Experimental section

Materials and Synthesis. The anatase TiO_2 cubes were prepared via hydrothermal processing of a quaternary solution consisting of tetrabutyl titanate (TBT), deionized water (H_2O), acetic acid (HAc) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmin][BF_4]). Specifically, 1 mL of [bmin][BF_4], 2.5 mL of H_2O, 40 mL of HAc and 5 mL of TBT were well blended, meanwhile the solution appealed to be light white, and turned back into colorless transparent after ultrasonic treatment. Afterwards, it was transferred into a Teflon-lined autoclave with a volume capacity of 50 mL and heated at 180℃ for 24 hours. When it cooled down to room temperature, the white precipitate was harvested by centrifugation, rinsed with water and ethanol for several times and dried in a vacuum oven at 100℃.

Characterization. The as-prepared samples were characterized by scanning electron microscope (SEM, FEI Quanta 200), transmission electron microscope (TEM, JEM-2100F), X-ray diffractometer (XRD, Rigaku D/max 2500 VB) with Cu Kα radiation and X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, K-Alpha 1063).

Electrochemical measurements. The electrochemical measurements were carried out using CR2016 coin-type cells with sodium plate serving as the counter and reference electrode. The samples were mixed with super-P and sodium carboxyl methyl cellulose (CMC) at a weight ratio of 70:15:15 in deionized water to form a slurry, and then pasted uniformly on copper foil. The electrode was dried in a vacuum oven at 100℃ overnight and pressed under a pressure of 20 MPa. The mass loading of active materials is around 1 mg cm^{-2}. The cells were assembled in a glove box filled with hi-purity argon using a polypropylene separator (Celgard 2400) and electrolyte of 1M $NaClO_4$ in propylene carbonate. Cyclic voltammetry (CV) and potentiostatic impedance tests were performed by Solartron Analytical, while galvanostatic charge/discharge tests by Arbin battery cycler (BT2000) in the voltage of 2－0.1V.

Methods. The calculation was performed within the framework of density functional theory (DFT) implanted in the plane wave code CASTEP.[1] The generalized gradient approximation (GGA) was employed with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE). The cutoff energy for the plane wave basis set using ultrasoft pseudopotentials was set to be 410 eV. The convergence thresholds for the energy change, maximum force, maximum stress and maximum displacement were set as 1×10^{-5} eV/atom，0.03 eV/Å 0.05 GPa and 1×10^{-3} Å. We have confirmed the reliability of the adopted method. As can be seen in Table S1 and S2, the optimized lattice parameters are very close to experimental data, and the calculated surface energy is consistent to some highly cited works in trend, while the difference is expected as the optimized structure and convergence standard are different. The total energy calculations of surface-containing crystals (slab models) were conducted with surface atoms relaxed.[1-5] The k-point mesh density for slab models of {100}, {001} and {101} were set to be 4×1×1, 4×4×1 and 3×4×1 respectively ("fine" quality).

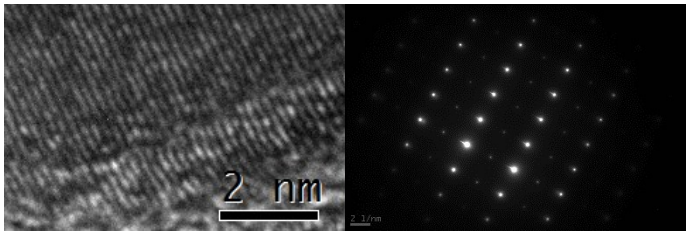

Figure S1. The HRTEM (High-resolution TEM) image and ED (electron diffraction) patterns of as-prepared anatase TiO_2 nanocubes. It displayed typical characters of {001} facets

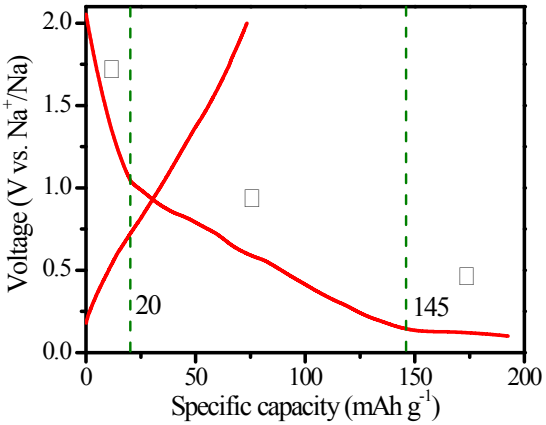

Figure S2. The discharge curve can be roughly divided into three sections.

