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Nanocrystalline Anatase TiO_2: a New Anode Material for Rechargeable Sodium Ion Batteries

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Experimental details

Preparation of nanocrystalline anatase TiO_2

Filter paper (Qualitative Grade 1, Whatman) was used as received without further treatment. In a typical process, 30 ml methanol, 3 ml hydrochloric acid (37 wt%), and 6.66 ml titanium isopropoxide ($C_{12}H_{28}O_4Ti$) were added into a beaker and stirred to form a homogeneous solution. The concentration of Ti was 0.57 M. 5 pieces of filter paper were immersed into the above solution, followed by stirring for 3 h at room temperature. Then the Ti-impregnated filter paper was held between two pieces of glass and dried at 60 ˚C overnight under vacuum. After that, they was hydrolyzed in deionized water at 95 ˚C for 3 h, followed by drying at 60˚C overnight under vacuum. Finally, anatase TiO_2 nanocrystals were obtained by annealing the filter paper in air at 550 ˚C for 2 h at a heating rate of 2 ˚C min^{-1}. For comparison, a composite of anatase TiO_2 nanocrystals intermixed with amorphous carbon was obtained by annealing in Ar

under the same conditions. Pure carbon sample was also obtained by annealing filter paper in Ar under the same conditions.

Characterization

X-ray diffraction (XRD) analysis was performed using a Bruker AXS D8 Discover diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) analysis was performed using a Hitachi H9500 transmission electron microscope with an accelerating voltage of 1000 kV. Scanning electron microscopy (SEM) analysis was conducted using a Hitachi S-4800 field emission scanning microscopy. X-ray photoelectron spectroscopy (XPS) analysis was performed using an Axis Ultra spectrometer with a base pressure of 5×10^{-10} Torr. The measurement of the nitrogen adsorption-desorption isotherms was perfomed using Nova 2000. Thermal gravimetric analysis was performed on a SDT Q600, TA Instruments TGA, in air with a heating rate of 10 ˚C min^{-1}.

Electrochemical measurement

The electrodes were fabricated by mixing the active material, carbon black (super P), and poly(vinylidenedifluoride) binder at a weight ratio of 80:10:10, and then coated uniformly (doctor-blade) on a copper foil with roughly 1.5 mg cm^{-2} mass loading. The electrodes were dried at 110 ˚C under vacuum for more than 12 h. Electrochemical tests were carried out using a coin cell configuration, CR2032, with a diameter and thickness of 20 mm and 3.2 mm, respectively, which were assembled in an argon-filled glove box in which oxygen and moisture concentrations were kept below 0.1 ppm. Sodium metal foil used as a counter electrode was separated from the working electrode with a polyethene separator (MTI Corporation, porosity of

36~44% and mainly 0.03 μm pore size) with a diameter of 19 mm. The electrolyte was 1 M sodium perchlorate ($NaClO_4$) salt in ethylene carbonate (EC) and dimethyl carbonate (DEC) solution with a 1:1 volumetric ratio. Cyclic voltammetry (CV) was performed on a Versa STAT 3 potentiostat using a scan rate of 1 mV S^{-1} in the potential range of 0.01 to 2.5 V (vs. Na/Na^+). Galvanostatic discharge/charge cycling was carried out on a BT2000 Arbin potentiostat with the cutoff potentials set to 0.01 ~ 2.5 V (vs. Na/Na^+). Electrochemical impedance spectroscopy (EIS) measurement was conducted on a Solartron 1470E Multichannel Potentiostat in a frequency range of 10M Hz to 0.01 Hz at open circuit potential condition with an AC perturbation of 10 mV.

Table S1. Parameters of anatase TiO_2 crystal structure

Crystal system	Tetragonal							
Unit cell	a = 3.785 Å, c = 9.514 Å, α = β = γ = 90°							
Volume	136.29 $Å^3$							
Z	4							
Space group	I 4_1/amd							
Atomic positions	Atom	#	Ox	Site	x	y	z	SOF
	Ti	1	+4	4a	0	0	0	1
	O	1	-2	8e	0	0	0.2064	1

