Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Free–Standing N,Co-Codoped TiO_2 Nanoparticles for LiO_2–Based Li–O_2 Batteries

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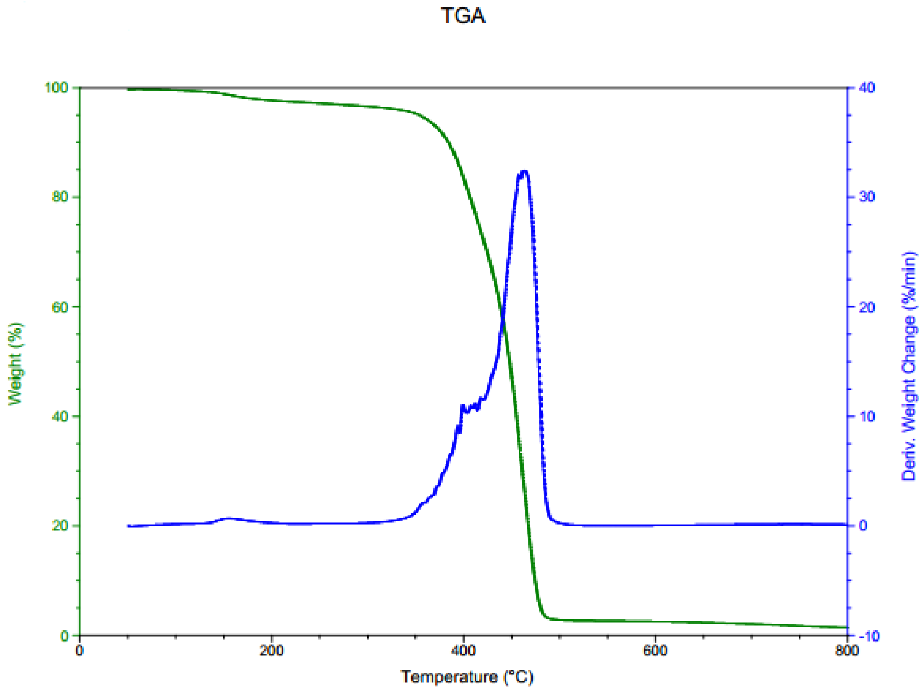

Figure S1. TGA curve of N, Co-TiO_2/CFs.

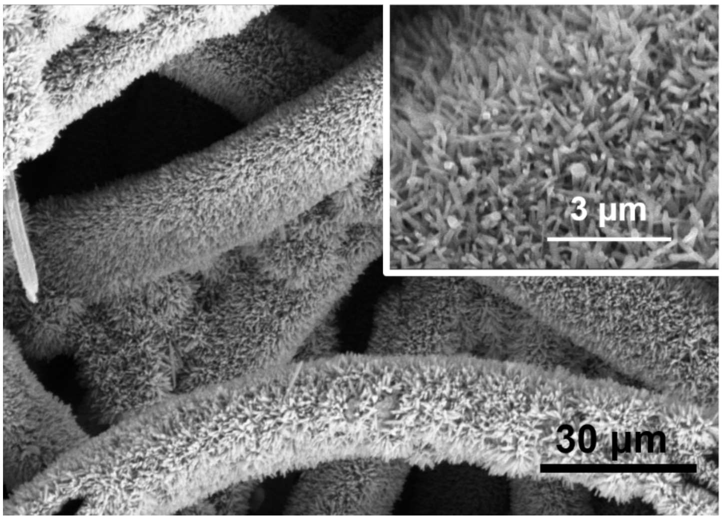

Figure S2. SEM image of TiO_2/CFs.

