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Communication

Binder-free carbon fiber/$TiNb_2O_7$ composite electrode as superior high-rate anode for lithium ions batteries

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ABSTRACT

Construction of advanced high-rate anodes is critical for the development of high-power lithium ion batteries (LIBs). In this work, we report a binder-free carbon fiber (CF)/titanium niobium oxide ($TiNb_2O_7$ (TNO)) composite electrode *via* a simple solvothermal method combined with heat treatment. Continuous TNO film consisting of cross-linked TNO nanoparticles of 30–50 nm is strongly anchored on the carbon fiber forming integrated CF/TNO composite electrode. Owing to the intimate three-dimensional structure, the as-prepared CF/TNO electrode presents exceptional high-rate performance (245 mAh/g at 1 C, and 138 mAh/g at 80 C) and enhanced cyclability with a capacity of 150 mAh/g at the current density of 10 C after 1000 cycles. Our results demonstrate the CF/TNO electrode as efficient anode for application in high-power lithium ion batteries.

The worsening environmental problems spur on us to develop green energy storage devices [1]. Particularly, lithium ion batteries (LIBs) have conquered the markets of electronics and electric vehicles without controversy and become the most popular battery since 1990s [2–4]. Though, as compared to supercapacitors, LIBs have the advantage of larger energy density, they suffer from relatively low power density [5–7]. It is accepted that the performance of LIBs is largely dependent on innovation/optimization of electrode materials [8]. Currently, various alternative anode candidates (such as graphite [9], Sn [8], Si [10], $Li_4Ti_5O_{12}$ [11,12] and titanium niobium oxide (TNO) [13,14]) have been the subject of intense research.

Of these candidates, titanium niobium oxide ($TiNb_2O_7$, TNO) have attracted tremendous attentions due to the following advantages: 1) Relative high working voltage platform (1.6 V *vs.* Li/Li^+) can hinder the formation of SEI layers. 2) Large theoretical capacity of 388 mAh/g due to multi-redox couples (Nb^{4+}/Nb^{5+}, Nb^{3+}/Nb^{4+} and Ti^{3+}/Ti^{4+}), higher than that of $Li_4Ti_5O_{12}$ (175 mAh/g). 3) High lithium ion diffusion coefficient owing to Wadsley-Roth shear structure of $TiNb_2O_7$ (Ti^{4+} and Nb^{5+} ions with molar ratios of 1:2 randomly occupy the octahedral sites connected by edges and corners and no cations are resided at the tetrahedral sites). However, the poor electron/ion transfer in bulk TNO limits its further commercial application. As a result, appropriate steps must be taken to improve the electrochemical performance of $TiNb_2O_7$. To date, a variety of improved TNO electrodes have been reported by doping or introducing conductive layers on TNO nanostructures. Liu *et al.* [15] synthesized Ag coated $TiNb_2O_7$ composites by a facile solid-state reaction showing a capacity of 170 mAh/g at 30 C. Ru doped $TiNb_2O_7$ proposed by Lin *et al.* [16] obtained a capacity of 181 mAh/g after 100 cycles at 5 C with a capacity retention of 90.1%. $TiNb_2O_7$ hollow nanofiber prepared by Yu *et al.* [17] possessed superior electrochemical performance with a reversible capacity of 158 mAh/g at a current density of 10 C after 900 cycles. $TiNb_2O_7$ nanoparticles synthesized by Li *et al.* [18] showed enhanced rate performances with 175 mAh/g at 5 C and 138 mAh/g at 10 C, respectively. The above works are mainly focused on the TNO powder electrode. The presence of insulating binders in the powder electrode would undermine the electrochemical performance [19]. Therefore, there is still huge room left to construct flexible and binder-free TNO electrodes [20–23].

