

Supporting Information

“Bubble-in-Bowl” Structured Metal Phosphide@N, P Codoped Carbon *via* Bio-Assisted Combustion Synthesis for High-Performance Potassium-Ion Hybrid Capacitor in a Wide Temperature Range

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Part I: Experimental details, Calculations & Discussions

S-1-1: Preparation of the TMP@NPC BIB composite

i) *Aspergillus oryzae* spore cultivation

The *Aspergillus oryzae* (*A. oryzae*) spore are cultivated in the Bio-organism Artificial Cultivation Laboratory of Harbin Normal University (HANU, 126°42'E, 45°24'N). The simplified process is showed in Figure S1. Firstly, the wasted rice is collected and cooked as the culture medium for the growth of *A. oryzae*. After inoculation with *A. oryzae* strain, the inoculated rice is transferred to the incubator with a constant temperature and humidity (25 °C, 65%) for a week. Next, the spores are harvest by filter screen several times to remove the residual moldy rice. Finally, the fallen spores are collected, purified and stored at 5~10 °C.

ii) Preparation of bio-precursor

Firstly, the cleaned spores are added to (0.5 mol L⁻¹) cobalt nitrate solution. The suspension was initially maintained at room temperature for three hours and then elevated to 45 °C for another eight hours. Then, the obtained suspension was centrifuged and washed three times. After that, the suspensions are frozen completely in liquid nitrogen and followed by freeze-dried for 24 hours. The resultant powders are denoted as the bio-precursors.

iii) Preparation of the CoP@NPC BIB composite

The bio-precursor was calcinated at 700 °C for four hours in the nitrogen atmosphere to achieve the final product.

iv) Preparation of Ni₂P@NPC BIB composite

The preparation of Ni₂P@NPC BIB was the same as the CoP@NPC BIB (S-1-1, *ii, iii*). In the first step, the nickel nitrate solution is used as the react solution to form the product.

v) Preparation of Fe₂P@NPC BIB composite

The preparation of Fe₂P@NPC BIB was the same as the CoP@NPC BIB (S-1-1, *ii, iii*). In the first step, the iron nitrate solution is used as the react solution to form the product.

S-1-2: Preparation of the reference samples

i) Preparation of the B-CoP reference sample

The commercial cobalt acetate was firstly oxidized in air at 450 °C for 3 hours to achieve the cobalt oxide. Then the obtained powder and NaH₂PO₂ with the mass ratio of 1:15 were put in two boats within a tube furnace, with NaH₂PO₂ placing at the upstream. Then the tube furnace was heat at 400 °C for 3 hours with the slow heating rate of 2 °C min⁻¹ to achieve the final product.

ii) Preparation of the M-CoP reference sample

The M-CoP reference sample was prepared by mixing the B-CoP sample with desirable activated carbon to achieve the same carbon content as the CoP@NPC BIB composite.

iii) Preparation of the R-CoP reference sample

Firstly, the cobalt nitrate and the citric acid were dissolved in the distill water to form a mixture. Then it was frozen-dried for 24 hours and the resultant powders were calcinated in N₂ atmosphere at 650 °C for 4 hours. The resultant intermediate product and excess

amount of NaH_2PO_4 were put in two boats within a tube furnace. Then the tube furnace was heat at $400\text{ }^\circ\text{C}$ for 3 hours with the slow heating rate of $2\text{ }^\circ\text{C min}^{-1}$ to achieve the final product.

S-1-3: Preparation of the bowl-like bio-derived carbon (MBC)

In the S-1-1-*i*, the collected spores were frozen completely in liquid nitrogen and followed by freeze-dried for 24 hours. The resultant powders were calcinated at $700\text{ }^\circ\text{C}$ for four hours in the nitrogen atmosphere to achieve the MBC sample.

