

## Supplementary Information

### Metal-Organic Framework Derived 3D Graphene Decorated $\text{NaTi}_2(\text{PO}_4)_3$ for Fast Na-ion Storage

***Lei Wang <sup>a,b</sup>, Zhennan Huang <sup>b</sup>, Bo Wang <sup>a,\*</sup>, Hao Luo <sup>a</sup>, Meng Cheng <sup>b</sup>, Yifei Yuan <sup>b</sup>, Kun He <sup>b</sup>, Tara Foroozan <sup>b</sup>, Ramasubramonian Deivanayagam <sup>b</sup>, Guijing Liu <sup>c</sup>, Dianlong Wang <sup>a,\*</sup>, and Reza Shahbazian-Yassar <sup>b,\*</sup>***

<sup>a</sup> MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 150001 Harbin, China.

<sup>b</sup> Department of Mechanical and Industrial Engineering, University of Illinois at Chicago (UIC), Chicago, IL 60607, USA

<sup>c</sup> School of Chemistry and Materials Science, Ludong University, Yantai, 264025, P R China

\*Corresponding author. Fax: +86 45186413721; Tel: +86 45186413751.

E-mail address:

[wangbo19880804@163.com](mailto:wangbo19880804@163.com) (B. Wang),  
[wangdianlonghit@163.com](mailto:wangdianlonghit@163.com) (D. L. Wang),  
[rsyassar@uic.edu](mailto:rsyassar@uic.edu) (R. S. Yassar).

**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.

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

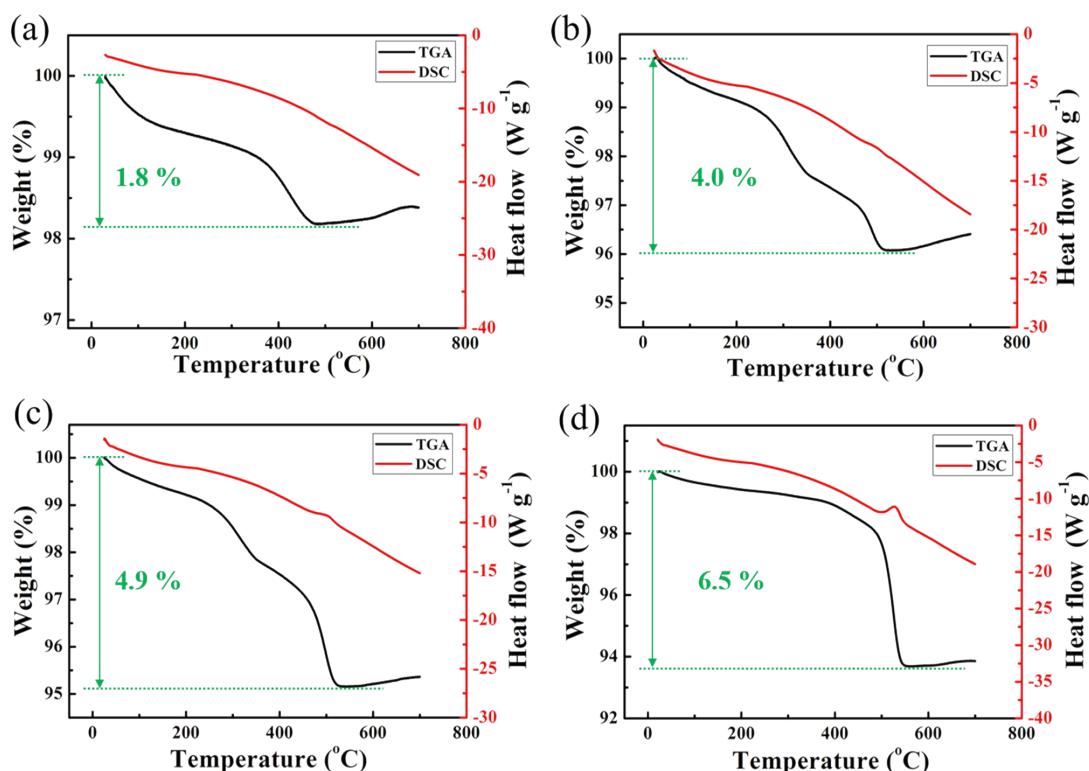


Fig. S1† TGA/DSC curves of all samples (a) NTP, (b) NTP-rGO-10, (c) NTP-rGO and (d) NTP-rGO-30.

