

## Electronic Supplementary Information

Chemically grafting nanoscale UIO-66 onto polypyrrole nanotubes for  
long-life lithium-sulfur batteries

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### Experimental Section

#### 1. Chemicals

Pyrrole ( $\geq 98.0\%$ ) and 1,4-dibromobutane ( $\geq 98.0\%$ ) were of chemical grade and purchased from Sinopharm Chemical Reagent Co., Ltd, and were distilled under vacuum before use. 2-Methylimidazole (MI) and 1,4-benzene dicarboxylic acid (BDC) were purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents were of analytical grade and used without further purification, such as methyl orange (MO) (Tianjin Damao Chemical Factory, IND);  $\text{FeCl}_3$  ( $\geq 99.0\%$ ),  $\text{KOH}$  ( $\geq 85.0\%$ ), and dimethylformamide (DMF) ( $98.0\%$ ) obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol and ethanol were obtained from Tianjin Damao Chemical Factory,

Z99.7%. Deionized water was used for all experiments. Zirconium tetrachloride ( $\text{ZrCl}_4$ ,  $\geq 99.5\%$ ), chromic nitrate nonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), iron chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), copper nitrate hydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), vanadyl sulfate ( $\text{VOSO}_4$ ), cobaltous nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), manganese chloride ( $\text{MnCl}_2$ ), and zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were obtained from Sigma-Aldrich Co., Ltd. All starting materials and solvents, unless otherwise specified, were used without further purification.

## **2. Synthesis**

### **2.1 Synthesis of PPy Nanotubes (PPyNTs)**

PPyNTs were synthesized using a template method as reported in the literature.<sup>1</sup> In a typical procedure, 0.243 g (1.5 mmol) of  $\text{FeCl}_3$  was dissolved in 30 mL of 5 mM MO solution (0.15 mmol), and a flocculent precipitate appeared immediately. Pyrrole monomer (105  $\mu\text{L}$ , 1.5 mmol) was then added, and the mixture was stirred at room temperature for 24 h. The formed PPy precipitate was washed with deionized water/ethanol several times until the filtrate was colourless and neutral. The produced PPyNTs were dried under vacuum at 60 °C for 24 h.

### **2.2 Synthesis of PPyNTs-( $\text{CH}_2$ )<sub>4</sub>Br**

A mixture of PPyNTs (0.030 g), KOH powder (0.050 g), and 1,4-dibromobutane (0.143 g) was dispersed in 25.0 mL DMF, sonicated for 5 min and then held at 60 °C for 24 h under vigorous agitation. The product was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed KOH and unreacted 1,4-

dibromobutane from the surface of PPyNTs. The final product, denoted as PPyNTs-(CH<sub>2</sub>)<sub>4</sub>Br, was then dried in a vacuum oven at 60 °C overnight to remove residual solvent.

### 2.3 Synthesis of PPyNTs-(CH<sub>2</sub>)<sub>4</sub>-MIBr

A mixture containing PPyNTs-(CH<sub>2</sub>)<sub>4</sub>Br (0.025 g) and MI (0.200 g) in 25.0 mL DMF with KOH (0.050 g) was sonicated for 5 min and then held at 80 °C for 24 h under vigorous agitation. The product was concentrated and washed with ethanol several times to thoroughly remove physically absorbed MI. Then the black precipitate was denoted as ILs/PPyNTs and was dried in a vacuum oven at 60 °C overnight to remove the residual solvent.

### 2.4 Synthesis of PPyNTs-(CH<sub>2</sub>)<sub>4</sub>-BDC

As can be seen from Scheme 1, a mixture containing PPyNTs-(CH<sub>2</sub>)<sub>4</sub>Br (0.025g), K<sub>2</sub>CO<sub>3</sub> (0.050g) powder, and dimethyl 2-aminoterephthalate (prepared by BDC and methanol, 0.050g) was dispersed in 25.0 mL DMF and sonicated for 5 min and then held at 80 °C for 24 h under vigorous agitation. The product was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed K<sub>2</sub>CO<sub>3</sub> and unreacted dimethyl 2-aminoisophthalate from the surface of PPyNTs-(CH<sub>2</sub>)<sub>4</sub>Br. The final product, denoted as PPyNTs-(CH<sub>2</sub>)<sub>4</sub>Br-aminoisophthalate, was then dried in a vacuum oven at 60 °C overnight to remove residual solvent. Subsequently, a mixture containing PPyNTs-(CH<sub>2</sub>)<sub>4</sub>Br-aminoisophthalate (0.025 g) and H<sub>2</sub>SO<sub>4</sub> (0.200 g) in 25.0 mLH<sub>2</sub>O was sonicated for 5 min and then held at 80 °C for 24 h under vigorous agitation. The product was concentrated and washed with deionized water several

times. Then the black precipitate, denoted as PPyNTs-(CH<sub>2</sub>)<sub>4</sub>-BDC, was dried in a vacuum oven at 60 °C overnight to remove residual solvent.

### **2.5 Synthesis of PPyNTs@ZIF-8**

A mixture containing Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (110.00 mg, 0.370 mmol) and PPyNTs-(CH<sub>2</sub>)<sub>4</sub>-MIBr (50.00 mg) was added to a methanol solution (25 mL) of 2-methylimidazole (122.00 mg, 1.48 mmol) at ambient temperature. This mixture was kept at room temperature for a period of 12 h with stirring. The resultant black precipitate was collected using centrifugation and washed five times with methanol. The obtained samples, denoted as PPyNTs@ZIF-8, were activated at 80 °C overnight under vacuum.

