Supporting Information

PANa/Covalent Organic Framework Composites with Improved Water Uptake and Proton Conductivity

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Materials and physical measurements.

All the chemical reagents were commercially available and used without further purification. 1,3,5-Triformylphloroglucinol (99.9%) was bought from Sigma Aldrich (China). Hydrazine hydrate (80% weight in water) and ammonium persulphate were purchased from Sinopharm Chemical Reagent Co., Ltd. Acrylic acid (99%) and N, N'-methylene diacrylamide (99%) were supplied by Sahn Chemical Technology (Shanghai) Co., Ltd. 1,4-Dioxane was obtained from (>99.5%) Tianjin Fuyu Fine Chemical Co., Ltd.

Synthesis of UCOF

UCOF was synthesized according to a previous report.[1] 1,3,5-triformylphloroglucinol (21.0 mg, 0.1 mmol) and hydrazine hydrate (0.01 mL 80% weight in water, 0.15 mmol) were dissolved in deionized water (1 mL) in a glass ampoule. This mixture was sonicated for 10 min in order to obtain a homogenous dispersion which was then degassed via three freeze-pump-thaw cycles (vacuum <50 mTorr) in a liquid nitrogen bath. The tube was sealed off and then heated at 120 °C for 20 hours to yield a red solid at the bottom of the ampoule. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 °C for 10 hours to afford a red powder in ~80% isolated yield.

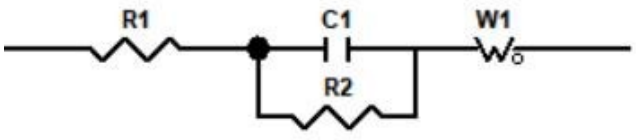
Synthesis of PANa@UCOF-x

acrylic acid, ammonium persulphate, N, N'-methylene diacrylamide were utilized as monomer, initiator, cross-linker, respectively.[2] Specifically, 3.6 mL acrylic acid was mixed with 5 mL deionized water to form solution A. 2 g NaOH was dissolved in 5 mL deionized water to form solution B. The solution B was added into solution A dropwise with stirring and ice-bath cooling. Then, 55 mg ammonium persulphate was added into the mixed solution, followed with 2 mg N, N'-methylene diacrylamide added.

50 mg of ground UCOF was weighed on a glass slide, the above mixed solution (50, 100, 150 μL) was added dropwise to the UCOF, and mixed evenly with a glass rod. Subsequently, a typical reaction of radical polymerization proceeded, and the mixture was placed in an oven at 65°C for 2 hours to allow PANa to grow in situ on UCOF. After the reaction is completed, the solid was washed with deionized water for 3 times which to remove excess initiator, cross-linker and sodium hydroxide, then dried under dynamic vacuum at 65 °C for 2 hours. The product was collected and weighed.

Proton conductivity measurement

The as-synthesized sample was placed in mold and pressed into a pellet with a diameter of 3 mm (UCOF and PANa@UCOF-x) and a thickness range of 1-2 mm by a tableting machine. The pellet was placed in the center of the glass pellet and fixed horizontally with two 20 cm of gold wires, and two sides of the pellet were coated with silver glue, and then waited for about 30 minutes to dry. Impedance analysis was performed with a 1260A Impedance/Gain-Phase Analyzer from 10 MHz to 0.1 Hz with an input voltage 200 mV in a constant temperature and humidity, which were controlled using a BPS-50CL humidity control chamber. Each sample was pressed at least three tablets, and repeated cyclic tests were performed on each tablet. Typically, the impedance at each temperature were measured after equilibration for a period of 6-10 hours. The resistance values were obtained by fitting the impedance profile using zview software. The circuit equivalent used for fitting is as follows:



R1 corresponds to the resistances of wire and electrode, while R2 accounts for the bulk resistance of the pellet. Proton conductivity (σ, S cm^{-1}) of each sample was obtained by the following equation:

$$\sigma = \frac{l}{RS}$$

Where l and S are the length (cm) and area (cm^2) of the pellet, respectively, and R is the intrinsic resistance value (Ω) of the material fitted by the equivalent circuit of the first semicircle using zview software. The activation energy (E_a) of the material is estimated according to the following Arrhenius equation:

$$\sigma T = \sigma_0 \, exp(-\frac{E_a}{k_B T})$$

Where σ_0 is the pre-exponential factor, T is the temperature, and k_B is the Boltzmann constant.

