

## Supplementary Information

### Metal-Organic Framework Derived 3D Graphene Decorated NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> for Fast Na-ion Storage

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**Calculation Methods:** The specific capacity of electrode materials was calculated from galvanostatic charge-discharge (GCD) tests according to the equations S1, where SC is the specific capacity,  $I$  is the discharge current,  $\Delta t$  is the discharge time, and  $m$  is the mass loading of active materials (for example, the mass of NTP-rGO composites includes the mass of NTP and rGO), respectively.

$$SC = \frac{I\Delta t}{m} \quad (S1)$$

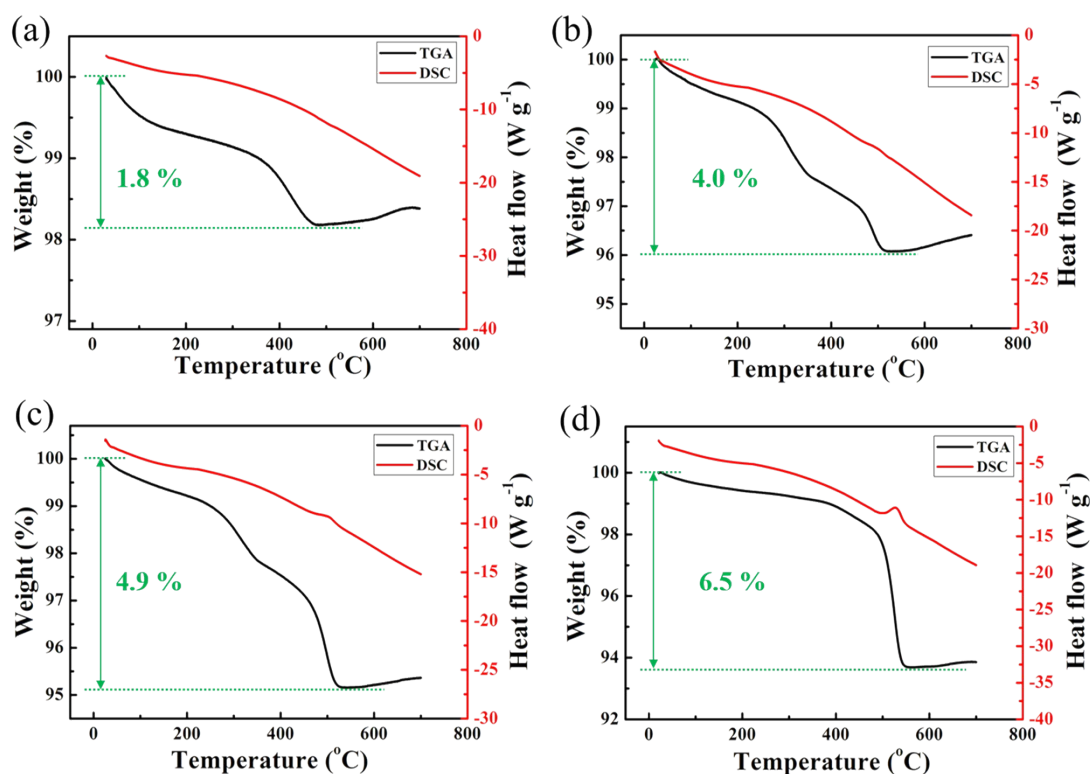


Fig. S1† TGA/DSC curves of all samples (a) NTP, (b) NTP-rGO-10, (c) NTP-rGO and (d) NTP-rGO-30.

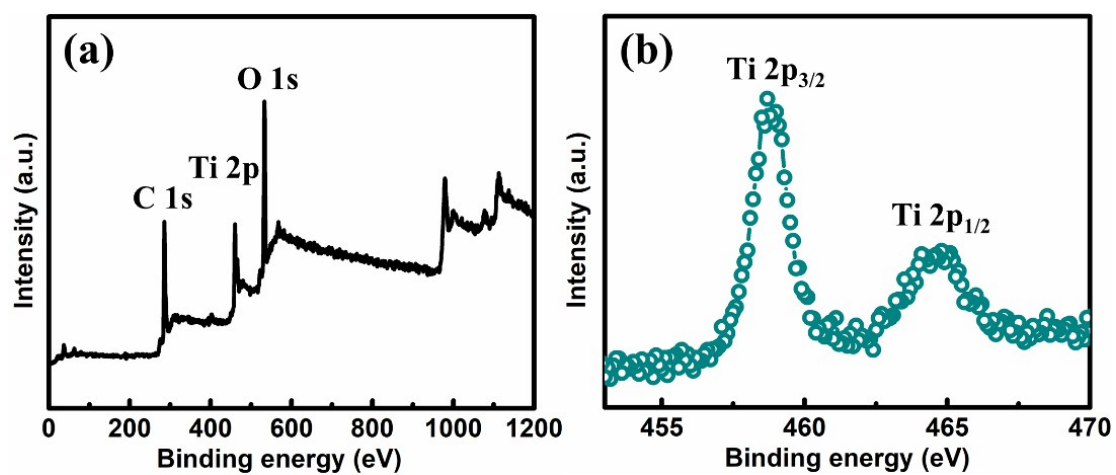


Fig. S2† XPS survey spectrum of MIL-125 and the corresponding high-resolution Ti 2p XPS spectrum.

