

Boosting Fast-Charging Performance of TiNb_2O_7 via Graphdiyne

Coating

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Experimental Procedures

Synthesis of TiNb_2O_7 (TNO) :

TNO can be prepared using a straightforward sol-gel method. Specifically, 4.8 g of F127 is added to a mixed solution containing 90 mL of ethanol, 6 mL of hydrochloric acid, and 7 mL of acetic acid. The mixture is stirred until uniform, followed by the addition of 5.4 g of NbCl_5 and 3.4 mL of titanium butoxide $\text{Ti}(\text{OC}_4\text{H}_9)_4$. Stirring continues until the solution becomes colorless. The solution is then transferred to a Petri dish and heated at 60°C to evaporate the solvent, forming a gel. The gel is transferred to a crucible and heated in a muffle furnace at a rate of $5^\circ\text{C}/\text{min}$ up to 750°C , where it is held for 2 hours. The resulting white solid, TNO, is ground and stored for later use.

Synthesis of TNO@GDY :

The synthesis of the graphdiyne (GDY) precursor, hexakis[(trimethylsilyl)ethynyl]benzene (HEB-TMS), follows previously reported procedures¹. In a dry three-neck flask, 100 mL of anhydrous THF is added under argon protection. With the flask kept in an ice-water bath and shielded from light, 300 mg of HEB-TMS is dissolved, and 4 mL of tetrabutylammonium fluoride (TBAF) is added. After approximately 10 minutes of reaction, an appropriate amount of ether is added for extraction, followed by three washes with saturated saline. The solution is dried over anhydrous sodium sulfate, yielding an ether solution of HEB (approximately 1 mg/mL), which is stored in the refrigerator, protected from light. For the synthesis of TNO@GDY , 6 mg of the HEB ether solution is mixed with 200 mg TNO, 100 μL pyridine and 2 mg CuCl . The mixture is stirred at room temperature for 24 hours. The product is then centrifuged and washed three times with ethanol, resulting in the in situ coated GDY on TNO, designated as TNO@GDY . Detailed steps are provided in Figure S1.