Water uptake and swelling ratio of PANa@UCOF-x pellets

The pellet' water uptake was calculated from the weight difference between the dry pellet and wet pellet (eqn (2.1)), and their swelling ratio was tested by measuring the difference of length and thickness between dry and wet pellets (eqn (2.2)). The dry and wet pellets were prepared in the same way as those used for proton conduction measurements.

$$Water\ uptake(\%) = 100 \times \frac{W_{wet} - W_{dry}}{W_{dry}} \qquad (2.1)$$

$$Swelling\ ratio(\%) = 100 \times \frac{L_{wet} - L_{dry}}{L_{dry}} \qquad (2.2)$$

Where W_{dry} is the weight of the pellet dried in a vacuum until the weight is constant, and W_{wet} is the weight of the pellet by putting it under 95% RH and 80℃ for different time.

The water vapor adsorption tests

The water vapor adsorption and desorption curves were measured by IGA-100B intelligent gravimetric analyzer of (Hiden) Company of Hyde Company, UK. The test of UCOF and PANa@UCOF-10 was performed after heating the sample for 5 hours at 100 ℃ under vacuum. At every humidity point, the samples were stabled for different time to reach adsorption equilibrium.

Other measurements

The date of powder X-ray diffraction (PXRD) were recorded on an X-Pert PRO MPD diffractometer with Cu-Kα radiation (l = 0.15418 nm). Thermal gravimetric analysis (TGA) was used by Mettler Toledo thermal analyzer with a heating rate of 10 ℃ min^{-1} in the range of 40-900 ℃ under N_2 atmosphere. Elemental analysis was conducted on a PerkinElmer 240C elemental analyzer for C, H, and N determination. N_2 adsorption and desorption tests were performed on a Tristar 2460 surface area analyzer. Field-emission scanning electron microscopy (FESEM) images were obtained on a Hitachi SU-8000 instrument.

Table S1. The water uptake and swelling ratio of PANa@UCOF-x under 95% RH and 80 ℃ for different times.

PANa/UCOF (%)	Water uptake[%]			Swelling ratio[%]		
	1h	6h	12h	1h	6h	12h
UCOF	2.61	2.81	2.82	4.31	4.43	4.71
PANa@UCOF-5	4.11	4.21	4.51	5.28	5.31	5.45
PANa@UCOF-10	6.04	6.31	6.38	6.24	6.28	6.53
PANa@UCOF-15	9.43	9.53	9.83	7.41	7.45	7.54
PANa@UCOF-20	12.55	12.51	12.75	8.17	8.27	8.66
PANa@UCOF-25	15.82	15.84	15.88	9.29	9.29	9.34
PANa@UCOF-30	20.41	21.61	20.82	10.41	10.51	10.54
PANa@UCOF-35	25.30	26.30	26.90	11.11	11.15	11.18
PANa@UCOF-40	34.11	34.63	34.94	12.13	11.74	11.82
PANa@UCOF-50	50.65	51.65	51.85	13.33	13.55	13.81
PANa@UCOF-60	81.38	81.46	81.98	14.57	14.68	14.74
PANa@UCOF-70	126.27	128.28	130.47	16.21	16.23	16.94
PANa@UCOF-80	181.21	183.21	184.71	17.35	17.65	18.33

Table S2. The water uptake, swelling ratio and proton conductivity of PANa@UCOF-x and reference materials under 95% RH and 80 ℃.

Material	Water uptake[%]	Swelling ratio[%]	σ (S cm^{-1})	
UCOF	2.6	4.3	5.93×10^{-7}	This work
PANa@UCOF-10	6.0	6.3	1.61×10^{-2}	This work
PANa@UCOF-28	15.9	9.3	5.13×10^{-2}	This work
PANa@UCOF-40	34.1	12.1	1.13×10^{-1}	This work
SPAEK-35	8.7	3.8	1.89×10^{-2}	Ref 3
L-SPAEK	15.1	6.6	1.64×10^{-2}	Ref 4
SBP-Cz-10	21.1	8.2	2.93×10^{-2}	Ref 5

Ph-SPEEKK	46.7	14.6	7.80×10^{-2}	Ref 6
Nafion® 117	38.0	17.2	1.00×10^{-1}	Ref 7

Table S3. Humidity-dependent proton conductivity (S cm^{-1}) of UCOF and PANa@UCOF-x.

