Supporting Information

Few Layer Covalent Organic Frameworks with Graphene Sheets as Cathode Materials for Lithium-Ion Batteries

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1. Materials and method

Pyromellitic dianhydride (PMDA, Aladdin, 99%), tris(4-aminophenyl)amine (TAPA, Aladdin, 99%), 1,3,5-tris(4aminophenyl)benzene (TAPB, Aladdin, 99%), *N*-methyl-2-pyrrolidone (NMP, J&K, 99.9%), mesitylene (J&K, 99%) and isoquinoline (Aladdin, 98%) were used as received. FT-IR was carried out with a Nicolet 380 FT-IR spectrometer. ^{13}C CP/MAS spectra (NMR) of COFs was recorded on an Agilent DD2 600 Solid NMR System with 4 mm zirconia rotors. Powder X-ray diffraction (PXRD) measurement was carried out with a PANalytical X'Pert Powder system using monochromated Cu/Kα (λ = 0.1542 nm). Nitrogen adsorption- desorption isotherm measurement were carried out using a Micromeritics ASAP 2020 system (samples were degassed at 200°C for 4 h). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the BJH model, the pore size distributions were derived from the sorption curves. Atomic force microscopy (AFM) images were acquired in air in tapping mode using a JPK NanoWizard Sense system.

2. Synthetic procedures

2.1 Synthesis of PI-COF-1

PI-COF-1 was synthesized according to a reported procedure with slight modification. A 20 mL pyrex tube was charged with PMDA (327 mg, 1.5 mmol) and TAPA (290 mg, 1.0 mmol) in a solution of 5.0 mL mesitylene/5.0 mL NMP/0.50 mL isoquinoline. The tube was degassed by three cycles of freezing-pumping-thawing

and sealed off and heated at 200°C for 5 days to afford a brown-red precipitate, which was isolated by filtration and washed with anhydrous THF (50 mL). The product was immersed in anhydrous THF (50 mL) for 8 h, during which the activation solvent was decanted and replaced four times. The solvent was removed under vacuum at 80°C to afford PI-COF-1 as a brown red powder (500 mg, 81%).

2.2 Synthesis of PI-COF-2

PI-COF-2 was synthesized according to a reported procedure with slight modification. A 20 mL pyrex tube was charged with PMDA (327 mg, 1.5 mmol) and TAPB (351 mg, 1.0 mmol) in a solution of 5.0 mL mesitylene/5.0 mL NMP/0.50 mL isoquinoline. The tube was degassed by three cycles of freezing-pumping-thawing and sealed off and heated at 200°C for 5 days to afford a brown yellow precipitate, which was isolated by filtration and washed with anhydrous THF (20 mL). The product was immersed in anhydrous THF (50 mL) for 8 h, during which the activation solvent was decanted and replaced four times. The solvent was removed under vacuum at 80°C to afford PI-COF-2 as a brown yellow powder (521 mg, 77%).

2.3 Preparation of PI-ECOF-1 and PI-ECOF-2

PI-ECOFs were prepared by balling-milling method to exfoliate the bulk COFs. In a typical experiment, 60 mg of bulk PI-COFs were placed in a milling pot with six steel ball (φ = 3 mm), and then the mixture was balling at 50 Hz (Jingxin, Tissuelyser-24) for 30 min to afford PI-ECOFs.

2.4 Synthesis of reduced GO (rGO)

Graphite oxide (GO) was prepared from purified natural graphite by the Hummers method.[1] rGO was synthesized by the reduction of GO with hydrazine hydrate[2]. In a typical procedure, GO (400 mg) was loaded in a 500 mL round-bottom flask and water (200 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was stirred at room temperature until it became clear with no visible particular matter. Then, $NH_3 \cdot H_2O$ (0.3 mL, 25% ~ 29%), hydrazine hydrate (0.36 mL, 80%) were added and the solution was heated in an oil bath at 100°C under a water-cooled condenser for 80 min over which rGO gradually precipitated out as a black solid. The product was isolated by filtration over a medium fritted glass funnel, washed copiously with water (100 mL×5), and then the product was freeze-dried to give a black powder.

