

Electronic Supplementary Information (ESI)

Porous TiN nanoparticles embedded in N-doped carbon composite derived from metal-organic frameworks as a superior anode in lithium-ion batteries

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Experimental

Material preparation

MIL-125 (Ti) was synthesized as described in our previous work. To prepare the porous TiN/N-doped C composite, MIL-125 (Ti) and melamine were ground together at a mass ratio of 1:5 using a mortar and pestle to form a uniform mixture. The mixture was first heated at 400 °C for 3 h, then heated to 900 °C at a speed of 5 °C min⁻¹, maintaining the temperature for 4 h in an argon (Ar) atmosphere.

For comparison, MOF-derived TiO₂/C composite was prepared by pyrolysis of MIL-125 (Ti) in argon as the same procedure used for preparing the porous TiN/N-doped C composite.

Materials characterization

The crystal structures of the obtained samples were identified using an X-ray diffractometer (XRD, Shimadzu, Chonnam National University, South Korea) with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the prepared sample was characterized using field-emission scanning electron microscopy (FE-SEM, S-4700, Hitachi, Chonnam National University, South Korea) and field-emission transmission electron microscopy (FE-TEM, Philips Tecnai F20 at 200 keV, KBSI, Chonnam National University, South Korea). The surface area was determined based on the nitrogen adsorption and desorption isotherms measured using the Brunauer–Emmett–Teller method (BET, Micromeritics ASAP2010 Instrument Co., Norcross, GA, USA, Chonnam National University, South Korea). Surface analysis of the composite was carried out using an X-ray photoelectron spectroscope (XPS, Thermo VG Scientific instrument, Multilab 2000, Chonnam National University, South Korea). The Raman measurement of the composite was conducted with an NRS-5100 device (JASCO, Tokyo, Japan, Chonnam National University, South Korea). Thermogravimetric analysis (TGA) was performed using a TA instrument SDT Q600 thermobalance (USA, Chonnam National University, South Korea) under an Ar atmosphere with a temperature change of 5 °C min⁻¹.

Electrochemical measurements

The electrochemical performance was investigated using coin-type cells (CR2032) with lithium metal as the counter electrode. The working electrode was prepared by mixing 70 wt% active material, 20 wt% conductive carbon (carbon black, Super P), and 10 wt% binder

(polyvinylidene fluoride, PVDF). The slurry was coated on a copper foil as an anode, and the electrode was assembled into a coin cell in an Ar-filled glove box. The electrolyte was 1 M LiPF_6 dissolved in an equi-volume mixture of ethylene carbonate and dimethylcarbonate (1:1 volume ratio).

The cells were tested using a BTS-2004H battery tester (Nagano, Japan) within the voltage range from 0.005 to 3.0 V (vs. Li^+/Li). Cyclic voltammetry (CV) curves and Nyquist plots were obtained on an AUTOLAB potentiostat (PGSTAT302N).

