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Enhanced supercapacitive performance of manganese oxides doped two-dimensional titanium carbide nanocomposite in alkaline electrolyte

Yi Tang [a, *], JianFeng Zhu [a], ChenHui Yang [b, **], Fen Wang [a]

[a] School of Materials Science & Engineering, Shaanxi University of Science & Technology, Xi'an 710021, PR China
[b] Electronic Materials Research Laboratory, School of Electronic & Information Engineering, International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, PR China

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ABSTRACT

Two-dimensional transition metal carbides MXenes, one of promising electrode materials for electrochemical capacitors (ECs), process unique layered structure, high surface area, remarkable chemical stability, and electrical conductivity for energy storage. However, the low capacity of MXene electrodes limits their further application in ECs. Herein, with excellent electrochemical performance of MnO_2, Ti_3C_2 nanosheets decorated with MnO_2 nanoparticles were synthesized through a simple liquid phase precipitation method and heat treatment process, and were subsequently employed to the electrode for ECs. TEM and XRD results demonstrate that MnO_2 nanoparticles, about 20–40 nm in diameter size, have been homogeneously inserted into the interlamination of Ti_3C_2 matrix for cation intercalation. Due to the synergistic effect between MnO_2 and Ti_3C_2 matrix, the nanocomposite exhibits a superior areal capacitances of 377 mF cm^{-2} at scan rate of 5 mV s^{-1}, which is significantly higher than that of Ti_3C_2 (306 mF cm^{-2}), and shows excellent cycling stability with capacitance retaining 95% after 5000 cycles. Even at a high scan rate of 200 mV s^{-1} (310 mF cm^{-2}), MnO_2–Ti_3C_2 nanocomposite displays a high rate capability of 83%. These results demonstrate that MnO_2–Ti_3C_2 nanocomposites offer fascinating potential for high-performance ECs.

1. Introduction

The development of novel, low-cost, environmentally friendly, and high-performance energy storage systems has been under an ever increasing demand as a result of the needs of modern society and emerging ecological concerns [1]. Electrochemical capacitors (ECs), which are also called supercapacitors (SCs) or ultracapacitors [2], have attracted tremendous amounts of attention as energy-storage devices due to their high power density, fast charge–discharge ability, excellent reversibility, and long cycling life [3–6]. There are two charge storage mechanisms in ECs: the first one are known as electrical double-layer capacitors (EDLCs), in which the capacity is resulted from the electrosorption of ions on porous carbon electrodes, such as activated carbon, carbon nanotubes, and graphene-based active materials [4,6,7]. The second one are known as pseudocapacitors, in which the capacity is due to redox reactions. They provide higher energy densities but usually suffer from shorter cyclic lifetimes [5,6,8]. The typical pseudocapacitor materials have transition metal oxides and conductive polymers [3,5,9]. To overcome the obstacles, the intensive approaches are the exploration of new materials [10], hybrid structure [11,12], surface modification [13], for EC electrodes.

Recently, MXenes (of the formula $M_{n+1}X_nT_x$, where M is a transition metal, X is C and/or N, and T_x denotes –OH, –F, and =O surface groups), are a novel family of two-dimensional (2D) metal carbides [14–19]. MXenes have already demonstrated their potential as promising electrode materials for Li-ion batteries [20–23], supercapacitors [11,12,24,25], and sensors [18,26,27], because of their high electrical conductivity, large surface area, layered structure, remarkable chemical stability, and environment-friendly characteristics [11,14,28]. Particularly, Ti_3C_2 is one of the most widely studied and promising members of this family [11,14], which is frequently applied in ECs. Ti_3C_2 is one of very few materials which exhibits "true" pseudocapacitive behavior. It presents a continuous change in the titanium oxidation state during charge/

* Corresponding author.
** Corresponding author.
E-mail addresses: tangyi150@163.com (Y. Tang), ych488@163.com (C. Yang).

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discharge, producing rectangular-shaped CVs. Such kind of behavior can be attributed to the 2D nature of Ti_3C_2 MXene: (1) spontaneous ion intercalation naturally provides access to electrochemically active transition metal oxide surfaces; (2) the conductive carbide layer ensures rapid charge transfer [10].

To further enhance electrochemical performance of the 2D Ti_3C_2 electrode material, one straightforward strategy that has been extensively investigated is introducing interlayer spacers [11]. Notably, one of the most effective ways is employing various transition metal oxides to insert among the nanosheets [6,29]. Among the transition metal oxides, manganese oxides, basically including MnO, Mn_3O_4, Mn_2O_3, MnO_2 with different allotropes, exhibit the advantages of low cost, no toxicity, easy to obtain and high specific capacitances, and therefore have been taken for granted as the most promising materials in the application of supercapacitors [8,30]. Over the past few years, various nanostructured MnO_2, including dendritic clusters, nanocrystals with different morphologies including nanowires, nanotubes, nanobelts, and nanoflowers, have been successfully synthesized and characterized [2,8,30–34]. For example, MnO_2 with α-, β-, γ-, δ-, and λ-type crystal structures exhibited specific capacitances of 70–150 F g^{-1} at 5 mV s^{-1} [35]. Yan et al. used the reduction of permanganate by surface carbon to prepare graphene/MnO_2 composite electrodes with necessary binder and conductor agents and obtained specific capacitance of 310 F g^{-1} at the scan rate of 2 mV s^{-1} [36].

