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Porous NiCoP nanosheet as efficient and stable positive electrode for advanced asymmetric supercapacitors

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The materials with good capacitance performance at high loading is desirable for the application of supercapacitors at device level. Here, we have reported the synthesis of sheet-like porous NiCoP (S-NiCoP) by controllable phosphorization of 2-D NiCo hydroxide precursor. In the synthesis, the NiCo hydroxide sheets were firstly prepared through a solvothermal process in large quantity. Under the phosphorization, the PH₃ released by NaH₂PO₂ could react with NiCo in precursor to form NiCoP. The release of gas by decomposition of hydroxide could lead to the formation of pores, thus making the formation of 2-D porous NiCoP with high specific surface areas (216.39 m² g⁻¹). The S-NiCoP have combined the advantages of porous nanosheets (faster ion transport along the pores) and metal phosphides (TMPs) (good conductivity), thus are promising for supercapacitors. The S-NiCoP-300 have shown the high capacitance (1206 F g⁻¹ at 1A g⁻¹) and good rate performance (612 F g⁻¹ at 20 A g⁻¹), much superior to corresponding NiCo hydroxide (566 F g⁻¹), NiP-300 (436 F g⁻¹) and CoP-300 (404 F g⁻¹). Notably, the electrode still exhibit a high capacitances of 1095 F g⁻¹ at high loading of 13.5 mg cm⁻², ascribing to the ability for easily transferring electrolyte along the pores. In this case, the area capacitance can reach high values of 14.78 F cm⁻². A asymmetric supercapacitor composed of active carbon and S-NiCoP could achieve a high specific capacitance, good cycling stability and high energy density. A white LED (3 V) can be lighted for more than 2 h by charging two S-NiCoP-2-300//AC ASC devices about 170 s. The easy synthesis process and good performance makes 2-D NiCoP promising in portal energy systems.

1. Introduction

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The rapid growth of portable electronic devices has resulted in an increasing demand for clean and renewable energy storage devices. Supercapacitors (SCs) have the advantage of density, fast charge/discharge high power ability. environmental friendliness and long life span, thus drawing considerable attention. However, the SCs have relatively low energy density in comparison with batteries, which limited their practical application.^[1-3] According to the equation $E = 1/2 \text{ CV}^2$, the expansion of operating voltage or improvement of capacitance of materials are two feasible routes to enhance the energy density of SCs.^[4] In this regard, the voltage can be amplified by matching the potential voltage of two electrodes in a asymmetric supercapacitor (ASC), thereby increasing the energy density of devices.^[5] The performance can also be improved by optimizing the capacitance through tuning the structure of electrode materials.^[6,7] In addition, there are usually need of thick coating of active components (high loading) on current collector for the practical application at the device level.

This needs good ability for easily transferring electrolyte along the vertical direction of electrode. Thus, it is desired to designed synthesis of materials that can satisfy the above the demand to promote the practical application of SCs.

Based on the charge storage mechanism, the SCs can be divided into electrical double-layer capacitors (EDLCs),^[8] which storing energy by ion adsorption on the active materials, and pseudocapacitors worked through fast surface redox reactions.^[9-11] The pseudocapacitive materials have usually shown higher capacitance than that of EDLCs, thus receiving intensive attention. The transition metal-based hydroxides and oxides are of particular interest owing to their high theoretical pseudocapacitances and earth abundance.^[12] However, they suffer from a limited kinetics during redox reactions due to its intrinsic low conductivity, which can result in poor rate performance and stability. The development of material with well designed structure and improved conductivity is important to overcome such drawback. Transitional metallic phosphides (TMPs) are of promising in catalytic and energy field lithiumion battery,^[13,14] hydrodesulfurization (HDS)^[15] and hydrogen evolution reaction (HER).^[16,17] The TMPs have metalloid structure and good conductivity compared with corresponding oxides. The advantages make large potential of TMPs for capacitors. The phosphide nanoparticle,^[18] nanowire^[19,20] and nanosheet have shown good performance as pseudocapacitance electrode. Typically, the NiCoP@C nanowire arrays can give a specific capacitance much superior to NiCo-nanowire and

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 $Ni_xCo_{1-x}O@C$ nanowire.^[21] Chen and co-workers have designed a 3D networked Ni_2P nanosheets grown on Ni foam with a specific capacitance much larger than those of $Ni(OH)_2$ $NS/NF.^{[22]}$ A 3D electrode consisting of self-supported NiCoP/NiCo-OH/carbon cloth can give a seven fold increase of capacitance compared to that of NiCo-OH alone.^[23]