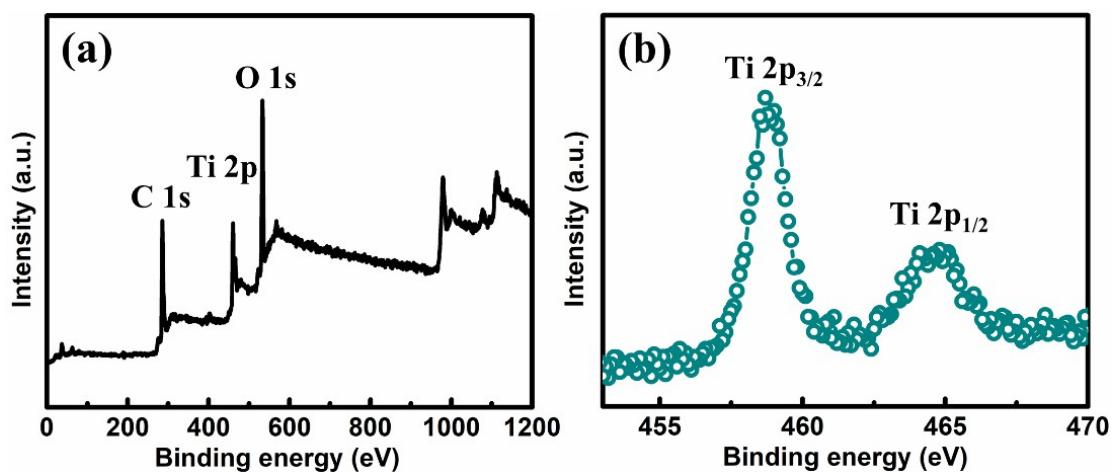
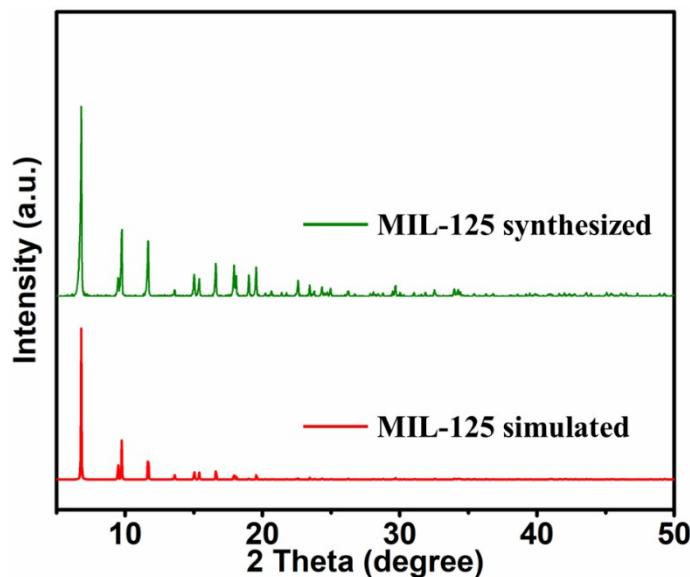
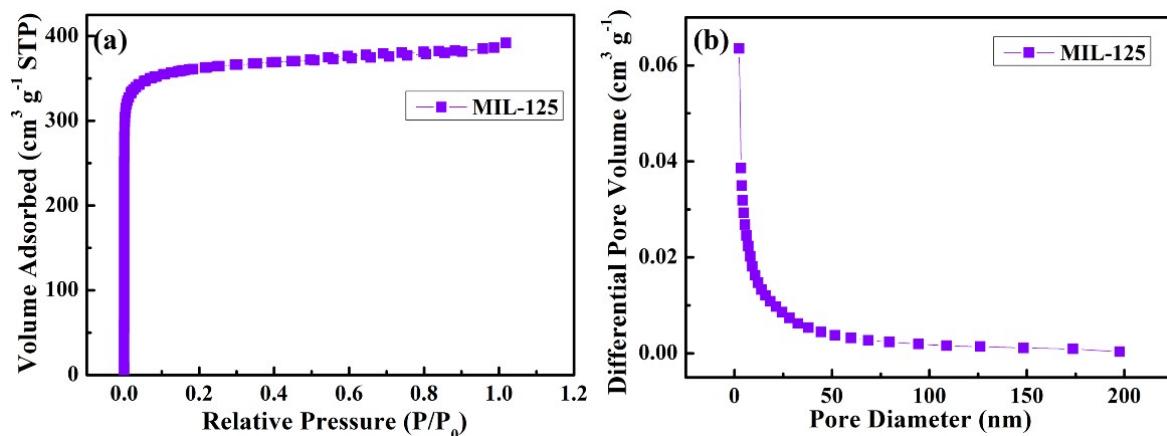


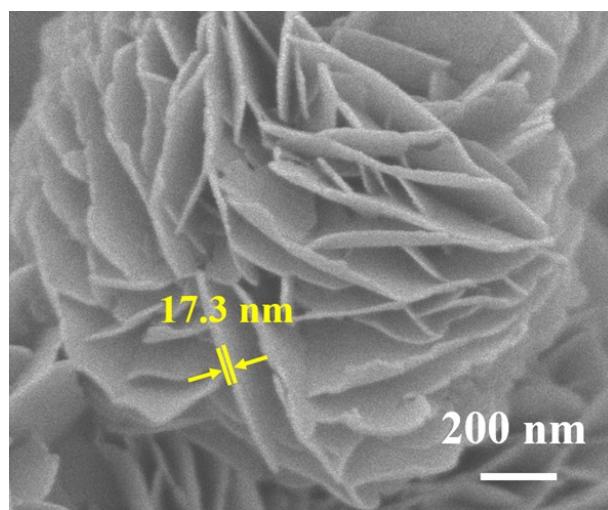
Fig. S2† XPS survey spectrum of MIL-125 and the corresponding high-resolution Ti 2p XPS spectrum.



