An Excellent Full Sodium-Ion Capacitor Derived From a single Ti-based Metal-Organic Frameworks

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1. Experimental Section

Synthesis and characterization of TiO_xN_y: TiO_xN_y nanowires were obtained by annealing hydrogen titanate nanowires ($H_2Ti_3O_7$) in ammonia flow at 800 °C. $H_2Ti_3O_7$ NWs were firstly synthesized by hydrothermal method reported elsewhere.[1] Briefly, TiO_2 anatase (2 g) was added into NaOH solution (30 mL, 15 M) under magnetic stirring for 1 h. Then, the suspension was transferred to a Teflon-lined stainless steel autoclave and heated in an electric oven at 180 °C for 72 h. After cooling down at room temperature, the product was stirred in 0.1 M HCl solution for 24 h. The material was filtered, washed with deionized water and alcohol, and dried at 70 °C for 12 h. Finally, $H_2Ti_3O_7$ were converted to TiO_xN_y by annealing in NH_3 flow at 800 °C for 4 h with a heating rate of 5 °C min^{-1}.

2. Calculations of specific capacity, energy density and power density

The half-cell specific capacity (mAh g^{-1}) is calculated by **Equation S1**;

$$Q = i \times t \quad (1)$$

Q (mAh g^{-1}) is the half-cell specific capacity; i (mA g^{-1}) is the current density; t (h) is the charge or discharge time.

The Na-ion capacitors specific capacity (F g^{-1}), energy density (E) and power density (P) are calculated based on **Equations S2, S3** and **S4**;

$$C = I \times \Delta t / (\Delta V) \quad (2)$$

$$E = (C \times \Delta V^2)/2 \quad (3)$$

$$P = E / \Delta t \quad (4)$$

C (F g^{-1}) is the Na-ion Capacitors specific capacity; I (A g^{-1}) is the current density; Δt (s) is the discharge time. ΔV is the charge-discharge potential window; E (Wh kg^{-1}) is the energy density and P (W kg^{-1}) is the power density.

3. Calculate methods and details of capacitive effect contribution and diffusion-controlled contribution

Using the scan-rate-dependent CV curves (**Fig. 4**A) to quantify the contribution from capacitive effects (both surface pseudocapacitance and doublelayer capacitance) and diffusion-controlled Na^+ insertion process to the current response according to the following equation;

$$\boldsymbol{I(V)=k_1v+k_2v^{1/2}}$$

Where I (V), k_1v and $k_2v^{1/2}$ represent the total current response at a given potential V, current due to surface capacitive effects, and current due to diffusion-controlled Na^+ insertion process, respectively. The above equation can also be reformulated as;

$$\boldsymbol{I\ (V)/\ v^{1/2}=k_1v^{1/2}+k_2}$$

By plotting I (V)/ $v^{1/2}$ *vs*. $v^{1/2}$ at different potentials, we can calculate the values of k_1 (slope) and k_2 (intercept) from the straight lines. This allows one to quantify the fraction of the current at specific potentials to the capacitive effect (k_1v) and diffusion-controlled insertion ($k_2v^{1/2}$) at fixed potential (see **Fig. S13** A, B). After integration of the enclosed CV area, the amount of stored charge from different energy storage modes can be distinguished, expressed by the following equation;

$$\mathbf{Q=Q_s + Q_d}$$

Where, Q, Q_s, and Q_d represent the total stored charge included in the enclosed CV area at set scan rate, surface capacitive effects, and diffusion controlled Na^+ insertion process, respectively.

