

Catalytic effect of nitrogen-doped TiO₂ nanofibers for rechargeable Li-O₂ batteries

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Supporting Information

Experimental section; Synthesis of TiO₂ and N-TiO₂

The two kinds of samples were prepared by simple solution mixture and electrospinning as reported elsewhere¹. Typically for both samples, 1.6ml of Titanium (v) iso-propoxide was mixed with 5ml of ethanol and 0.5ml of acetic acid. After an hour of stirring, the mixture was added to 5ml of ethanol containing 0.5g of PVP (Polyvinylpyrrolidone Mw=1,300,000) followed by 1 hour stirring. For nitrogen doping varying amount (0.1ml, 0.15ml) of Diethylenetriamine as nitrogen precursor was added to the solution. A yellow transparent spinning solution was obtained after 3 hour stirring and loaded into a plastic syringe equipped with a 23 gauge stainless steel needle. The needle was connected to a high voltage supply and the feeding rate was set at 0.5ml/h at a distance of 10cm between the needle and the collector. After spinning the as spun nanofibers were left in air for 24hours to obtain anatase phase. The nanofiber were then heat treated at 450°C for 1 hour in air to remove PVP.

Material Characterization

The morphology and structural characterization were conducted using field emission-scanning electron microscope (FE-SEM), TEM, X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Electronic properties were characterized using ultraviolet photoemission spectroscopy (UPS) and UV-Visible spectroscopy by spin-coating onto ITO and bare glass respectively.

Air-electrode fabrication and cell assembly

The prepared TiO₂ and N-TiO₂ nanofibers (0.016g respectively), conducting agent (ketjen black) and binder (HFP-PVDF) in a ratio of 40% : 45% : 15 % respectively were dispersed in NMP (N-methyl-2-pyrrolidone). The mixture was cast onto a GDL current collector and dried in vacuum at 120°C for 5 hours. Lithium foil and one sheet of glass fiber were used for anode and separator respectively. Lithium metal, the separator and as prepared air electrode were stacked into a Swagelok-type Li-air cell in sequence. The electrolyte was made up of 1 M lithium Bis(trifluoromethane) sulphonamide (LiTFSI) in tetraethylene glycol dimethylether (TEGDME). To elucidate the effect of TiO₂ nanofiber amount on the electrochemical performance, an electrode with the ratio of 75%(TiO₂ nanofiber) : 10%(ketjen black) : 15% (HFP-PVDF) was also prepared using the aforementioned procedure.

Electrochemical Measurement

The cell was galvanostatically charged and discharged at a current density of $200\text{mA/g}_{(\text{carbon})}$ over a range of 2.0 - 4.5 V. For the stabilization of cycling, the cell was also tested using a constant current – constant voltage (CC – CV) mode with potentiostatic steps at 4.2 V under limited capacity condition ($1000\text{mAh/g}_{(\text{carbon})}$). To clearly distinguish the electrochemical performance of the doped and pristine TiO_2 , a higher current density of $500\text{mA/g}_{(\text{carbon})}$ was also demonstrated.

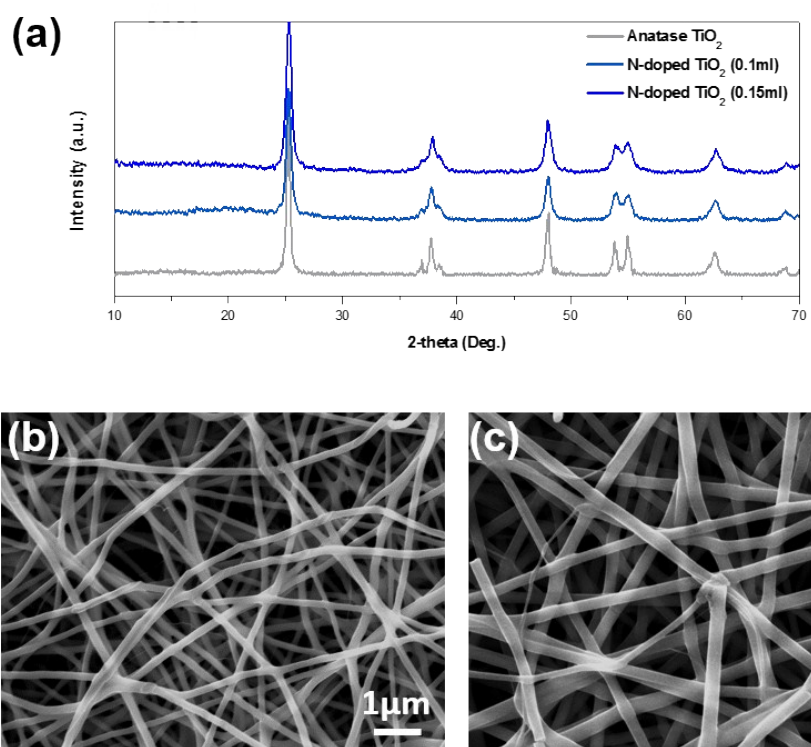
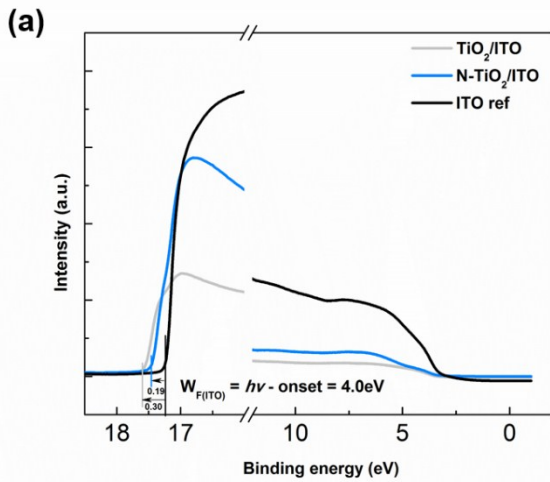