S-2: Materials characterizations

Powder X-ray diffraction (XRD, Bruker D8/Germany) using $\text{Cu K}\alpha$ radiation was employed to identify the crystalline phase of the material. The morphology was observed with a scanning electron microscope (SEM, HITACHIS-4700) and a transmission electron microscope (TEM, JEOS-2010 PHILIPS). The element distribution of the sample was confirmed by energy dispersive X-ray detector (EDX). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was employed to measure the chemical or electronic state of each element. Thermogravimetric analysis (TGA, NETZSCH STA 449C) was used to investigate the carbon content of the sample. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 2010. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

S-3: Electrochemical measurements

S-3-1: Electrochemical properties in potassium half cell

The electrochemical characteristics were measured in CR2032 coin cells. Active material, acetylene black, and poly(vinylidene fluoride) were mixed at a weight ratio of 80:10:10

in N-methyl-2-pyrrolidinone solvent to a uniform slurry. The electrodes were prepared by covering above slurry onto the stainless-steel sheet and further dried in a vacuum drying oven at 80 °C for 12 h. The fresh metal potassium film was used as the counter electrode and the Whatman glass microfiber filters were used as the separator. The electrolytes of 1M KPF₆ dissolved in ethylene carbonate and diethyl carbonate (EC/DEC = 1:1 in volume). The coin cells were assembled in an Ar filled glovebox. Galvanostatic charge/discharge tests and galvanostatic intermittent titration technique (GITT) were performed using a Land battery testing system (Wuhan, China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted using a Zivelab electrochemical workstation.

S-3-2: Electrochemical properties in full PIHC

The CoP@NPC BIB//MBC PIHC were fabricated with the CoP@NPC BIB electrode as anode and the MBC electrode as cathode. Glass fiber was used as the separator. 1M KPF₆ in a mixture of EC/DEC (1:1, volume ratio) were used as electrolyte. Before the assembling of the full device, the anode was activated in a half cell by five charge/discharge cycles. The cathode/separator/anode sandwich was put into an aluminum plastic bag to assemble the sandwich-type cell. After the electrolytes were injected, the cells were vacuum sealed.

S-3-3: Electrochemical properties in modified PIHC

i) Preparation of the polymer electrolyte

The polymer electrolyte membrane was prepared by a facile method.^{S1} In a typical process, the perfluorinated sulfonic resin power, K form (PFSA-K) was initially prepared

by dissolving the PFSA-Li in hot KOH solution. The product was washed and dried in the vacuum oven to achieve the PFSA-K powder (Figure S21a). Next, obtained PFSA-K powder was dissolved in DMF to achieve the homogeneous solution, followed by adding the liquid electrolyte (Figure S21b). After homogeneous solution was achieved, the solution blade coating method was employed and the polymer membrane was obtained (Figure S21c~f).

ii) Assembling the modified PIHC

Firstly, the prepared polymer membrane was wetted by the ethylene carbonate and propylene carbonate mixed solution. Next, the modified PIHC device was assembled by the CoP@NPC BIB anode, the MBC cathode and the polymer electrolyte. The anode was activated in a half cell before assembling the full cell. The coin-type cells were assembled in an Ar filled glovebox. Galvanostatic charge/discharge tests of both the PIHC and the modified devices were performed using a Land battery testing system (Wuhan, China).

S-4: Calculation of the sodium diffusion coefficient based on the GITT results

The ion intercalation coefficients of all the samples are investigated based on the GITT measurements. According to the Fick's second law of diffusion, D_K can be calculated from the following equation,^{S2}

$$D_K = \frac{4}{p} \left(\frac{m_B V_m}{M_B A} \right)^2 \left(\frac{\Delta E_s}{t \left(\frac{dE_t}{d\sqrt{t}} \right)} \right)^2 \quad (t \ll L^2 / D_{Na}) \quad (1)$$

where D_K ($\text{cm}^2 \text{s}^{-1}$) is the ion diffusion coefficient; m_B , M_B and V_m are the mass, molecular weight and molar volume of the electrode material, respectively; A is the interfacial area between electrode and electrolyte; τ is the duration of the current pulse. As the

relationship between E and $\tau^{1/2}$ is linear in this study, equation 1 can be simplified as following:

$$D_K = \frac{4}{pt} \left(\frac{m_B V_m}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (2)$$

S-5 Computational methods

The theoretical calculations were carried out using the density functional theory and the plane-wave pseudopotential method^{S3}. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange correlation function^{S4} was adopted with the plane-wave cutoff energy set at 500 eV. All geometric optimizations and energy calculations were performed using periodic boundary conditions with adjacent adsorbents and adsorbents at least 15 Å apart to prevent configurational interactions. The convergence criteria of energy and the residual force calculations are set to 10⁻⁶ eV and 0.01 eV/Å, respectively.

