Supporting Information

Highly conductive PEDOT:PSS threaded HKUST-1 thin films

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Experiment section:

Materials and Chemicals: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS), aminoethanol (AE), and 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3BTC) were purchased from Sigma Aldrich. Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was purchased from Acros Chemicals. Ultrapure water of 18.2 MΩ produced by a Millipore direct-Q system was used throughout the experiments.

Preparation of PEDOT:PSS@HKUST-1 composite thin film: The positively charged copper hydroxide nanostrands were synthesized by quickly mixing equal volume 4 mM copper nitrate aqueous solution with 1.6 mM AE aqueous solution at room temperature and aged for 24 hours. Diluted the purchased water soluble PEDOT:PSS solution by 500 times with water, 0.22 wt‰ PEDOT:PSS aqueous solution was obtained. The negatively charged PEDOT:PSS was easily fixed on the highly positively charged CHNs by simply mixing. Then the mixed solution was filtered on a porous polycarbonate (PC) substrate with a pore size of 200 nm, to form a PEDOT:PSS/CHNs composite thin film, which was further peeled off from PC substrate and transferred to a piece of clean glass (2.5 cm×2.5 cm) or ITO-glass (glass for conductivity measurement and ITO-glass for electro-chemical evaluation). The PEDOT:PSS@HKUST-1 composite thin film was prepared by immersing PEDOT:PSS/CHNs composite thin film into H_3BTC ethanol–water (vol:vol=1:1) solution at room temperature for 1h. By controlling the weight ratio of PEDOT:PSS to CHNs, PEDOT:PSS@HKUST-1 composite thin film with different amount of PEDOT:PSS were obtained. By controlling the weight ratio of PEDOT:PSS to CHNs (Mixing 6.44, 12.88, 19.32 ml PE-

DOT:PSS aqueous solution with 30 ml CHNs respectively) PEDOT:PSS@HKUST-1 composite thin film with different weight ratios of PEDOT:PSS to HKUST-1 (10 wt%, 20 wt% and 30 wt%, respectively) were obtained and denote as PPH-1, PPH-2, PPH-3.

Characterization: The morphology and structure analyses were characterized by SEM (Hitachi S-4800) equipped with X-ray energy dispersive analysis and transmission electron microscopy (TEM) (JEM 2100F) equipped with X-ray energy dispersive analysis (Oxford). The TEM samples were prepared from a resin embedded ultrathin section (EM UC7, LEICA) of the PPH membrane. The phase of the as-prepared thin film was characterized by powder XRD at 0.02° step at room temperature using an X'Pert PRO (PANalytical, Netherlands) instrument with Cu *Kα* radiation. FTIR spectroscopy was recorded on FTIR TENSOR 27 equipment. X-ray photoelectron spectroscopy (XPS, ESCALAB_250Xi X-ray photoelectron spectrometer), The N_2 sorption analysis was conducted with a Micromeritrics specific area analyzer (Micromeritics, 3Flex, SN#340) at 77 K. Electrical conductivity was obtained from CHI 660D electrochemical workstation and a four-point probe resistivity measurement system (RTS-8 Four Probes Tech).

Conductivity Evaluation:

(1) Two-probe method. Two Ag electrodes were evaporated onto the surface of the thin film on glass by ZHD-300S film preparation system (BEIJING TECHNOL CO. LTD) with current of 65 A. The linear sweep voltammetry measurements were carried out by using CHI660D electrochemical workstation. The electrical conductivity was calculated based on the measured physical dimensions of the samples (thin film samples: 300 μm (channel length) × 3 mm (width) ×3 μm (thickness for PEDOT:PSS@HKUST-1) using the equation $\sigma = L/RS$， where σ is the conductivity, L is the channel length (here is 300 μm), R is the resistance calculated from I-V plots of samples, and S is the cross-section of the flow transportation surface (here is 3 mm (width) ×3 μm).

