Nanoscale

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Cheng, H. Fan, Y. Xu, R. Wang and X. Zhang, *Nanoscale*, 2017, DOI: 10.1039/C7NR04464J.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Hollow Co₂P nanoflowers organized by nanorods for ultralong cycle-life supercapacitors

Ming Cheng^{a,b}, Hongsheng Fan^{a,b}, Yingying Xu^c, Rongming Wang^{c,*}, Xixiang Zhang^{b,*}

^a Department of Physics, Beihang University, Beijing 100191, P. R. China

^b King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia

^c Beijing Key Laboratory for Magneto-Photoelectrical Composite and Interface Science, School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, P. R. China

* Corresponding authors: rmwang@ustb.edu.cn, xixiang.zhang@kaust.edu.sa

Abstract

Hollow Co₂P nanoflowers (Co₂P HNF) are successfully prepared via a one-step, template-free method. Microstructure analysis reveals that Co₂P HNF is assembled by nanorods, possesses abundant mesopores and a amorphous carbon shell. Density functional theory calculation and electrochemical measurements demonstrate the high electrical conductivity of Co₂P. Benefiting from the unique nanostructures, when employed as electrode material for supercapacitors, Co₂P HNF exhibits a high specific capacitance, an outstanding rate capability, and an ultralong cycle stability. Furthermore, the constructed Co₂P HNF//AC ASC yields a high energy density of 30.5 Wh kg⁻¹ at a power density of 850 W kg⁻¹, along with an superior cycling performance (108.0% specific capacitance retained after 10000 cycles at 5 A g⁻¹). These impressive results make Co₂P HNF a promising candidate for supercapacitor applications.

Keywords: Co₂P; hollow nanoflower; pseudocapacitive; asymmetric supercapacitor;

ultrahigh stability

1. Introduction

To fulfill ever-increasing environmental and societal demands for energy storage, various strategies have been developed, such as lithium-(ion, sulfur, air) batteries, solar energy technology, and fuel cells.¹⁻⁵ Among them, supercapacitors play a crucial role on account of their high power density, reliable safety, and long lifetime.⁶⁻⁸ The main limitation of supercapacitors is their low energy density, which seriously impedes their widespread application.⁹⁻¹¹ Based on their fundamental energy storage mechanisms, supercapacitors are usually classified into two categories: electrode double layer capacitors (EDLCs), which store energy by accumulating the surface charges of the electrode materials, and pseudocapacitors, which deliver energy through reversible faradaic redox reactions.^{7, 12} Pseudocapacitors possess a much higher energy density than EDLCs.^{6, 7} Therefore, exploiting high performance pseudocapacitive materials is a feasible strategy to gain high performance supercapacitors.

High performance pseudocapacitive materials should possess four features: multiple oxidation states, a large specific surface area, good electronic conductivity, and a robust structure.¹³ Cobalt phosphides, which have been extensively studied in many fields (e.g., as electro-catalysts in water splitting, as anode materials in lithium-ion batteries, and as catalysts in hydrodesulfurization reactions), exhibit

metalloid properties and superior electronic conductivity.¹⁴⁻²¹ Since both cobalt phosphates and nickel phosphides have delivered high specific capacitance for supercapacitors in previous demonstrations,^{11, 22, 23} cobalt phosphides can be reasonably believed to produce rich redox reactions in alkaline solution. Moreover, considering the relationship between cobalt oxides and nickel oxides,^{24, 25} cobalt phosphides should have a higher theoretical capacity than nickel phosphides. So, cobalt phosphides are a promising alternative material for supercapacitors. Also, constructing nanostructured cobalt phosphides is an effective way to realize their specific capacitance by engineering a larger specific surface area. So far, cobalt phosphides with diverse structures, such as nanoparticles,^{14, 26-28} nanowires,^{20, 29} nanorods,^{15, 30-32} nanoflowers,^{30, 33} urchin-like microspheres,³⁴ and grass-like superstructures,³⁵ have been synthesized. However, unlike cobalt hydroxide, oxide, or sulfide, there is scanty research about the use of cobalt phosphides as the electrode materials for supercapacitors. Therefore, it's significant and meaningful to develop the application of cobalt phosphides for supercapacitors.

Compared with zero, one, or two-dimensional nanostructures, three-dimensional (3D) nanostructures should possess a larger specific surface area and more effectively prevent particle aggregation; therefore, they are preferable for energy storage.^{9, 30, 36, 37} Currently, there are two main techniques for synthesizing nanostructured transition metal phosphides, namely the solution-phase reaction and gas-solid reaction.^{38, 39} However, the process for synthesizing 3D transition-metal phosphides using the gas-solid method is too tedious and usually requires prepared

precursors.^{22, 34, 40} In addition, the nanostructure directly determines the cycling performance of electrode materials; thus, a robust structure is important in energy storage fields. The structure obtained from the gas-solid reaction may suffer from performance decay.²² Therefore, a simple solution-phase reaction must be developed to directly construct 3D transition-metal phosphides with a robust structure.

