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Enhanced reversible Li-ion storage in Si@Ti_3C_2 MXene nanocomposite

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ABSTRACT

The Si@Ti_3C_2 MXene nanocomposite was prepared in this paper by simply ultrasonic mixing of commercially available nanosized Si and Ti_3C_2 MXene. The introduction of Ti_3C_2 makes the aggregation of silicon nanoparticles relieved. Electrochemical measurements show that the nanocomposite maintains a reversible capacity of 188 mAh·g^{-1} at 0.2 A·g^{-1} after 150 cycles and exhibits improved capacity retention, which are significantly better than those of pure Si. The enhanced cycling stability and rate capability are attributed to the good electrical connection between silicon and Ti_3C_2. This study provides a new available matrix and guidance for the applications of MXenes in Si-based anode LIBs.

1. Introduction

Silicon is considered as the most promising anode material for rechargeable lithium ion batteries (LIBs), mainly due to: (i) the highest theoretical capacity (4200 mAh·g^{-1}) [1], which is far beyond that of graphite (372 mAh·g^{-1}); (ii) the low lithium insertion potential (~0.12 V) [2]; (iii) the high natural abundance and similar properties with carbon [3,4]. However, several rigorous challenges of Si must be addressed when used as the anode material, including: (i) the huge volume changes (> 300%) [5] during lithiation/delithiation process that results in significant capacity loss; (ii) the intrinsically poor electrical conductivity (1.56×10^{-3} S·m^{-1}) [3] and low diffusivity of Li-ion (~10^{-14}–10^{-13} cm^2·s^{-1}) [6], which eventually leads to poor rate performance; (iii) regeneration of the unstable solid electrolyte interphase layers [7], which would consume the electrolyte continually.

To tackle these challenges, numerous approaches have been implemented, such as decreasing Si particles into nanoscale size [8,9], covering protecting layer on Si surface [10,11], fabricating silicon/carbon composites [12,13], and so on. Among the above methods, dispersing silicon into carbon matrix to accommodate the volume changes and enhance the conductivity is believed to be an effective strategy. A variety of carbon materials have been selected as matrix to improve the capacity retention of Si-based materials, mainly including graphene [14,15], graphite [16], carbon fibers [17], carbon nanotubes [18] and mesoporous carbon [19].

Recently, a novel graphene-like carbide, Ti_3C_2, has been paid tremendous attentions in energy storage applications owing to its specific structure and chemistry properties [20–23]. Ti_3C_2 belongs to a class of two-dimensional materials named MXenes, where M is an early transition metal and X is carbon and/or nitrogen [24]. Ti_3C_2 has the advantages of high conductivity (4600 S·cm^{-1}) [25], excellent diffusion mobility for Li-ion (~10^{-10}–10^{-9} cm^2·s^{-1}) [26], and good mechanical properties [27], which make it a potentially ideal substrate for silicon.

To our knowledge, this is the first report about the combination of Si and Ti_3C_2 MXene for the application in LIBs. In this work, the Si@Ti_3C_2 nanocomposite was fabricated by dispersing Si nanoparticles into Ti_3C_2 through ultrasonic mixing for understanding its electrochemical behaviors. The preparation process of Ti_3C_2 is simpler than that of graphene, which reduces the difficulty of preparing composite materials. Owing to the high conductivity and good mechanical properties offered by Ti_3C_2, the prepared nanocomposite shows much better electrochemical performance than that of pure Si. Considering the vast varieties of MXenes to which Ti_3C_2 belongs, this work provides guidance for the application of MXenes in Si-based anode LIBs.

2. Experimental

The Si@Ti_3C_2 nanocomposite was fabricated through ultrasonic mixing of commercially available Si (~40 nm, Aladdin) and Ti_3C_2 with a weight ratio of 1:5. Ti_3C_2 was synthesized via a wet-chemical method, as previously reported by our group [26,28]. In detail, 30 mg Si powders and 150 mg Ti_3C_2 were ultrasonically dispersed in 20 mL alcohol for 2 h, respectively. After that, both of them were mixed together followed by strong stirring for 8 h. Finally, the resulting product after

