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In Situ Construction of Redox-Active Covalent Organic Frameworks/Carbon Nanotube Composites as Anode of Lithium-Ion Batteries

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Instrumental Characterization. ^{1}H-NMR spectra were measured using a JEOL model JNM-LA400 NMR spectrometer, wherein the chemical shifts (δ in ppm) were determined using a residual proton of the solvent as the standard. FT-IR spectra were recorded using a JASCO model FT IR-6100 infrared spectrometer. XRD data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on a glass substrate, and was recorded in the range from $2\theta = 1.5$ to 30° with a 0.02° increase. Elemental analysis was performed using a Yanako CHN CORDER MT-6 elemental analyzer. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo model TGA/SDTA851e under N_2 by heating the sample to 800 °C at a rate of 10 °C min^{-1}. Raman spectra were obtained using RM-1000 (Renishaw) at a laser excitation of 632.8 nm. The microstructures and EDS maps were obtained using scanning electron microscopy (Zeiss Merlin Compact). XPS and ex-situ XPS analysis were performed using an energy spectrometer (Thermo Scientific K-Alpha). Nitrogen sorption isotherms were measured at 77 K using a Micromeritics Instrument Corporation model 3Flex surface characterization analyzer. Before measurement, the samples were degassed in a vacuum at 100 °C for more than 10 h. The specific surface area was calculated using the BET method. The pore volume was derived from the sorption curve using the NLDFT model.

Electrochemical Measurements. COFs electrodes were prepared by mixing COFs, acetylene black, and Polyvinylidene Fluoride (PVDF) at a weight ratio of 8:1:1, and 1-methyl-2-pyrrolidone (NMP) was used as the solvent. Subsequently, the slurry was uniformly coated on a copper foil, and dried at 60 °C for 12 h. Thereafter, the foil was rolled using a roller press, after which the copper foil was cut into wafers with a diameter of 8 mm. The mass loading of the active material was approximately 1–2 mg cm^{-2}. The COFs electrodes were used as the working electrodes, Li foil was used as the counter electrodes, 1.0 M $LiPF_6$ in EC/DEC (v/v = 1:1) was used as the electrolyte, and glass fiber filters (Whatman GF/D) were used as the separators. Subsequently, CR-2032-coin cells were assembled in an Ar filled glove box. The galvanostatic charge/discharge test was performed using a multichannel battery tester (LAND CT2001A, Wuhan), and all the specific capacities were based on the weight of the

COFs composite. The test was performed in the voltage range from 0.01-3.0 V, and the specific capacity was based on the total mass of the COFs samples. The voltage range was selected after a comprehensive consideration of the high capacity and long life. The CV test was performed using an electrochemical workstation (CHI 660e, chenhua, Shanghai) at a scan rate of 0.2 mV s^{-1} with a voltage range of 0.01-3 V. Electrochemical impedance spectrum (EIS) and in-situ EIS was performed using an electrochemical workstation (Zennium-pro, Germany, Zahner) in a frequency range from 0.1 to 100 kHz.

Materials. Mesitylene, 1, 4-dioxane, tetrahydrofuran, dimethylacetamide, acetic acid, Pyrazine-2,5-diamine were purchased from Aladdin chemicals and used without further purification unless otherwise noted. 1,3,5-triformylpholoroglucinol (TP) were synthesized according to the reported method.[1]

Section C. Supporting Figures

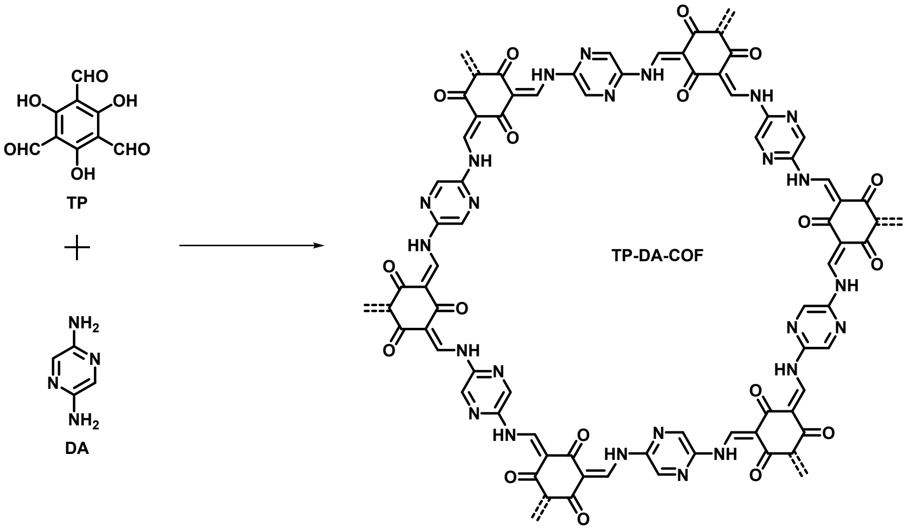

Figure S1. Schematic synthesis of TP-DA-COF.

