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Reduced graphene oxide bridged, TiO_2 modified and Mn_3O_4 intercalated $Ti_3C_2T_x$ sandwich-like nanocomposite as a high performance anode for enhanced lithium storage applications

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ABSTRACT

$Ti_3C_2T_x$, a novel two-dimensional metal carbide, is regarded as a promising candidate for lithium-ion batteries (LIBs) due to its unique layered structure, good conductivity and low barrier for Li^+ diffusion. However, $Ti_3C_2T_x$ has low capacity and poor rate capability due to the severe interlayer stacking and functionalization group of hydroxyl, oxygen or fluorine existing in $Ti_3C_2T_x$ particles, limiting its widespread applications. Herein, we have firstly offered a relatively simple and rapid synthetic method to fabricate a 3D quaternary $rGO/TiO_2/Mn_3O_4/Ti_3C_2T_x$ nanocomposite as LIBs anode material. $Ti_3C_2T_x$ acts as a conductive framework to enhance the electronic transport properties. Besides, this unique layered structure contributes partially to the enhancement of the total theoretical capacity of the active material. Mn_3O_4 functions as the dominant part of the active material to contribute an extraordinarily high theoretical capacity. TiO_2 nanoparticles and rGO nanosheets can effectively shorten the electron/ion diffusion channels and construct a highly conductive matrix for the fast transfer of electron and Li^+. Meanwhile, both of them can also efficaciously buffer the volume change effect during lithiation/delithiation process. As expected, $rGO/TiO_2/Mn_3O_4/Ti_3C_2T_x$ material has presented significantly outstanding lithium ion storage capabilities, high Coulombic efficiency, excellent long-term cyclability and superior rate capability. For an example, the $rGO/TiO_2/Mn_3O_4/Ti_3C_2T_x$ anode exhibits high specific capacity of 887.2 mA h g^{-1} at 0.05 A g^{-1}, almost 2.2 times as much as that of raw $Ti_3C_2T_x$ anode (404.9 mA h g^{-1}). Even after 100 cycles at a current density of 0.5 A g^{-1}, the $rGO/TiO_2/Mn_3O_4/Ti_3C_2T_x$ anode can still deliver a capacity of 221.5 mA h g^{-1}. Thus the $rGO/TiO_2/Mn_3O_4/Ti_3C_2T_x$ anode can be ascribed to have a novel 3D sandwich-like collective benefit from the 0D/2D/3D particles/sheets/layers nanoarchitecture and can be used as a promising anode material for high performance LIBs.

1. Introduction

Lithium ion batteries (LIBs) are currently considered as the dominant power source owing to long cycle life, high energy density, and environmental benignity [1–5]. Graphite has been used as the most important commercial lithium ion anode material for a long time. However, poor rate performance, serious safety problems and low theoretical capacity (372 mA h g^{-1}) have limited its further application [5–9]. In recent years, a two-dimensional layered structured material of $Ti_3C_2T_x$ has been applied in many areas, such as LIBs [4,5,7–11], supercapacitors [12,13], photocatalysis [14], etc. Theoretical studies have indicated that the Li diffusion within the graphite interlayers needs to overcome a relatively high energy barrier of 0.3 eV. However, $Ti_3C_2T_x$ monolayer exhibits a much lower barrier for Li diffusion (the predicted diffusion barrier is 0.07 eV for Ti_3C_2). The exceptional properties, including unique layered structure similar to that of graphite, good electronic conductivity, fast Li diffusion and low operation voltage (~0.2 eV), make $Ti_3C_2T_x$ a promising anode material for Li ion batteries [15–18]. $Ti_3C_2T_x$ is commonly synthesized by selectively etching the Al element layers with hydrofluoric acid from Ti_3AlC_2. Surface functional groups (T_x) of hydroxyl, oxygen or fluorine