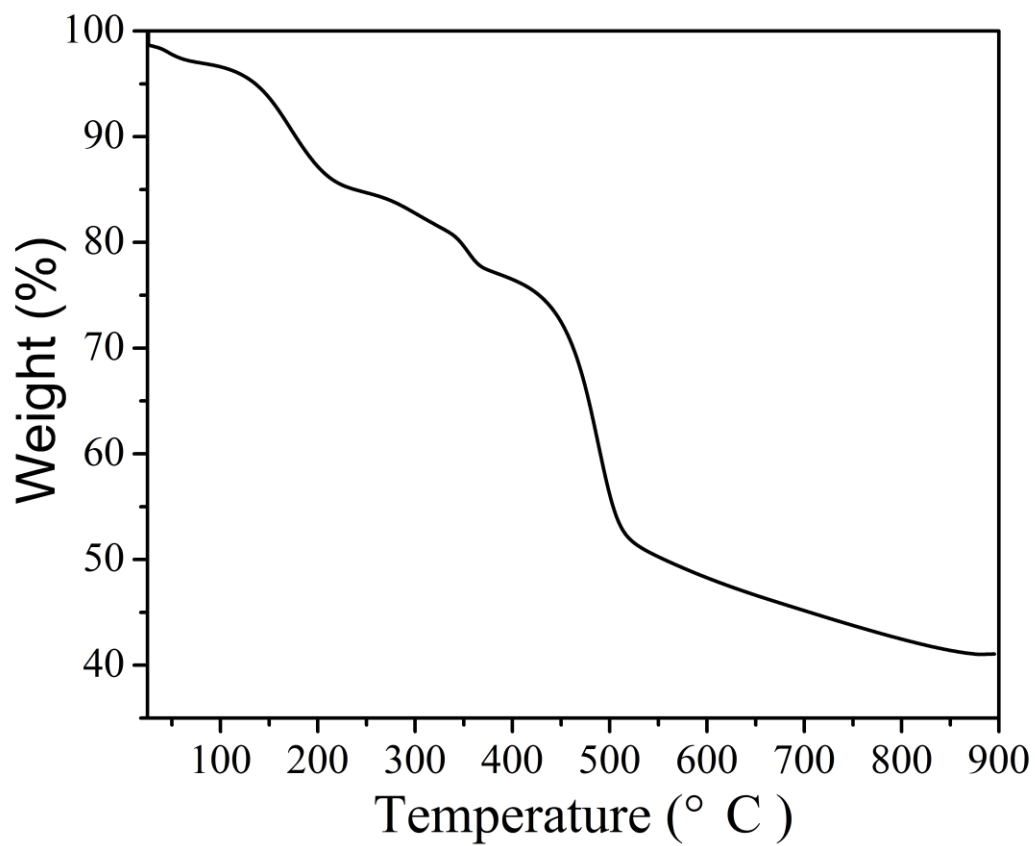


Fig. S1 TGA curve of TiMOF heated under an Ar atmosphere

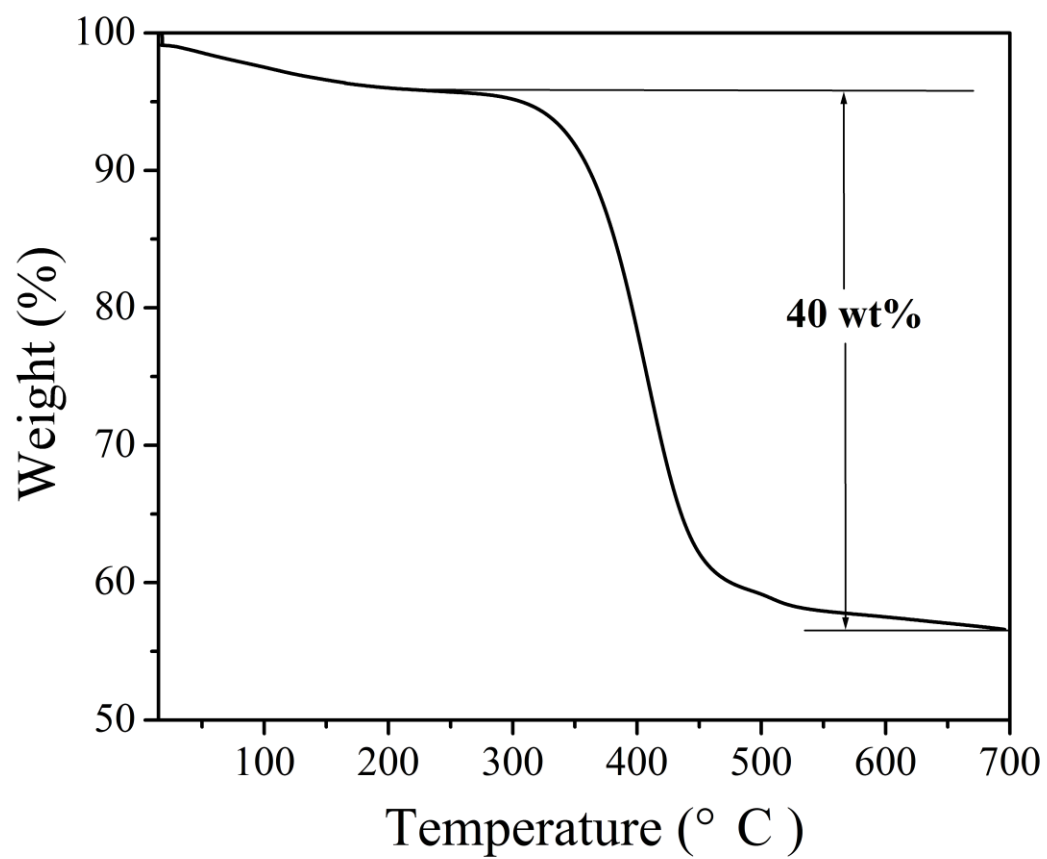


Fig. S2 TGA curve of the porous TiN/N-doped C composite heated in air.