To exploit the potential of MXene-based materials for supercapacitor applications, in this work, we have doped active materials in the MXene nanosheets to obtain hybrid electrodes for the supercapacitors to further increase the specific capacitances as well as the energy density while maintaining its good power performance. Ti_3C_2 nanosheets doped with MnO_2 nanoparticles have been synthesized *via* a simple liquid phase reaction of $Mn(NO_3)_2$ and $KMnO_4$, and followed by a heat treatment process in N_2, and subsequently used as a novel electrode material for supercapacitor. The two-dimensional titanium carbide material before/after incorporated with manganese oxides were systematically investigated by means of SEM, TEM, XRD, and XPS techniques. In addition, the electrochemical behaviors of the pristine titanium carbide as well as the derivates doped with manganese oxides were measured by a three-electrode system, using 6M KOH solution as electrolyte.

2. Experimental

2.1. Instrumentation and chemicals

Field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray analysis (EDAX) were performed using a Hitachi S-4800 &Hiroba energy dispersive X-ray electron microscope. Transmission electron microscopy (TEM; FEI company Tecnai G220 S-twin, 200 kV) was used to observe the morphology of the samples. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2200pc diffractometer using Cu Kα radiation of wavelength λ = 0.15418 nm at 40 kV and 40 mA. Raman spectroscopic measurements were carried out at both room temperature and 100 K using a Lab Ram Aramis Raman spectrometer with a He–Ne laser having an excitation wavelength of 633 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Thermo ESCALAB 250 spectrometer with an exciting source of Al Kα.

Unless otherwise noted, all the chemicals (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. In all experiments deionized water was used.

2.2. Synthesis of MnO_2–Ti_3C_2 nanocomposite

The main process of synthesizing MnO_2–Ti_3C_2 nanocomposite is illustrated in Fig. 1. Ti_3C_2 was successfully prepared by etching Al from Ti_3AlC_2 in HF at room temperature [16,18]. Firstly, 3.0 g as-prepared Ti_3AlC_2 powders were immersed in 60 mL 40% HF solution under magnetic stirring at room temperature for 24 h. Then the resulting MXene suspension was repeatedly washed 6 times using deionized water until the pH value of the liquid reached ~6. After decantation, the resulting powder was washed for 3 times by absolute ethanol and centrifuged to separate the powders. Finally, the powders were dried in the vacuum oven (<0.09 MPa) at 60 °C for 48 h.

MnO_2–Ti_3C_2 nanocomposite was synthesized by the combination of liquid-phase precipitation reaction method and a high temperature sintering process. Firstly, 200 mg of Ti_3C_2 powders were dispersed in 100 mL 1 mM $Mn(NO_3)_2$ aqueous solution under magnetic stirring at room temperature for 6 h. Then, the 100 mL 1 mM $KMnO_4$ aqueous solution was slowly added in the previous mixed solution and was then stirred for 30 min. At the end of the reaction, a precipitate was collected by centrifugation and rinsed sequentially with ethanol for 3 times and deionized water for 3 times. Then the powders was dried in the vacuum oven (<0.09 MPa) at 80 °C for 24 h. Afterward, the dried product was heated at 300 °C for 3 h in N_2 to prepare the MnO_2–Ti_3C_2 nanocomposites.

2.3. Electrochemical measurements

All electrochemical experiments were performed with a CHI

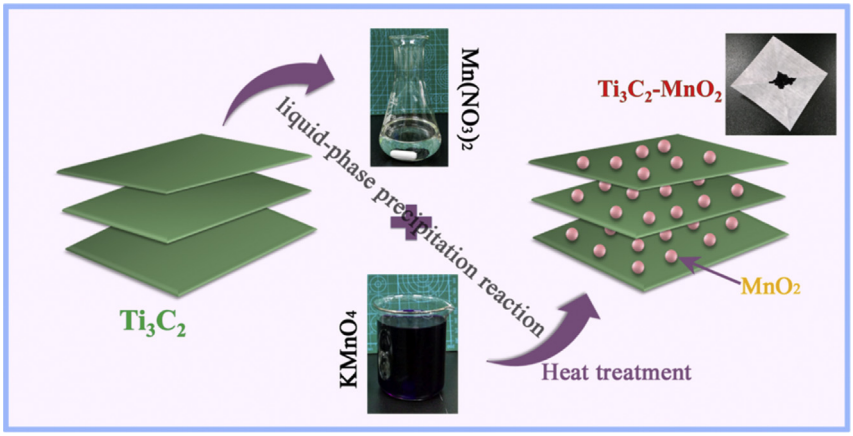

Fig. 1. Schematic illustration of the synthesis process of MnO_2–Ti_3C_2 nanocomposite.