

## High areal capacity sodium-ion battery anode enabled by free-standing red phosphorus@N-doped graphene/CNTs aerogel

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### Experimental Section

#### *Materials synthesis*

#### *Synthesis of GA, GCA, and NGCA*

80 mg of graphene oxide was dissolved in 40 ml of deionized water followed by stirring for 12 hours and sonication for 3 hours, named as solution 1. 80 mg of graphene oxide and 16 mg of carbon nanotubes were dissolved in 30 ml of deionized water and 10 ml of ethanol solution respectively, stirred for 12 h and sonicated for 3 h. The graphene oxide solution and the CNTs solution were mixed and stirred for 3 h to obtain solution 2. On the basis of solution 2, 2.6 ml of ammonia water was added and stirred for 10 min to obtain solution 3. 1.3 ml of solutions 1, 2, and 3 were added into glass bottles and keep it at 120°C for 12 h to obtain graphene hydrogel, graphene-CNTs hydrogel, and N-doped graphene-CNTs hydrogel. Then the hydrogels were soaked in a 10% hydroalcoholic solution for 2 h. The soaked hydrogels were pre-frozen at -55°C for 6

h, and then dried under vacuum (<50 Pa) for 24 h to obtain graphene aerogel (GA), graphene-CNTs aerogel (GCA), and N-doped graphene-CNTs aerogel (NGCA).

#### *Synthesis of P@NGCA and P<sub>L</sub>@NGCA*

50 mg NGCA and 50 mg red phosphorus were encapsulated in a quartz glass tube, and then kept at 600°C for 3 h at a heating rate of 3°C/min. Then the glass tube was opened in the glove box filled with Ar, and the sample was washed several times with CS<sub>2</sub>. The cleaned sample was vacuum dried at 60°C for 12 h to obtain P@NGCA. The only difference between the preparation method of P<sub>L</sub>@NGCA and P@NGCA is that the ratio of RP to NGCA is 1:2.

#### **Structure characterizations**

The morphologies of the sample were investigated by scanning electron microscope (SEM Gemini 500) and transmission electron microscope (TEM JEM1400 FLASH). The structure of the sample was characterized by XRD (PANalytical X-Pert PRO MPD) using Cu- K $\alpha$  radiation (0.1541 nm) and Raman spectra (LabRAM HR Evolution) using 532 nm argon laser. N<sub>2</sub> adsorption/desorption isotherms were recorded on Quantachrome autosorb IQ-C. The pore size distributions plots were recorded from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model and non-local density functional theory (DFT) model, respectively. The chemical components were obtained by X-ray photoelectron spectroscopy (XPS America Thermo ESCALAB250).

#### **Mechanical testing**

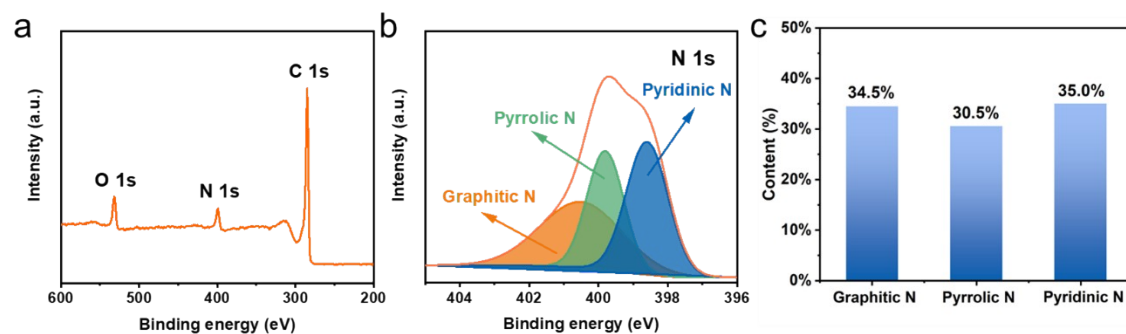
Compressive and stretching tests were performed by using an Haida HD-B609B-S with

two flat-surface compression stages and 10 N and 500 N load cells. All hysteresis curves were obtained at the strain ramp rate of  $60 \text{ mm min}^{-1}$  without prestrain of the tested samples.