The performance of materials can be tuned by the microstructure besides the components.^[24] The 2-D materials represented by graphene (or reduced graphene oxides)^[25] and some non-graphene 2-D materials (oxides and sulfides)^[26, 27] can be used as effective electrode materials for SCs. Our previous work have demonstrated the good performance of 2D nanosheets for electrochemical storage-energy^[28-30] and for HER.^[31] Especially, the engineering of pores (or holes) on 2-D materials can facilitate faster reagent transport into the inner structure of the electrodes, and shorten ion transport pathway, which is favorable to improve the application performance of materials.^[32] Especially, the holey (porous) structure can make the easy transfer of electrolyte, even at thick coating of active species,^[33] which is favourable for practical application at the device level. Considering the advantage of the porous sheets and phosphides, the construction of 2-D porous phosphides will provides an avenue for giving a high-effective electrode materials. In this study, we have demonstrated that 2-D porous NiCoP can be used as effective electrode materials for supercapacitor. The 2-D NiCo hydroxide were selected as precursor based on 1) the 2-D structure can provide a template for 2-D NiCoP, and 2) the release of water from hydroxide under heating can result in the formation of the porous structure. The synergistic action of two metals in bimetallic compounds can making the enhanced performance than corresponding single metal compounds.^[34, 35] So, we choose the synthesis of bimetallic phosphides rather than monometallic phosphides in this study. The S-NiCoP have shown good electrochemical performance with high specific capacitance (1206 F g⁻¹ at 1A g⁻¹) superior to corresponding NiCo hydroxide (566 F g⁻¹), NiP-300 (436 F g^{-1}) and CoP-300 (404 F g^{-1}). The electrode still exhibit a high discharge specific capacitances of 1095 F g⁻¹ even at high loading mass of S-NiCoP (13.5 mg cm⁻²), implying its potential for practical application. The area capacitance can reached to 14.78 F cm⁻² in this case, much higher than previous reports. An ASC composed of a active carbon and 2-D porous sheets could achieve a high specific capacitance, good cycling stability and high energy density of 36.32 W h kg⁻¹ at an power density of 375 W kg⁻¹. A white LED (3V) can be lighted for more than 2h by using two S-NiCoP-2-300//AC ASC devices charged about 170 s. The ASC devices can also effectively operate an electrical motor fan. The good performance makes the 2-D NiCoP promising for portal energy-storage derives for advanced application.

2. Experimental section

2.1. Materials and chemicals

Nickel nitrate hexahydrate (Ni(NO₃)₂· $6H_2O$) was purchased from Shanghai Chemical Technology Co., Ltd. China. Cobalt nitrate hexahydrate (Co(NO₃)₂· $6H_2O$), polyethylene glycol 200 (PEG-200), sodium monophosphate (NaH₂PO₂) and NaCH₃COO was supplied by Aladdin Chemical Reagent Con-Ltd. Alcohol was purchased from Tianjit^{0.1}Catangfa^{0.5}Fine Chemical Research Institute. Activated carbon (YEC-8) was purchased from Fuzhou Yihuan Carbon Co., Ltd. All of the chemicals in the experiments were used as received without any further purification.

2.2. Material synthesis

2.2.1 The synthesis of 2-D NiCo oxide sheets

The 2-D porous NiCoP were obtained by the phosphorization of 2-D NiCo hydroxide precursor. Firstly, the 2-D NiCo hydroxides were synthesized in a large quantity based on a solvothermal method. In detail, 15 mmol $Co(NO_3)_2 \cdot 6H_2O$ (4.365g), 15 mmol Ni(NO_3)_2 \cdot 6H_2O (4.365g) and 60 mmol of NaCH₃COO (4.92 g) were added into 40 mL polyethylene glycol 200 (PEG-200). The mixture was stirred to form a homogeneous solution at room temperature. Followed this, the solution was transferred into a Teflon-lined stainless autoclave (50 mL volume) and heated at 200 °C for 16 h in an electric oven. The NiCo-precursor was taken out, washed with alcohol for several times to remove residues, and finally dried for 12 h.

2.2.2 The synthesis of 2-D porous NiCoP sheets (S-NiCoP)

To prepare S-NiCoP, 0.25g NiCo-precursor and 1g NaH₂PO₂ were putted at two separate porcelain boat and then placed in a quartz tube (NaH₂PO₂ at the upstream side of the furnace). The tube was setted on a tube furnace, in that the centre of tubular furnace is close to the boat loaded with precursor. Under N₂ atmosphere, the furnace was heated to 300 °C (heating speed of 5 °C min⁻¹) and remained at this temperature for 2 h. After naturally cooling to ambient temperature, the solids were washed with deionized water and then dried in oven. The products were denote as S-NiCoP-2-300.

The phosphating temperature was tuned as 250 °C and 350 °C to obtain S-NiCoP-2-250 and S-NiCoP-2-350 to study the effect of calcination temperature on the structure of final samples. A series of other control samples were also fabricated by tuned mass ratio of Ni(NO₃)₂· 6H₂O and Co(NO₃)₂· 6H₂O as 1:0, 1:2, 2:1 and 0:1 with remaining total molar amount of 30 mmol. The phosphorization condition is same to that for S-NiCoP-2-300. The detail for the preparation of different samples are listed in Table S1.