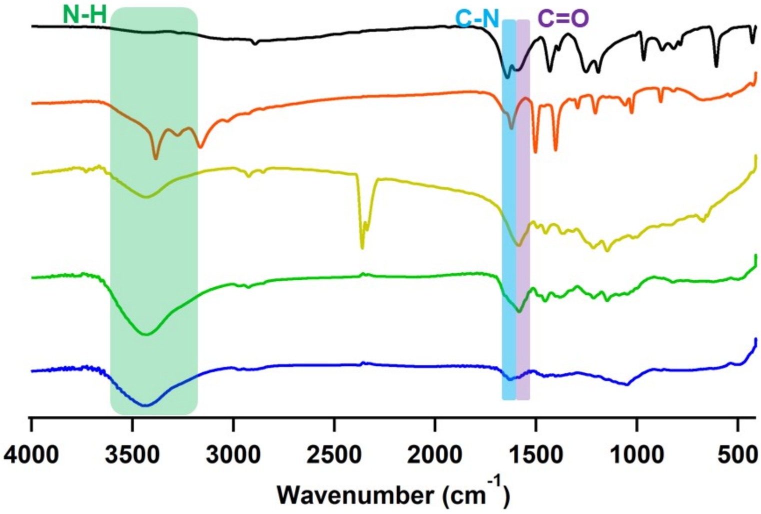

Figure S2. FT-IR spectra of TP (black), DA (red), TP-DA-COF (yellow), COF@CNT-1 (green), and COF@CNT-2 (blue).

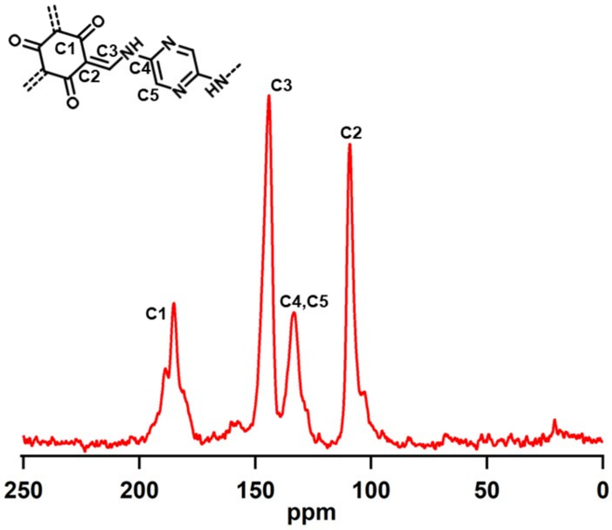

Figure S3. Solid State ^{13}C CP-MAS NMR spectrum of TP-DA-COF.

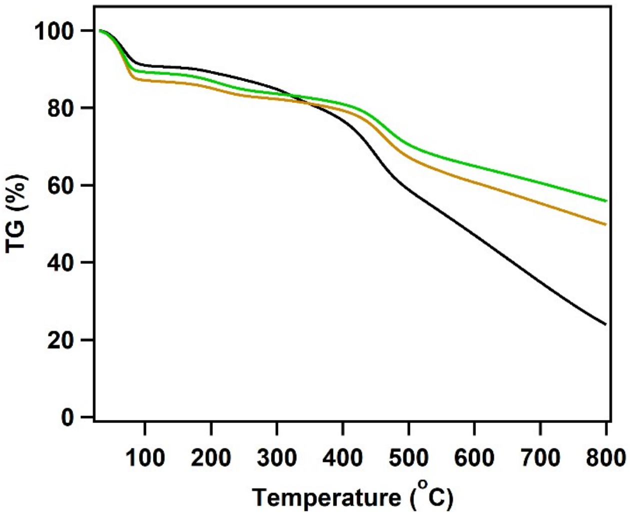

Figure S4. Thermal properties of TP-DA-COF (black), COF@CNT-1 (orange), and COF@CNT-1 (green) in the N_2.