In this work, we report the synthesis of Co₂P with a robust, hollow nanoflower structure using a simple, one-step thermal decomposition method. Transmission electron microscopy (TEM) analysis reveals that the hollow Co₂P nanoflowers (Co₂P HNF) are composed of nanorods. When employed as the electrode material for supercapacitor, Co₂P HNF delivers a high specific capacitance of 412.7 F g⁻¹ at 1 A g⁻¹. Co₂P HNF also shows an ultrahigh cycling stability, with 124.7% of the initial specific capacitance retained after 10000 charge-discharge cycles. Furthermore, a Co₂P HNF//AC asymmetric supercapacitor (ASC) is successfully fabricated, and shows a superior specific capacitance, rate capacity, and cycling life-span. These results suggest that Co₂P HNF has potential as an alternative electrode material for supercapacitors.

2. Experimental

2.1. Material preparation

Cobalt(III) acetylacetonate (Co(acac)₃, chemical purity), triphenylphosphine (TPP, 99.0%), oleylamine (OAm, 98.0%), toluene (99.5%), and acetone (99.5%) were purchased from Beijing Chemical Reagents Company. Active carbon was purchased

from Nanjing JCNANO Tech Co., Ltd. All reagents were chemical grade and used without further purification.

The hollow Co₂P nanoflowers (Co₂P HNF) were synthesized in a one-step process by the thermal decomposition of Co(acac)₃ in a solution containing OAm and toluene, with TPP as the phosphorus source. First, 0.5 g Co(acac)₃ was dissolved in a three-neck flask containing a solution of 10 mL OAm and 5 mL toluene, before being heated to 100 °C and subjected to magnetic stirring and nitrogen bubbling for 0.5 h. Subsequently, 1.0 g TPP was added into the homogeneous solution, which continued under magnetic stirring and nitrogen bubbling for an additional 0.5 h. Then, the mixed solution was rapidly heated up to 280 °C, which was maintained for 2 h. Finally the obtained black solution was naturally cooled to room temperature, acetone was added to dilute the solution. The products were collected by centrifugation and washed several times with acetone.⁴¹

2.2. Material characterization

The crystal structure, morphology, elemental composition, and chemical valence state of the Co₂P HNF were studied using X-ray diffraction (XRD, X'Pert Pro MPD system, Cu K α , λ =0.154 nm), X-ray photoemission spectra (XPS, ESCALAB MK II, Al K α photon source, C1s 284.8eV), field-emission scanning electron microscopy (FESEM, HITACHI, S4800) and high-resolution transmission electron microscopy (HRTEM, FEI Titan G2 80-300 ST equipped with X-ray energy-dispersive spectroscopy (EDS)). The specimen for the TEM study was prepared by dispersing a drop of toluene solution containing the as-synthesized product onto a porous carbon film supported by a

copper grid, which was then dried in a vacuum drying oven.⁴² The specific surface areas of the products were determined by N₂ adsorption–desorption isotherm measurements at 77K (Micrometrics, ASAP 2020).

2.3. Electrochemical measurements

For preparation of the working electrodes, the prepared active material was mixed with carbon black and polyvinylidene fluoride (PVDF) with a mass ratio of 7:2:1 in N-methyl-2-pyrrolidinone solution. The mixture was pasted on a clean nickel-foam current collector (area ~1 cm²) and dried overnight at 80 °C in a vacuum oven. This dried electrode was pressed using a hydraulic press at a pressure of 10 MPa. The electrochemical tests were carried out in both three-electrode and two-electrode configurations using a 6 M KOH aqueous solution as the electrolyte. In the three-electrode electrochemical cell, a Pt wire and a saturated calomel electrode were used as the counter and reference electrodes, respectively.⁴¹ The loading mass of the active material in the working electrode was about 2.45 mg cm⁻². In the two-electrode electrochemical system, an ASC was constructed by using Co₂P HNF as the positive electrode and AC as the negative electrode. Electrochemical measurements were performed on an electrochemical workstation (CHI760E) using the cyclic voltammetry (CV) and chronopotentiometry (CP). Electrochemical impedance spectroscopy (EIS) measurements were also carried out using this apparatus over a frequency range between 100 kHz to 0.01 Hz at open-circuit voltage with an AC amplitude of 5 mV.⁴²

The specific capacitance (C , F g⁻¹), energy density (E , Wh Kg⁻¹) and power density (P ,

W Kg⁻¹) are calculated from the charge-discharge curves based on the following equations:^{43, 44}

$$C=I\Delta t/\Delta V \quad (1)$$

$$E=C\Delta V^2/7.2 \quad (2)$$

$$P=3600E/\Delta t \quad (3)$$

where I (A g⁻¹) is the current density, Δt (s) is the discharge time, ΔV (V) is the applied potential window. For the asymmetric supercapacitor, the current density I is defined by the total mass of the active materials on both the positive and negative electrodes.

3. Results and discussion

Co₂P hollow nanoflowers (Co₂P HNFs) were synthesized through a simple one-step process by the thermal decomposition of cobalt acetylacetonate in the solution containing oleylamine and toluene with triphenylphosphine as phosphorus source. The low-magnification SEM image in Fig. 1a shows that the prepared samples were uniform in size and shape. Detailed morphological information can be obtained from the high-magnification SEM image of two representative nanoparticles in Fig.1b. The nanoparticles had a spherical morphology with many protuberances and a diameter of about 110 nm. Besides, a thin carbon shell also can be observed on the surface.

