

Supporting information:

Figure S1

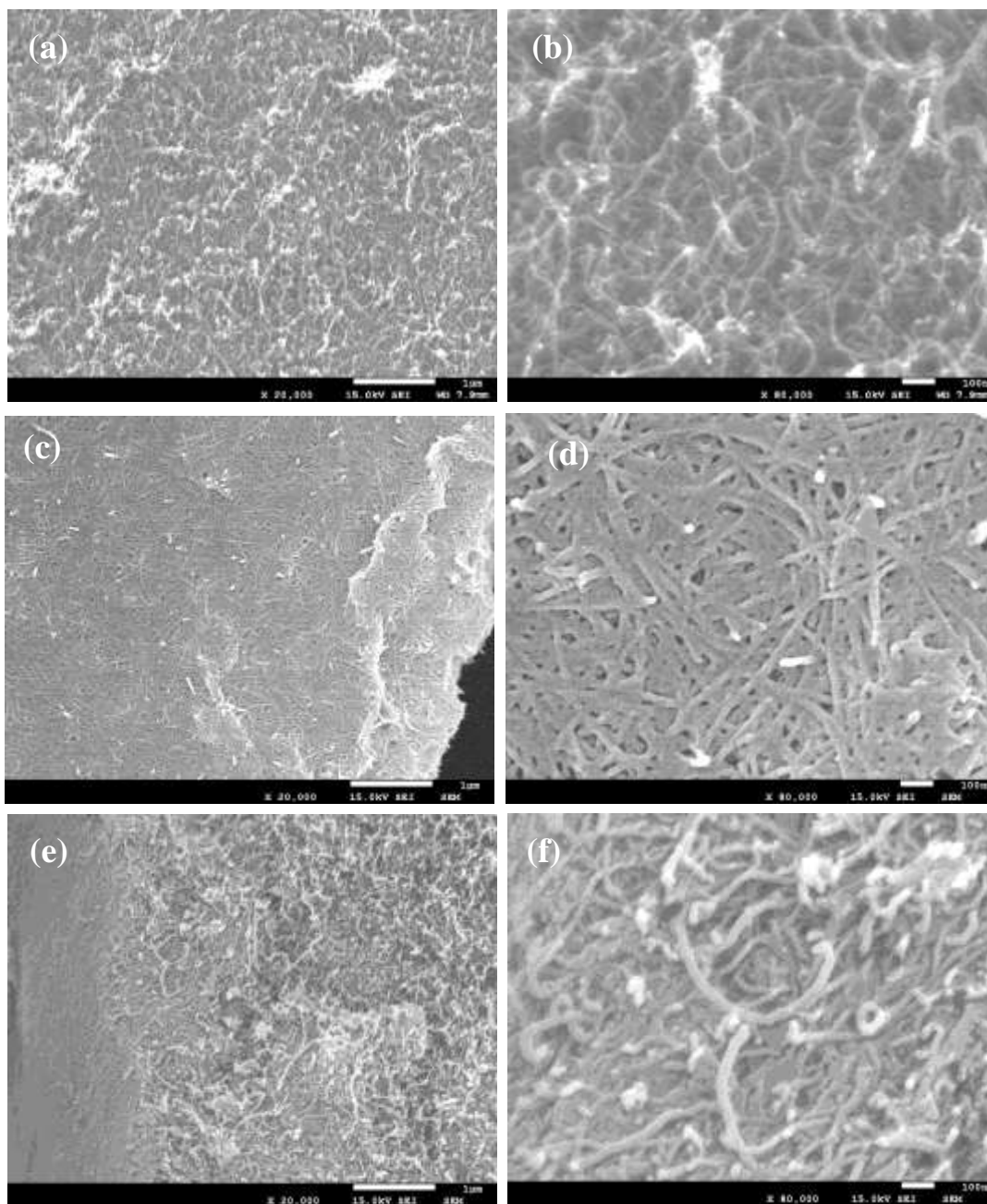


Figure S1 SEM images with different magnifications: The top view of pure CNT film (a,b) and conformal CNT-TiO₂ film (c,d); The cross-section view of conformal CNT-TiO₂ film (e,f).