3. Electrochemical tests

Electrochemical tests were performed using CR2025 coin type cells, which were assembled in an argon-filled glove box. The active materials, including PI-COF-1, was mixed with Ketjen black (KB, EC-600JD) by grinding using hands; The active materials, including PI-ECOF-1, PI-ECOF-2 were mixed with KB by using a high-energy ball-milling mixer (50 Hz, 30 min); The active materials, including PI-ECOF-1/rGO, PI-ECOF-2/rGO were mixed with different weight percentage of rGO (10%, 30%, 50%) and KB by using a high-energy ball-milling mixer (50 Hz, 30 min). Then PVDF solution (poly(vinylidene fluoride) in N-methyl-2-pyrrolidone, 20 g/L) was

added to above mixture to afford a slurry. The cathode was prepared by casting a slurry on Al foils and then vacuum dried at 80°C for 12 h. the weight ratio of active materials, KB, PVDF in the cathode pellets is 6:3:1. The cathode pallets are 12 mm in diameter. The average loading of active materials in each pallet was uniform and about 1 mg/cm^2. The cells were fabricated from the cathode, a Celgard 2400 membrane separator, a lithium plate anode and 1.0 M of lithium bis(trifluoro-methanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/dimethoxyethane (DME) (1:1 v/v) or 1.0 M LiPF$_6$ in dimethyl carbonate (DMC)/ethylene carbonate (EC)/ethyl methylcarbonate (EMC) (1:1:1 v/v/v). The charge-discharge measurements were carried out on a Neware CT4008 battery tester in the potential range of 1.5 V to 3.5 V (*vs*. Li). Cycling voltammetry (CV) was conducted on a CHI660E electrochemical workstation at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a CHI660E electrochemical workstation by sweeping the frequency from 100 kHz to 10^{-2} Hz.

4. Calculation of theoretical capacity[1]

Theoretical capacity C_t (mAh g^{-1}) was calculated using the equation of $C_t = F/(3600(M_w/1000))$, where F and M_w is Faraday constant (96500 C mol^{-1}) and the molecular weight per active specie, respectively.

As for PI-COF-1, the molecular weight of the repeating imide units (M_A) and tris(4-aminophenyl) amine (M_B) in the COF is 214 and is 242, respectively. In the COF unit cell, the number of imide unit is calculated to be 6×1/2 =3, and the number

of tris(4-aminophenyl）amine unit is calculated to be $6 \times 1/3 = 2$, the molecular weight of unit cell is calculated to be $M_{\text{unit cell}} = 3 \times M_A + 2 \times M_B = 3 \times 214 + 2 \times 242 = 1126$. The number of electrons (n) involved in the unit cell is given by the equation of $3 \times 2 = 6$, taking into account of the fact that two electrons are involved in each diimide unit. Therefore, the equivalent molecular weight $M_w = M_{\text{unit cell}}/n = 1126/6 = 187.67$. The theoretical capacity is calculated using the equation of $C_t = F/(3600(M_w/1000)) = 142$ mAh g^{-1}.

