

## Supporting Information

### **Protein-assisted Assembly of Mesoporous Nanocrystals and Carbon Nanotubes for Self-supporting High-Performance Sodium Electrodes**

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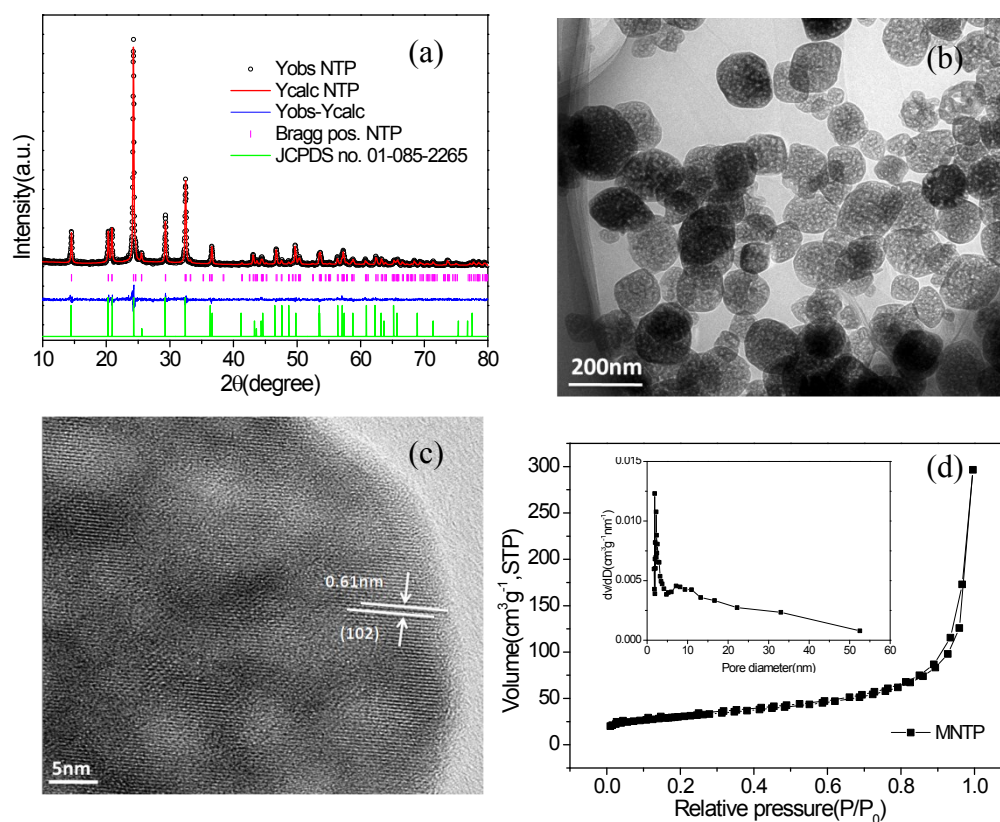
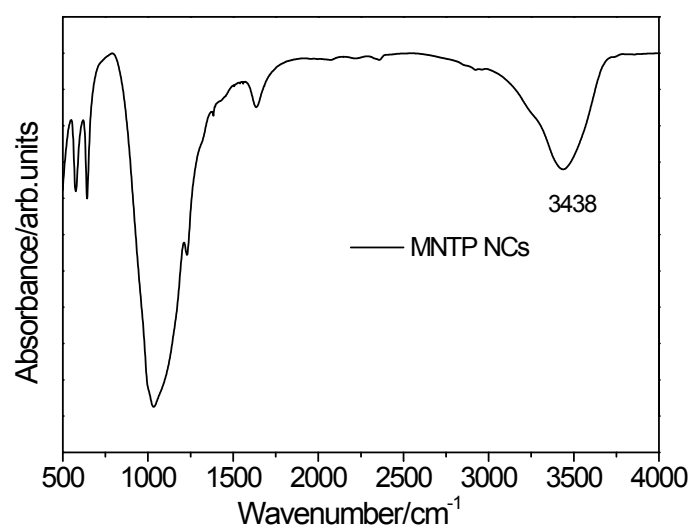


Figure S1. (a)-(c) XRD patterns with Rietveld refinement, TEM and HRTEM images of the MNTP NCs; (d) Nitrogen adsorption–desorption isotherms and corresponding pore size distribution of the MNTP NCs. The results indicate that the MNTP NCs have high crystallinity, a diameter of about 100nm, and pore size between 2 and 10 nm.