Conditions	UCOF	PANa@UCOF-10	PANa@UCOF-28	PANa@UCOF-40
80°C, 50%RH	9.06×10^{-9}	1.20×10^{-5}	2.22×10^{-4}	5.06×10^{-4}
80°C, 60%RH	1.98×10^{-8}	6.01×10^{-5}	1.45×10^{-3}	3.45×10^{-3}
80°C, 70%RH	4.13×10^{-8}	1.98×10^{-4}	5.90×10^{-3}	1.24×10^{-2}
80°C, 80%RH	9.39×10^{-8}	7.10×10^{-4}	1.69×10^{-2}	3.30×10^{-2}
80°C, 90%RH	3.04×10^{-7}	5.31×10^{-3}	3.54×10^{-2}	7.93×10^{-2}
80°C, 95%RH	5.93×10^{-7}	1.61×10^{-2}	5.13×10^{-2}	1.13×10^{-1}

Table S4. Proton conductivity (S cm^{-1}) of UCOF, PANa and PANa@UCOF-x under 50% RH and 80 °C.

UCOF	PANa	PANa@UCOF-10	PANa@UCOF-28	PANa@UCOF-40
9.06×10^{-9}	1.81×10^{-6}	1.20×10^{-5}	2.22×10^{-4}	5.06×10^{-4}

Table S5. Temperature-depedent proton conductivity (S cm^{-1}) of UCOF and PANa@UCOF-x.

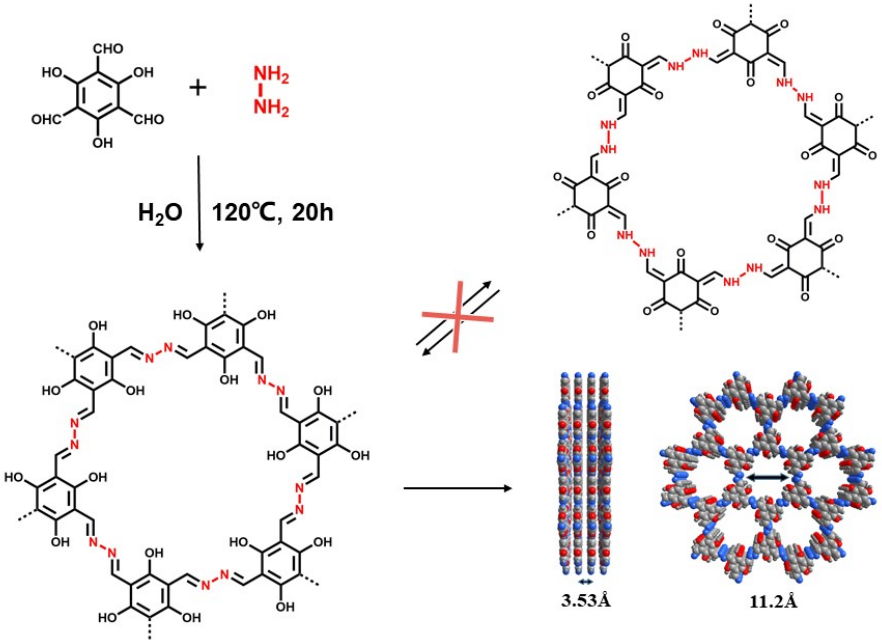
Conditions	UCOF	PANa@UCOF-10	PANa@UCOF-28	PANa@UCOF-40
40°C, 95%RH	1.63×10^{-7}	2.48×10^{-3}	2.56×10^{-2}	2.93×10^{-2}
50°C, 95%RH	2.19×10^{-7}	3.49×10^{-3}	3.07×10^{-2}	3.83×10^{-2}
60°C, 95%RH	3.07×10^{-7}	5.15×10^{-3}	3.56×10^{-2}	4.96×10^{-2}
70°C, 95%RH	4.42×10^{-7}	7.21×10^{-3}	4.04×10^{-2}	6.29×10^{-2}