As for PI-COF-2, the molecular weight of the repeating imide units (M_A) and tris(4-aminophenyl) benzene (M_B) in the COF is 214 and is 303, respectively. In the COF unit cell, the number of imide unit is calculated to be $6 \times 1/2 = 3$, and the number of tris (4-aminophenyl) benzene unit is calculated to be $6 \times 1/3 = 2$, the molecular weight of unit cell is calculated to be $M_{\text{unit cell}} = 3 \times M_A + 2 \times M_B = 3 \times 214 + 2 \times 303 = 1248$. The number of electrons (n) involved in the unit cell is given by the equation of $3 \times 2 = 6$, taking into account of the fact that two electrons are involved in each diimide unit. Therefore, the equivalent molecular weight $M_w = M_{\text{unit cell}}/n = 1248/6 = 208$. The theoretical capacity is calculated using the equation of $C_t = F/(3600 (M_w/1000)) = 128$ mAh g^{-1}.
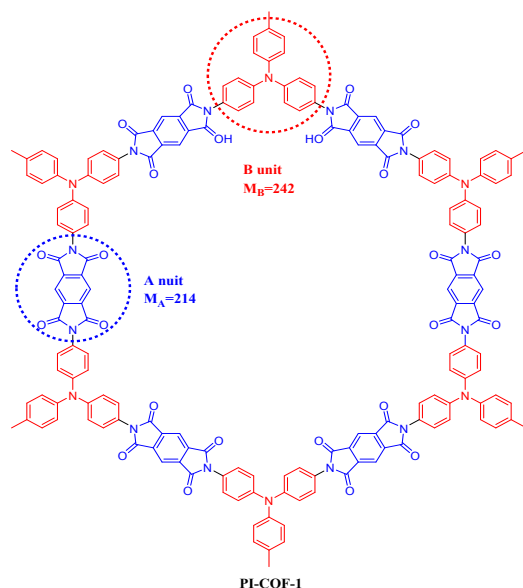
Scheme S1. Chemical structure of PI-COF-1.
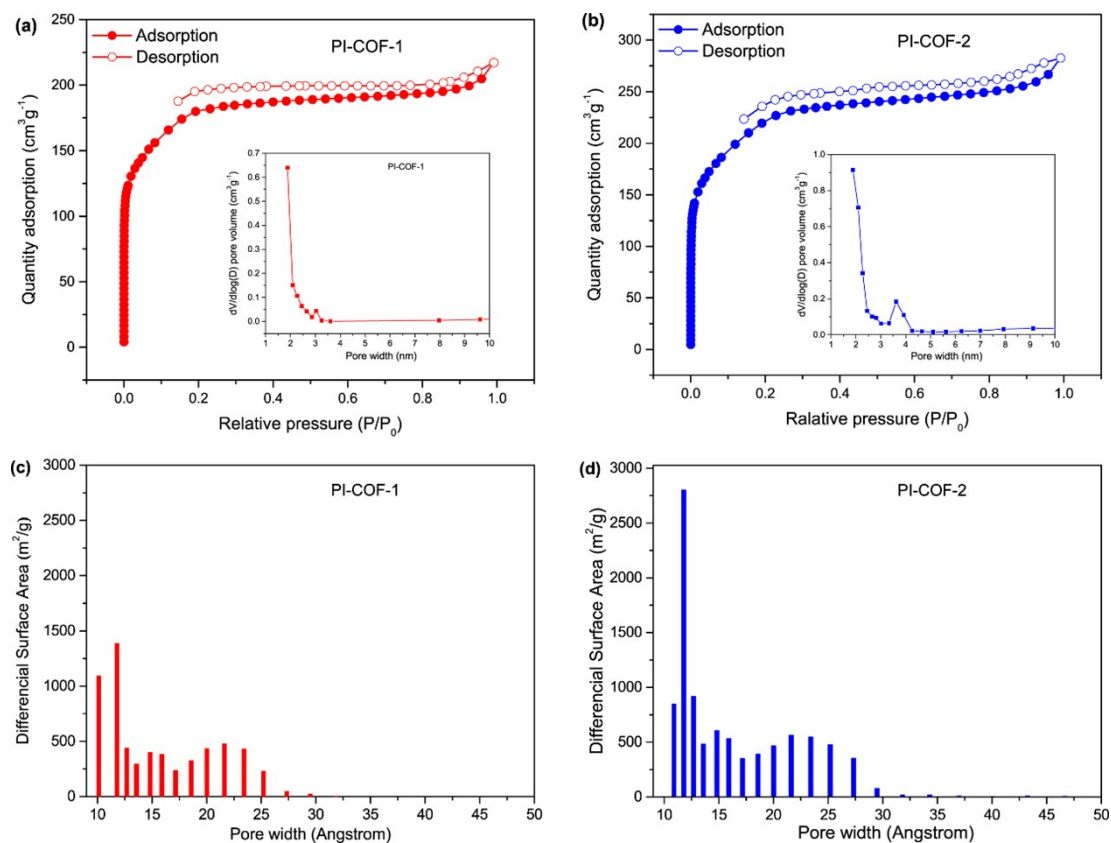
5. Supplementary Figures