(2) Four-point probe method. Four Ag electrodes were evaporated onto the surface of the thin film on glass by ZHD-300S film preparation system (BEIJING TECHNOL CO. LTD) with current of 65 A. The electrical conductivity was calculated by the equation $\sigma = 1/\rho = FI/2\pi LV$, where σ is the conductivity, ρ is the resistivity, L is the channel length (here is 300 μm), I is the electrical current, V is the applied voltage, F is a correction factor.

Electrochemical performance: In order to evaluate the electrochemical performance of PEDOT:PSS@HKUST-1 composite thin film used as electrode for supercapacitor. The PE-

DOT:PSS/CHNs composite thin film was transfer onto an ITO-glass (act as current collector), after reacting with H_3BTC ethanol–water (vol:vol=1:1) solution at room temperature for 1 hour, the PEDOT:PSS@HKUST-1 composite thin film on ITO-glass was obtained. It was directly used as the electrode without any additives. Electrochemical experiments for individual electrodes were performed in a three-electrode configuration with Pt foil as counter electrode, $Hg/HgCl_2$ as reference electrode and 1M Na_2SO_4 as electrolyte. The cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) data were recorded using a CHI660D electrochemical workstation (Chinstruments, China) at room temperature. The specific capacitance (C) of a half-cell supercapacitor electrode calculated from the galvanostatic charge–discharge(GCD) curves by following equation $C = \frac{I\Delta t}{m\Delta V}$, where I is an applied current for the charge–discharge testing, m is the mass of the active composite materials, Δt is the discharging time, and ΔV is the potential window excluding the iR drop.[1]

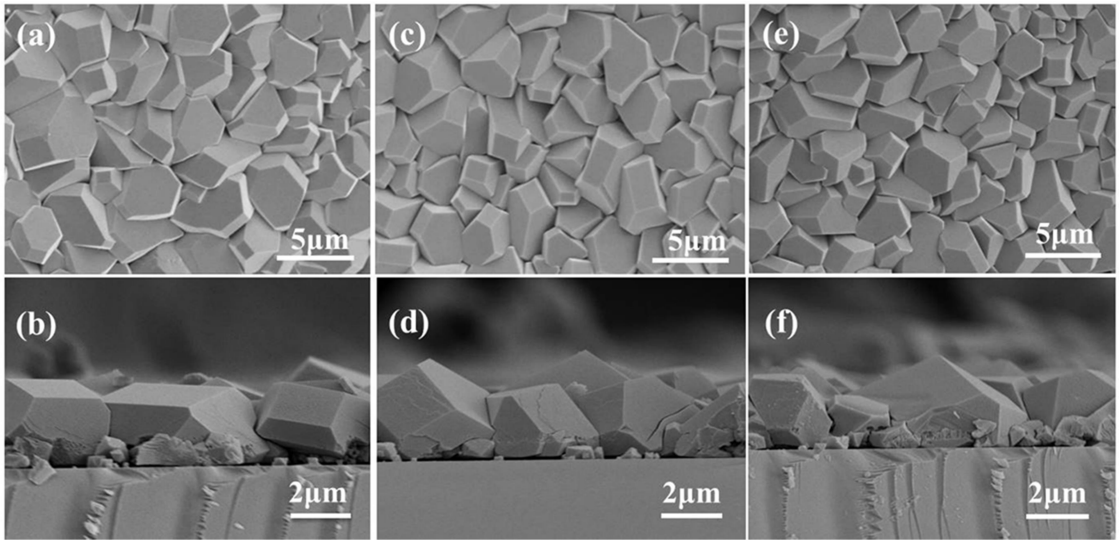

Fig. S1 (a, b), (c, d) and (e, f) are the corresponding surface and Cross-Section SEM images of pristine HKUST-1 thin film, PPH-1 thin film and PPH-3 thin film, respectively.