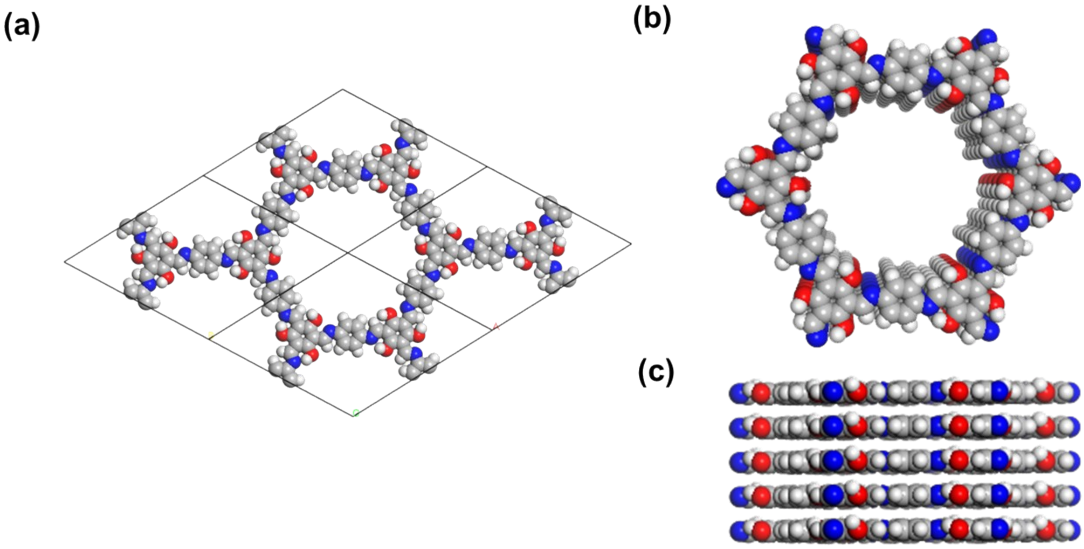

Figure S5. (a) AA stacking mode of TP-DA-COF; (b) Top and (c) side view of TP-DA-COF.

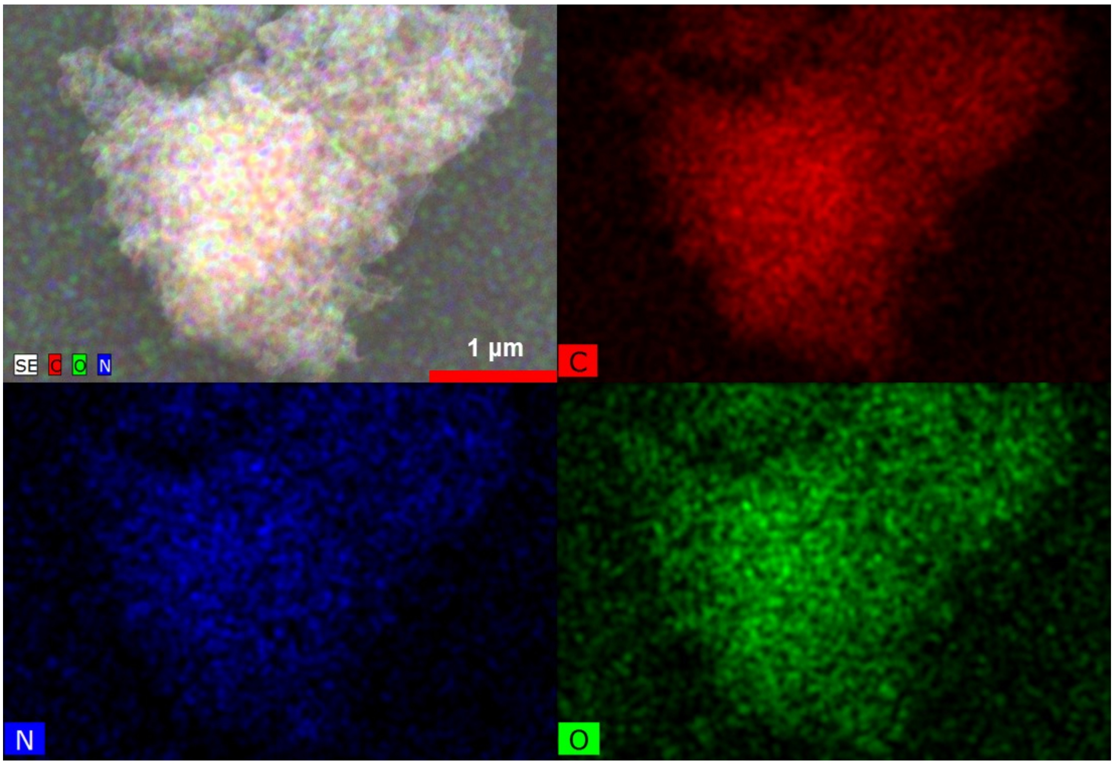

Figure S6. Elemental mapping images of TP-DA-COF using silicon as substrate.