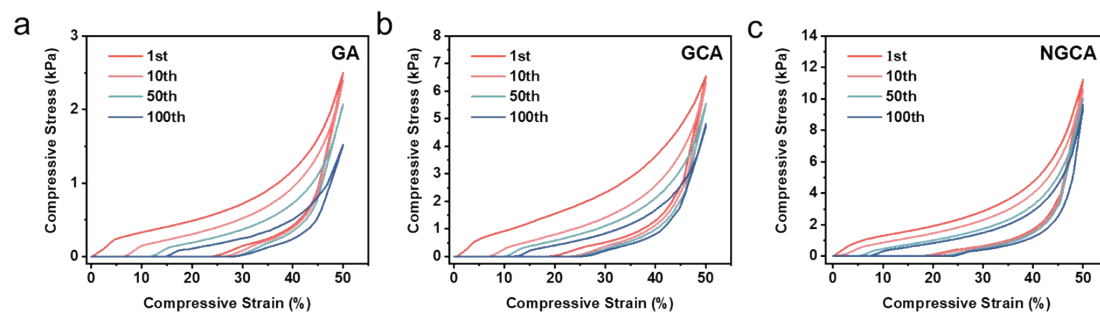
### **Electrochemical measurements**

The pure red P electrodes were fabricated by mixing 60 wt% active materials, 20 wt% Super P, and 20 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The mixed slurry was then coated uniformly on copper foil and subsequently dried at  $80^\circ\text{C}$  overnight under vacuum. After drying, the laminate was punched into disks with a radius of 7 mm. The loading mass of the active materials was controlled around  $1 \text{ mg/cm}^2$ . The free-standing P@NGCA was used as electrode without treatment. The mass loading of the electrode is  $\sim 4.2 \text{ mg cm}^{-2}$ . The coin-type cells half cells (CR2032) were assembled in Argon filled glove box using a sodium metal sheet as counter electrode, P@NGCA electrode and pure red P electrode as working electrodes, glass fiber (GF/D, Whatman) as separator, and a solution of 1 M  $\text{NaClO}_4$  dissolved in ethylene carbonate (EC) and dimethyl carbonate (DEC) (1:1, v/v) with fluoroethylene carbonate (FEC) as additive (10 wt %) as electrolyte. All the electrochemical tests were conducted at  $25^\circ\text{C}$ . The cells were cycled on the LAND cycler (BT2000 battery test system) in a voltage range of 0.001–3.0 V. For GITT measurements, the cell was cycled at  $0.2 \text{ A g}^{-1}$  with current pulse duration of 0.5 h and interval time of 2 h. CV test was performed on the electrochemical workstation (Chenhua CHI660E) in a voltage range of 0.01–2.0 V with the frequency from 100 kHz to 1 Hz. All the electronic conductivity tests were conducted on the Four-Point Probes

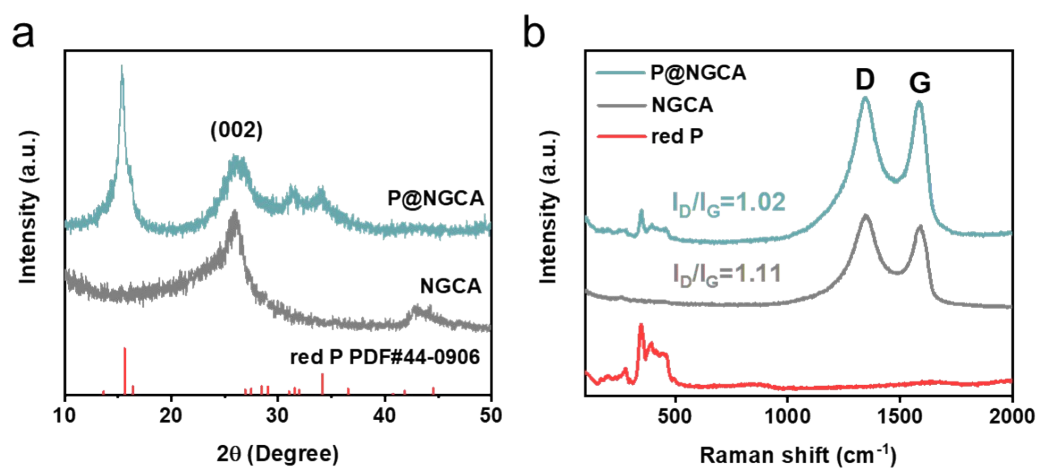
tester (Keithley 2001).



