Supporting Information:

Facile Synthesis of nanostructured $TiNb_2O_7$ anode materials with superior performance for high-rate lithium ion batteries

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Experimental Section

Preparation of $TiNb_2O_7$: $TiNb_2O_7$ nanorods were prepared through a simple sol-gel method. First, Nb_2O_5 (Sinopharm Chemical Reagent, analytically pure) was added to a hydrofluoric acid solution (Sinopharm Chemical Reagent, 40 wt.%) and stirred for about 4 hours at 70℃. After the solution became transparent, excess ammonium hydroxide was added and then a white $Nb(OH)_5$ precipitated. The solid was filtered, washed and dried. 1.78g of the obtained $Nb(OH)_5$ was added in an oxalic acid solution at 80°C to form transparent solution including Nb^{5+}, with the pH value adjusted by controlling the amount of oxalic acid. Meanwhile, 1.7 ml tetrabutyltitanate (Sinopharm Chemical Reagent, analytically pure) was added into absolute ethanol with a little oxalic acid and then stirred vigorously. Subsequently, The resulted light yellow solution was added to the Nb^{5+}-contained oxalic acid solution slowly. The mixed solution was then stirred and heated at 90℃ to completely remove ethanol and water. The obtained white powder was calcined at 900°C in air to obtain the slightly yellow $TiNb_2O_7$ product.

Materials characterization: The size and morphology of the $TiNb_2O_7$ powders were characterized

using a Helios Nanolab 600i high-resolution Field emission Scanning Electron Microscope (FESEM) operated at 10 kV. X-ray powder diffraction (XRD) was carried out on a Rigaku D/max-γA X-ray diffractometer with Cuκα radiation (λ=1.54178 Å). The FTIR spectra was collected using a ThermoNicolet iS10 FT-IR spectrometer with an attenuated total reflectance(ATR) unit. Transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) images were taken with a TecnaiG2F30 transmission electron microscope with an acceleration voltage of 300 kV. X-ray photoelectron spectra (XPS) was recorded on a PHI 5700 ESCA system fitted with Al κα radiation. The energy calibration and deconvolution of XPS peaks were calculated using a XPSPEAK software.

***Electrode fabrication and electrochemical measurements*:** The working electrodes were fabricated as follows. First, the $TiNb_2O_7$ nanostructured materials (70 wt.%), acetylene black (20 wt.%), and polyvinylidene fluoride (PVDF, 10 wt.%) were mixed and then stirred in N-methyl-2-pyrrolidone (NMP) to form a black slurry. Then, the black slurry was spread onto a Cu foil by a doctor blade method, followed by drying in vacuum at 120°C for 12 h. The average loading weight of the active material in the coin cell fabrication is ~2 mg. Lithium metal was used as both the counter electrode and the reference electrode, and a porous polypropylene membrane (Celgard 2500) was used as the separator. CR2025-type coin cells were assembled in an argon-filled glove box with both moisture and oxygen contents below 0.5 ppm. The electrolyte was 1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC, 1:1:1 by volume). The galvanostatic charge/discharge test (1.0-3.0V) was performed on a Neware-CT3008 test system under ambient temperature.