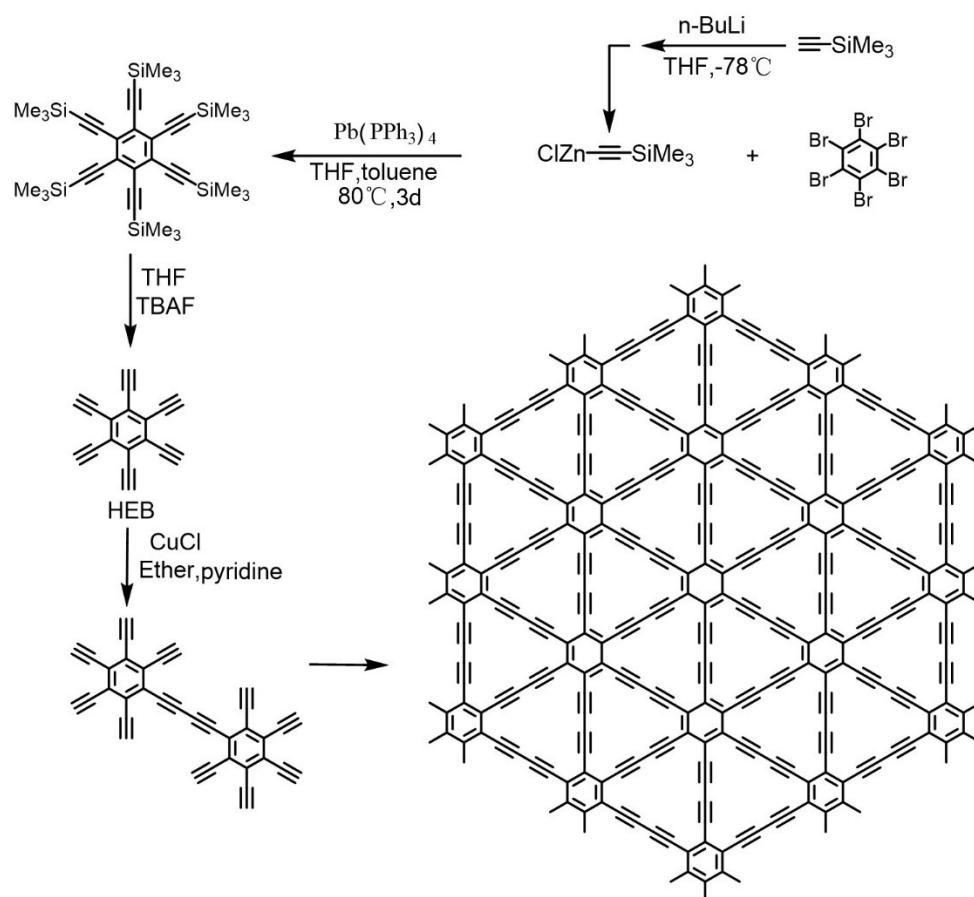


Figure S1. Detailed synthesis steps of GDY.

Materials characterization :

The powder X-ray diffraction (XRD) patterns were collected using a Panalytical Empyrean diffractometer set to 45 kV and 40 mA. Scanning electron microscopy (SEM) was carried out on a Carl Zeiss Auriga 40 SEM microscope, while transmission electron microscopy (TEM) images were obtained with a Carl Zeiss Libra 200 MC TEM microscope. Raman spectra were recorded with a WITec GmbH Alpha 300 confocal Raman microscope, utilizing a solid-state 532 nm excitation laser. Fourier-transform infrared (FTIR) spectra of the samples were recorded using a Nicolet Nexus iS50 FTIR instrument, covering a spectral range of 4000 to 500 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific spectrometer, equipped with a monochromated Al K α (1486.6 eV) X-ray source focused to a 400-micron spot under a pressure of less than 1×10^{-7} mbar. The calibration and deconvolution of XPS peaks were processed using Avantage software. The thermal gravimetric analysis (TGA) was performed on TGA Q50 thermogravimetric analyzer at 10° /min in air atmosphere.

Electrochemical Testing :

First, a binder solution was prepared by mixing PVDF with NMP solvent at a mass ratio of 1:10, stirring with a magnetic stirrer until the mixture was uniform. Next, the electrode preparation was carried out. The active material (TNO or TNO@GDY),

Super P carbon black, and PVDF were mixed in a mass ratio of 70:20:10 to obtain the experimental slurry. This slurry was then spread onto copper foil using a doctor blade and vacuum-dried at 110°C for 12 hours. The electrodes were cut into small circular discs (1 cm in diameter) with a mass loading of 1.3~2.1 mg cm⁻². CR2032 coin-type half-cells were assembled in an argon-filled glove box, using lithium metal as the counter electrode and Celgard 2500 as the separator. The electrolyte was a solution of 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, V/V). The electrochemical performance of TNO and TNO@GDY was evaluated within a voltage window of 1.0V~3.0V using a Neware testing system.

