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MXene-coated silk-derived carbon cloth toward flexible electrode for supercapacitor application

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ABSTRACT

Flexible supercapacitors are promising energy storage devices in wearable smart electronics. Exploring cost-efficient electrodes with high capacitance would promote the wide-scale application of such capacitors. Herein, in order to explore a methodology for preparing low cost, flexible, tough, and up-scalable supercapacitor electrodes, silk textile is directly carbonized to make a conductive free-standing textile substrate. Through mildly baking the surfactant-free $Ti_3C_2T_x$ flakes suspension loaded on the carbonized silk cloth, a uniform and adhesive coating consisting of nanometer-thick $Ti_3C_2T_x$ flakes is well established on the conductive fabric support, forming a MXene-coated flexible textile electrode. The fabricated electrode exhibits a high areal capacitance of 362 mF/cm^2 with excellent cyclability and flexibility. Moreover, capacitance changes neglegibly under the bending deformation mode. This study elucidates the feasibility of using silk-derived carbon cloth from biomss for MXene-based flexible supercapacitor.

1. Introduction

Nowadays, the demand for flexible, wearable, and even implantable electrical devices, such as intelligent bracelets, wearable sensors, implantable clinical devices, and electric pills, has led to an upsurge in the development of corresponding energy storage systems for power supply [1–5]. Supercapacitors, also known as electrochemical capacitors, as energy storage devices with high power density and long cycle life, have attracted great attention [6,7]. Great efforts have been dedicated to fabricating flexible electrodes of supercapacitors [8], which are generally made from carbon-based materials like carbon nanotube [9,10], graphene [11] and analog as well [12]. However, they are limited to the chemistry of carbon, do not tap into metal redox reactions as in ruthenium oxide (RuO_2), and their electrical conductivity is substantially decreased by the addition of redox-active functional groups [13].

In search for alternatives, MXenes, a recently explored two dimensional materials family of early transition metal carbides and carbonitrides, have shown much promise in electrochemical energy storage applications [14–18], especially in supercapacitor electrodes [19–23]. $Ti_3C_2T_x$ is the most widely studied MXene to date. It was usually obtained by selectively etching off the Al element from Ti_3AlC_2, a layered ternary carbide among a family referred to as MAX phases [24]. At the expense of removing the Al element layers, the Ti_3C_2 layers left in the etchants are spontaneously terminated with O, F, OH, or H groups, giving a general formula $Ti_3C_2T_x$, where T_x stands for a general surface termination [25]. Due to their metallic conductivity [26], hydrophilic nature, and excellent ion intercalation behavior, MXenes have proven to be promising candidates for supercapacitors with high capacitance exceeding most previously reported materials. Recent results also showed that $Ti_3C_2T_x$ is suitable for fabricating flexible electrodes. For instance, MXene-on-paper supercapacitors made by Meyer rod coating of MXene slurry on commercially available printing paper showed the areal capacitance of 25 mF/cm^2 and can be foldable [27]. The flexible electrode based on MXene nanosheets and electrochemically exfoliated graphene delivered an areal capacitance of 3.26 mF/cm^2 with excellent flexibility [28]. The freestanding polypyrrole/$Ti_3C_2T_x$ film has also been demonstrated [29]. However, their very low capacitances, expensive cost and complex synthesis processes limit the further development for flexible purpose. As the self-supported MXene films are used as flexible electrodes, they are not mechanically tough enough to suffer from bending

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cycle for a long time. Thus, exploring flexible MXene-based electrodes that have simultaneously both high capacitance and high mechanical strength remains challenging.

Carbon-based materials from natural biomaterials have received extensive interests owing to their good electrical conductivity, large-scale, and low-cost production capability as well as environmental benignity [30]. Silk, as a kind of widely used natural material, is composed of sericin and fibroin, among which fibroin is the major component and consists of repetitive crystalline heavy chains (forming discrete β-sheet crystallites) and noncrystalline light chains (forming amorphous domains). Silk fibroin has been reported to transform into graphitic nanocarbon by thermal treatment because of the fact that the β-sheet crystallites in the silk polypeptides could be aromatized or cyclized into sp^2-hybridized carbon structure [31]. It has been reported that carbonized silkworm cocoon or regenerated silk fibroin, showed good electrical conductivity [32,33]. We surmised that carbonized silk fibers, based on their unique carbon nanoplate structures, might work as conductive substrates. Silk fiber with the advantages of outstanding mechanical performance, high resilience, and large-scale production, has been widely used as raw material in textile and clothing around the world for thousand years [34,35]. The output of the silk fabric amounts to 132.9 ktonne in the first 10 months of 2015 [36]. This means definitely that there is a huge amount of discarded silk textile leaving unused. Therefore, it is environmental friendly to reuse this biomass by converting the discarded silk textile into conductive carbon fiber cloth working as a flexible current collector for MXene. However, the application of carbonized silk cloth (CSC) in preparing free-standing electrode for energy storage devices has never been reported before, to the best knowledge of the present authors.