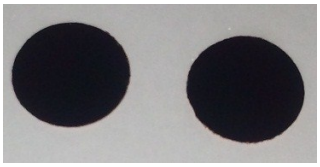

Figure S3. The photo of electrode film after activation.

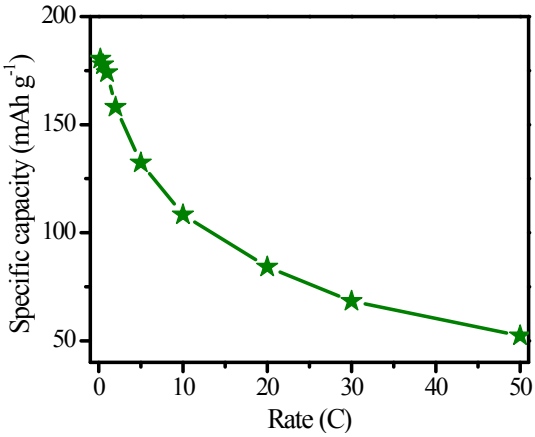

Figure S4. Charge capacity at various rates.

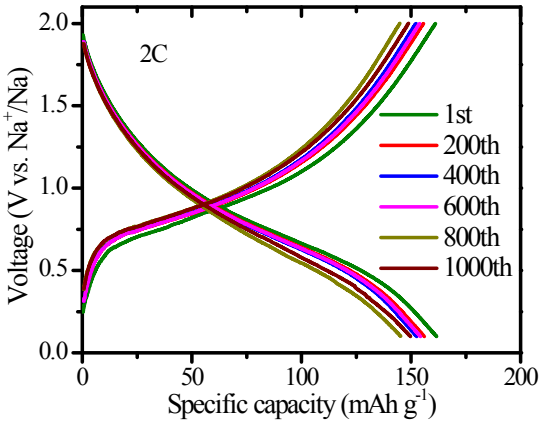

Figure S5. The voltage profiles at selected cycles during the cycle stability test at 2C.

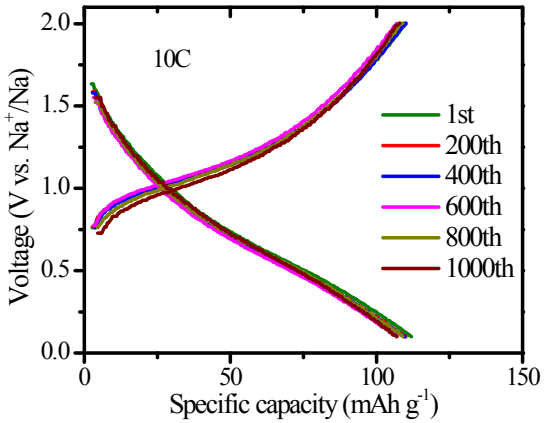

Figure S6. The voltage profiles at selected cycles during the cycle stability test at 10C.

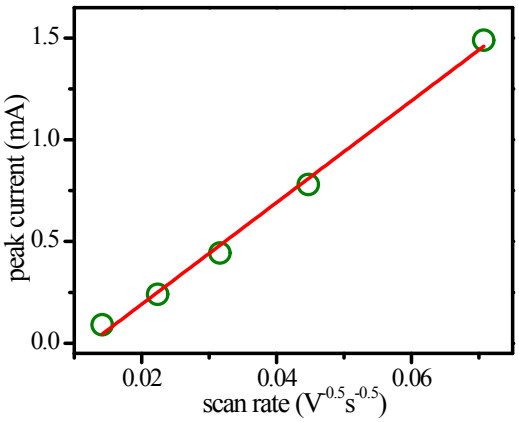

Figure S7. The cathodic peak current is linearly dependent on the scan rates.