Figures

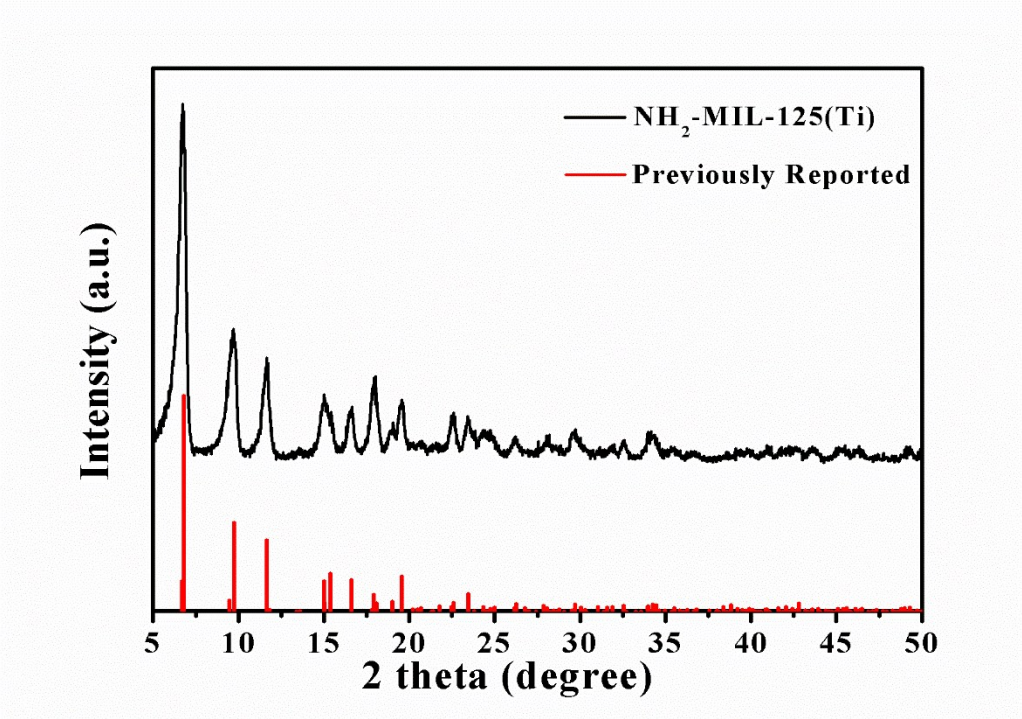

Fig. S1. XRD pattern of as-prepared NH_2-MIL-125(Ti).

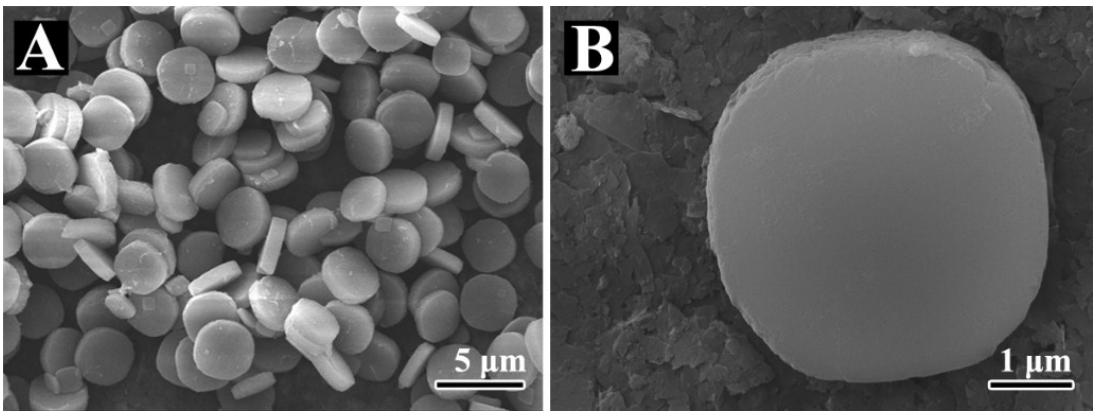

Fig. S2. (A and B) FESEM images of NH2-MIL-125(Ti) with different resolution.

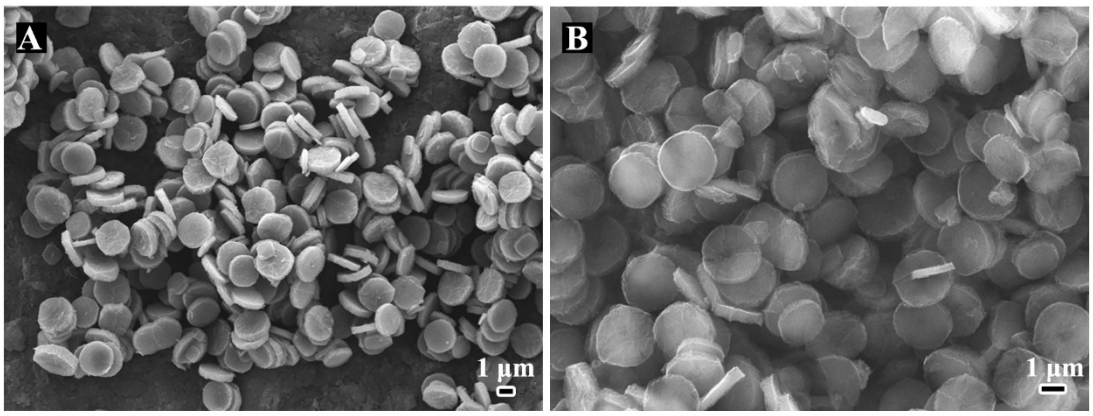

Fig. S3. (A and B) low resolution FESEM images of TiO_xN_y/C and NHPC, respectively.