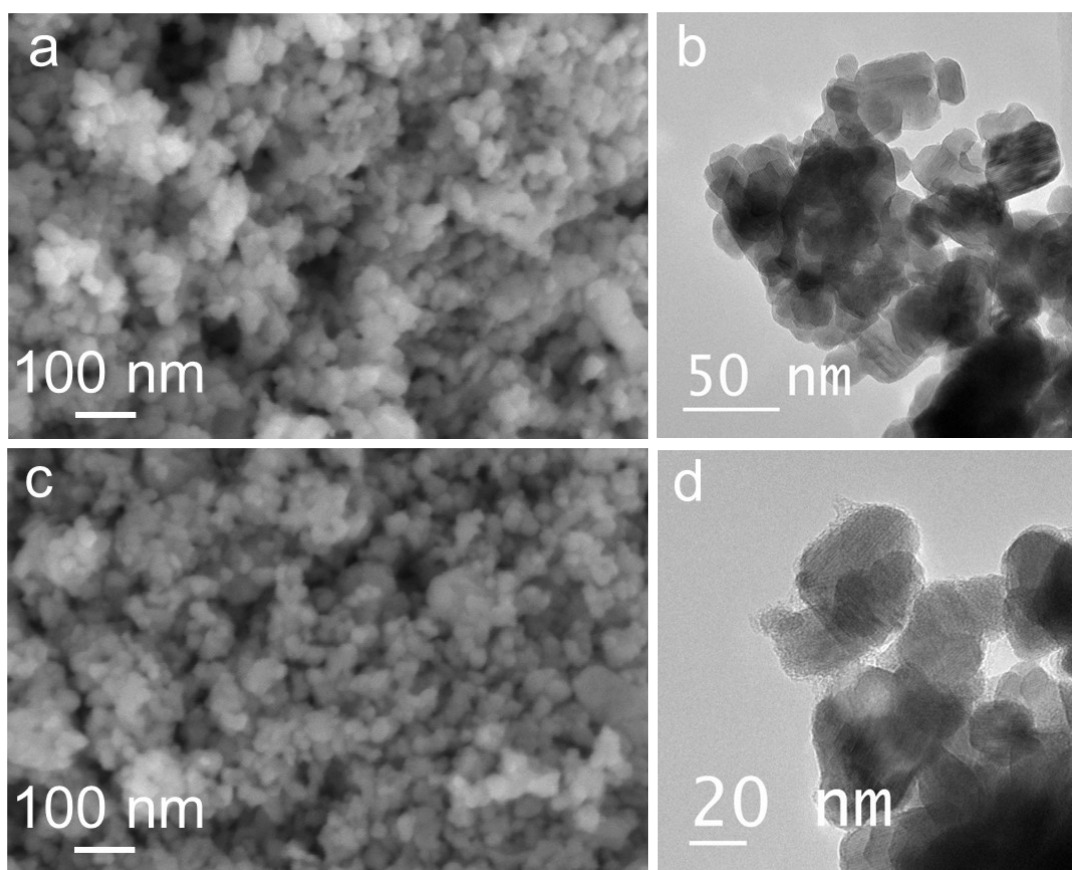


Figure S2. SEM images and TEM images of (a, b) TNO (c, d) TNO@GDY.

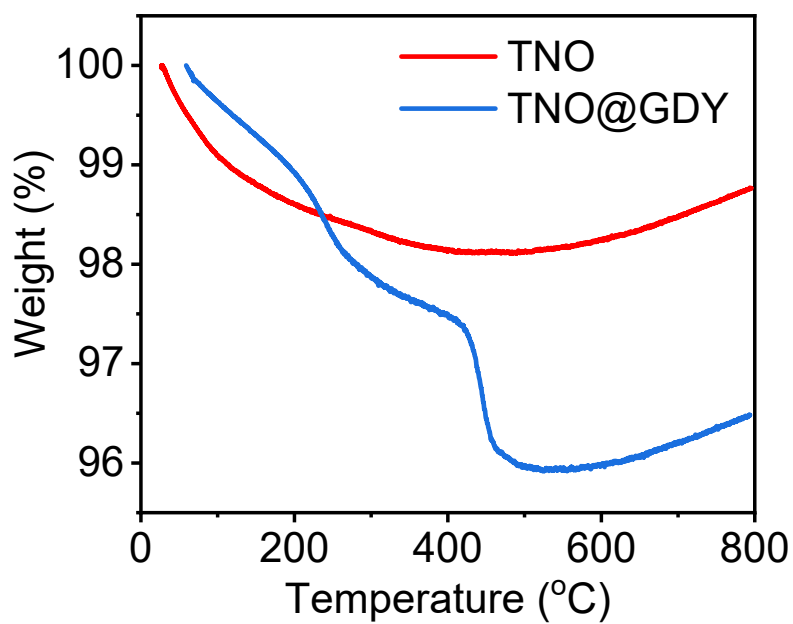


Figure S3. TGA results of TNO and TNO@GDY under air with a ramping rate of 10 °C min⁻¹.