### **2.6 Synthesis of PPyNTs@ZIF-67**

In a typical synthesis process, A mixture containing Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (174.60 mg) and PPyNTs-(CH<sub>2</sub>)<sub>4</sub>-MIBr (50.00 mg) was added to methanol (25 mL) and denoted solution A. 2-Methylimidazole (197.00 mg, 1.48 mmol) was dissolved in methanol (25 mL) and denoted solution B. Solutions A and B were mixed rapidly and then kept at room temperature for 24 h. The resultant precipitate was centrifuged and washed with ethanol several times, and finally dried in air at 80 °C, and the final product was denoted as PPyNTs@ZIF-67.

### **2.7 Synthesis of PPyNTs@UIO-66**

A mixture containing ZrCl<sub>4</sub> (28.80 mg, 0.12 mmol), PPyNTs-(CH<sub>2</sub>)<sub>4</sub>-BDC (50.00 mg), and acetic acid (0.34 mL) was firstly added to DMF (5 mL) and sonicated for 10 min. Subsequently, BDC (19.94 mg, 0.12 mmol) was added to the clear dispersion in

an equimolar ratio with regard to  $\text{ZrCl}_4$ . Afterwards, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and kept in an oven for 24 h at 120 °C under static conditions. When the reaction temperature cooled to room temperature, the precipitate was isolated by centrifugation. Finally, the sample dried in air at 80 °C, and the product was denoted as PPyNTs@UIO-66.

### **2.8 Synthesis of PPyNTs@MIL-101**

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (48.00 mg, 0.12 mmol), PPyNTs-( $\text{CH}_2$ )<sub>4</sub>-BDC (50.00 mg), and BDC (19.94 mg, 0.12 mmol) were added to DMF (10 mL) with brief stirring, resulting in a black suspension. The suspension was placed in a Teflon autoclave and kept in an oven at 200 °C for 10 h under static condition. The precipitate was harvested through centrifugation and then washed with methanol and  $\text{H}_2\text{O}$ . Finally, the product was dried in air at 80 °C and was denoted as PPyNTs@MIL-101.

### **2.9 Synthesis of PPyNTs@MIL-53**

A mixture containing  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (45.01), PPyNTs-( $\text{CH}_2$ )<sub>4</sub>-BDC (50.00 mg), and BDC (19.94 mg, 0.12 mmol) was added to DMF (10 mL) with brief stirring, resulting in a black suspension. The suspension was placed in a Teflon autoclave and kept in an oven at 200 °C for 10 h under static condition. The precipitates were harvested through centrifugation and then washed with methanol and  $\text{H}_2\text{O}$ . Finally, the product dried in air at 80 °C, and denoted as PPyNTs@MIL-53.

### **2.10 Synthesis of PPyNTs@MIL-100**

These reaction details are the same as those for PPyNTs@MIL-53, except for a substitution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  by  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

### **2.11 Synthesis of PPyNTs@HKUST-1**

These reaction details are the same as those for PPyNTs@MIL-53, except for a substitution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  by  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .

### **2.12 Synthesis of PPyNTs@Mn-BDC**

The reaction details are the same as that for PPyNTs@MIL-53, except for the change of metal salts by  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  to  $\text{MnCl}_2$ .

### **2.13 Synthesis of PPyNTs@V-BDC**

These reaction details are the same as those for PPyNTs@MIL-53, except for a substitution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  by  $\text{VOSO}_4$ .

### **2.14 Synthesis of PPyNTs@MOF-125**

1,4-Benzenedicarboxylic acid (250.00 mg, 1.5 mmol) and titanium isopropoxide  $\text{Ti}(\text{OiPr})_4$  (0.3 ml, 1 mmol) (Acros Organics, 98%) were introduced in a solution of 4.5 ml of dimethylformamide (Acros Organics, extra-dry) and 0.5 ml of dry methanol (Aldrich, 99.9%). This mixture was stirred gently for 5 minutes at room temperature and then was introduced into a 23 ml Teflon-lined autoclave at  $150^\circ\text{C}$  for 15 hours. After cooling to room temperature, the white solid was recovered by filtration, washed twice with acetone, and dried in air at room temperature. Finally, the product was dried in air at  $80^\circ\text{C}$ , and denoted as PPyNTs@MOF-125.

## **3. Characterization**

The crystal structures were determined using a powder X-ray diffraction (XRD) analysis (Philips X'Pert PRO) with  $\text{Cu K}\alpha$  radiation. The Ni content of Ni/PCNF and S loading of Ni/PCNF-S were determined using thermogravimetric analysis (TGA 4000

PerkinElmer Co., Ltd) under N<sub>2</sub> and air at a heating rate of 5 °C min<sup>-1</sup>. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM Hitachi S-4700) and high-resolution transmission electron microscopy (HRTEM FEI Tecnai G2 F20) fitted with an energy dispersive spectrometer (EDS) detector, STEM, and selected area electron diffraction (SAED). The chemical compositions and surface chemistry of the samples were examined using an X-ray photoelectron spectroscopy (XPS-7000) spectrometer with Al K $\alpha$  radiation. N<sub>2</sub> adsorption–desorption isotherm measurements were performed with a Micromeritics ASAP 2020 instrument using the Brunauer–Emmett–Teller (BET) method, and pore-size distributions (PSD) were calculated using the Barrett–Joyner–Halenda (BJH) model. Raman spectra were recorded using a LabRAM HR800 in a range of 100 to 3500 cm<sup>-1</sup>.