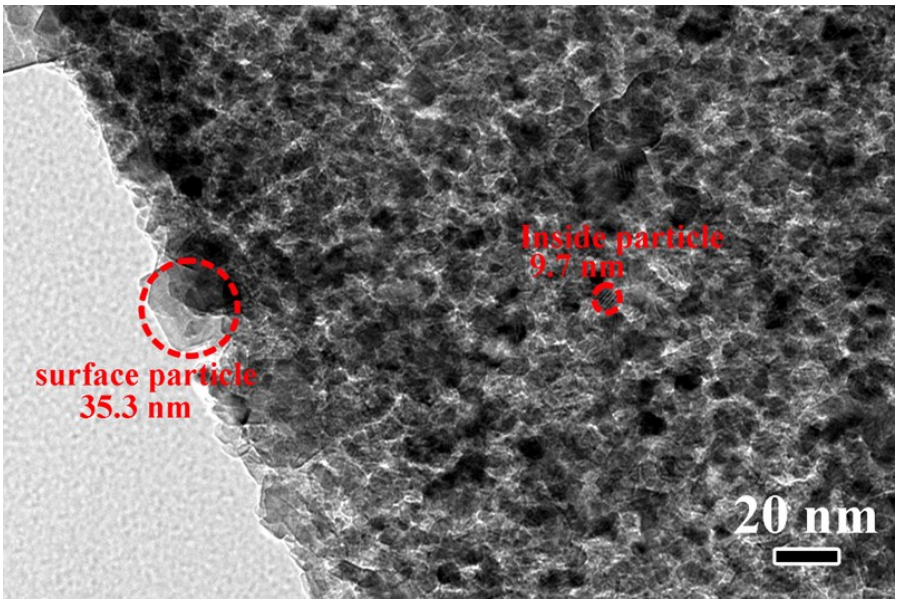

Fig. S4. bright-field TEM image of TiO_xN_y/C inside structure.

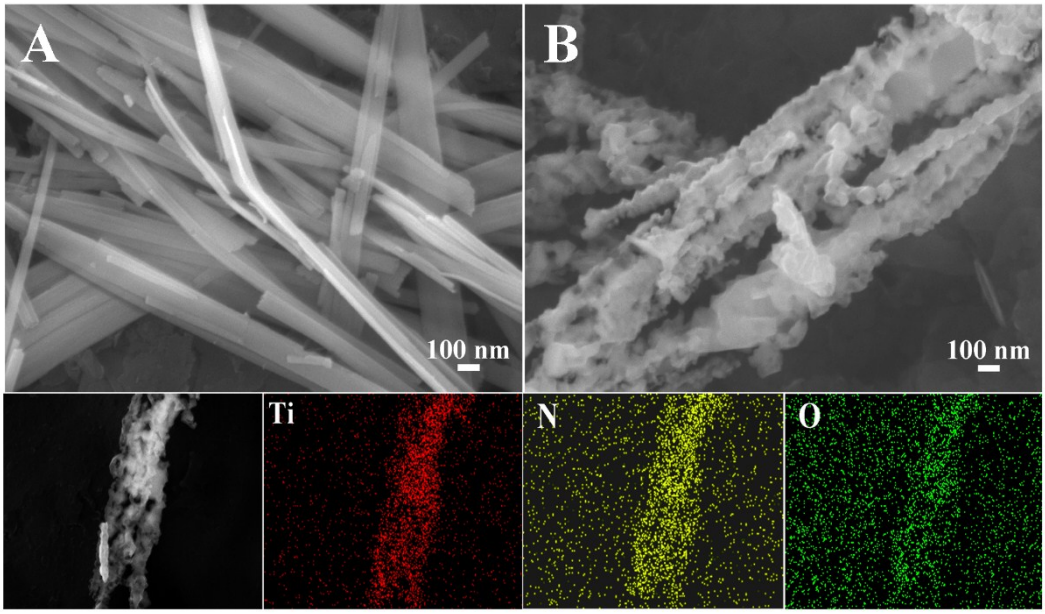

Fig. S5. (A) FESEM image of nanowires precursor, (B) FESEM image of TiO_xN_y nanowires and corresponding FESEM element mapping image.