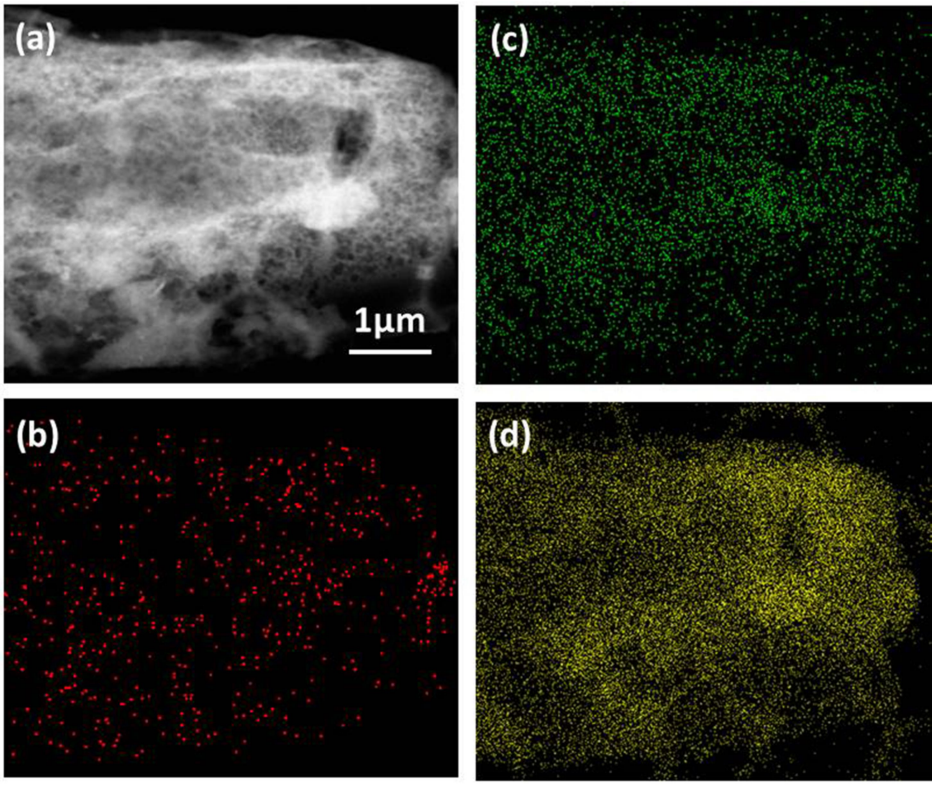

Fig. S2 (a) Cross-Section TEM image of PPH-2 thin film. **(b, c, d)** The distribution of element S (b), element Cu (c) and element C (d) in EDS mapping of (a).

