MXene encapsulated titanium oxide nanospheres for ultra-stable and fast sodium storage

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ABSTRACT

Sodium-ion batteries with high power density present tremendous potential for large-scale energy storage applications. However, it remains a big challenge to develop suitable anode materials for ultrafast and highly reversible sodium ion storage. Herein, for the first time, we report a novel strategy to fabricate highly conductive MXene $Ti_3C_2T_x$ encapsulated titanium oxide spheres ($TiO_2@Ti_3C_2T_x$) as an excellent anode material for sodium-ion batteries. The MXene layers significantly improve the electronic conductivity of the whole electrode and protect the structural integrity of the TiO_2 spheres from electrochemical pulverization, which hence contributes to the formation of a stable solid-electrolyte interface. Meanwhile, the pseudocapacitance of the as-fabricated $TiO_2@Ti_3C_2T_x$ composites enables high-rate capability and long cycle life in sodium-ion batteries. As a result, the hybrid electrode delivers a high reversible capacity of 116 mAh g^{-1} at 960 mA g^{-1} up to 5000 cycles. By coupling with a $NaCrO_2$ cathode, a prototype Na-ion full cell achieved a capacity of 103.4 mAh g^{-1} at 960 mA g^{-1} and an excellent cycling performance with 73.5% capacity retention after 1000 cycles.

1. Introduction

Lithium-ion batteries (LIBs), the current technology of choice for portable electronics and electric vehicles (EVs), have been very thoroughly developed since their commercialization in 1990s [1–3]. The size of the battery market is estimated to triple from 2010 to 2020, with remarkable growth of EVs and renewable energy storage systems [4]. Up to now, the manifold consumption of lithium has resulted in an exponential price rise in the past decade, and it also brings fears of a potential lithium shortage in the future [5]. Hence, sodium-ion batteries (SIBs), as a promising alternative to Li-ion batteries, would become more competitive in the coming half century because of the low cost and abundance of sodium sources [6].

Although much knowledge and experience accumulated in the LIBs can be translated to SIBs due to the similar chemical and physical properties of the Li and Na ions, the larger size of Na^+ has proved problematic to the development of advanced electrode materials for SIBs. Several promising types of SIB cathode materials have been reported so far, but there is still a shortage of suitable anode materials with high capacity, good rate performance and long cycling life [7–11]. At present, disordered carbon (mainly hard carbons) and alloy-based materials have been widely investigated for sodium-ion anodes, but these still suffer from either a low rate capability or a poor cycle life [12–16]. Attentions have

also shifted to titanium-based materials because of their decent capacity and good cycling stability. Titanium dioxide (TiO_2), is an especially ultra-stable, abundant, inexpensive and environmental benign material, and has attracted intense interest since its first introduction for SIB anodes in 2011 [17]. However, the low conductivity of semi-conductive TiO_2 limits its rate capability and long-term electrochemical performances. Substantial efforts has been made to address these issues, including fabrication of various nanostructures of TiO_2 materials to shorten electron and ion pathways and addition of highly conductive material or carbon coating to improve the conductivity [18–21]. Recently, Huang et al. and Lu et al. separately demonstrated that the Na^+ insertion pseudocapacitance dominated the charge storage in the both graphene/TiO_2-bronze and graphene/anatase-TiO_2 composites, which enables the SIBs with high rate capability and good cycling performance [22,23]. These results encouraged the exploration of high performance SIBs based on titania electrodes by utilizing the pseudocapacitive charge storage mechanism. *However, the reported TiO_2/graphene composites have a low tap density because of their highly porous structures, and these open architectures are still vulnerable and prone to pulverization during the charge-discharge processes. To tackle these challenges, one of the effective routes is to fabricate solid TiO_2 spheres confining by conductive materials, which could help to improve the electronic conductivity and tap density [24,25].*