The XRD results revealed the as-prepared product to be orthorhombic Co₂P, as shown in Fig. 1c. Four discernible peaks at 40.4°, 43.5°, 52.0°, and 55.6° are ascribed to the (112)/(210), (211), (020) and (302) planes of Co₂P (JCPDF No. 89-3030),

respectively. Fig. 1e presents a crystal structure model of the Co_2P crystal structure.

In orthorhombic Co_2P , the Co atoms have two occupied sites, which are tetrahedral and pyramidal geometries surrounded by four P and five P atoms, respectively. Each P atom is shared by three Co atoms, forming a tricapped trigonal prismatic configuration.⁴⁵⁻⁴⁷ The complicated structure of Co_2P endows it with abundant physicochemical properties.^{14, 15, 20, 30, 31, 35, 48} Moreover, the calculated densities of states of Co_2P show the Fermi level within the conduction band (Fig. S1). The result demonstrates the metallic feature of Co_2P , which benefits Co_2P as electrode material for energy storage.^{40, 44}

The energy dispersive X-ray spectroscopy (EDS) results of the Co_2P HNFs are shown in Fig. 1d. The atomic ratio of Co/P was measured to be 1.7, within the experimental error of stoichiometric ratio of Co_2P , further confirming the formation of Co_2P phase. Oxygen was detected, originating from the oxide layer that commonly forms on the surface of cobalt phosphide.^{17, 28, 31} The carbon signal came from the carbon film and the formed carbon shell on the surface of the nanoparticles, while the copper signal was from the copper network.

TEM revealed the microstructure of the prepared sample. A typical TEM image of the prepared Co_2P sample in Fig. 2a shows the flower-shaped structure with a hollow core, made up of nanorods with good monodispersity. A TEM image of an individual Co_2P HNF in Fig. 2b more clearly reveals its nanostructure. The diameter of the nanostructure was measured to be about 110 nm, consistent with the SEM results. The hollow flower structure and uniformity of Co_2P HNF were further

confirmed by HAADF STEM (Fig. 2c). Fig. 2d displays the selected area electron diffraction pattern of Co_2P HNF. The several diffraction rings observed in Fig. 2d correspond to the (112)/(210), (211), (020) and (302) planes of Co_2P , coinciding with the XRD data. A HRTEM image of Co_2P HNF in Fig. 2e clearly reveals its good crystallinity and lattice fringes. The lattice fringes with interplane distances of 0.221 and 0.174 nm correspond to the (112) and (020) planes of Co_2P , respectively. Fig. 2f shows the STEM image of Co_2P HNF and the corresponding EDX elemental mapping images of cobalt, phosphorus, and oxygen for the Co_2P HNF. In accordance with the EDS result (Fig. 1d) and the XPS spectrum (Fig. 3), both cobalt and phosphorus were uniformly distributed throughout each HNF, and oxygen was detected on the surface of the Co_2P HNF.

The multi-species on the surface of Co_2P determined its abundant electrochemical performance. To confirm the surface elemental composition and electronic states of the Co_2P HNF, XPS experiments were conducted. Cobalt, phosphorus, and oxygen were detected, and an overlapping peak resolving strategy was employed to analyze the valence state of the elements in-depthly, as shown in Fig. 3. For the high-resolution XPS spectrum of Co 2p, two species of Co can be clearly recognized in Fig. 3a. The fitting peaks at 777.9 and 792.8 eV are ascribed to the $2p_{3/2}$ and $2p_{1/2}$ binding energies of the reduced Co species in Co_2P .^{14, 15, 27} The peaks at 781.3 ($2p_{3/2}$) and 797.2 ($2p_{1/2}$) eV, which are accompanied by two shake-up satellite peaks at 785.6 and 802.5 eV, correspond to the oxidized Co species, which originated from the cobalt phosphate that formed on the surface of Co_2P .^{17, 18} Fig. 3b

shows the high-resolution P 2p spectrum, which was deconvoluted to three fitting peaks. The doublet at 192.2 and 130.2 eV indicates the phosphidation of cobalt as it formed Co₂P, while the peak at 133.4 eV is attributed to the phosphate and P-C bonding.^{14, 18, 27, 40} The obvious peak at 285.5 eV in the C 1s spectrum confirms the P-C bonding (Fig. S2).¹⁴ The spectrum of O 1s was also fitted to two peaks at 531.2 and 532.5 eV, corresponding to the lattice oxygen and the chemisorbed oxygen species, respectively.^{17, 21, 49}

Fig. 3d displays the N₂ adsorption-desorption isotherm of the as-prepared Co₂P HNF. The specific surface area was measured to be 19.37 m² g⁻¹ by the Brunauer-Emmett-Teller method. The Barrett-Joyner-Halenda pore size distribution plot shown in the inset of Fig. 3d reveals that Co₂P HNF possesses abundant mesopores, which substantially facilitate contact between the electrolyte and the active sites.