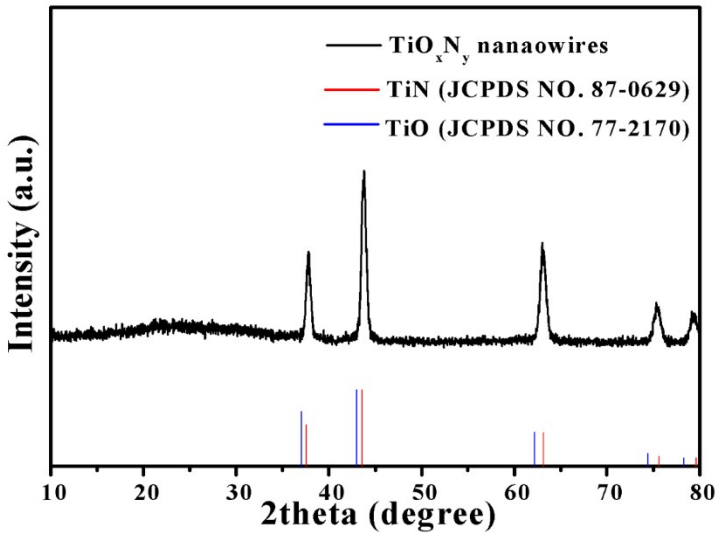

Fig. S6. XRD pattern of TiO_xN_y nanowires.

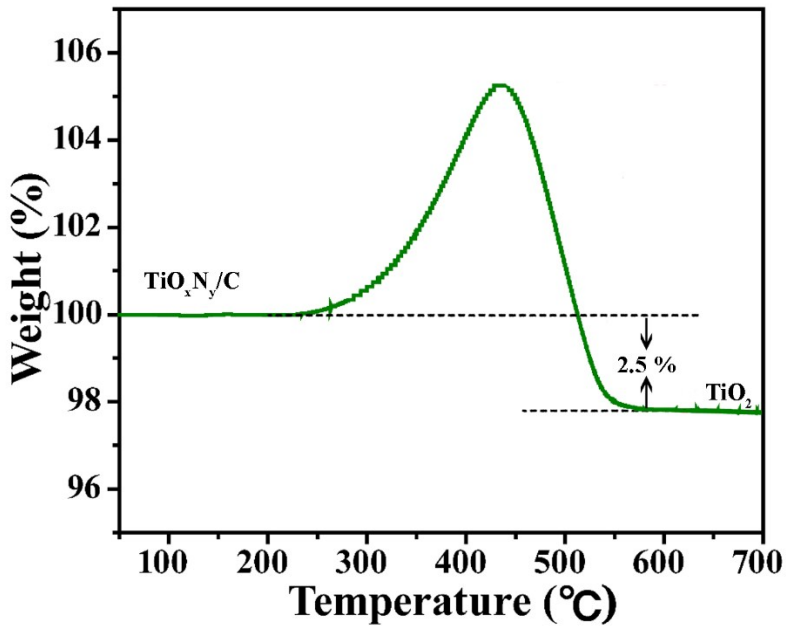

Fig. S7. Thermogravimetric analysis curves of TiO_xN_y/C.

The TGA data was obtained by annealing in O_2 flow. In the detail, the original specimant is TiO_xN_y(x+y=1) and carbon. The speciment converted to pure TiO_2 phase after TG test. So, according to the the finnal mass of TiO_2 and Invariance Principle of Ti elements in this process, the carbon contents in the TiO_xN_y/C is approximately 22 % by calculated.