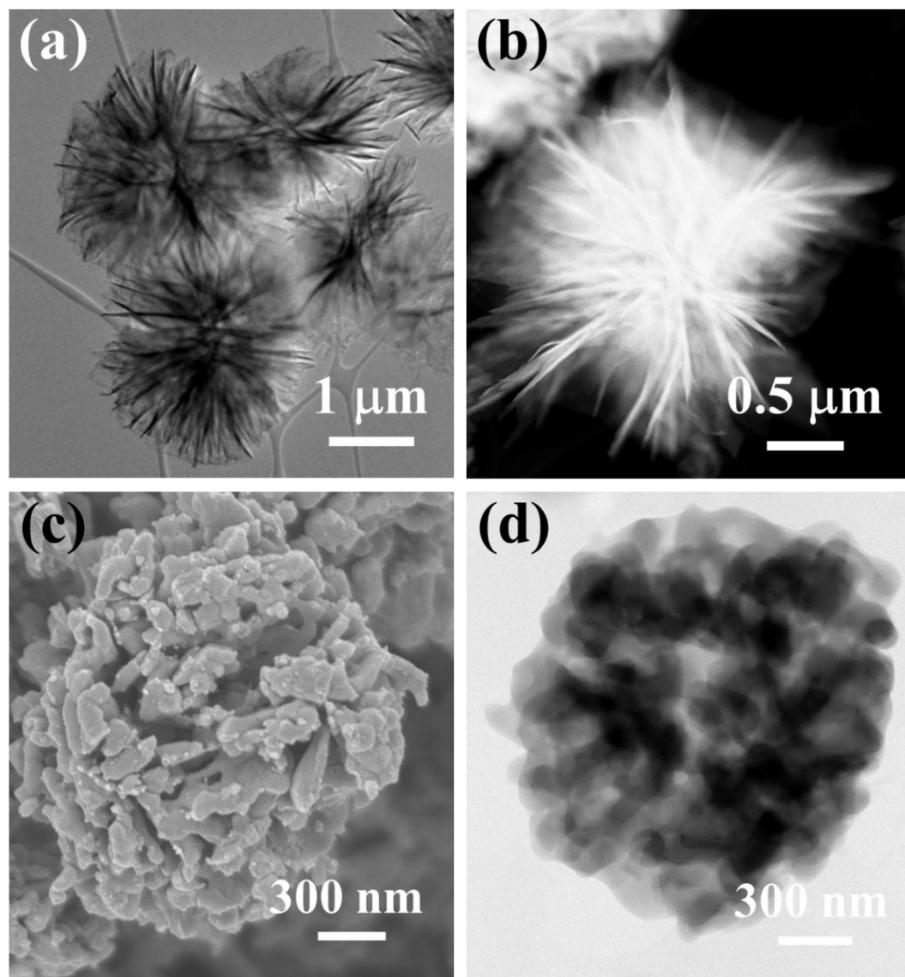
**Fig. S3†** XRD pattern of MIL-125 compared with the MIL-125 simulated.



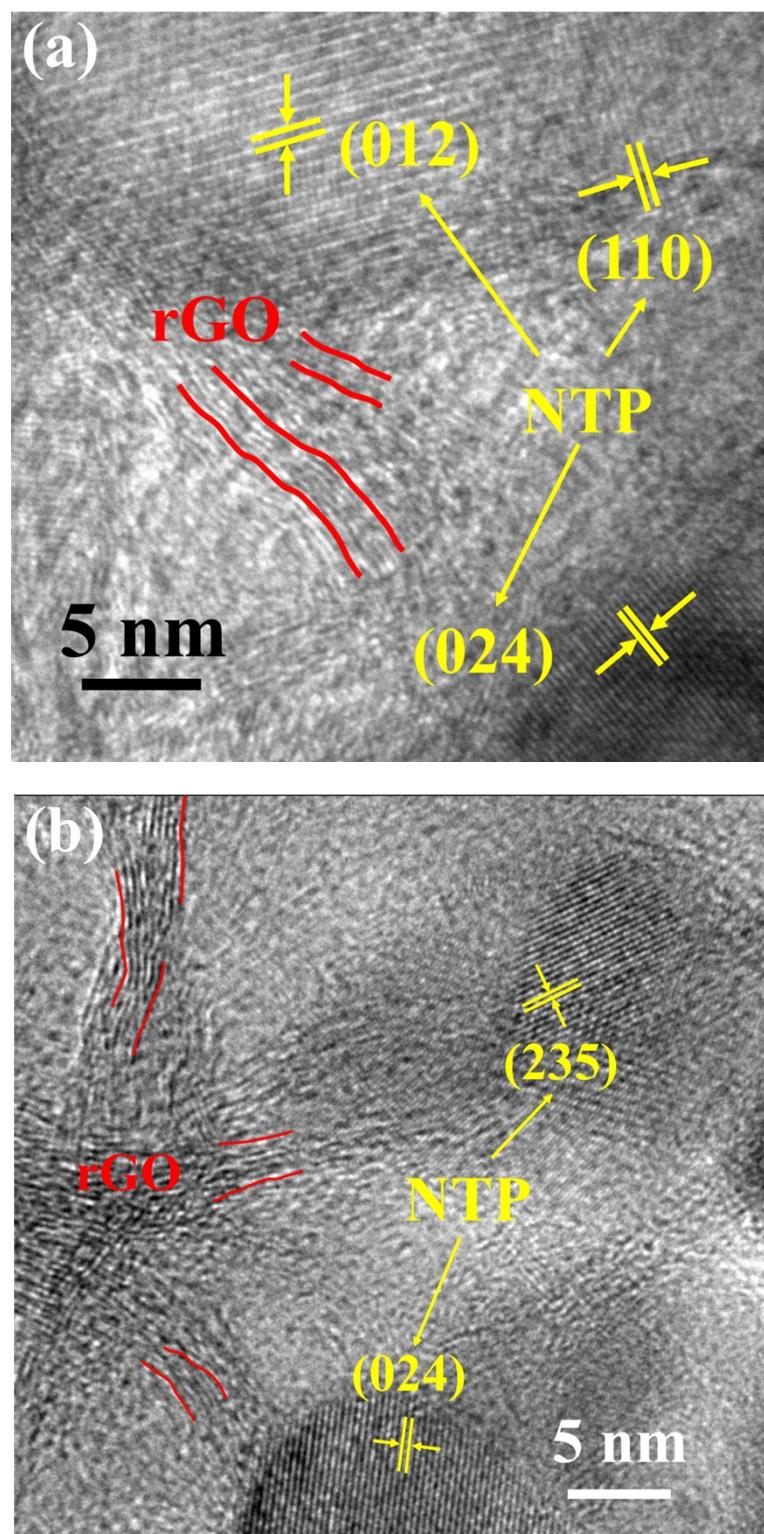
**Fig. S4†** (a) Nitrogen adsorption-desorption isotherms of MIL-125; (b) The pore size distribution plot of MIL-125