Figure S2

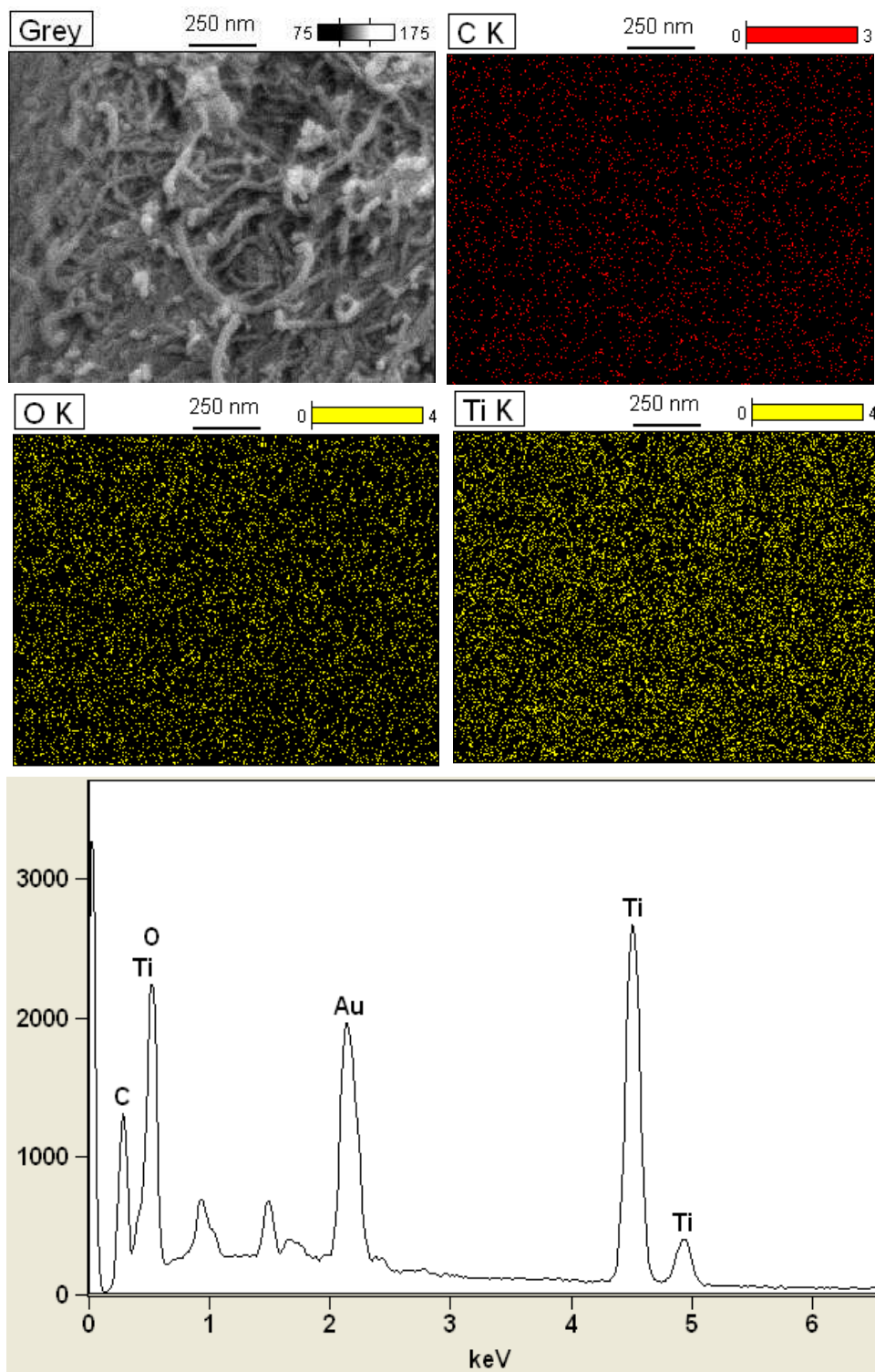


Figure S2 EDS maps of Ti, O and C elements from cross-section view (The Au is from sputter coating).

