General formation of Prussian blue analogue microtubes for high-performance Na-ion hybrid supercapacitors

Xuemin Yin, Hejun Li*, Ruimei Yuan, Leilei Zhang and Jinhua Lu*

ABSTRACT One-dimensional (1D) hollow-structured nanomaterials with desirable compositions have aroused huge attention in the field of electrochemical energy storage. In the present study, 1D hierarchical cobalt hexacyanoferrate (CoHCF) microtubes were initially fabricated using a facile self-templated method with the electrospun polyacrylonitrile (PAN)-cobalt acetate ($\text{Co}(\text{Ac})_2$) as templates. After the chemical reaction was performed between the templates and a potassium ferricyanide solution, the core-shell PAN- $\text{Co}(\text{Ac})_2$ @CoHCF nanofibers were successfully fabricated. Subsequently, the CoHCF microtubes were finally obtained via the selective dissolution of the PAN- $\text{Co}(\text{Ac})_2$ cores. Benefiting from the unique structural characteristic, the CoHCF microtubes electrode exhibited prominent electrochemical characteristics in Na_2SO_4 aqueous electrolyte, including a high specific capacitance of 281.8 F g^{-1} (at 1 A g^{-1}), and good rate capability as well as long cycling stability (93% capacitance retention after 5000 cycles). The hybrid supercapacitor assembled with CoHCF microtubes and activated carbon (AC) as the positive and negative electrodes, respectively, exhibited a high energy density of $43.89 \text{ W h kg}^{-1}$, a power density of 27.78 kW kg^{-1} , as well as a long cycle life. Note that this versatile self-templated synthetic strategy could be extended to fabricate other 1D hollow Prussian blue (PB) or its analogues (PBA) with controllable composition, which have a potential application in a range of fields.

Keywords: electrospinning, microtubes, cobalt hexacyanoferrate, hollow structures, hybrid supercapacitors

INTRODUCTION

It is a notable saying in materials science that the performance and characteristics of a material are dependent on its structure. Recently, hollow structures exhibiting the unique structural characteristics of high surface area and

low density have aroused huge attention from researchers [1–4]. Besides, the hollow-structured materials have been extensively applied in many fields (e.g., catalysis, gas/ion adsorption, sensor, electromagnetic shielding, energy storage and conversion) [5–11]. For the area of energy storage, as compared with the solid or bulk materials, hollow structures exhibit the following advantages. First, porous structures exhibiting open channels and high surface area could create considerable electrochemical active sites for the rapid charge transfer reaction. Second, hollow structures composed of nanoparticles are capable of narrowing the diffusion distance for ions/electrons. Third, the hollow interior could relax the structural strain and alleviate the volume change attributed to the ion insertion/extraction [10–15]. Considering the mentioned merits of hollow structures, researchers have been committed to developing novel hollow structures applied in a range of energy storage-related areas.

Prussian blue (PB) is a material with a long history, which could be used as pigment in painting and photographs. The PB with a cubic crystal structure has the typical chemical formula $\text{A}_x\text{M}_y[\text{M}'(\text{CN})_6]_z$, where $\text{A} = \text{K}^+$, Na^+ , etc., and $\text{M} = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , etc. [16–18]. Recently, PB and its analogues (PBA) have been extensively employed in various fields, such as energy storage, electrocatalysis, bio-sensor and bio-medical applications, mainly benefiting from their structural superiority in accommodating metal cations [19–23]. Note that considerable interest has been generated in PB/PBA for their applications in energy storage (supercapacitors, batteries) in view of their structural superiority [24–28]. However, the electrochemical performance could not satisfy the requirements. As mentioned above, constructing hollow structures can effectively enhance the electrochemical performance of materials. Accordingly,

State Key Laboratory of Solidification Processing, C/C Composites Research Center, Northwestern Polytechnical University, Xi'an 710072, China

* Corresponding authors (emails: lihejun@nwpu.edu.cn (Li H); lujinhua@nwpu.edu.cn (Lu J))

the hollow-structured PB/PBA for energy storage should be developed. Though some studies on hollow structures of PBA have been reported [22], one-dimensional (1D) PBA structures have been rarely reported. Thus, it is still a challenge to fabricate 1D PBA with tunable composition using a novel method.