Fig. S1. (a) XRD patterns of pristine anatase TiO_2 and N- TiO_2 , SEM images of as-spun (b) pristine TiO_2 , (c) N- TiO_2 nanofibers.



(b)

Sample	Work Function (ϕ)
ITO ref	4.0
N-TiO ₂	4.19
TiO ₂	4.30

Fig. S2. UPS spectra (He I, $h\nu = 21.2\text{eV}$) of N-TiO₂/ITO, TiO₂/ITO samples and bare ITO substrate. The ITO work function (4.0eV) and the vacuum shift were determined by using the onset of photoemission. (b) Table comparing the obtained work function values of N-TiO₂/ITO, TiO₂/ITO samples and bare ITO substrate.

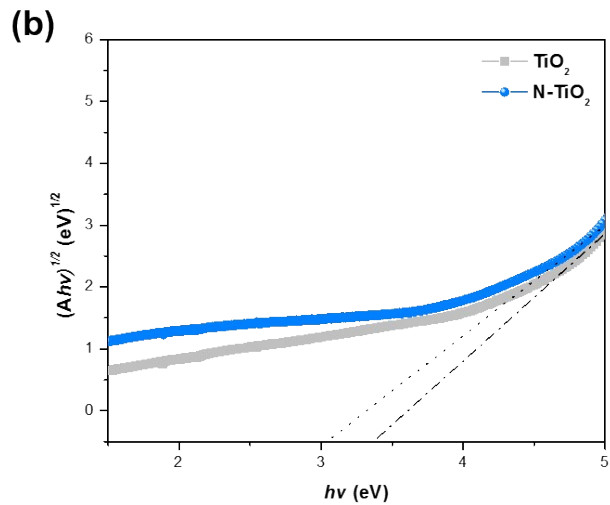
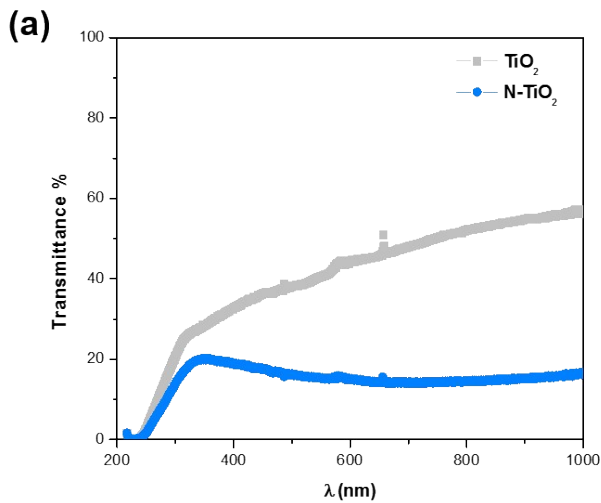


Fig. S3. Transmittance spectra of TiO₂ thin film on glass substrate; (a) Optical transmittance spectra of N-TiO₂ and pristine TiO₂, (b) Tauc's plot showing the band gaps (E_g) of N-TiO₂ and pristine TiO₂ obtained from UV-visible spectroscopy.