Part II: Supporting Figures

Figure S1

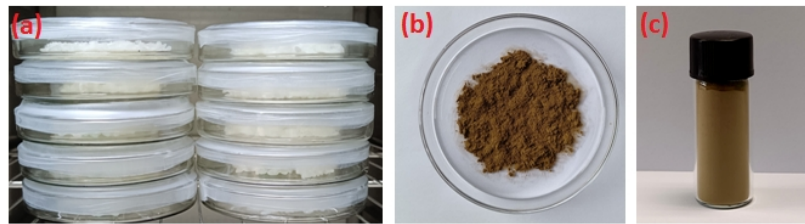


Figure S1 Schematic illustration of the synthesis process of *A. oryzae* spore.

(a) Cultivation of the inoculated rice at 25 °C and 60% of humidity; (b) the moldy rice with *A. oryzae* after a week of cultivation; (c) the collected *A. oryzae* spores.

Figure S2

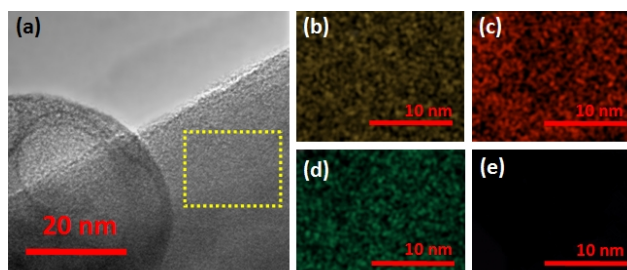


Figure S2 TEM image of the shell of CoP@NPC BIB composite. The corresponding EDS results of the nitrogen (b), carbon (c), phosphate (d) and cobalt (e) elements.

Figure S3

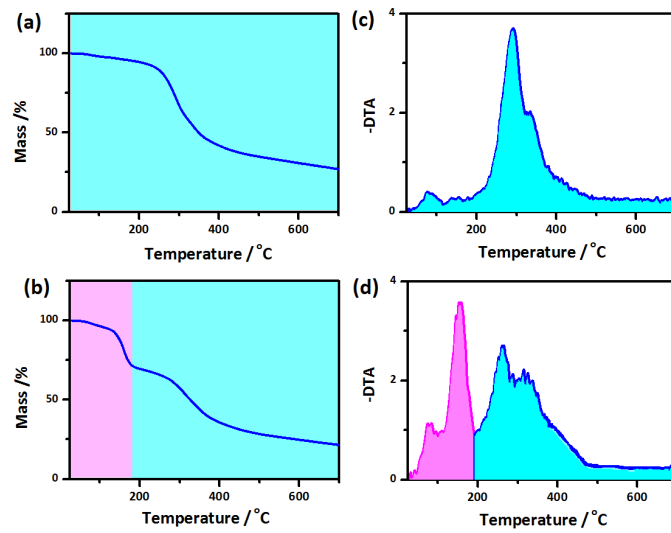


Figure S3 (a, b) TG and (c, d) DTA results of the pure spore (a, c) and the bio-precursor (b, d).