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terminate the Ti_3C_2 surface in the exfoliation process. Unfortunately, the existence of functionalization groups leads to a high diffusion barrier and decreased conductivity to a certain degree, particularly in the *c*-lattice direction, limiting its full utilization. In addition, the large interlayer spaces in the vertical-to-layer direction of $Ti_3C_2T_x$ particles also cause a slight decrease in the bulk electrical conductivity [15,16]. In addition, widespread interlayer stacking is often observed to exist in $Ti_3C_2T_x$ particles, which greatly hinders the accessibility of interlayers to electrolyte ions. Recent researches indicate that the electrical conductivity of $Ti_3C_2T_x$ depends on the sample preparation method. The conductivity of $Ti_3C_2T_x$ ranges from less than 1000 S cm^{-1} for HF-etched powders to 6500 S cm^{-1} for delaminated vacuum filtered films. These values exceed those of other solution-processed materials, including graphene [5]. Density functional theory (DFT) calculations have predicted that the corresponding theoretical specific capacity of Ti_3C_2, $Ti_3C_2F_2$ and $Ti_3C_2(OH)_2$ are 320, 130, and 67 mA h g^{-1}, respectively [17,18], limiting the application of $Ti_3C_2T_x$ as an anode material for lithium ion batteries. Therefore, it is urgently needed to develop novel $Ti_3C_2T_x$-based composites.

Metal oxides like Co_3O_4 [2,3,19], SnO_2 [20–22], Fe_2O_3 [23] and Mn_3O_4 [24–27] have been attractive anodes due to their high theoretical capacities. Among them, Mn_3O_4 is a promising modifier because of its great natural abundance, environmental benignity and high theoretical capacity (936 mA h g^{-1}). Unfortunately, the main limiting factors to its practical application for LIBs are extremely low electrical conductivity (~10^{-7} to 10^{-8} S cm^{-1}), large volume expansion and pulverization occurring during lithiation/delithiation process, which lead to a drastic reduction in capacity retention, poor cycling performance and rate capability [26–38]. To overcome these shortcomings, an effective way is to combine Mn_3O_4 into composites with lightweight and electronically conducting materials, such as carbon [28–31], carbon nanotubes [32,33], graphene [34–38], polymer [39], etc.

Intriguingly, titanium dioxide (TiO_2) has features such as low cost, low volume change (only ~4%), excellent cycling stability and high environmental compatibility [40–43]. It has been reported in the previous literatures that TiO_2 as an appealing additive has exhibited excellent electrochemical performance by the growth of TiO_2 branches on Fe_2O_3 [42], Co_3O_4 [43] and Mn_3O_4 [40,41] advanced anode nanomaterials. In these composites, Fe_2O_3, Co_3O_4 and Mn_3O_4 as typical transitional metal oxides offer a high theoretical capacity but suffer from severe volume change that the issue could be effectively addressed by the growth of TiO_2 on their surface because of the small volume change. Fortunately, $Ti_3C_2T_x$, a compound of titanium and carbon, affords a natural platform to grow TiO_2 nanoparticles. Naguib et al. [44] have reported that an oxidation of laminar $Ti_3C_2T_x$ resulted in TiO_2 nanocrystals decorated on disordered carbon sheets, making the product a good LIB anode material.

$Ti_3C_2T_x$ has large inner surface area to provide plenty of lithium storage space and enhance the fast transfer of Li^+. Simultaneously, Ti_3C_2 has good electrical conductivity. Hence, Ti_3C_2 was chosen as a 2D substrate, meanwhile several measures were taken to improve its electrochemical performance in this work. An effective strategy by introducing spacers between the $Ti_3C_2T_x$ layers is adopted to directly improve the electrochemical performance of multi-stacked $Ti_3C_2T_x$ particles. rGO nanosheets bridge the gap between $Ti_3C_2T_x$ interlayers, providing effective conductive pathways to effectively facilitate rapid diffusion and transport among $Ti_3C_2T_x$ flakes, forming a 3D conductive network. Herein, we firstly conceive a new concept to design and fabricate reduced graphene oxide bridged, TiO_2 modified and Mn_3O_4 intercalated $Ti_3C_2T_x$ hybrid sandwich-like nanocomposite via a simple hydrothermal process.