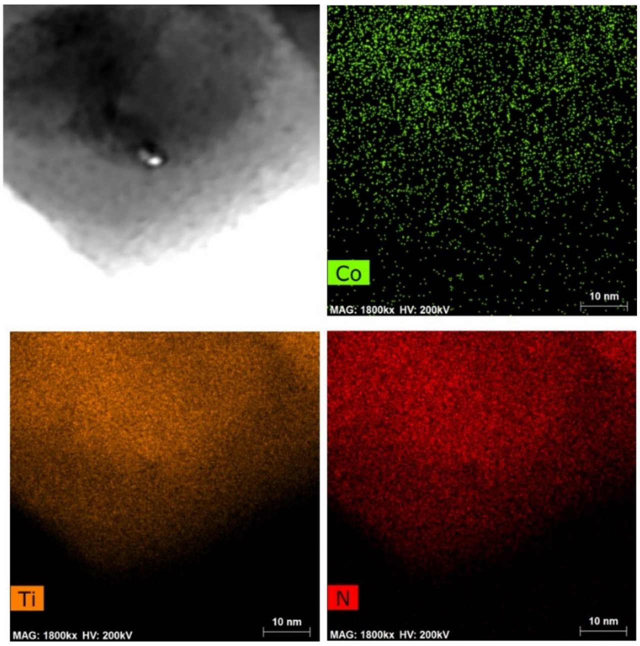

Figure S3. EDX elemental mapping of Co, Ti, and N of the N,Co-TiO_2/CFs.

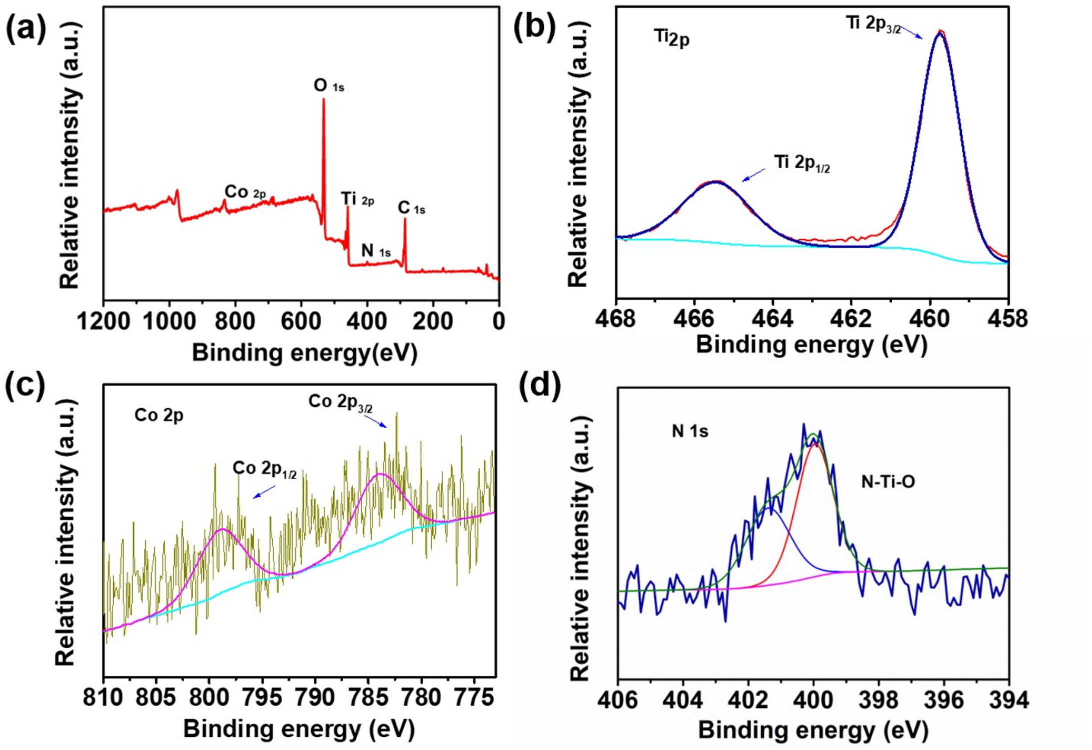

Figure S4. XPS patterns of N,Co-TiO_2/CFs

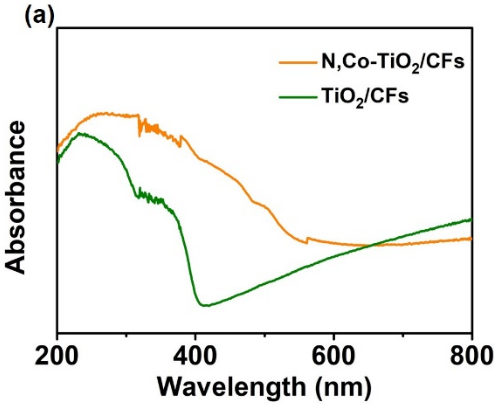

Figure S5. (a) UV-vis diffuse reflectance spectra of N,Co-TiO_2/CFs and TiO_2/CFs. (b) The band gaps of N,Co-TiO_2/CFs and TiO_2/CFs.