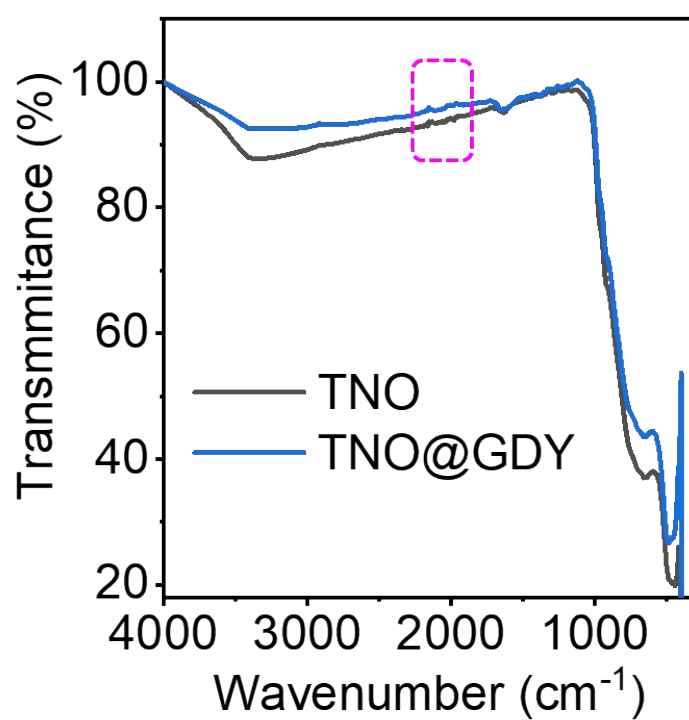


Figure S4. FTIR spectra of TNO and TNO@GDY.

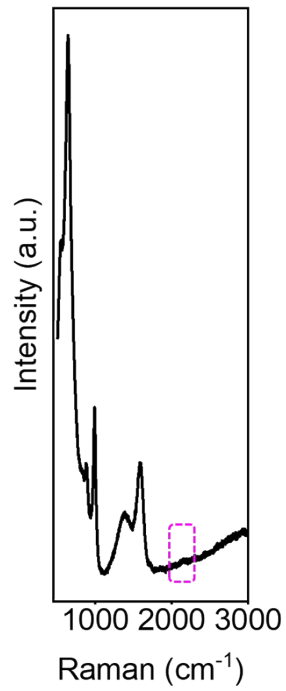


Figure S5. Raman spectra of TNO@GDY.

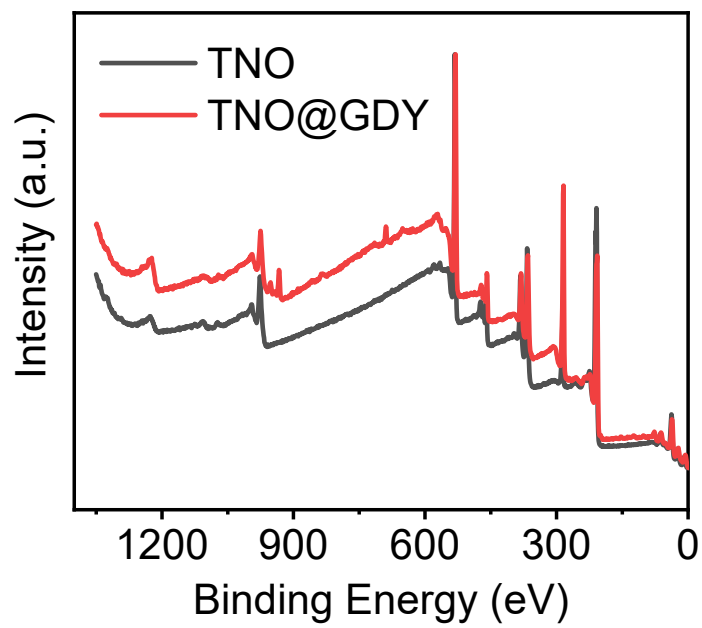


Figure S6. XPS survey spectra for TNO and TNO@GDY.