2.3 Sample characterization

The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM, Hitachi S-4800, acceleration voltage of 5 kV) and transmission electron microscopy (TEM: JEM-2100, acceleration voltage of 200 kV). BET test was performed at 77 K with a Micro-meritics Tristar II surface area and a porosimetry analyzer. In the test, the catalyst (more than 100 mg) was degassed under vacuum at 150 °C for 5 h before the measurement. The pore size distribution and surface area were determined from desorption isotherms by the BJH and BET methods, respectively. X-ray diffraction (XRD) patterns were collected on a Bruker D8 diffractometer using Cu Ka ($\lambda = 1.5406$ Å) radiation. XPS (X-ray photoelectron spectroscopy) analysis was performed on a VG

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ESCALABMK II with an Mg Ka achromatic X-ray source (1253.6 eV).



Figure 1. Schematic fabrication process of S-NiCoP-2-300. 2.4 Electrochemical measurements

The electrochemical measurements were carried out using a CHI 760E electrochemical workstation (CH Instruments Inc, China) in a 2 M aqueous potassium hydroxide (KOH) electrolyte with a typical three electrode confirguration. A Hg/HgO electrode and platinum electrode were used as the reference electrode and counter electrode, respectively. The working electrode were prepared by mixing the samples with 5 wt% polytetrafluoroethylene (PTFE) binder and 5 wt% acetylene black. The mixture is grinded to form a welldispersed slurry. The slurry was pasted on a piece of nickel foam current collector (1.0 \times 1.0 cm²) and dried in a vacuum oven. The foamed nickel with active materials was pressed under 15 Mpa. The active material loading of the nickel foam was estimated to be about 4 mg cm² in most case. All capacitance performances were tested at least for three times, and a intermediate value was used in the paper. The mass loading of S-NiCoP on Ni foam are changed from 0.32 to 13.5 mg cm⁻² to study the effect of loading amount.

2.5 Preparation of asymmetric supercapacitor (ASC) device

A asymmetric supercapacitor was assembled by using a active carbon as positive electrode and S-NiCoP negative electrode. The positive electrode was prepared by a route described above (2.4 section). The negative electrode was prepared by mixing the activated carbon with 5 wt% polytetrafluoroethylene (PTFE) binder and 5 wt% acetylene black. The slurry was coated onto the nickel foam current collector and dried overnight at 120 $\,^\circ$ C in vacuum oven. All of the fabricated electrode was pressed under 15 Mpa. The mass loading of active materials on electrode is controlled by weighting its mass before the dispersion in slurry. The active materials can combined with foamed nickel firmly with the mass loading increasing by compression and add of proper amount of binder. ACS device was assembled with a configuration of 2025type coin cell by integrating the as-prepared positive electrode and negative electrode. A piece of NKK placed was placed between the two electrodes as separator in 2 M KOH electrolyte. The mass ratio of the positive and negative electrodes for an ACS full cell can be calculated based on the principle of charge balance. According to the equation (1):

$$\mathbf{m}^{+}/\mathbf{m}^{-} = \left(\mathbf{C}^{-} \times \Delta \mathbf{V}^{-}\right) / \left(\mathbf{C}^{+} \times \Delta \mathbf{V}^{+}\right) \tag{1}$$

where m^+ , C^+ , and ΔV^+ are represent mass specific capacitance, and potential window of positive electrode material may $C_{\rm S}$ and $\Delta W^$ are represent mass specific capacitance, and potential window of positive electrode material. The optimized mass ratio of S-NiCoP-2-300/AC is about 2 based on the equation.

3. Results and discussion

3.1. Morphology and Structure

The preparation procedure for S-NiCoP is illustrated in Figure 1. Firstly, the 2-D NiCo-precursors were prepared through reaction of Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O in the presence of NaCH₃COO in PEG-200. The process is simple and well-reproductive. The products can be obtained with good uniformity in large quantity (about 3g for one time synthesis), which should be favourable for practical application of the materials. Under heating, the NiCo-precursor can react with PH₃ released from NaH₂PO₂, thus forming corresponding 2-D NiCoP. The pore can be formed by the release of water from the decomposition of hydroxide. The synthetic parameters for S-NiCoP and other control samples are listed in Table S1 in detail.



Figure 2. (a) SEM images of NiCo-precursor; (b) TEM images of NiCo-precursor, (c)
(d) are the HRTEM images of the selected areas; (e) SEM images of S-NiCoP-2-300; (f) TEM images of S-NiCoP-2-300, (g) (h)are the HRTEM images of the selected areas; (i) Dark-field TEM image showing the area for which elemental maps were obtained for S-NiCoP-2-300 and (j-l)corresponding STEM/EDS elemental mapping.