Figure S3

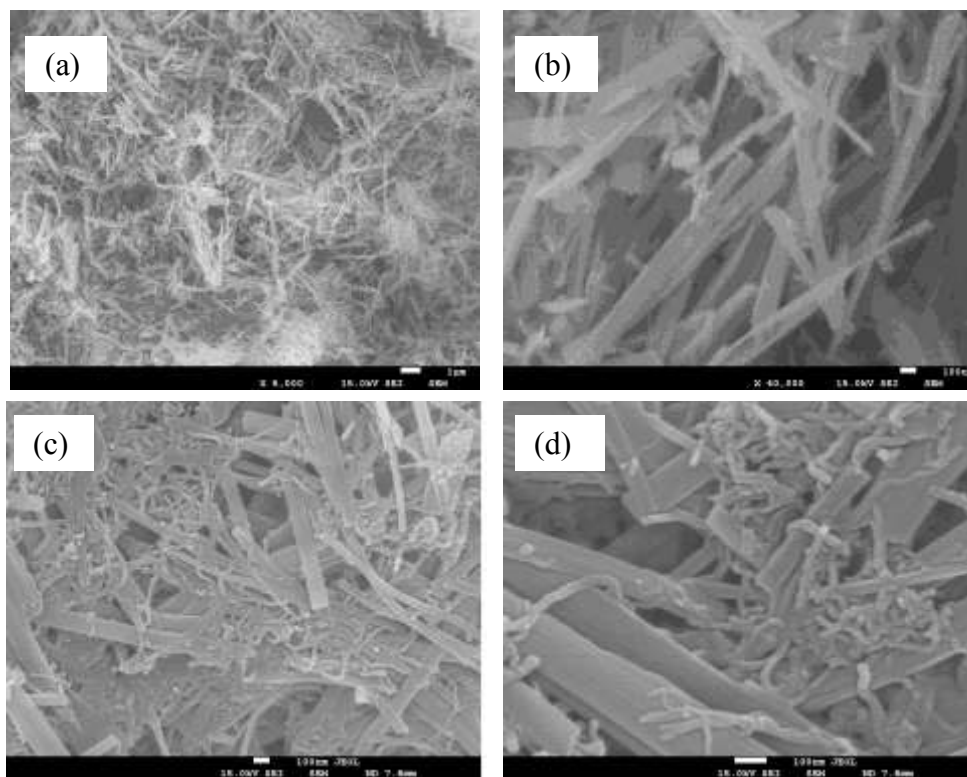


Figure S3 (a,b)TiO₂ nanofibers were synthesized by hydrothermal treatment of TiO₂ particles in 10M NaOH solution; (c,d) TiO₂ nanofiber/CNT composite was synthesized by hydrothermal treatment of TiO₂ and CNTs in 10M NaOH solution (both TiO₂ and CNTs were dispersed in 10M NaOH solution under ultrasonication).

During the hydrothermal treatment of TiO₂ in 10M NaOH solution, TiO₂ particles dissolve in the NaOH solution, which breaks the Ti-O-Ti bonds. The resulting Ti-containing complex precipitates in the strong alkaline environment and bonds to form lamellar sheets and then completely transforms to nanorods/nanofibers.¹ Consistent with the reported results, TiO₂ nanofibers were synthesized by hydrothermal treatment of TiO₂ in 10M NaOH solution, shown in Figure S3a-b. By the addition of CNTs in 10M NaOH solution, a part of the resulting Ti-containing complex precipitates on the CNTs surface;

while, most of the Ti-containing complex prone to self-nucleate, leading to form nanorods/nanofibers, shown in Figure S3c-d.

However, in the CNT/TiO₂ mixed film, the TiO₂ particles are confined in the CNT network, self-nucleation of the Ti-containing complex is greatly suppressed, which results in most of the Ti-containing complex to coat on the CNT networks. So, the 3-D CNT film acts as a nanoreactor to confine the chemical reactions in its network and the interconnected cross-stacking CNT backbone also works as nucleation sites for the new growing of Ti-containing complex.

[1] S. T. Myung, N. Takahashi, S. Komaba, C. S. Yoon, Y. K. Sun, K. Amine, H. Yashiro, *Adv Funct Mater* 2011, 21, 3231.