Figure S4

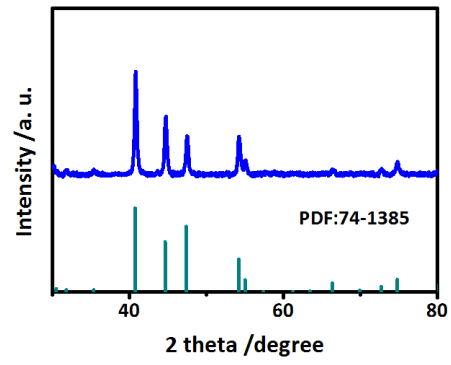


Figure S4 XRD pattern of the Ni₂P@NPC BIB composite and standard pattern of Ni₂P (PDF: 74-1385).

Figure S5

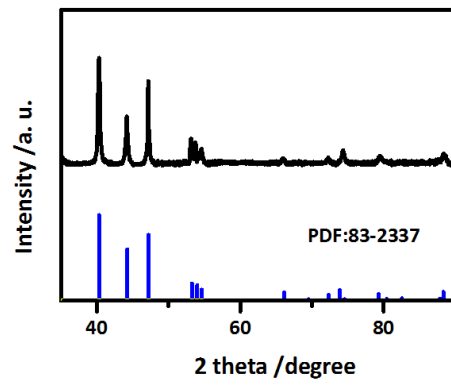


Figure S5 XRD pattern of the Fe₂P@NPC BIB composite and the standard pattern of

Fe₂P (PDF: 83-2337)..

Figure S6

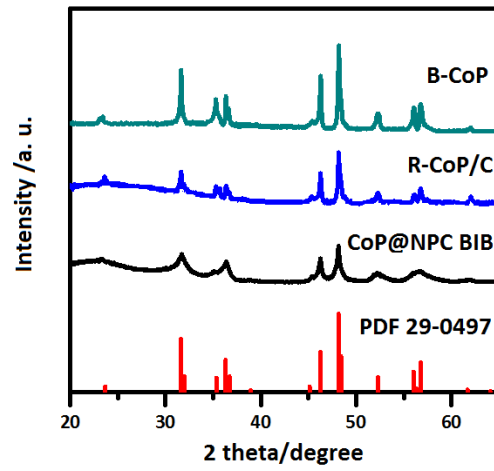


Figure S6 XRD pattern of the B-CoP reference, R-CoP/C reference and CoP@NPC BIB samples with the standard pattern of CoP (PDF: 29-0497).

Figure S7

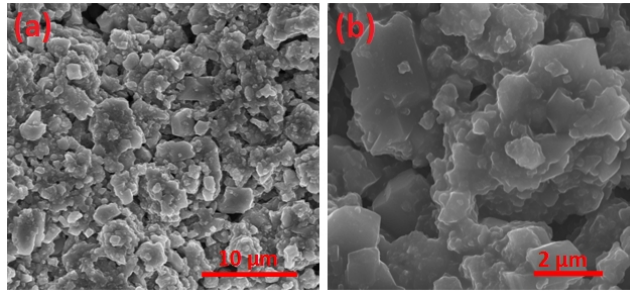


Figure S7 SEM images of the B-CoP reference sample.

Figure S8

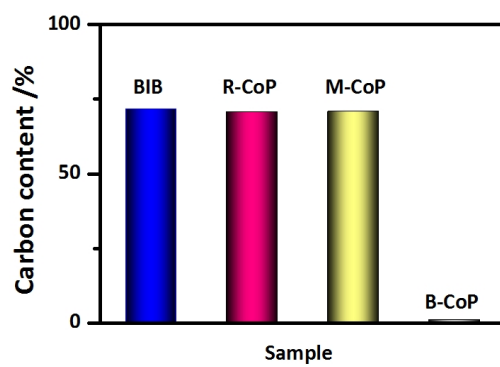


Figure S8 Comparison of the carbon contents of the B-CoP reference, M-CoP/C reference, R-CoP/C reference and CoP@NPC BIB samples

Figure S9

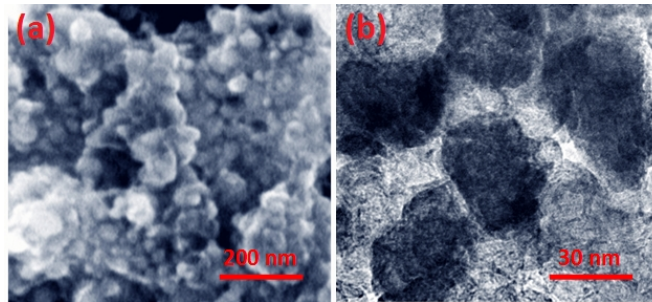


Figure S9 (a) SEM and (b) TEM images of the R-CoP reference sample.