**Fig. S1** XPS (a) full spectra and (b) high-resolution N 1s spectra of NGCA. (c) The content of graphitic N, pyrrolic N, and pyridinic N in NGCA.



**Fig. S2** The compressive stress-strain curves of different cycles for (a) GA, (b) GCA and (c) NGCA at 50% strain.



**Fig. S3** (a) XRD patterns and (b) Raman spectra of red P, NGCA, and P@NGCA.

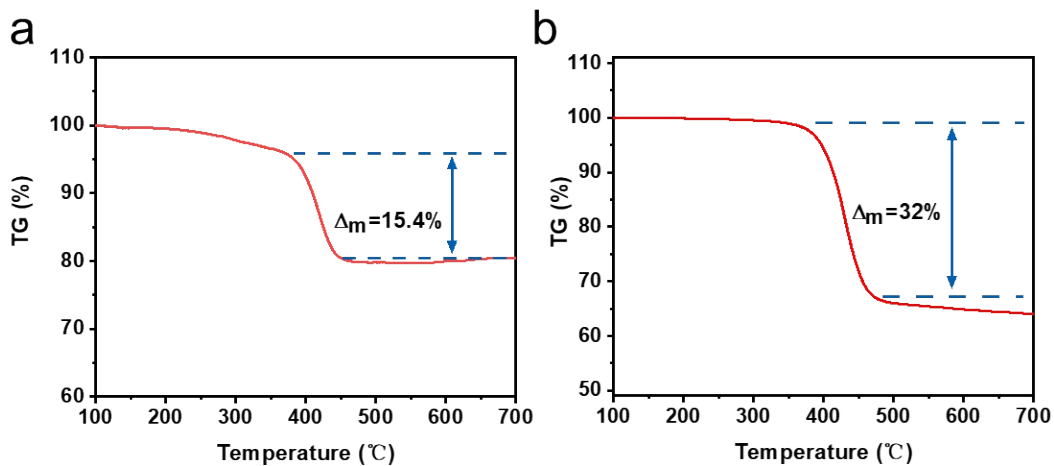


Fig. S4 TGA curves of (a) P<sub>L</sub>@NGCA and (b) P@NGCA with different loading.

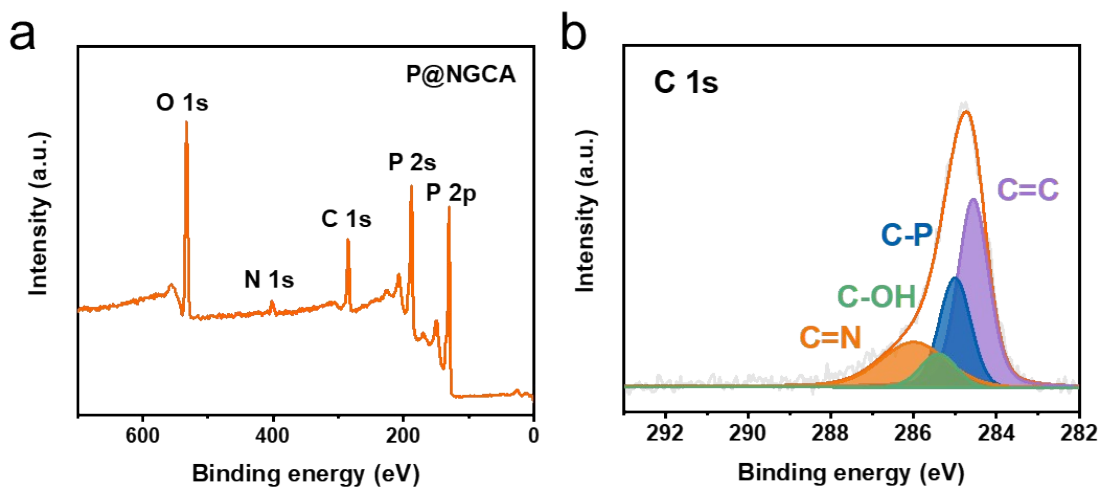


Fig. S5 (a) XPS full spectra and (b) high-resolution C 1s spectra of P@NGCA.