#### **4. Electrochemical Section**

##### **4.1 Sulfur impregnation in PPyNTs@UIO-66, PPyNTs, and UIO-66**

PPyNTs@UIO-66/sulfur composite cathodes were prepared by a melting-diffusion strategy. In brief, sulfur and PPyNTs@UIO-66, PPyNTs, and UIO-66 with a mass ratio of 85:15 were heated at 155 °C for 20 h. The resultant sulfur composite cathodes were denoted as PPyNTs@UIO-66-S, PPyNTs-S, and UIO-66-S, respectively. For the quantification of the accurate loading content of sulfur in the three carriers, a dissolution followed by weighting method was used to calculate the sulfur content. PPyNTs@UIO-66-S (1 g), PPyNTs-S (1 g), and UIO-66-S (1 g) cathodes dissolved in adequate carbon disulfide at vigorous stirring for 12h, and dried at 100 °C in a vacuum for 12h,

respectively. The weight of the obtained PPyNTs@UIO-66, PPyNTs, and UIO-66 were identified to 173, 186, and 168 mg, and the corresponding loading content of sulfur are 75.7, 76.4, and 81.2 wt%, respectively. It has to point out that thermogravimetry measurement for the quantification of sulfur content in this work is not feasible because the PPyNTs (Figure S13) and UIO-66 would occur to pyrolysis above 300 °C, and this in turn leads to relatively big error.

#### **4.2 Li-S Batteries Assembly and Electrochemical Test**

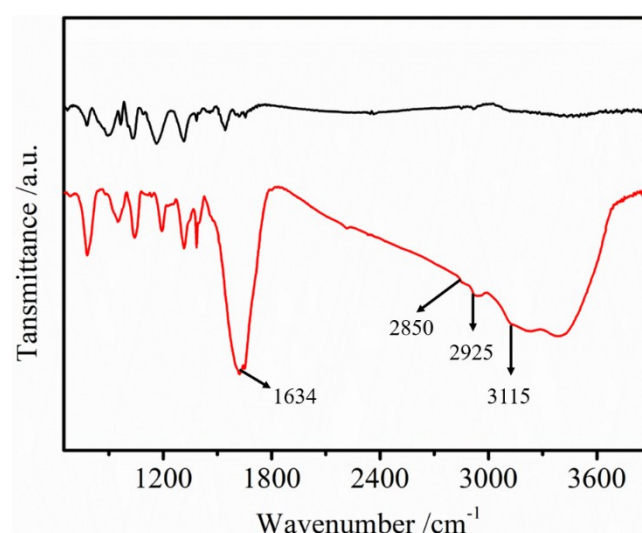
Sulfur composite cathodes were prepared by mixing the active materials (PPyNTs@UIO-66-S, PPyNTs-S, and UIO-66-S), acetylene black, and binder (polyvinylidene fluoride, PVDF) in N-methyl-pyrrolidinone (NMP) at a weight ratio of 8:1:1, respectively. This mixture was then ground for 30 min, spread on aluminum foil, and then dried in a vacuum oven at 80 °C for 24 h to remove the NMP. The average area of electrodes made this way was 1.3 mg cm<sup>-2</sup>. Coin-type Li-S batteries (CR 2016) were assembled in an Ar-filled glove box by using S composite cathodes, lithium foil anodes, and a Celgard 2400 separator. We used an electrolyte composed of 1.0 M bis-(trifluoro-methane) sulfonylimide (LiTFSI) and 1 wt% LiNO<sub>3</sub> dissolved in a mixed solvent of 1,3-dioxolane and 1,2-dimethoxyethane (DOL and DME, 1:1 in volume). The amount of electrolyte was approximately 15 μL mg<sup>-1</sup> sulfur. Chemical performance parameters were measured using a LAND CT2001A electrochemical analyzer at various current rates. Cyclic voltammograms (CV) curves were recorded using a CHI660C electrochemical workstation with a scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) measurements were made at frequencies ranging from



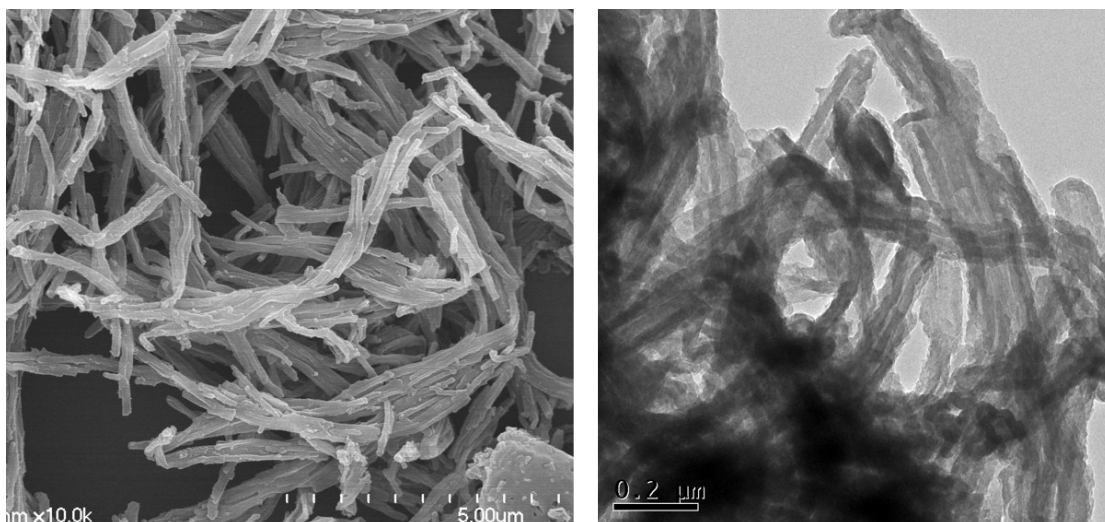
100 kHz to 0.01 Hz.