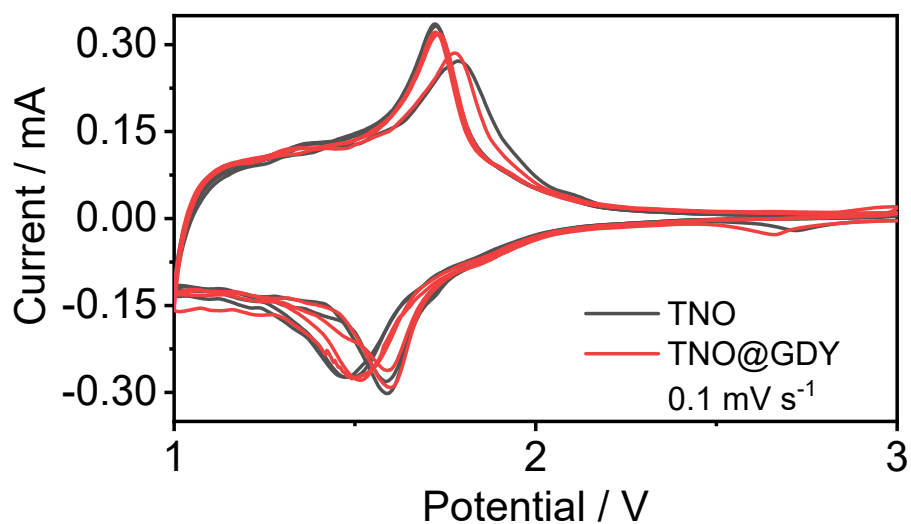


Figure S7. Cyclic voltammograms of TNO and TNO@GDY half-cell at a scan rate of 0.1 mV s⁻¹.

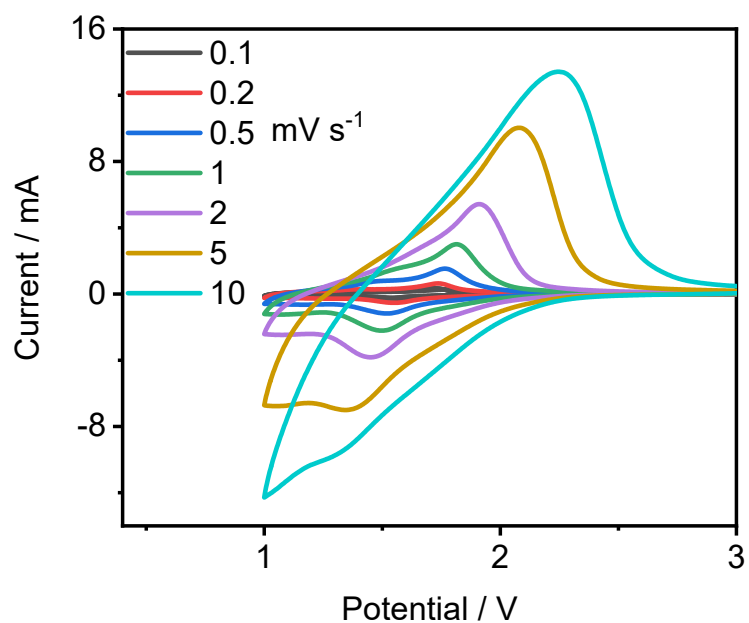


Figure S8. CV curves of TNO measured at sweep rates from 0.1 to 5 mV s⁻¹.