The electrochemical properties of Co₂P HNF as a positive electrode material for supercapacitors were estimated in a 6 M KOH aqueous solution. Fig. 4a shows the typical CV curves of Co₂P HNF at different scan rates, from 5 mV s⁻¹ to 50 mV s⁻¹. The CV curves of Co₂P HNF possess distinct redox peaks, unlike the rectangular CV curves of conventional EDLCs, highlighting the faradaic pseudocapacitive characteristics of a Co₂P HNF electrode.⁵⁰ Also, the anodic and cathodic peaks continuously shifted toward higher and lower potentials, respectively, with the current density peaks augmented by the increasing scan rates. The faradaic pseudocapacitive property of an electrode derives from the reversible redox of metal ions at the surface of the

active material. Based on previous studies of cobalt phosphide and phosphate, the complicated faradaic reversible redox reactions of Co₂P HNF were caused by the surface formation of different Co-based species, including the cobalt phosphate (denoted as Co²⁺_xP_yO_z) detected by XPS and EDX, and the cobalt hydroxide that originated from the oxidation of Co₂P in a KOH electrolyte at low voltage.^{11, 20, 30, 51, 52}

A possible reaction mechanism is proposed based on the CV curve measured at 5 mV s⁻¹ containing one small oxidation peak and four pairs of redox peaks (Fig. S3). The single one comes from the oxidation of Co₂P (Co^{δ+}) into Co(OH)₂ (Eq. (4)).^{20, 44} The two pairs of redox peaks at 0.10/0.07 V and 0.50/0.46 V can be assigned to the reversible transformation process of Co(OH)₂ ↔ CoOOH (Eq. (5)) and CoOOH ↔ CoO₂ (Eq. (6)), respectively.⁴⁴ Whereas the two couples of redox peaks at 0.35/0.27 V and 0.38/0.31 V can be assigned to the reversible conversion of Co²⁺_xP_yO_z ↔ Co³⁺_xP_yO_z(OH)_x (Eq. (7)) and Co³⁺_xP_yO_z(OH)_x ↔ Co⁴⁺_xP_yO_z(OH)_{2x} (Eq. (8)), respectively.^{11, 43, 51, 53}

Fig. 4b shows the CP curves of the Co₂P HNF electrode measured at current densities ranging from 1 A g⁻¹ to 10 A g⁻¹. The distinct plateaus in the potential further indicate the pseudocapacitive performance of the Co₂P HNF electrode, and

the number of plateaus also corresponds well with the number of redox peaks.

View Article Online
DOI: 10.1039/C7NR04464J

Meanwhile, the high symmetry of the CP curves reveals the excellent reversibility of the faradic redox processes.^{54, 55} Based on the discharging curves, the specific capacitances of Co₂P HNF were calculated to be 412.7, 370.4, 321.1, 284.9, 276.5, and 266.9 F g⁻¹ at the current densities of 1, 2, 4, 6, 8, and 10 A g⁻¹, respectively (Fig. 4c). Co₂P HNF exhibited an excellent rate capacitive property. Moreover, the specific capacitance of Co₂P HNF was higher than that of some reported cobalt-phosphorus-based materials, such as Co₂P nanorods (284 F g⁻¹ at 1 A g⁻¹),³⁰ Co₂P₂O₇ nanosheets (286 F g⁻¹ at 1 A g⁻¹),⁵³ Co₃(PO₄)₂ nanoflakes (188 F g⁻¹ at 3 A g⁻¹),⁵¹ Co₁₁(HPO₃)₈(OH)₆ microarchitecture (321 F g⁻¹ at 1.25 A g⁻¹),⁵⁵ NH₄CoPO₄ • H₂O microflowers (369.4 F g⁻¹ at 0.625 A g⁻¹),⁵⁶ Co₂P₂O₇ hierarchical architecture (367 F g⁻¹ at 0.625 A g⁻¹),⁵⁷ and flower-like Co₃(PO₄)₂ • 8H₂O (350 F g⁻¹ at 1 A g⁻¹).⁵⁰ Fig. 4d shows the plot of the voltage drops of Co₂P HNF electrode versus current density and the corresponding linear fitting function. The small absolute value of the slope indicates the low internal resistance of the Co₂P HNF electrode.

Cycling stability is a significant parameter to evaluate the performance of energy storage material. Fig. 3e shows the repeated charging-discharging process of the Co₂P HNF electrode at a constant high current density of 5 A g⁻¹. The Co₂P HNF electrode displayed impressive cycling stability and coulombic efficiency. During the first 4000 cycles, the specific capacitance continuously increased from 285.9 F g⁻¹ to 360.9 F g⁻¹. More importantly, the specific capacitance remained at 356.6 F g⁻¹ even after the subsequent 6000 cycles. This means that the Co₂P HNF electrode retained

124.7% of the initial specific capacitance after 10000 cycles at a high current density of 5 A g^{-1} .

