Supplementary information

Porous NiCoP *in-situ* grown on Ni foam using molten-salt electrodeposition for asymmetric supercapacitors

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Method S1: Calculation details

a. The three-electrode test:

The mass specific capacity (Q_m) and areal capacitance (C_s) are estimated by galvanostatic charge-discharge profiles. The Q_m and C_s are calculated by the following equation:

$$Q_m = \frac{I \cdot t}{m} \tag{1}$$

$$C_s = \frac{I \cdot t}{S \cdot \Delta V} \tag{2}$$

where Q_m (C g⁻¹) is the mass specific capacity, C_s (F cm⁻²) is the areal capacitance, I (A), t (s), m (g), S (cm²) and ΔV (V) represent the charge-discharge current, the discharge time, the mass loading of active materials, the geometric surface area of electrode and the voltage window of charge-discharge, respectively.

b. The two-electrode test:

The C_m of p-NiCoP/NF//AC device is calculated by the following equation:

$$C_m = \frac{I \cdot t}{m \cdot \Delta V} \tag{3}$$

The C_s of p-NiCoP/NF//AC device is calculated from the galvanostatic charge-discharge profiles by the equation (2).

The mass energy density (E_m) and the mass power density (P_m) are calculated by the following equations:

$$E_m = \frac{1}{2} C_m \cdot \Delta V^2 \tag{4}$$

$$P_m = \frac{E_m}{\Delta t} \tag{5}$$

where E_m (W h kg⁻¹), P_m (W kg⁻¹) and Δt (h) are the mass energy density, the mass power density and the discharge time, respectively.

The areal energy density (E_s) and the areal power density (P_s) are calculated by the following equations:

$$E_{s} = \frac{1}{2}C_{s} \cdot \Delta V^{2}$$

$$P_{s} = \frac{E_{s}}{\Delta t}$$
(6)
(7)

where E_m (mW h cm⁻²) and P_m (mW cm⁻²) are the areal energy density and the areal power density, respectively.



Fig. S1 XRD patterns of (a) CoAl/NF, (b) NiCoP/NF, Ni₂P/NF and p-NiCoP/NF.

To demonstrate the existence of Co/Al alloy, XRD measurement of electrode after electrodeposition was conducted in Fig. S4a. The diffraction peaks located at 31.2 ° and 44.8 ° can be indexed to the (100) and (110) planes of AlCo phase (JCPDS card no.44-1115). Fig. S4b indicates that the NiCoP electrode and the Ni₂P electrode are successfully synthesized. Comparing XRD patterns of p-NiCoP/NF and NiCoP/NF, the stronger peaks of NiCoP are shown in the pattern of p-NiCoP/NF. This result demonstrates convincingly that Al acts as an intermediate of phosphorization.



Fig. S2 CV curves of p-NiCoP/NF and its peak separation with different current densities of electrodeposition at a scan rate of 10 mV s⁻¹.

Herein, current densities of electrodeposition were optimized. The CV curve of 100 mA cm⁻² shows the largest redox peaks, indicating the largest capacitance. Although the CV curve of 200 mA cm⁻² also shows a pair of large redox peaks, the large potential difference of redox peaks indicates its poor reversibility. We therefore choose a current density of 100 mA cm⁻² to conduct electrodeposition.



Fig. S3 (a) XRD patterns of active materials on NF from different amount of Co in molten-salt; (b) CV curves of active materials on NF from different amount of Co in molten-salt; (c) Charge-discharge curves of active materials on NF from different amount of Co in molten-salt.

To study the influence of molten salt concentration on the final loading of active materials, we change the additive amount of Co in the molten-salt. As shown in Fig. S3a, the diffraction peaks of $Ni_{12}P_5$ disappears with the increase of Co. The electrochemical performance tests show that the electrode materials possess the highest areal capacitance and superior reversibility when the amount of Co in molten-salt is 0.4 g. This result can be attributed to the different electrochemical

characteristics of Co, Ni-based compounds, where Co-based compounds possess high reversibility but with low specific capacity and Ni-based compounds can deliver high specific capacity but with poor rate capability and cycling performance.¹ Fortunately, the bimetallic NiCo compounds can combine the advantages of both, which has been demonstrated by NiCo chalcogenides and oxides.²⁻⁴



Fig. S4 SEM images of NiCoP/NF (a, b) and CoAl/NF (c, d).



Fig. S5 N_2 adsorption-desorption isotherms of p-NiCoP/NF before and after activation.



Fig. S6 XPS survey spectrum for (a) CoAl/NF, (b) unactivated p-NiCoP/NF and (c) activated p-NiCoP/NF; (d) A12p regions for p-NiCoP/NF before and after activation.



Fig. S7 HRTEM image of activated p-NiCoP/NF.