80°C, 95%RH	5.93×10^{-7}	1.61×10^{-2}	5.13×10^{-2}	1.13×10^{-1}

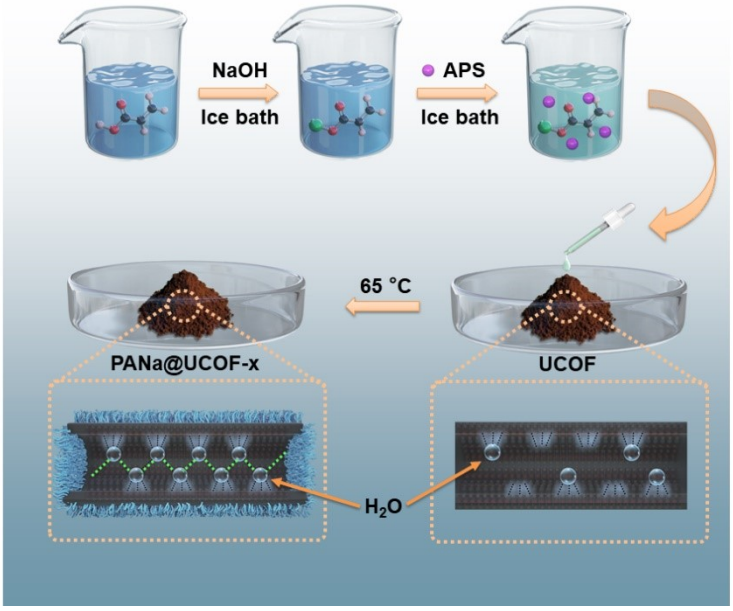
Table S6. Comparison of proton conductivity of the PANa@UCOF-x and other COF-based materials.

Compound name	σ (S cm^{-1})	Year	Refs.
PA@Tp-Azo	9.90×10^{-4} (25 ºC, 98% RH)	2014	8
PA@Tp-Stb	2.30×10^{-5} (60°C, 98% RH)		
EB-COF:PW_{12}	3.32×10^{-3} (25°C, 97% RH)	2016	9
NUS-9 (COF)	1.24×10^{-2} (25 ºC, 97% RH)	2016	10
NUS-10 (COF)	3.96×10^{-2} (25 ºC, 97% RH)		
RT-COF-1	1.83×10^{-5} (40 ºC, 100% RH)	2017	11
LiCl@RT-COF-1	6.45×10^{-3} (40 ºC, 100% RH)		
PTSA@Tp-Azo	7.80×10^{-2} (80 ºC, 95% RH)	2018	12
PTSA@TpBpy	6.20×10^{-2} (80 ºC, 95% RH)		
PTSA@$TpBD(Me)_2$	5.30×10^{-2} (80 ºC, 95% RH)		
aza-COF-2	8.78×10^{-6} (50 ºC, 97% RH)	2019	13
aza-$COF\text{-}2_H$	4.80×10^{-3} (50 ºC, 97% RH)		
H_3PO_4@NKCOF-1	1.13×10^{-1} (80 ºC, 98% RH)	2019	14
H_3PO_4@NKCOF-2	4.28×10^{-2} (80 ºC, 98% RH)		
PA@NKCOF-2-M	1.38×10^{-2} (80 ºC, 98% RH)	2020	15
COF-1-Li	2.70×10^{-2} (80 ºC, 98% RH)	2020	16
COM (COF membrane)	1.60×10^{-3} (90 ºC, 100% RH)	2021	17
S-COF-1	7.50×10^{-4} (25 ºC, 95% RH)	2021	18
S-COF-2	1.50×10^{-2} (25 ºC, 95% RH)		
etidronic acid@COF-300	6.50×10^{-1} (90 ºC, 100% RH)	2021	19
UCOF	5.93×10^{-7} (80 ºC, 95% RH)	-	This work
PANa@UCOF-10	1.61×10^{-2} (80 ºC, 95% RH)	-	This work

PANa@UCOF-28	5.13×10^{-2} (80 ºC, 95% RH)	-	This work
PANa@UCOF-40	1.13×10^{-1} (80 ºC, 95% RH)	-	This work



Scheme S1. Scheme for the synthesis of UCOF.



Scheme S2. Scheme for the synthesis of PANa@UCOF-x and the formation of ordered hydrogen bond chains in PANa@UCOF-x.

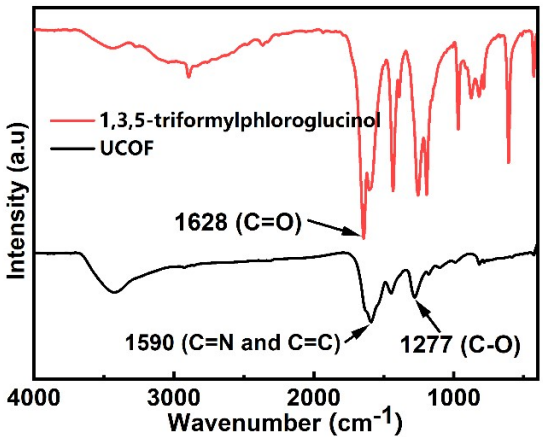


Figure S1. FT-IR spectra of UCOF and 1,3,5-triformylphloroglucinol.