**Table S1** MOFs prepared by using various metal ions and ligands.

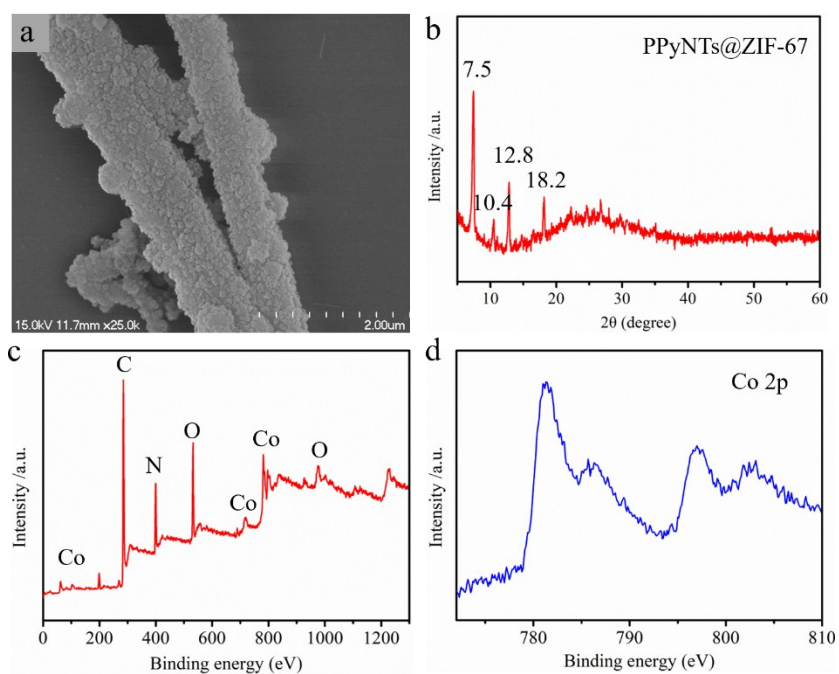
Number	Metal ion	Ligand	Product
(1)	Co <sup>2+</sup>	2-methylimidazole	ZIF-67
(2)	Zn <sup>2+</sup>	2-methylimidazole	ZIF-8
(3)	Cu <sup>2+</sup>	1,4-benzene dicarboxylic acid	HKUST-1
(4)	Mn <sup>2+</sup>	1,4-benzene dicarboxylic acid	Mn-BDC
(5)	Fe <sup>3+</sup>	1,4-benzene dicarboxylic acid	MIL-100
(6)	Al <sup>3+</sup>	1,4-benzene dicarboxylic acid	MIL-53
(7)	Ti <sup>4+</sup>	1,4-benzene dicarboxylic acid	MOF-125
(8)	V <sup>4+</sup>	1,4-benzene dicarboxylic acid	V-BDC
(9)	Cr <sup>4+</sup>	1,4-benzene dicarboxylic acid	MIL-101



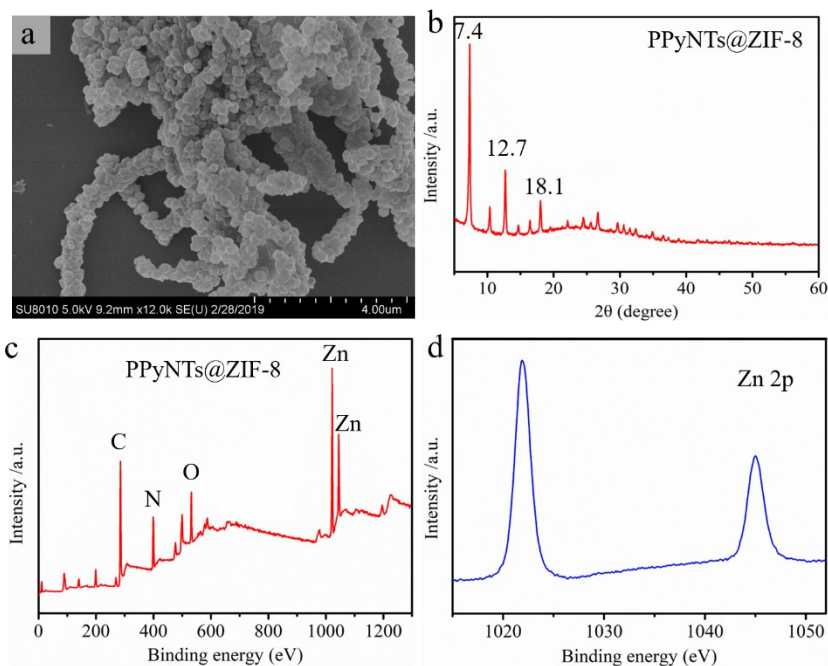
**Fig. S1** FTIR spectra of PPyNTs (black) and 2-methylimidazole functionalized PPyNTs (red).