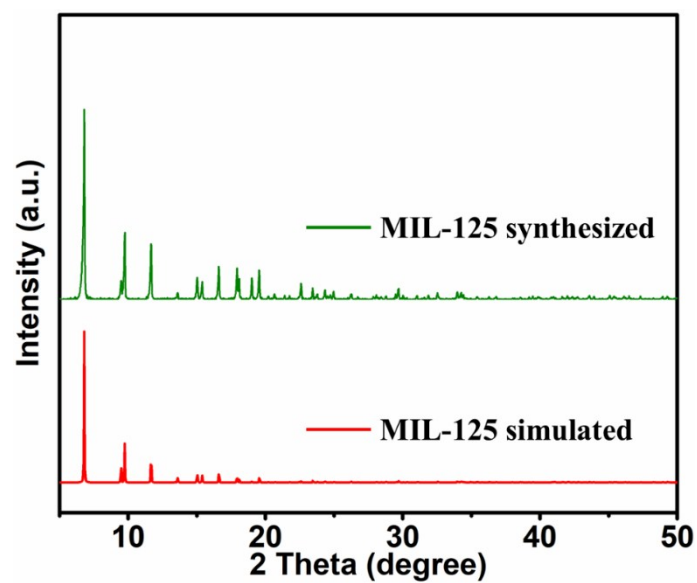
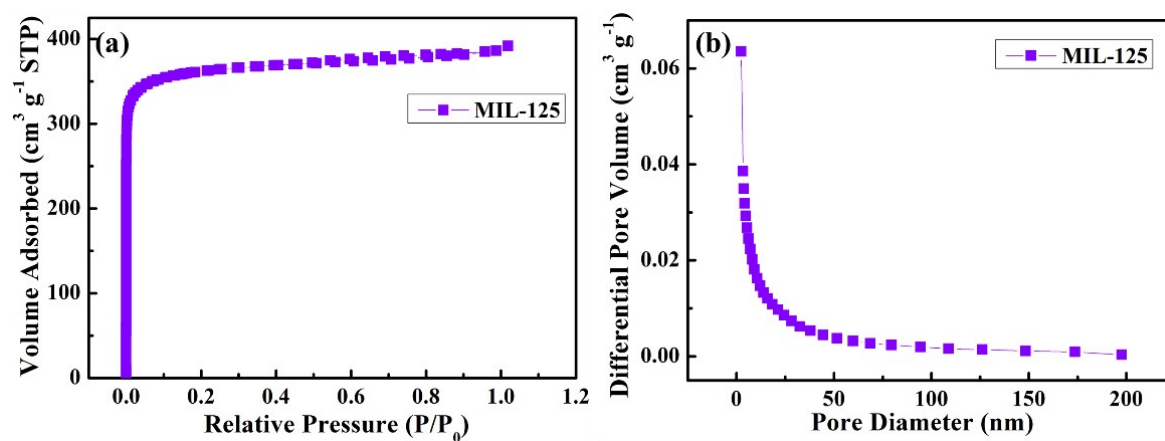
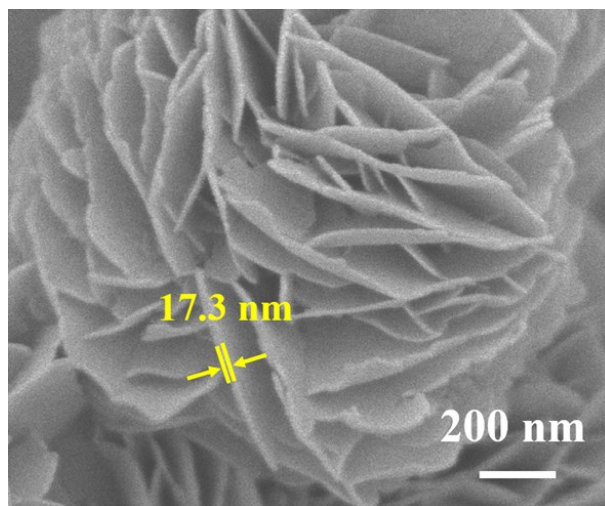