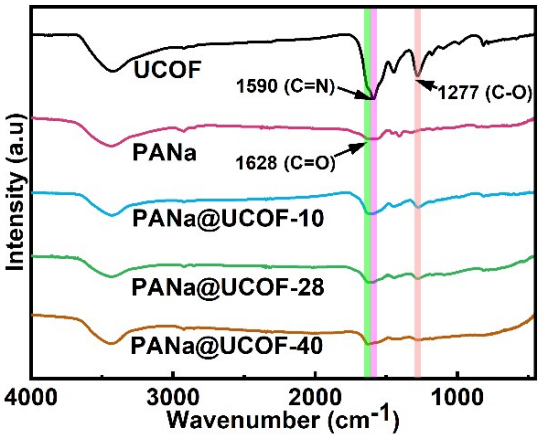


Figure S2. FT-IR spectra of UCOF, PANa, and PANa@UCOF-x.

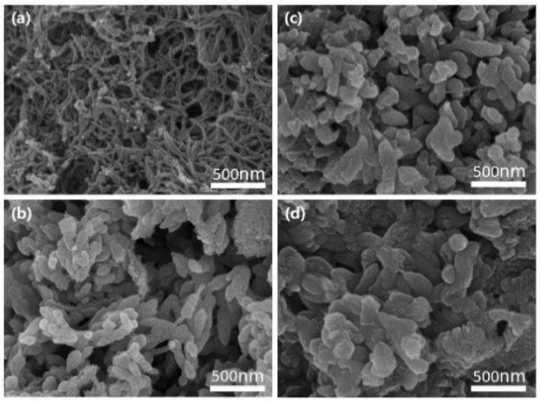


Figure S3. FESEM image comparison of (a) UCOF, (b) PANa@UCOF-10, (c) PANa@UCOF-28 and (d) PANa@UCOF-40.

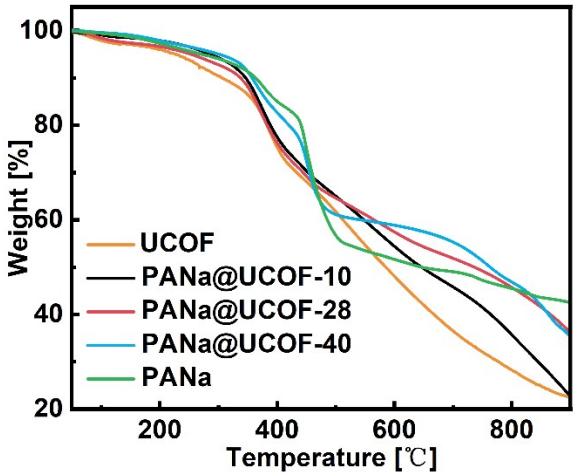


Figure S4. Thermal gravimetric analysis of UCOF, PANa@UCOF-10, PANa@UCOF-28 and PANa@UCOF-40, and PANa.

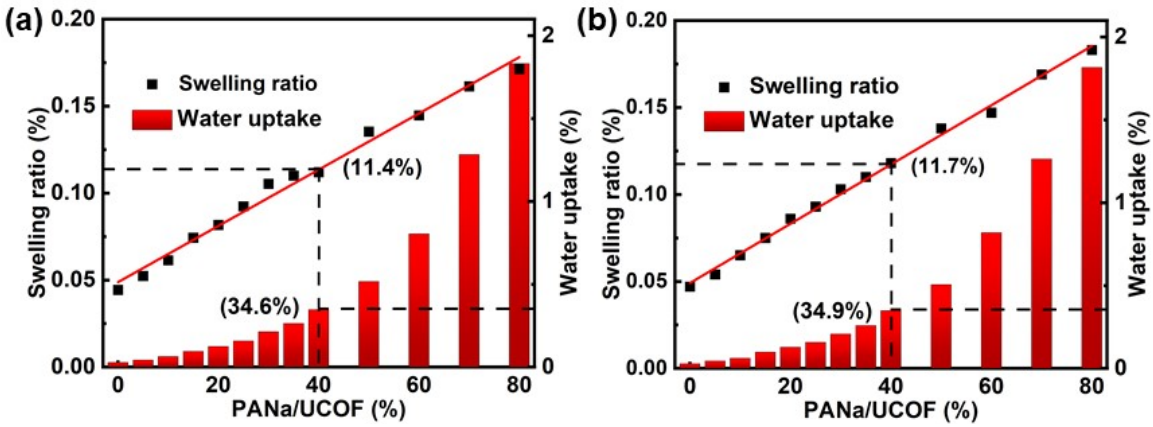


Figure S5. Water uptake and swelling ratio of different proportions of PANa@UCOF-x under 95% RH at 80℃ for 6 and 12 hours.