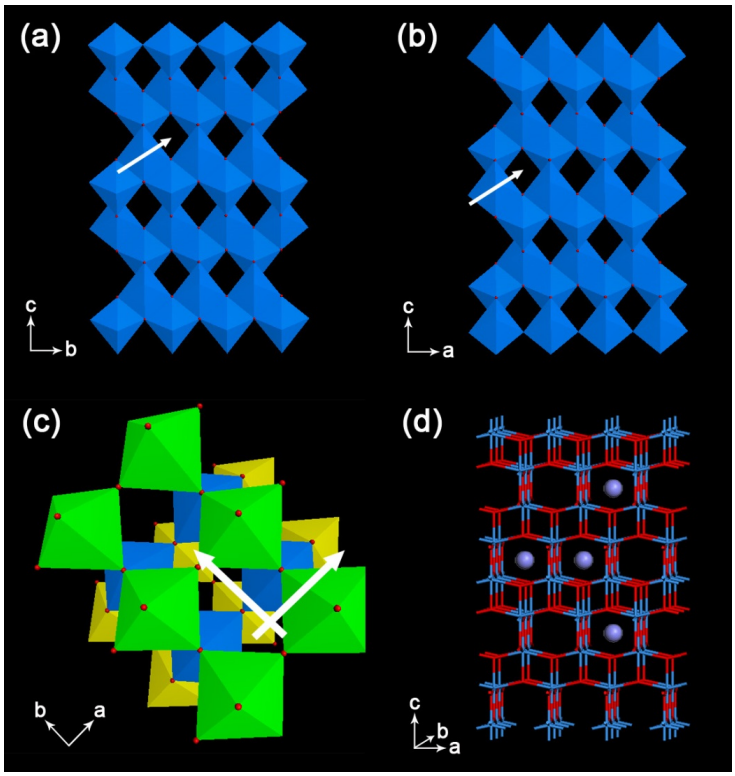

Fig. S1 Atomic supercell structures of anatase TiO_2 projected along (a) [100] and (b) [010], showing Na ions diffusion path; (c) perspective view projected along [001] (each layer of TiO_6 octahedra is shown in different colors), showing the interconnection between the diffusion paths along [100] and [010]; (d) supercell structures in ball-stick mode, showing the possible filling sites of Na ions.

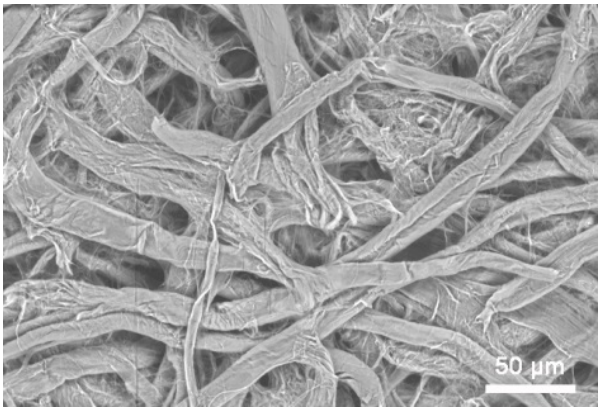

Fig. S2 SEM micrograph of the filter paper, highlighting the belt-like cellulose fibers.

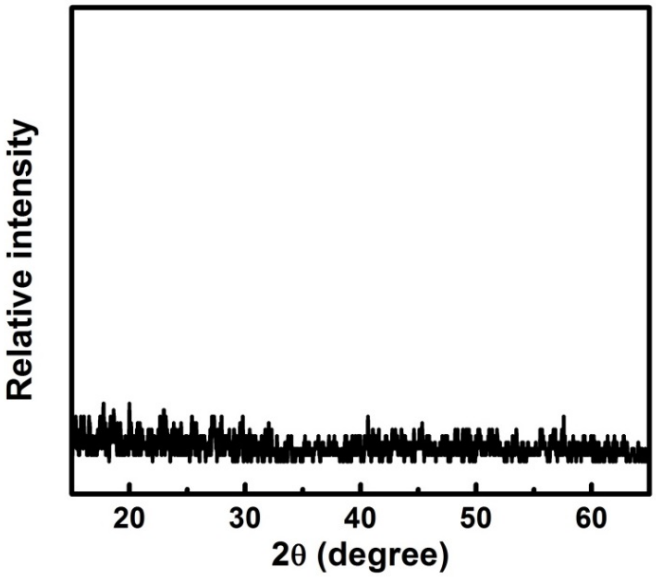

Fig. S3 XRD pattern of the amorphous carbon sample obtained by annealing filter paper in Ar at 550 ˚C for 2 h with a heating rate of 2 ˚C min^{-1}.