Figure S4

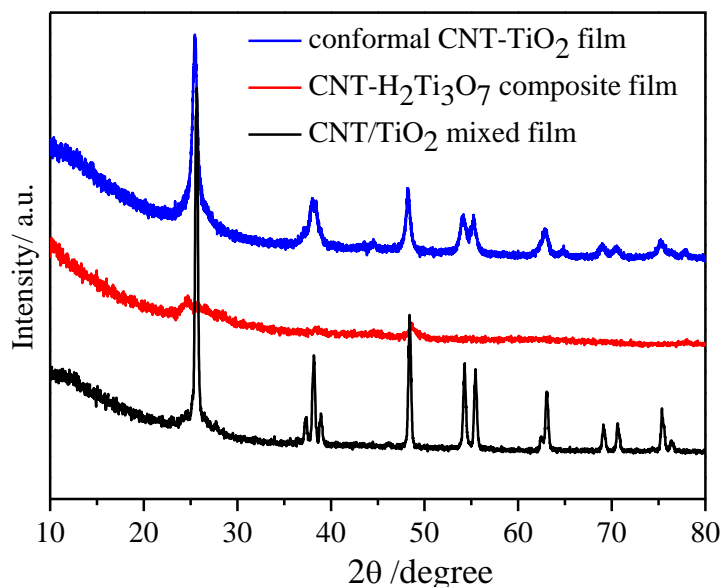


Figure S4 XRD patterns of the CNT/TiO₂ mixed film (precursor), CNT-H₂Ti₃O₇ composite film (intermediate product) and conformal CNT-TiO₂ film (final product).

As shown in Figure S4, anatase TiO₂ changed to hydrogen titanate, H₂Ti₃O₇ after the hydrothermal treatment and the following ion exchange in HCl (Figure S4 in red), which is in good agreement with the reported result.¹ Then, the heat treatment makes the

$\text{H}_2\text{Ti}_3\text{O}_7$ transferred to anatase TiO_2 , forming CNT- TiO_2 film (Figure S4 in blue). The diffraction peaks of the TiO_2 in the conformal CNT- TiO_2 film greatly broaden as compared with that of the TiO_2 precursor, indicating smaller crystal size. The change of the crystal size further proves that the dissolving and recrystallization of TiO_2 particles do occur in our system.

Figure S5

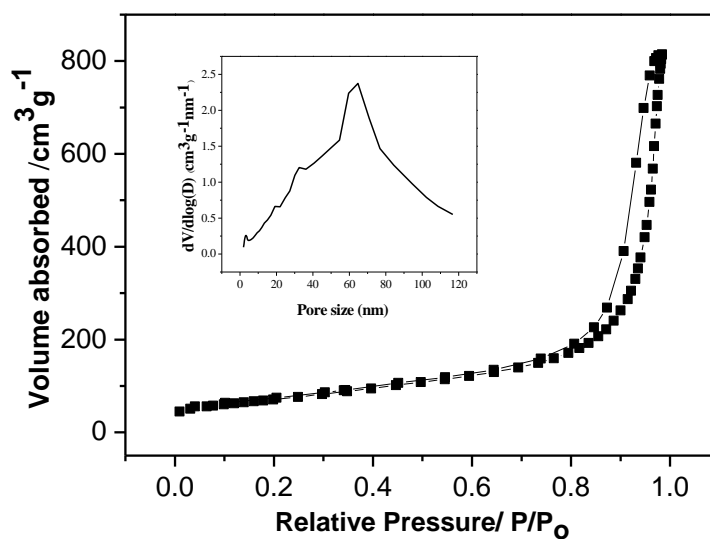


Figure S5 Nitrogen adsorption and desorption isotherm of the conformal CNT- TiO_2 film (the inset is the pore size distribution).

Figure S6

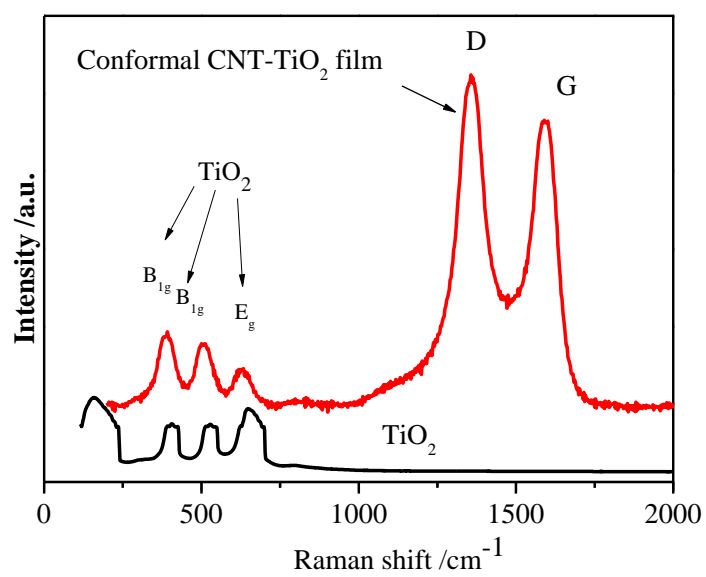


Figure S6 Raman spectra of the conformal CNT-TiO₂ film and the precursor TiO₂ particle.