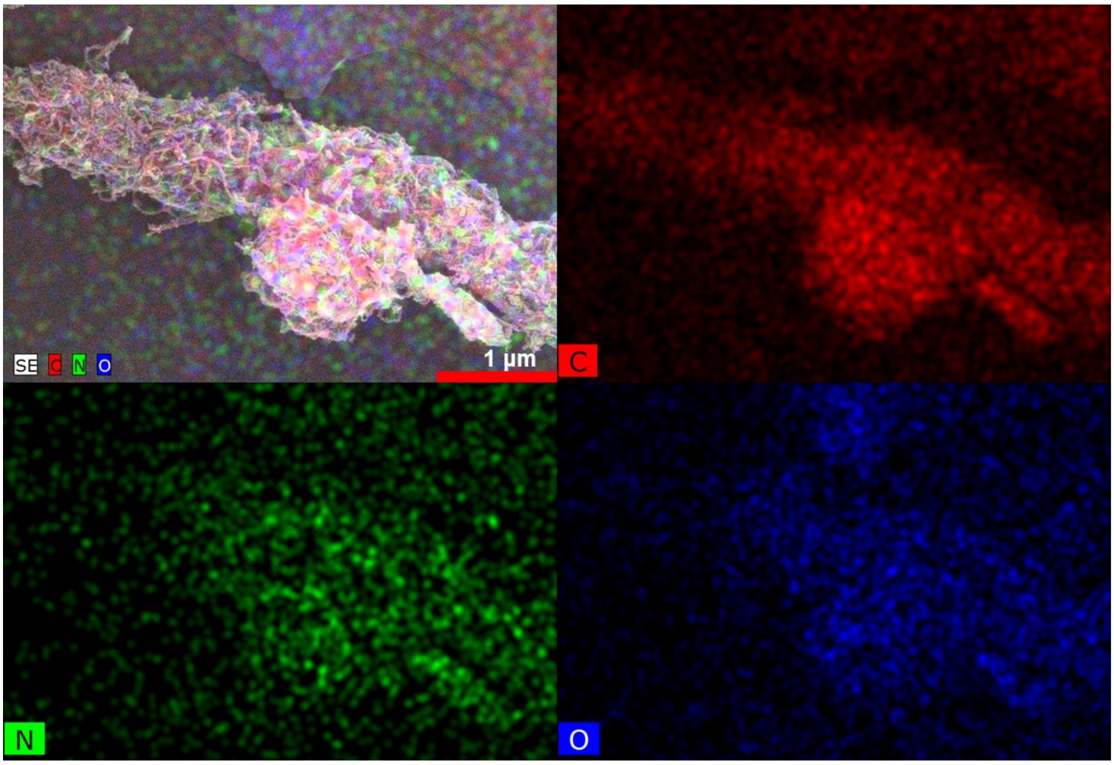

Figure S7. Elemental mapping images of COF@CNT-1 using silicon as substrate.