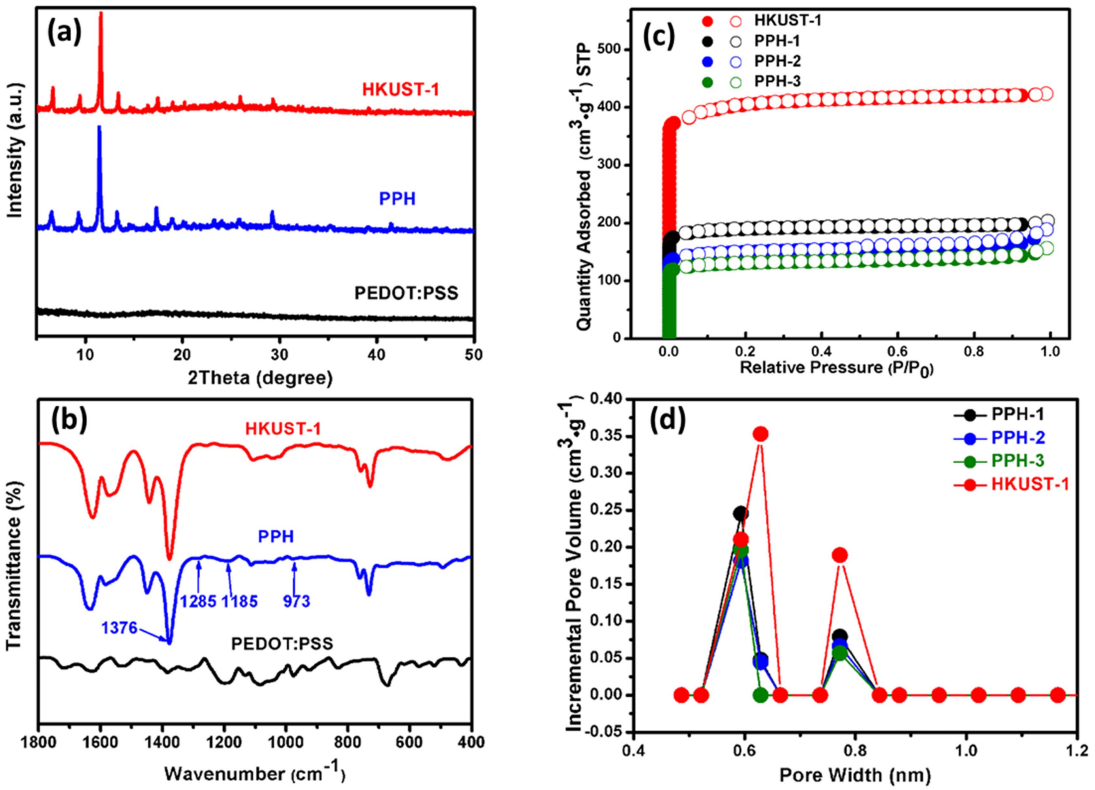

Fig. S3 (a, b) XRD patterns (a) and FTIR spectra (b) of pristine HKUST-1, PPH and PEDOT:PSS. **(c)** BET surface area and **(d)** Pore size distribution of pristine HKUST-1, PPH-1, PPH-2 and PPH-3, respectively.