Figure S10

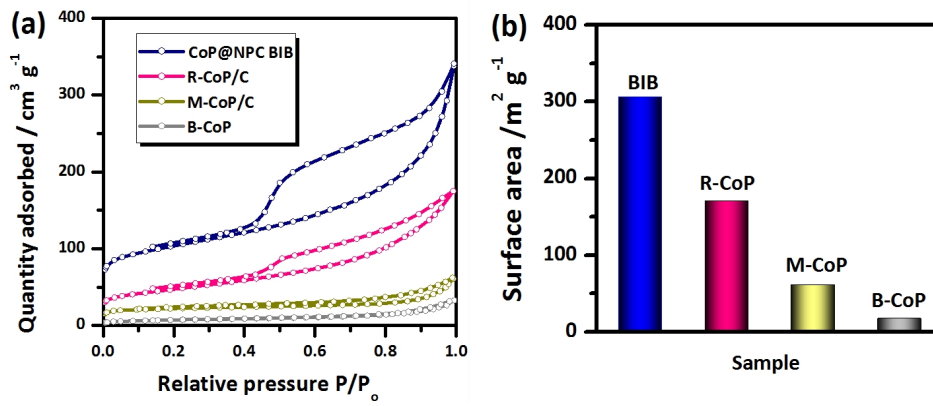


Figure S10 (a) N₂ adsorption/desorption isotherms and (b) the surface areas of the B-CoP reference, M-CoP/C reference, R-CoP/C reference and CoP@NPC BIB samples

Figure S11

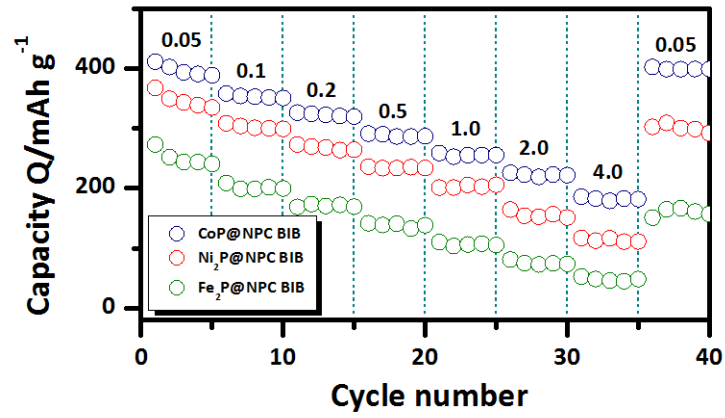


Figure S11 Comparison of the rate capability of the CoP@NPC BIB, Ni₂P@NPC BIB and Fe₂P@NPC BIB samples.