FigureS2. FTIR spectrum of the MNTP NCs revealing abundant OH groups on the MNTP NCs.

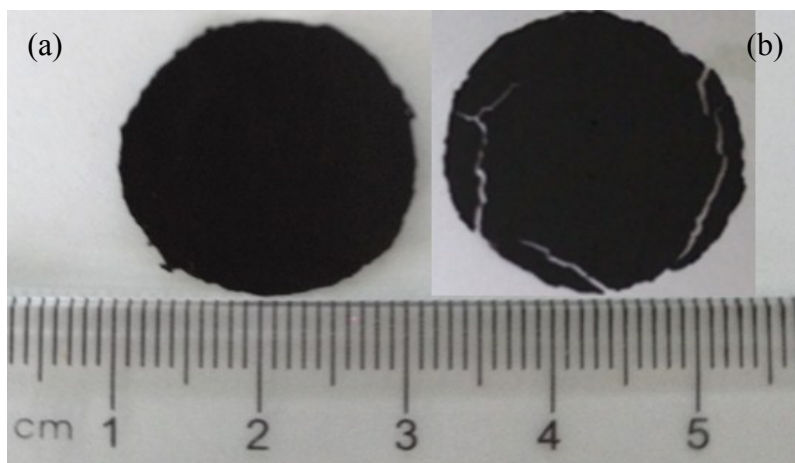


Figure S3. Optical images of (a) Self-supporting MNTP/MWCNTs film and (b) p-MNTP/MWCNTs control sample.

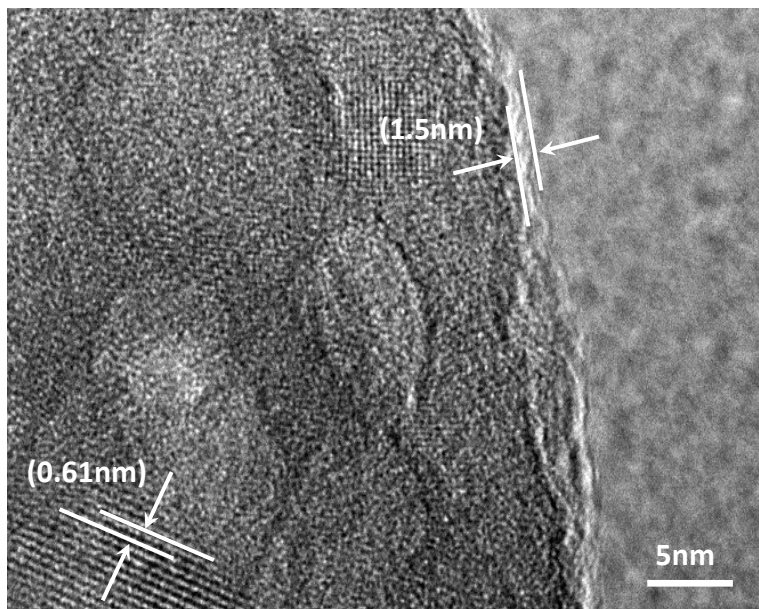


Figure S4. Representative HRTEM image of the MNTP NCs in the self-supporting MNTP-MWCNTs film, demonstrating mesoporous characteristic as well as (102) lattice plane of the NASICON-type phase with a lattice spacing of 0.61nm.

