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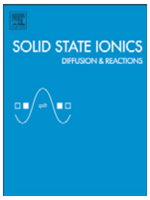

Hybrid nanoarchitecture of rutile TiO_2 nanoneedle/graphene for advanced lithium-ion batteries

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ABSTRACT

In this paper, rutile TiO_2 nanoneedle/graphene composites with a unique one dimensional/two dimensional (1D/2D) hybrid nanostructure were prepared *via* a facile hydrothermal route. These obtained rutile TiO_2 nanoneedles with the length of ~500 nm have a homogeneous dispersion on the interlayers of graphene nanosheets. As the anodic materials, the as-prepared sample exhibited the superior Li storage capability with good cycling stability (over 94% capacity retention) and remarkable rate performance (149 mA h g^{-1} at a 5 C rate). The improved electrochemical performance can be attributed to the unique microstructure. On the one hand, 1D rutile TiO_2 nanoneedles shorten the length of Li^+ transport paths to achieve a higher Li^+ diffusion rate. On the other hand, 2D graphene sheets provide good electronic contacts to reduce the contact resistance, as well as keep the structural integrity of the electrode materials.

1. Introduction

With the rapid development of portable electronic devices and hybrid electric vehicles, rechargeable lithium-ion batteries are considered as one of the most promising energy storage devices owing to their high energy density, long cycling lifetime and excellent safety. Over the past decades, metal oxides (*e.g.* Co_3O_4 [1,2], NiO [3,4], Fe_3O_4 [5,6] and TiO_2 [7]) have been regarded as anode materials for lithium-ion batteries. In particular, TiO_2 has attracted considerable interests because of its abundance in nature, environmental friendliness and low cost [8–10]. Up to date, three common polymorphs of TiO_2 (*e.g.* rutile, anatase and TiO_2-B) have been widely investigated since TiO_2 has the high theoretical capacity of 335 mA h g^{-1} corresponding to the insertion of one lithium per formula unit ($TiO_2 + Li^+ + e^- \rightarrow LiTiO_2$) and the superior safety arising from the structural stability and electrolyte insensitivity [11]. In this regard, anatase TiO_2 and TiO_2-B are considered as the promising candidates, which have been well studied in many literatures [12–14]. At room temperature (RT), anatase TiO_2 has a distinct plateau at ~1.8 V corresponding to 0.5–1 mol Li^+ per TiO_2 unit, which has no major structural changes [15]. Meanwhile, TiO_2-B presents a stable channel structure for the Li^+ mobility, which has a low potential of 1.6 V associated with the Li^+ insertion [15,16]. Compared with anatase TiO_2 and TiO_2-B, rutile TiO_2 has the most stable structure with the highest density of 4.25 g cm^{-3} in which the Li^+ insertion into rutile TiO_2 is commonly considered to be negligible at RT [17]. In spite of this, Macklin and Neat reported that Li^+ can be reversibly inserted/extracted into/from bulk rutile TiO_2 at 120 °C [18]. The kinetic limitations have been demonstrated that rutile TiO_2 only has 1D Li^+ transport channel along *c*-axis (10^{-6} cm^2 S^{-1}), whereas Li^+ diffusion in the *ab*-planes is very low (10^{-14} cm^2 S^{-1}) [19]. This highly anisotropic Li^+ insertion/extraction mechanism causes low electronic and ionic conductivity of rutile TiO_2 during the charge–discharge cycling [11,19].

Up to date, great efforts have been made to solve these above issues. An effective strategy is to synthesize 1D TiO_2 such as nanorods [20], nano-needles [21], nanotubes [22], and nanowires [23], which could shorten the diffusion length for electrons and lithium ions. Wang et al. synthesized 1D nanostructured TiO_2 of various morphologies and structures, which exhibited remarkable electrochemical performance [24]. Another approach is adding various kinds of metals (*e.g.* Ag [25] and Sn [26]), metal oxides (*e.g.* RuO_2 [27]) and carbonaceous materials (*e.g.* CNTs [28] and carbon [29], graphene [30]) as matrices or conductive layers. Unlike other additives, graphene, a one-atom thick structure of sp^2-bonded carbon atoms that are densely packed in honeycomb crystal lattice, is considered as one of the most promising hosts. Owing to the high carried mobility (~10,000 cm^2 V^{-1} s^{-1}), large specific surface area (~2630 m^2 g^{-1}) and exceptional mechanical properties (Young's modulus ≈ 1.0 TPa) [31,32], graphene will be favourable in enhancing the electrochemical performance of TiO_2. Cao et al. [33] demonstrated that TiO_2 nanoparticles coupled with conducting graphene nanosheets could provide faster electronic transport and Li^+ diffusion during the lithium insertion/extraction process, leading to a high rate

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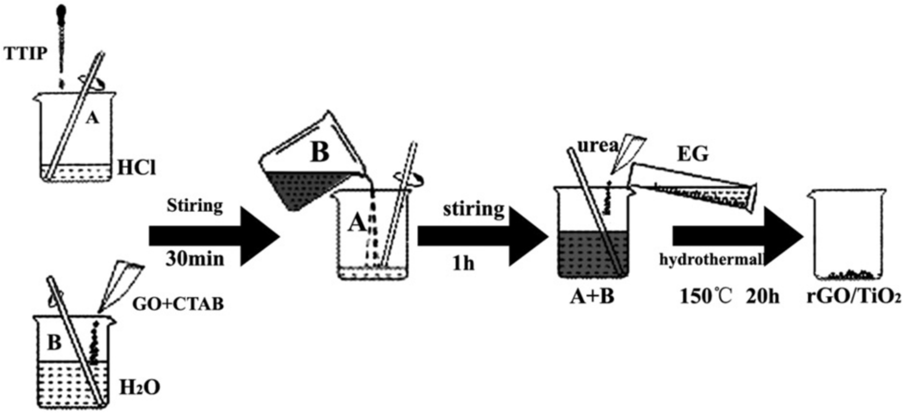