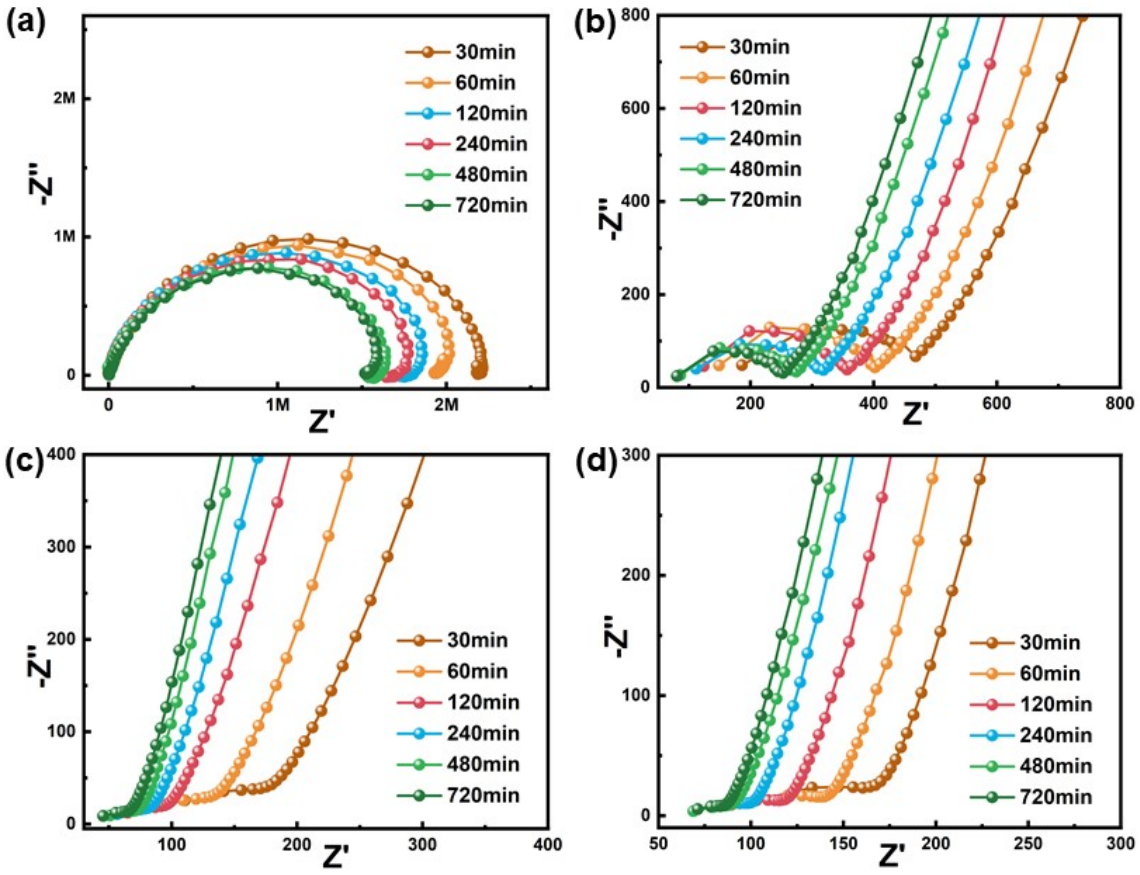


Figure S6. The time-dependent Nyquist plot of UCOF, PANa@UCOF-10, PANa@UCOF-28 and PANa@UCOF-40 at 80 °C and 95% RH.

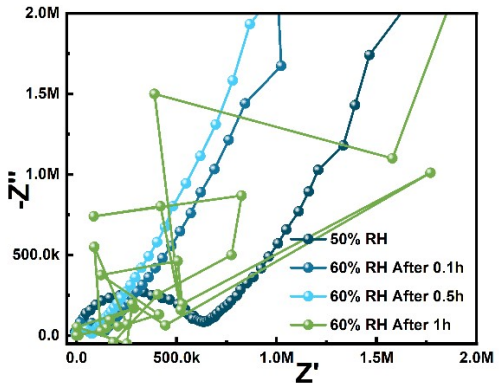


Figure S7. The humidity-dependent Nyquist plot of PANa at 80 °C.