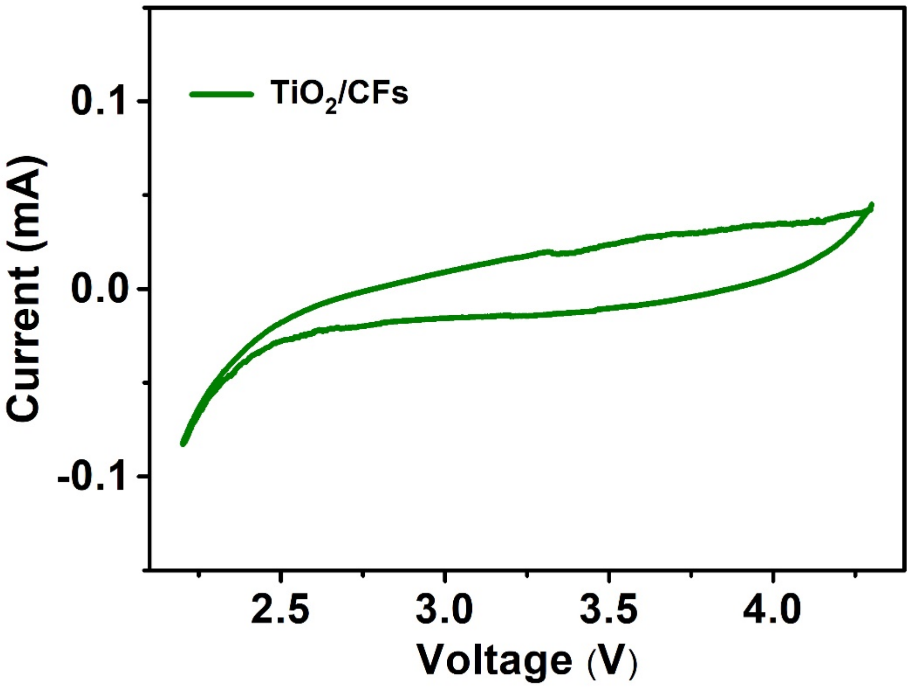

Figure S6. Cyclic voltammetry (CV) curve of TiO_2/CFs at a constant scan rate of 0.1 mV s^{-1}.