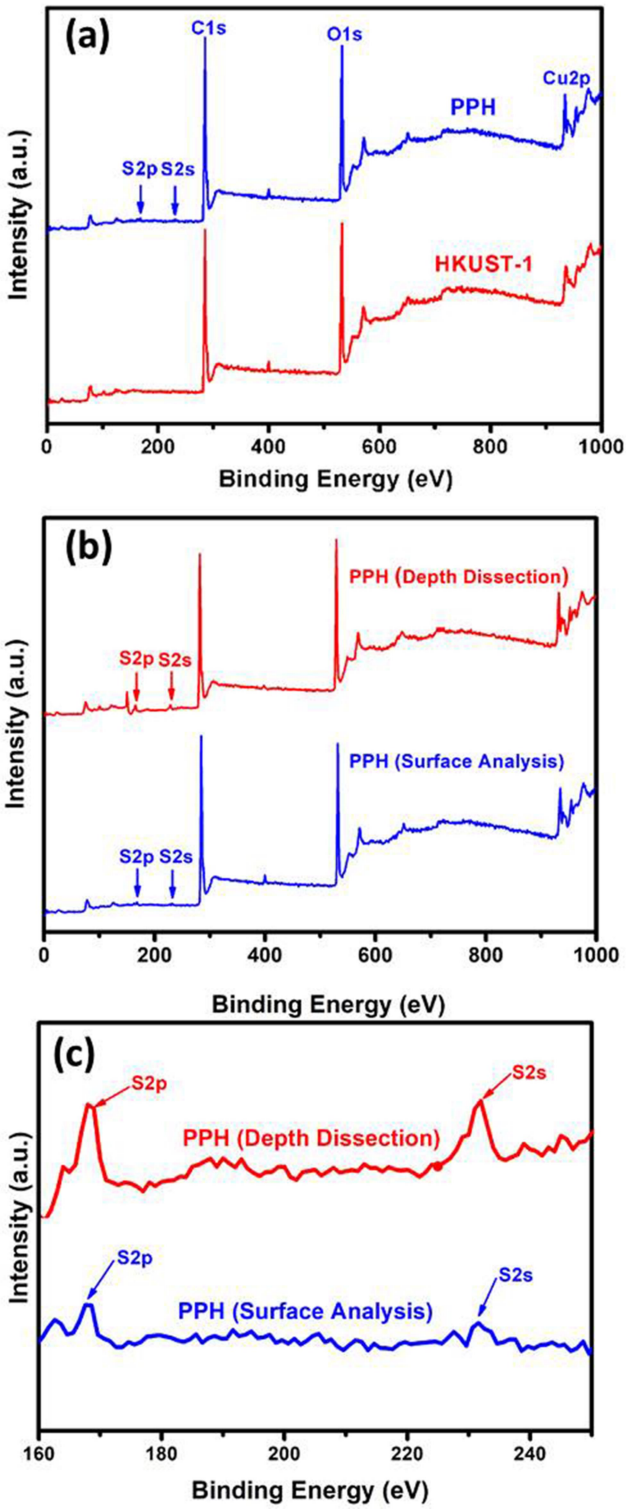

Fig. S4 (a) XPS spectra of PPH and HKUST-1. **(b)** XPS spectra of PPH thin film before and after using the depth dissection method of XPS. **(c)** Magnified spectra of PPH in (b).

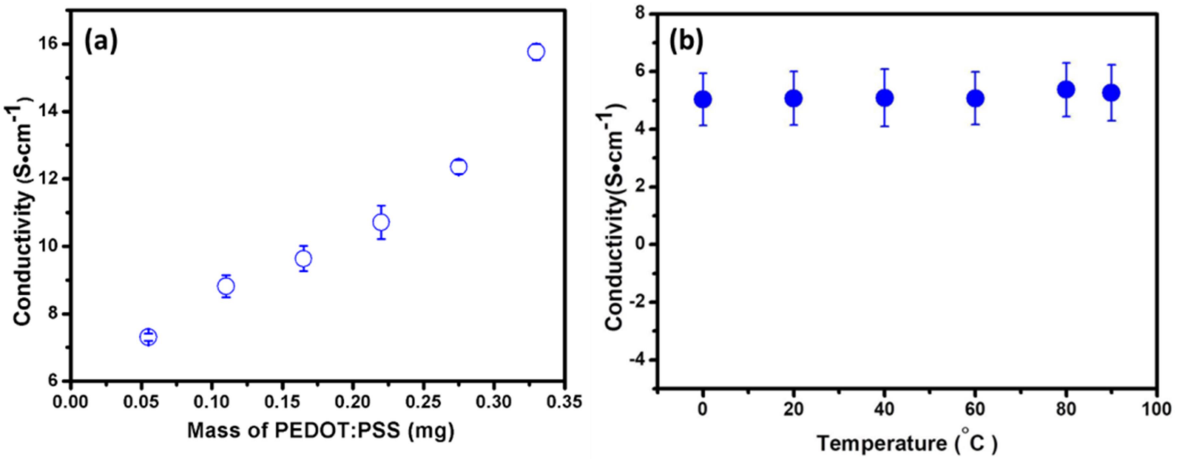

Fig. S5 (a) Conductivity of pure PEDOT:PSS thin films drop casting and drying on glass with different mass that equal to the mass of PEDOT:PSS contained in PPHs with different weight percent of PEDOT:PSS(5%, 10%, 15%, 20%, 25% and 30%, respectively). **(b)** Conductivity of PPH-2 at different temperature.