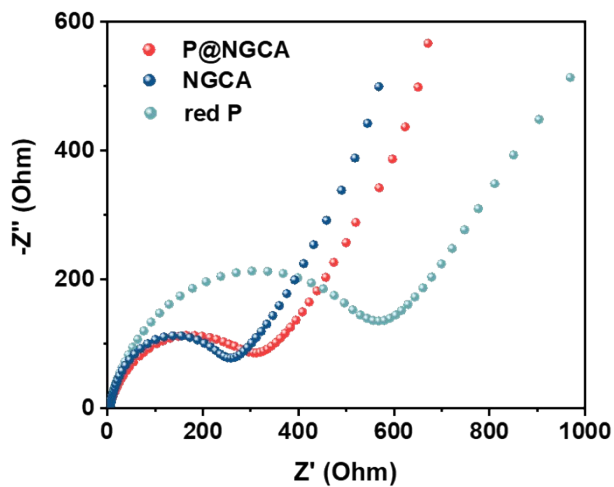


Fig. S6 Nyquist plot of red P, NGCA, and P@NGCA.

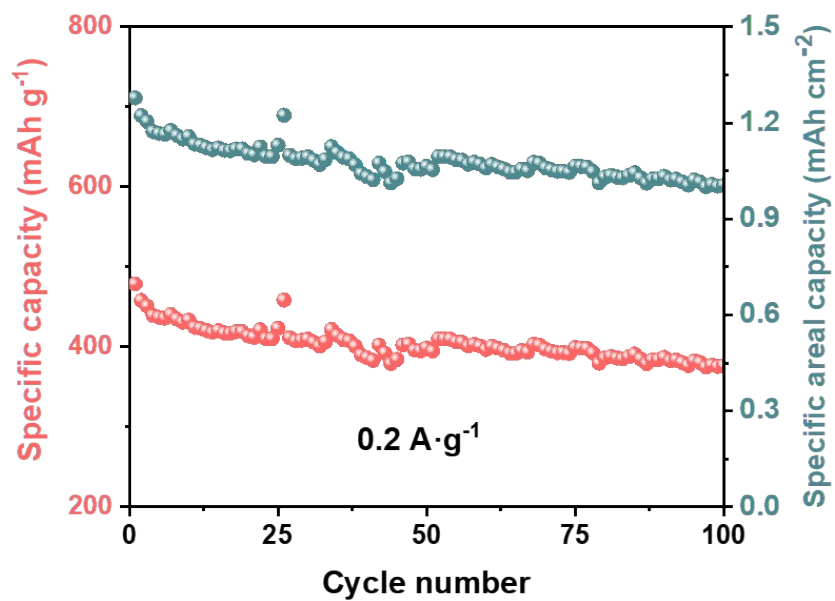


Fig. S7 Cycling properties of PL@NGCA.