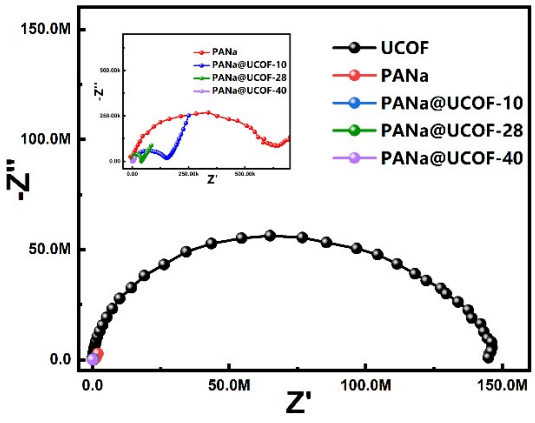


Figure S8. Nyquist plots of UCOF, PANa and PANa@UCOF-10, PANa@UCOF-28 and PANa@UCOF-40 under 50% RH at 80 ℃.

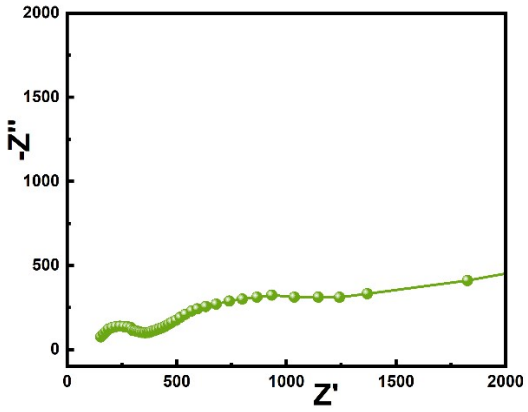


Figure S9. Nyquist plots of PANa and UCOF with weight ratio of 1:9 by directly grinding together.

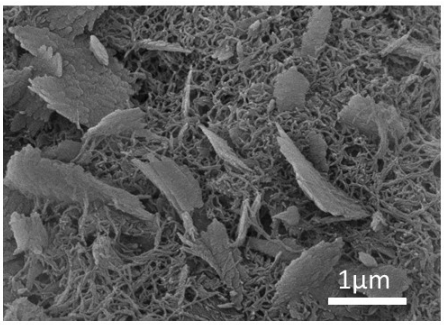


Figure S10. FESEM image of UCOF and 10% PANa by directly grinding together.