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MXenes, a new family of 2D materials, are considered a rising star for energy storage due to their unprecedented combinations of properties: excellent electronic conductivity, hydrophilicity, mechanical flexibility and compositional adaptability [26–32]. In particular, the Na^+ intercalation pseudocapacitance of MXenes has been proven by Yamada's group and their materials delivered reasonable capacity and high rate performance in sodium-ion capacitors [33]. The major drawback of MXene materials for battery applications is their low specific capacities, despite substantial improvements achieved [34,35]. Many works has verified that MXenes could play an extraordinary synegistic role when combining with metal oxide materials [36,37]. In addition, compared with graphene, MXene with a lateral size from a few hundred nanometres to micrometres is expected to be a better choice that can individually constrain oxides nanomaterials because of the smaller difference between the lateral size of the MXene and oxide particles.

Herein, for the first time, we report a unique architecture of MXene $Ti_3C_2T_x$ encapsulated TiO_2 nanospheres ($TiO_2@Ti_3C_2T_x$) for ultrafast sodium storage. A novel strategy was employed for the preparation of $TiO_2@Ti_3C_2T_x$ composite by self-assembly between positively charged TiO_2 spheres and negatively charged $Ti_3C_2T_x$ nanosheets. The as-prepared $TiO_2@Ti_3C_2T_x$ composites exhibit several advantages: (i) MXene $Ti_3C_2T_x$ shells improve the ionic and electronic conductivity of the whole anode; (ii) the design architecture enables high oxide content in the composite, lowering the cost and increasing the density of composites; (iii) TiO_2 spheres are individually confined within MXene shells, which protect the TiO_2 spheres from pulverization during the charge-discharge processes and contribute to the formation of a ultra-stable solid-electrolyte interphase film. As a result, the $TiO_2@Ti_3C_2T_x$ nanospheres exhibit superior sodium storage capability and ultrastable cyclability upon long term cycling.

2. Materials and methods

2.1. Synthesis of TiO_2-$Ti_3C_2T_x$ composites

First, monodispersed amorphous spherical TiO_2 were prepared *via* a controlled hydrolysis of tetra-isopropoxide (TTIP, 97%) in ethanol (see details in Supplementary Information). Then the TiO_2 nanospheres (0.5 g) were homogenously dispersed in 50 mL of anhydrous ethanol via sonication. Aminopropyl-trimethoxysilane (0.5 mL) APS was added into the above solution and refluxed at 65 °C for 4 h. Amine-functionalized TiO_2 spheres were obtained after washing via centrifugation and drying in air. Secondly, the $Ti_3C_2T_x$ colloidal solution with a quantified concentration was prepared by an etching process of Ti_3AlC_2, followed by exfoliation in water. The details have been described in our previous report. [36] Thirdly, 10 mL of aqueous $Ti_3C_2T_x$ colloidal solution (1.0 mg mL^{-1}) was added into 40 mL of amine-modified TiO_2 spheres (1 mg mL^{-1}, dispersed homogenously via sonication) under stirring. After 1 h, the mixture was centrifuged at 6000 r/ppm, and then collected and dried at room temperature. The $TiO_2@Ti_3C_2T_x$ product was obtained after calcination at 400 °C for 5 h under Ar atmosphere. As a comparison, the pure TiO_2 spheres were prepared via calcination of amorphous titanium oxide precursor at 400 °C for 5 h in air; and the bare $Ti_3C_2T_x$ materials were acquired *via* drying process of exfoliated $Ti_3C_2T_x$ colloidal solution at room temperature.

2.2. Characterization

Zeta potential measurements were performed on a Malvern Zetasizer Nanoseries analyser. X-ray diffraction was conducted on a Bruker D8 Discovery X-ray diffractometer using Cu Kα radiation (λ=0.15406 nm). Raman spectra were obtained by a Renishaw inVia Raman spectrometer system (Gloucestershire, UK) equipped with a Leica DMLB microscope (Wetzlar, Germany) and using a 633 nm

wavelength laser. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB250Xi (Thermo Scientific, UK) equipped with mono-chromated Al K alpha (energy 1486.68 eV). The morphologies of samples were observed on field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 55VP) and scanning transmission electron microscopy (STEM, JEOL JEM-ARM200F); energy dispersive X-ray spectroscopy was also acquired on the STEM.