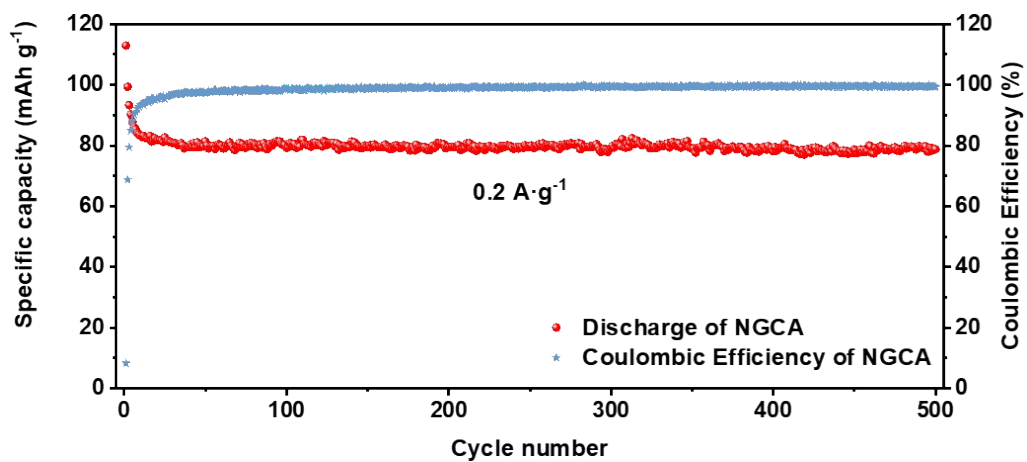
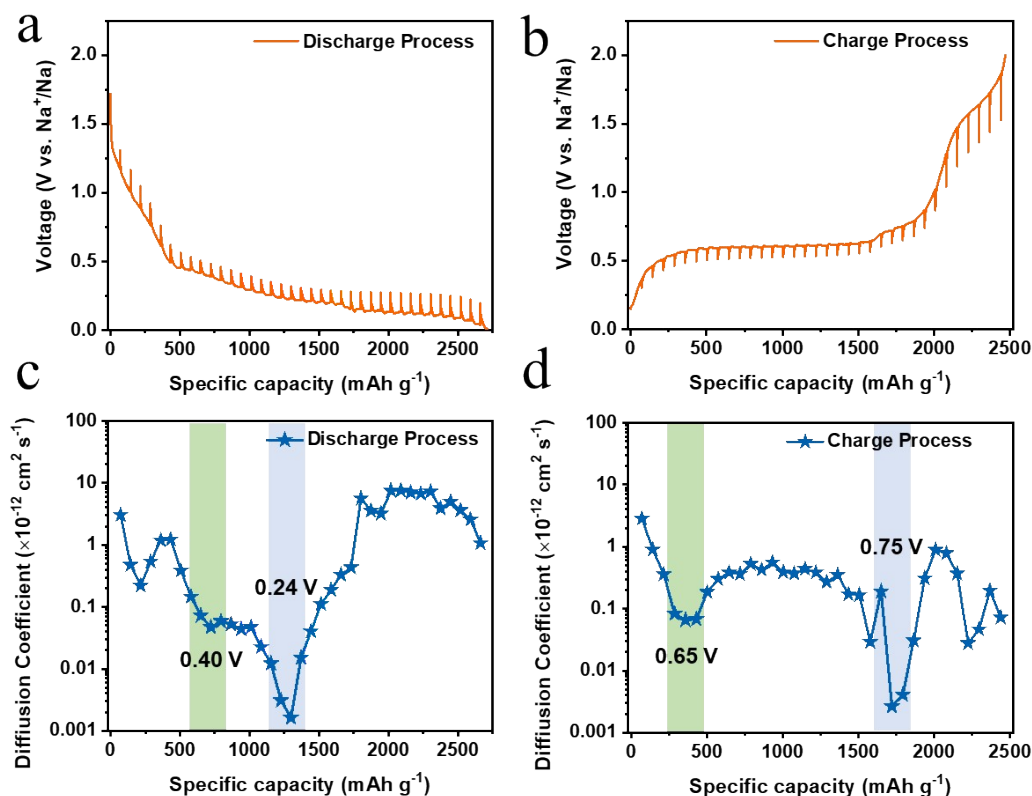
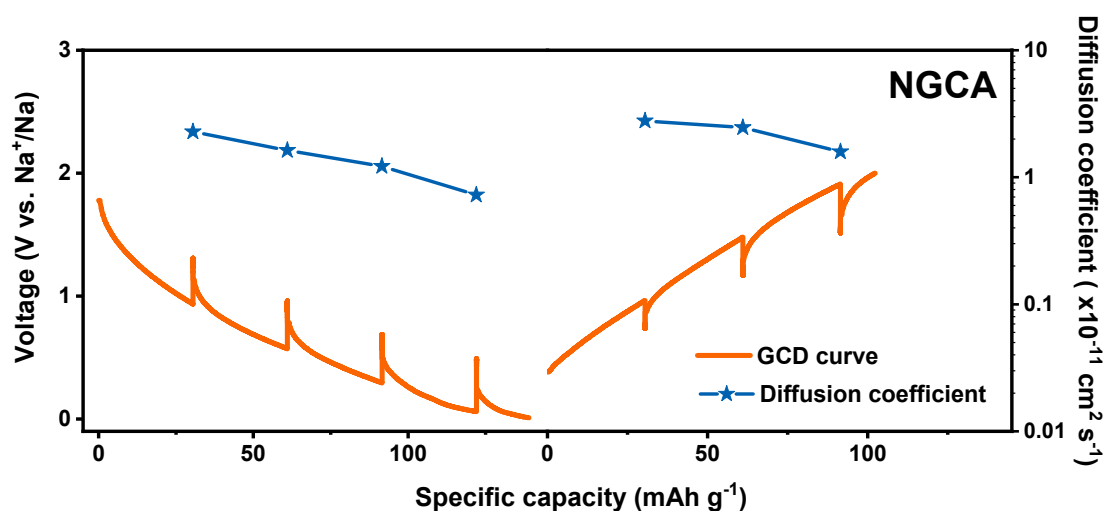