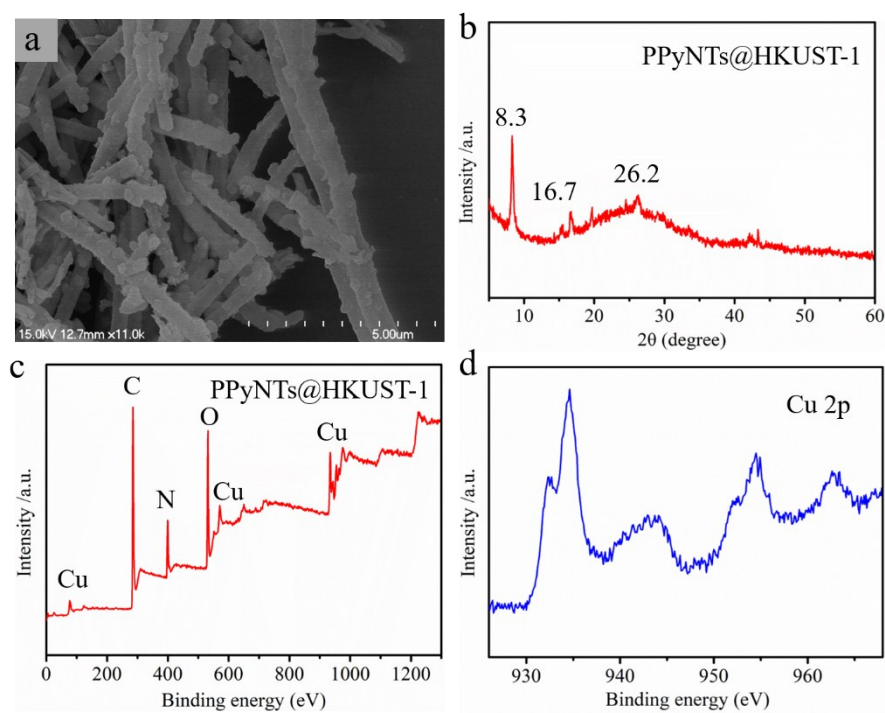
**Fig. S2** SEM (left) and TEM (right) images of 1,4-benzene dicarboxylic acid functionalized PPyNTs.



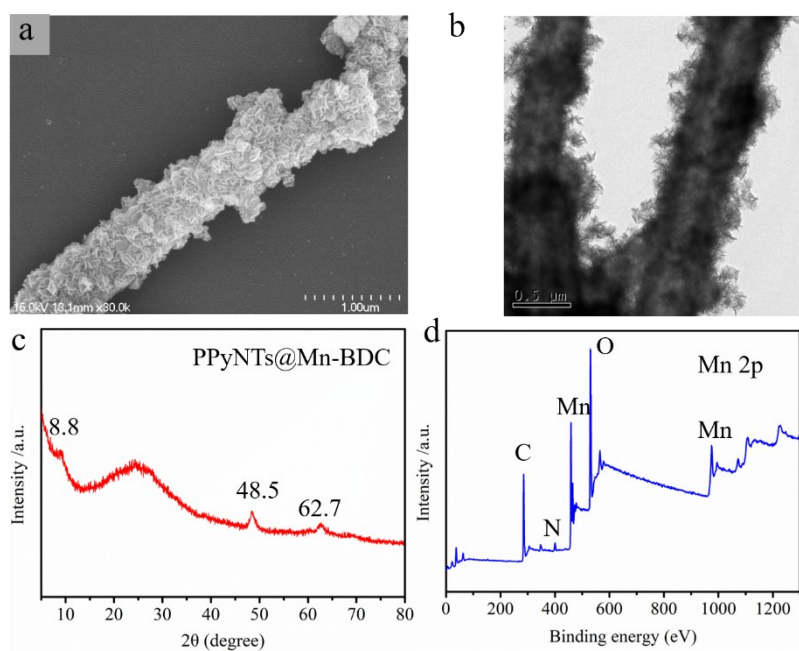
**Fig. S3** (a) SEM image, (b) PXRD, (c) XPS, and (d) high-resolution Co 2p XPS of PPyNTs@ZIF-67.



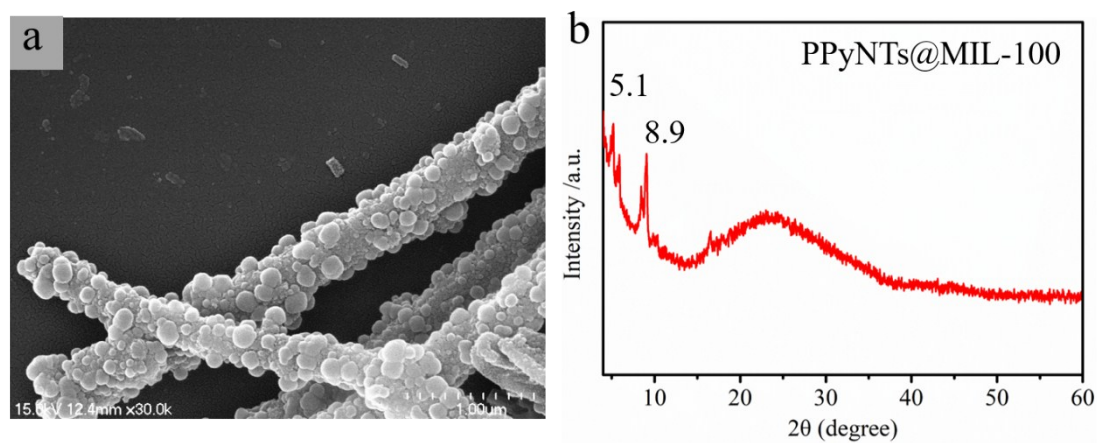
**Fig. S4** (a) SEM image, (b) PXRD, (c) XPS, and (d) high-resolution Zn 2p XPS of PPyNTs@ZIF-8.