In this study, a novel and general multi-step strategy was proposed to fabricate PBA microtubes by using a self-templated method with electrospun nanofibers as precursors. After the chemical reaction was performed, numerous of hierarchical cobalt hexacyanoferrate (CoHCF) nanocrystals were fabricated on the surface of as-electrospun nanofibers to form a core-shell structure. Lastly, the CoHCF microtubes were fabricated *via* a selective etching process. It is noteworthy that this method can be adopted as a novel method of fabricating 1D hollow PB/PBA with tunable composition. For the merits of hollow structures, the as-fabricated CoHCF microtubes exhibited excellent electrochemical properties as an electrode material for supercapacitors. Furthermore, the hybrid supercapacitor assembled with CoHCF microtubes and activated carbon (AC) displayed remarkable performance with enhanced energy/power densities and good cycling stability.

EXPERIMENTAL SECTION

Synthesis of polyacrylonitrile (PAN)-Co(Ac)₂ composite nanofibers

The PAN-Co(Ac)₂ composite nanofibers were fabricated *via* a facile electrospinning process. Typically, 1 g of polyacrylonitrile (PAN, molecular weight ~1,300,000, AR) and 3 g of cobalt acetate tetrahydrate (Co(Ac)₂·4H₂O, AR) were dissolved into 20 mL of *N,N*-dimethylformamide (DMF, AR) at 80°C with vigorous stirring to obtain a pink solution. Subsequently, the mixed solution was transferred to a 50-mL syringe for electrospinning. The electrospinning process was conducted at an applied working voltage of 15 kV and a feeding rate of 1.0 mL h⁻¹ with an electrospinning distance of 15 cm. The electrospun PAN-Co(Ac)₂ nanofibers were dried at 60°C and collected for further use.

Fabrication of CoHCF microtubes

Typically, 20 mg of the as-fabricated PAN-Co(Ac)₂ composite nanofibers were soaked into 20 mL of ethanol and 20 mg of potassium hexacyanoferrate (K₃[Fe(CN)₆], AR) was dissolved into 20 mL of deionized water. Then, the K₃[Fe(CN)₆] solution was poured into the PAN-Co(Ac)₂ ethanol solution, and maintained at room tem-

perature for 24 h. Afterwards, the core-shell PAN-Co(Ac)₂@CoHCF composite nanofibers were obtained. Lastly, the CoHCF microtubes were fabricated by dispersing the core-shell nanofibers into DMF at 60°C to dissolve the PAN-Co(Ac)₂ core.

Materials characterization

The crystal structures of the as-fabricated samples were analyzed by X-ray diffraction (XRD, X'Pert Pro MPD, Philips). The morphology and microstructure were characterized by field emission scanning electron microscopy (FESEM, FEI Nano SEM 450) and transmission electron microscopy (TEM, FEI Tecnai F30G2). The element composition and distribution of the samples were analyzed by an energy dispersive X-ray spectrometer (EDX, X-act, Oxford). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific) was adopted to ascertain the surface chemical states of the samples. The Fourier-transform infrared (FT-IR) spectra were collected by using a Nicolet iS50 spectrometer (Thermo Fisher Scientific).

Electrochemical measurements

Before the electrochemical tests, the slurry of working electrodes was fabricated by mixing the active materials (CoHCF microtubes, AC), conductive carbon black and polytetrafluoroethylene (PTFE) in a weight ratio of 7:2:1 with constantly stirring. The working electrodes were prepared by painting the above slurry on Ni foam and drying at 80°C and the typical mass loading of active materials was nearly 1.5 and 3.0 mg cm⁻² for CoHCF and AC electrodes, respectively. The electrochemical measurements were performed on a CHI660E electrochemical station with a conventional three-electrode system with a Pt foil and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. The electrolyte was 0.5 mol L⁻¹ Na₂SO₄ aqueous solution.

The hybrid supercapacitor was constructed by assembling CoHCF as the positive electrode and the AC as the negative electrode. The electrolyte was 0.5 mol L⁻¹ Na₂SO₄ aqueous solution. Based on the charge balance equation ($q^+ = q^-$), the mass balance of positive and negative electrodes can be expressed by the following equation: $m_+/m_- = C_+ \Delta V_- / C_- \Delta V_+$, where m , C , and ΔV are the mass, specific capacitance and voltage range of the positive (+) and negative (-) electrodes, respectively.