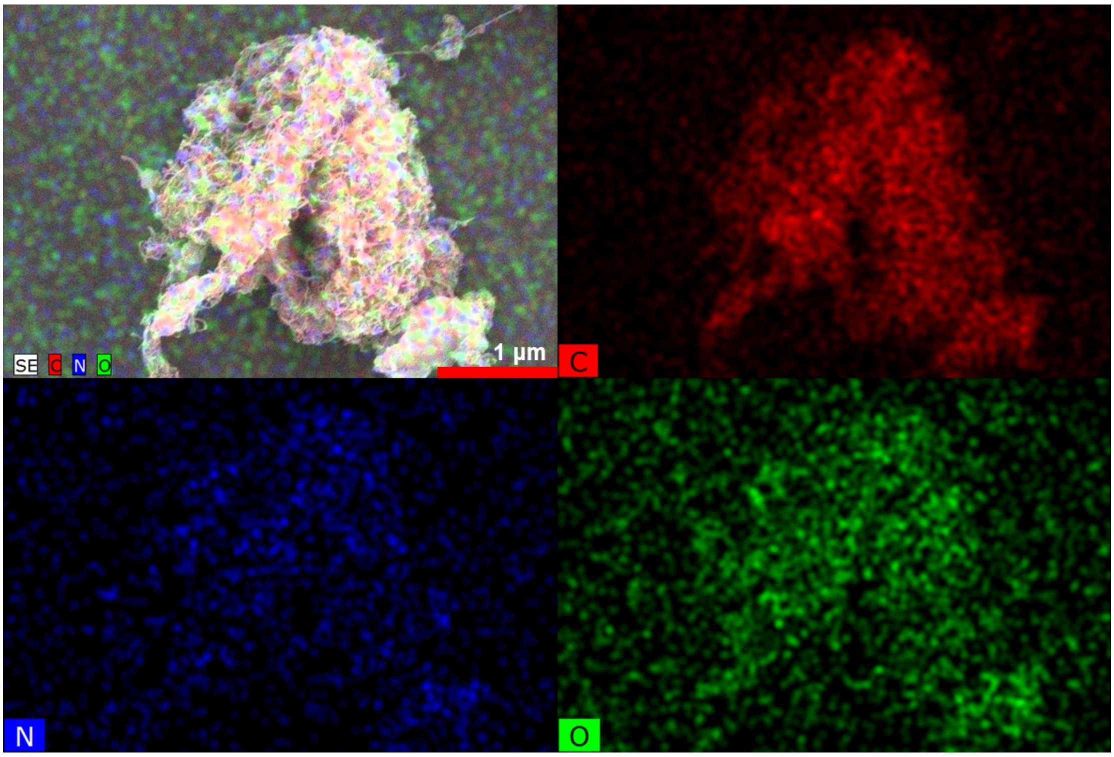

Figure S8. Elemental mapping images of COF@CNT-2 using silicon as substrate.

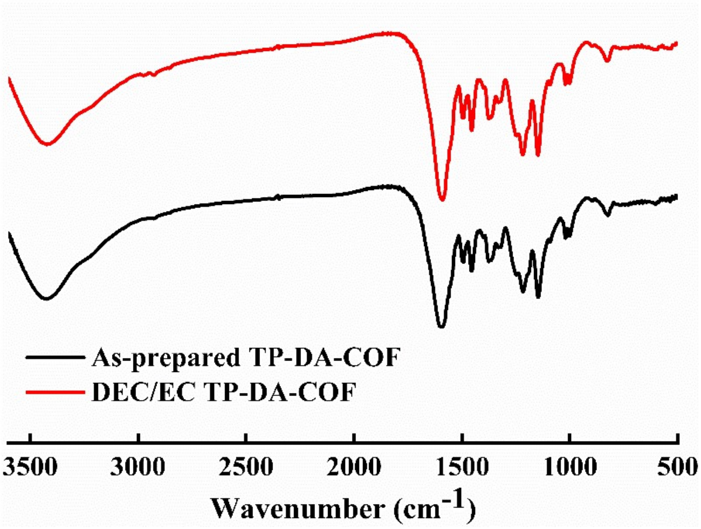

Figure S9. FT-IR spectra of the TP-DA-COF after being immersed EC and DEC (1:1) for 3 days at room temperature.

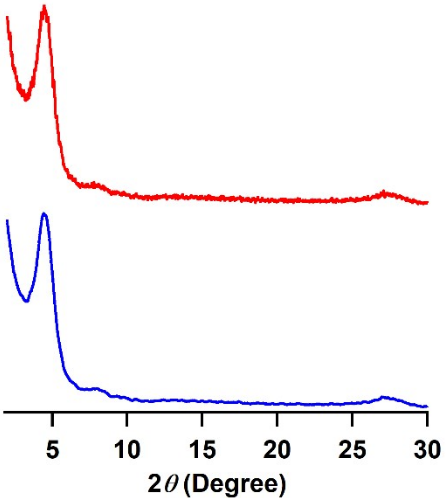

Figure S10. XRD spectra of the TP-DA-COF before (red) and after (blue) being immersed EC and DEC (1:1) for 3 days at room temperature.