2.3. Electrochemical measurements

The electrochemical performance of the materials was firstly evaluated in CR2032-type half cells with Na metal as the counter/reference electrode. The working electrodes were prepared by the following procedure. First, a uniform slurry containing 80 wt% active material, 10 wt% carbon black and 10 wt% carboxymethyl cellulose (CMC) dispersed in water was pasted onto a current collector (copper foil for anode materials and aluminium foil for $NaCrO_2$ cathode material) with a doctor blade. After vacuum drying at 80 °C for 12 h, the electrodes were pressed and cut into square pieces (1×1 cm^2). The typical active material loading was around 1 mg cm^{-2} for anodes and 2 mg cm^{-2} for cathodes. The electrolyte was a solution of 1 M $NaClO_4$ in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (1:1, v/v) to which was added 5% fluoroethylene carbonate (FEC), and glass fibers (Whatman) were selected as separators. Galvanostatic discharge/charge measurements were conducted on a Neware battery testing system. The current densities and specific capacities were all calculated based on the mass of active material except carbon black and binder. CV and EIS tests were performed on a Biologic VMP3 workstation. For EIS measurements, an AC amplitude of 5 mV was applied to the cells in the range from 100 kHz to 10 mHz.

3. Results and discussion

Fig. 1a illustrates the preparation process of the $TiO_2@Ti_3C_2T_x$ nanospheres. In the first step, the as-synthesized amorphous titanium oxide spheres were amine-modified by amino-propyl-trimethoxysilane (APS) to render the TiO_2 surface positively charged (Fig. S1a, Supporting Information) [38]. After then, the amine-functionalized titanium oxide nanospheres (denoted as TiO_2-NH_2) were mixed with the certain amount of MXene $Ti_3C_2T_x$ colloidal solution at PH ≈ 6−7 in an aqueous solution (an optimised weight of $Ti_3C_2T_x$ that accounts for 15 wt% of the composites was used here). The $Ti_3C_2T_x$ nanosheets are negatively charged owing to the presence of the surface functional groups (*e.g.* −OH, -F, and -O) (Fig. S1b). Consequently, the $Ti_3C_2T_x$ nanosheets were attracted to the surface of TiO_2-NH_2 nanospheres until the positive charges were fully balanced. Both TiO_2-NH_2 spheres and $Ti_3C_2T_x$ nanosheets were finally aggregated in the bottom of the container and a clear aqueous supernatant could be observed, indicating the successful co-assembly between the positive charged TiO_2-NH_2 spheres and negative charged $Ti_3C_2T_x$ nanosheets (Fig. S2a). *On the contrary, the TiO_2 spheres without APS modification precipitated at the bottom of vessel and still stay separately with the $Ti_3C_2T_x$ MXene colloidal solution even after thoroughly sonication (Fig. S2b).* The $TiO_2@Ti_3C_2T_x$ composites were obtained after thermal treatment, which can remove the residual organics and surface groups, and improve the crystallinity of the product. *Bare TiO_2 nanospheres, $Ti_3C_2T_x$ nanosheets and mechanically mixed $TiO_2/Ti_3C_2T_x$ were also prepared using the same preparation conditions as "control" references (Fig. S3).*

Fig. 1b shows that well-defined TiO_2 nanospheres with sizes of 250 to 350 nm were successfully prepared *via* a controlled hydrolysis process. From Fig. 1c, we observe that $TiO_2@Ti_3C_2T_x$ composites present a similar morphology to that of the amorphous TiO_2 nanospheres, excepting that a few $Ti_3C_2T_x$ sheets are observed on the surface of spheres. However, the high magnification SEM image (Fig. 1d) clearly demonstrates that TiO_2 spheres are individually