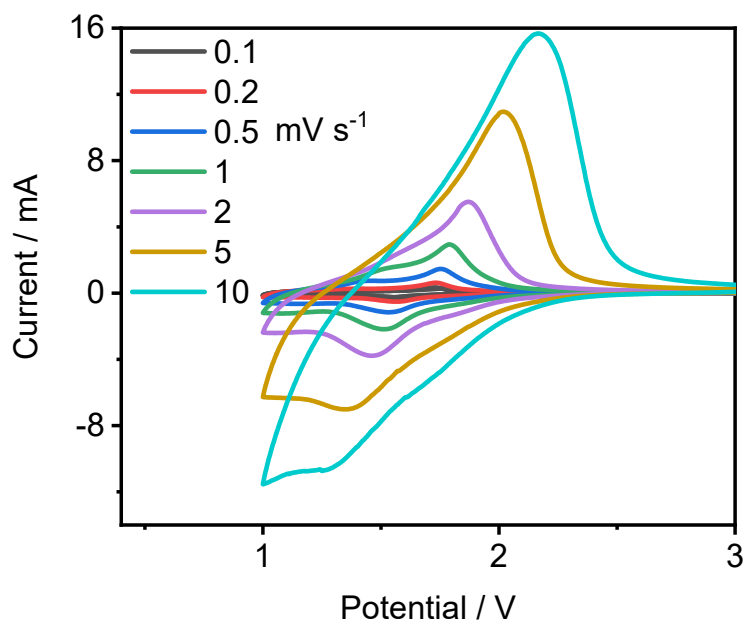


Figure S9. CV curves of TNO@GDY measured at sweep rates from 0.1 to 5 mV s⁻¹.

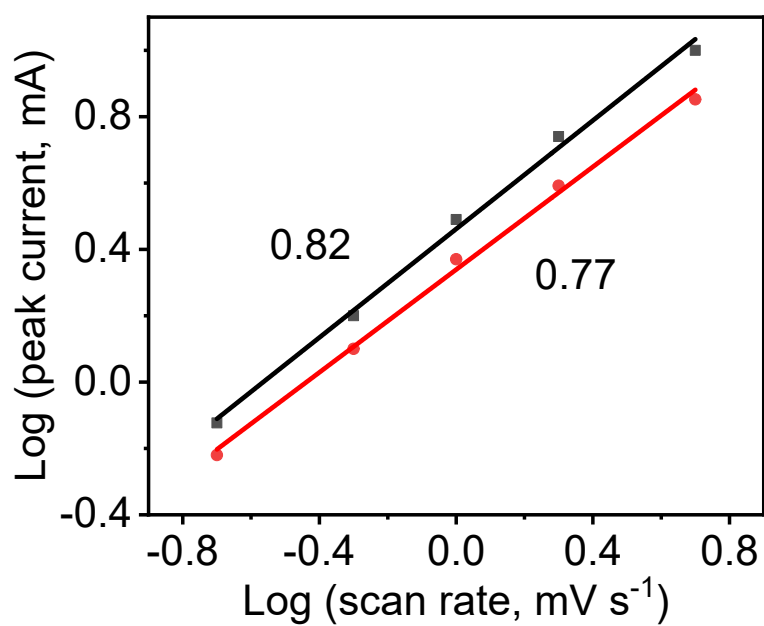


Figure S10. The corresponding peak currents of TNO measured at sweep rates from 0.2 to 5 mV s⁻¹.