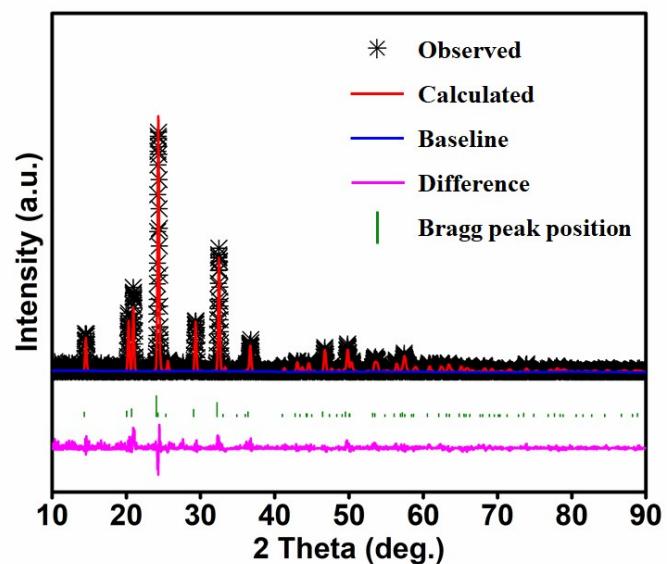
**Fig. S5†** SEM image of the NTP precursor.



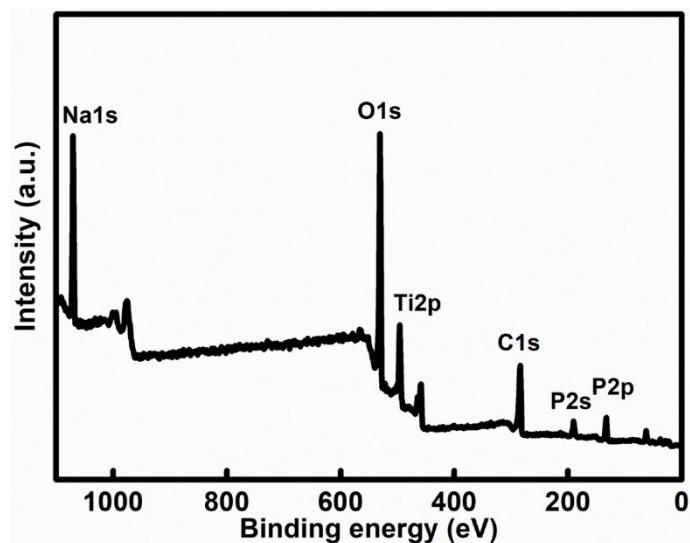
**Fig. S6†** TEM images of (a) NTP precursor and (b) NTP-rGO precursor; (c) SEM image of NTP; (d) TEM image of NTP sample.