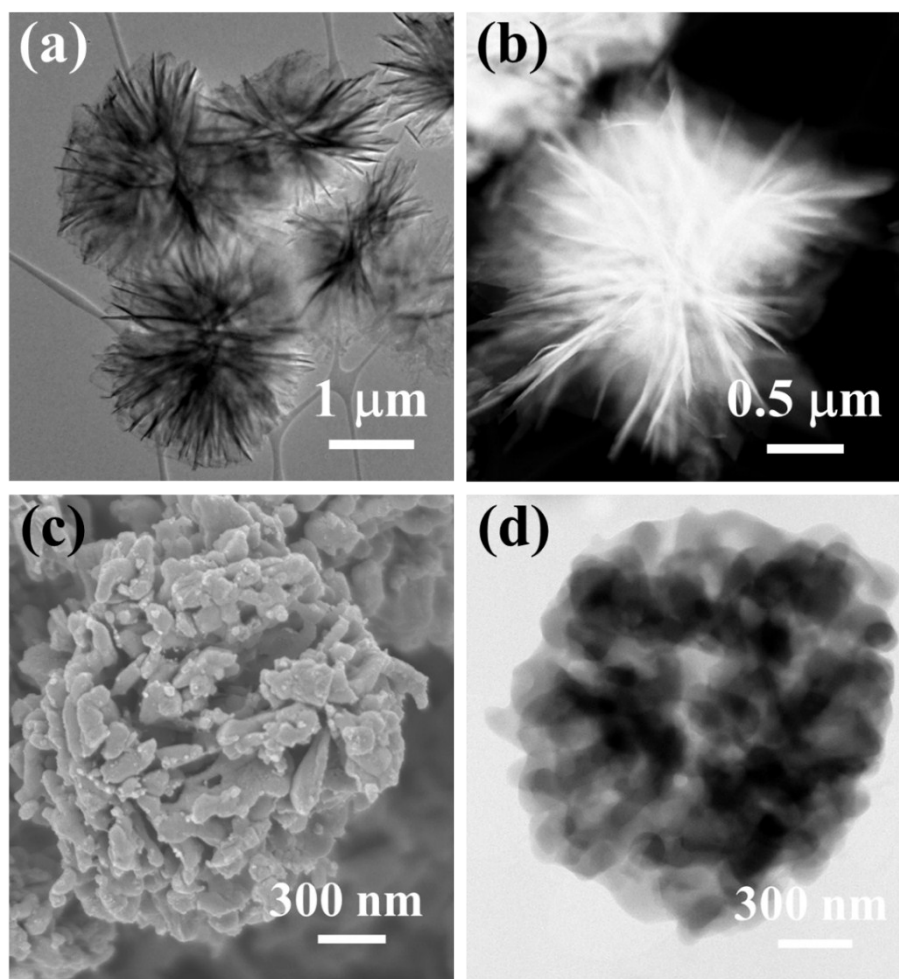
Fig. S3† XRD pattern of MIL-125 compared with the MIL-125 simulated.



**Fig. S4†** (a) Nitrogen adsorption-desorption isotherms of MIL-125; (b) The pore size distribution plot of MIL-125



**Fig. S5†** SEM image of the NTP precursor.



**Fig. S6†** TEM images of (a) NTP precursor and (b) NTP-rGO precursor; (c) SEM image of NTP; (d) TEM image of NTP sample.

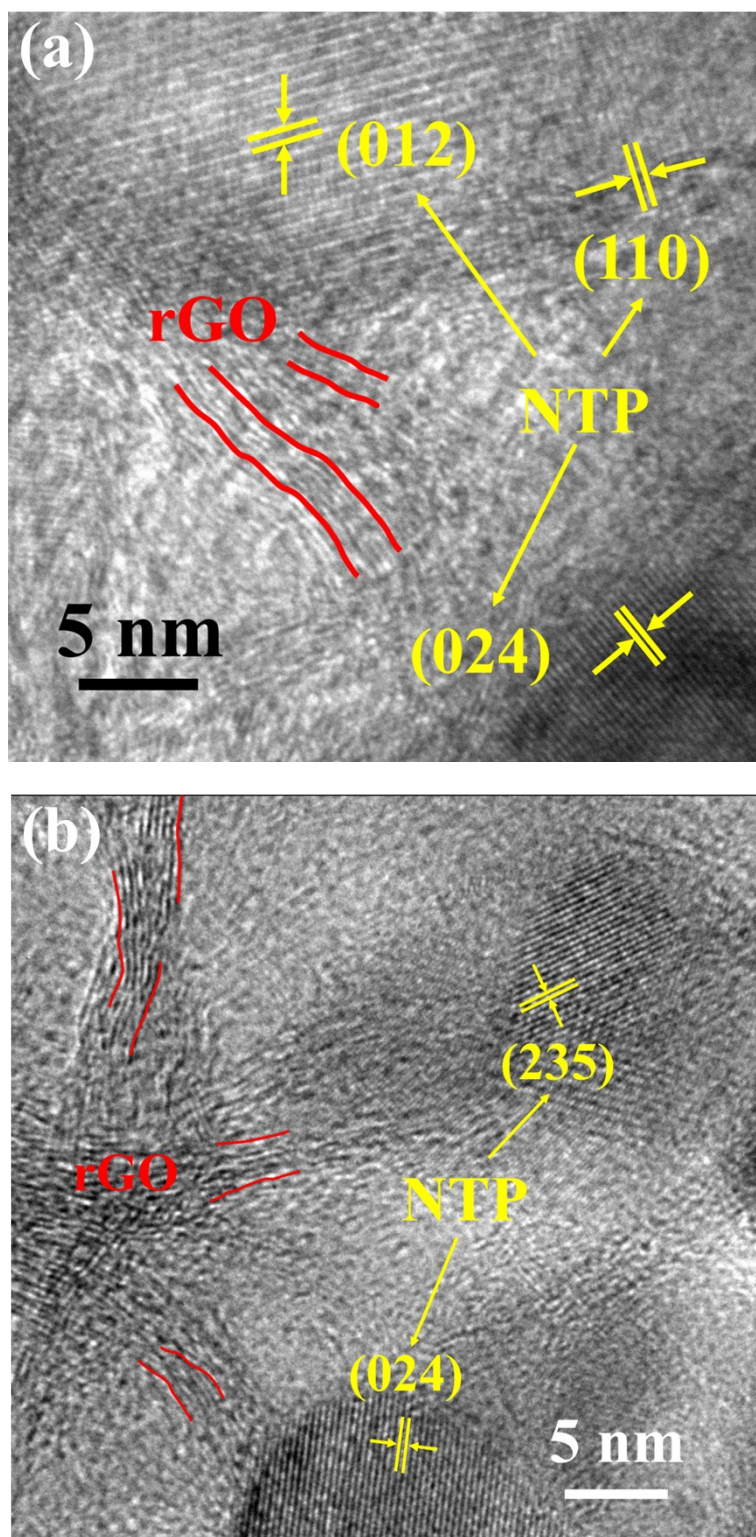
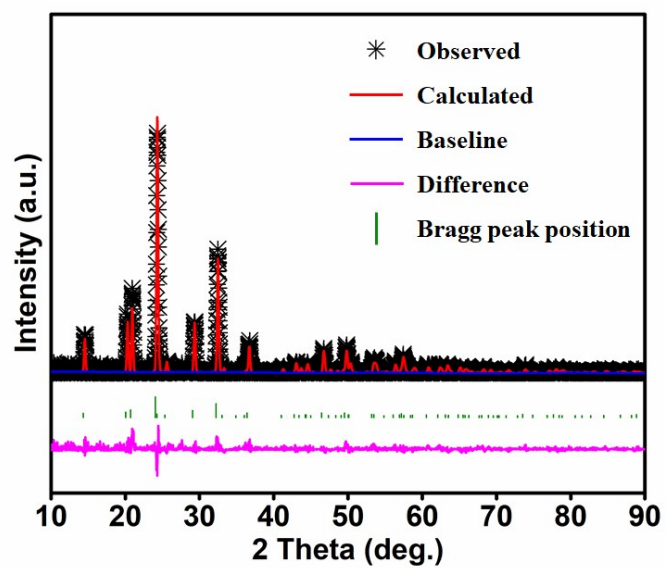