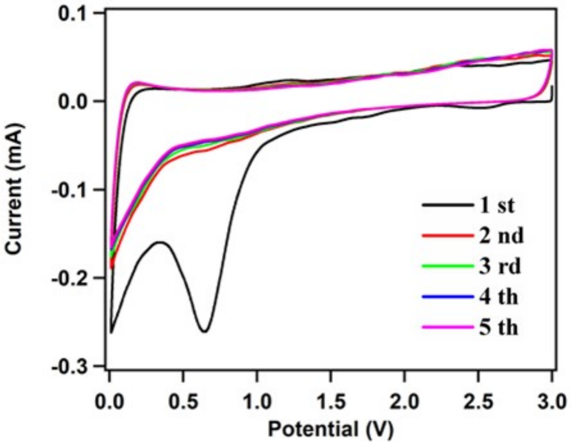

Figure S11. CV curves of COF@CNT-2 anode material at 0.2 mV s^{-1}.

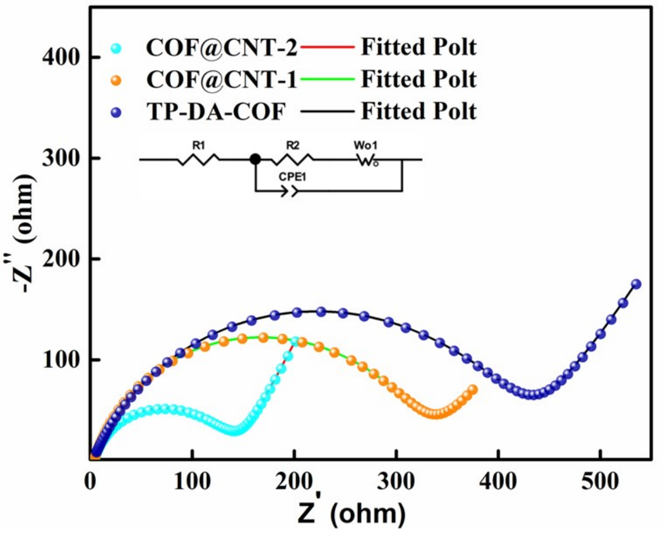

Figure S12. Nyquist plots fitting results of the TP-DA-COF (blue), COF@CNT-1(orange), and COF@CNT-2 (green) anodes.

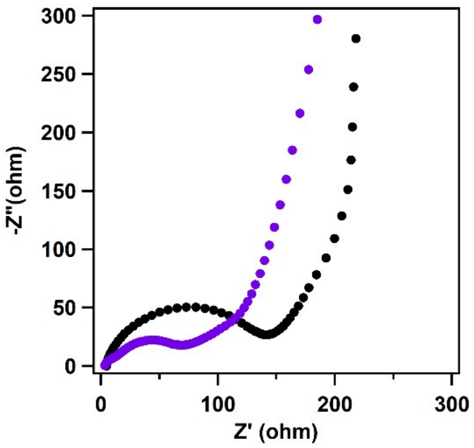

Figure S13. AC-impedance measurements of the COF@CNT-2 anode materials after first cycle (black) and 2000 cycles (purple) at 1 A g^{-1}.

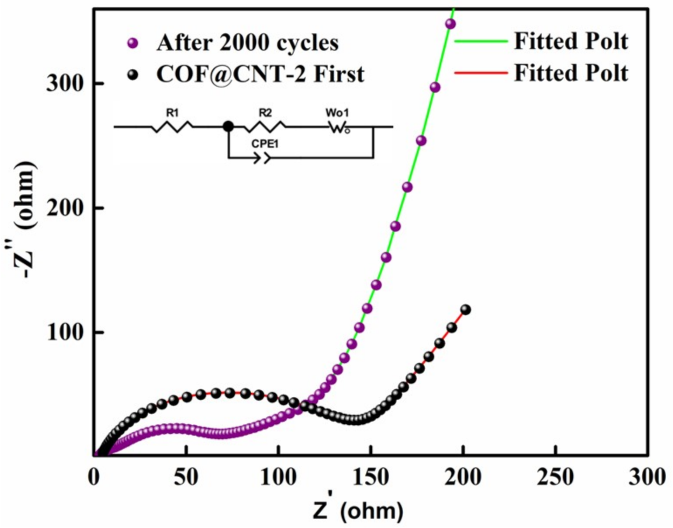

Figure S14. Nyquist plots fitting results of the COF@CNT-2 anode before (black curve) and after (purple curve) the cycling test (2000 cycles at 1.0 A g^{-1}).