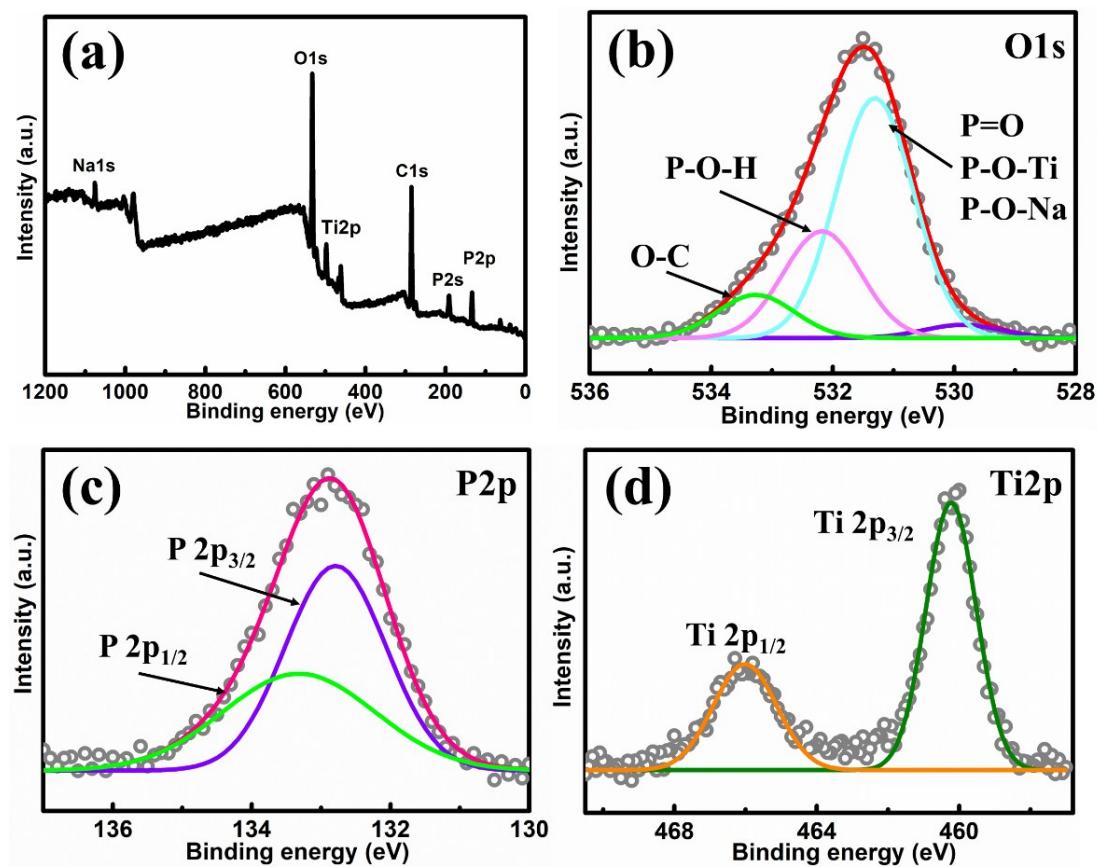
**Fig. S7†** HRTEM image of the NTP-rGO.



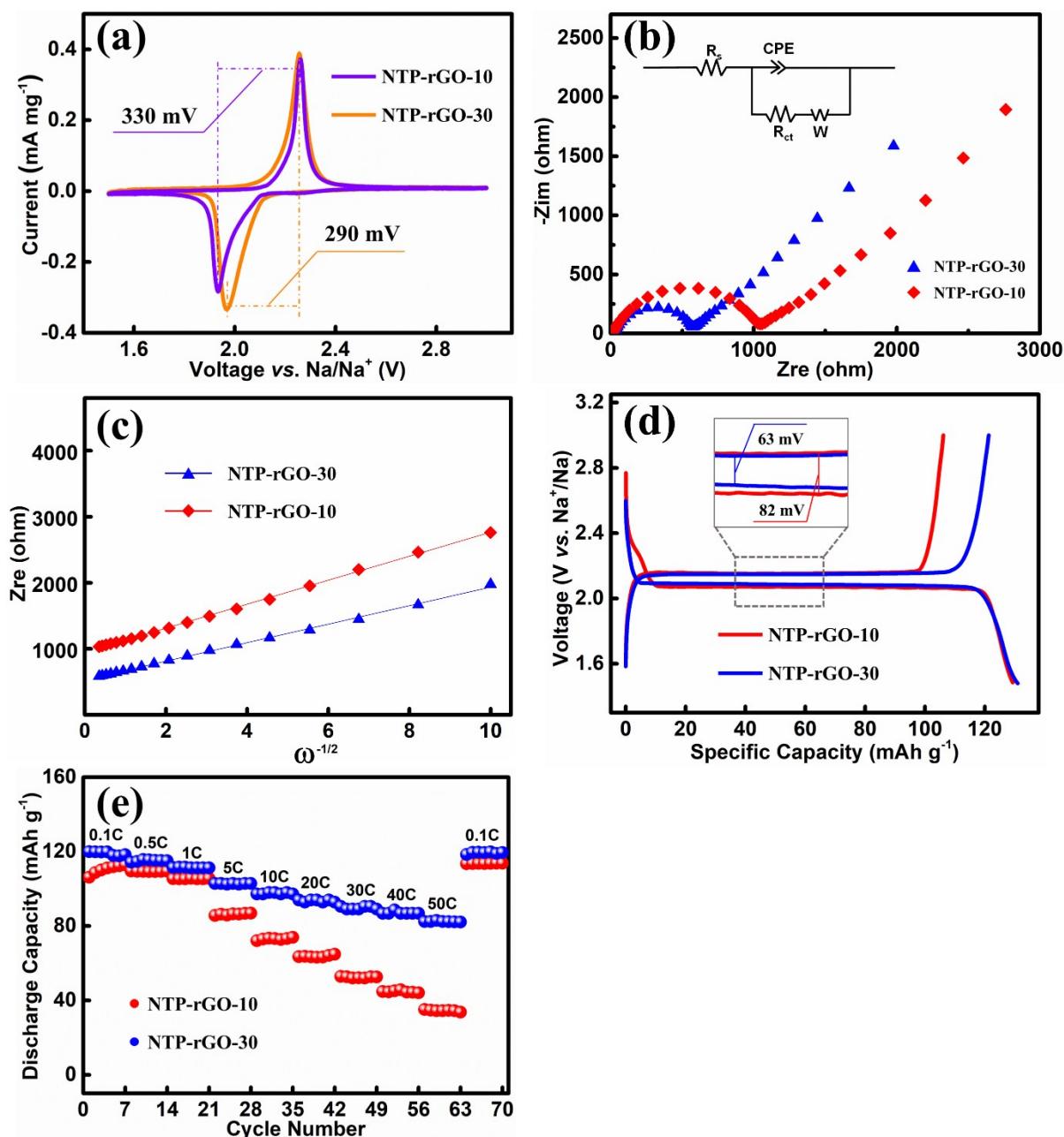
**Fig. S8†** XRD pattern of the NTP-rGO and its Rietveld refinement.