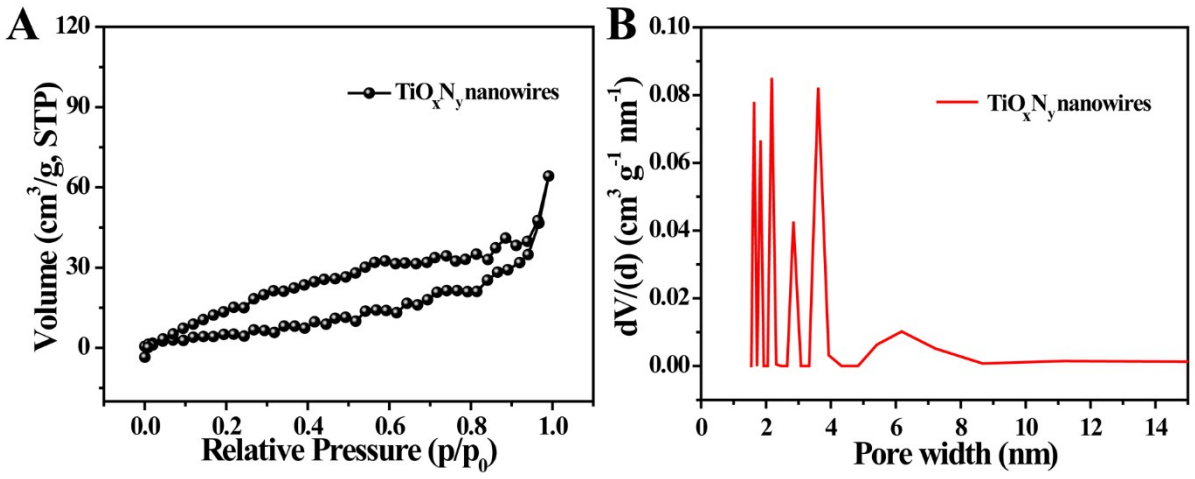

Fig. S8. (A) The nitrogen adsorption-desorption isotherms of TiO_xN_y, and (B) the corresponding pore distribution.

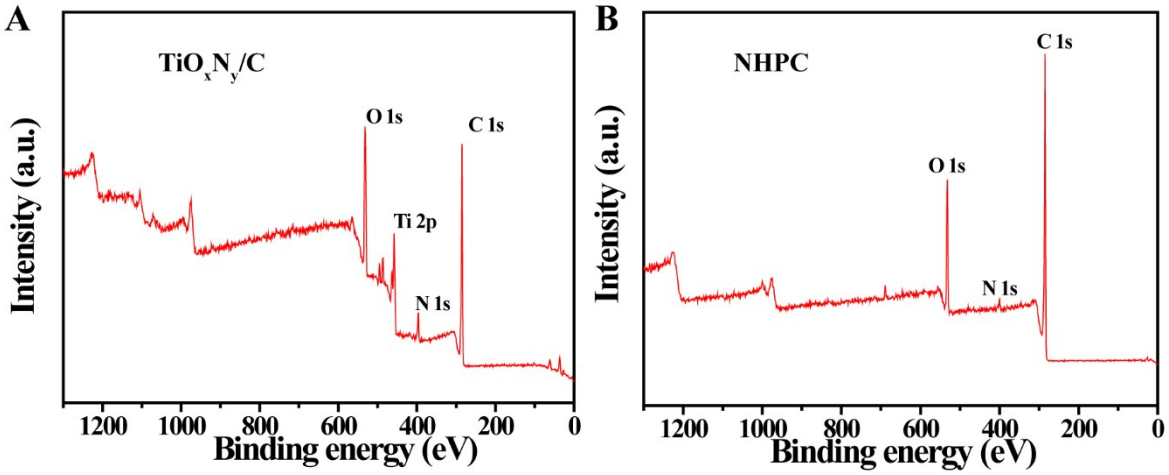

Fig. S9. (A and B) XPS spectra of TiO_xN_y/C and NHPC, respectively.