Fig. S7† HRTEM image of the NTP-rGO.





**Fig. S8†** XRD pattern of the NTP-rGO and its Rietveld refinement.

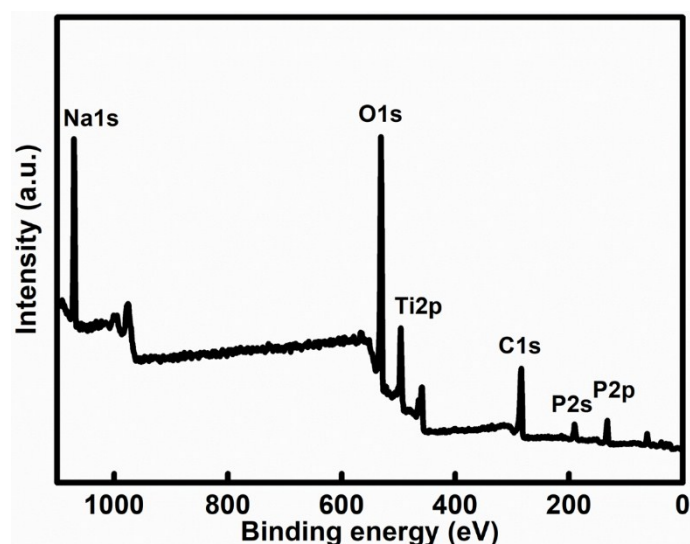
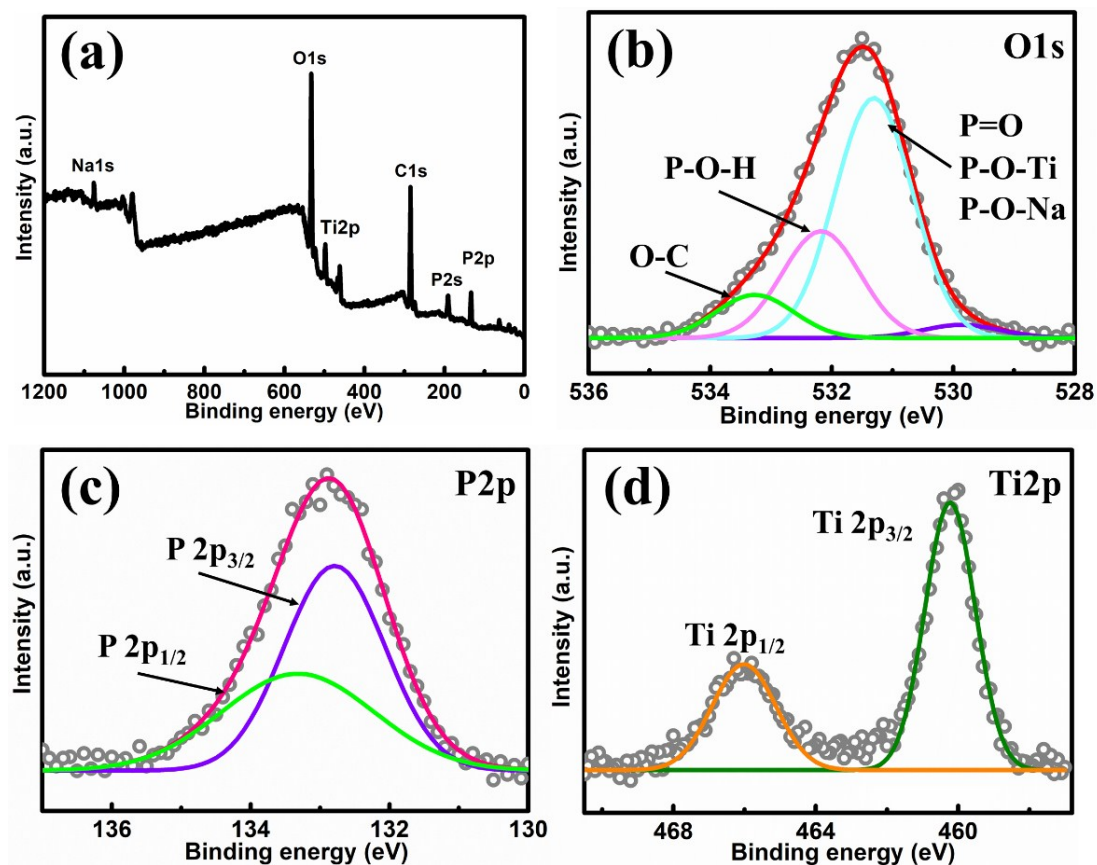
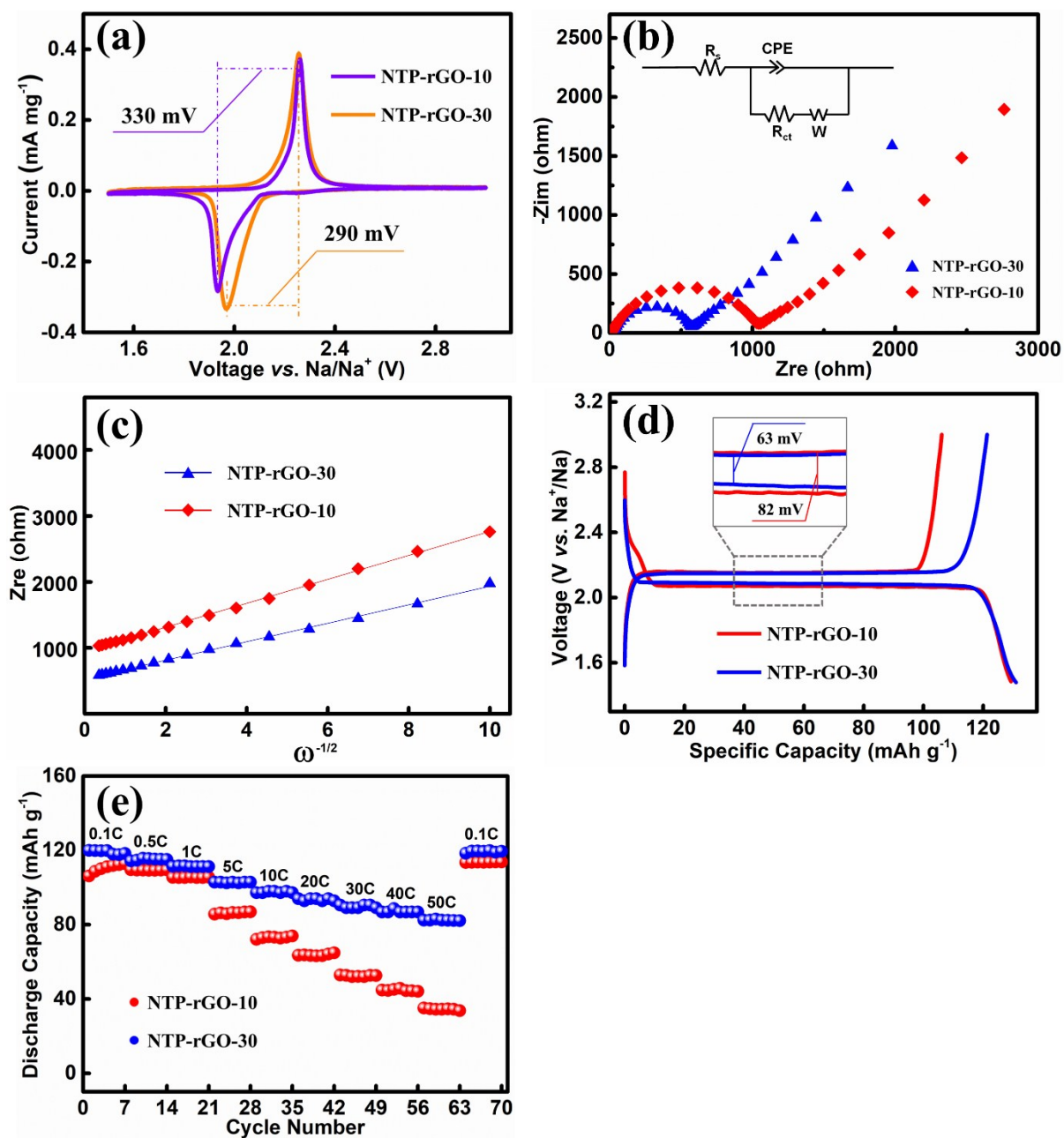