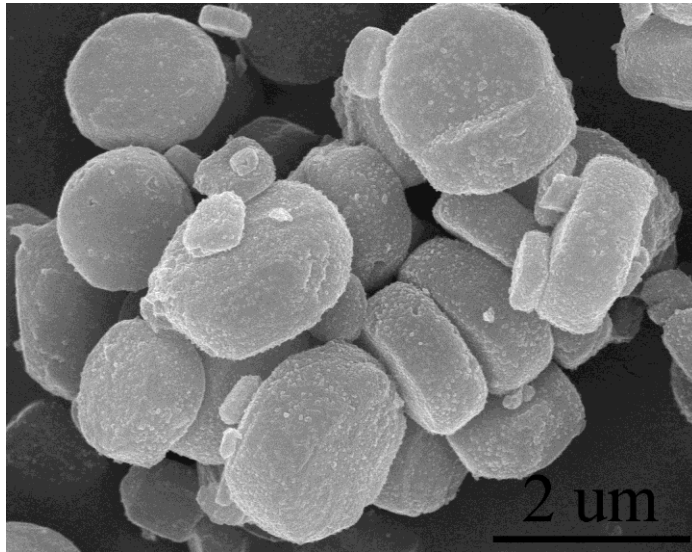


Fig. S3 SEM image of the porous TiN/N-doped C composite.

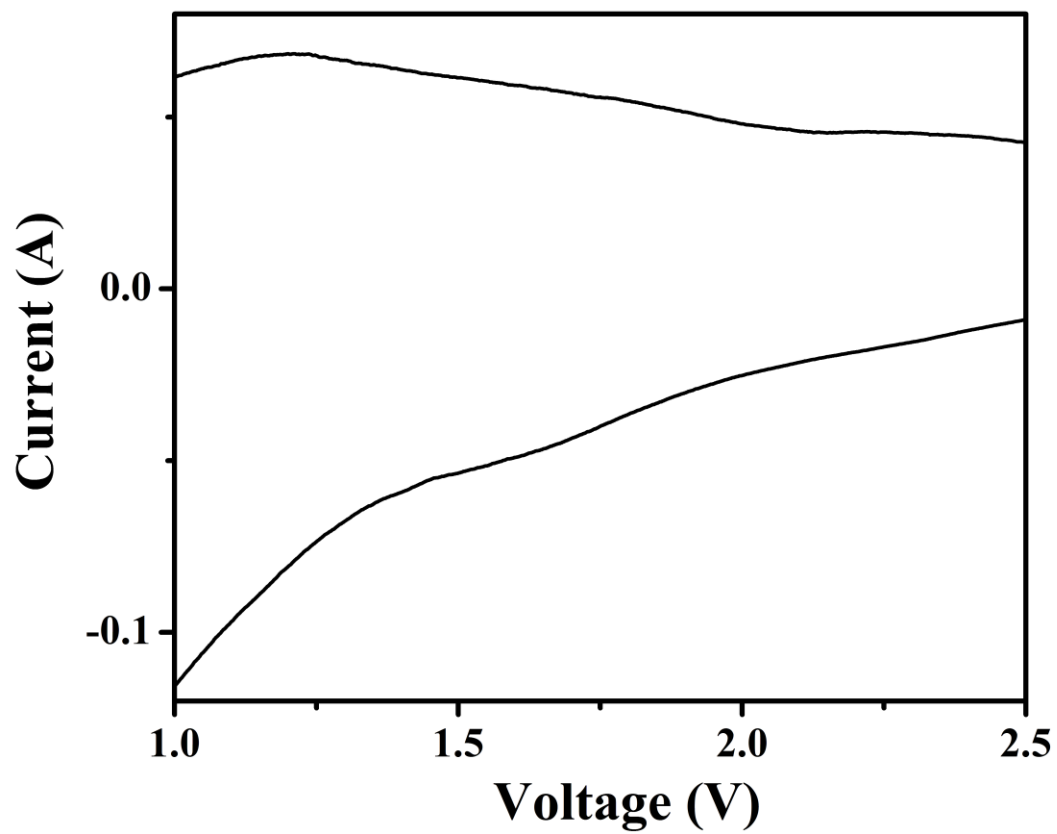


Fig. S4 A close-up view of the first CV curve of the porous TiN/N-doped C composite in the range of 1.0-2.5 V.