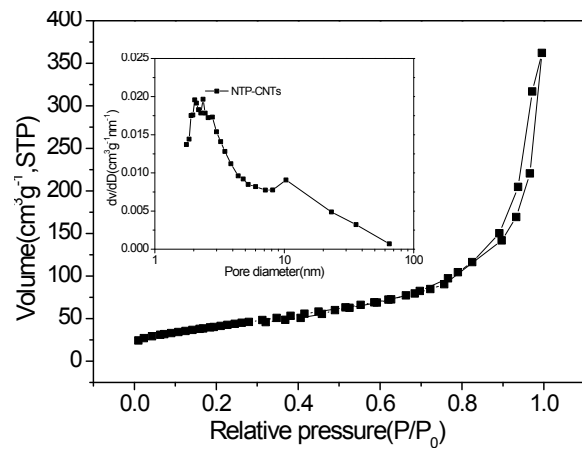


Figure S5. Nitrogen adsorption–desorption isotherms and corresponding pore size distribution of the p-MNTP/MWCNTs control sample.

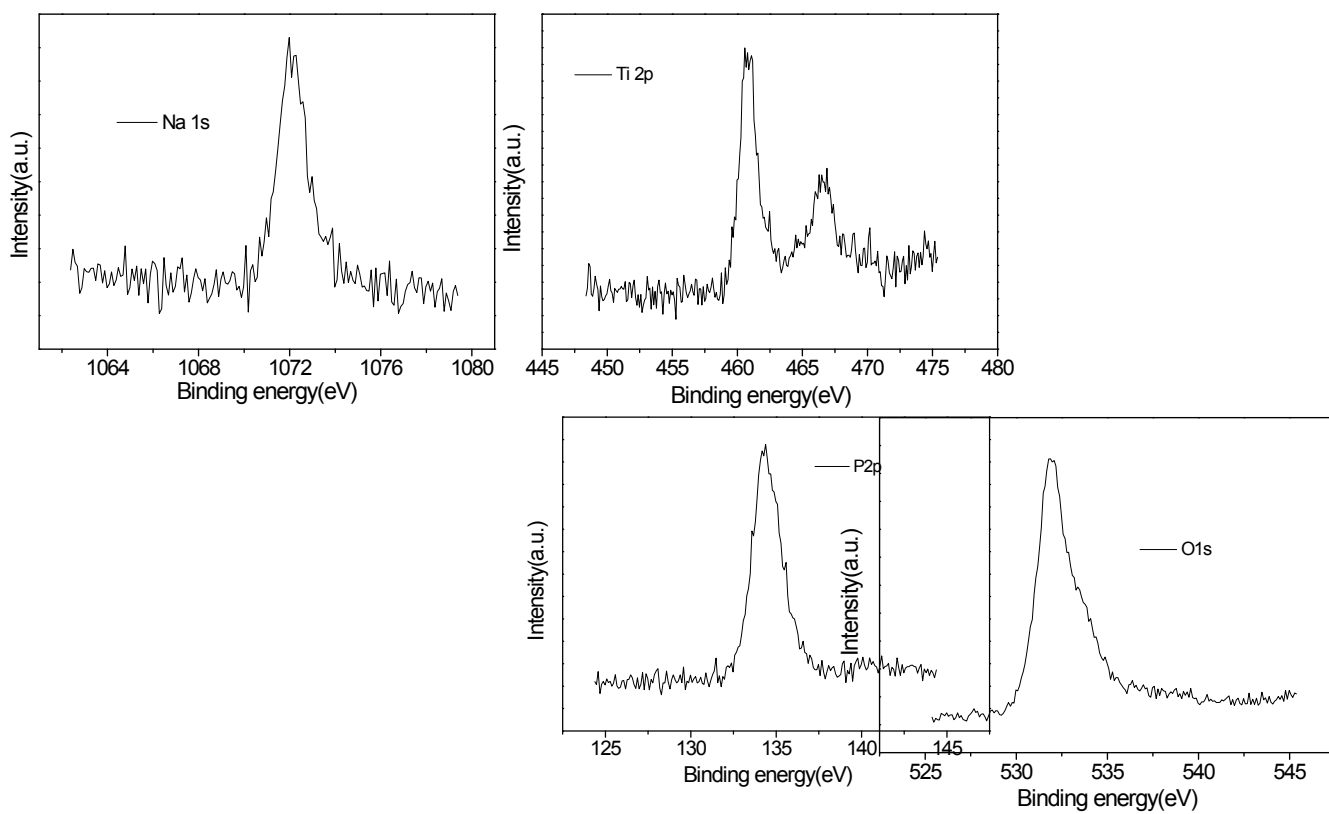