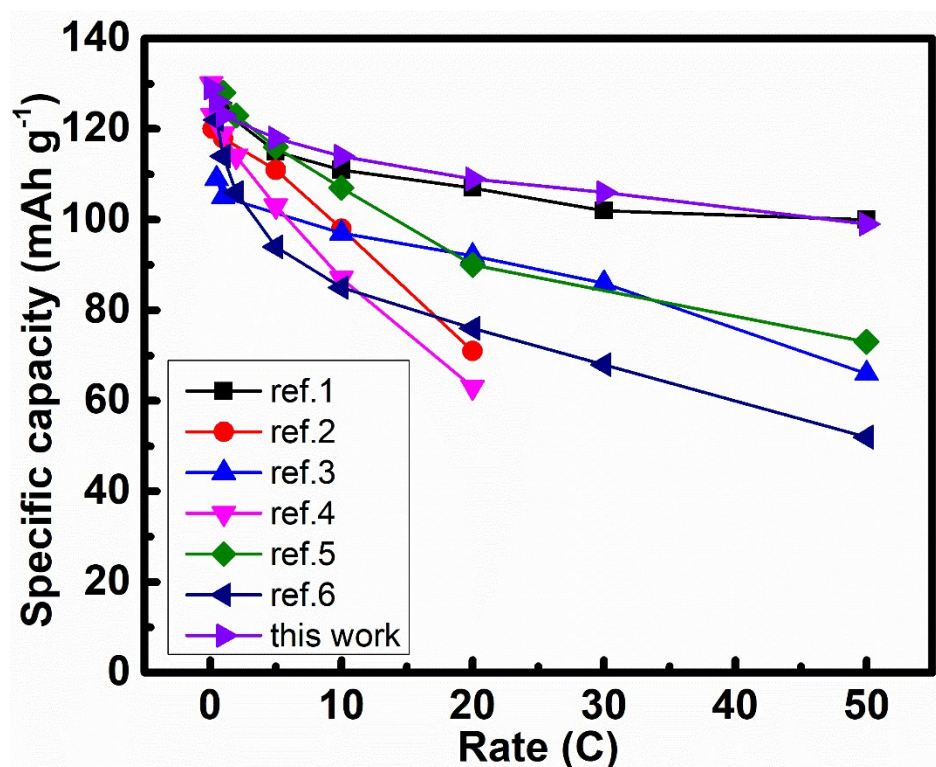
Fig. S9† XPS survey spectrum of the NTP-rGO.



**Fig. S10†** (a) XPS survey spectrum of the NTP and high-resolution spectra for (b) O 1s, (c) P 2p and (d) Ti 2p, respectively.



**Fig. S11†** The electrochemical performance of NTP-rGO-10 and NTP-rGO-30. (a) CV curves. (b) Nyquist plots and the equivalent circuit (the inset). (c) The relationship between  $Z_{re}$  and  $\omega^{-1/2}$  at low frequency from EIS test. (d) The first cycle of the discharge-charge curves. (e) Rate performance.



**Fig. S12†** The comparison of specific capacity and rate capability of NTP-rGO in this work with others published recently. <sup>[1-6]</sup>

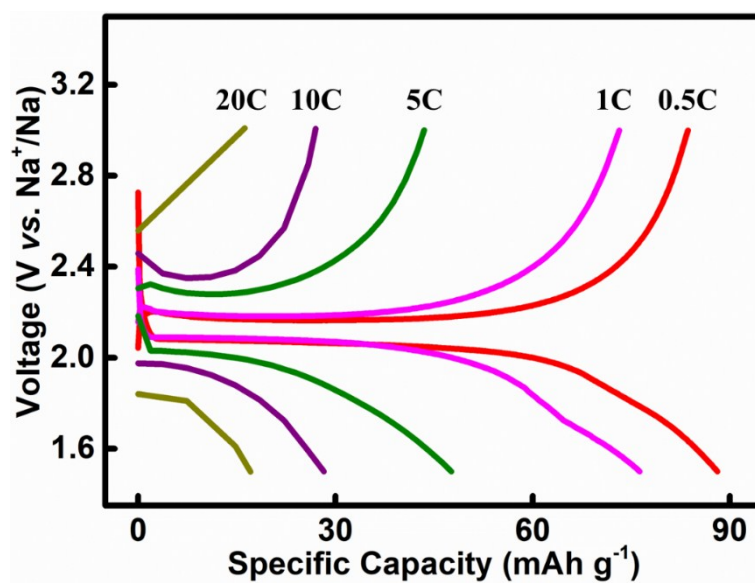


Fig. S13† The discharge-charge curves of NTP electrode at various current densities.