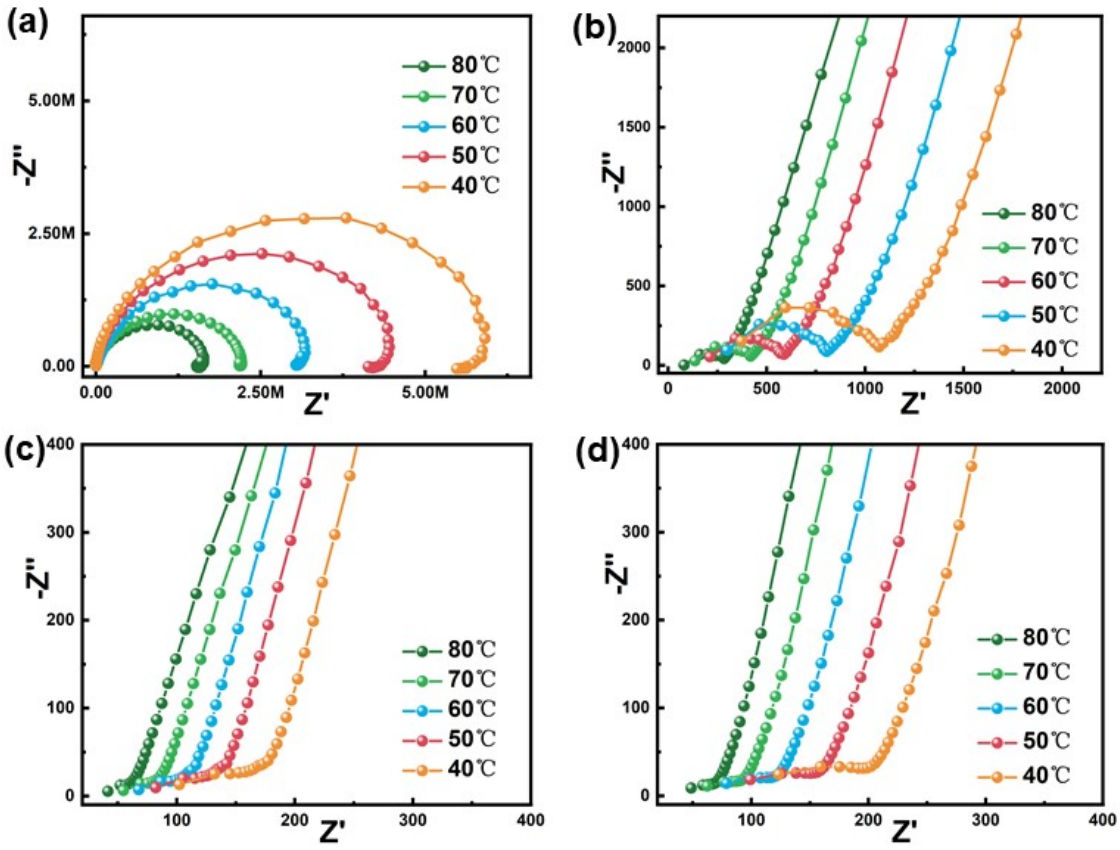


Figure S11. Temperature-dependent Nyquist plots of UCOF (a), PANa@UCOF-10 (b), PANa@UCOF-28 (c) and PANa@UCOF-40.

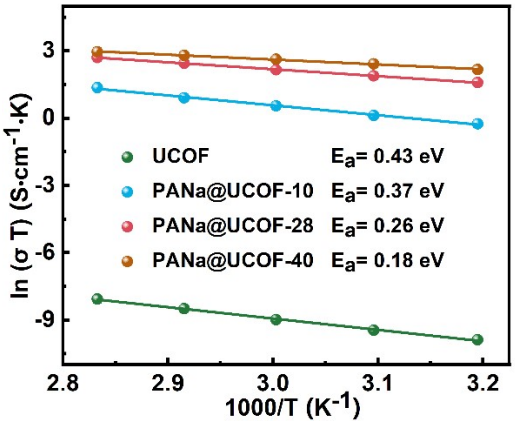


Figure S12. Arrhenius plots of UCOF, PANa@UCOF-10, PANa@UCOF-28 and PANa@UCOF-40 under 95%RH.

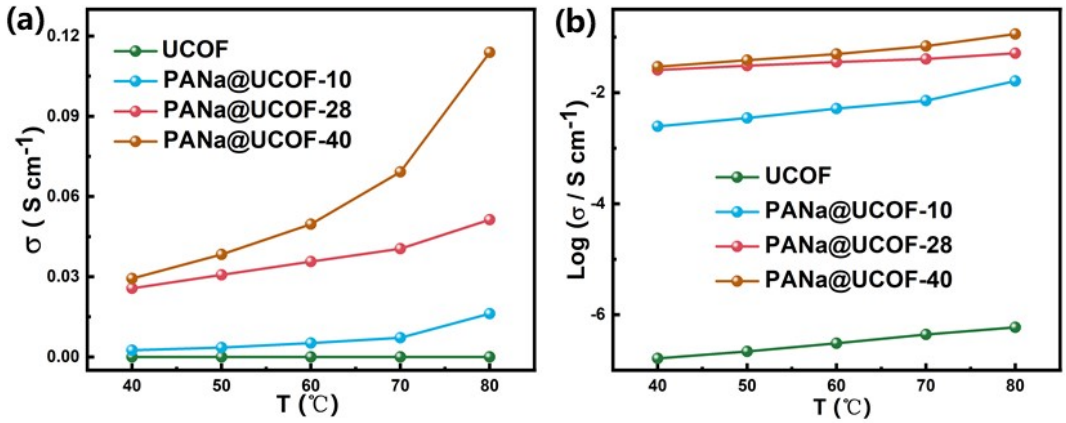


Figure S13. Proton conductivities (a), and Log-scaled proton conductivities (b) of UCOF, PANa@UCOF-10, PANa@UCOF-28 and PANa@UCOF-40 under 95% RH and different temperature.

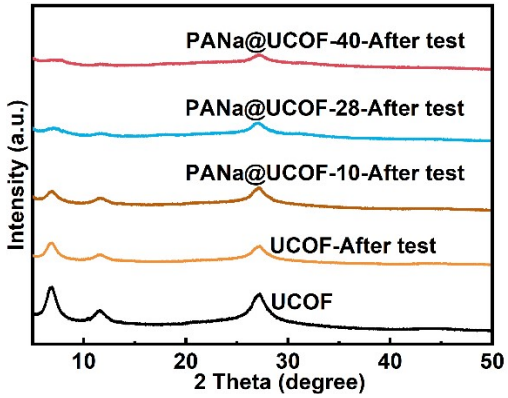


Figure S14. PXRD patterns of UCOF, PANa, PANa@UCOF-10, PANa@UCOF-28 and PANa@UCOF-40 after conducting impedance tests.

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