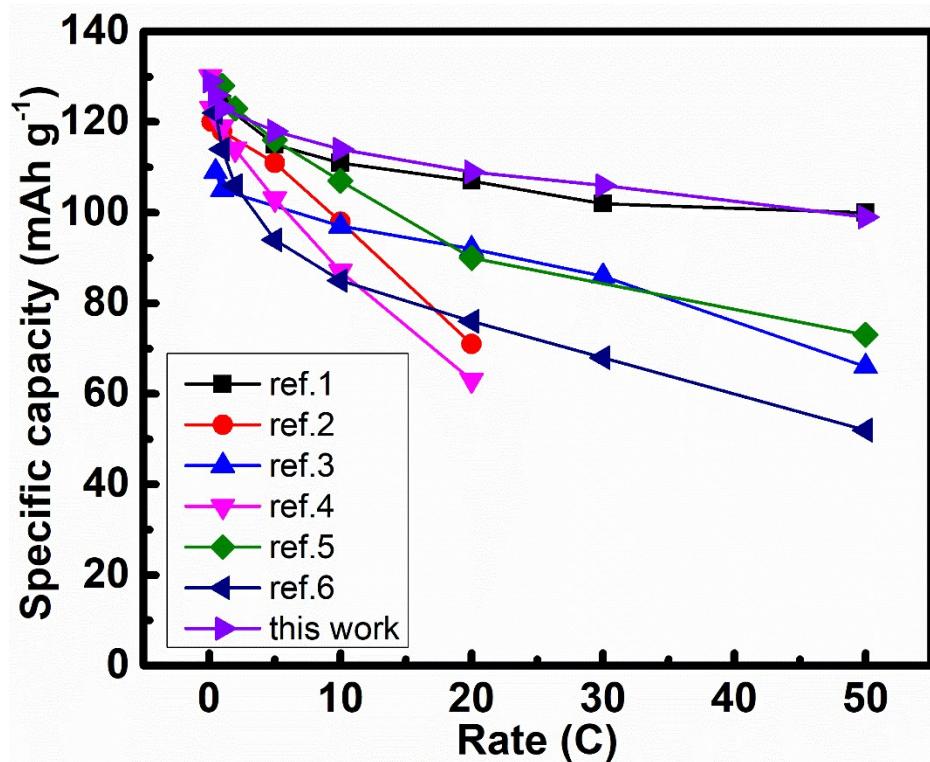
**Fig. S9†** XPS survey spectrum of the NTP-rGO.



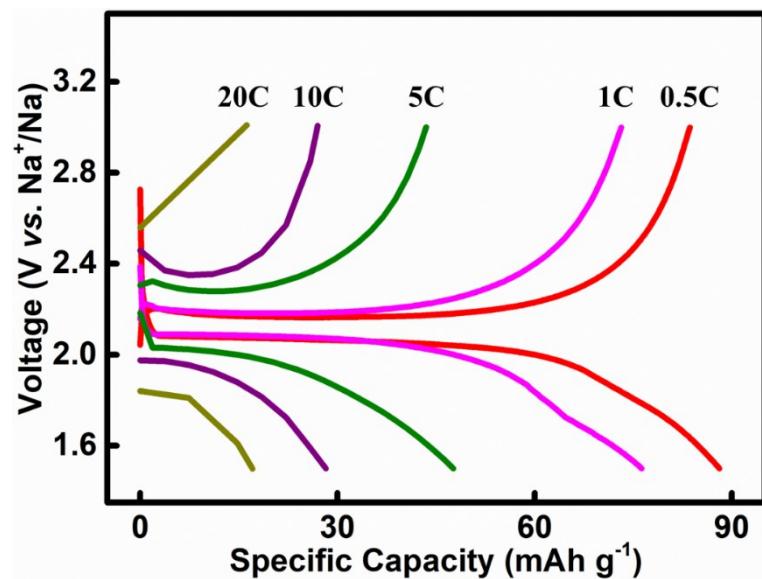
**Fig. S10†** (a) XPS survey spectrum of the NTP and high-resolution spectra for (b) O 1s, (c) P 2p and (d) Ti 2p, respectively.