Figure S12

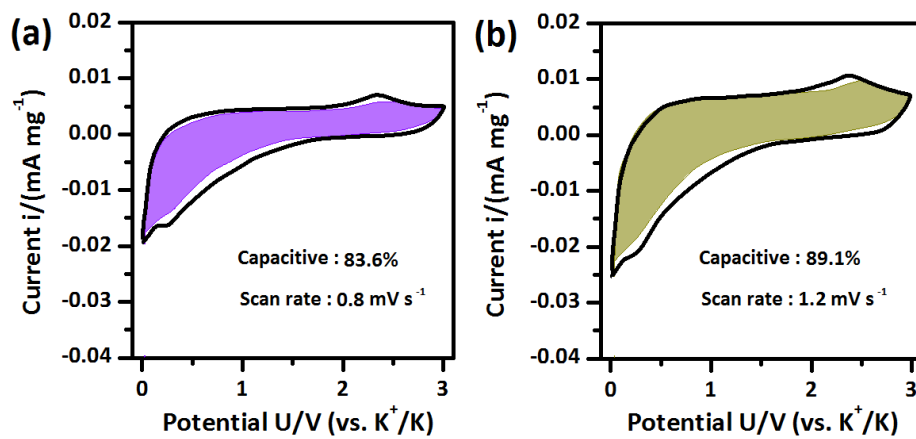


Figure S12 Capacitive contributions of the CoP@NPC BIB samples at the scan rates of (a) $0.8\ mV\ s^{-1}$ and (b) $1.2\ mV\ s^{-1}$.

Figure S13

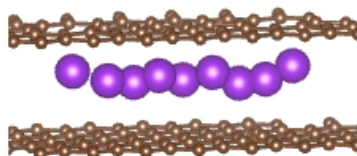


Figure S13 Schematic illustration of the diffusion pathways of potassium ion on BC.

Figure S14

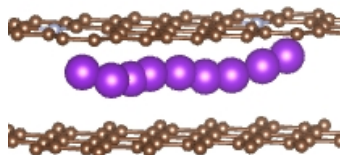


Figure S14 Schematic illustration of the diffusion pathways of potassium ion on NC.

Figure S15

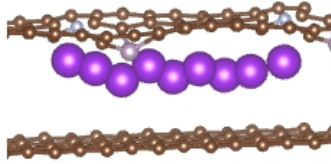


Figure S15 Schematic illustration of the diffusion pathways of potassium ion on NPC.

Figure S16

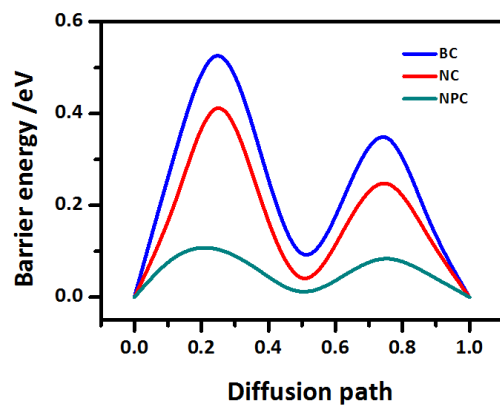


Figure 16 Comparison of the energy barriers of a potassium ion on the BC, NC and NPC.

Figure S17

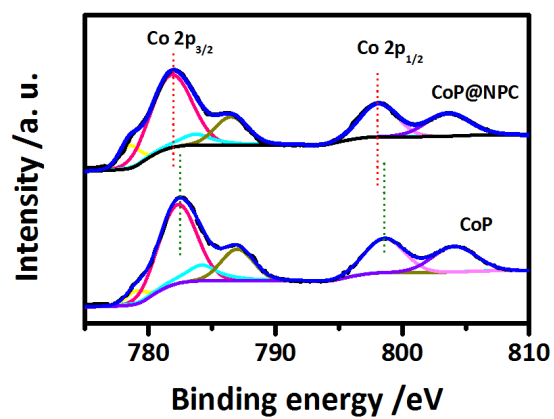


Figure S17 Comparison of the Co 2p XPS spectra of CoP@NPC and bare CoP.