Fig. 1. Schematic illustration of the preparation process of TiO2/rGO composite.

performance. The previous works mainly focused on anatase TiO_2, however, literatures relating on rutile TiO_2 coupled with graphene for lithium-ion batteries are rarely reported [15,17,19,34].

In the present work, a facile hydrothermal route is developed to fabricate rutile TiO_2 nanoneedle/graphene composites with a unique 1D/2D hybrid structure. The electrochemical performance clearly demonstrates that these composites exhibit high initial discharge capacity (427.6 mA h g^{-1}, 0.1 C), high-rate discharge capability (149 mA h g^{-1}, 5 C), and enhanced cycling stability. Hereby, graphene-supported rutile TiO_2 nanoneedle composite will be very attractive as a prospective anode material for advanced lithium-ion batteries.

2. Experimental section

2.1. Materials and preparation

Graphite powder was purchased from Alfa Aesar (325 mesh). $NaNO_3$, H_2SO_4 (98 wt.%), $KMnO_4$, HCl (36–38 wt.%), hexadecyl trimethyl ammonium bromide (CTAB), titanium tetraisopropoxide (TTIP, 98 wt.%), ethylene glycol (EG), H_2O_2 (30 wt.%) and urea were purchased from Aladdin chemical reagent company. All the reagents were used as received without further purification.

Graphene oxide (GO) was synthesized by a modified Hummers' method [35,36]. In detail, 5 g of graphite powder and 3.75 g $NaNO_3$

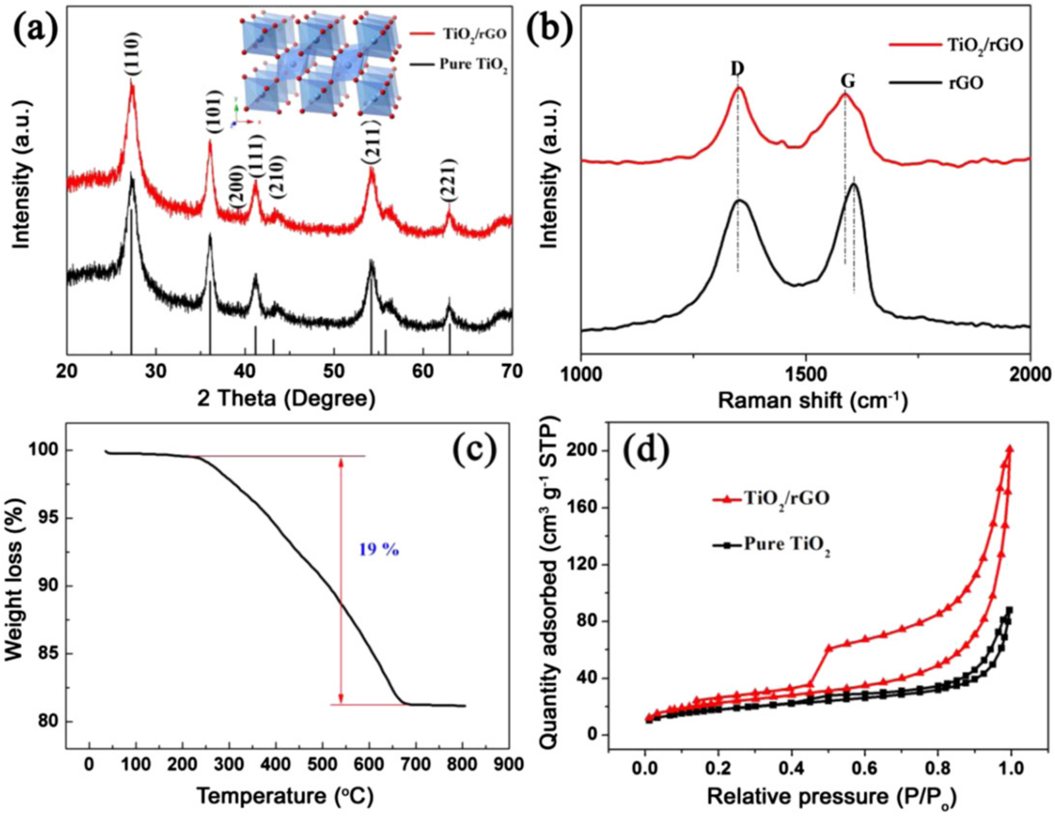

Fig. 2. (a) XRD patterns of pure TiO_2 and TiO_2/rGO composite. The inset is crystal structure of rutile TiO_2 (red is oxygen atom; blue is TiO_6 octahedra). (b) Raman spectra of TiO_2/rGO composite and rGO. (c) TG curve of TiO_2/rGO composite. (d) Nitrogen adsorption–desorption isotherms of pure TiO_2 and TiO_2/rGO composite.