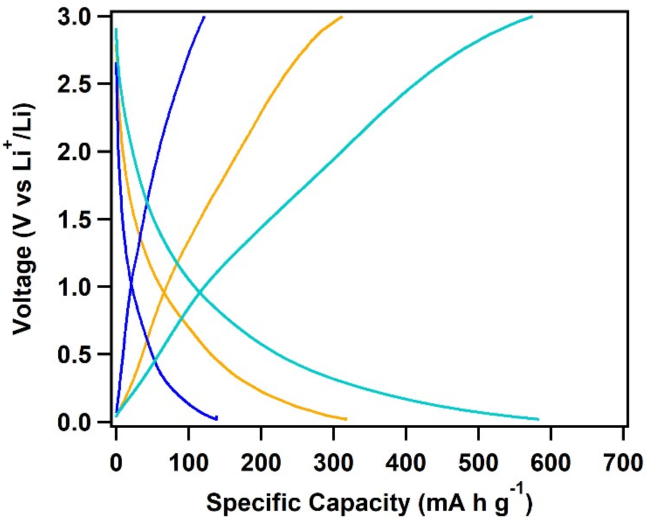

Figure S15. Charge-discharge curves of TP-DA-COF (blue), COF@CNT-1 (yellow), COF@CNT-2 (cyan) for the first cycle at 0.1 A g^{-1}.

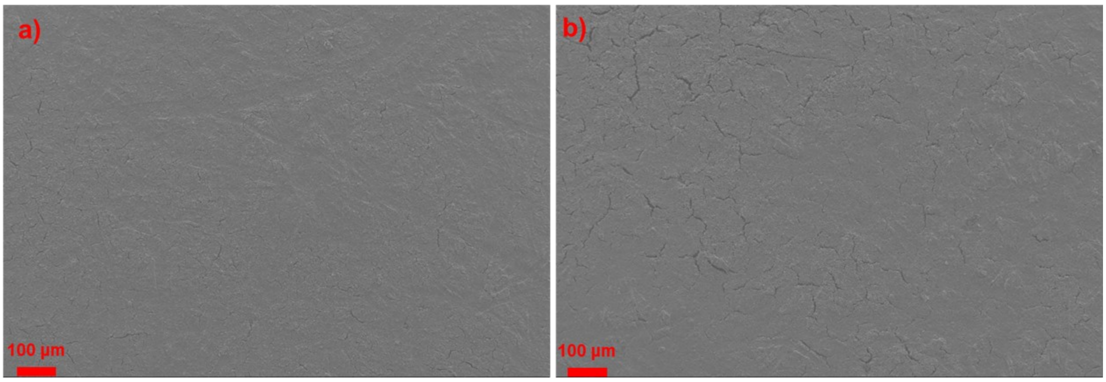

Figure S16. FE SEM images of the COF@CNT-2 anode: surface before (a) and after (b) the cycling test (2000 cycles at 1 A g^{-1}).

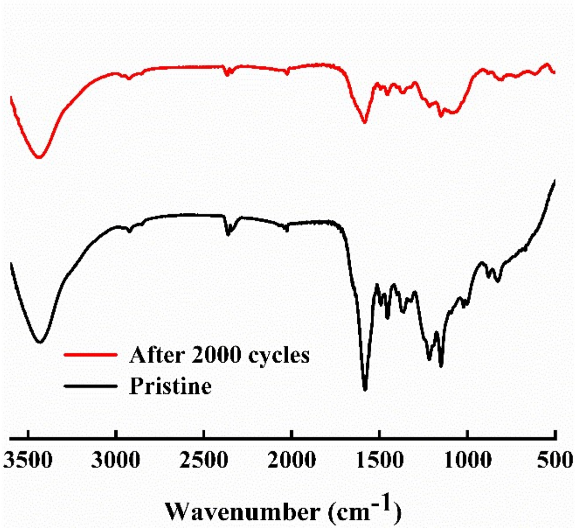

Figure S17. FT-IR spectra of the COF@CNT-2 anode: before (red) and after (black) the cycling test (2000 cycles at 1 A g^{-1}).

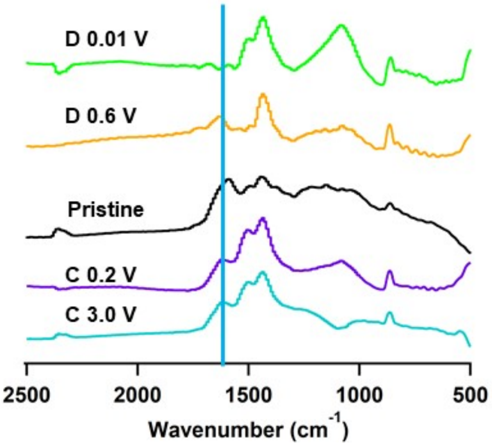

Figure S18. FT-IR Spectra of COF@CNT-2 electrode materials at different states of lithiation/delithiation.