Figure S1. N_2 sorption isotherms of PI-COF-1 (A) and PI-COF-2 (B), and the pore

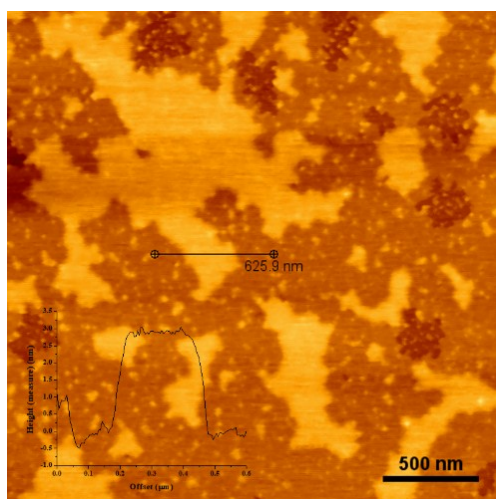size distributions derived from BJH (inset) and NLDFT (C and D) model.

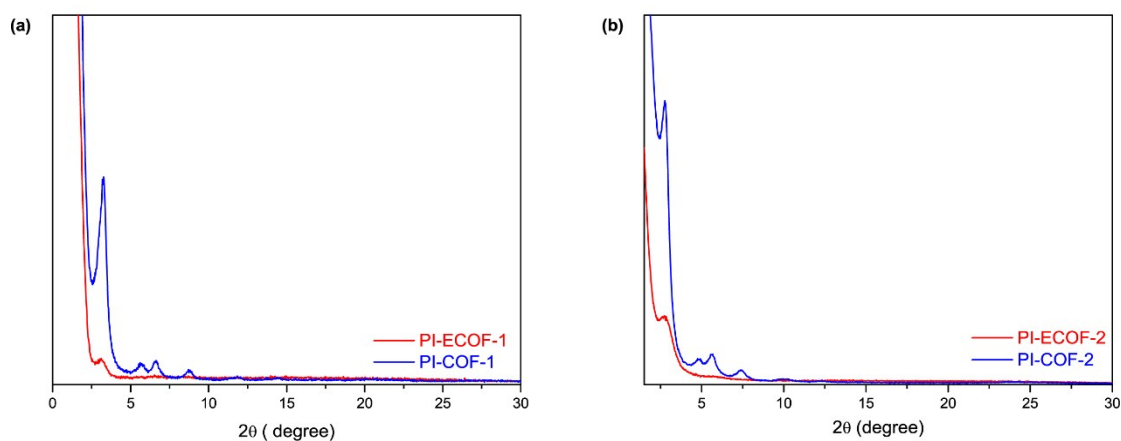**Figure S2**. AFM imagine and height profile of PI-ECOF-2.

Figure S3. PXRD patterns of (A) PI-COF-1 (blue) and PI-ECOF-1 (red), and (B) PI-
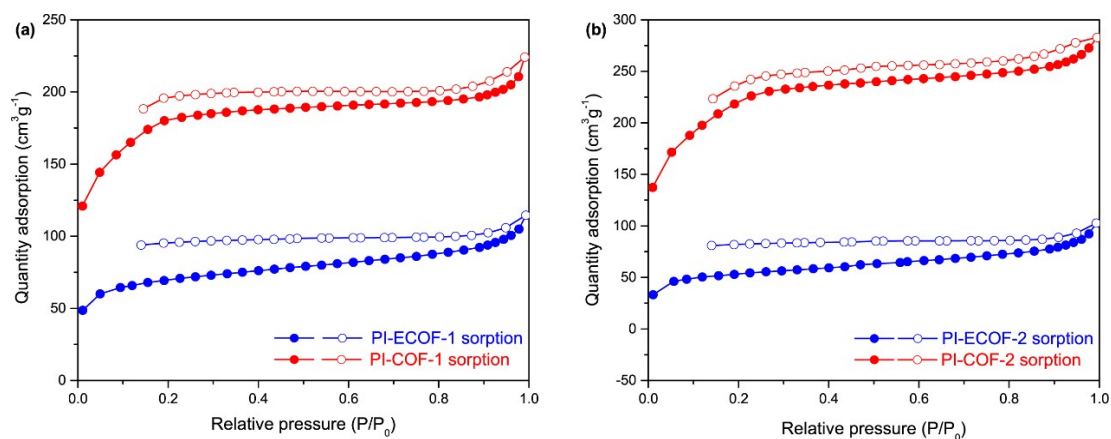
COF-2 (blue) and PI-ECOF-2 (red).