The mass ratio of the positive electrode relative to the negative electrode in this work was determined to be 0.5. The specific capacitance (C_{cell}), energy density (E) and power density (P) of the two-electrode hybrid super-

capacitor were calculated according to the following equations: $C_{\text{cell}} = I\Delta t / m_{+-}V$, $E = C_{\text{cell}}\Delta V^2/2$, $P = E/\Delta t$, where I , Δt , ΔV and m_{+-} represent the discharge current density, the discharge time, the voltage range and the total mass of active materials on both electrodes, respectively.

RESULTS AND DISCUSSION

The synthetic procedures of CoHCF microtubes in this experiment are illustrated in Fig. 1, consisting of three steps. First, the PAN-Co(Ac)₂ composite nanofibers were fabricated by electrospinning, serving as the templates and cobalt source for the formation of CoHCF. Subsequently, after the reaction between the PAN-Co(Ac)₂ nanofibers and [Fe(CN)₆]³⁻ solution, CoHCF layer composed of numerous nanocrystals was uniformly grown on the surface of the nanofibers. Lastly, the cores of the as-obtained core-shell PAN-Co(Ac)₂@CoHCF nanofibers were dissolved by DMF, and hierarchical CoHCF microtubes were successfully generated.

As shown in Fig. S1, the PAN-Co(Ac)₂ composite nanofibers, with a diameter of about 700 nm and a smooth surface, were successfully synthesized *via* an electrospinning method. The EDX mapping spectrum indicated that the Co(Ac)₂ was uniformly distributed in the PAN nanofibers. After the reaction with [Fe(CN)₆]³⁻, the color of nanofiber textile turned from light pink into tan (Fig. S2). From the SEM images (Fig. S3), lots of CoHCF nanoparticles were grown on the PAN-Co(Ac)₂ nanofibers to form a CoHCF layer. The as-synthesized PAN-Co(Ac)₂@CoHCF nanofibers showed a core-shell structure with a rough surface. From the XRD pattern of the core-shell nanofibers (Fig. S3d), the typical diffraction peaks of CoHCF could be detected, demonstrating the formation of CoHCF. After being dipped into the DMF solution, the core of PAN-Co(Ac)₂ could be completely removed, successfully forming a microtube structure

(Fig. 2a–c, Figs S4 and S5). Compared with the PAN-Co(Ac)₂ nanofibers, the CoHCF microtubes synthesized using the precursors without the supporting cores could not maintain the length, and they could be broken in the positions of weak and thin wall, forming the relatively short microtubes. According to Fig. 2c and d, the CoHCF microtubes with a diameter of 700 nm could be observed, displaying a rough surface. The thickness of tube wall, composed of lots of CoHCF nanocrystals with a particle size of several nanometers, was about 20 nm. From the high resolution TEM (HRTEM) image shown in Fig. 2e, the lattice fringe with an interplanar distance of 0.514 nm was indexed to the (200) plane of cubic CoHCF. The selected area electron diffraction (SAED) pattern of microtubes (Fig. 2f) could also confirm the formation of CoHCF. EDX analysis (Fig. 2g and Fig. S5c) revealed that the element composition of the product was K, C, N, Fe and Co, further suggesting the successful formation of CoHCF microtubes.

The crystal structure of the microtubes was further investigated by XRD and FT-IR. The peaks located at 17.5°, 25.0° and 35.5° could be indexed to the (200), (220) and (400) planes of the face-centered cubic CoHCF (JCPDS No. 46-0907), respectively, which further ascertained the formation of CoHCF (Fig. 3a). The FT-IR spectrum (Fig. 3b) shows the characteristic peaks of PBA at 2089 and 593 cm⁻¹, corresponding to the stretching vibrations of C≡N triple bond and the bending modes of Fe–C≡N, respectively [22]. The elemental composition and surface chemical states of the CoHCF were investigated by XPS. As shown in Fig. 3c, the Co, Fe, C, O, and N elements were detected, which was basically consistent with the EDX results. The C–N bond at 285.8 eV and C≡N at 398.1 eV were observed in C 1s and N 1s spectra (Fig. 3d and e). As shown in Fig. 3f, the Co 2p could be deconvoluted into two major peaks and two