The electrochemical impedance spectrum (EIS) was also determined to explore the electrical conductivity of the Co_2P HNF electrode over a frequency range between 100 kHz and 0.01 Hz under open-circuit conditions as shown in Fig. 4f. The diameter of the semicircle in the high frequency region, which is a decisive parameter for an electrode material, represents the charge-transfer resistance (R_{ct}); the intercept on the real Z axis in the high-frequency region is the internal resistance (R_s).^{37, 41} The values of R_{ct} and R_s were about 0.17Ω and 0.64Ω , respectively. The steep slope of the straight line in the low frequency region suggests a good capacitive behavior and a low electrolyte diffusion impedance.^{54, 56, 58} Therefore, the Co_2P HNF electrode exhibited fast charging and ion transfer behavior. The high-performance of the as-prepared Co_2P HNF can be attributed to the unique robust hollow structure, multiple oxidation states and high conductivity. Moreover, when as electrocatalyst for oxygen evolution reaction (OER), Co_2P HNF also exhibited moderate electrocatalytic performance (Fig. S4).

To further evaluate the Co_2P HNF electrode for use in supercapacitors in a practical application, an ASC was fabricated using Co_2P HNF as the positive electrode and AC as the negative electrode (Co_2P HNF//AC).²³ The electrochemical performance of the AC electrode was also tested in a 6 M KOH aqueous solution (Fig. S5). Based on the discharge curves, the specific capacitance of the AC electrode is calculated to be 246.3, 235.3, 225.4, 218.8, 213.8, 209.6 F g^{-1} at the current densities

of 1, 2, 4, 6, 8, 10 A g⁻¹. Thus, AC is an excellent negative electrode material for supercapacitors.

For optimal performance, the two electrodes should satisfy the charge balance relationship, $q^+ = q^-$.^{11, 30} The optimal loading mass ratio between Co₂P HNF and AC electrodes is $m_+/m_- = (C_- \times \Delta V_-)/(C_+ \times \Delta V_+) = (246.3 \times 1)/(412.7 \times 0.75) = 0.8$. Fig. 5a shows the CV curves of the Co₂P HNF electrode and the AC electrode at a scan rate of 10 mV s⁻¹, which indicate that the potential window of the Co₂P HNF//AC ASC could be enlarged to 1.6 V. Because the large potential window is significant to improve the energy density of ASC, a series of CV curves of the Co₂P HNFs//AC ASC with different potential windows at 20 mV s⁻¹ is presented in Fig. 5b, to determine the optimal operating potential of the ASC.⁵⁹ Remarkably, the operating potential of the ASC could be enlarged up to 1.7 V without obvious polarization curves. To further ascertain the potential window, the CP curves of the ASC under potential windows from 0.8 to 1.7 V at 1 A g⁻¹ were measured.⁵⁹ As expected, no obvious polarization appeared when the potential window increased to 1.7 V, consistent with the results in Fig. 5b. The specific capacitance of the ASC increased from 44.8 to 75.8 F g⁻¹ when the potential window increased from 0.8 to 1.7 V (Fig. 5d). As the potential window increasing from 0.8 to 1.7 V, the energy density of the ASC also increased dramatically from 4.0 to 30.4 Wh kg⁻¹. So an operation potential window of 1.7 V is deserved to study the electrochemical performance of the Co₂P HNFs//AC ASC.

Fig. 6a shows the CV curves of the Co₂P HNF//AC ASC at different scan rates from 5 to 50 mV s⁻¹ within the potential window of 0-1.7 V in 6 M KOH aqueous

View Article Online
DOI: 10.1039/C7NR04464J

electrolyte. The distorted, rectangular CV curves found at all of the scan rates indicate that both the pseudocapacitance from Co₂P HNF and the electric double-layer capacitance from AC contributed to the total capacitance of the ASC.²³ An absence of obvious shifts in the CV curve peaks indicates the excellent rate capability of the ASC. Fig. 6b shows the typical CP curves of the ASC measured at different current densities from 1 to 10 A g⁻¹. Based on the discharge curves, the specific capacitance of the ASC was calculated to be 75.9, 70.9, 66.0, 61.8, 58.8, and 56.9 F g⁻¹ at the current densities of 1, 2, 4, 6, 8, and 10 A g⁻¹, respectively (Fig. 6c). A capacitance of 75.0% was maintained even at a high current density of 10 A g⁻¹, demonstrating the excellent rate capability of the Co₂P HNF//AC ASC. Fig. 6d presents the cycling performance of the Co₂P HNF//AC ASC measured at a current density of 5 A g⁻¹. Within the initial 4000 cycles, the specific capacitance of the ASC slightly increased from 62.1 to 66.4 F g⁻¹, and remained at 67.1 F g⁻¹ even after completing the subsequent 6000 cycles. That means the Co₂P HNF//AC ASC delivered 108.0% of its initial specific capacitance after 10000 continuous cycles. The coulombic efficiency of the ASC remained at about 99% throughout all 10000 cycles. These results reveal the outstanding cycling performance of the Co₂P HNF//AC ASC.