Figure S4. N_2 sorption isotherms of (A) PI-COF-1 (red) and PI-ECOF-1 (blue), and

(B) PI-COF-2 (red) and PI-ECOF-2 (blue).
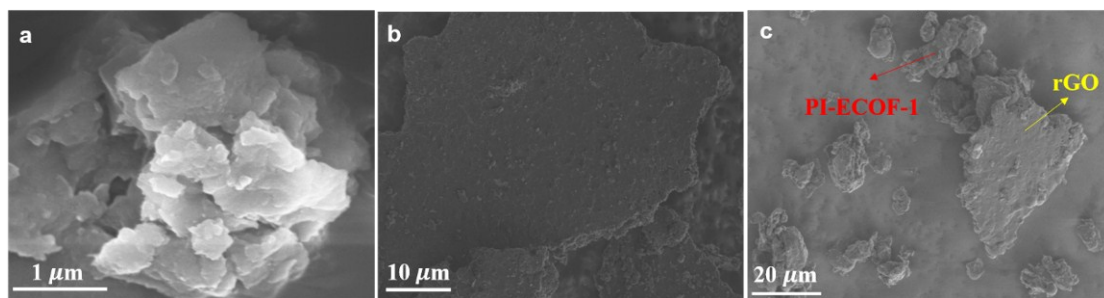
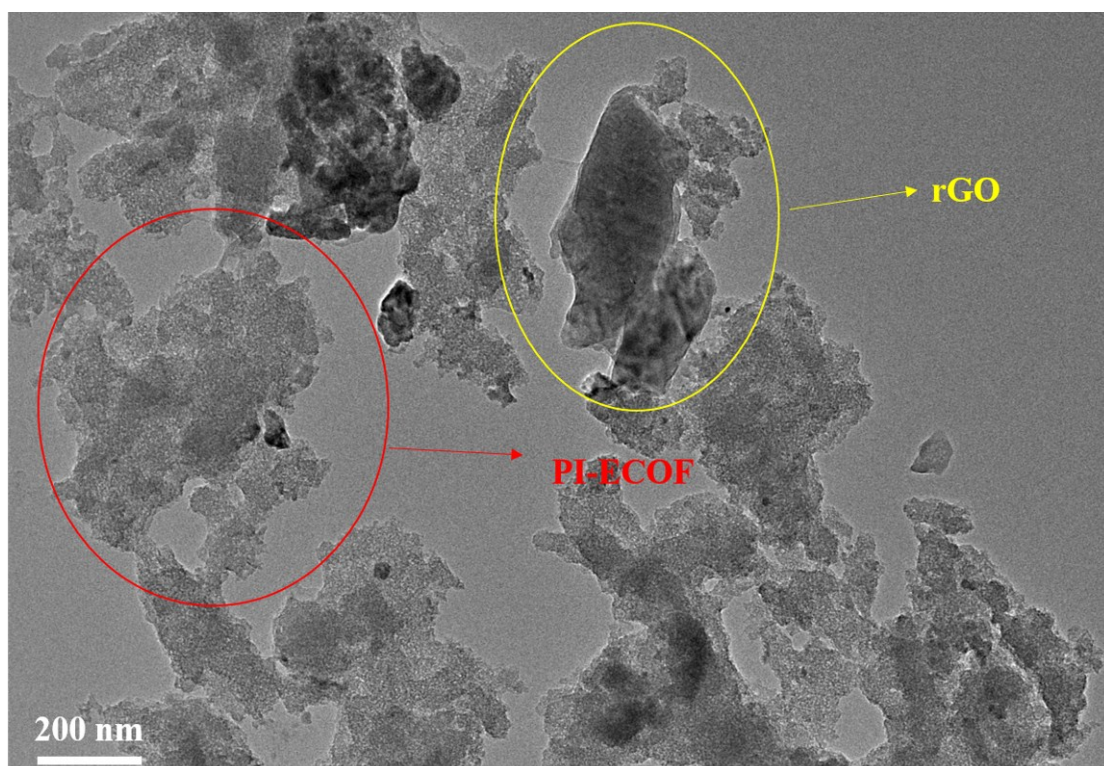**Figure S5**. SEM images of pure PI-ECOF-1 (A), rGO (B) and PI-ECOF-1/rGO30 composite (C).

