Electronic Supplementary Information (ESI)

$Ti_2Nb_{10}O_{29}$ microspheres coated with ultrathin N-doped carbon layer by atomic layer deposition for enhanced lithium storage

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Experimental

Preparation of TNO@N-C and TNO microspheres

The TNO@N-C microspheres were synthesized via a facile solvothermal method combined with ALD technology plus high temperature sintering process. 0.284 g titanium isopropoxide ($C_{12}H_{28}O_4Ti$, TIP; 97%, Aladdin) and 1.35 g niobium chloride ($NbCl_5$; 99.99%, Aladdin) were dissolved into 70 mL of ethanol with continuous stirring for 20 min. Then, the above solution was transferred into a Teflon-linked steel autoclave and kept at 190 ^{o}C for 20 h. The obtained powder was washed three times with ethanol. After that, the samples were dried at 80 °C. The polyimide film was prepared by using ethylenediamine (EDA) and 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) as precursors in a homemade, closed type, hot wall ALD reactor. Finally, the precursor was calcined in the tube furnace at 800 °C for 2 h in Ar with the heating rate of 5 °C min^{-1}. For comparison, the pure TNO microspheres were prepared by a same solvothermal method combined with high temperature sintering process.

Characterization of materials

The crystal structures of the as-prepared powder were monitored by using X-ray diffraction (XRD, D8 Advance with Cu Kα radiation). Raman spectra were detected by using an inVia Reflex Raman system (Renishaw, England) with a laser wavelength of 532 nm (2.33 eV). The Si peak at 520 cm^{-1} was used as a reference to correct the wavenumber. The chemical composition was characterized by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA). The morphologies of the as-prepared TNO@N-C microspheres and pure TNO microspheres were investigated by using field emission scanning electron microscopy (FESEM, Hitachi S4800). The TEM images were revealed by using a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010F) operating at 200 kV.

Electrochemical characterizations

Electrochemical performance of the TNO@N-C and TNO microspheres were tested by using CR2016 coin cells prepared in an argon-filled glove box. 65 wt. % TNO@N-C microspheres or pure TNO microspheres, 25 wt. % Super P conductive carbon, 10 wt. % polyvinylidene fluoride (PVDF) and a certain amount of N-methylpyrrolidone (NMP) mixed into a homogeneous slurry coted on Cu foil and used as the working electrode. The above working electrodes were dried in a vacuum oven at 100 ^{o}C for 12 h before cell assembly. Meanwhile, microporous polypropylene films (Celgard 2400, Celgard LLC, USA) and pure Li foil were taken as the separators and counter electrode, respectively. A mixture of ethylene carbonate, dimethyl carbonate and diethylene carbonate (1: 1: 1 by weight) with 1 M $LiPF_6$ were used as the electrolyte. Galvanostatic charge/discharge tests were performed in the voltage range from 1.0 to 2.5 V vs. Li/Li^+ at room temperature by using battery testing system (LAND). Cyclic voltammorgams tests were carried out by CHI660C electrochemistry workstation (Chenhua instrument, Shanghai, China) at the voltage range from 1.0 to 2.5 V vs. Li/Li^+. EIS tests were also conducted with amplitude of the sine perturbation signal of 10 mV between 0.01 Hz and 100 kHz.

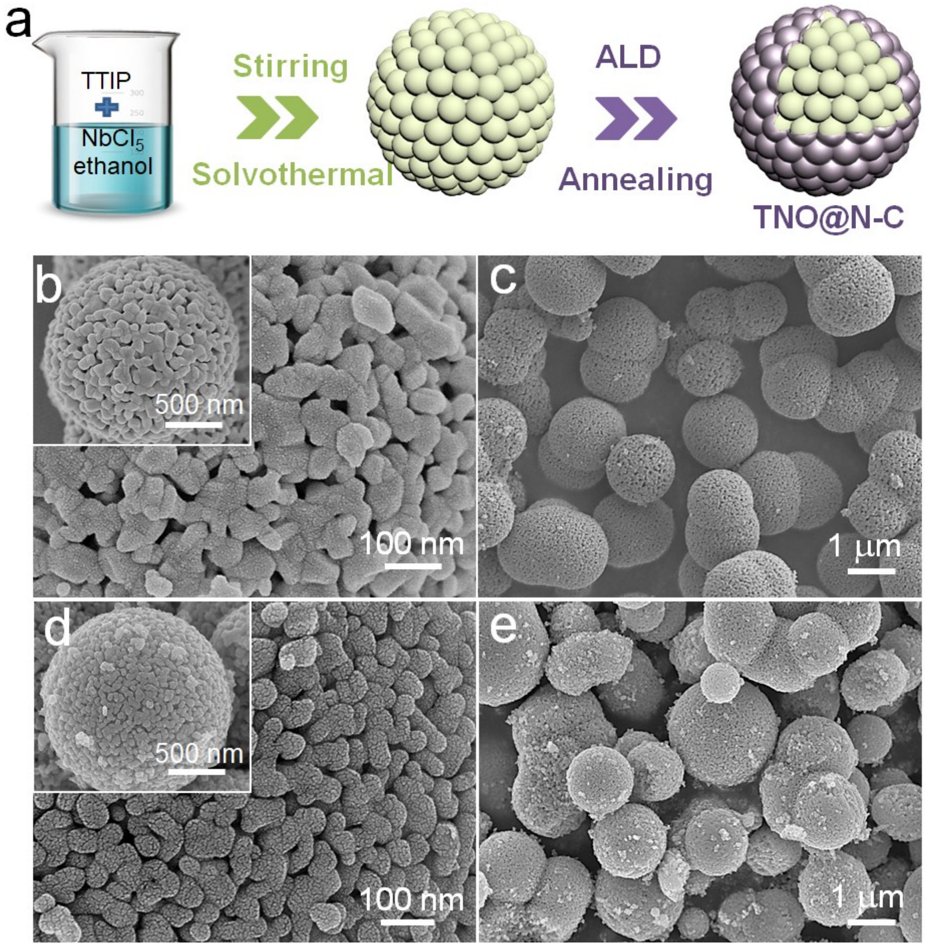

Fig. S1 (a) Schematic illustration of the preparation process of TNO@N-C microspheres; SEM images of samples: (b, c) TNO microspheres, (d, e) TNO@N-C microspheres.