The formation of 2-D NiCoP sheets were demonstrated by XRD, TEM and SEM. XRD of the precursor shows the peaks located at 33.6° and 60.9°, indexing to (110) and (301) planes of NiCo hydroxide (JCPDS no. 22-0444) (Figure S1). The SEM image shows the presence of large-scale, uniform nanosheets with thickness of several tens of nanometers and lateral size above micrometers (Figure 2a). In TEM image, we can clearly see the presence of 2-D nanosheet (Figure 2b). An enlarged TEM image of NiCo-precursor (Figure 2c and d) clarified the formation of thin sheet structure with many folds. In Figure 2d, we can see the lattice fringe of 0.26 nm, matching well with (110) lattice planes of NiCo hydroxide. After phosphorization, the NiCo hydroxide can be transformed into S-NiCoP. In XRD patterns (Figure S1), the sharpest diffraction peaks located at

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41.0° can be assigned to (111) plane of hexagonal NiCoP (JCPDS no. 71-2336).^[36] Other peaks, corresponding to (201), (210), (300), (002), and (211) planes, can be observed at 44.9°, 47.6°, 54.4°, 54.7° and 55.3°, respectively. The SEM image (Figure 2e) shows the presence of sheet-like structure, but with more rougher surface than NiCo-precursor. The roughness should be ascribed to the formation of small particles in phosphorization process. The TEM test can give more information about the structure of nanosheets. Low resolution image of S-NiCoP-2-300 shows a sheet-like structure with wrinkling surface (Figure 2f), being consistent with SEM test. Notably, an enlarged TEM image of S-NiCoP-2-300 proves the presence of a large number of pores on sheets (Figure 2g and h). It is obvious different with NiCo precursor that have a smooth surface. The formation of pore on sheets should be relative with the release of water under heating process. Similar phenomenons were observed in previous reports.^[37,38] The pores can provide suitable avenues for electrolyte diffusion and charge transportation, being favorable to improve the performance for energy storage and catalysis.^[39, 40] Further details were revealed by high resolution transmission electron microscopy (HRTEM) (Figure 2h). The interplanar spacing of 0.28 nm is indexed to (111) plane of NiCoP. The EDS elemental mapping analysis indicates the uniform distributions of Ni, Co, and P throughout the sheet (Figure 2i-l). The XRD, SEM and TEM results confirm the formation of 2-D Co-Ni precursor and its transformation into 2-D porous NiCoP nanosheets.

The transformation of 2-D Co-Ni precursor to 2-D porous NiCoP nanosheets have also be reflected by XPS method. From Figure 3a, one can see the presence of Ni, Co, O, C elements in NiCo-precursor. Further information can be gained by highresolution XPS spectra. In the Figure 3b, we can see the obvious shakeup satellites (shortened as sat.) at 878.9 and 860.9 eV, which is consistent with the Ni 2p1/2 and Ni 2p3/2 of Ni(OH)₂ at 872.6 and 855.0 eV, respectively.^[41] The peaks at 797.2 and 781.3 eV were ascribed to Co 2p1/2 and Co 2p3/2 in Co(OH)₂. The binding energies at around 795.4 and 779.6 eV are indexed to Co³⁺ (Figure 3c).^[42] After phosphorization, the Ni/Co/P elements can be observed in ternary S-NiCoP-2-300. The test implies the conversion of NiCo-precursor into NiCoP, being consistent with XRD results. In high resolution XPS spectra (Figure 3d-f), the Ni 2p1/2 and Ni 2p3/2 (Figure 3d) can be observed at 872.2 and 854.5 eV with the energy gap of 17.7 eV. Two sat. peaks of Ni 2p located at 878.5 and 860.5 eV are also observed. These results are consistent with that reported for Ni₂P.^[33,43] The Co 2p spectrum (Figure 3e) shows the peaks at 778.9, 782.2 eV with one sat. at 786.0 eV, corresponding to spin-orbit splitting values of Co 2p_{3/2}. The peaks at 798.2 and 794.3 eV with one sat. peak at 802.9 eV can be index to the spin-orbit splitting value of Co $2p_{1/2}$. The results can be observed for CoP-based materials.^[44,45] The weak sat. peak corresponding to Co^{3+} should be due to the easy surface oxidation of phosphide in air.[46-48] The P 2p peaks can be divided into two peaks at 129.8 (P $2p_{1/2}$) and 129.0 eV (P $2p_{3/2}$)



Figure 3. (a) XPS full profiles for S-NiCoP-2-300 and NiCo-precursor; High-resolution XPS spectra of NiCo-precursor for (b) Ni 2p, (c) Co 2pand High-resolution XPS spectra of S-NiCoP-2-300 for (d) Ni 2p, (e) Co 2p, (f) P 2p.