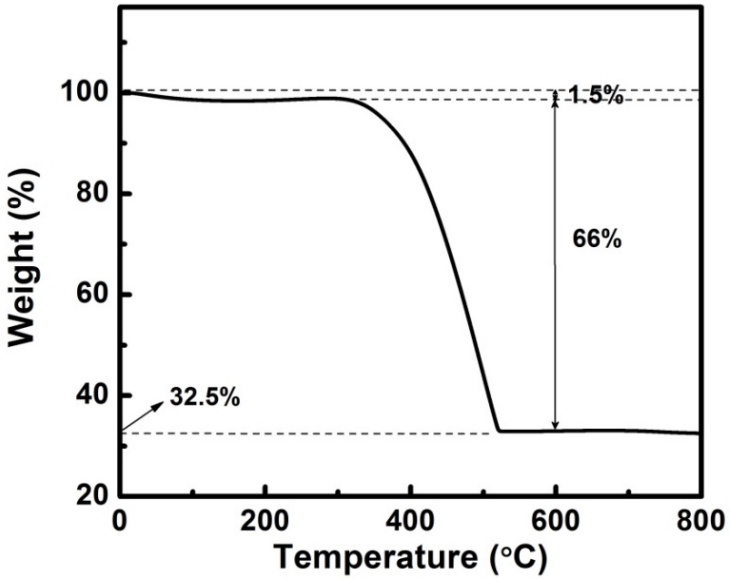

Fig. S4. TGA curve of the ANC-C sample obtained by annealing the Ti-impregnated filter paper at 550 ˚C for 2 h in Ar with a heating rate of 2 ˚C min^{-1}, giving the weight content of TiO_2 of 32.5%.

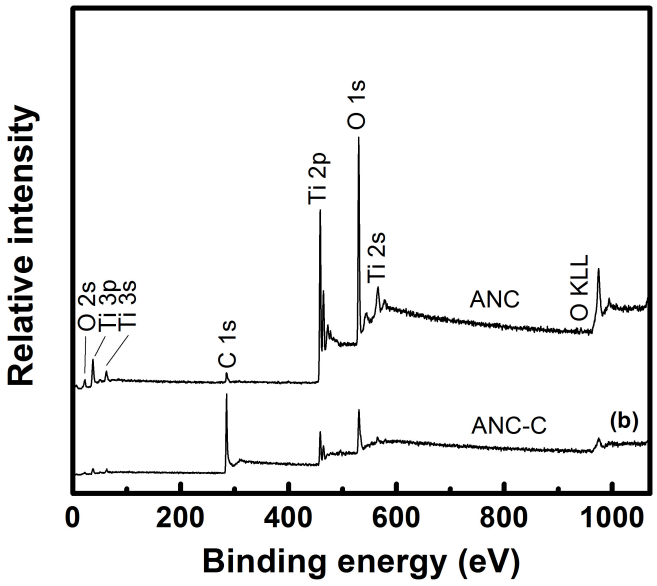

Fig. S5. Survey XPS spectra of the ANC and ANC-C samples.

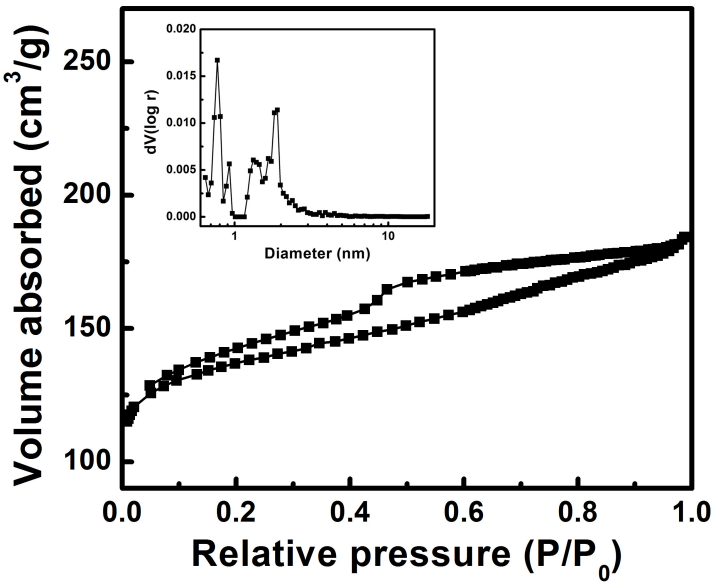

Fig. S6. N_2 adsorption-desorption isotherm and pore size distribution of the pure carbon sample.