Fig. S8 Galvanostatic charge-discharge curves of anode at different current densities.



Fig. S9 Circuit connection of galvanostatic charge-discharge test of four-electrode system.

To investigate their change of potential, we used two groups of reference electrodes and voltmeters to measure and record the potential of anode and cathode. Their potential can be obtained by a parallel connection with a voltmeter and a reference electrode. One reference electrode acts independently on one electrode, which achieves the measurement of bipolar potential on condition that their potential is not effected by each other.



Fig. S10 Galvanostatic charge-discharge test of four-electrode system at a current density of 20 mA cm^{-2} .

Motoriola	E_m / W h kg ⁻¹	Def	
Materials	$(P_m/W kg^{-1})$	Kei.	
S. N.C., D. 2. 200//A.C.	43.54	7	
S-NiCoP-2-300//AC	(150)	/	
meso-NiO/Ni-3//CNCs	19.1	20	
	(700)		
	32		
AC//NiCoP	(351)	41	
	41	10	
PMNC/G-2//AC	(216)	42	
	33.2	10	
CoS _{1.097} /GF//GF	(374.7)	43	
NiCo2S4@PPy-50/NF//AC	34.62	4.4	
	(120.2)	44	
NC D//AC	45.54	This	
p-NiCoP//AC	(124.2)	work	

Table S1 E_m and P_m of p-NiCoP//AC ASC and other Ni or Co-based ASC.

	E_s / mW h cm⁻²	E_s / mW h cm⁻²	Ref.	
Materials	$(P_s / \mathbf{mW cm}^2)$	$(P_s / \mathbf{mW cm}^{-2})$		
NiCoP//AC	1.16	0.59	40	
	(1.6)	(40)	40	
NC LDH NSs@Ag@CC//AC	0.079	0.04	15	
	(0.785)	(12.1)	43	
P-Ni(OH)2@MnO2/NF//AC	0.324	0.04		
	(0.8)	(16)	46	
Ni(OH) ₂ -Cu//RGO	0.95	0.57		
	(2.01)	(44.78)	47	
RGO//NCO	0.8	0.5	40	
	(4.2)	(13)	48	
NiCo ₂ S ₄ @Co(OH) ₂ //AC	1		40	
	(11.15)	—	49	
p-NiCoP//AC	2.93	1.27	This	
	(8.00)	(80.0)	work	

Table S2 E_s and P_s of p-NiCoP//AC ASC and other Ni or Co-based ASC.



Fig. S11 LED demos of p-NiCoP/NF//AC asymmetric supercapacitor at 0 min (a), 1 min (b), 5 min (c), 10 min (d), 20 min (e) and 30 min (f).



Fig. S12 Area demo of every p-NiCoP.

Method S2: Optimization details



Fig. S13 (a, b) Illustration of the traditional matching method. (a) Discharge curve of ASC with the traditional matching method; (b) Dishcharge curves of anode and cathode with the traditional matching method. (c, d) Illustration of the optimized matching method. (c) Discharge curve of ASC with the optimized matching method; (d) Dishcharge curves of anode and cathode with the optimized matching method.

When the mass of cathode is fixed, the discharge time of cathode (t_1) is constant. According to the formula of energy:

$$e = \int U(t) \cdot I(t) \cdot dt = I \cdot \int U(t) \cdot dt \approx I \cdot S_{ABC}$$
(8)

Where *e* is the energy of ASC, *I*, *U*, *t* and S_{ABC} represent the discharge current, the discharge voltage, the discharge time and the area surrounded by A, B and C, respectively. When mass of anode is excess, the formula (8) becomes the following formula:

$$e = I \cdot S_{A_1 B_1 C_1 D_1} \tag{9}$$

The corresponding formula of energy density is as follows:

$$E(m_1) = \frac{e}{M} = \frac{I \cdot S_{A_1 B_1 C_1 D_1}}{M} = \frac{I \cdot S_{A_1 B_1 C_1 D_1}}{m_1 + m_2}$$
(10)

where $E(m_1)$ is the energy density of ASC, *M*, m_1 and m_2 represent the mass of ASC, the mass of anode and the mass of ASC without the anode, respectively. $S_{A1B1C1D1}$ can be expressed as the following equation:

$$S_{A_1B_1C_1D_1} = E \cdot t_1 - \frac{I \cdot t_1^2}{2m_1 \cdot C}$$
(11)

where *E*, t_1 and *C* represent discharge voltage window of ASC, discharge time of cathode and mass specific capacitance of anode, respectively. Combine the formula (10) with the equation (11) to obtain the following energy density function:

$$E(m_1) = \frac{I \cdot E \cdot t_1}{m_1 + m_2} - \frac{I^2 \cdot t_1^2}{2C} \cdot \frac{1}{m_1^2 + m_2 \cdot m_1}$$
(12)