Figure S6. TEM image of PI-ECOF-1/rGO30 composite.
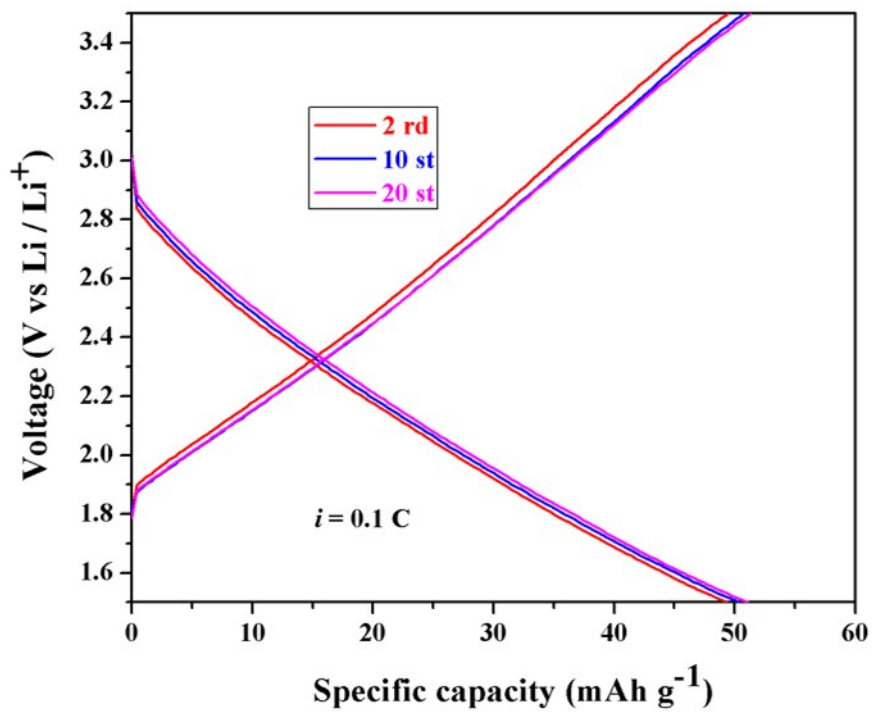
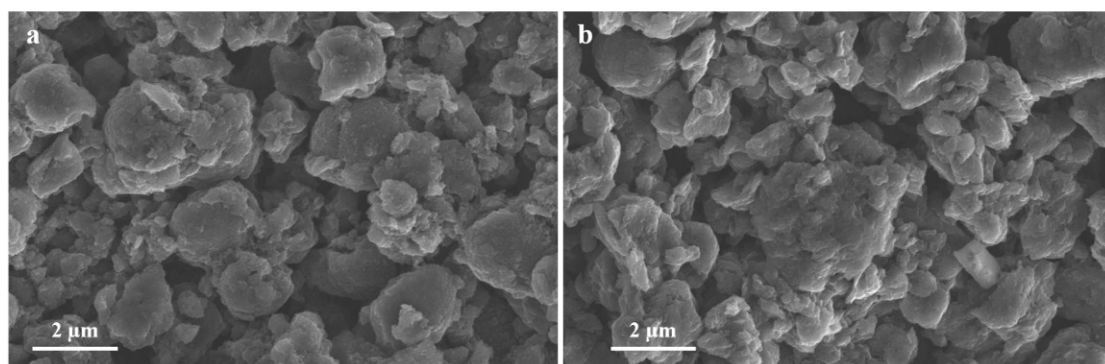**Figure S7**. Discharge-charge curves of rGO at the rate of 0.1 C.