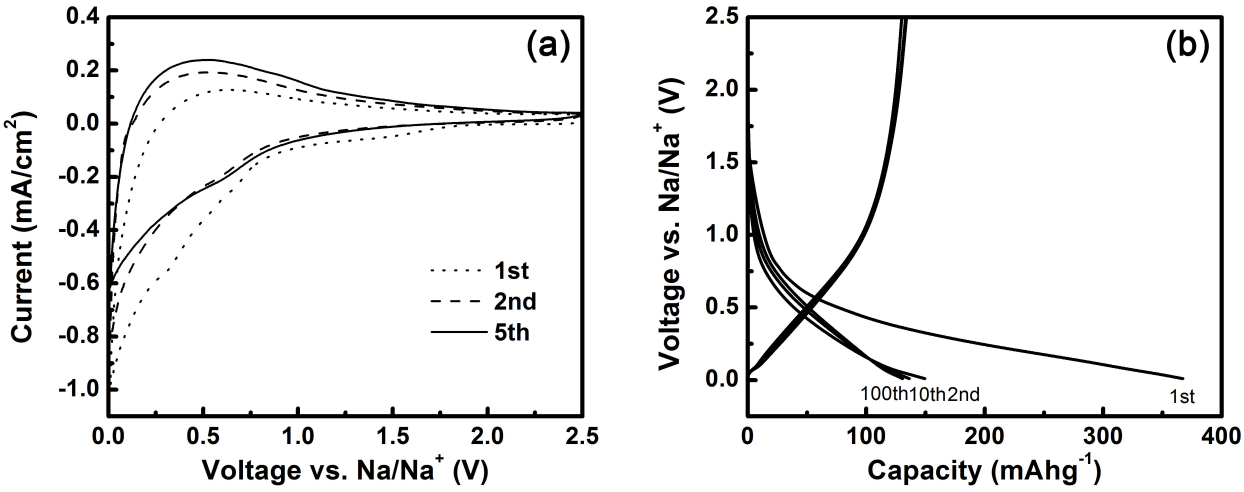

Fig. S7 Electrochemical performance of the ANC-C anode: (a) CV curves (tested at a rate of 1 mV s^{-1}) and (b) charge-discharge profiles (tested at a rate of 50 mA g^{-1}).

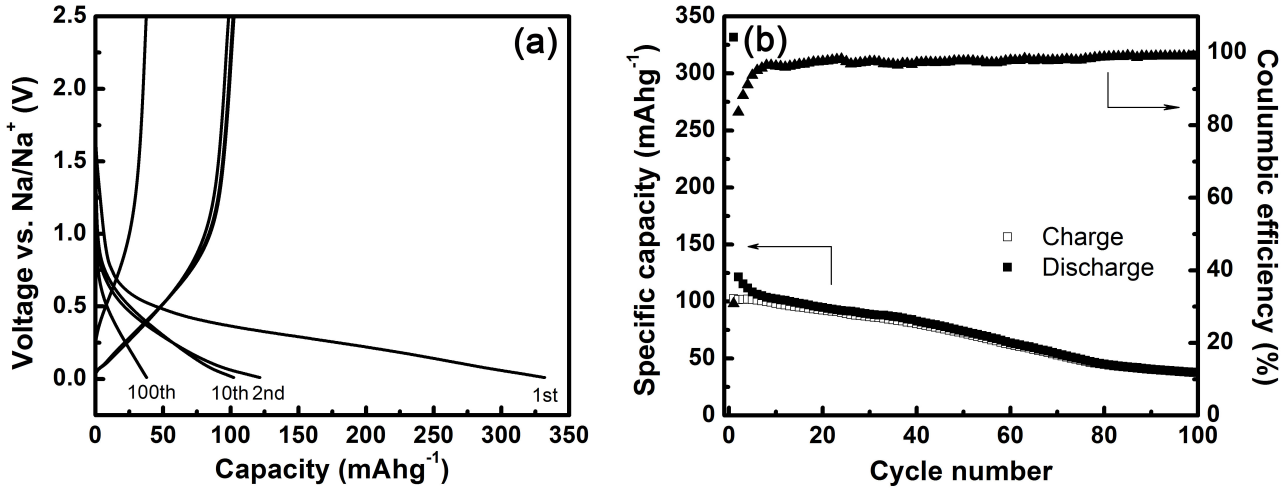

Fig. S8 Electrochemical performance of the amorphous carbon anode: (a) Charge-discharge profiles, tested at a rate of 50 mA g^{-1}. (b) Charge-discharge capacity and coulombic efficiency vs. cycle number, tested at a rate of 50 mA g^{-1}.