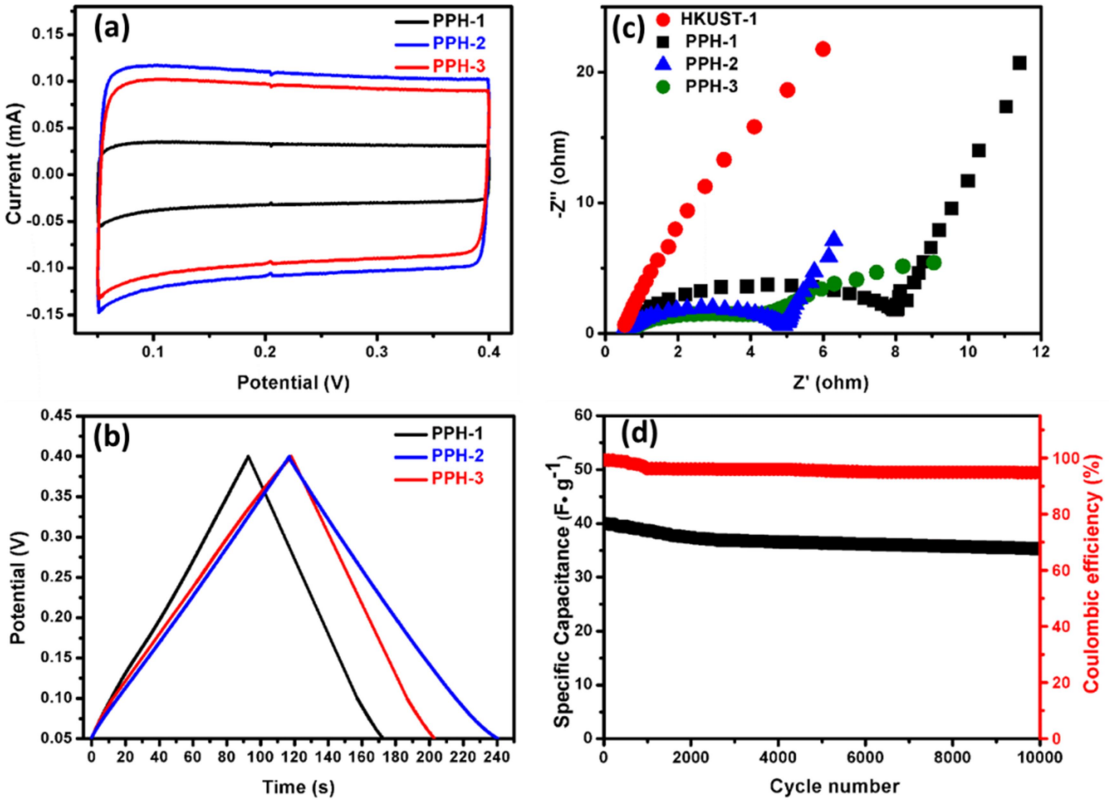

Fig. S6 (a) CV curves of PPH-1, PPH-2 and PPH-3 at 10 mV/s. **(b)** GCD curves of PPH-1, PPH-2 and PPH-3 at 0.1 A/g. **(c)** EIS spectra of pristine HKUST-1, PPH-1, PPH-2 and PPH-3. **(d)** Cycling performance of PPH-2.