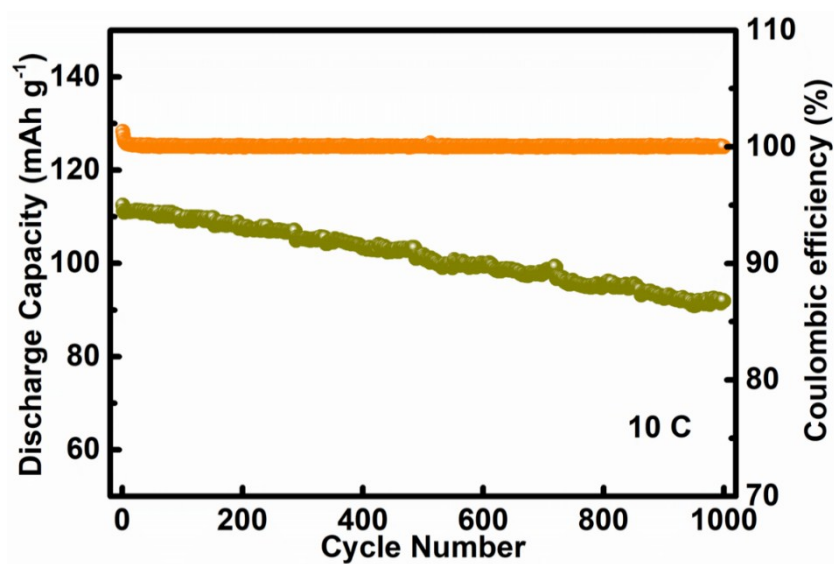
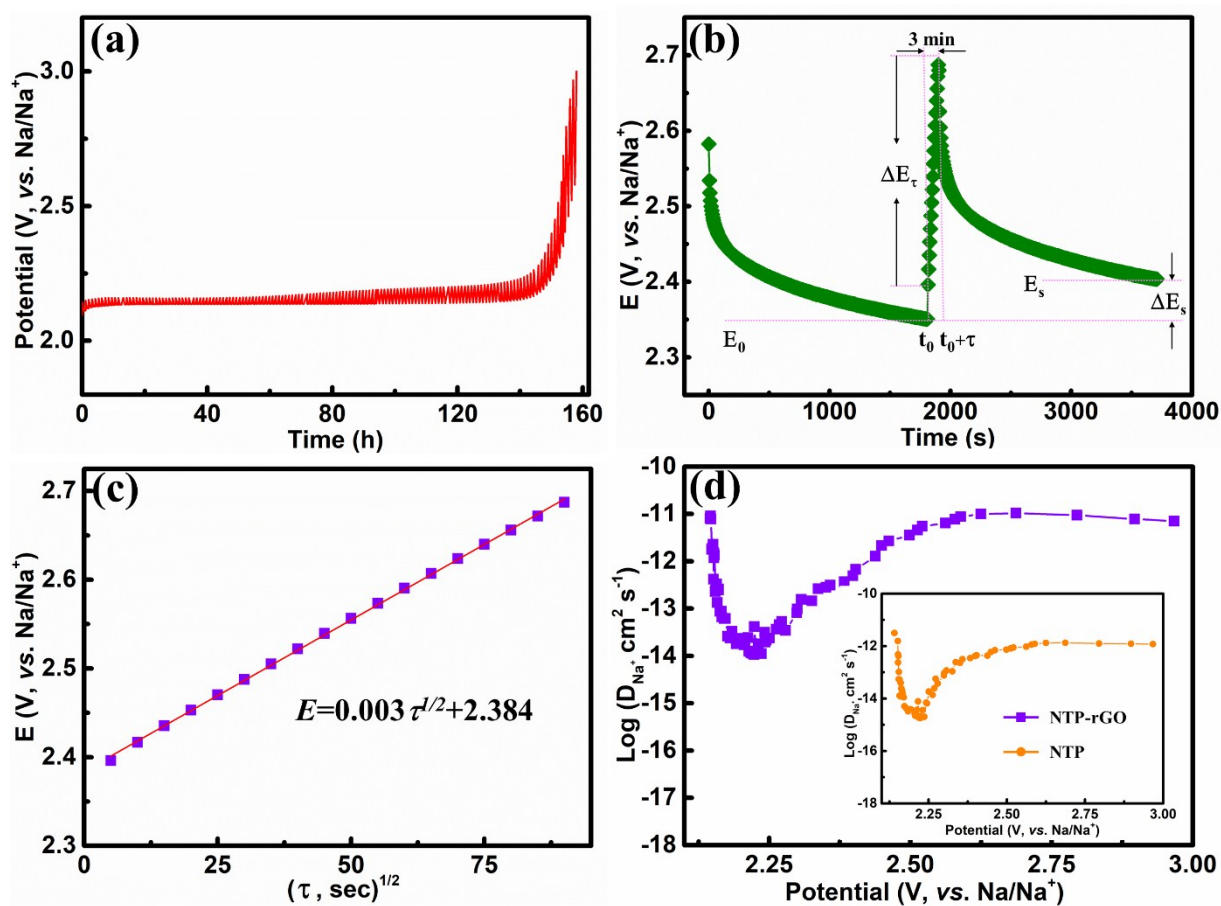
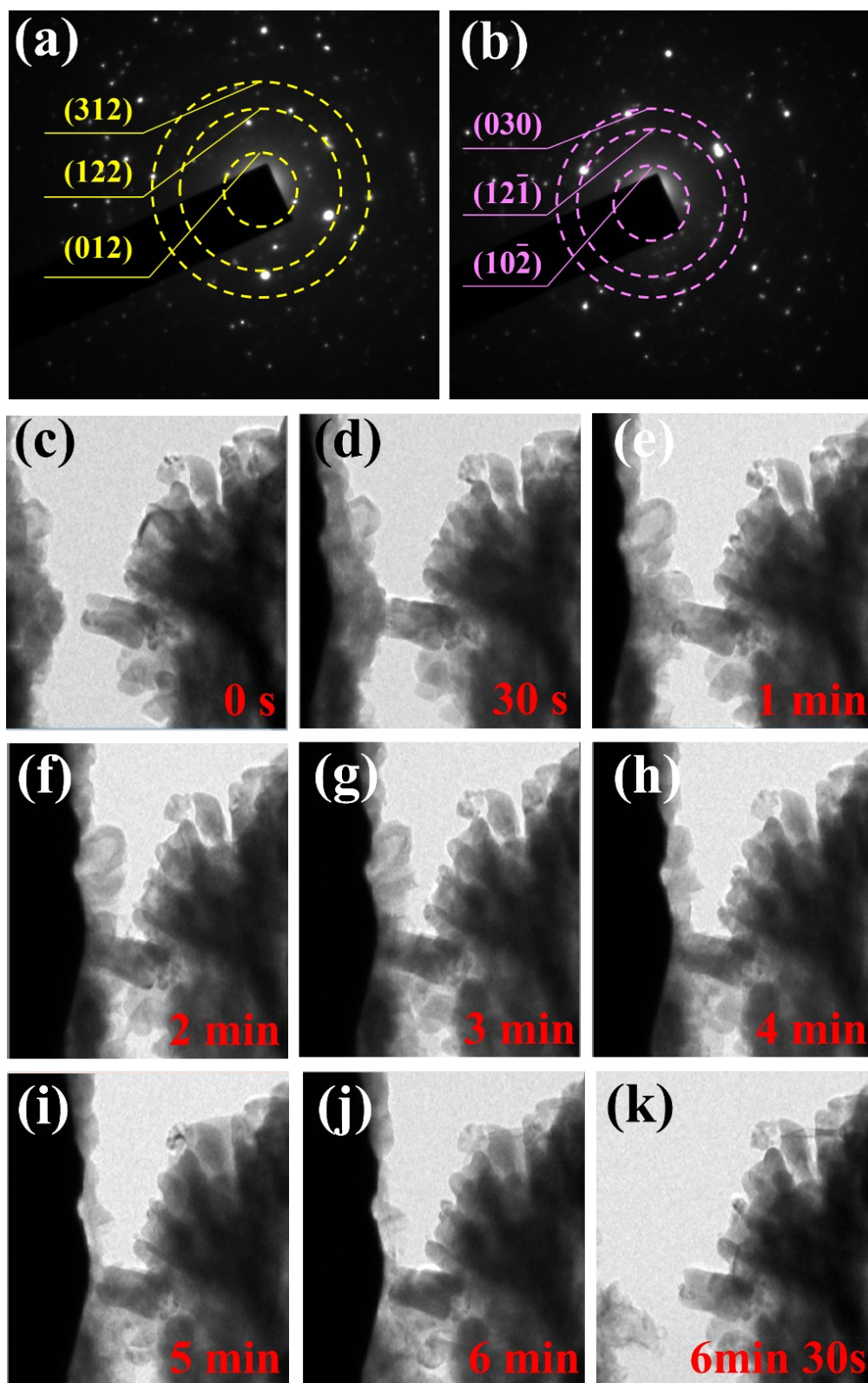


Fig. S14† Cycling stability test at 10 C for NTP-rGO electrode.



**Fig. S15†** (a) The charge GITT curves of NTP-rGO. (b)  $t$  vs.  $E$  profile for a single GITT titration. (c) Linear behavior of  $E$  vs.  $\tau^{1/2}$  relationship. (d) The calculated  $D_{\text{Na}^+}$  from GITT data for the NTP-rGO electrode and the NTP electrode (the inset).





**Fig. S16†** SAED pattern of the NTP a) before sodiation and b) after sodiation. c-k) *In-situ* TEM of the NTP during the sodiation/desodiation process.



**Table S1** The comparison of CE of NTP-rGO in this work with recent published works.

Materials	Current density (C)	Coulombic efficiency (%)	Ref.
This work	0.1 C	96.8%	-
NTP $\subset$ GN	1 C	79%	[7]
NTP@C@PC	1 C	95%	[8]
NTP-NBA	1 C	83%	[9]
NTP $\subset$ rGO-CNTs	1 C	90%	[5]
NTP/C P2	0.1 C	95%	[10]
h-MNTP/WMCNTs	0.5 C	96.6%	[11]

## Reference

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