Figure S7

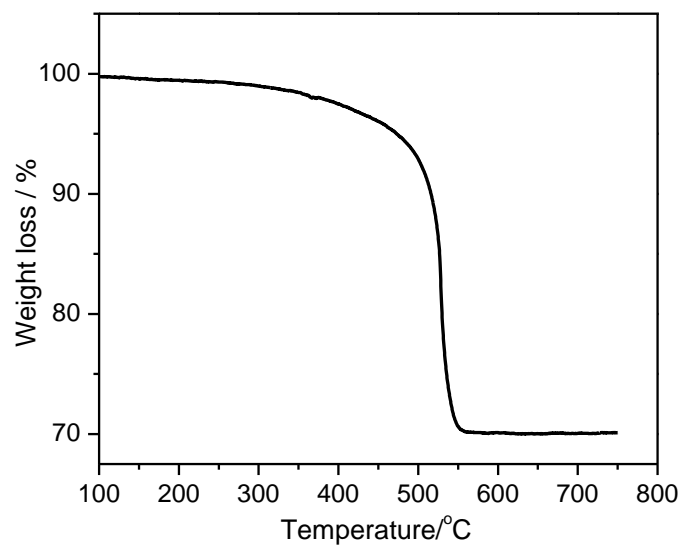


Figure S7 Thermogravimetric analysis of conformal CNT-TiO₂ film

Figure S8

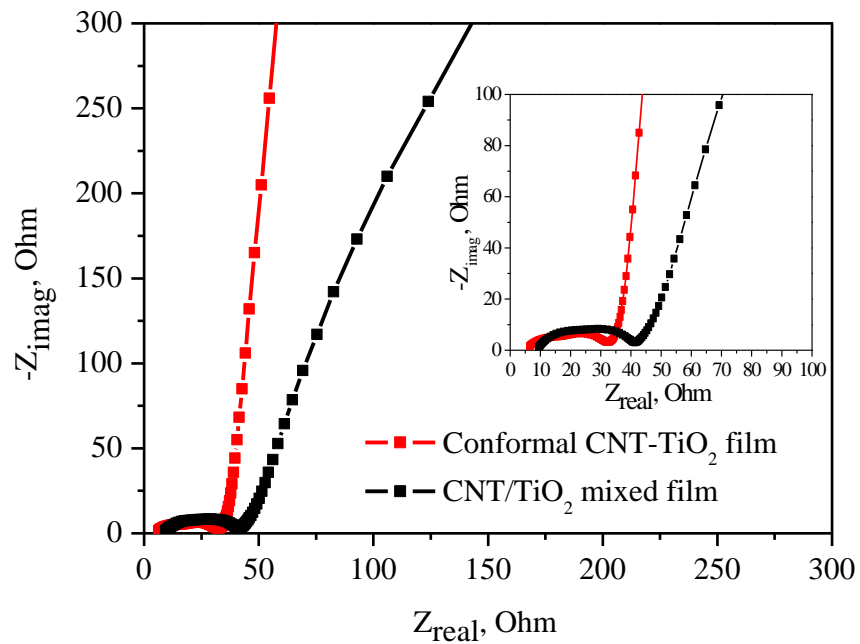


Figure S8 Nyquist plots of conformal CNT-TiO₂ film and CNT/TiO₂ mixed film electrodes after rate cycling test.