(Figure 3f). The P 2p_{1/2} peak at 129.8 eV is lower than that for elemental P (130.2 eV). This implies that P species in NiCoP has a negative charge,^[49] which is related with the formation of metal (Co, Ni)-P bond. In addition, the peaks at 133.1 eV show that the P-metal species (like Ni and Co) is oxidized due to the exposure of sample in air.^[45] Besides the S-NiCoP, other samples can also be prepared as control. The synthetic parameters for different samples (NiP-300 and CoP-300 etc.) are listed in Table S1. The formation of NiP-300 and CoP-300 are also supported by XPS analyses (Figure S2, S3).^[50]

For electrochemical capacitance, the ions adsorption and redox are mainly processed on the surface.^[51] Therefore, the high surface areas and plentiful pores are favourable to improve the capacitance, which can be verified by N₂ isothermal adsorption-desorption isotherm of different samples (Figure 4 and Figure S4). The specific surface area (S_{BET}) of NiCo-precursor is about 147.9 m²g⁻¹ with average pore size of 16.41 nm. After phosphating, the samples with different SBET can be obtained based on the calcination condition. Typically, the S_{BET} and pore volume of the S-NiCoP-2-300 are about 216.4 m²g⁻¹ and 0.62 cm³g⁻¹, respectively (Table S2). For S-NiCoP-2-250 and S-NiCoP-2-350, the S_{BET} is about 148.0 m²g⁻¹ and 104.3 m²g⁻¹. The S-NiCoP-2-300 have highest surface area, implying the important effect of calcination temperature on the microstructure of materials. The low calcination temperature of S-NiCoP-2-250 makes the incomplete conversion of NiCo hydroxide precursor, thus giving a low SBET values (148.0 m²g⁻¹) close to Ni-Co precursor

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Figure 4. Nitrogen adsorptio-desorption isotherms of (a) NiCo-precursor, (b)S-NiCoP-2-300, (c) NiP-300 and (d) CoP-300 (inset: corresponding pore size distribution).

(147.9 m²g⁻¹). Indeed, the XRD of S-NiCoP-2-250 shows a similar pattern with that of NiCo-precursor. On the other hand, the high calcination temperature can make the full phosphorization, but can also results in growth of particles and aggregation of nanosheets. So, the S-NiCoP-2-350, composed of NiCo phosphide, have low specific surface area of 104.3 m²g⁻¹. The S-NiCoP-2-300 from suitable calcination temperature have given a large specific surface area with plentiful pores. Further, our results also indicated the ratio of Co and Ni in samples have obvious effect on the surface area. The SBET of S-NiCoP-1-300 is about 163.3 m²g⁻¹, and S-NiCoP-3-300 is about 91.7 m²g⁻¹. In addition, the CoP-300 and NiP-300 have a low SBET of 55.4 m²g⁻¹ and 88.1 m²g⁻¹, respectively. Based on above results, we can obviously see that 1) the bimetallic phosphides have shown the larger surface area than any corresponding singe metal phosphides. It implies that the combination of Co and Ni in precursor are favourable for its decomposition in phosphorization process to give TMPs a suitable pore structure.^[52] 2) the suitable ratio of Co and Ni is important to give a materials with high SBET. The bi-transition meta phosphides (BTMPs) from the phosphorization of the precursor synthesized with 1:1 Co/Ni molar ratio have a higher specific area than those with 2:1 and 1:2 molar ratio. It is ascribed to that the precursor synthesized with 1:1 Co/Ni molar ratio are favourable to give S-CoNiP with little impurity of single metal phosphide. In contrast, the precursor synthesized with 2:1 and 1:2 Co/Ni molar ratio is inclined to form monometal Co or Ni species. So, after the phosphorization, the corresponding mono-transition metal phosphides (MTMPs) can also be formed besides BTMPs. The presence of MTMPs can result the decrease of SBET of final materials because its lower SBET value than BTMPs. In general, the high surface area of the material is favorable to improve the specific capacitance.^[52] The high SBET of S-NiCoP-2-300 and large pore volume would be beneficial to the exposure of more active sites and rapid mass transfer, making its potential useful for supercapacitance.

3.2. The test of electrochemical properties



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Figure 5. Electrochemical performance of NiCo-precursor, S-NiCoP-2-300, CoP-300 and NiP-300 for supercapacitors:(a) CV curves at 10mV s⁻¹; (b) Galvanostatic charge/discharge curves at a current density of 1 A g⁻¹. (c) CV curves of the S-NiCoP-2-300 at different scan rate; (d) Galvanostatic charge/discharge curves of the S-NiCoP-2-300 at different current densities; (e) The specific capacitances at different current densities;(f) The EIS curves. Inset: an expanded high-frequency region of the plots.

The electrochemical performance of the samples was evaluated in a three-electrode system in 2 M KOH aqueous electrolyte. Figure 5a shows CV curves of NiCo-precursor, S-NiCoP-2-300, CoP-300 and NiP-300. All samples show a couple of the prominent faradaic redox peaks within the potential window (vs Hg/HgO), implying the presence of a faradaic behavior during the electrochemical process. ^[23,50]. Specifically, the emergency of redox peaks around a potential range of 0.3 to 0.5 V (vs Hg/HgO) is ascribed to the conversion of $Co^{(\delta+)}/Ni^{(\delta+)}$ state in S-NiCoP to Co^{3+}/Ni^{3+} state. ^[53] Also, the similarity of anodic and cathodic peaks implied the good reversibility of the system. The redox reaction mechanism of the NiCoP with respect to the potential involved in a three-electrode system and the electrochemical reactions corresponding are as follows^[53]:

