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Ni foam supported quasi-core-shell structure of ultrathin Ti_3C_2 nanosheets through electrostatic layer-by-layer self-assembly as high rate-performance electrodes of supercapacitors

Yapeng Tian [a, 1], Chenhui Yang [a, 1], Wenxiu Que [a, *], Yucheng He [a], Xiaobin Liu [a], Yangyang Luo [a], Xingtian Yin [a], Ling Bing Kong [b, **]

[a] Electronic Materials Research Laboratory, International Center for Dielectric Research, Key Laboratory of the Ministry of Education, School of Electronic & Information Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, People's Republic of China
[b] School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore

HIGHLIGHTS

- Ni foam supported quasi-core-shell structure of ultrathin Ti_3C_2 nanosheets was prepared.
- FL-Ti_3C_2@NF was prepared by an electrostatic layer-by-layer self-assembly method.
- Binder-free FL-Ti_3C_2@NF exhibited a specific capacitance of 370 F g^{-1} at 2 mV s^{-1}.
- A high rate performance at 1000 mV s^{-1} was obtained in the 1 M Li_2SO_4 electrolyte.
- The capacitive contribution was calculated to understand the underlying mechanism.

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ABSTRACT

Supercapacitor, as an important energy storage device, is a critical component for next generation electric power system, due to its high power density and long cycle life. In this study, a novel electrode material with quasi-core-shell structure, consisting of negatively charged few layer Ti_3C_2 nanosheets (FL-Ti_3C_2) and positively charged polyethyleneimine as building blocks, has been prepared by using an electrostatic layer-by-layer self-assembly method, with highly conductive Ni foam to be used as the skeleton. The unique quasi-core-shell structured ultrathin Ti_3C_2 nanosheets provide an excellent electron channel, ion transport channel and large effective contact area, thus leading to a great improvement in electrochemical performance of the material. The specific capacitance of the binder-free FL-Ti_3C_2@Ni foam electrodes reaches 370 F g^{-1} at the scan rate of 2 mV s^{-1} and a specific capacitance of 117 F g^{-1} is obtained even at the scan rate of 1000 mV s^{-1} in the electrolyte of Li_2SO_4, indicating a high rate performance. In addition, this electrode shows a long-term cyclic stability with a loss of only 13.7% after 10,000 circles. Furthermore, quantitative analysis has been conducted to ensure the relationship between the capacitive contribution and the rate performance of the as-fabricated electrode.

1. Introduction

With the exhaustion of traditional fossil energy and the emergence of clean energy, like wind energy and solar energy, electric energy storage has become an urgent issue to be solved. Supercapacitors (SCs), among the most promising energy storage devices, have attracted extensive research interest, due to their high power density, fast recharge capability and long cycle life [1,2]. Especially, two dimensional (2D) materials-based SCs are a rising star because of their excellent electrochemical performance [3,4].

MXenes, a novel family of transition metal carbides or carbonitrides, have emerged as a newly developed 2D materials in recent years, which exhibited excellent capacitance performance as electrodes of SCs [5–7]. MXenes are usually prepared by selectively

* Corresponding author.
** Corresponding author.
E-mail addresses: wxque@mail.xjtu.edu.cn (W. Que), elbong@ntu.edu.sg (L.B. Kong).
[1] These authors contributed equally to this work.

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etching the layer of A element from MAX ceramic powders, where M represents an early transition metal, A stands for a group of IIIA or IVA elements and X could be carbon and/or nitrogen, which result in the presence of oxygen and fluorine-containing surface function groups (e.g., -O, -OH, and/or -F) [8]. To date, Ti_3C_2, one of the family members of MXenes, has been widely and extensively studied for its unique electrochemical performance in the fields of Li-ion batteries [9–11], supercapacitors [12–16] and biosensors [8,17]. Furthermore, other types of MXenes also have widely studied for the applications in energy storage, such as Nb_2CT_x [18], Ti_2C [15], Nb_4C_3 [11], $Mo_{1.33}C$ [19], Mo_2TiC_2 [7] etc. Few-layer Ti_3C_2 (FL-Ti_3C_2) nanosheets have been obtained by delaminating the multi-layered Ti_3C_2. The d-Ti_3C_2 nanosheets displayed a negatively charged surface due to the presence of -F and -OH surface groups [5,20].

However, in most of reports on Ti_3C_2, high specific capacitances were only observed at low current densities (<1 A/g) in the galvanostatic charge/discharge (GCD) process or low scan rates (<50 mV/s) in the cyclic voltammetry (CV) process, which have defeated the initial purpose - the applications in supercapacitors for high power densities [8,21,22]. This problem is closely related to the non-uniform distribution of Ti_3C_2 on current collectors in the traditional slurry-derived electrode and the restacking of the Ti_3C_2 nanosheets during the preparation process of materials and electrodes [23]. As a consequence, the Ti_3C_2-based electrodes usually do not have adequate transport channels for the access of electrolyte to surface of the active material, thus delivering a relatively slow redox reaction rate and hence low rate performance [24,25]. What's worse, the poor contact among the bulk Ti_3C_2 and binder or the Ti_3C_2 nanosheets leads to an extra electrical resistance [26].