Figure 1 Schematic illustration of the synthesis procedure of CoHCF hollow microtubes using electrospun PAN-Co(Ac)₂ nanofibers as the templates. I, the preparation of PAN-Co(Ac)₂ nanofiber templates by electrospinning; II, the growth of CoHCF on the PAN-Co(Ac)₂ nanofibers; III, selective etching of the PAN-Co(Ac)₂ cores in DMF solution.

Figure 2 (a–c) SEM images, (d) TEM image, (e) HRTEM image, (f) SEAD pattern and (g) EDX mappings of the synthesized CoHCF microtubes.

Figure 3 (a) XRD pattern and (b) FT-IR spectrum, and (c–f) XPS spectra of the synthesized CoHCF microtubes. (c) Survey scan spectrum; high-resolution spectra of (d) C 1s, (e) N 1s and (f) Fe 2p and Co 2p.

shakeup satellites (Named as “Sat.”), in which the peaks at 780.2 and 783.6 eV belong to $\text{Co}^{3+} 2p_{3/2}$ and $\text{Co}^{2+} 2p_{3/2}$ and those at 794.8 and 797.0 eV refer to $\text{Co}^{3+} 2p_{1/2}$ and $\text{Co}^{2+} 2p_{1/2}$. In the high resolution Fe 2p spectrum, two obvious peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ at around 706 and 719 eV could be detected [29,30]. Combining the XRD pattern, FT-IR spectrum and XPS spectra, all results above confirmed the successful preparation of CoHCF.

It is noteworthy that the self-templated method in this work was extended to prepare other PBA microtubes, as exemplified by NiHCF and MnHCF microtubes. As show

in Fig. 4, Figs S6 and S7, the XRD, SEM and TEM and EDX measurements were performed to characterize the NiHCF and MnHCF microtubes. It is evident that based on this preparation mechanism, the NiHCF and MnHCF microtubes could be successfully fabricated, just by regulating the composition of the electrospinning solution. Notably, by regulating the experimental parameters (e.g., the ions ratio of electrospinning solution, the kinds of reaction solution, and the electrospinning parameters), it is easy to fabricate 1D PBA hollow microtubes with different kinds, compositions and sizes. From the above

Figure 4 (a, d) FESEM, (b, e) TEM images and (c, f) XRD patterns of (a–c) NiHCF and (d–f) MnHCF microtubes.

analyses, this self-templated strategy is versatile in fabricating 1D PBA hollow microtubes.

In this work, the electrochemical performance of the as-fabricated CoHCF microtubes was firstly investigated by a three-electrode cell in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ neutral electrolyte. The cyclic voltammetry (CV) curves of the CoHCF microtubes at various scan rates are exhibited in Fig. 5a. Along with the insertion/extraction of Na^+ into/from the framework structure, reversible Faradaic redox reactions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ occurred, showing pairs of reduction/oxidation peaks in all CV curves, which could be expressed as follows: $\text{Co}_{1.5}[\text{Fe}^{\text{III}}(\text{CN})_6] + \text{e}^- + \text{Na}^+ \leftrightarrow \text{NaCo}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and $\text{KCo}[\text{Fe}^{\text{III}}(\text{CN})_6] + \text{e}^- + \text{Na}^+ \leftrightarrow \text{NaKCo}[\text{Fe}^{\text{II}}(\text{CN})_6]$. Moreover, the CV curves display high shape retention and prominent symmetry with a rise in the scan rates, suggesting the rapid reaction rate, remarkable reversibility and high coulombic efficiency of electrochemical reaction. It is known that the peak current density (i_p) to the scan rate (ν) in a CV measurement, will vary depending on whether the redox reaction is diffusion-controlled or surface-controlled, which agrees with the following general relationship: $i_p = a\nu^b$. For a redox reaction controlled by semi-infinite linear diffusion, the b -value is 0.5; for a capacitive process, a b -value of 1 is obtained [31,32]. From Fig. S8, the slopes of plots of $\log(i_p) - \log(\nu)$ are around 0.65, demonstrating that the electrochemical reaction in this experiment is diffusion-controlled. Fig. 5b exhibits the galvanostatic charge/discharge (GCD) curves at different current densities ranging from 1 to 20 A g^{-1} , showing obvious pseudocapacitive characteristics. The voltage plateaus at about 0.8