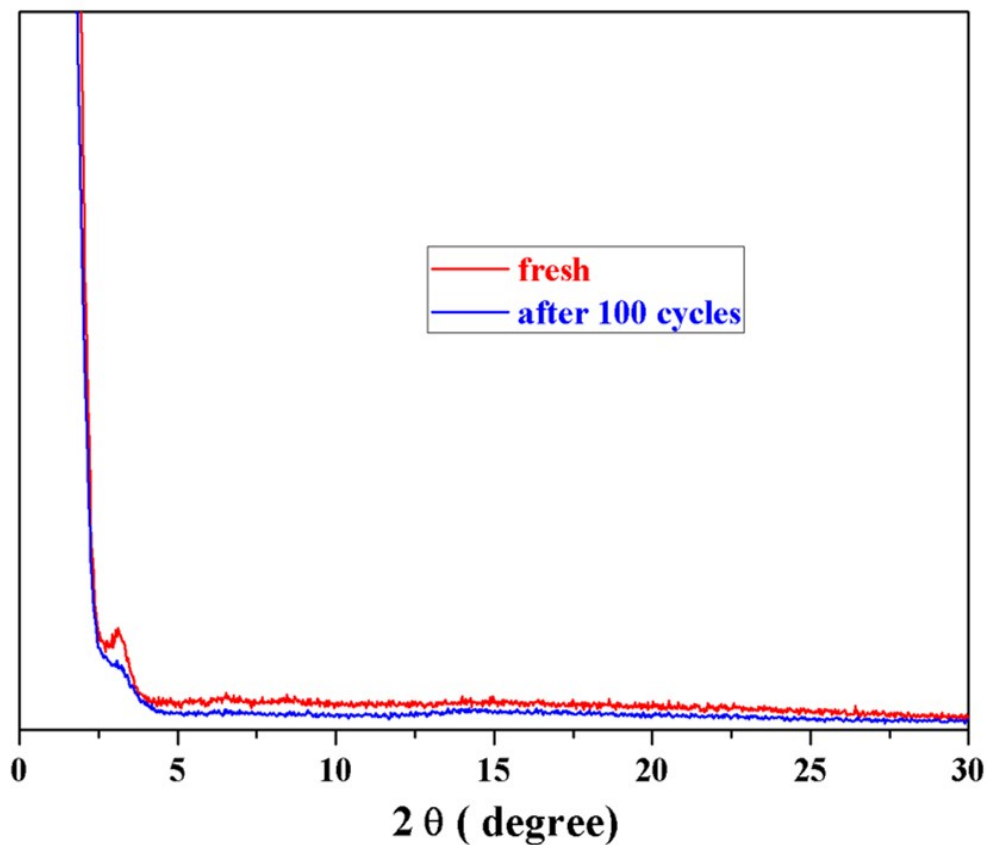**Figure S8**. SEM images of PI-ECOF-1/rGO30 before (A) and after (B) 100 cycles at

the rate of 1 C.

Figure S9. PXRD patterns of PI-ECOF-1/rGO30 before (red) and after (blue) 100 cycles at the rate of 1 C.

Reference

1. J. P. Zhao, S. F. Pei, W. C. Ren, L. B. Gao, H. M. Cheng, *ACS Nano* 2010, **4**, 5245.

2. R. L. Jay, D. D. Condell, V. K. Dmitry, H. Wen-Fang, M. T. James, *J. Am. Chem. Soc.* 2008, **130**, 16201.

3. F. Xu, S. Jin, H. Zhong, D. Wu, X. Yang, X. Chen, H. Wei, R. Fu, D. Jiang, *Sci. Rep.* 2015**, 5**, 8225.