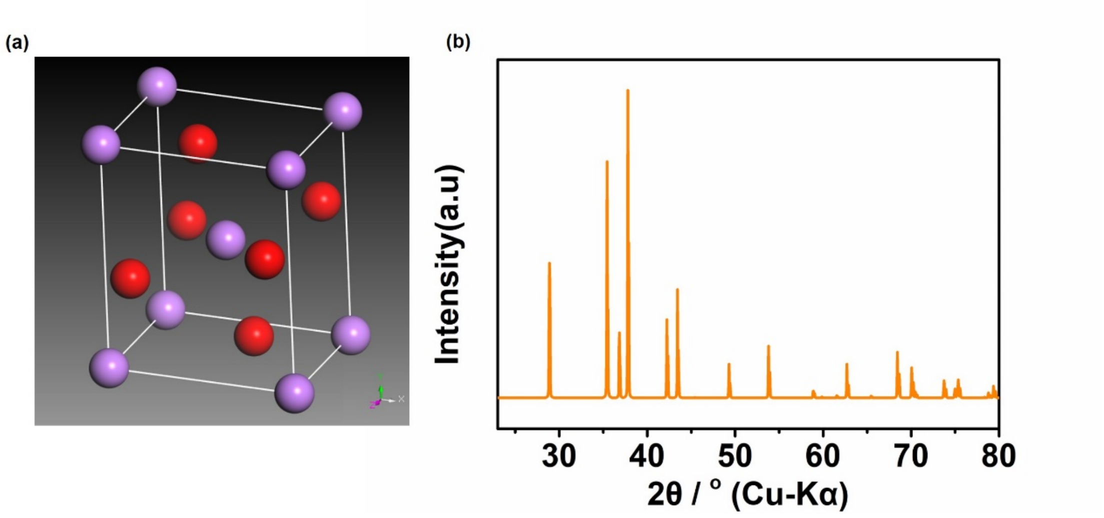

Figure S7. (a) The crystal structure of the DFT predicted LiO_2 crystal with an orthorhombic lattice. The purple and red colors are lithium and oxygen, respectively. (b) The simulated XRD pattern of the DFT structure of orthorhombic LiO_2 crystal structures under the wavelength 1.540562 Å (λ_1) and 1.54439 Å (λ_2). Atomic coordinates for the LiO_2 crystal structure from DFT calculation can be obtained from the ICSD-Database. The X-ray tube is Cu target.

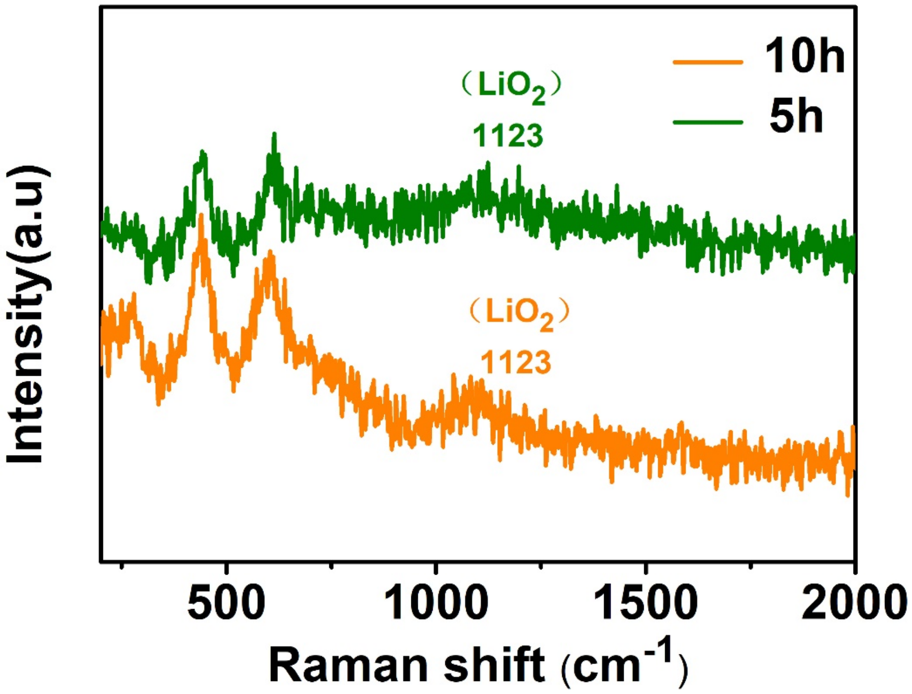

Figure S8. Raman spectra of N,Co-TiO_2/CFs cathode after discharged for 5h and 10h of GITT experiment.