To evaluate the energy storage ability of the Co₂P HNF//AC ASC, Ragone plots based on the galvanostatic discharge curves are displayed in Fig. 7. The energy density of the prepared ASC reached 30.5 Wh kg⁻¹ at a power density of 850 W kg⁻¹, and maintained 22.8 Wh kg⁻¹ at a higher power density of 8500 W kg⁻¹. Thus, the Co₂P HNF//AC ASC outperformed many previously reported ASCs (Fig. 7), such as

Co₂P nanoflowers//AC (24 Wh kg⁻¹ at 300 W kg⁻¹),³⁰ amorphous Ni-P//AC (29.2 Wh kg⁻¹ at 400 W kg⁻¹),²³ NiCo₂O₄//AC (14.7 Wh kg⁻¹ at 175 W kg⁻¹),³⁶ NiCo₂O₄ hollow submicrospheres//AC (27.2 Wh kg⁻¹ at 375 W kg⁻¹),⁶⁰ NiCoO₂/Ni foam//rGO (25.7 Wh kg⁻¹ at 1500 W kg⁻¹).⁶¹ And the Co₂P HNF//AC is also comparable with some recently reported high-performance transition metal phosphide-based or phosphate-based ASC.^{44, 62-65} The high energy storage of the Co₂P HNFs//AC ASC benefited from the large cell voltage of 1.7 V and the high specific capacitance. These results reinforce the promise of Co₂P HNF as an alternative material for supercapacitors.

4. Conclusions

In summary, we developed a simple, one-step method to synthesize robust Co₂P HNF. Structural characterizations disclosed that Co₂P HNF was composed of by nanorods and possessed abundant mesopores. Applied as an electrode material for supercapacitors, Co₂P HNF delivered a high specific capacitance of 412.7 F g⁻¹ at 1 A g⁻¹, a superior capacity retention at increased current densities, and an ultrahigh cycling stability. Additionally, the fabricated Co₂P HNF//AC ASC possessed a long cycling lifespan, and exhibited a high energy density of 30.5 Wh kg⁻¹ at a power density of 850 W kg⁻¹. More importantly, the energy density output was 22.8 Wh kg⁻¹ even at a high power density of 8500 W kg⁻¹. These results attest to the great potential of the Co₂P HNFs material for electrochemical energy storage fields.

[†] Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51371015, 51331002, 51501004), the Beijing Municipal Science and Technology Project (No. Z17111000220000), and King Abdullah University of Science and Technology (KAUST).

Notes and references

1. G. Gao, H. B. Wu and X. W. Lou, *Adv. Energy Mater.*, 2014, **4**, 1400422.
2. M. P. Yu, J. S. Ma, H. Q. Song, A. J. Wang, F. Y. Tian, Y. S. Wang, H. Qiu and R. M. Wang, *Energy Environ. Sci.*, 2016, **9**, 1495.
3. D. S. Geng, N. Ding, T. S. A. Hor, S. W. Chien, Z. L. Liu, D. Wu, X. L. Sun and Y. Zong, *Adv. Energy Mater.*, 2016, **6**, 14.
4. H. P. Zhou, Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, Z. R. Hong, J. B. You, Y. S. Liu and Y. Yang, *Science*, 2014, **345**, 542.
5. G. Wu, K. L. More, C. M. Johnston and P. Zelenay, *Science*, 2011, **332**, 443.
6. J. Zhang and X. S. Zhao, *ChemSusChem*, 2012, **5**, 818.
7. N. Choudhary, C. Li, J. Moore, N. Nagaiah, L. Zhai, Y. Jung and J. Thomas, *Adv. Mater.*, 2017, **25**, 1605336.
8. D. Chen, Q. F. Wang, R. M. Wang and G. Z. Shen, *J. Mater. Chem. A*, 2015, **3**, 10158.
9. F.-X. Ma, L. Yu, C.-Y. Xu and X. W. Lou, *Energy Environ. Sci.*, 2016, **9**, 862.
10. G. Zhang and X. W. Lou, *Adv. Mater.*, 2013, **25**, 976.
11. B. Li, P. Gu, Y. Feng, G. Zhang, K. Huang, H. Xue and H. Pang, *Adv. Funct. Mater.*, 2017, **27**, 1605784.
12. P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845.
13. X. Leng, L. Wu, Y. Liu, C. Li, S. Wei, Z. Jiang, G. Wang, J. Lian and Q. Jiang, *J. Mater. Chem. A*, 2016, **4**, 17171.
14. D. Das and K. K. Nanda, *Nano Energy*, 2016, **30**, 303.
15. Z. Huang, Z. Chen, Z. Chen, C. Lv, M. G. Humphrey and C. Zhang, *Nano Energy*, 2014, **9**, 373.
16. D. Yang, J. Zhu, X. Rui, H. Tan, R. Cai, H. E. Hoster, D. Y. Yu, H. H. Hng and Q. Yan, *ACS Appl. Mater. Inter.*, 2013, **5**, 1093.
17. J. Chang, Y. Xiao, M. Xiao, J. Ge, C. Liu and W. Xing, *ACS Catal.*, 2015, **5**, 6874.
18. Y.-P. Zhu, Y.-P. Liu, T.-Z. Ren and Z.-Y. Yuan, *Adv. Funct. Mater.*, 2015, **25**, 7337.
19. M. C. Lopez, G. F. Ortiz and J. L. Tirado, *J. Electrochem. Soc.*, 2012, **159**, A1253.
20. M. Chen, W. Zhou, M. Qi, J. Yin, X. Xia and Q. Chen, *J. Power Sources*, 2017, **342**, 964-969.
21. G. Xia, J. Su, M. Li, P. Jiang, Y. Yang and Q. Chen, *J. Mater. Chem. A*, 2017, **5**, 10321.
22. K. Zhou, W. Zhou, L. Yang, J. Lu, S. Cheng, W. Mai, Z. Tang, L. Li and S. Chen, *Adv. Funct. Mater.*, 2015, **25**, 7530.
23. D. Wang, L.-B. Kong, M.-C. Liu, W.-B. Zhang, Y.-C. Luo and L. Kang, *J. Power Sources*, 2015, **274**, 1107.