In the present work, we construct a novel binder-free carbon fiber/titanium niobium oxide (CF/TNO) composite electrode *via* a simple solvothermal method combined with heat treatment. Benefiting from the smart three-dimensional structure and highly

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conductive carbon fibers, the as-prepared CF/TNO electrode presents superior high-rate performance (245 mAh/g at 1 C, and 138 mAh/g at 80 C) and improved cyclability with a capacity of 150 mAh/g at the current density of 10 C after 1000 cycles. Our work demonstrates the flexible and binder-free CF/TNO electrode as efficient anode for high-power lithium ion batteries.

The fabrication schematics of CF/TNO electrode is shown in Fig. 1a. The carbon fibre cloth is used as the substrate for the growth of TNO film *via* a facile hydrothermal method (detailed information see Supporting information). To check the structure information, phase evolution and elementary composition, X-ray diffraction (XRD), Raman spectra and XPS spectra are employed. Fig. 1b shows the XRD patterns of CF and as-prepared CF/TNO composite electrode. The diffraction peaks at 23° and 43° in both samples are corresponding to (002) and (004) crystal planes of graphitic carbon (JCPDS No. 65-6212) [24]. Compared with the XRD pattern of CF, it can be clearly observed that the other strong diffractions of CF/TNO are index well with $TiNb_2O_7$ phase (JCPDS No. 77-1374). The above results are supported by Raman result. As shown in Fig. 1c, apart from the peaks of CF (1355 cm^{-1} and 1590 cm^{-1} for D band and G band, respectively), new peaks appear at 993, 890, 648 and 261 cm^{-1}, which belong to $TiNb_2O_7$ phase. XPS spectra (Fig. 2a) proving the presence of Ti, Nb, O, C elements and testify again the successful grown of TNO films on CF. According to Ti 2p spectrum (Fig. 2b), there are two peaks respectively located at 465 eV and 459 eV with about 6 eV binding energy separation confirming the existence of Ti^{4+} [25]. In Nb 3d spectra (Fig. 2c), core levels of Nb 3b 5/2 (210 eV) and Nb 3d 3/2 (207 eV) are corresponding to the state of Nb^{5+}. The high-resolution spectrum of O 1s consists of one peak at 531 eV (Fig. 2d), which demonstrates the existence of O element in TNO phase and is related to the binding energy of Nb/Ti-O. The C 1s spectrum is resolved into three components located at 284.6 eV, 286.2 eV and 288.6 eV (Fig. 2e). The main peak at 284.6 eV is corresponding to the binding energy of C=C, and the other two small peaks can be indexed as the oxidative forms of hydrocarbons (COOH and C=O) [26]. All results mutually support the formation of an integrated electrode with TNO film grown on carbon fiber substrates. To further calculating the weight content of TNO on carbon fibers, TG measurement is performed with a temperature window of 20–1000 °C in air. As shown in Fig. 3f, the carbon fibers are oxidized to CO_2 while TNO keeps intact. The proportion of TNO is calculated to be 4.9% with a mass area of ~1 mg/cm^2.

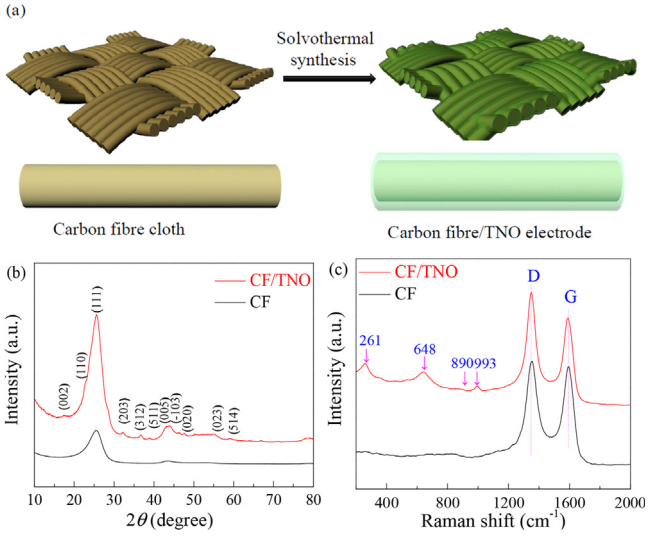

Fig. 1. (a) Schematic illustration of the formation of CF/TNO electrode; (b) XRD patterns of pure CF and CF/TNO; (c) Raman spectra of pure CF and CF/TNO electrodes.

