte

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HIGHLIGHTS

- The introduction of carbon nanotube can impede the stacking of MXene sheets.
- Introducing carbon nanotube can improve the electrical conductivity of MXenes.
- The d-Ti_3C_2/CNT composites exhibit excellent supercapacitive performance.

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ABSTRACT

MXenes, a new family of two-dimensional materials, are terminated by O, OH and F groups. The existence of the oxygen-containing functional groups indicates a potential application in supercapacitor based on a redox mechanism. However, the irreversible stacking of MXenes will lead to an insufficient utilization of these functional groups and thus a decrease in the supercapacitive performance. To solve the problem, we synthesized a composite material comprised of carbon nanotube (CNT) and Ti_3C_2 sheets (d-Ti_3C_2) delaminated from MXenes by ultrasonic stirring. The FTIR result suggests that the ultrasonication has no significant effect on the oxygen-containing functional groups. The resultant composites exhibit significantly higher volumetric capacitance and better capacitance retention (during 5 –100 mv s^{-1}) than d-Ti_3C_2. A highest volumetric capacitance of 393 F cm^{-3} at 5 mv s^{-1} in KOH electrolyte can be obtained when the weight ratio of d-Ti_3C_2 to CNT is 2:1. In addition, the volumetric capacitance has no significant degradation even after 10000 cycles in cycling stability test, showing an excellent cycling stability compared with metal oxides. These enhanced electrochemical performances can be ascribed to the introduction of CNTs, which impede the stacking of Ti_3C_2, enlarge the distance between Ti_3C_2 sheets and improve the electrical conductivity.

1. Introduction

Supercapacitors, a new energy storage device, bridge the gap between batteries and conventional capacitors and have been attracting considerable interest in the energy storage field [1–4]. Suitable electrode materials are key ingredients enabling the search for high performance supercapacitors. Up to now, many materials used as electrodes have been investigated, such as activated carbon [5,6], carbide-derived carbon [7–9], metal oxides [10,11], graphene/metal oxide composite materials [12], conducting polymers [13] and so on.

Recently, a new family of two-dimensional (2D) materials (i.e., MXenes) have attracted increasing attention, and shown a potential application in the fields of hydrogen storage [14], lead adsorption [15] and energy storage [16–18]. The MXenes are synthesized by selective removal the A-element from MAX phases (such as Ti_3AlC_2 [19]), where M is an early transition metal, A is a

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III or IV A-group element and X is carbon and/or nitrogen [20]. It is worth noting that the termination of the 2D MXene surfaces mainly contain a lot of oxygen-containing functional groups (such as −OH/=O) and some fluorine (−F) [18,21], which are introduced after etching with aqueous hydrofluoric acid (HF). The existence of the oxygen-containing functional groups shows a promising application in the supercapacitor based on the redox mechanism. However, the MXene sheets are easy to form irreversible agglomerations due to the strong van der Waals interactions between individual MXene sheets, leading to the insufficient utilization of the MXene surface and oxygen-containing functional groups, and, as a result, a poorer electrochemical performance of pseudocapacitors.

One-dimension carbon nanotubes (CNTs) have attracted much attention in energy storage applications. Most researches have proved that the introduction of the CNTs in the graphene structures can effectively impede the aggregations of individual graphene sheets and exhibit enhanced supercapacitive performance [22–24]. Therefore, in this work, through introducing the CNT into a Ti_3C_2-MXene, which is graphene-like structure [21], we synthesized a delaminated 2D Ti_3C_2/CNT composite material and investigated the electrochemical performance for the resultant composite.

2. Experimental

2.1. Sample preparation

A MXene (2D Ti_3C_2) used in the present work was produced by immersing Ti_3AlC_2 in HF [18]. In order to obtain the delaminated Ti_3C_2 sheets [20], 0.3 g of 2D Ti_3C_2 were mixed with 6 ml dimethyl sulfoxide (DMSO, Shanghai Lingfeng Chemical Reagent Co. Ltd., China) and then magnetically stirred for 18 h at room temperature. The resultant suspension was centrifuged to separate the powder from the liquid DMSO. The obtained powder was mixed with deionized water and the suspension was under intermittent ultrasonication for designated time (e.g. 2 h and 6 h). After that, the larger particles were removed by centrifuging and the supernatant were collected as the samples for further investigation. The samples obtained after ultrasonication for 2 h and 6 h were denoted as ex-Ti_3C_2 and d-Ti_3C_2, respectively. The CNTs with 20–40 nm in diameter were obtained from the Shenzhen Nanotech Co. Ltd. of China. The stable suspension of CNTs (0.3 mg ml^{-1}) was produced by ultrasonication in the presence of dispersant. Thereafter, the d-Ti_3C_2 (0.3 mg ml^{-1}) and CNTs were thoroughly mixed (denoted as d-Ti_3C_2/CNT) at different weight ratios of d-Ti_3C_2 to CNT (6:1, 2:1 and 1:1) by ultrasonic stirring. The mixed suspension was filtered using a polytetraflouroethylene (PTFE) filter (0.2 μm in pore size) and dried at 70 °C, achieving the d-Ti_3C_2/CNT composite materials. Besides, the weight ratio of d-Ti_3C_2/CNT is 2:1 if no particular explanation.