 $\begin{array}{rll} NiCoP + 4(OH^{-}) + x(OH^{-}) \leftrightarrow NiP(OH^{-})_{2} + CoP(OH^{-})_{2} + \\ x(OH^{-}) + 4e^{-} \end{array} \tag{2}$

The CV curves of S-NiCoP-2-300 electrode exhibit an larger CV curve area compared to other electrodes. This is a indicative of the increased area specific capability for S-NiCoP-2-300. The increased CV area of S-NiCoP-2-300 are related to their high surface areas and plentiful pore. Galvanostatic charge/discharge (GCD) curves at 1 A g⁻¹ (Figure 5b) show the longest discharging time for S-NiCoP-2-300 among all samples. The capacitance calculated are about 1206 F g⁻¹ for S-NiCoP-2-300, much higher than those for Ni-Co precursor (566

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F g⁻¹), CoP-300 (404 F g⁻¹) and NiP-300 (436 F g⁻¹). The advantage of S-NiCoP over CoP and NiP indicate that the synergism of two metals can large promote the performance of electrode materials; It is further supported by the better performance of the NiCo hydroxide precursor than the CoP-300 and NiP-300. On the other hand, the improved performance of S-NiCoP-2-300 than NiCo hydroxide precursor demonstrates the superiority of the phosphide over corresponding oxides, which should be related to the good conductivity of former than later,^[12] as well of specific structure of phosphide.

Figure 5c shows CV curves of S-NiCoP-2-300 electrode at various scan rates of 5, 10, 20, 50, and 100 mV s⁻¹. With the increase in scan rate, the anodic peak is shifted toward a higher potential and the cathodic peak is shifted toward a lower potential due to polarization.^[54] The redox peaks have no obvious change in shape, implying high reversibility of electrode material. Figure 5b shows GCD curves of S-NiCoP-2-300 electrode at different current density from 1 to 20 A g^{-1} . All curves have good symmetry, indicating the high coulombic efficiency due to the highly reversible redox reactions of S-NiCoP-2-300 in the electrochemical charging and discharging process. The specific capacitances of S-NiCoP-2-300 are 1206 F g⁻¹, 1080 F g⁻¹, 1050 F g⁻¹, 962 F g⁻¹, 825 F g⁻¹, 709 F g⁻¹ and 612 F g^{-1} at the current densities of 1, 2, 5, 10, 15, and 20 A g $^{-1}$, respectively(Table S3). It implies the good rate performance in fast electrochemical response process (Figure 5e). At various current densities, the S-NiCoP-2-300 shows higher capacitance than other samples. The capacitance retention at 20 A g⁻¹ are 50.75% of that at 1A g⁻¹ for S-NiCoP-2-300, which are 17.66%, 43.26%, 29.33%, 39.83%, 43.24%, 60.40% and 23.17% for Ni-Co precursor, S-NiCoP-1-300, S-NiCoP-3-300, S-NiCoP-2-250, S-NiCoP-2-350, CoP-300 and NiP-300. The samples from phosphorization shows higher retention than that of NiCo precursor, whatever they are higher or lower capacitance at 1 A g-1, further demonstrating the good rate performance of phosphide. In addition, we can see that CoP-300 have highest retention of 60.40% at 20 A g⁻¹, while NiP-300 have low retention of 23.17%. Correspondingly, the capacitance retention increases with the increase of ratio of Co in the samples. The results imply the important of Co in designing the high-stable electrode. It is also indicates that one can design suitable bimetal based electrode materials by tuning the ratio of metal ions and kind of counter ions. The specific capacitance for S-NiCoP-2-300 is not only significantly higher than those for Ni-Co precursor and other contrast samples, but also superior to those for metal phosphide, such as Ni₂P nanoparticles (668.7 F g⁻¹ at 1 A g^{-1}),^[55] Ni₂P/rGO nanoparticles (672.4 F g^{-1} at 1 A g^{-1}),^[56] Au/Ni₁₂P₅ core/shell nanoparticles (571.4 F g^{-1} at 0.2 A g^{-1}),^[57] Co₂P nanoflowers (284 F g^{-1} at 1 A g^{-1}),^[45] Ni₂P (843.25 F g^{-1} at 1 A g⁻¹),^[58] etc (see Table S4). The 2-D sheet-like porous structure, suitable ratio of Co and Ni are responsible for enhanced redox reaction kinetics of S-NiCoP-2-300.