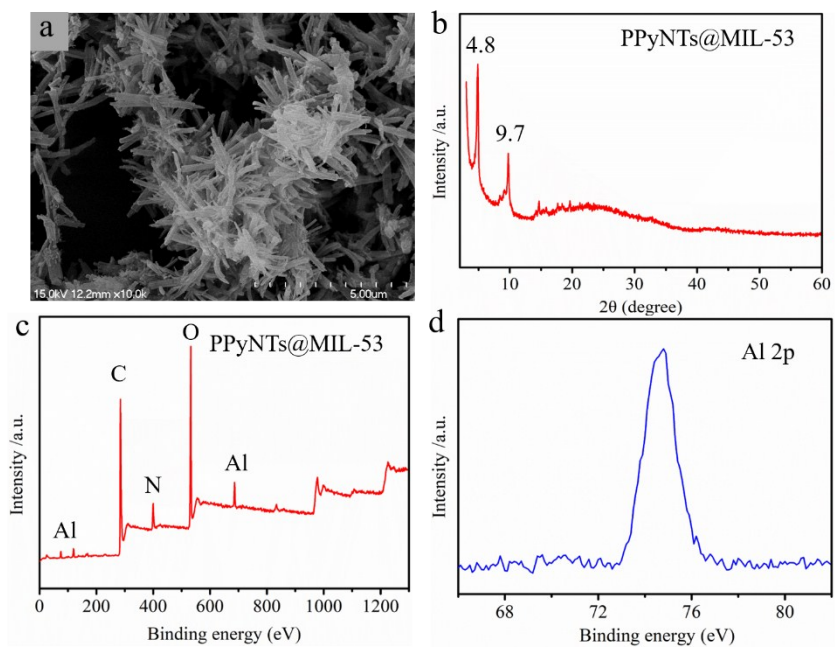
**Fig. S5** (a) SEM image, (b) PXRD, (c) XPS, and (d) high-resolution Cu 2p XPS of PPyNTs@HKUST-1.



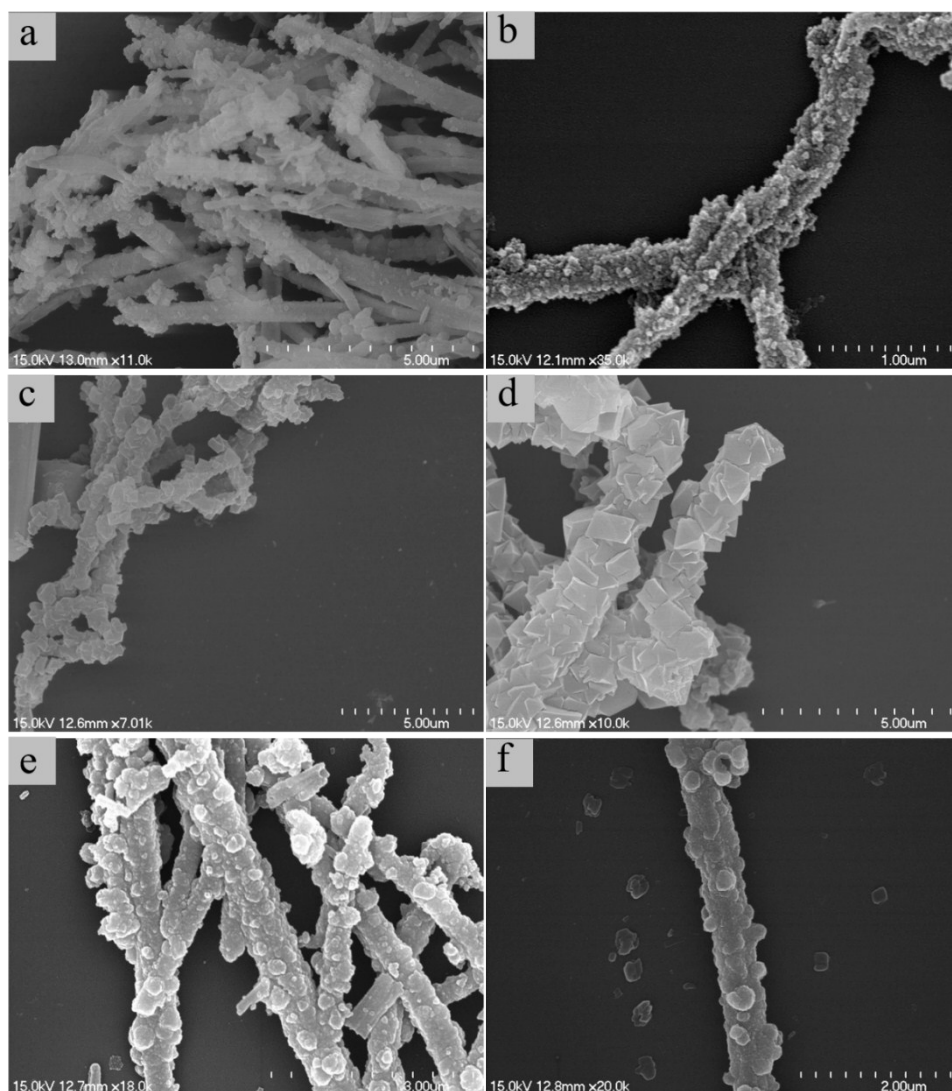
**Fig. S6** (a) SEM image, (b) PXRD, (c) XPS, and (d) high-resolution Mn 2p XPS of PPyNTs@Mn-BDC.