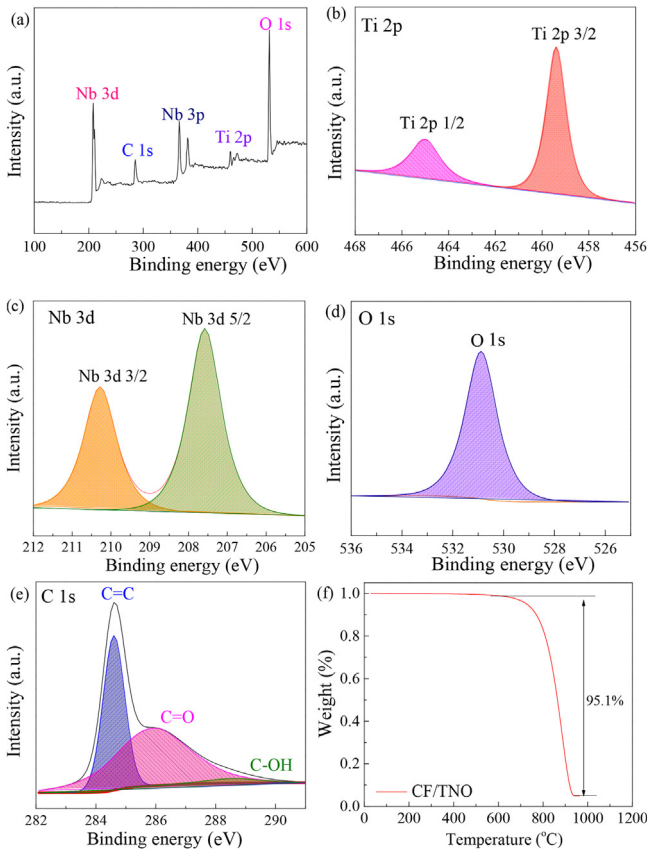

Fig. 2. (a) XPS spectra of wide survey scan and (b) Ti 2p, (c) Nb 3d, (d) O 1s, and (e) C 1s of the CF/TNO composite electrode; (f) TG curve of CF/TNO electrode.

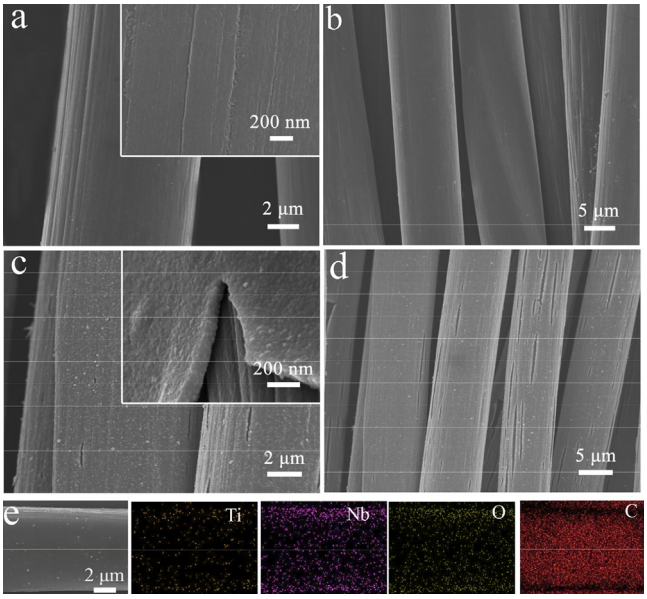

Fig. 3. SEM images of pure CF (a and b) and CF/TNO (c and d); (e) EDS elemental mapping images Ti, Nb, O and C in the CF/TNO composite electrode.

The microstructures and morphologies of bare CF and CF/TNO composite electrodes are shown in Fig. 3a–d. Cross-linked carbon fibers with diameters of ~10 μm can be clearly seen in Fig. 3a and

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