Supporting Information

Tunnel-structured $Na_{0.54}Mn_{0.50}Ti_{0.51}O_2$ and $Na_{0.54}Mn_{0.50}Ti_{0.51}O_2$/C nanorods as advanced cathode materials for sodium-ion batteries

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Experimental Section

Synthesis Method

$Na_{0.54}Mn_{0.50}Ti_{0.51}O_2$ nanorods were synthesized by a modified molten salt method. First, appropriate amounts of $NaCH_3COO$, $Mn(CH_3COOH)_2$, and TiO_2 (Sinopharm, AR) were dissolved in droplets of deionized water and added to a mixture of NaCl-KCl (molar ratio = 0.59:0.41, total mass = 1 g). The mixture was mixed in a mortar, transferred to an alumina crucible, and dried at 180 °C for 3 h. The powders were then ground for another 20 min, then heated to 800 °C at a rate of 2 °C min^{-1} in air. After stayed at 800 °C for 10 h, the powders were cooled to room temperature at a rate of 3 °C min^{-1}. The obtained product was thoroughly washed with deionized water to remove the salts, dried at 60 °C in a vacuum oven overnight. The obtained sample was named as NMTO. For the carbon coating experiment, the power was mixed with 50 wt% citric acid by ball-milling and heated treated at 400 °C for 4 h under a flow of Ar(95 %)/H_2(5 %). The final black powder was $Na_{0.54}Mn_{0.50}Ti_{0.51}O_2$/C composite, marked as NMTO/C. All the powers were collected for structural characterization and electrochemical measurements. The specific surface areas of NMTO and NMTO/C are 16.3 and 22.0 m^2 g^{-1}, based on Brunauer-Emmett-Teller (BET) model.

Structural Characterization

X-ray powder diffraction (XRD) pattern of the product was recorded on a Bruker D8 advance X-ray diffractometer with Cu Kα line as a radiation (λ=1.5418 Å). SEM, TEM and HRTEM images were achieved from a scanning electron microscope (JSM-7600F, Japan), a transmission electron microscope (JEM-1011, Japan) and an analytic transmission electron microscope (JEOL-2100, Japan). The molar ratio of Na, Mn and Ti was determined by inductively coupled plasma-atomic emission spectroscopy (ICP –AES, IRIS Intrepid II XSP, USA). The carbon content of NMTO/C was obtained from a Mettler Toledo TGA/SDTA851 thermal analyzer. Raman spectrum was recorded by a NEXUS 670 FT-IR Raman spectrometer with an excitation wavelength of 632 nm.

Electrochemical measurements

The working electrode was prepared by a recipe of 10 wt.% polyvinylidene fluoride (PVDF), 20 wt.% acetylene black and 70 wt.% active material (NMTO and NMTO/C) in N-methylpyrrolidinone (NMP). The slurry based on the above recipe was bladed on aluminum foil and dried in vacuum at 80 ^{o}C. The resulting film was roll-pressed and punched into the discs with a diameter of 12 mm. These discs typically have active material of ~1.8 mg cm^{-2}. The tap densities of NMTO and NMTO/C are 1.82 and 1.79 g cm^{-3}, respectively. The discs were assembled together with a Na metal foil as the counter electrode, a glass fiber as the separator and 1 M $NaClO_4$ in a mixture of EC-DEC (1:1 volume) as the electrolyte in an argon-filled glove box. Cyclic voltammograms (CV) was acquired from an LK2005A electrochemical workstation between 2 and 4.2 V versus Na^+/Na at a scan rate of 0.1 mV s^{-1}. As to C-rate, 140 mA g^{-1} is assumed to be 1 C.

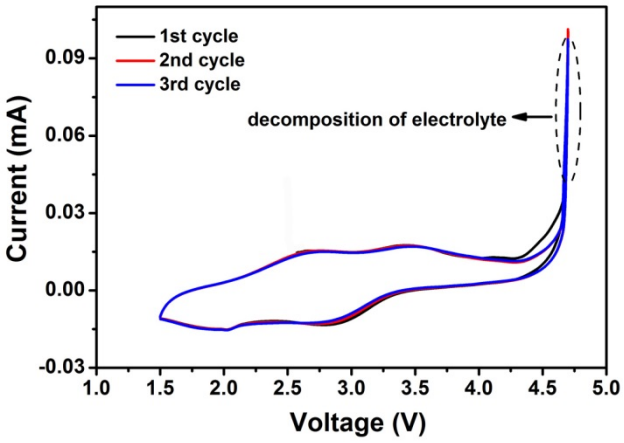

Figure S1. The CV curves of NMTO nanorods between 2.0-4.7 V at a scan rate of 0.1 mV s^{-1}.