**Fig. S7** (a) SEM image and (b) PXRD of PPyNTs@MIL-100.

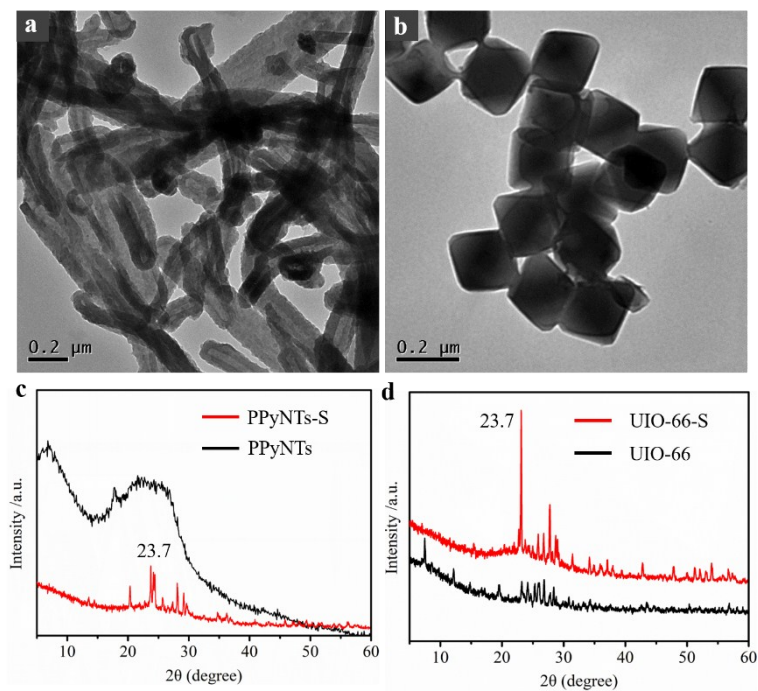


**Fig. S8** (a) SEM image, (b) PXRD, (c) XPS, and (d) high-resolution Al 2p XPS of PPyNTs@MIL-53.

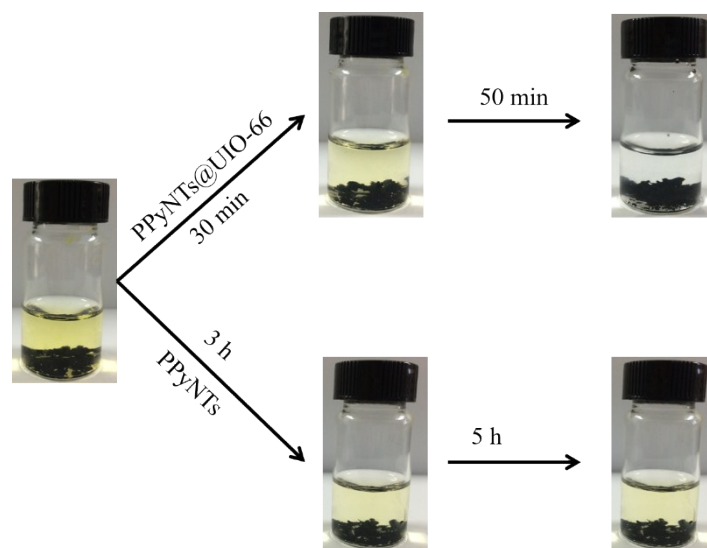


**Fig. S9** SEM images of (a,b) PPyNTs@MOF-125, (c,d) PPyNTs@V-BDC, and (e,f) PPyNTs@MIL-101.



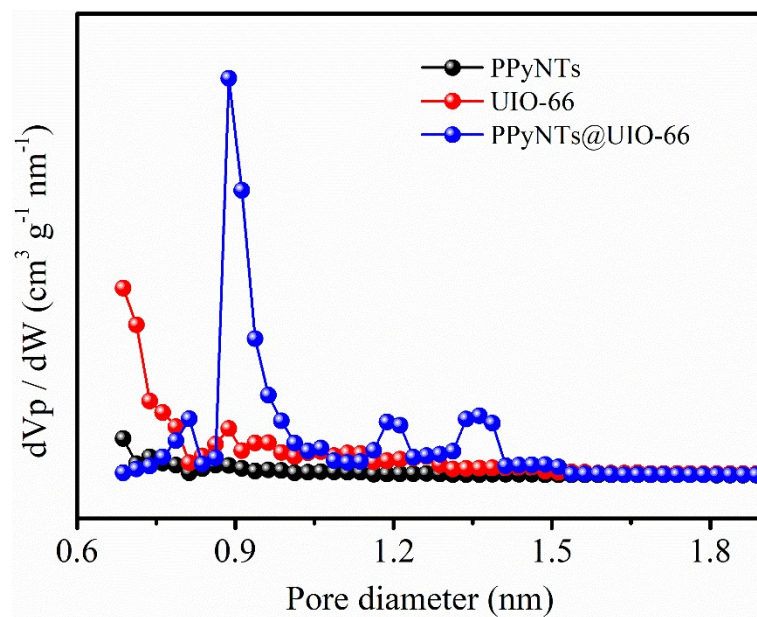


**Fig. S10** TEM images (a), (b) and PXRD patterns (c), (d) of PPyNTs-S and UIO-66-S cathodes, respectively.

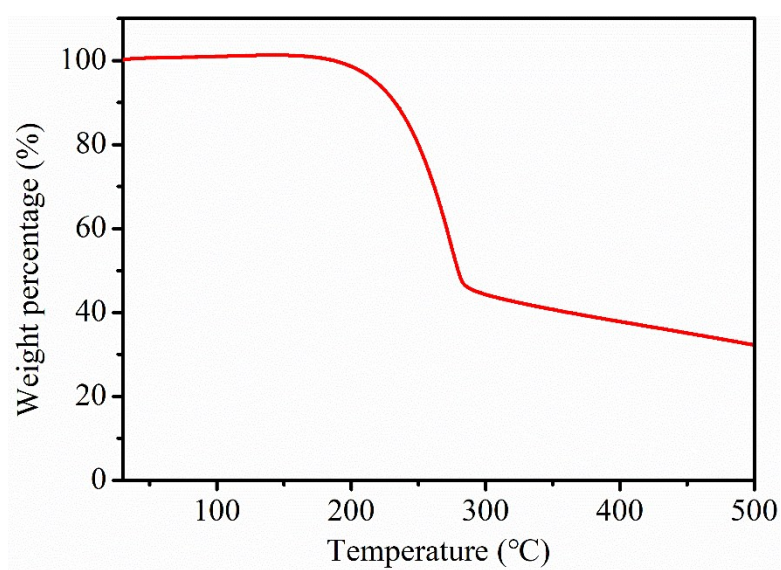


**Fig. S11** Adsorption ability tests of PPyNTs@UIO-66 and PPyNTs with polysulfides as a representative lithium polysulfide.