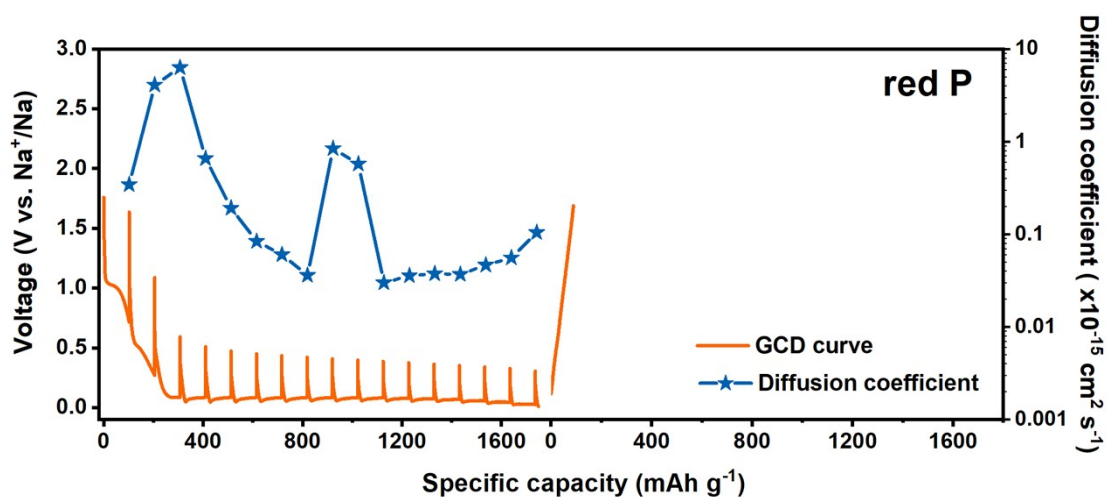
Fig. S8 Cycling properties of NGCA.



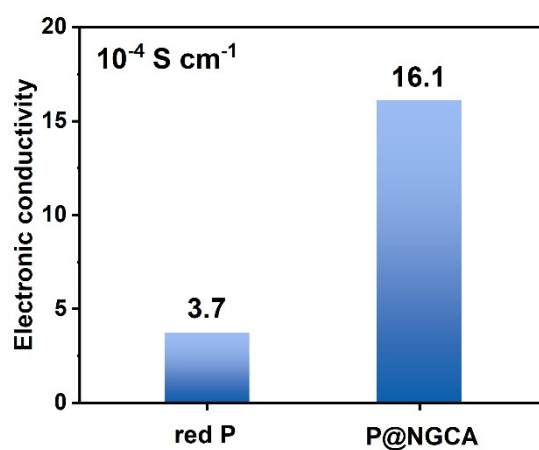
**Fig. S9** (a, b) Galvanostatic intermittent titration technique (GITT) potential profiles and (c, d) Na<sup>+</sup> apparent diffusion coefficients of P@NGCA using a pulse current of 0.2 A g<sup>-1</sup> for 0.5 h accompanied by a rest interval of 2.0 h during the third cycle.



