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Effects of etching temperature and ball milling on the preparation and capacitance of Ti_3C_2 MXene

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ABSTRACT

Two-dimensional Ti_3C_2 MXene is prepared by a combination of ball milling and HF etching of Ti_3AlC_2 powder. Effects of etching temperature and ball milling duration on the preparation and electrochemical performance of as-prepared Ti_3C_2 MXene are investigated in detail. It is found that higher etching temperature and longer ball milling duration lead to faster transformation from Ti_3AlC_2 to Ti_3C_2 MXene. The ball milling treatment can improve the capacitive of Ti_3C_2 MXene. This improvement in the performance is attributed to higher carbon content for better conductivity and faster transportation of electrons, and the larger surface area for more access of aqueous electrolyte to the electrode.

1. Introduction

Since the discovery of graphene in 2004 [1], two-dimensional (2D) materials such as hexagonal boron nitrides [2], transition metal dichalcogenides [3], metal oxides [4], have drawn tremendous attention owing to unprecedented physical and chemical properties originating from their ultrathin structure and ultrahigh surface areas.

MXenes are a new family of 2D materials first described in 2011 [5]. These materials are comprised of transition metal carbides, carbonitrides and nitrides with a general chemical formula of $M_{n+1}X_n$ (M = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta; X = C, N; n = 1–3) [6]. Due to the high conductivities and hydrophilic surfaces, MXenes exhibit promising performance in many applications, including energy storage [7–10], water purifier [11,12], catalysts [13], electromagnetic interface shielders [14].

MXenes are usually prepared by chemical etching method using layered ternary carbides, carbonitrides and nitrides (known as MAX phases) as the starting materials [15–17]. Employing the HF or fluorides salts as the etching reagents, A layers (elements from the group 13 and 14) of MAX phases are selectively removed by breaking the M-A metallic bond. When the A layers are extracted, surfaces of $M_{n+1}X_n$ layers are terminated by functionalities such as –O, –F or –OH [18]. Ti_3C_2 MXene is the first MXene material prepared by chemical etching method [5], and probably the most studied MXene. Many MXenes, such as Nb_4C_3, V_2C, Zr_3C_2, Nb_2C, Ti_4N_3, Mo_2TiC_2, $Mo_2Ti_2C_3$, Cr_2TiC_2, Ta_4C_3, $(Ti_{0.5}Nb_{0.5})_2C$, $(V_{0.5}Cr_{0.5})_3C$, Ti_3CN, have been prepared by the similar chemical etching method [10,19–23].

Since HF etching is a most widely used method to synthesize the MXenes, it is of great importance to study the effect of the etching temperature on the structure, morphology and electrochemical properties of MXenes. Ball milling method is a facile strategy used for the preparation of 2D nanosheets [24,25]. However, as far as we know, there is no investigation of the ball milling on the preparation and electrochemical properties of MXenes.

In the present work, Ti_3C_2 MXene is prepared by the combination of the ball milling method and HF etching process. The effects of etching temperature and ball milling duration on the preparation and capacitance of Ti_3C_2 MXene are studied. The results demonstrate that relatively higher etching temperature and longer ball

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milling duration lead to faster conversion of Ti_3C_2 MXene. Meanwhile, it is found that ball milling treatment can improve the capacitance performance of Ti_3C_2 MXene. The present study is important for the scale-up production of Ti_3C_2 MXene with high electrochemical performance.

2. Experimental procedures

2.1. Low-energy ball milling of Ti_3AlC_2 powder

Ball milling of Ti_3AlC_2 powder was performed on a horizontal planetary ball mill with a rotation speed of 100 rpm. In a typical procedure, 4 g Ti_3AlC_2 powder (98%, Forsman company, Beijing, China) and 30 mL deionized water were mixed and transferred to a 500 mL glass bottle with zirconia balls (1–2 mm in diameter). The glass bottle was sealed and filled with Ar gas to avoid contamination of Ti_3AlC_2. The milling duration was set to 3 h and 12 h, respectively.

2.2. Preparation of Ti_3C_2 MXene

Ti_3C_2 MXene was prepared by HF etching process. In detail, 4 g of the ball milled Ti_3AlC_2 powder was slowly added into 40 mL of 40% HF aqueous solution (Macklin Chemical, Shanghai, China). Then the suspension was stirred at different temperatures (35 °C and 60 °C) for different time. After that the suspension was washed for several times with deionized water until a pH value of approximately 6 was reached. Finally, the product was separated from the supernatant suspension by centrifugation and then dried at 60 °C for 12 h in vacuum. For comparison, the pristine Ti_3AlC_2 powders were also etched at different temperatures (6 °C, 25 °C, 35 °C, and 60 °C) using the same procedure.

2.3. Material characterization

The crystal structures of the as-prepared samples were investigated by X-ray diffraction (XRD) on a powder diffractometer (Bruker D8 Davinci, Germany) using Cu K_α radiation. The high-resolution images of samples were obtained using a field emission scanning electron microscopy (FESEM, Hitachi S-4800, Tokyo, Japan). Raman spectra were recorded on a Raman spectrometer (JY HR800, Horiba Jobin Yvon, France) using 514.5 nm laser excitation. Nitrogen adsorption-desorption isotherms were measured at 77 K on an Autosorb iQ Station 1 (Quantachrome Instruments, FL, USA) and the samples were outgassed in vacuum at 120 °C for 6 h before the test.