To achieve the maximum energy density, the derivative of function (12) is found as $follows:^{5}$

$$E'(m_1) = \frac{I^2 \cdot t_1^2}{2C} \cdot \frac{2m_1 + m_2}{m_1^2 + m_2 \cdot m_1} - \frac{I \cdot E \cdot t_1}{(m_1 + m_2)^2}$$
(13)

According to the property of function (12), $E(m_1)$ is the maximum when its derivative

(13) satisfies the condition of " $E'(m_1) = 0$ ". Finally, the mass of anode (m₁) can be expressed as the following equation:

$$m_{1} = \frac{\overline{I \cdot t_{1}}}{C \cdot E} + \sqrt{\left(\frac{I \cdot t_{1}}{C \cdot E}\right)^{2} + \frac{2I \cdot t_{1} \cdot m_{2}}{C \cdot E}}$$
(14)



Fig. S14 Galvanostatic charge-discharge curves of anode at different current densities.



Fig. S15 Galvanostatic discharge of different mass of anode at current density of 60 mA cm⁻².



Fig. S16 Galvanostatic charge-discharge test of four-electrode system with different mass of anode at a current of 10 mA.



Fig. S17 CV curves of matching process at the scan rate of 10 mV s⁻¹. (a-g) The capacitance contribution area (red area) of cathode and the potential window of anode with the different anode mass. (h) The change of its potential window with the increasing of anode mass.

To obtain the information of potential changes of two poles, we performed the galvanostatic charge-discharge test of four-electrode system with the different mass of anode at a current of 10 mA (Fig. S14). With the increment of anode mass, the potential window of cathode firstly increases, and then maintain at the maximum (0.6 V). Interestingly, the potential window of anode always decreases with the increasing of anode mass. To clearly exhibit this phenomenon, we firstly carried out CV tests of anode with different mass at the scan rate of 10 mV s⁻¹ (the potential windows are

selected according to Fig. S14). Then, the capacitance contribution areas (red areas) of cathode were marked out by equal to the area of anode. As shown in Fig. S15h, the potential windows of anode ceaselessly shrink with the increasing of anode mass. The capacitance contribution areas of cathode, meanwhile, continue to increase until the whole CV curves are filled. Moreover, CV curves of cathode were conducted with the different potential windows at a scan rate of 10 mV s⁻¹ (Fig. S16-22).



Fig. S18 CV curves and the charge-discharge curves with the anode mass of 4 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.



Fig. S19 CV curves and the charge-discharge curves with the anode mass of 9 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.



Fig. S20 CV curves and the charge-discharge curves with the anode mass of 14 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.



Fig. S21 CV curves and the charge-discharge curves with the anode mass of 16 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.



Fig. S22 CV curves and the charge-discharge curves with the anode mass of 19 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.



Fig. S23 CV curves and the charge-discharge curves with the anode mass of 22 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.



Fig. S24 CV curves and the charge-discharge curves with the anode mass of 26 mg. (a) The capacitance contribution area of cathode and CV curves of anode; (b) CV curves of anode and cathode; (c) The galvanostatic charge-discharge curves at a current of 10 mA.

Anode mass	Potential window of cathode	Potential window of anode	Rate of shrink
4 mg	0.40 V	1.40 V	_
9 mg	0.45 V	1.10 V	0.060 V mg^{-1}
14 mg	0.50 V	0.95 V	0.030 V mg^{-1}
16 mg	0.55 V	0.80 V	0.075 V mg^{-1}
19 mg	0.58 V	0.70 V	0.033 V mg^{-1}
22 mg	0.58 V	0.60 V	0.033 V mg^{-1}
26 mg	0.58 V	0.50 V	0.025 V mg^{-1}

 Table S3 The potential window of cathode and anode and the rate of shrink with different mass of anode.

Herein, we used the rate of shrink to represent the shrinkage level of anode potential window. Its calculation method was the narrowed potential window of anode divided by the increased anode mass.



Fig. S25 The relationship between the potential window of anode and the redox reaction depth of cathode.

