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Improved capacitance of nitrogen-doped delaminated two-dimensional titanium carbide by urea-assisted synthesis

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ABSTRACT

Two-dimensional transition metal carbides (MXenes) were recently emerged as promising electrode materials for energy storage applications. Herein, we report a high-capacity supercapacitor material based on nitrogen-doped delaminated titanium carbides (N-d-Ti_3C_2) synthesized through the facile urea-assisted delamination of large-scale Ti_3C_2 and carbonization of delaminated Ti_3C_2 (d-Ti_3C_2) mixed with urea. The two-dimensional N-d-Ti_3C_2 nanosheets exhibit a high specific capacitance of 266.5 F g^{-1} at the scan rate of 5 mV s^{-1} in 6 M KOH electrolyte solution, with a high capacitance retention capability. This new type of nitrogen-doped delaminated titanium carbide could be a promising electrode material for high-performance supercapacitors.

1. Introduction

Supercapacitors (SCs) have attracted considerable attention as energy-storage sources, due to their high power density, fast charge-discharge ability, excellent reversibility, and long cycling life [1–5]. Two charge storage mechanisms have been observed in SCs so far. One is known as electrical double-layer capacitors (EDLCs). The capacity of EDLCs is resulted from the electrosorption/desorption of ions on the surface of electrode materials, such as activated carbon, carbon nanotubes, graphene, and carbon-based active materials [2,6–9]. The other one is known as pseudocapacitors (PCs), because highly reversible redox reaction can contribute to the capacity at/near the surface of active materials. Typical pseudocapacitive materials include transition metal oxides [10,11], conductive polymers [3,12], and a kind of carbon based materials with rich oxygen- and nitrogen-containing surface groups, which provide exceedingly high capacitance than the EDLCs by at least 2 times [13–16].

Recently, MXenes emerged as a novel two-dimensional (2D) materials with potential applications as electrode materials [17,18], because of layered structure, relatively large surface area, high electroconductivity, remarkable chemical durability, hydrophilic property, and environment-friendly characteristics [17,19,20]. Until now, Ti_3C_2 as one of this MXenes family members, have been extensively studied as promising electrode materials for Li-ion batteries [21,22], supercapacitors [23,24], and biosensors [18,25]. Although Ti_3C_2 as electrode material in SCs showed a capacity up to 98 F g^{-1} [23], the restacking Ti_3C_2 nanosheets have a relatively low surface area than other carbon materials [26,27]. Therefore, it is expected that the performance of Ti_3C_2 can be further enhanced by delaminating the restacking flakes, adjusting the surface functional groups, or introducing extra carbon element [20,28,29]. Delamination can be used to increase surface area of materials by more than 6 times, which has been applied to electrodes of supercapacitors in particular [30]. A flexible additive-free delaminated Ti_3C_2 'paper', with an excellent volumetric capacitance, has been produced by filtering its colloidal solutions in water, which were obtained by using simple sonication [31]. Delaminated Ti_3C_2 electrodes containing carbon nanotubes have also been reported, showing noteworthy performance in aqueous supercapacitors [20,32].

To further improve the performance of SCs, introducing pseudocapacitive characteristics into the electrode materials is a vital strategy [33,34]. For example, it is an effective method that heteroatoms (such as nitrogen, boron, sulfur) have been incorporated into the carbon based materials to enhance their electrochemical performances [34,35]. It has been demonstrated that nitrogen functionalized carbon-based materials not only have improved surface wettability and electronic conductivity, but also can be used as electrode materials for high-performance SCs [26,33,36].

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Herein, we report a simple and controllable method to prepare 2D nitrogen-doped delaminated titanium carbide (N-d-Ti_3C_2), with urea as intercalant and nitrogen source, in order to develop MXene-based supercapacitor with an improved performances. The as-obtained N-d-Ti_3C_2 shows a 2D layered structure, relatively high surface area, favorable mesopores, appropriate N content and high conductivity. These results indicate that the as-prepared N-d-Ti_3C_2 exhibits beneficial electrochemical performances as electrodes of supercapacitors, especially, a relatively high specific capacitance, good rate performance and cycling stability, when compared with the popular N-containing carbon based materials reported in the open literature. Furthermore, all precursors used in this process either can be synthesized at large-scale or are commercially available, which ensures scale-up capability for industrial applications.

2. Experimental

2.1. Instrumentation and Chemicals

Scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDAX) was usually employed in the analysis of microstructure and elements by using a JSM-6390 (JEOL Inc., Japan). Transmission electron microscopy (TEM, JEM-2010, JEOL Inc., Japan) was used to further observe the morphology of the samples. X-ray diffraction (XRD) patterns of samples were tested by using a Rigaku D/max 2200 pc diffractometer with Cu Kα radiation, and the XRD data were analyzed by using the Jade 5.0 softwave. Raman spectroscopic measurements were performed by using a LabRam Aramis Raman spectrometer with a He-Ne laser (λ = 633 nm). X-ray photoelectron spectroscopy (XPS) measurements were fulfilled by utilizing a VG Thermo ESCALAB 250 spectrometer with an exciting source of Al Kα. Nitrogen sorption isotherms were measured by using an automatic N_2 adsorption/desorption instrument (ASAP 2460, Micromeritics Inc., USA) at 77 K and the samples need be outgassed in vacuum at 200 °C for 3 h before test. Specific surface areas of the nanopowders were calculated by using the Brunauere Emmette Teller (BET) method. Pore size distributions were obtained from the desorption branch using the Barrette Joynere Halenda (BJH) model. Except as otherwise specified, all the chemicals with analytical grade were bought from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water was used in all experiments.