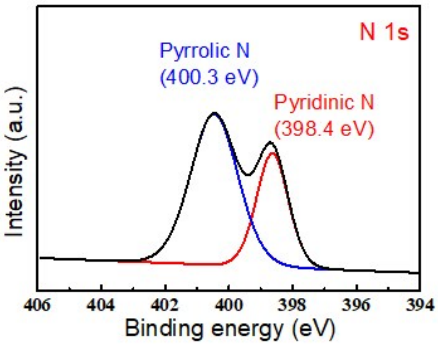

Fig. S2 XPS spectra of N 1S in the TNO@N-C.

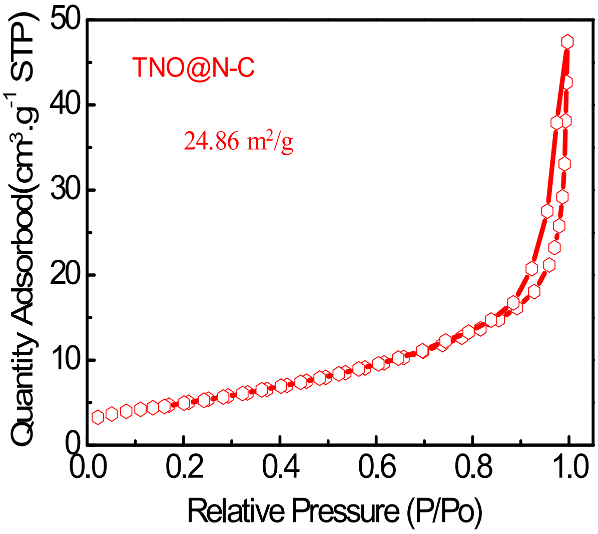

Fig. S3 Nitrogen adsorption–desorption isotherms.

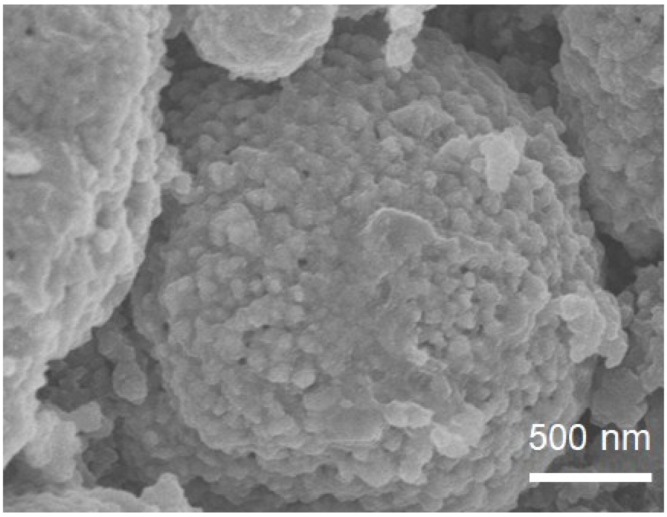

Fig. S4 SEM image of TNO@N-C after cycle stability test.

Table S1. The comparison of electrochemical performance for different samples

Active materials	Rate capability	Cyclability	Ref.
$Ti_2N_{10}O_{29}$ particles	10 C (144 mAh g^{-1})	800 cycles (10 C, 144 mAh g^{-1})	[1]
$Ti_2N_{10}O_{29}$	10 C (130 mAh g^{-1})	/	[2]
Porous $TiNb_{24}O_{62}$	20 C (181 mAh g^{-1})	500 cycles (10, 183 mAh g^{-1})	[3]
$Ti_2N_{10}O_{29}$/C	10 C (194 mAh g^{-1})	100 cycles (5 C, 214 mAh g^{-1})	[4]
$TiNb_6O_{17}$/C	10 C (199 mAh g^{-1})	500 cycles (10 C, 165 mAh g^{-1})	[5]
V-$Ti_2N_{10}O_{29}$	10 mA cm^{-2} (150 mAh g^{-1})	/	[6]
$Ti_2Nb_{10}O_{29}$/rGO	500 mA g^{-1} (165 mAh g^{-1})	/	[7]
$Ti_2Nb_{10}O_{27.1}$	5 C (180 mAh g^{-1})	100 cycles (5 C, 180 mAh g^{-1})	[8]
$TiNb_2O_7$ Microspheres	100 C (143 mAh g^{-1})	1000 cycles (5 C, 190 mAh g^{-1})	[9]
$Ru_{0.01}Ti_{0.99}Nb_2O_7$	5 C (181 mAh g^{-1})	100 cycles (5 C, 162 mAh g^{-1})	[10]
$TiNb_2O_7$ Nanospheres	50 C (167 mAh g^{-1})	10000 cycles (5 C, 160 mAh g^{-1})	[11]
TNO@N-C	**40 C (199** mAh g^{-1}**)**	500 cycles **(10 C, 241** mAh g^{-1}**)**	**This work**

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