Figure S6. High-resolution Na1s, Ti2p, P2p and O1s XPS spectra of the self-supporting MNTP-MWCNTs film.

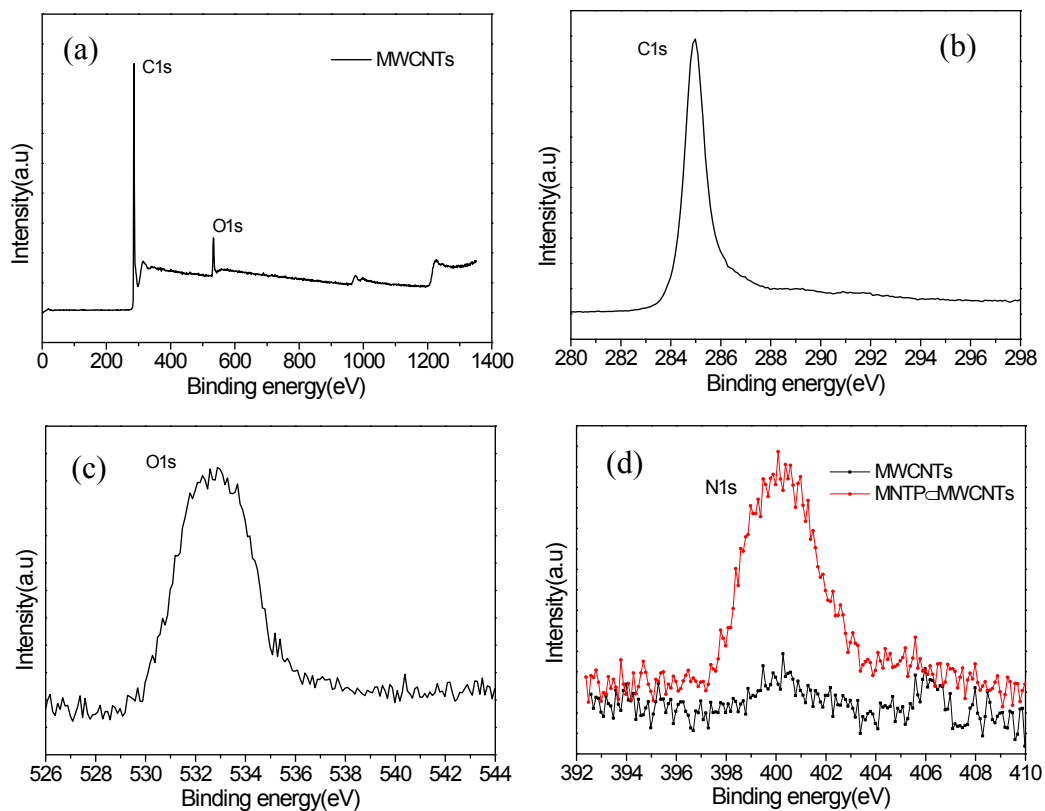
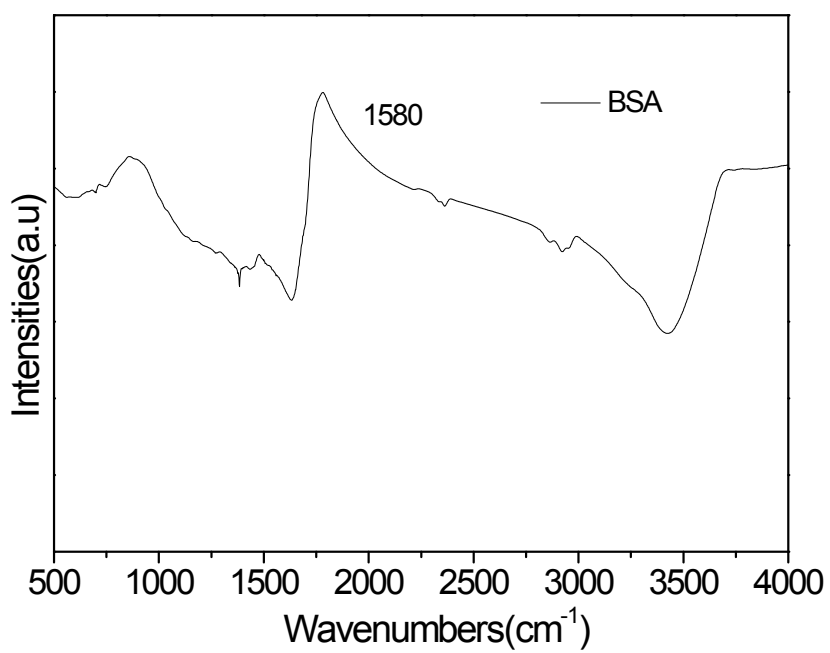