2.2. Synthesis of Nitrogen-doped Delaminated Ti_3C_2

Ti_3C_2 was typically prepared by etching Ti_3AlC_2 in HF at ambient temperature to remove Al (see Supporting Information) [18,37]. The main synthesis process of the nitrogen-doped delaminated Ti_3C_2 is illustrated in Fig. 1. Firstly, the delaminated Ti_3C_2 (d-Ti_3C_2) was synthesized by a simple intercalation and delamination in liquid. For intercalation, 600 mg of Ti_3C_2 were mixed with 10 mL of 50 wt.% aqueous solution of urea. The mixture was then magnetically stirred for 24 h at 60 °C. For delamination, deionized water were added to the resulting solutions to 200 mL. After bath sonication of the suspension for 6 h, the precipitate was collected by centrifugation, which was rinsed sequentially with ethanol for 3 times and deionized water for 3 times. Then, the powders were dried in the vacuum oven at 80 °C for 24 h. For nitrogen functionalization, the dried d-Ti_3C_2 nanopowders were mixed with urea of the same quality, and then annealed in an alundum tube in N_2 at a flow of 200 mL min^{-1}. Carbonization was conducted at 500 °C for 3 h at a heating rate of 2 °C min^{-1} to obtain the nitrogen-doped delaminated Ti_3C_2 (N-d-Ti_3C_2). For comparison, Ti_3C_2 without delamination was also annealed with urea under the same conditions to obtain the nitrogen-doped Ti_3C_2, which its SEM images are shown in Fig. S1.

2.3. Electrochemical Measurements

All electrochemical testing was carried out by using a CHI 660E electrochemical workstation (CH Instruments, Shanghai, China) at ambient temperature. In a traditional three-electrode setup, a platinum plate (1 × 1 cm^2) was applied as the counter electrode, an Ag/AgCl/3 M KCl electrode as the reference electrode, and the Ti_3C_2 based active material as the working electrode. The working electrode was fabricated by pressing a mixture of 85 wt.% active material, 10 wt.% acetylene black, and 5 wt.% polyvinylidene fluoride (PVDF) onto a piece of nickel foams (1 × 1 cm^2) under a pressure of 20 MPa for 1 min. The as-prepared working electrodes were dried in a vacuum oven at 80 °C for 12 h. Mass loading of active material in each current collector was about 1.8 mg cm^{-2}. 6 M KOH solution was employed as electrolyte for all the electrochemical measurements. Cyclic voltammograms (CVs) were acquired in the potential range from −1.0 V to −0.4 V at a sweep rate from 5 mV s^{-1} to 200 mV s^{-1}. Galvanostatic charge-discharge (GCD) measurements were performed at a current density from 0.2 A g^{-1} to 10 A g^{-1}, over potential range between −1.0 V and −0.4 V. Galvanostatic cycling testing was performed at 2 A g^{-1} at the same potential window. Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential, with a 5 mV amplitude, at frequencies ranging from 10 mHz to 100 kHz.

3. Results and discussion

As shown in Fig. 2a, the Ti_3C_2 sample has an accordion-like layered morphology. After delamination, relatively thin lamellas of the Ti_3C_2 layers is apparently glued together by the intercalant as shown in Fig. 2b. After nitrogen doping, a number of nanoparticles or small nanosheets can be observed on the thin Ti_3C_2 lamellas (Fig. 2c). From Fig. 2d–f, it can be also observed that the Ti_3C_2 nanolayers are derived from a restacked layered structure, leading to perfect nanoscale lamellas, and rough carbonized lamellas. Meanwhile, as evidenced by the inset of Fig. 2f, the N-d-Ti_3C_2 sample has a 2D hexagonal structure. To confirm the presence of N between the layers, energy dispersive spectroscopy (EDS)

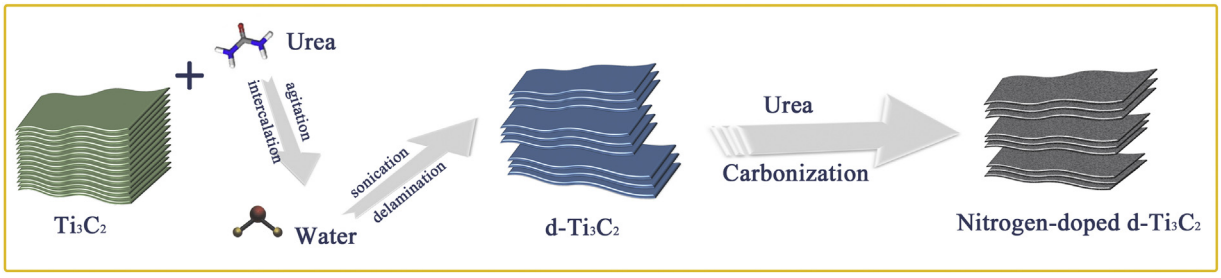

Fig. 1. Schematic illustration of the synthesis process of the nitrogen-doped delaminated Ti_3C_2 nanosheets.