24. C. Zhou, Y. Zhang, Y. Li and J. Liu, *Nano Lett.*, 2013, **13**, 2078.
25. G. Cheng, W. Yang, C. Dong, T. Kou, Q. Bai, H. Wang and Z. Zhang, *J. Mater. Chem. A*, 2015, **3**, 17469.
26. Y. Cao, W. Zhou, X. Li, X. Ai, X. Gao and H. Yang, *Electrochim. Acta*, 2006, **51**, 4285.
27. S. Cao, Y. Chen, C.-C. Hou, X.-J. Lv and W.-F. Fu, *J. Mater. Chem. A*, 2015, **3**, 6096.
28. J. Ryu, N. Jung, J. H. Jang, H.-J. Kim and S. J. Yoo, *ACS Catal.*, 2015, **5**, 4066.
29. J. Tian, Q. Liu, A. M. Asiri and X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587.
30. X. Chen, M. Cheng, D. Chen and R. Wang, *ACS Appl. Mater. Inter.*, 2016, **8**, 3892.
31. V. V. T. Doan-Nguyen, S. Zhang, E. B. Trigg, R. Agarwal, J. Li, D. Su, K. I. Winey and C. B. Murray, *ACS Nano*, 2015, **9**, 8108.
32. F. Yuan, Y. Ni, L. Zhang, X. Ma and J. Hong, *J. Clust. Sci.*, 2013, **24**, 1067.
33. E. J. Popczun, C. W. Roske, C. G. Read, J. C. Crompton, J. M. McEnaney, J. F. Callejas, N. S. Lewis and R. E. Schaak, *J. Mater. Chem. A*, 2015, **3**, 5420.
34. H. C. Yang, Y. J. Zhang, F. Hu and Q. B. Wang, *Nano Lett.*, 2015, **15**, 7616.
35. H. Wu, Y. Ni, F. Hong, D. Lu and Y. Xiao, *RSC Adv.*, 2016, **6**, 5154.
36. R. Ding, L. Qi, M. Jia and H. Wang, *Electrochim. Acta*, 2013, **107**, 494.
37. H.-W. Shim, A.-H. Lim, J.-C. Kim, E. Jang, S.-D. Seo, G.-H. Lee, T. D. Kim and D.-W. Kim, *Sci. Rep.*, 2013, **3**, 2325.
38. Y. Shi and B. Zhang, *Chem. Soc. Rev.*, 2016, **45**, 1529.
39. Y. Lu, T. Wang, X. Li, G. Zhang, H. Xue and H. Pang, *RSC Adv.*, 2016, **6**, 87188.
40. J. Song, C. Zhu, B. Z. Xu, S. Fu, M. H. Engelhard, R. Ye, D. Du, S. P. Beckman and Y. Lin, *Adv. Energy Mater.*, 2017, **7**, 1601555.
41. M. Cheng, S. Duan, H. Fan and R. Wang, *CrystEngComm*, 2016, **18**, 6849.
42. S. Duan and R. Wang, *NPG Asia Mater.*, 2014, **6**, e122.
43. R. Bendi, V. Kumar, V. Bhavanasi, K. Parida and P. S. Lee, *Adv. Energy Mater.*, 2016, **6**, 1501833.
44. H. Liang, C. Xia, Q. Jiang, A. N. Gandhi, U. Schwingenschlögl and H. N. Alshareef, *Nano Energy*, 2017, **35**, 331.
45. S. Fujii, S. Ishida and S. Asano, *Journal of Physics F Metal Physics*, 1988, **18**, 971.
46. J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney and R. E. Schaak, *Chem. Mater.*, 2015, **27**, 3769.
47. D. R. Liyanage, S. J. Danforth, Y. Liu, M. E. Bussell and S. L. Brock, *Chem. Mater.*, 2015, **27**, 4349.
48. Y. Ni, J. Li, L. Jin, J. Xia, J. Hong and K. Liao, *New J. Chem.*, 2009, **33**, 2055.
49. H. Zhang, T. Ling and X.-W. Du, *Chem. Mater.*, 2015, **27**, 352.
50. H. Li, H. Yu, J. Zhai, L. Sun, H. Yang and S. Xie, *Mater. Lett.*, 2015, **152**, 25.
51. J. Theerthagiri, K. Thiagarajan, B. Senthilkumar, Z. Khan, R. A. Senthil, P. Arunachalam, J. Madhavan and M. Ashokkumar, *ChemistrySelect*, 2017, **2**, 201.
52. W. Peng, L. Jiao, Q. Huan, L. Li, J. Yang, Q. Zhao, Q. Wang, H. Du, G. Liu, Y. Si, Y. Wang and H. Yuan, *J. Alloy. Compd.*, 2012, **511**, 198.
53. Z. Khan, B. Senthilkumar, S. Lim, R. Shanker, Y. Kim and H. Ko, *Adv. Mater. Inter.*, 2017, 1700059.
54. H. Pang, S. Wang, W. Shao, S. Zhao, B. Yan, X. Li, S. Li, J. Chen and W. Du, *Nanoscale*, 2012, **4**, 5946.