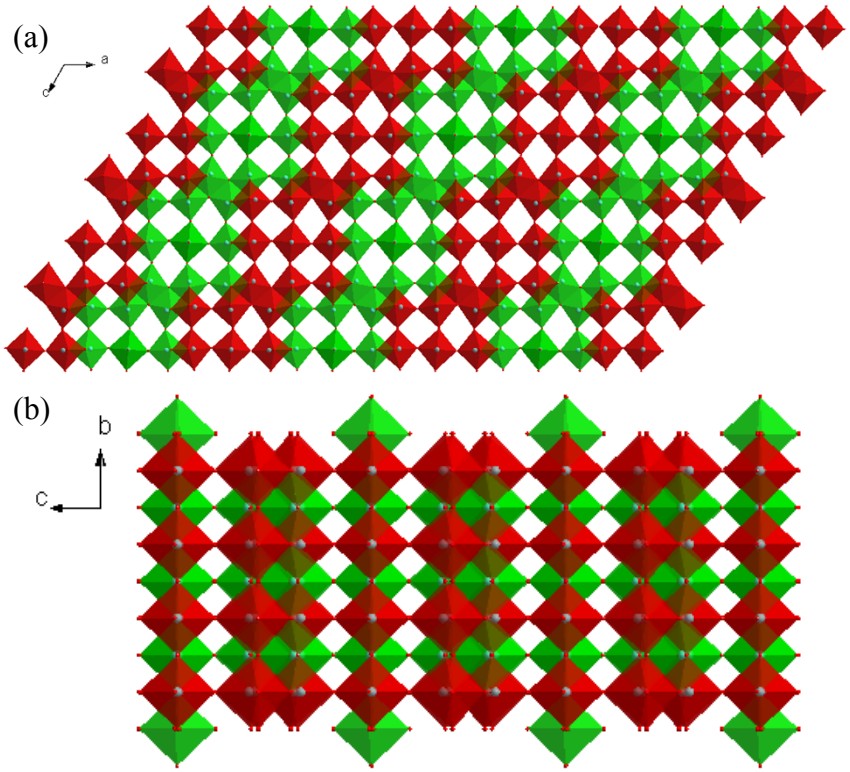

Fig. S1 Crystal structure of $TiNb_2O_7$ oxide with a ReO_3-type structure, (a) *ac* plane and (b) *bc* plane.

The red blocks and green blocks represent the MO_6 (M=Ti, Nb) octahedra (TiO_6 and NbO_6 octahedra show a random arrangement) on the adjoining layers, and each of these blocks contains nine MO_6 (3×3) octahedra.

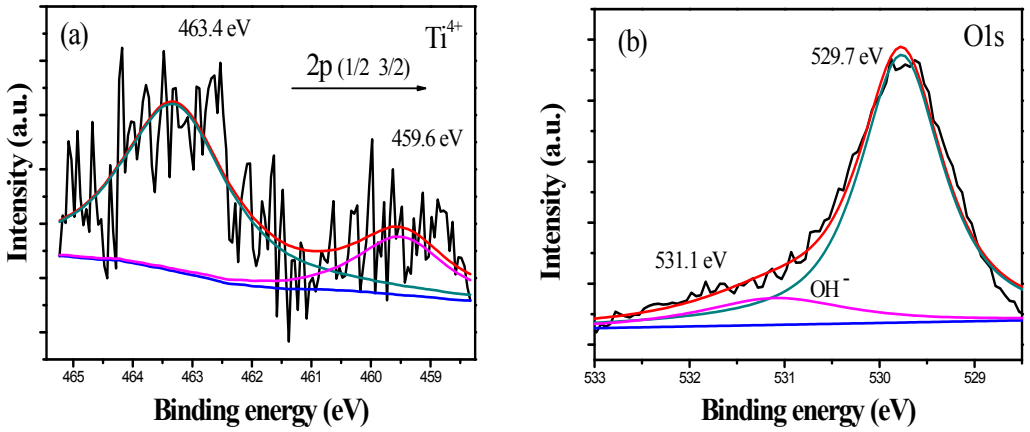

Fig. S2 XPS spectra of Ti and O elements in nanostructured $TiNb_2O_7$.

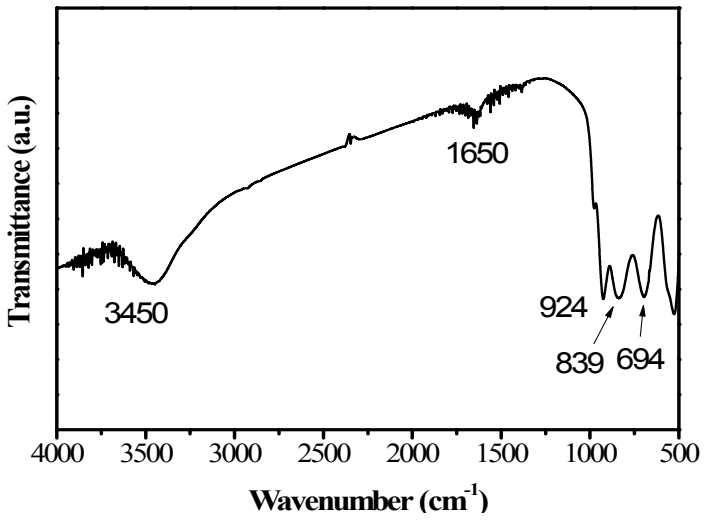

Fig. S3 FTIR of $TiNb_2O_7$ nanostructured materials.