In this paper, we report the fabrication of a low cost, flexible, and up-scalable supercapacitor electrode for wearable smart electronics. In the electrode, a uniform and adhesive coating consisting of nanometer-thick $Ti_3C_2T_x$ flakes is well established on the conductive CSC support. The fabricated electrode exhibits a high areal capacitance of 362 mF/cm^2 with excellent cyclability and flexibility, and capacitance changes negligibly under the bending deformation mode.

2. Experimental

2.1. Carbonization of silk textile

Commercially available silk fabrics were utilized as raw materials. The fabrics were rinsed in alcohol to remove the contamination from the fabric surface, followed by drying. The dried fabrics were subjected to carbonization in a mixed atmosphere of argon (95%) and hydrogen (5%) in a quartz tube furnace. The gas flow is 200 sccm. The heating schedule is: (i) heat from room temperature up to 350 °C at a rate of 5 °C/min and keep for 1 h; (ii) then heat up to 800 °C at a rate of 2.5 °C/min and keep for 4 h; (iii) naturally cool the system to room temperature. The as-obtained CSCs were then cut into rectangular strips for further treatment.

2.2. Synthesis of $Ti_3C_2T_x$ MXene

The preparation of porous Ti_3AlC_2 monolith used in this work followed the previously reported method by means of solid–liquid reaction [37]. The as-prepared monolith was drilled into powders (1.5 g) and poured carefully into a solution (HCl 6 mol/L, 20 mL) containing LiF (1.0 g). Note that the Ti_3AlC_2 powders were added over a time period of 5 min to avoid initial overheating of the solution due to the exothermic nature of the reaction between Ti_3AlC_2 and the solution. After 20 days, the resulting particulates were separated by vacuum filtration with a porous membrane filter (0.22 μm pore size) and washed with deionized water until the pH of the supernatant reached approximately 4.0. The separated wet sediment was immersed in deionized water, after which the mixture was sonicated in a pulse mode for 1 h by an ultrasonic homogenizer (JY96-IIN, Scientz).

2.3. Fabrication of CSC@$Ti_3C_2T_x$ electrodes

The CSC strips were exposed to oxygen plasma for 5 min to make them hydrophilic. The $Ti_3C_2T_x$ colloidal suspension was loaded dropwise with a pipette on the CSC strip that was placed on a hot plate kept at 50 °C. To prevent the hot plate surface from contamination, a hydrophobic polytetrafluoroethylene film was placed between the CSC and the hot plate. Upon mild baking, water in the suspension evaporated and the remaining flakes self-assembled into a coating on the fibers of the CSC. The mass of the $Ti_3C_2T_x$ was determined by measuring the weight change after the mild baking.

2.4. Characterization and electrochemical measurements

Three-dimensional (3D) confocal microscopy images were recorded on a 3D measuring laser microscope (LEXT OLS4000, Olympus) with a light source of 405 nm. Microstructural characterization was conducted on a scanning electron microscope (LEO Supra35, Zeiss) working at an accelerating voltage of 20 kV. The electrochemical performance was evaluated using a three-electrode test cell at room temperature: CSC or CSC@$Ti_3C_2T_x$ served as the working electrode, platinum was used as the counter electrode, Ag/AgCl in saturated KCl was the reference electrode and 1 mol/L H_2SO_4 was the electrolyte. Cyclic voltammogram (CV), electrochemical impedance spectroscopy (EIS) measurements were all performed on an electrochemical workstation (PARSTAT 2273, Princeton Applied Research). The voltage ramp rates ranged from 2 to 50 mV/s. EIS spectra were recorded from 100 kHz to 10 mHz at 0 V with an amplitude of 10 mV. For the all-solid-state supercapacitor, the gel electrolyte was prepared by dissolving 10 g of polyvinyl alcohol (PVA) in a solution of 100 mL H_2SO_4 with a concentration of 1 mol/L under vigorous stirring at 90 °C to form a transparent gel. After being coated with the gel electrolyte, two CSC@$Ti_3C_2T_x$ core/shell electrodes were assembled together in a face-to-face manner to produce the capacitor. The CV curves were evaluated using a two-electrode test cell on the electrochemical workstation. The bending of the capacitor was controlled manually.

3. Results and discussion

The preparation process of CSC and CSC@$Ti_3C_2T_x$ electrode is illustrated in Fig. 1. The pristine silk textile used was rinsed in alcohol to clean the fabric surface. After the carbonization of silk textile through a temperature control program (see Section 2), flexible carbon fiber cloth was obtained with a carbon yield of 30% and a 65% contraction. From the scanning electron microscopy (SEM) characterization shown in Fig. S1, the surface of the as-prepared carbon fibers was covered by some impurities which may originate from inorganic salts taken in during their preparation. The impurities can be removed by acid treatment and the fiber surface became clean and smooth (Fig. 2a and b). We all know that silk has excellent mechanical strength [38]. After carbonization, the as-obtained CSCs still have good mechanical properties (Fig. S2). Then, we adopted the solution-processed method [39] to fabricate the CSC@$Ti_3C_2T_x$ electrode. Firstly, the $Ti_3C_2T_x$ MXene was obtained through etching Ti_3AlC_2 in a mixture of HCl and LiF followed by delamination through sonication (Fig. S3). Then, the as-prepared CSCs were exposed to oxygen plasma to decorate them with

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