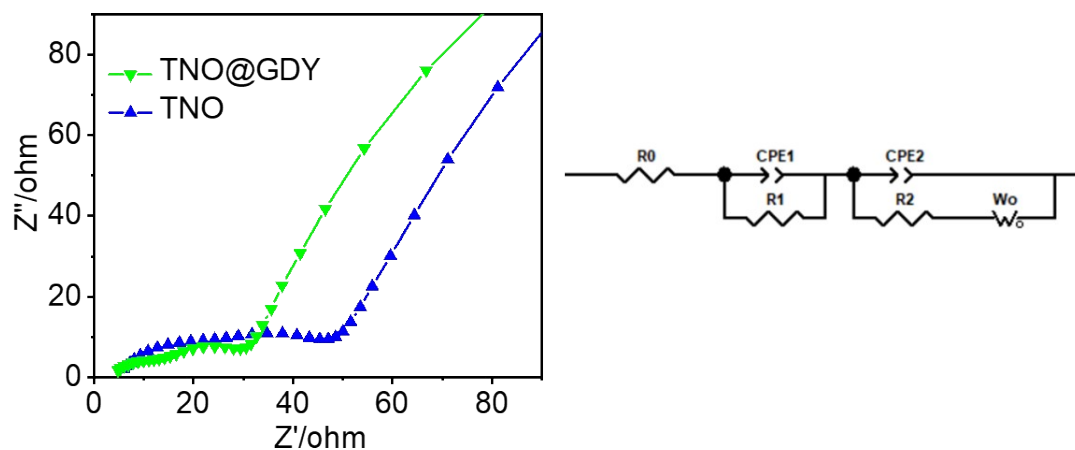


Figure S11. Nyquist plots of TNO and TNO@GDY and equivalent circuit model after CV activation.

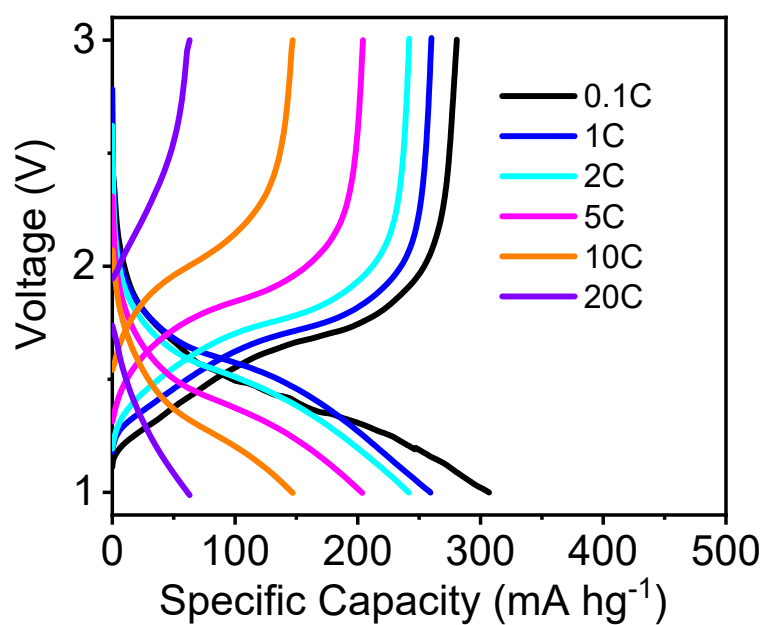


Figure S12. Discharge-charge curves of the TNO anode at different current rates.

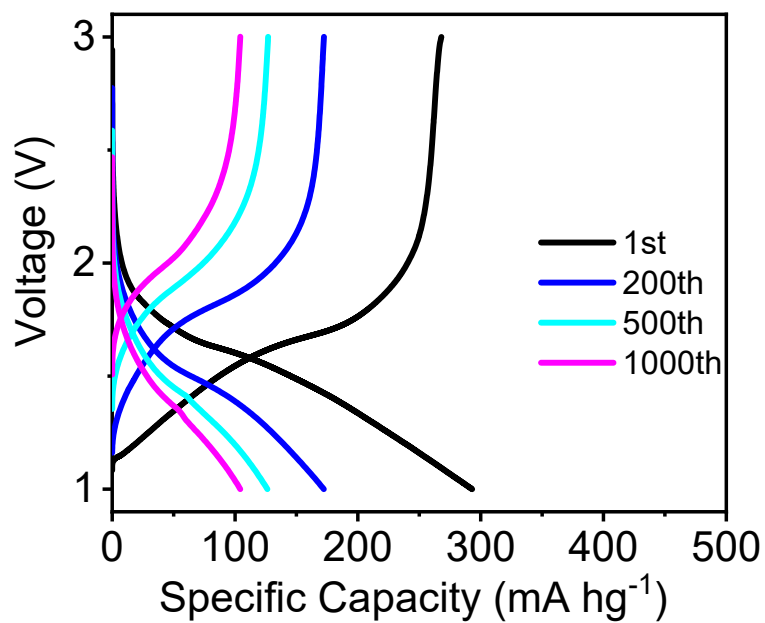


Figure S13. Charge and discharge profiles of TNO at 5C rate.