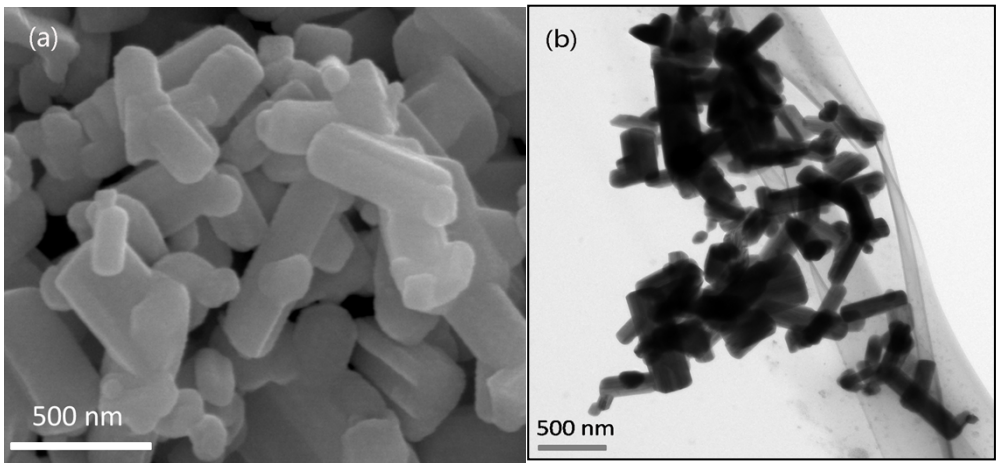

Fig. S4 (a) The SEM and (b) TEM image of $TiNb_2O_7$ nanostructured materials.

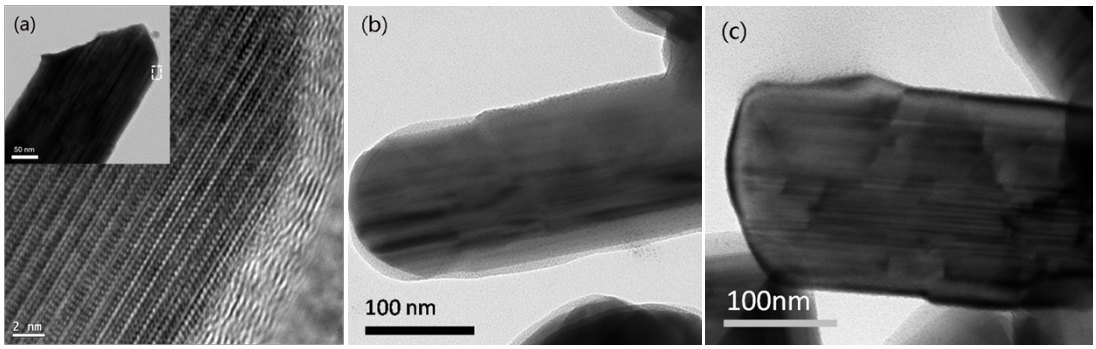

Fig. S5 The orientation of $TiNb_2O_7$ nanorod materials.

The structural orientation shows a consistency results that crystal lattice fringes are parallel to the axial direction of the $TiNb_2O_7$ rod. Fig. S5(a) is the enlarge image of the box in the inset image. Fig. S5 (b) and (c) are the representational TEM images in the products.

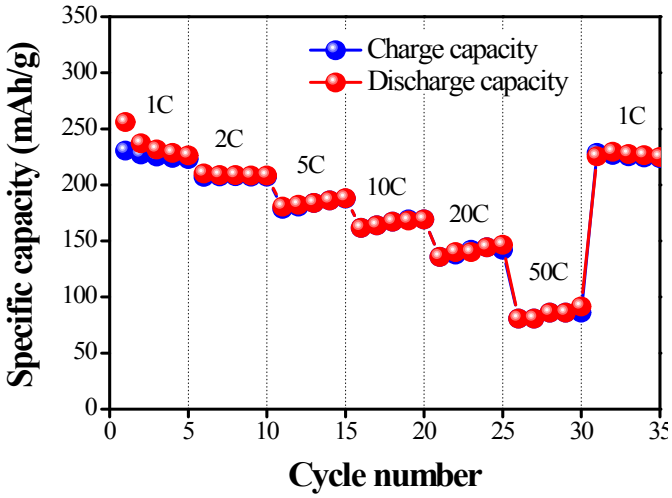

Fig. S6 Rate performance of $TiNb_2O_7$ electrodes at various rates (1 C, 2 C, 5 C, 10 C, 20 C, 50 C)