There are usually need of thick coating of active components (high loading) on current collector in the practical application. Generally, the performance of electrode can be decreased with the increase of mass loading (especially at high loading), which is not favourable for the practical application. The mass loading of S-NiCoP-2-300 on Ni foam are changed from 0.32 to 13.5 mg cm⁻² to study the effect (Figure SS), 5We can see that the high capacitance can be obtained in the case of low mass loading (2687 Fg⁻¹). However, too little loading amount of active components are not real for practical application. The specific mass capacitance gradually decreased with the increase mass loading until the mass reached to 2.65 mg cm⁻². Further increase mass loading can not induce obvious change of capacitance value. For example, the value is about 1240 F g⁻¹ and 1095 F g⁻¹ for the loading mass of 2.65 mg cm⁻² and 13.5 mg cm⁻². Notably, even at high loading mass of 13.5 mg cm⁻², the electrode still exhibit a high discharge specific capacitances of 1095 F g⁻¹, being similar to that at 4.06 mg cm⁻². In this case, the area capacitance can increased from 4.89 F cm⁻ ² to 14.78 F cm⁻², which is much higher than previous reports (see Table S5). The capacitance behavior is related with the ability of the transmission of ions and the transfer of electrons. The excellent capacitance behavior at large mass loading is intimately related with the structure of 2-D S-NiCoP materials as follows (1) the S-NiCoP have good conductivity due to its metalloid structure. Also, the S-NiCoP can form dense, stacked structure due to its sheetlike structure. Therefore, the electrons can easily transfer from the electrode surface to the current collector at at large mass loading (thick coating), which is favorable for improving the capacitance behavior; (2) the porous structure of S-NiCoP materials is favourable for the transmission of electrolyte, which is positive for giving the good performance even at thick coating of active species.

The conductivity and ion migration ability have important effect for a electrode materials. The electrochemical impedance spectroscopy (EIS) of Ni-Co precursor, S-NiCoP-2-300, CoP-300 and NiP-300 are tested to give the information of ion migration characteristics and conductivity of the materials (Figure 5f). The test was carried out in the frequency range of 0.01 Hz to 100 kHz, and the inset diagram is a magnification of the high frequency region. We can see that all of EIS spectra were composed of a semicircle in high frequency area and a sloped line in low frequency area. The slope of the straight line for S-NiCoP-2-300 is much larger than that of Ni-Co precursor, CoP-300 and NiP-300 at low frequency region, which reveal the lower diffusion limitations, and consequently, the efficient electrolyte ions diffusion during redox reaction. The easy ions diffusion should be related to the proper porous structure. Besides, the charge transfer resistance (Rct value) of S-NiCoP-2-300 (0.70 Ω) is lower than those of Ni-Co precursor (1.88 Ω), CoP-300 (1.90 Ω) and NiP-300 (0.87 Ω), which should be favourable for fast charge transfer during charge/discharge processes. The lower resistance of S-NiCoP than NiCo hydroxide originated good charge and mass transfer ability conductivity of phosphide. Also, the bi-metal phosphide shows lower the electronic and ionic resistances which can also contribute on the good energy-storage ability.[36] The EIS analytical results further verify that S-NiCoP-2-300 exhibits favorable reaction kinetics and the internal resistance compared with other samples.

To evaluate the potential of S-NiCoP-2-300 for the practical application in portable electronic devices, an asymmetric supercapacitor (ASC) was assembled in a CR2025

b 40 5 30 AC S-NiCoP-2-300 4 20 density 10 0 20-10-20--30 -1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 Potential / V C d 6 03 SerVa 0 timVe Current density / A 4 20mVs 2 density 0 .2 D, 0.4 0.6 0.8 1.0 1.2 1.4 1.6 Potential / V -0.20.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 Potential / V -0.2 0.0 0.2 0.4 0.6 0.8

Figure 6. Electrochemical performances of the S-NiCoP-2-300//AC ASC device: (a) Schematic of the assembled structure of energy storage device based on S-NiCoP-2-300 as positive electrode and AC as negative electrode. (b) CV curves of the S-NiCoP-2-300 and AC electrodes at a scan rate of 20 mV s⁻¹ in 2 M KOH electrolyte. (c) CV curves of the ASC device at 20 mV s⁻¹ with different voltage windows. (d) CV curves of the ASC device at different scan rates.

cell by utilizing S-NiCoP-2-300 and AC as the positive and negative electrodes with a piece of NKK as the separator (denoted as S-NiCoP-2-300//AC). Figure 6a shows the assembled structure of ASC device. The CV tests of S-NiCoP-2-300 and AC electrodes in 2M KOH at 20 mV s⁻¹ was performed to estimate total voltage of devices (Figure 6b). According to CV curve, the voltage window of S-NiCoP-2-300 and AC is from 0 V to 0.6 V and -1.0 V to 0 V, respectively. Figure 6c shows CV curves of ASC device within different potential windows (from 0-1.3 V to 0-1.7 V) at a scan rate of 20 mV s⁻¹. With the increase of the potential windows from 0-1.3 V to 0-1.7 V, the redox humps can be observed. Obvious polarization occurred when the voltage was further extended to 1.6 V. Thus, the optimum operating potential window of 0-1.5 V was used to investigate the performance of S-NiCoP-2-300//AC ASC device. The CV curves at various sweep rates (5 to 50 mV s⁻¹) in a potential window of 0-1.5 V shows a quasirectangular shape coupled with distinguished redox peaks, which is typical for hybrid capacitive behavior (Figure 6d).