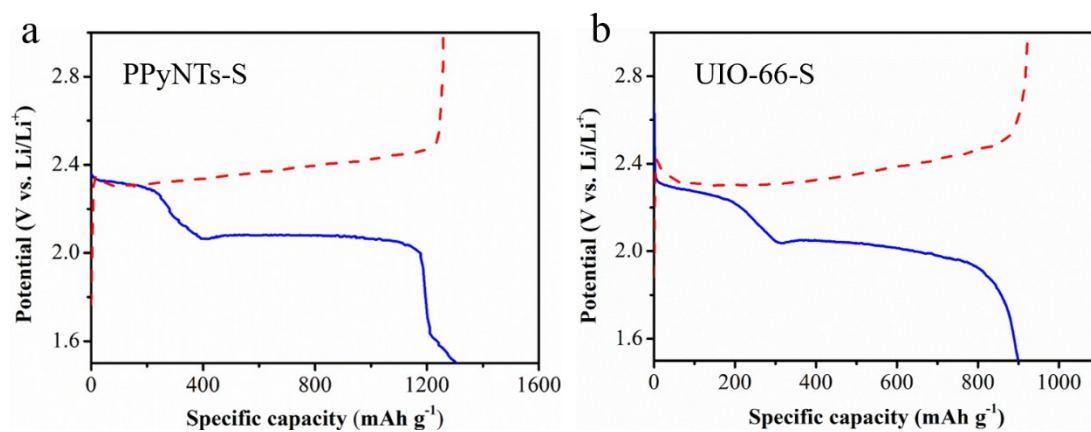




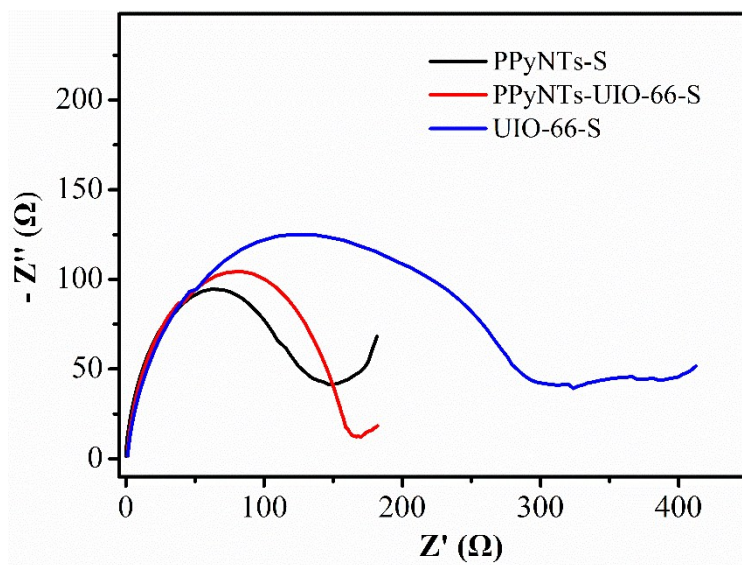
**Fig. S12** Pore size distribution of PPyNTs, UIO-66, and PPyNTs@UIO-66.



**Fig. S13** TG curve of PPyNTs at N<sub>2</sub> flow with a heating rate of 10 °C min<sup>-1</sup>.



**Fig. S14** Galvanostatic charge/discharge curves of PPyNTs-S and UIO-66-S cathode with area sulfur loading of 1.3 mg cm<sup>-1</sup> at a scan rate of 0.1 C.



**Fig. S15** Electrochemical impedance spectroscopy of PPyNTs-S, PPyNTs@UIO-66-S, and UIO-66-S cathodes.

**Table S2** Electrochemical cycling performances of the representative sulfur composite cathodes based PPy and MOF.

Sulfur structure	hosts	Sulfur loading (mg cm <sup>-2</sup> )	Current rate (C)	Initial capacity (mAh g <sup>-1</sup> )	Cycle number	Capacity retention (mAh g <sup>-1</sup> /C)	Ref.
ZIF-8		-	0.5	738	300	553	1
HKUST-1		-	0.5	431	300	286	1
NH <sub>2</sub> -MIL-53		-	0.5	568	300	332	1
UIO-66/CNTs		1.0	0.5 A g <sup>-1</sup>	925	300	765	2
Hollow Spheres	PPy	-	0.5	1426	100	620	3
Tubular PPy		-	-	1151	80	650	4
PPy-MWCNT		-	-	1275	100	725	5
Highly ordered nitrogen-rich mesoporous carbon		0.7-1.0	1.0	1209	200	600	6
Acetylene black		1.5	0.1	935	50	500	7
Carbon black nanoparticles		2.0	0.1	1250	100	865	8
Graphitized porous carbon		0.8-1.0	0.1	908	100	739	9
Porphyrin-derived graphene-based nanosheets		0.1	0.2	1212	300	798	10
PPyNTs@UIO-66		1.2	0.1	1225	200	998	This work

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