Herein, we firstly conceive a new concept to design and fabricate reduced graphene oxide bridged, TiO_2 modified and Mn_3O_4 intercalated $Ti_3C_2T_x$ hybrid sandwich-like nanocomposite via a simple hydrothermal process. In this 3D rGO/TiO_2/Mn_3O_4/$Ti_3C_2T_x$ nanostructure, each component plays unique, indispensable and different roles. $Ti_3C_2T_x$ has large inner surface area to provide plenty of lithium storage space and enhance the fast transfer of Li^+. Simultaneously, $Ti_3C_2T_x$ has good electrical conductivity. Hence, $Ti_3C_2T_x$ was chosen as a 2D substrate to enhance the electronic transport properties. Besides, this unique layered structure contributes partially to the enhancement of the total theoretical capacity of the active material. Mn_3O_4 functions as the dominant part of the active material to contribute an extraordinarily high theoretical capacity. TiO_2 nanoparticles and rGO nanosheets can potentially construct a conductivity network and effectively buffer the volume change effect. Furthermore, rGO nanosheets bridge the gap between $Ti_3C_2T_x$ interlayers, providing effective conductive pathways to effectively facilitate rapid diffusion and transport among $Ti_3C_2T_x$ flakes, forming a 3D conductive network. As expected, rGO/TiO_2/Mn_3O_4/$Ti_3C_2T_x$ anode material can display significantly outstanding lithium ion storage capabilities, high Coulombic efficiency, excellent long-term cyclability and superior rate capability. Fig. 1 schematically illustrates the typical 3D nanostructure. Firstly, 2D-layered $Ti_3C_2T_x$ is formed by wet HF treatment of inexpensive Ti_3AlC_2 (step 1), then TiO_2 and Mn_3O_4 nanoparticles branch on $Ti_3C_2T_x$ matrix (step 2). Whereafter the rGO nanosheets are deposited on TiO_2/Mn_3O_4/$Ti_3C_2T_x$ nanocomposite (step 3).

2. Experimental section

Ti_3AlC_2 powders (>98 wt%, −325 mesh) were supplied by the Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, China. Natural flake graphite (45 mm, 99.95%) was provided by XFNANO Materials Tech Co., Ltd, Nanjing, China. All of the other chemical reagents were of analytical reagent grade and used without further purification. And all the aqueous solutions were prepared using distilled water.

1 g Ti_3AlC_2 particles were immersed into 20 mL 49–51% HF solution at room temperature for 24 h to exfoliate the Al layers. Then the resulting powders were repeatedly rinsed by distilled water until pH value of the solution reached ~6. The obtained sediment was allowed to desiccate under vacuum at 90 °C for 24 h. A rudimentary yield by mass was 88%.

Graphite oxide (GO, concentration: 1 mg mL^{-1}) was prepared from the natural flake graphite prepared by a modified Hummers method [6,36,45]. Certain amount of MnO_2 powders (e.g., 0.1 g) were well dispersed in 15 mL of distilled water, and the suspension was stirred for 0.5 h. Then the 0.5 g $Ti_3C_2T_x$ powders were dispersed into the MnO_2 suspension and stirred for another 0.5 h. Subsequently, 10 mL of GO solution (0.01 g) was added dropwise into $Ti_3C_2T_x$/MnO_2 mixture suspension under ultrasonication for 0.5 h. Then the suspension containing the rGO, MnO_2 and $Ti_3C_2T_x$ at a weight ratio of 1:10:50 was stirred for another 2 h. The homogeneous suspension was then transferred into a 50 mL Teflon-lined autoclave and kept at 180 °C in an oven for 12 h. During that time the GO and MnO_2 were reduced to rGO and Mn_3O_4, respectively. Meanwhile, the titanium atoms on $Ti_3C_2T_x$ act as nucleating sites to allow the growth of TiO_2. TiO_2 resulted from the partial oxidation of $Ti_3C_2T_x$ during the hydrolysis and post heat-treatment processes under the atmosphere containing oxygen. Whereafter, the precipitate was obtained after the Teflon-lined autoclave was naturally cooled down to room temperature. The final product was rinsed with distilled water for several times, and finally dried at 80 °C for 12 h.

X-ray diffraction (XRD) patterns were performed by a Bruker D8