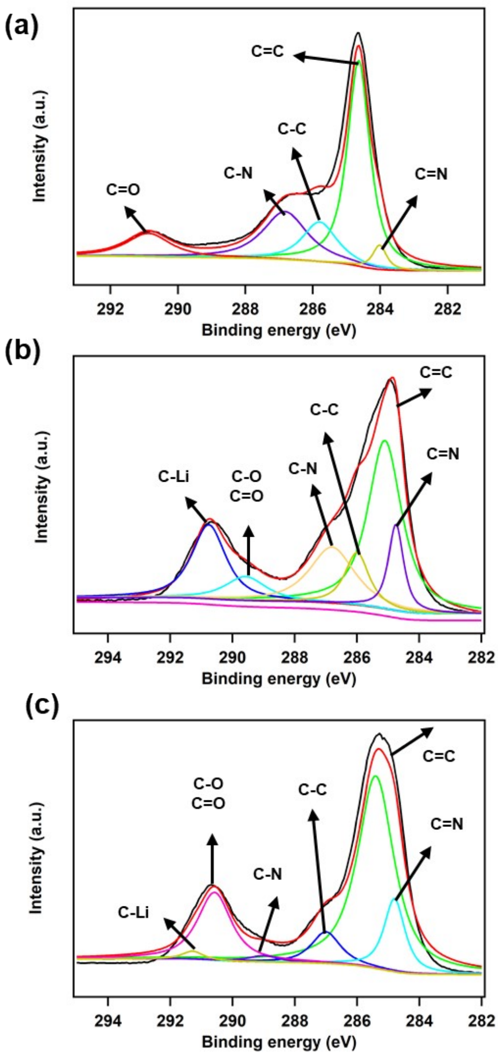

Figure S19. XPS investigation: C 1s of COF@CNT-2: (a) pristine; (b) lithiation; (c) delithiation.

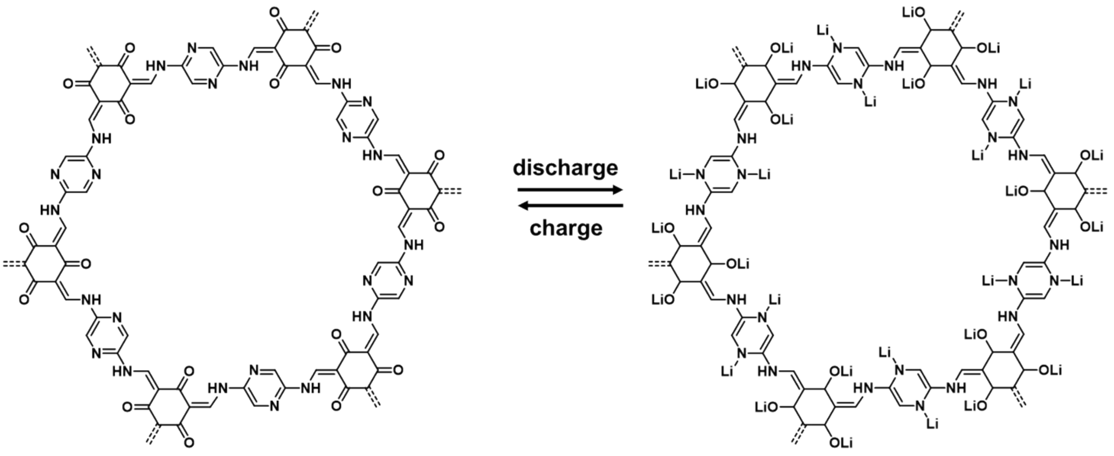

Figure S20. Proposed electrochemical mechanism of lithiation/delithiation for COF@CNT-2.

Table S1. Elemental analysis of TP-DA-COF.

Sample		C (wt.%)	N (wt.%)	H (wt.%)
TP-DA-COF	Calcd.	56.07	26.17	2.80
	Found	55.17	25.41	2.35

Supporting references

1. Chandra, S, Chowdhury. D. R, Addicoat. M, Heine. T, Paul. A and Banerjee. R. *Chem. Mater*. 2017, **29**, 2074-2080.