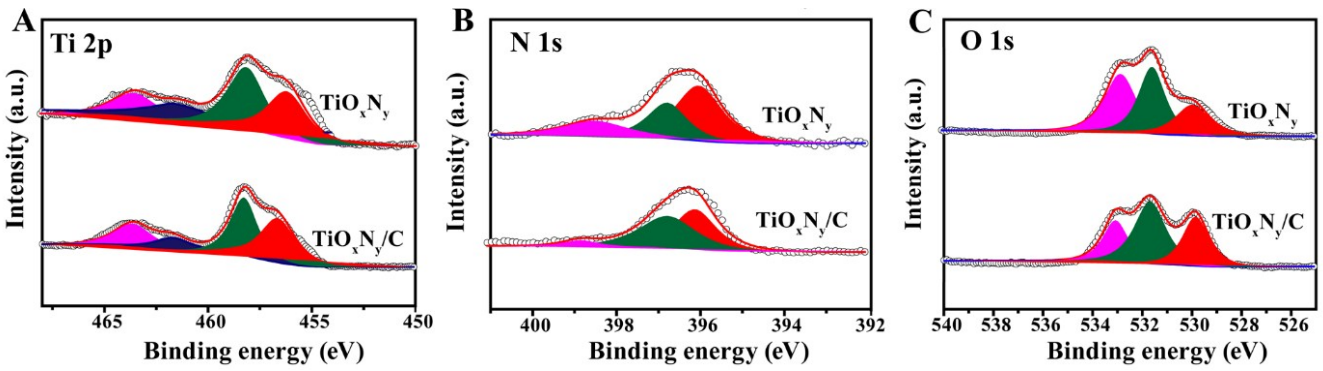

Fig. S10. (A, B and C) the contrast of Ti 2p, N 1s and O 1s XPS spectra between TiO_xN_y/C and TiO_xN_y nanowires, respectively.

Sample	Textural properties	
	$S_{BET}^{a}(m^2g^{-1})$	$V_t^{b}(cm^3g^{-1})$
C	1731	1.12
TiO_xN_y/ C	248	0.5
TiO_xN_y	20.921	0.11

Table S1. the structure information of as-prepared samples.

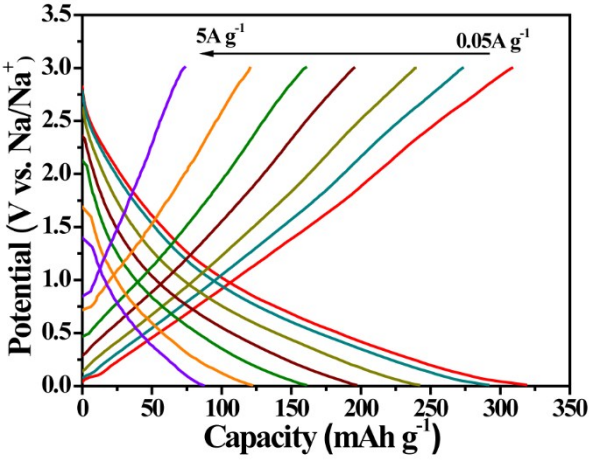

Fig. S11. Charge and discharge curves of TiO_xN_y/C at different current density.