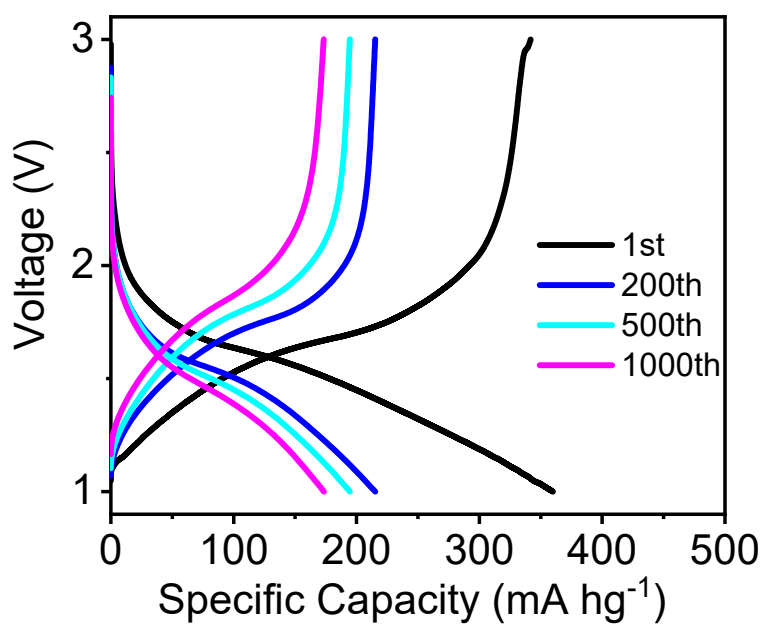


Figure S14. Charge and discharge profiles of TNO@GDY at 5C rate.

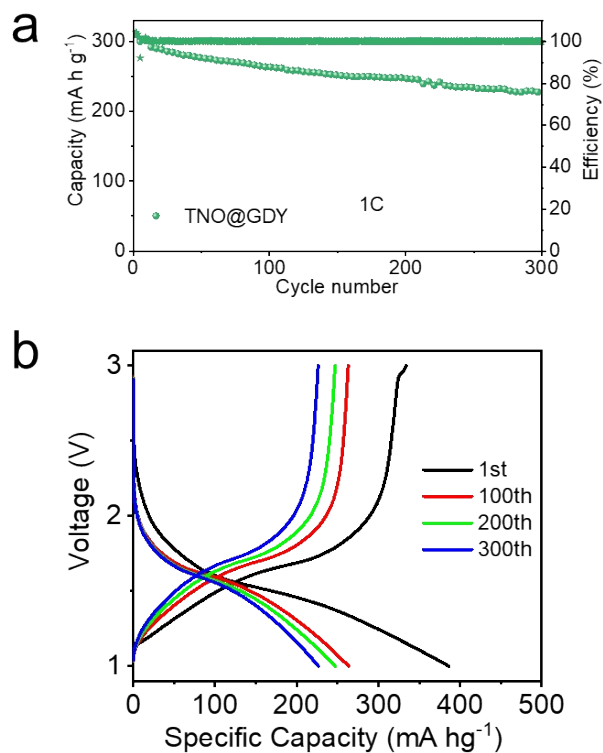


Figure S14. (a) Cyclic performance of the TNO@GDY anode at a current rate of 1 C (active substance loading 16.3 mg cm⁻²); (b) charge and discharge profiles of TNO@GDY at 1C rate.

Table S1. Surface composition of TNO and TNO@GDY.

	C	Nb	O	Ti
TNO	31.1	14.6	49.2	4.9
TNO@GDY	56.1	6.5	31.2	2.4

Table S2. EIS equivalent circuit model of TNO and TNO@GDY.

Sample	R0 (ohm)	R1(ohm)	R2(ohm)
TNO	4.76	17.69	21.88
TNO@GDY	3.46	11.97	13.93

References

1. G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*, 2010, **46**, 3256-3258.