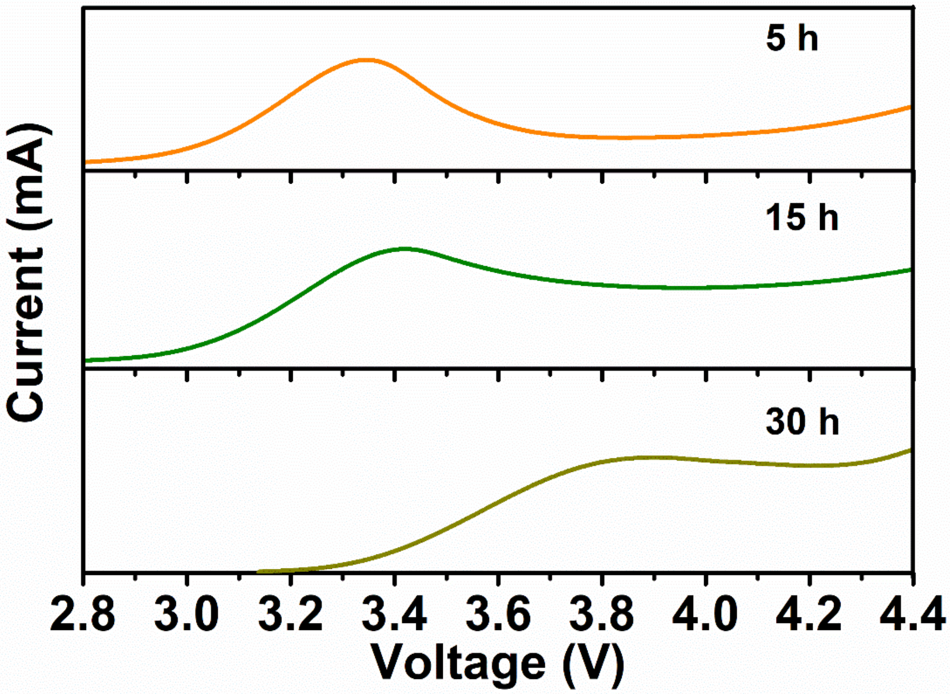

Figure S9. Linear sweep voltammetry measurement of N,Co-TiO_2/CFs under different discharge time.

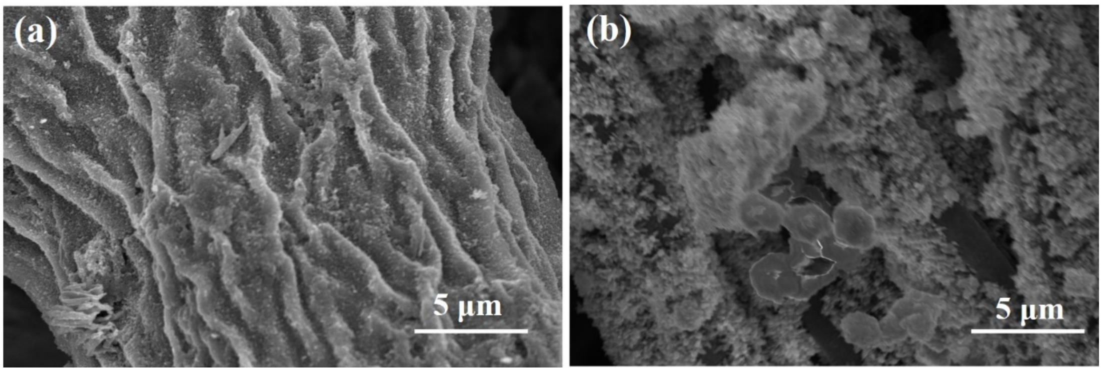

Figure S10. SEM images of (a) N,Co-TiO_2/CFs and (b) TiO_2/CFs after the first charging.