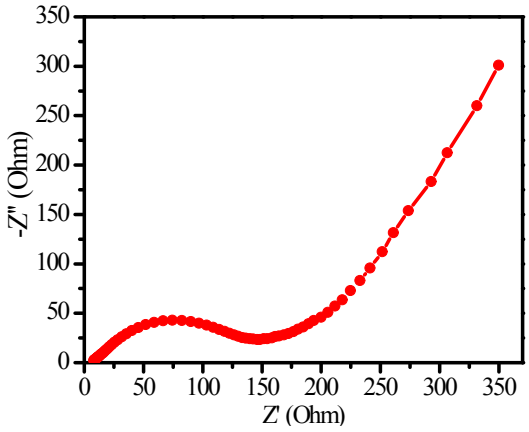

Figure S8. The Nyquist plot of the electrical impedance spectroscopy (EIS).

Table S1. The optimized structure parameters of anatase TiO_2 from different initial conditions.

	a (Å)	c (Å)
experimental[6]	3.784	9.514
Ref[7]	3.786	9.737
Here	3.782	9.584

Table S2. The surface energy with surface atoms relaxed.

Relax surface energy	E_{100} (J m^{-2})	E_{001} (J m^{-2})	E_{101} (J m^{-2})
PBE[7]	0.53	0.98	0.49
PBE[8]	Not given	0.93	0.39
PBE	0.72	1.00	0.53

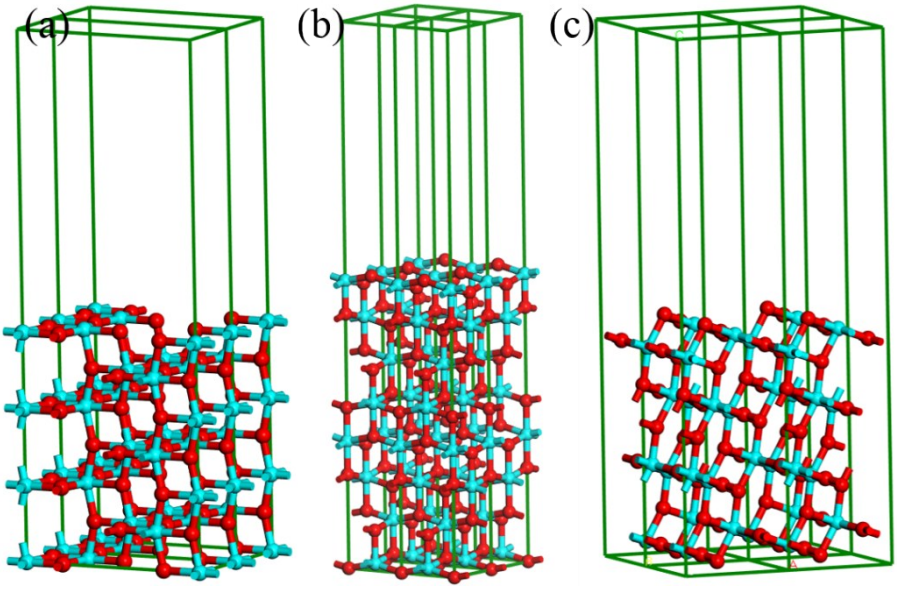

Figure S9. The surface-containing crystals for {100}, {001} and {101} (a-c).