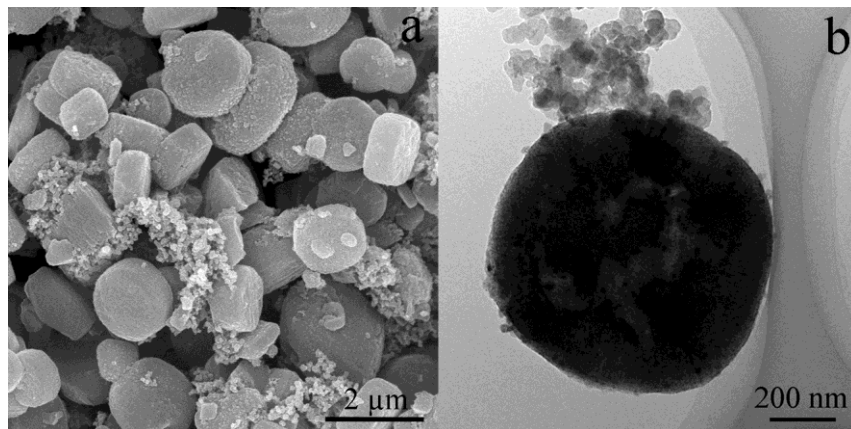


Fig. S5 SEM and TEM images of the cycled electrode

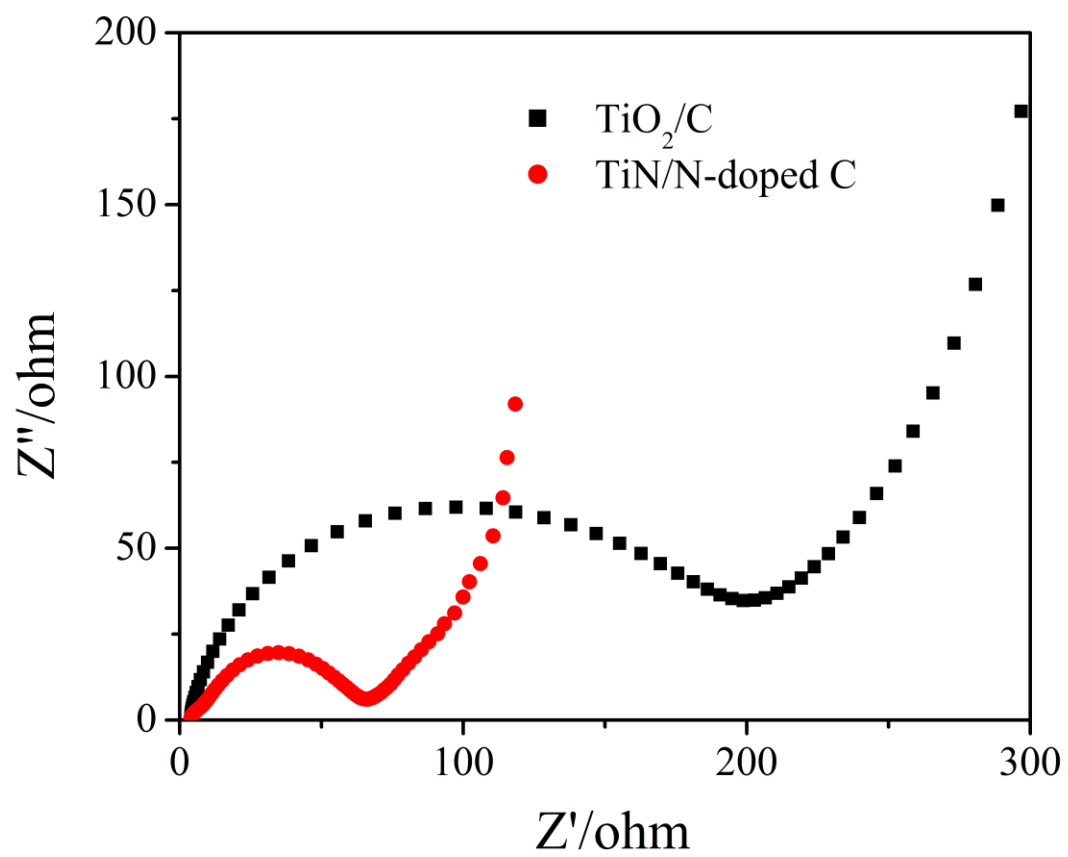


Fig. S6 Nyquist plots of the cycled $\text{TiN}/\text{N-doped C}$ electrode and the cycled TiO_2/C electrode

Table S1 Comparison of the capacities of the porous TiN/N-doped C composite electrode presented in this work with those of electrodes recently reported in the literatures

Sample	Discharge capacity (mA h g ⁻¹)	Current density (mA g ⁻¹)	Reference
Porous carbon Nanofibers	491	50	1
Porous carbon	400 306	372 744	2
Porous carbon	277.9 200 ^a 139 ^a	18.6 74.4 167.4	3
Porous carbon sphere	378 270	37.2 372	4
N-doped hollow carbon sphere	462 363 286 230	372 744 1116 1860	5
Graphitized porous carbon microspheres	453 410 ^a 350 ^a 300 ^a	50 100 500 1000	6
TiVN/C-2	596 400 ^a 300 ^a	74.4 744 1860	7
TiN nanowires/ carbon fabric	460 385 332 288	335 670 1005 1675	8
Porous TiN/ N-doped C	561 492 364 326 281	50 100 500 1000 2000	This work

^aThe discharge capacity was estimated according to the literatures.

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