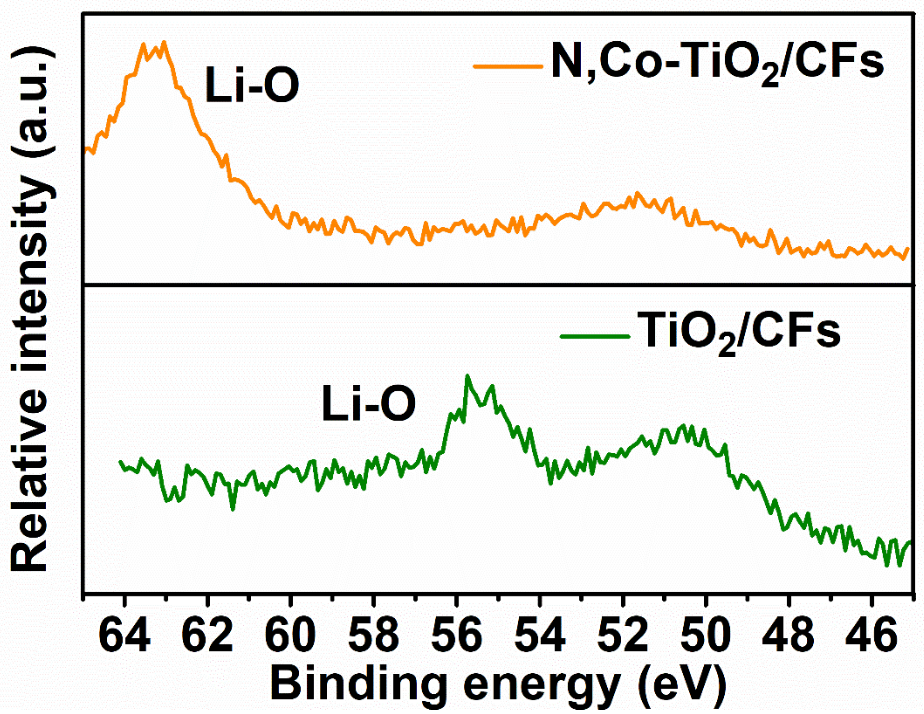

Figure S11. XPS patterns of Li 1s in N, Co-TiO_2/CFs and in TiO_2/CFs.

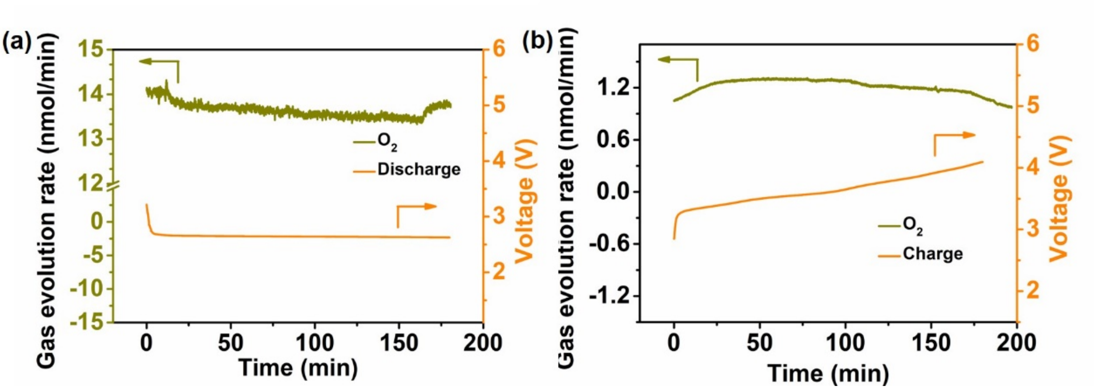

Figure S12. DEMS analyses of gas consumption and evolution during (a) discharge and (b) charge of N, Co-TiO_2/CFs.

The e^-/O_2 ratio is based on the amount of reaction charge and O_2 consumption. Before the discharge and charge process, it is necessary to keep O_2 evolution rate stable for 6 hours. O_2 evolution rate of this stage is called the baseline. In the subsequent discharge process, the O_2 evolution rate decrease due to the consumption of O_2 in the reduction reaction. Therefore, the average O_2 consumption rate is the difference of these two stages. On the contrary, the O_2 evolution rate will increase due to the decomposition of Li_2O_2 in the charge process. The procedure can be calculated by using the following equations:

Charge process:

$$\frac{Qcharge}{NA(Vcharge - Vbaseline)ave}$$

Discharge process:

$$\frac{Qdischarge}{NA(Vbaseline - Vdischarge)ave}$$

V(discharge) is the average O_2 evolution rate of the charge process. V(discharge) is the average O_2 evolution rate of the discharge process. The V(baseline) is the average O_2 evolution rate of whole the stable stage. N_A is the Avogadro constant. Q(charge) and Q(discharge) are the amount of reaction charge.