Figure S7. (a) Survey XPS spectrum of the MWCNTs and (b-d) High-resolution C1s, O1s and N1s XPS spectra of the MWCNTs treated under the similar experimental condition. In (d), the N1s XPS spectra acquired from self-supporting MNTP-MWCNTs film is also shown.





FigureS8. FTIR spectrum of the thermally-treated BSA at 350°C exhibiting a strong absorption peak at about 1580  $\text{cm}^{-1}$ .

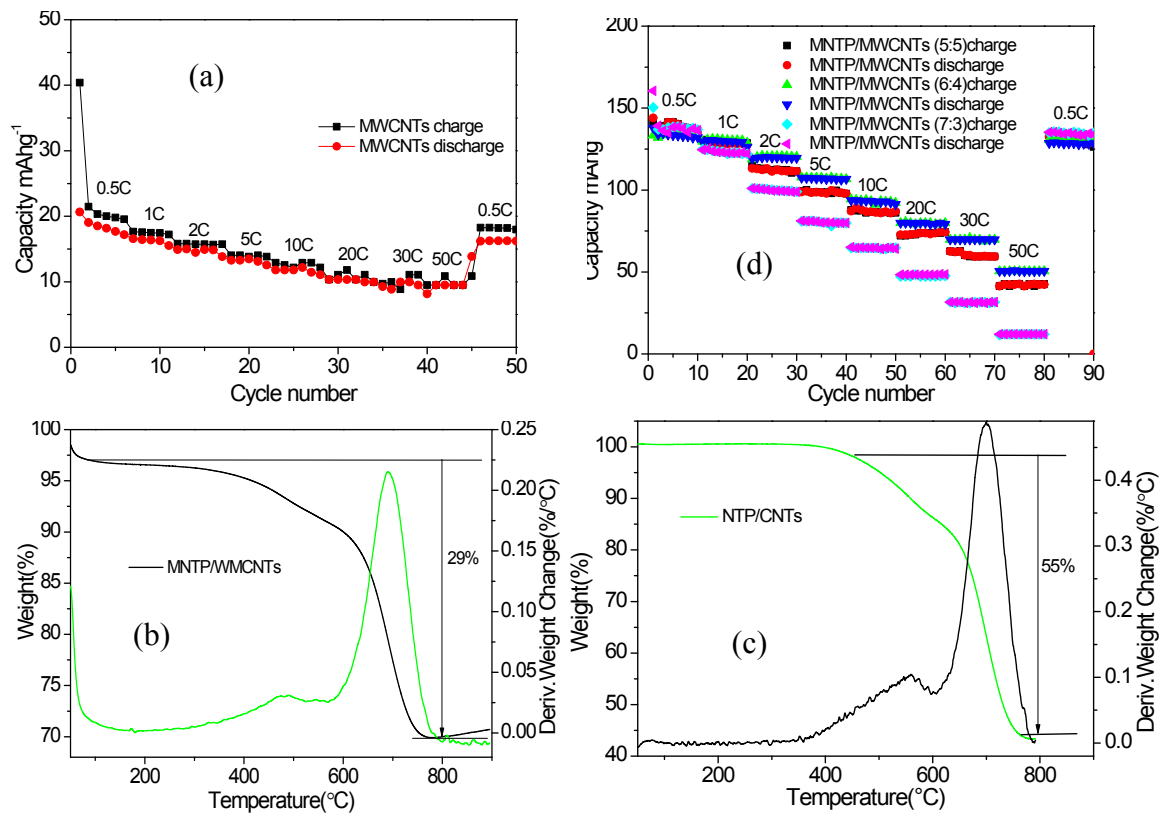