**Fig. S10** GITT potential profiles and Na<sup>+</sup> apparent diffusion coefficients of NGCA using a pulse current of 0.2 A g<sup>-1</sup> for 10 min accompanied by a rest interval of 2.0 h during the second cycle.



**Fig. S11** GITT potential profiles and  $\text{Na}^+$  apparent diffusion coefficients of red P using a pulse current of  $0.2 \text{ A g}^{-1}$  for 0.5 h accompanied by a rest interval of 2.0 h during the first cycle.



**Fig. S12** Electronic conductivity of red P and P@NGCA.

**Table S1** The charge transfer resistance ( $R_{ct}$ ) and SEI resistance ( $R_{SEI}$ ) of P@NGCA electrode before and after cycle.

Sample	$R_{ct}(\Omega)$	$R_{SEI}(\Omega)$
Before cycle	240.8	-
20th cycle	22.31	17.34
50th cycle	24.96	10.03



**Table S2** The comparison between P@NGCA and other works.

Sample	$m_a$ mg/cm <sup>2</sup>	Current mA g <sup>-1</sup>	$C_1$ mAh/g	$C_2$ mAh/cm <sup>2</sup>	ICE %
P <sub>2</sub> @N-SGCNT	1.3	0.1	1065.6	1.39	80.0
CRP-rGA	0.44	0.1	1498.3	0.75	81.8
NRP-rGO	0.35-0.49	0.1	1226.6	0.86	61.2
P/TiN/Gnps	1.2-1.6	0.1	888.4	1.42	86.8
RH-3-1-RP/CS	3.0-5.0	0.1	654.4	3.27	49.3
P/CFs@RGO	0.8-1.0	0.05	937.2	0.94	73.8
P@C	1.6	0.2	1308.5	2.09	75
P@RGO	1.29	1.6	1211.47	1.56	75.2
P@PMCNFs	1.2-1.6	0.1	1580.12	2.53	69.9
This work	4.2	0.2	786.9	3.30	80.0

$m_a$ : Mass loading of active material (mg/cm<sup>2</sup>)

$C_1$ : Specific capacity (mAh g<sup>-1</sup> based on P/C)

$C_2$ : Specific capacity (mAh cm<sup>-2</sup>)

The specific capacity ( $C_2$ ) was calculated according to the following equation:

$$C_2 = C_1 \times m_a$$

### GITT measurements

The diffusion coefficient of  $^{D}_{Na^+}$  was calculated according to Fick's second law:

$$D_{Na^+} = \frac{4}{\pi\tau} \left( \frac{m_B V_M}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

where  $\tau$  is the time for an applied galvanostatic current;  $m_B$ ,  $M_B$ ,  $V_M$ , and  $S$  are the mass, molecular weight, molar volume, and active surface area of the electrode, respectively. Additionally,  $\Delta E_\tau$  and  $\Delta E_s$  are the change of cell voltage  $E$  during the current pulse and the relaxation process, respectively.

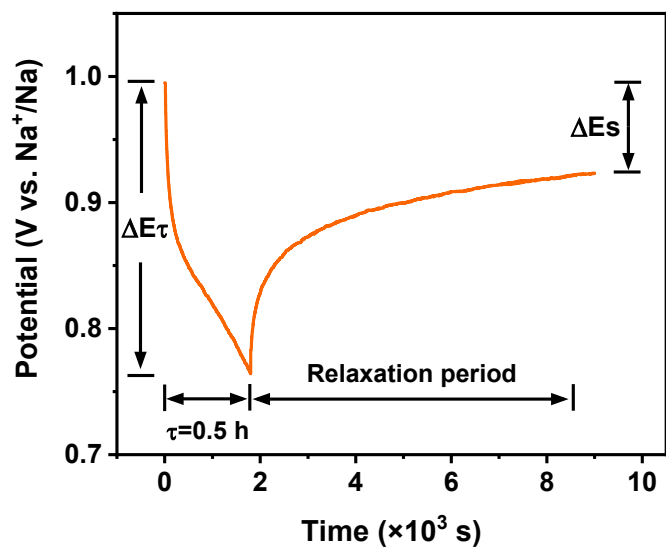


Fig. S13  $\tau$  vs E profile for a single GITT titration.