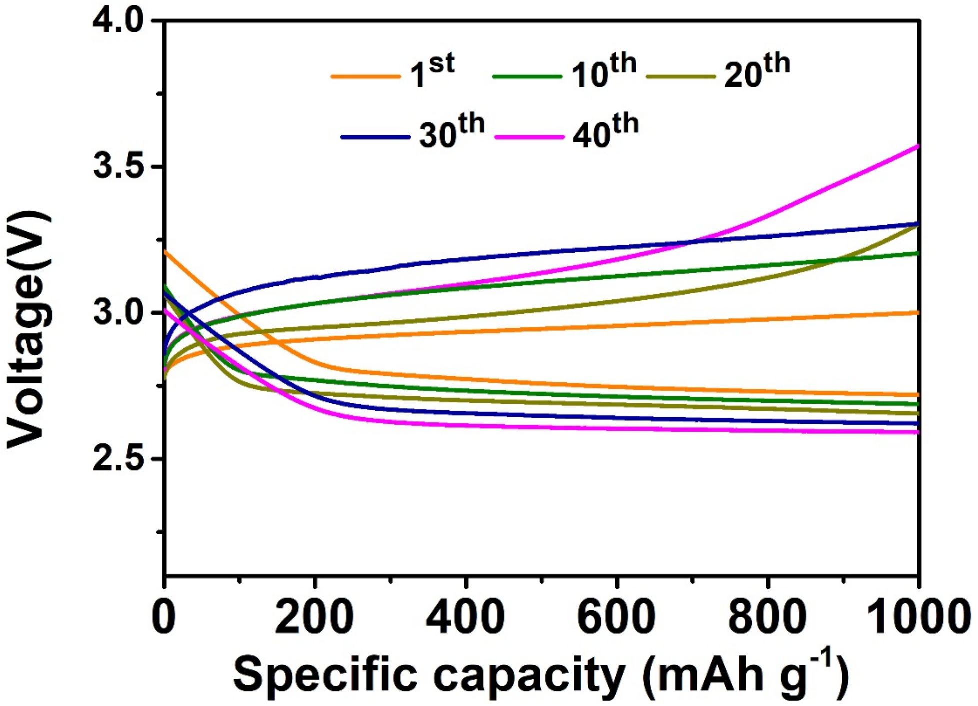

Figure S13. The discharge/charge profiles of N,Co-TiO_2/CFs at current density of 200 mA g^{-1} with a limited capacity of 1000 mAh g^{-1}.

The cycling performance with cut-off capacity of 1000 mAh g^{-1} was measured in Fig. S13. The initial discharge and charge overpotential of N,Co-TiO_2/CFs is only 0.1, and 0.2 V, respectively. After 40 cycles, the charge terminal potential of N,Co-TiO_2/CFs is still less than 3.7 V.

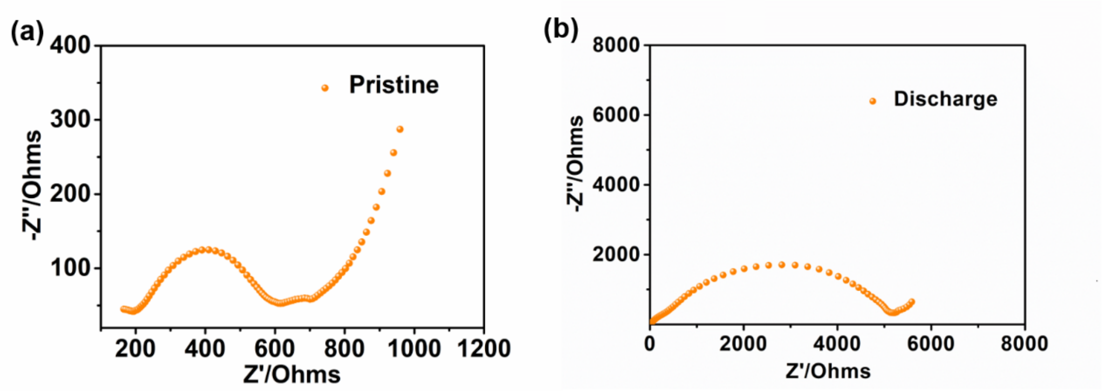

Figure S14. Electrochemical impedance spectra of (a) pristine and (b) discharged TiO_2/CFs.

Table S1. Adsorption energies (eV) of LiO_2 on the (110) surface of TiO_2/CF, N-TiO_2/CF, Co-TiO_2/CF and N,Co-TiO_2/CF.

	TiO_2/CF	N-TiO_2/CF	Co-TiO_2/CF	N,Co-TiO_2/CF.
LiO_2	-1.41 eV	-3.45 eV	-2.30 eV	-4.08 eV