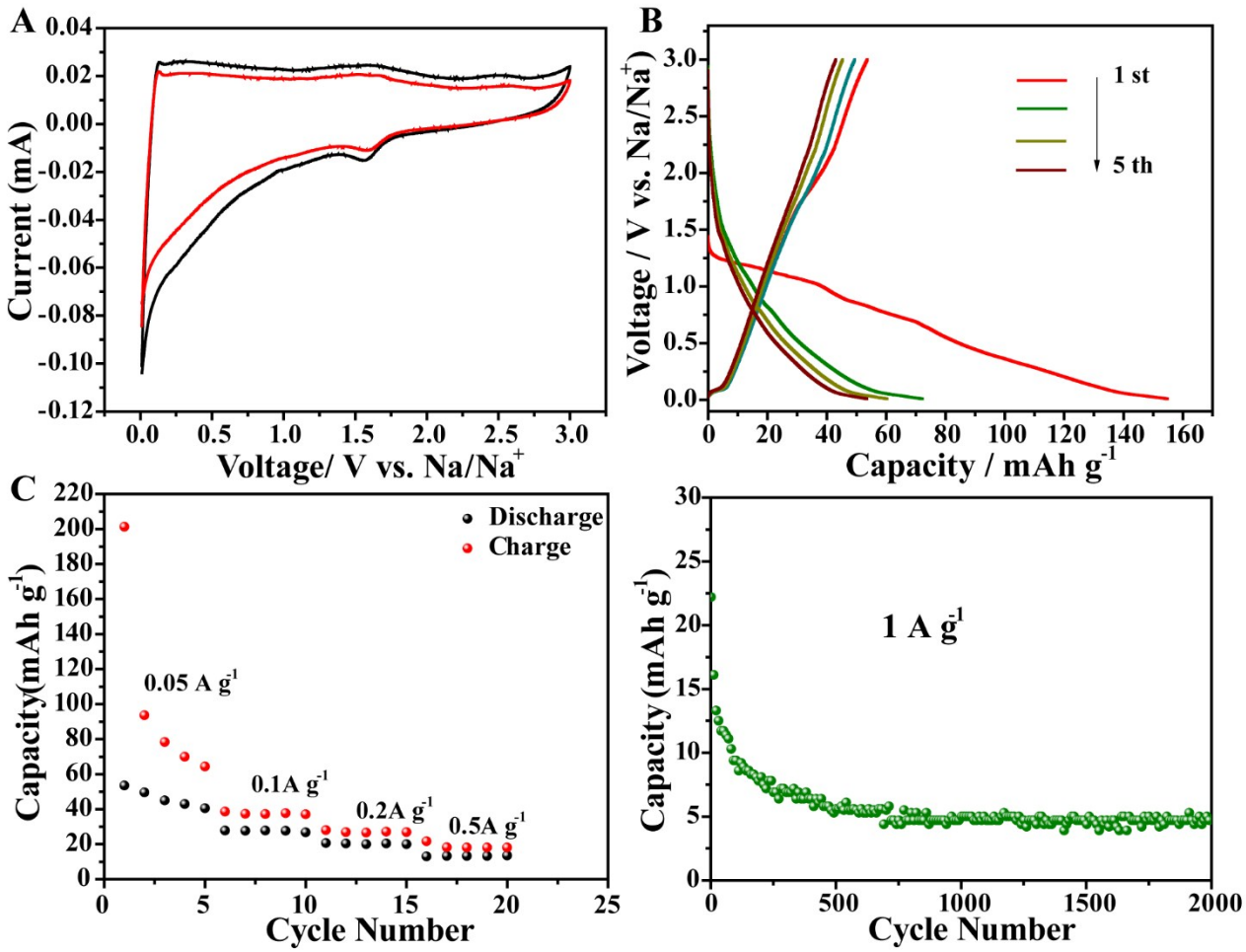

Fig. S12. CV curves (A), first five galvanostatic discharge–charge profiles at 0.05A g^{1} (B), rate performance (C) and the cycling stability of at 1A g^{-1} of TiO_xN_y nanowires.