Figure S18

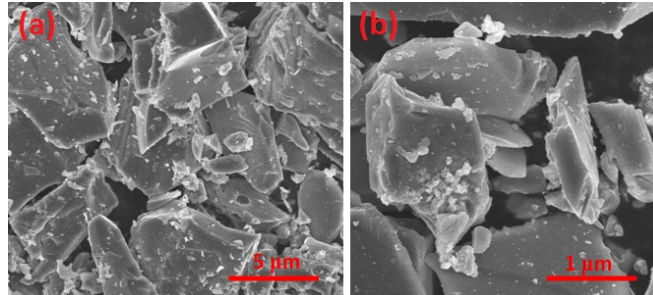


Figure S18 SEM images of the activated carbon

Figure S19

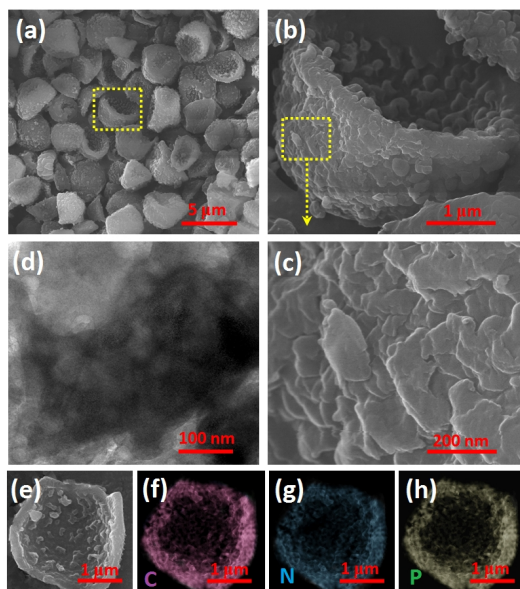


Figure S19 (a~c) SEM and (d) TEM images and (e~h) EDS mapping of the C (f), N (g) and P (h) elements of the MCB sample.

Figure S20

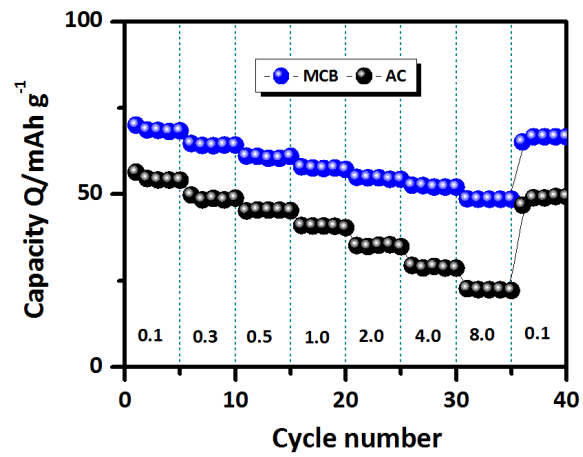


Figure S20 Rate capability of the AC and MCB samples.

Figure S21

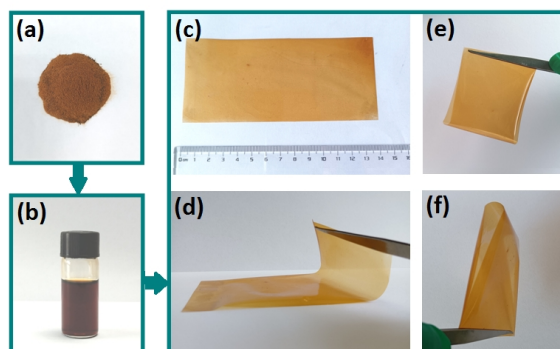


Figure S21 Digital photos of the PFSA-K powder (a), the homogenous solution (b) and the prepared membrane in flat (c), bend (d) and curved (e, f) states.

Part II: Supporting Tables

Table S1 Contents of N and P dopants in the TMP@NPC BIB composites

Dopant content /%	Samples		
	Ni ₂ P@NPC BIB	Fe ₂ P@NPC BIB	CoP@NPC BIB
N	6.45	6.13	5.82
P	3.69	3.12	2.49

Part IV: Supporting References

[S1] G. Y. Du, M. L. Tao, D. Y. Liu, M. K. Aslam, Y. R. Qi, J. Jiang, Y. T. Li, S. J. Bao, M. W. Xu, *J. Colloid Interf. Sci.* 2021, 582, 932-939.

[S2] H. H. Sun, J. G. Wang, Y. Zhang, W. Hua, Y. Y. Li, H. Y. Liu, *J. Mater. Chem. A* **2018**, 6, 13419-13427.

[S3] J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C* **2007**, 111, 14925-14931.

[S4] B. K. Lesel, J. S. Ko, B. Dunn, S. H. Tolbert, *ACS Nano* **2016**, 10, 7572-7581.