To explain the shrinkage of anode potential window, we take into account a redox reaction of quasi 2D. Energy storage of cathode makes up of two phases: ions diffusion and faradaic redox reaction.⁶ Firstly, ions in electrolyte (generally H⁺ or OH⁻) diffuse into electrode/electrolyte interface under an external electric field. The ions subsequently enter into bulk phase of electrode materials by interfacial faradaic redox reaction. With the increasing of diffusion length, the required external electric field is increasing. Therefore, the surface of materials has a higher reaction priority than the near-surface and the near-surface need a higher reaction electromotive force than the surface. The surface of cathode is firstly reduced during the discharge of ASC. If the anode mass is less, the reduction reaction of cathode is just conducted at a less depth. Thus, the low electromotive force can also trigger cathode reaction. With the increasing the discharge of reduction reaction is increasing. The potential window of anode, which is near to positive potential, cannot provide enough electromotive force for the deep reduction. This part of potential window is

useless. Moreover, when the anode mass is excess, the active materials of cathode have been completely reduced under high electromotive force during the discharge of ASC, leading to a part of unavailable potential window of anode. The capacitance of anode, which is near to negative potential, is increasing with the increment of anode mass, leading to an increase of unavailable potential window of anode. These result in the shrinkage of anode potential window. Thus, ASC cannot be exploited all capacitance of cathode by the traditional matching method as a result of the shrinkage phenomenon of potential window.



Fig. S26 The mass of parts of capacitor, including anode, separator, case and cathode.

To prove the rationality which we assume the mass of ASC without anode (m_2) is 0.02 g, a supercapacitor was divided into various parts (including anode, separator, case and cathode), and we measured their mass. As shown in Fig. S24, the mass of anode, separator, case and cathode are 120.3 g, 23.5 g, 158.9 g and 118.6 g, respectively. Therefore, it is possible to produce ASC that mass of non-energy-storage parts (including case, separator and electrolyte) is equal to mass of cathode in actual production. Herein, the mass of cathode we used is 0.01 g, to simplified calculation, we assume that the sum of mass of case, separator and electrolyte is equal to the mass of cathode. According to Method S2, the larger proportion of non-energy-storage parts in ASC, the more anode mass is needed to achieve the optimal state of ASC.

items	Mass
Anode (including electrolyte)	120.3 g
Separator	23.5 g
Case	158.9 g
Cathode (including electrolyte)	118.6 g
Whole supercapacitor	425 g

Table S4 The mass of each part of ASC.



Fig. S27 Circuit connection of free discharge test of four-electrode system.

In the free discharge tests, a 55 Ω resistor was series connection with ASC. Before tests, ASC was charged to 1.6 V with a current of 10 mA. The potential of cathode and anode can be obtained by a parallel connection with a voltmeter and a reference electrode. And the current can be obtained by a tandem galvanometer.



Fig. S28 (a) Illustration of matching process; (b) Energy density corresponding to each part; (c) Rate of shrink with different mass of anode. (d) Illustration of redox reaction.



Fig. S29 (a) Galvanostatic discharge curves of ASC with different mass of anode at a current of 10 mA. (b) Energy density of ASC with different mass of anode at a current of 10 mA. (c-h) Free discharge electrochemical measurement with different resistance values. (c) Current-time curves of ASC with different mass of anode at a resistance of 50 Ω . (d) Potential-time curves of ASC with different mass of anode at a resistance of 50 Ω . (e) Current-time curves of ASC with different mass of anode at a resistance of 50 Ω . (e) Current-time curves of ASC with different mass of anode at a resistance of 100 Ω . (f) Potential-time curves of ASC with different mass of anode at a resistance of 500 Ω . (h) Potential-time curves of ASC with different mass of anode at a resistance of 500 Ω . (h) Potential-time curves of ASC with different mass of anode at a resistance of 500 Ω . (h) Potential-time curves of ASC with different mass of anode at a resistance of 500 Ω . (h) Potential-time curves of ASC with different mass of anode at a resistance of 500 Ω . (h) Potential-time curves of ASC with different mass of anode at a resistance of 500 Ω . (i) Energy density of ASC with different mass of anode.

The mass of cathode which contains substrate was 0.015 g in the verification

experiment. The discharge time of cathode (t_1) was 260 s. The discharge voltage window of ASC (E) was 1.4 V. The mass specific capacitance of anode (C) was 130 F/g and the galvanostatic charge-discharge current (I) was 10 mA. According to the actual situation, the mass of ASC without anode (m_2) was reasonably assumed to be 0.03 g. In the free discharge tests, three resistors with different resistance values (50 Ω , 100 Ω and 500 Ω) were used in the experiments. Before tests, ASC was charged to 1.6 V with a current of 10 mA. As shown in Fig. S27i, the result of verification experiment come up to our expectation.



Fig. S30 Comparison diagram of ions transport and redox reaction with different matching method. According to galvanostatic charge-discharge test of four-electrode system, the potential window of anode with traditional matching is $-1.0 \text{ V} \sim 0 \text{ V}$. When ASC is matched by optimized matching method, the potential window of anode is $-1.0 \text{ V} \sim -10 \text{ V}$

-0.3 V. The shrinkage of anode potential window brings higher electromotive force during charge-discharge of ASC. The fast ions transport and the deep redox reaction can be achieved by high electromotive force, leading to the excellent rate capability of optimized matching ASC.

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