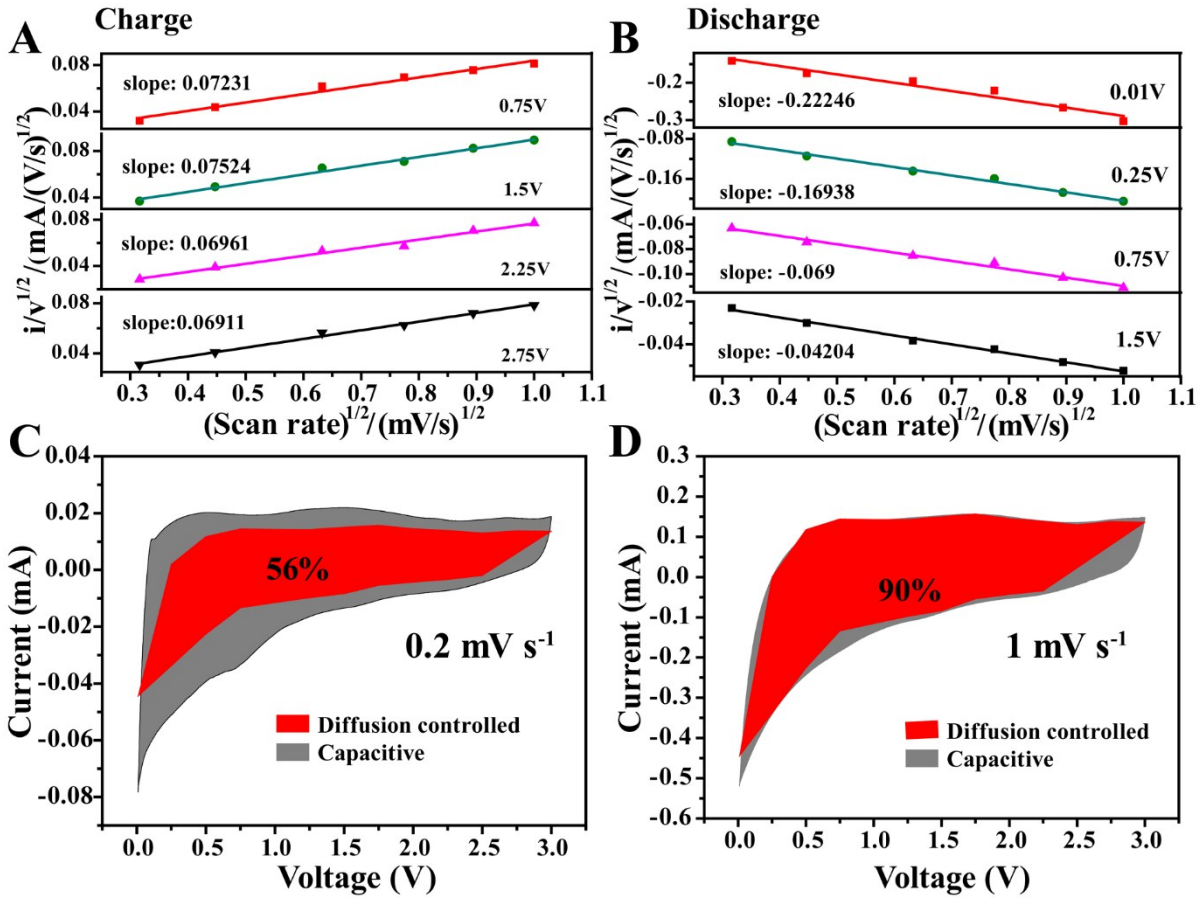

Fig. S13. (A and B) $I/v^{1/2}$ *vs.* $v^{1/2}$ plots of TiO_xN_y/C used for calculating constants k_1 and k_2 at different potentials, (C and D) Capacitive charge storage contributions at a scan rate of 0.2 mV s^{-1} and 1 mV s^{-1}.

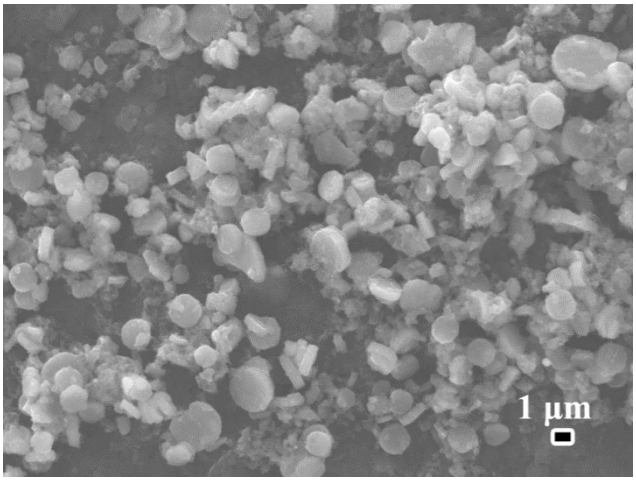

Fig. S14. FESEM images of TiO_xN_y/C after electrochemical cycles test.

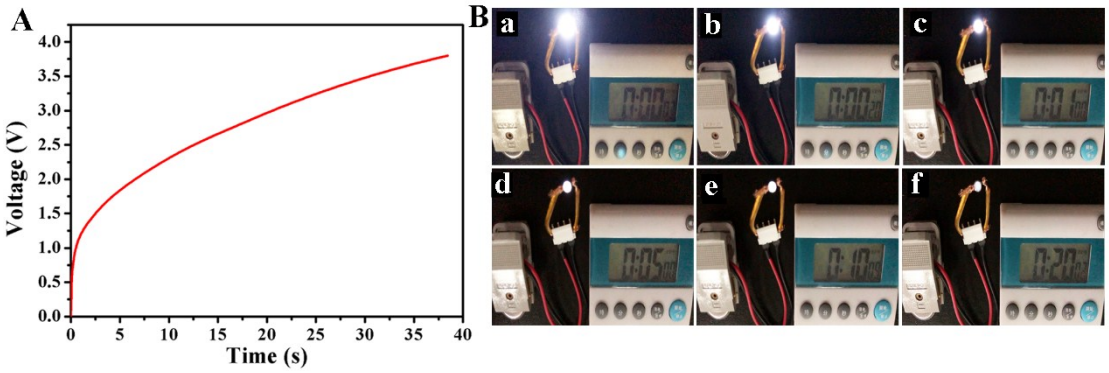

Fig. S15. The rapid charging curves in 40s of TiO_xN_y/C//NHPC SICs (B), and the Photographs of a light emitting diode powered by a rapid charging TiO_xN_y/C // NHPC SIC in 40 s under time recording by a timer.