Figure S9

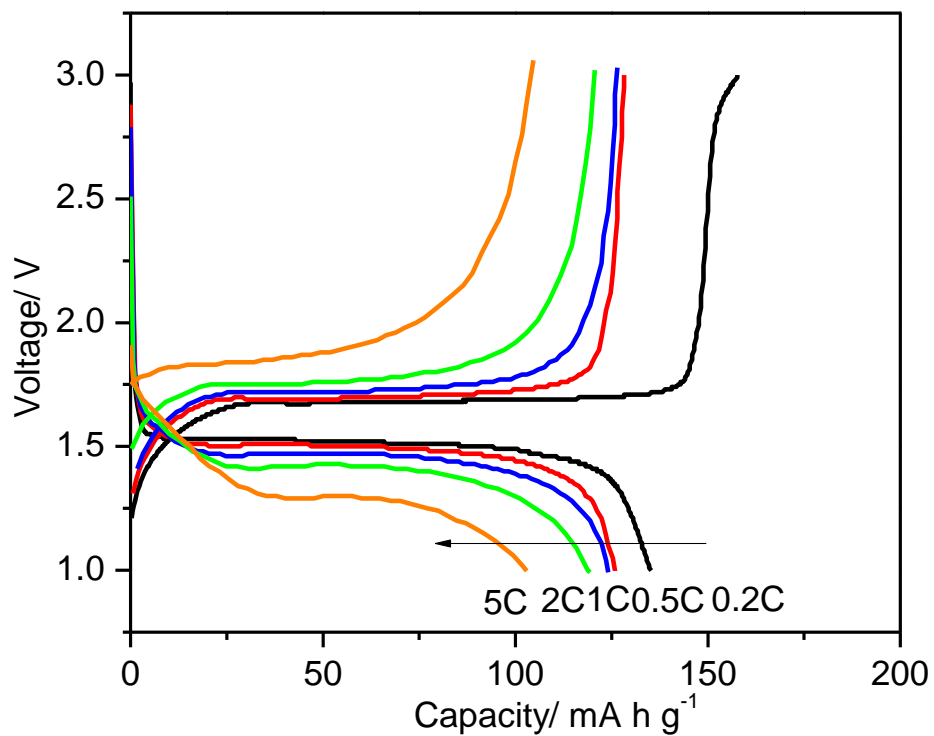


Figure S9 Charge-discharge voltage profiles of CNT-TiO₂/ LiFePO₄ full cell at different rates.

Figure S10

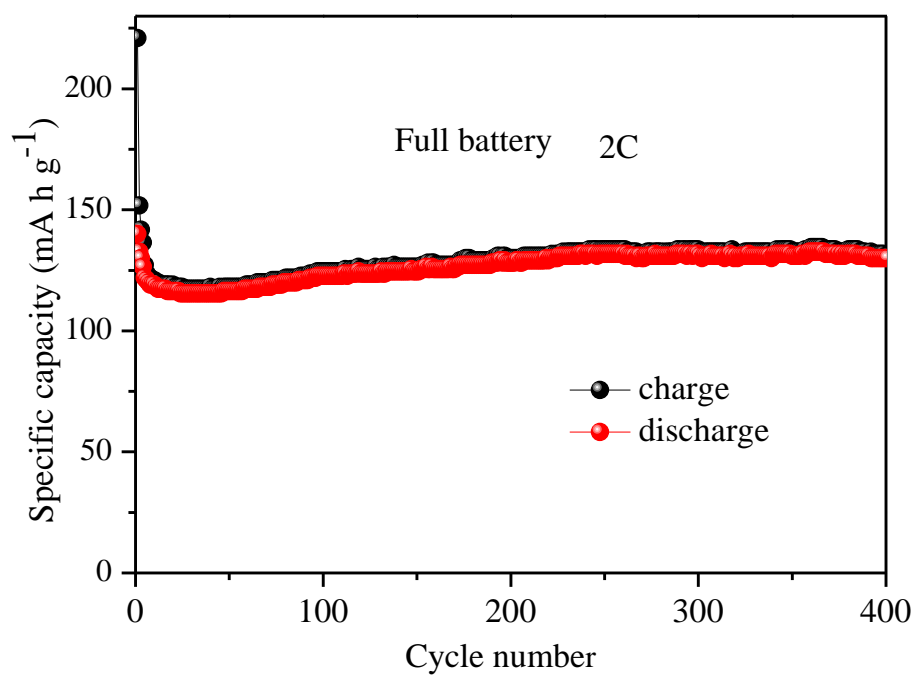


Figure S10 Cycling performance of CNT-TiO₂/ LiFePO₄ full cell at a rate of 2C in a voltage range of 1-3 V.

1. S. T. Myung, N. Takahashi, S. Komaba, C. S. Yoon, Y. K. Sun, K. Amine and H. Yashiro, *Adv Funct Mater*, 2011, **21**, 3231-3241.