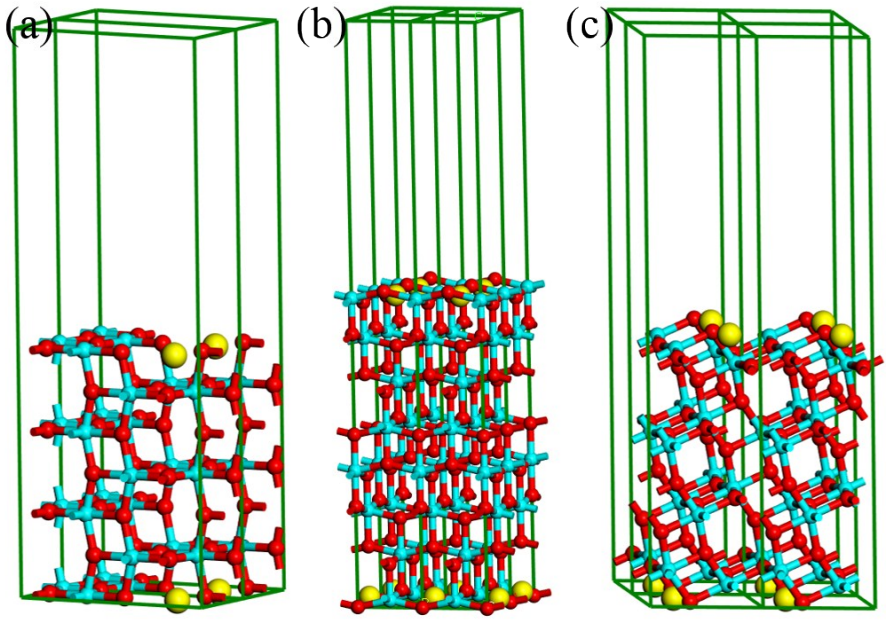

Figure S10. The surface-containing crystals with sodium atoms attached for {100}, {001} and {101} (a-c).

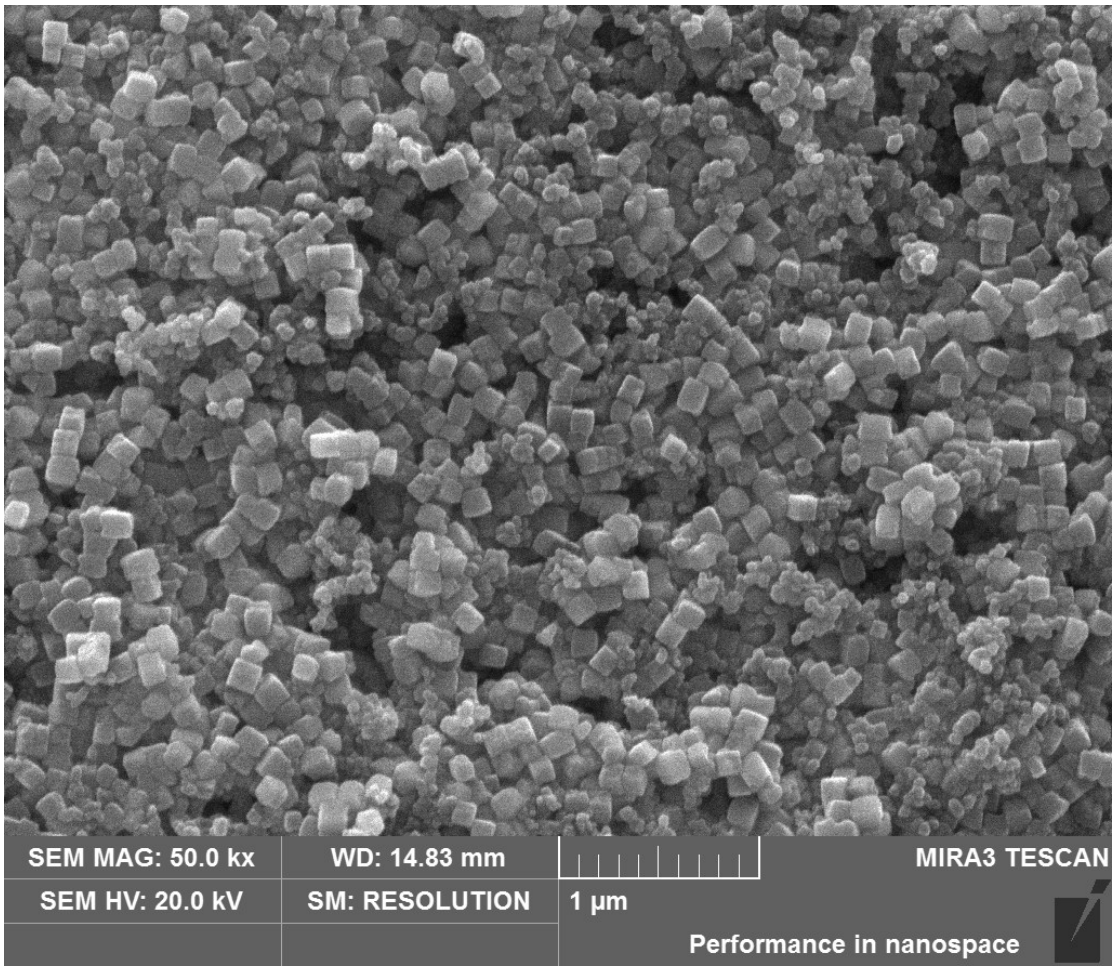

Figure S11: Ex situ SEM image of electrode materials after 1000 cycles.

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