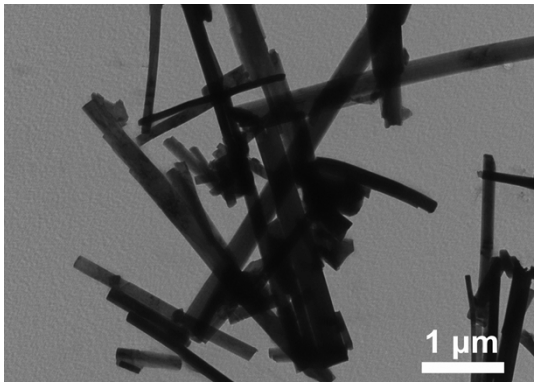

Figure S2. The TEM image of NMTO/C nanorods.

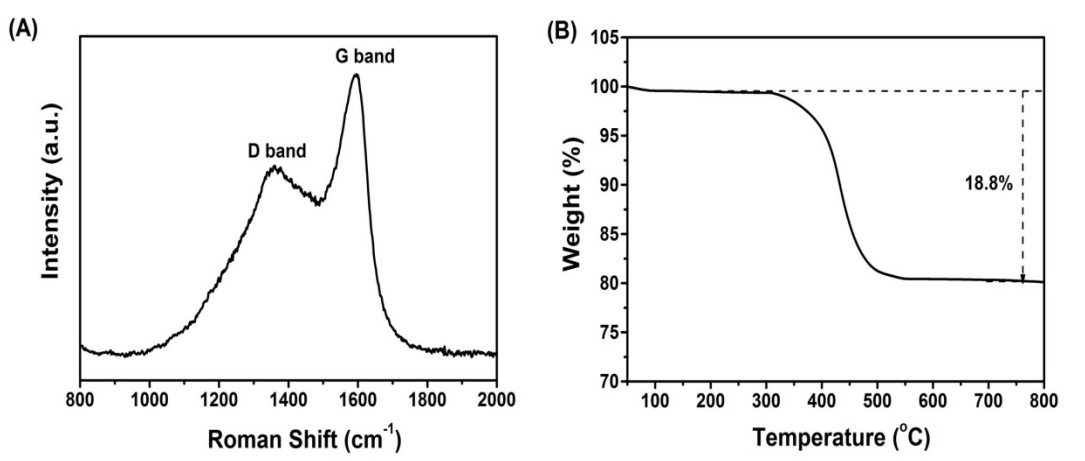

Figure S3. (A) Raman spectrum and (B) TG curve of NMTO/C nanorods. TG measurement was carried out at a heating rate of 10 °C min^{-1} in air.

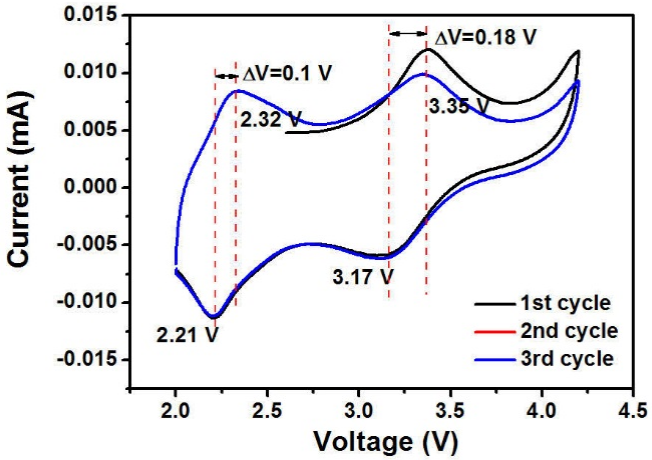

Fig. S4 CV curves of $Na_{0.54}Mn_{0.50}Ti_{0.51}O_2$/C.

Table 1. Lattice parameters of $Na_{0.54}Mn_{0.50}Ti_{0.51}O_2$ Nanorods after Rietveld refinement

Phase	$Na_4Mn_4Ti_5O_{18}$
Crystal system	Orthorhombic
Space group	Pbam (55)
Lattice constants:	
a ()	9.1817(4)
b ()	26.4451(5)
c ()	2.8746(7)
Cell volume (^{3})	698.01
R_B	3.92%
R_{wp}	5.14%
χ^2	1.13