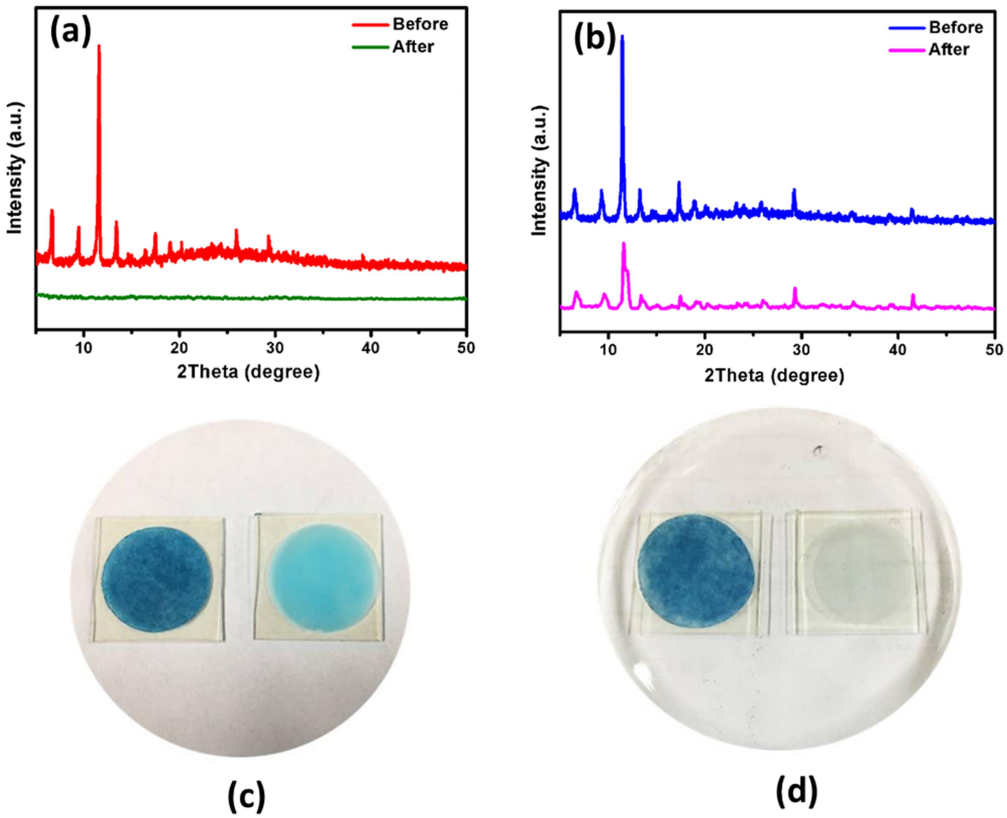

Fig.S7 (a,b) XRD patterns of pristine HKUST-1 (a) and PPH (b) thin film before and after immersing in 1M Na_2SO_4 for 4h. **(c)** The image of original PPH-2 and pristine HKUST-1 thin film. **(d)** The images of PPH-2 and pristine HKUST-1 thin film after immersing in 1M Na_2SO_4 for 4 hours.

Table S1. Conductivities of PEDOT:PSS@HKUST-1 thin film measured by different methods.

Weight percent of PEDOT:PSS in compound [wt%]	Conductivity [S cm^{-1}] (2-contact probe method)	Conductivity [S cm^{-1}] (4-point probe method)
0	6.90×10^{-8}	6.95×10^{-8}
10%	0.06753	0.06897
20%	5.528	5.617
30%	13.68	13.78

Table S2. Specific capacitances of different thin films calculated by GCD at 0.1 A/g .

Samples	Weight [mg]	Specific capacitance of thin films [$F\ g^{-1}$]	Calculated Specific capacitance of HKUST-1 [$F\ g^{-1}$] [a]	R_{ct} [Ω]	BET Surface Area [$m^2\ g^{-1}$]	Micropore volume [$m^3\ g^{-1}$]
HKUST-1	1.1	0.160	0.160	265.1	1235.1	0.5391
PPH-1	1.2	26.456	28.86	8.169	691.5	0.2656
PPH-2	1.3	39.943	47.202	5.946	547.5	0.2035
PPH-3	1.4	29.895	38.043	4.584	398.4	0.1779

[a]. The capacitance of HKUST-1 in PPH was calculated according to the equation $C_{PPH}\times m_{PPH}=C_{HKUST\text{-}1}\times m_{HKUST\text{-}1}+C_{PEDOT:PSS}\times m_{PEDOT:PSS}$, where C_{PPH} is the specific capacitance of PPH ($F\ g^{-1}$); $m_{HKUST\text{-}1}$ and $m_{PEDOT:PSS}$ are the masses of HKUST-1 and PEDOT:PSS in PPH, respectively; $C_{HKUST\text{-}1}$ is the specific capacitance of HKUST-1 in PPH ($F\ g^{-1}$), and $C_{PEDOT:PSS}$ is the specific capacitance of PEDOT:PSS ($F\ g^{-1}$).

Table S3. Specific capacitances of PPH-2 calculated by GCD at different current densities.

Current density [$A\ g^{-1}$]	Specific capacitance of thin films [$F\ g^{-1}$]
0.1	39.943
0.2	33.829
0.5	32.471
1	31.029
2	28.686

Notes and references

1 A. Ghosh and Y. H. Lee, *Chemsuschem*, 2012, **5**, 480-499.