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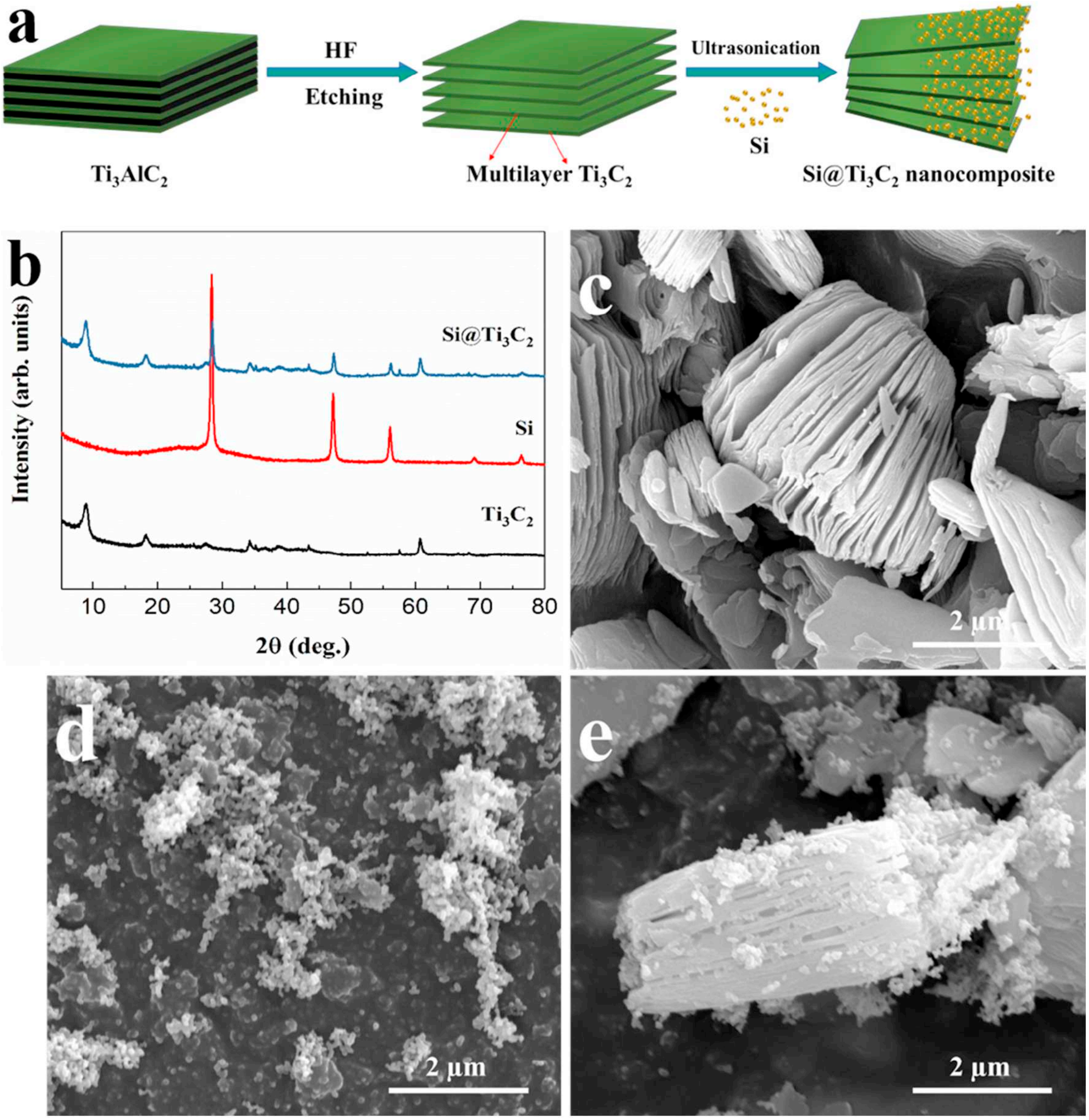

Fig. 1. (a) Schematic of Si@Ti_3C_2 nanocomposite preparation; (b) XRD patterns; SEM images of (c) Ti_3C_2, (d) Si nanoparticles, and (e) Si@Ti_3C_2 nanocomposite.

filtration and vacuum drying was Si@Ti_3C_2 nanocomposite.

X-ray diffraction (XRD) patterns of samples were obtained with an Empyrean (PANalytical, Cu K_α). The morphology of samples was investigated by a scanning electron microscope (SEM; HELIOS NanoLab 600i). The surface chemical properties of nanocomposite were characterized by X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi). To measure the electrochemical performance, pure Si and Si@Ti_3C_2 nanocomposite were respectively mixed with carbon black and sodium carboxymethyl cellulose (CMC, average Mw: ~250,000, Aladdin) binder in deionized water, at a weight ratio of 80:10:10. The processes of making electrodes and assembling coin cells can be found elsewhere [28]. The mass loadings of the working electrodes were about 0.5–0.8 mg/cm^2. The specific capacities were calculated based on the mass of active materials (pure Si or Si@Ti_3C_2 nanocomposite, i.e., 80% of the entire working electrodes mass). Galvanostatic cycling at 0.2 A·g^{-1} within the 0.05 V–2.5 V voltage range was tested on a Neware BTS instrument. Cyclic voltammetry (CV) was performed using a CHI860D Electrochemical Workstation (Chenhua) and electrochemical impedance spectroscopy (EIS) was conducted on a PARSTAT 2273 Electrochemical Workstation (Princeton Instruments).

3. Results and discussions

Fig. 1a exhibits the schematic of Si@Ti_3C_2 nanocomposite preparation, and the characterizations of samples are presented in Fig. 1b–e. In Fig. 1b, the XRD pattern of Ti_3C_2 is consistent with the reported results [21,29], indicating the successful fabrication of layered Ti_3C_2. The particle size of silicon is calculated to be about 22.4 nm by Scherrer formula using the half peak breadth of (111) peak. After ultrasonic mixing, the nanocomposite is composed of Ti_3C_2 and Si without new crystalline phase. SEM image in Fig. 1c exhibits the typical structure of Ti_3C_2 MXene. An obvious Si nanoparticles aggregation as