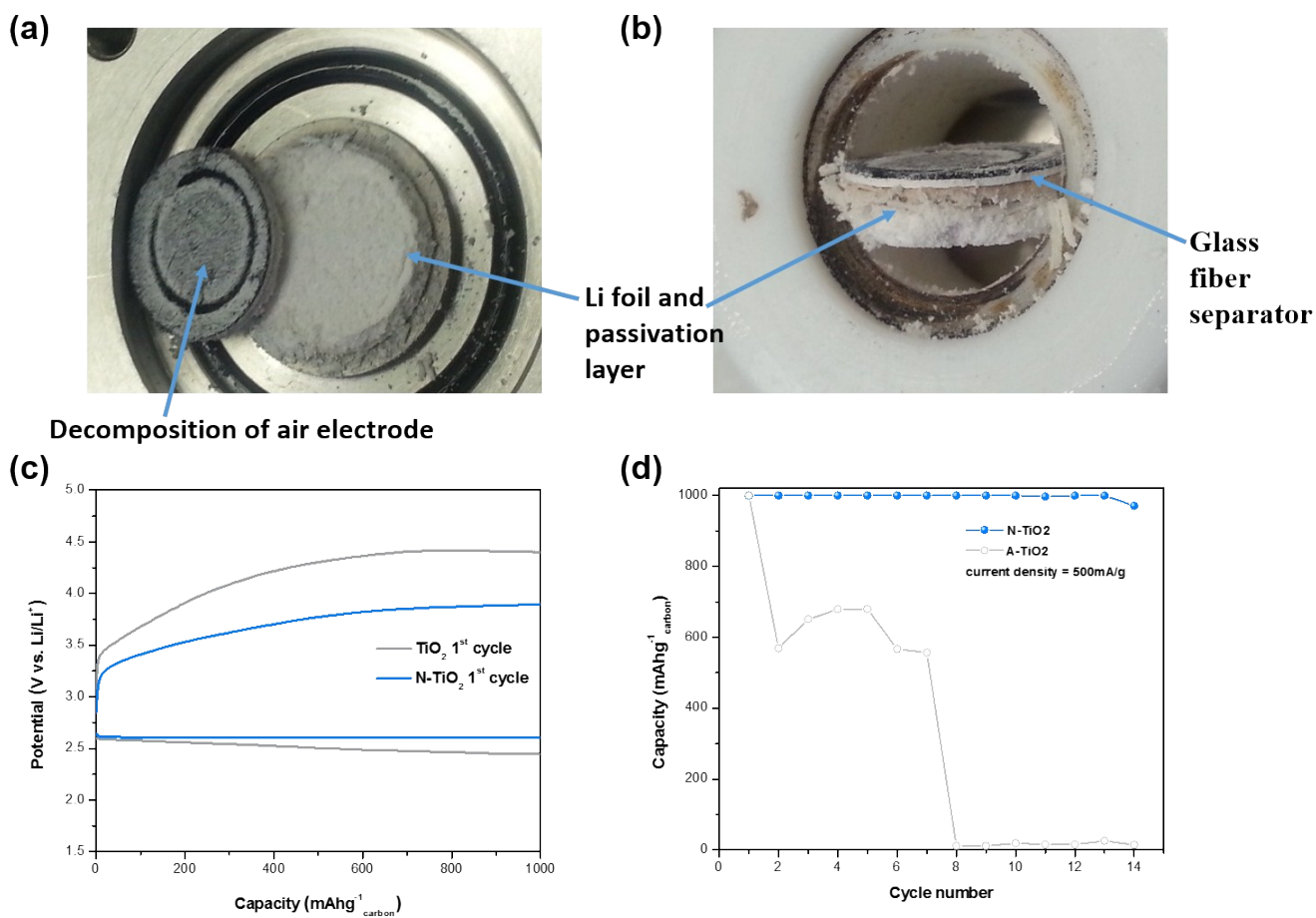


Fig. S4. (a & b) Pictorial images of N-TiO₂ electrodes after 20cycles showing the decomposition of lithium foil and the formation of passivation layer, which result in capacity fading upon cycling. (c) Discharge-charge curves and (d) cyclic retention at capacity cut-off of 1000mAh/g_(carbon) and current density of 500mA/g_(carbon).