2.2. Characterization

The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, Hitachi S4800, Japan) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan). X-ray diffraction (XRD) patterns between 5 (2θ) and 65 (2θ) degrees were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-Kα radiation ($\lambda = 0.154$ nm) operated at 40 kV and 200 mA. Existence of oxygen functional groups was examined by Fourier transform infrared spectroscopy (FTIR, Bruker Optiks E55 + FRA106, Germany). Electrical conductivity were measured by ST-2722 semiconductor resistivity of the powder tester (Changzhou Sanfeng instrument technology Co. Ltd., China).

2.3. Preparation of electrode and electrochemical measurement

The electrochemical investigations were carried out in a three-electrode system using platinum as counter electrode and Hg/HgO as a reference electrode. The working electrodes were prepared as follows: A slurry consisting of 80 wt.% active materials, 10 wt.% carbon black and 10 wt.% PTFE (60 wt.% suspension in water) binder was smeared into nickel foam and dried in vacuum at 120 °C for 10 h. Thereafter, the electrode was pressed at a pressure of 10 MPa. 6 M KOH solution was used as electrolyte. The active area of the electrode is 1 cm^2. Before each measurement, the working electrode was impregnated with electrolyte to ensure thoroughly wetted by electrolyte. Cyclic voltammograms (CV) were collected on CHI650D electrochemical workstation in a potential range of 0.1–0.55 V. The scan rates for all CV tests were in the range of 5–100 mV s^{-1}.

3. Results and discussion

The XRD patterns of 2D Ti_3C_2, ex-Ti_3C_2, d-Ti_3C_2, CNTs and d-Ti_3C_2/CNT composite are presented in Fig. 1. Fig. 1a shows the structural evolution from Ti_3AlC_2 to d-Ti_3C_2, demonstrating clearly a continuous decrease in crystallinity and the structural order when the pristine Ti_3AlC_2 is transformed to 2D Ti_3C_2, then to ex-Ti_3C_2, and finally to d-Ti_3C_2. The (002) peak of Ti_3AlC_2, which is initially at $2\theta = 9°$, broadens and shifts to $2\theta = 8°$ (for 2D Ti_3C_2) after etching with HF. When the ultrasonication on 2D Ti_3C_2 is carried out for 2 h, the (002) peak further shift to lower angle ($2\theta = 6°$ for ex-Ti_3C_2) and the lattice parameter c increases from 21.4 Å (2D Ti_3C_2) to 31.7 Å (ex-Ti_3C_2). When the ultrasonication is performed for 6 h, the (002) peak disappears, suggesting the full delamination of 2D Ti_3C_2 and thus the formation of individual Ti_3C_2 sheets. Furthermore, with the increasing of ultrasonic time, the gradually disappeared (110) peak at $2\theta = 61°$ also provides obvious evidence for the decrease of order and full delamination of 2D Ti_3C_2 [20]. By comparison to the XRD patterns of d-Ti_3C_2, CNTs and d-Ti_3C_2/CNT shown in Fig. 1b, it can be deduced that the d-Ti_3C_2/CNT composite material, which is comprised of Ti_3C_2 sheets and CNT, has been successfully synthesized.

Fig. 2 exhibits SEM images of these Ti_3C_2 samples. It is clear that the 2D Ti_3C_2 behaves a layered structure. Under ultrasonication, the layer number decreases and the surface becomes rougher (Fig. 2b for ex-Ti_3C_2), and then, the further ultrasonication will result in the formation and the pulverization of individual Ti_3C_2 sheets (Fig. 2c for d-Ti_3C_2). However, the pulverized individual Ti_3C_2 sheets are very easy to agglomerate. The introduction of the CNTs into the d-Ti_3C_2 can effectively impede the aggregation of individual Ti_3C_2 sheets (Fig. 2d). TEM observations further demonstrate (shown in Fig. 3) that the ultrasonication of 2D Ti_3C_2 can obtain delaminated Ti_3C_2 sheets and the CNTs and d-Ti_3C_2 are interweaved together in the d-Ti_3C_2/CNT composite.

The FTIR spectra of CNTs, d-Ti_3C_2 and d-Ti_3C_2/CNT are given in Fig. 4. It can be seen that the C=O (~1645 cm^{-1}) functional groups exist in all the samples. In addition, the C−O (~1051 cm^{-1}), C−F (~1090 cm^{-1}) and O−H (~1389 cm^{-1}) groups can be observed in the spectra of d-Ti_3C_2 and d-Ti_3C_2/CNT. Obviously, almost all the oxygen-containing functional groups in the MXenes can still be retained in the synthesized d-Ti_3C_2/CNT composite, suggesting that the ultrasonication has no significant effect on the oxygen-containing functional groups. This result also implies that the synthesized d-Ti_3C_2/CNT composite will exhibit pseudocapacitive performance due to the existence of the oxygen-containing functional groups.

The CV curves of 10 mv s^{-1} for d-Ti_3C_2 and d-Ti_3C_2/CNT composites at different weight ratios of d-Ti_3C_2 to CNT (6:1, 2:1 and 1:1)