50 mV s⁻¹, suggesting the good rate capability. The GCD curves at different current density were conducted to further explore the capacitive performance of ASC device. Almost symmetric GCD curves indicate a high coulombic efficiency and electrochemical reversibility of the devices (Figure 7a). It also can be seen that the ASC device exhibits a potential window of 1.5 V, which is much higher than those of conventional symmetric capacitors of activated carbon in aqueous solution. The capacitance values calculated from GCD curves are 116.2, 103.1, 87.8, 78.6, 67.3 and 53.3 F

Moreover, the shapes are almost the same even at high scan rate



Figure 7. Electrochemical performances of the S-NiCoP-2-300//AC ASC device: (a) GCD curves of the ASC device collected at various current densities; (b) The specific capacitances at different current densities; (c) Cycling performance of the ASC device at a current density of 5 A g⁻¹; (d) The fully charged ASC operates a white LED and an electric motor fan, demonstrating its potential suitability for wearable electronic applications.

g⁻¹ at current densities of 0.5, 1, 2, 3, 5 and 10 A g⁻¹, respectively. Even at high current density, the device still maintain a high capacitor value, indicating the remarkable rate capability (Figure 7b). The good rate performance of ASC device can be attributed to the porous 2D structure and increased conductibility of S-NiCoP-2-300. A cycling test was carried out over 8000 cycles at a current density of 5 A g⁻¹ to evaluate the cycling stability of ASC device. At initial cycles, the increase of the capacitance is probably due to the activation process that allows the electrolyte ions to diffuse into the bulk and increases the number of available electrochemically active sites. After 8000 cycles, the S-NiCoP-2-300//AC ASC device can deliver a capacitance retention of 90.6%, indicating an excellent cycling stability (Figure 7c). All of above tests reveal that the S-NiCoP-2-300//AC ASC device with favorable cycling stability and excellent energy density and power energy has a great potential application in the energy storage field. So it is suitable for driving realistic low-voltage devices. To demonstrate the potential, two same ACS device were connected together to achieve a higher operating voltage. As shown in Figure 7d, a 3 V white LED can be lighted using the two charged devices assembled here in series. In the long-term test, the device can power the white LED efficiently for more than 2h after charging within 170s (1 A g⁻¹ current density). Also, one ASC cell can effectively operate an electrical motor fan (Figure 7d). These results suggest the large potential of S-NiCoP-2-300 for construction of high-effective ASC devices for practical applications.

Figure 8 shows the Ragone plots of the ASC device, energy density and corresponding power density. The energy density (E) and the power density (P) are estimated using the following equations (3) and (4):

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Figure 8. Ragone plots of the S-NiCoP-2-300//AC and reported Ni or Co-based ASC devices.

$$E = 1/2 C \Delta V^2$$
(3)
$$P = E/\Delta t$$
(4)

Where C is specific capacitance, Δt is the discharge time, and ΔV is the potential window of S-NiCoP-2-300//AC ASC device. The GCD measurements indicate that the ASC device possesses an energy density of 43.54 W h kg⁻¹ at a low power density of 150 W kg⁻¹. A high value of 16.65 W h kg⁻¹ can be retained when the power density increases to 7500 W kg⁻¹. The energy density of S-NiCoP-2-300//AC ASC device is higher than a number of oxide-based hybrid super-capacitor, such as Ni-Co oxide//AC (7.4 Wh kg⁻¹ at 1.90 kW kg⁻¹),^[59] core-shell NiCo₂S₄ on Ni foam/porous carbon (10.6 Wh kg⁻¹ at 2.47 kW kg⁻¹),^[60] NiCo₂S₄/RGO(24.4 Wh kg⁻¹ at 750 W kg⁻¹)^[61] and Ni-Co sulfide//AC (25 Wh kg⁻¹at 0.45 kW kg⁻¹).^[62] It is also higher than Ni or Co-based phosphide ASC devices reported previously.^[22,45,63-65] (Table S4)

4.Conclusions

We have demonstrated that the 2-D porous NiCoP can be used as effective electrode for supercapacitance. The performance is intimately related with the components and structure of materials. The formation of the phosphide and the construction of bi-metallic components are essential to boost the performance of materials. Also, it is shown that the presence of Co is helpful to improve the rate performance. The optimized electrode can be obtained by controlling the phosphorization temperature, choosing the suitable ratio of Co and Ni. The material showed a high specific capacitance and good rate performance. By assembling the asymmetric supercapacitor composed of S-NiCoP as the positive electrode and AC as the negative electrode, the cell can deliver a high energy density of 43.54 Wh kg⁻¹ at power density of 150 W kg⁻¹ with good electrochemical stability. The ASC cell can light the LED and electrical motor fan after charging for short time, implying the large potential for practical application.

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Notes and references

[‡] Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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The porous TMP nanosheets have been prepared by the phosphorization of sheet-like NiCo hydroxide precursor, and can be used as efficient and stable positive electrode for advanced asymmetric supercapacitors with high specific capacitance, good rate performance and long-term stability.