Figure S9. (a) Cycling performance at different current rates from 0.5 to 50 C of the pure MWCNTs electrode; (b) and (c) TGA/DSC curves of the self-supporting MNTP/MWCNTs films with MWCNTs contents of 50wt% and 30wt%; (d) Cycling performances at different current rates from 0.5 to 50 C of the self-supporting MNTP/MWCNTs films with different contents of MWCNTs.

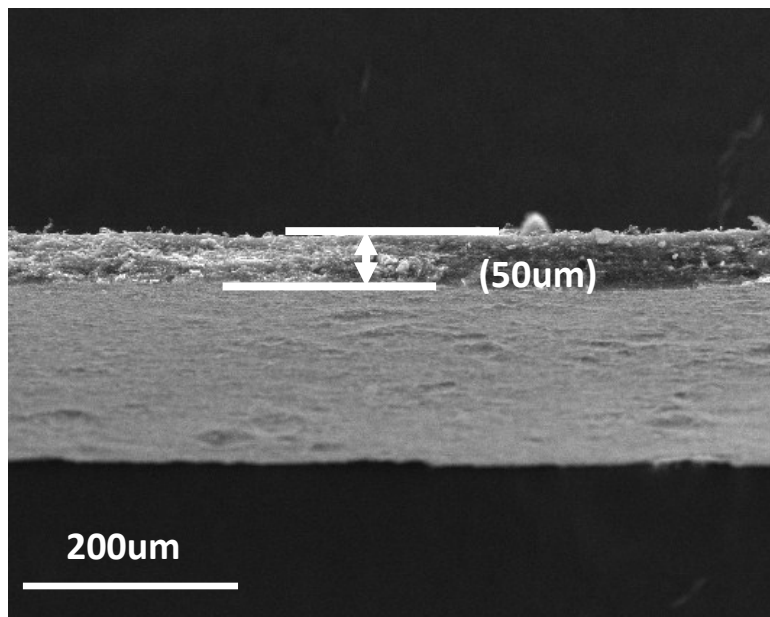


Figure S10. Typical SEM image of the self-supporting MNTP-MWCNTs film with a thickness of up to 50  $\mu\text{m}$ .