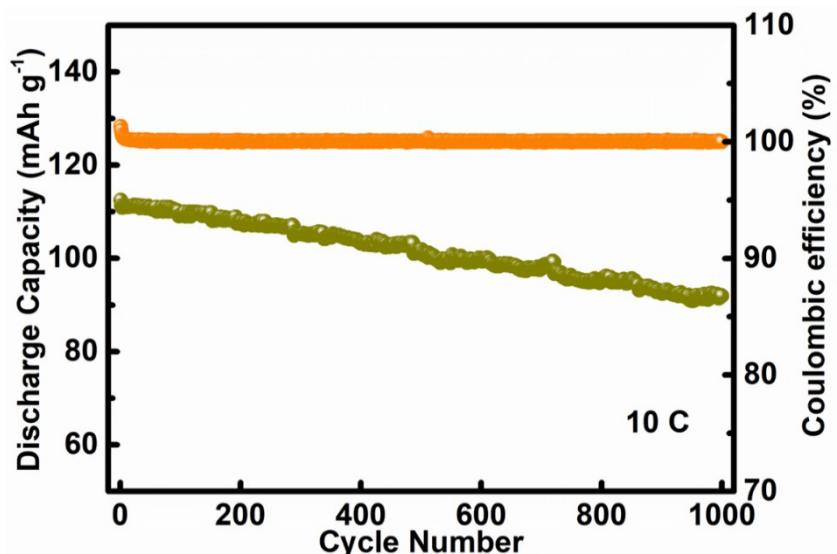
**Fig. S11†** The electrochemical performance of NTP-rGO-10 and NTP-rGO-30. (a) CV curves. (b) Nyquist plots and the equivalent circuit (the inset). (c) The relationship between  $Z_{re}$  and  $\omega^{-1/2}$  at low frequency from EIS test. (d) The first cycle of the discharge-charge curves. (e) Rate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



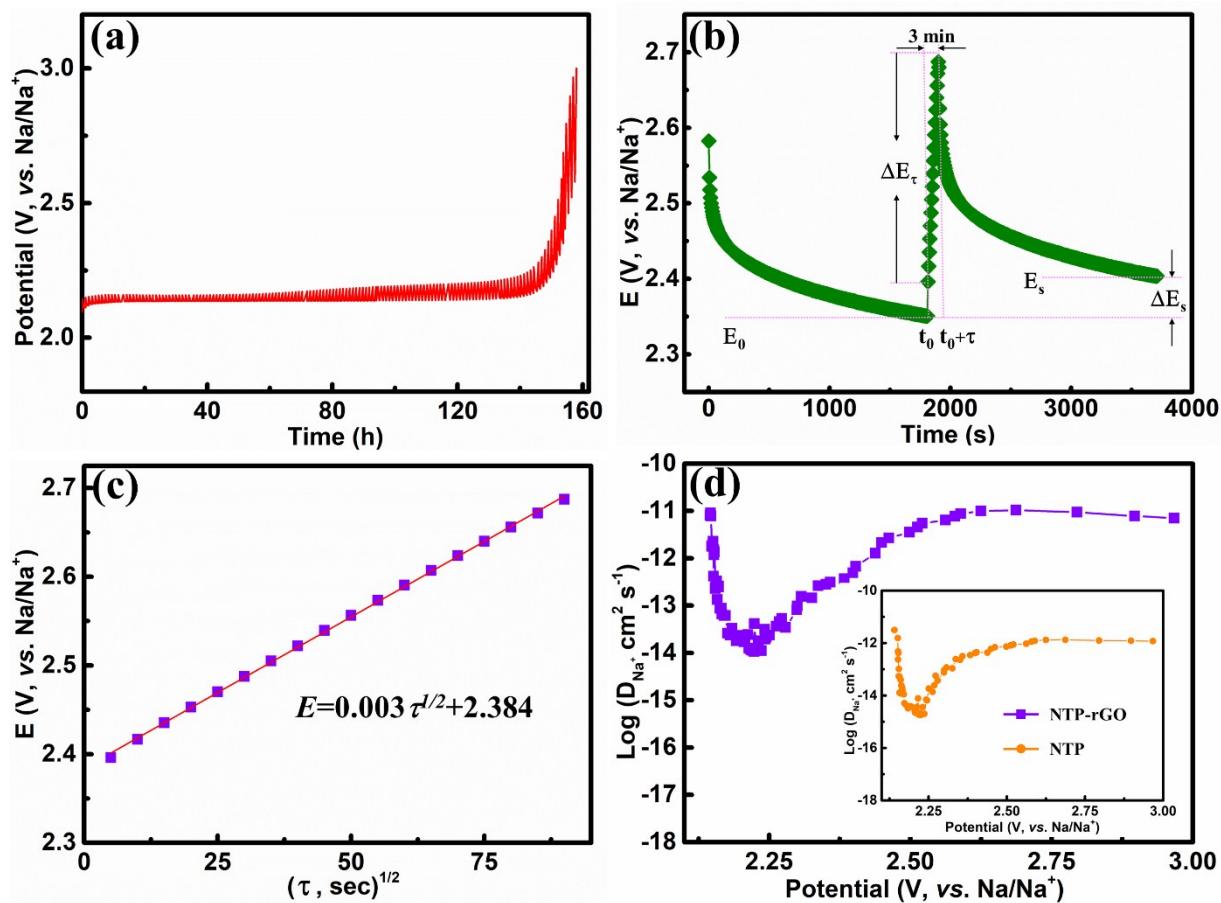
**Fig. S12†** The comparison of specific capacity and rate capability of NTP-rGO in this work with others published recently. [1-6]