A strategy of combining 3D conductive skeleton and active material has been proposed to improve the material structure stability and electron transport performance, for example, $NiCo_2O_4$ nanosheets supported on Ni foam [27], $NiCo_2O_4$@MnO_2 core-shell heterostructured nanowire arrays on Ni foam [28] and single-crystalline $NiCo_2O_4$ nanoneedle arrays on conductive substrates [29]. Inspired by these achievements, we developed a quasi-core-shell structure with ultrathin Ti_3C_2 nanosheets uniformly distributed on Ni foam. In this case, the non-uniform distribution and the restacking of the Ti_3C_2 nanosheets were effectively prevented, while the effective contact area was increased, so that the transport of electrons was promoted and the electrode materials were fully utilized [30–32]. More importantly, rate performance of the electrodes can be fiercely improved due to the introduction of the highly conductive 3D skeleton and the absence of binders [33]. Therefore, the binder-free Ti_3C_2 based quasi-core-shell structure with less agglomerated and effective electron channel could find practical applications in SCs.

Layer-by-layer (LBL) self-assembly is an effective synthetic technique, which offers both strong non-covalent integration and precise arrangement of homo- or hetero-phase compounds or oppositely charged nanomaterials, resulting in highly-ordered nanoscale structures with excellent functionalities and activities. This technology has been widely utilized to develop various novel materials and nanostructures from nanomanufacturing to nanomedicines [34].

Here, we firstly described the bottom-up strategy to prepare a quasi-core-shell structure in which the ultrathin Ti_3C_2 nanosheets deposited on highly conductive Ni foam (NF) with a controlled thickness. In the LBL self-assembly process, the NFs were alternatively immersed in cationic PEI solution and anionic d-Ti_3C_2 nanosheets suspension. Compared with the d-Ti_3C_2 films and the Ti_3C_2 electrodes prepared by the traditional slurry method (the accordion-like Ti_3C_2), the LBL strategy would provide highly conductive electron channel and relatively large contact area, thus leading to a significant improvement in electrochemical performances.

2. Experimental

2.1. Materials

Unless otherwise mentioned, all the chemicals (analytical grade) were purchased from Shanghai Aladdin Biochemical Polytron Technologies Inc, China. In all experiments, ultrapure water was used.

2.1.1. Preparation of Ti_3AlC_2

Ti_3AlC_2, the precursor of Ti_3C_2, was prepared by using atmosphere sintering method, with mixed powders of TiC (2-4 μm, 99% purity, Aladdin), Al (1-3 μm, 99.5% purity, Aladdin) and Ti (≤48 μm, 99.99% purity, Aladdin) in a molar ratio of 2:1.2:1 about 10 g in each mill pot. The ultimate mixture, including the mixed raw powders, absolute ethanol and the grinding balls with a mass ratio of 1:1:3, was ball-milled for 4 h at a speed of 350 rpm in atmosphere. Then, the mixture was sintered at 1400 °C for 2 h in Ar atmosphere in a tube furnace. The sintered product was further grinded with a mortar to obtain powders and then the milled powder was sieved through a 400 mesh screen, so that the initial particle size was <38 μm.

2.1.2. Preparation of delaminated Ti_3C_2 suspension

Delaminated Ti_3C_2 aqueous suspension was prepared according to the precious work with certain modification [20]. A mixed solution of HCl and LiF was first obtained by slowly adding 2 g LiF to 20 mL 9 M HCl aqueous solution under stirring for 5 min. Then, 2 g as-prepared Ti_3AlC_2 was slowly added, followed by stirring at 35 °C for 24 h at 200 rpm. After that, the mixture was washed several times with ultrapure water, shaken for 2 min and centrifuged at 3500 rpm for 2 min for each cycle, until pH value of the supernatant was >6. The as-prepared Ti_3C_2 sediment after the last centrifugation cycle was dispersed with deionized water up to 200 mL, which was deoxidized by using the vacuum degassing process for 1 h, followed by sonicating for 1 h and centrifuging for 1 h at 3500 rpm. Finally, the supernatant, named as d-Ti_3C_2 aqueous solution, was collected.

2.1.3. Preparation of FL-Ti_3C_2@NF electrode

FL-Ti_3C_2@NF was prepared by using LBL self-assemble method through the electrostatic interactions of positively charged polyethyleneimine (PEI, M_w = 70,000, 50 wt% in water) and negatively charged delaminated Ti_3C_2 nanosheets. 1 mg mL^{-1} PEI solution was obtained by diluting a 50 wt% PEI solution with ultrapure water. 0.5 mg mL^{-1} d-Ti_3C_2 suspension, measured by weighing the dried film after vacuum filtration, was obtained by diluting the prepared d-Ti_3C_2 solution with ultrapure water. Ni foams with a dimension of 1 × 1.5 cm^2 were carefully cleaned with 3 M HCl solution for 30 min to remove the NiO layer on the surface with the assist of ultrasonication and then washed with ultrapure water and absolute ethanol several times. Then, the NFs were alternately soaked in the cationic (PEI) solution and the anionic (FL-Ti_3C_2 nanosheets) suspension for 1 min. The excess adsorbed material (PEI and FL-Ti_3C_2 nanosheets) was removed by rinsing with ultrapure water for several times. The mass of the FL-Ti_3C_2 nanosheets assembled on surface of the NFs was precisely controlled by changing the number of the bilayers. Finally, the obtained FL-Ti_3C_2@NF samples were dried in a vacuum oven at 60 °C. The mass load of the FL-Ti_3C_2 nanosheets on the NFs was about 0.2 mg cm^{-2}.