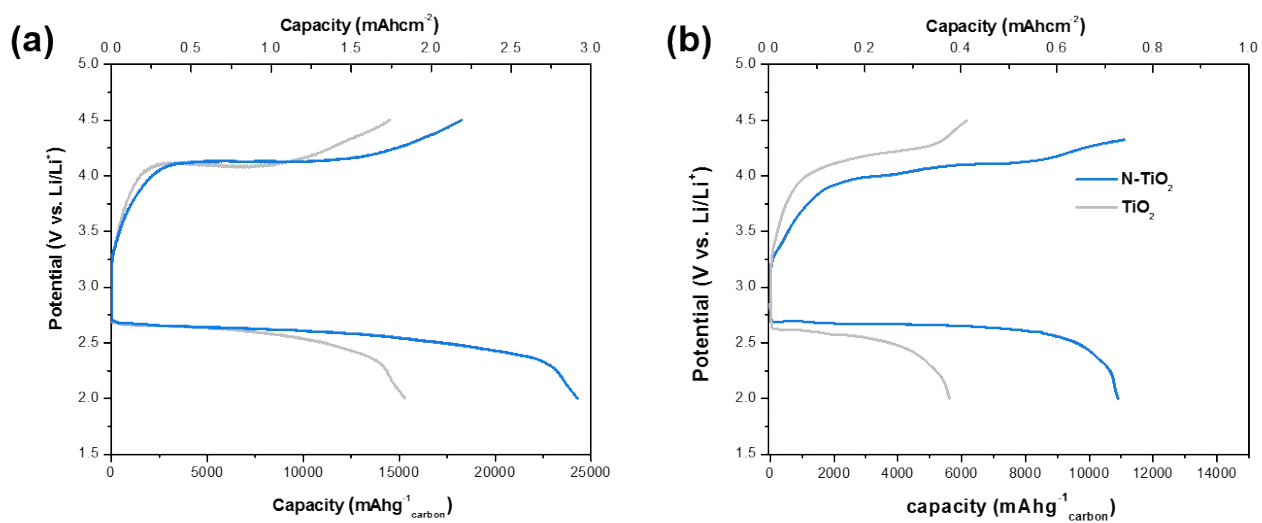


Fig. S5. The initial electrochemical performances of N-TiO₂ NF and TiO₂ NF electrodes in the electrode composition of (a) 75:10:15 and (b) 40:45:15 at current density of 200mA/g_(carbon)

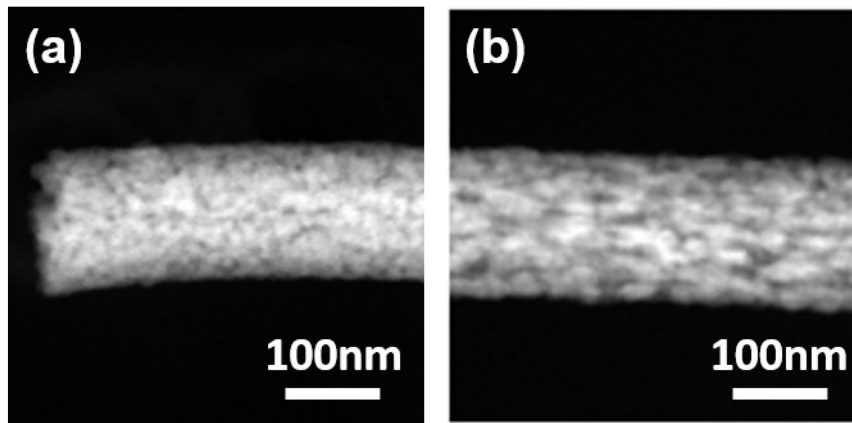


Fig. S6. High resolution STEM image of (a) N-doped TiO_2 (b) pristine TiO_2 NFs indicating the porosity of the samples which confirms the BET calculation.

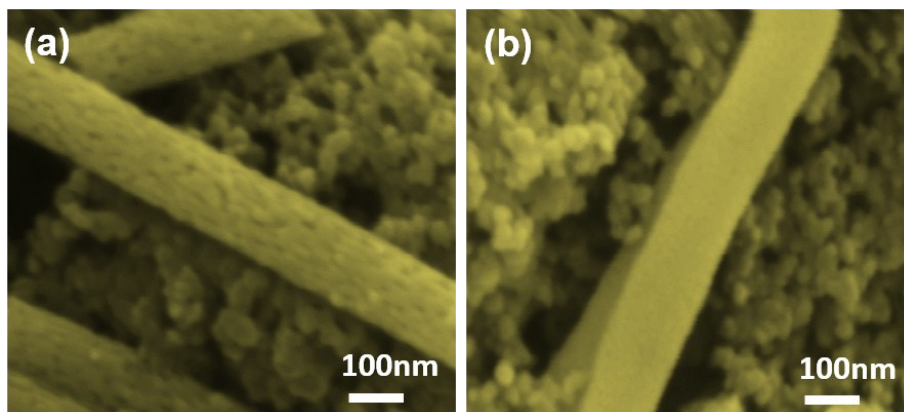


Fig.S7. High resolution SEM image of (a) pristine (b) N-doped TiO_2 pristine electrodes showing nanofibers retain their structure after electrode preparation.

Textural properties	Samples	
	TiO ₂	N-TiO ₂
S _{BET} (m ² ·g ⁻¹)	46.188	27.834
V _P (cm ³ ·g ⁻¹)	0.1483	0.0636

Table S1. The surface and pore properties of both N-TiO₂ and pristine TiO₂ characterized by adsorption/desorption measurements and results shown in table. The surface area is calculated by the Brunauer-Emmett-Teller (BET) method