2.4. Electrochemical measurement

Electrochemical measurements were carried out in a three-electrode configuration on CHI660E electrochemical workstation (CH Instruments, Shanghai, China). Working electrodes were fabricated by a convention process. Typically, the as-prepared Ti_3C_2 MXene, acetylene black, and polytetrafluoroethylene (PTFE, 60 wt% in H_2O, Aldrich) binder in a mass ratio of 80: 10: 10 were mixed using an agate mortar. Successively, the mixture was pressed onto nickel foam (1 × 1 cm) at a pressure of 20 MPa for 20 s, and dried at 60 °C for 12 h in vacuum. The loading mass of active material on nickel foam was 4.5–5 mg/cm^2. Platinum foil (1 × 1 cm) and Ag/AgCl/3 M KCl were used as the counter and reference electrodes, respectively. All the electrochemical measurements were performed in 6 M KOH electrolyte solution at room temperature. Cyclic voltammetry (CV) was measured at different scan rates (5, 10, 20, 50, 100, and 200 mV/s) in the voltage window of −1 to −0.4 V. Galvanostatic charge/discharge (GCD) measurements were conducted at different current densities (0.2, 0.5, 1, 2, 5, and 10 A/g) in the potential range −1 to −0.4 V. Electrochemical impedance spectroscopy (EIS) was conducted at open circuit voltage with an amplitude of 5 mV, within the frequency domain of 10 mHz–100 kHz.

The specific capacitance (C_s, F/g) is calculated from the CV curve using equation [26]:

$$C_s = \frac{\int IdV}{mv\Delta V} \tag{1}$$

where I (A) is the charging or discharging current, m (g) is the mass of active material, v (V/s) is the scan rate, ΔV (V) is the voltage window.

The specific capacitance (C_s, F/g) also can be calculated from the GCD curve using equation [26]:

$$C_s = \frac{I\Delta t}{m\Delta V} \tag{2}$$

where I (A) is the discharging current, Δt (s) is the discharge time, m (g) is the mass of active material, ΔV (V) is the voltage window.

3. Results and discussion

The XRD patterns of samples prepared by HF etching pristine Ti_3AlC_2 at 6 °C for different time are shown in Fig. 1(a). For comparison, the XRD pattern of the Ti_3AlC_2 powder is also illustrated. There is no obvious difference in XRD pattern between sample obtained by etching for 24 h and pristine Ti_3AlC_2. Increasing the etching time to 36 h, the (0 0 2) and (0 0 4) peaks of Ti_3AlC_2 at $2\theta = 9.78°$ and 19.47° bifurcated into two peaks, indicating the appearance of Ti_3C_2 MXene. The peaks at the original position correspond to Ti_3AlC_2. The peaks shifting to low angle are assigned to Ti_3C_2 MXene [5]. Further increasing the etching time to 96 h, the intensities of the diffraction peaks of Ti_3AlC_2 are decreased. The characteristic (1 0 4) peak of Ti_3AlC_2 at $2\theta = 39.18°$ can also be observed, indicating that the Ti_3AlC_2 cannot completely react with HF to form Ti_3C_2 even etching for long time when the etching temperature is low.

Fig. 1(b) shows the XRD patterns of samples prepared by HF etching pristine Ti_3AlC_2 at 25 °C for different time. For samples obtained by etching for 24 h and 48 h, the XRD patterns show the existence of both Ti_3AlC_2 and Ti_3C_2 MXene. The intensities of Ti_3C_2 MXene peaks are further increased by increasing the etching time from 24 h to 48 h. When the etching time increases to 72 h, the characteristic (1 0 4) peak of Ti_3AlC_2 at $2\theta = 39.18°$ disappears, and the diffraction peaks of Ti_3C_2 MXene become much stronger, implying that the Ti_3AlC_2 is completely converted into Ti_3C_2 MXene.

The etching temperature is further increased to 35 °C and 60 °C, and the XRD patterns of as-prepared samples are shown in Fig. 1(c) and (d), respectively. It is found that pure Ti_3C_2 MXene can be obtained after 48 h when the etching temperature is 35 °C. At 60 °C, the etching time can be significantly decreased to 24 h. Based on the XRD results shown in Fig. 1, it can be concluded that the etching temperature influences the elimination kinetics of Al layers from Ti_3AlC_2. High etching temperature is favorable for the preparation of Ti_3C_2 MXene in shorter time.

The ball milling method is demonstrated to be an efficient way for the preparation of 2D nanosheets by breaking the weak Van Der Waals interactions between layers [24–27]. In this work, the ball milling method is investigated for the preparation of Ti_3C_2 MXene. Briefly, before the HF etching step, the pristine Ti_3AlC_2 powder is first ball milled for different duration using a low-energy ball