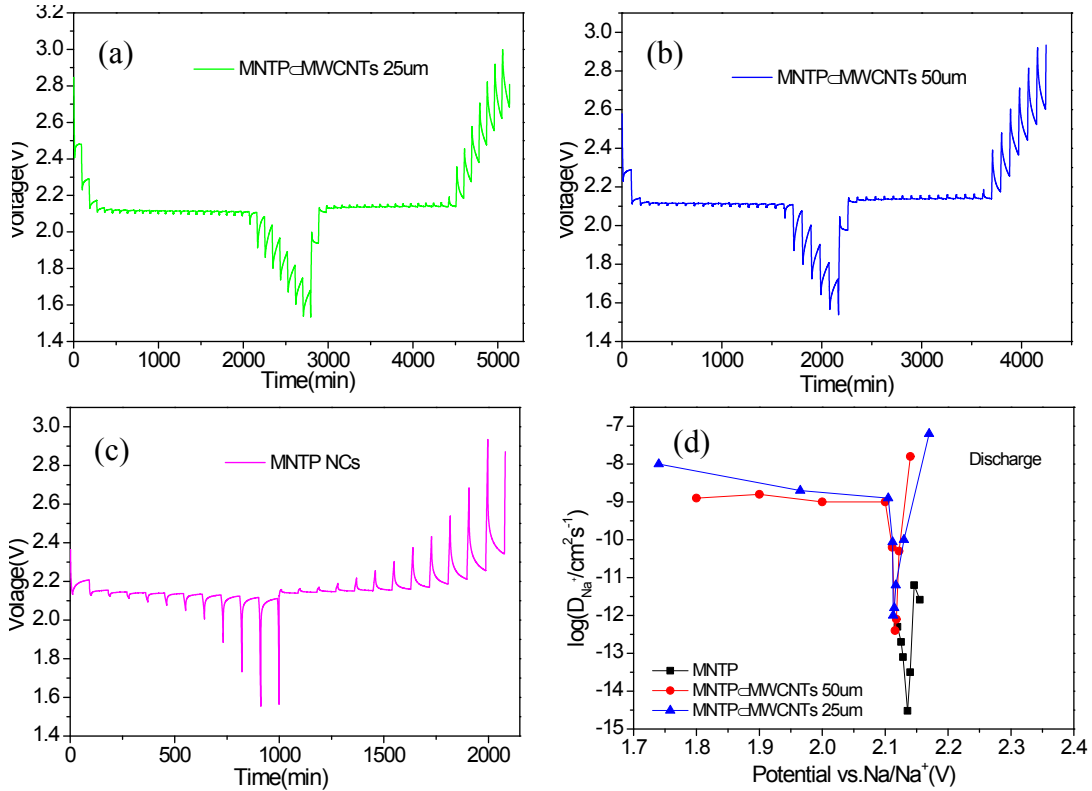


Figure S11. (a-c) GITT curves of the self-supporting MNTP@MWCNTs (25um), self-supporting MNTP@MWCNTs (50um) and MNTP NCs anodes as a function of time with a current of 0.2C in the voltage range of 1.5–3 V respectively. (d) The calculated chemical diffusion coefficients of Na<sup>+</sup> of all anodes as a function of the open-circuit voltage from GITT curves, according to the following equation:

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

, where  $V_M$  is the molar volume of NTP, which is 136.59 cm<sup>3</sup> mol<sup>-1</sup>,  $m_B$  and  $M_B$  are the mass and the molecular weight of the electrode material, respectively,  $A$  is the surface area of the electrode,  $\tau$  is the titration time and  $\Delta E_s$  is the difference of the two consequent stabilized open-circuit potentials [K. M. Shaju, G. V. Subba Rao and B. V. R. Chowdari, *Electrochim. Acta*, 48, 2691–2703(2003); Y. Niu, M. Xu, Y. Zhang, J. Han, Y. Wang, C. M. Li, *RSC Adv.* 6, 45605(2016)].

Table SI. Stimulated  $R_s$  and  $R_{ct}$  values for the MNTP $\subset$ MWCNTs and reference samples in the Na half-cells according to Fig. 7d.

Sample	$R_s(\Omega)$	$R_{ct}(\Omega)$
MNTP $\subset$ MWCNTs film (25um)	4.9	284.7
MNTP $\subset$ MWCNTs film (50um)	5.9	325
MNTP NCs	8.1	575