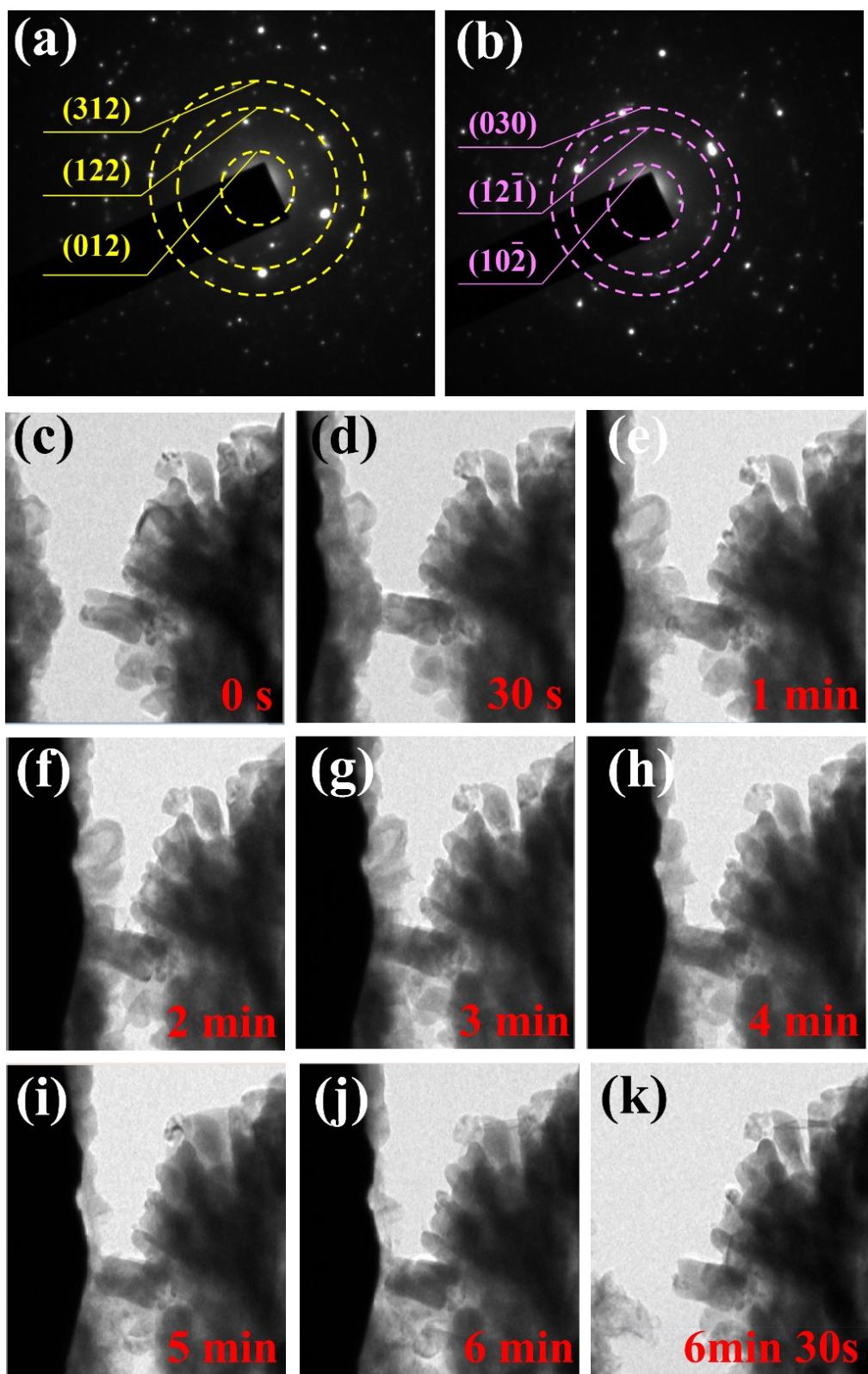
**Fig. S13†** The discharge-charge curves of NTP electrode at various current densities.



**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 <sub>c</sub> GN	1 C	79%	[7]
NTP@C@PC	1 C	95%	[8]
NTP-NBA	1 C	83%	[9]
NTP <sub>c</sub> 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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