View Article Online
DOI: 10.1039/C7NR04464J

55. H. Pang, Y. Liu, J. Li, Y. Ma, G. Li, Y. Ai, J. Chen, J. Zhang and H. Zheng, *Nanoscale*, 2013, **5**, 503. View Article Online
DOI:10.1039/C7NR04464J
56. H. Pang, Z. Yan, W. Wang, J. Chen, J. Zhang and H. Zheng, *Nanoscale*, 2012, **4**, 5946..
57. H. Pang, Z. Yan, Y. Ma, G. Li, J. Chen, J. Zhang, W. Du and S. Li, *J. Solid State Electr.*, 2013, **17**, 1383.
58. D. Zhou, X. Su, M. Boese, R. Wang and H. Zhang, *Nano Energy*, 2014, **5**, 52.
59. C. Qing, Y. Liu, X. Sun, X. OuYang, H. Wang, D. Sun, B. Wang, Q. Zhou, L. Xu and Y. Tang, *RSC Adv.*, 2016, **6**, 67785.
60. Y. Zhu, J. Wang, Z. Wu, M. Jing, H. Hou, X. Jia and X. Ji, *J. Power Sources*, 2015, **287**, 307.
61. X. Xu, H. Zhao, J. Zhou, R. Xue and J. Gao, *J. Power Sources*, 2016, **329**, 238.
62. M. Minakshi, D. Mitchell, R. Jones, F. Alenazey, T. Watcharatharapong, S. Chakraborty and R. Ahuja, *Nanoscale*, 2016, **8**, 11291.
63. S. Liu, K. V. Sankar, A. Kundu, M. Ma, J. Y. Kwon and S. C. Jun, *ACS Appl. Mater. Inter.*, 2017, **9**, 21829.
64. Y. Tang, Z. Liu, W. Guo, T. Chen, Y. Qiao, S. Mu, Y. Zhao and F. Gao, *Electrochim. Acta*, 2016, **190**, 118-125.
65. Y.-M. Hu, M.-C. Liu, Y.-X. Hu, Q.-Q. Yang, L.-B. Kong and L. Kang, *Electrochim. Acta*, 2016, **215**, 114-125.

Fig. 1 (a, b) SEM images, (c) XRD patterns, (d) EDS elemental spectrum, and (e) crystal structures of Co_2P HNF.

Fig. 2 (a, b) TEM images, (c) STEM image, (d) corresponding SAED pattern image, and (e) HRTEM image of Co_2P HNF. (g) STEM image and corresponding EDS elemental maps of Co, P, and O in a single Co_2P HNF.

Fig. 3 High resolution XPS spectra of (a) Co 2p, (b) P 2p, and (c) O 1s of Co₂P HNF. (d) Typical N₂ adsorption and desorption isotherms and the pore-size-distribution curves (inset) of Co₂P HNF.

Fig. 4 (a) CV curves at different scan rates and (b) charge-discharge curves at different current densities of Co_2P HNF. (c) Plot of the voltage drops of Co_2P HNF versus current density, and the corresponding linear fitting function. (d) Specific capacitance at different current densities of Co_2P HNF. (e) Cycling stability of Co_2P HNF at a current density of 5 A g^{-1} . (f) Electrochemical impedance spectra (EIS) of Co_2P HNF.

Fig. 5 (a) CV curves of Co₂P HNF and AC electrodes at a scan rate of 10 mV s⁻¹. (b) CV curves of the Co₂P HNF//AC ASC measured at different potential windows at a scan rate of 20 mV s⁻¹. (c) CP curves of the Co₂P HNF//AC ASC measured at different potential windows at a current density of at 1 A g⁻¹. (d) Specific capacitance of the Co₂P HNF//AC ASC measured at different potential windows at a current density of at 1 A g⁻¹.

Fig. 6 (a) CV curves of the Co_2P HNF//AC ASC at different scan rates in the potential window of 0–1.7 V. (b) CP curves of the Co_2P HNF//AC ASC at different current densities. (c) Specific capacitance of the Co_2P HNF//AC ASC at different current densities. (d) Cycling stability and coulombic efficiency of the Co_2P HNF//AC ASC at a constant current density of 5 A g^{-1} .

Fig. 7 Ragone plots of the Co_2P HNF//AC ASC and other previously reported ASCs.