and 0.35 V could be observed in the curves, corresponding to the voltage positions of the redox peaks in the CV curves. In addition, the charge curve is symmetrical with discharge curve, revealing the excellent reversibility and high coulombic efficiency. The specific capacitance of CoHCF microtubes electrode at various current densities are shown in Fig. 5c. The CoHCF microtubes electrode exhibited a high specific capacitance of 281.8 F g^{-1} at a current density of 1 A g^{-1} . With the increase of the current density, the electrode exhibited good capacitance retention (64.6%) and a capacitance of 182 F g^{-1} even at 20 A g^{-1} , suggesting its excellent rate performance. As shown in Fig. 5d, the cycling performance of CoHCF microtubes was also investigated, which is critical to supercapacitors in practical applications. The CoHCF microtubes electrode preserved 93% of the initial capacitance after 5,000 cycles at a current density of 5 A g^{-1} , indicating their prominent long-term cycling stability. Furthermore, the coulombic efficiency was maintained at about 100% during the cycling tests. Compared with the Nyquist plot before cycles, the curve after cycles shows a similar shape with tiny distortion, further confirming the cycling stability (Fig. S9) [33]. The good cycling stability of CoHCF microtubes electrode might be due to the stability of the hollow structure, so the volume expansion and contraction could be buffered during the long cycle tests. Fig. S10 displays the SEM images of CoHCF microtubes electrode after the charging-discharging cycles. The hollow structure of CoHCF microtubes could be well maintained, verifying our guess about the stability of hollow microtubes. More re-

Figure 5 (a) CV curves of the CoHCF microtubes at various scan rates. (b) GCD curves at various current densities. (c) The specific capacitance as a function of current density. (d) Cycling performance at a current density of 5 A g^{-1} .

markably, the electrochemical performance was superior to that of many previously reported CoHCF-based materials as supercapacitors, as illustrated in Table S1.

To further evaluate the practical application of CoHCF microtubes, a hybrid supercapacitor device was fabricated by assembling CoHCF microtubes with AC (Fig. S11) as the positive and negative electrodes, respectively, which can extend the voltage window to enhance the performance of the full cell. The typical CV curves of CoHCF and AC electrodes at a scan rate of 20 mV s^{-1} are plotted in Fig. 6a. The potential window of CoHCF was -0.1–1.0 V, which was compatible to that of AC (-1.0–0 V). Therefore, the potential window of the cell could be extended to 2.0 V, thereby improving the electrochemical performance of the full cell. In Fig. 6b, the CV curves of the CoHCF//AC at different scan rates from 2 to 100 mV s^{-1} are displayed, exhibiting both pseudo-capacitive and electrical double-layer capacitive characteristics at all scan rates. At a high scan rate of 100 mV s^{-1} , the CV curve could maintain the original shape of that at the low scan rate, revealing the good rate performance. As exhibited in Fig. 6c, GCD measurements at different current densities from 1 to 30 A g^{-1} were carried out. The discharge curves are basically symmetrical to the corresponding charge curves, suggesting

outstanding electrochemical reversibility and high coulombic efficiency of the device. Fig. 6d shows the specific capacitance calculated from the discharge curves of the device at different current densities. The hybrid device could achieve a high specific capacitance (based on the total mass of both electrodes) of 79, 76, 74, 72, 68, 61, 55, and 50 F g^{-1} at current densities of 1, 2, 3, 5, 10, 15, 20 and 30 A g^{-1} , respectively. About 63.3% of the capacitance was retained even at a high current density of 30 A g^{-1} , indicating an excellent rate capability. The cycling performance of the device was evaluated by repeated GCD tests at a current density of 5 A g^{-1} (Fig. 6e). Encouragingly, the device manifested outstanding cycling stability with a high capacitance retention of 91.1% after 3,000 cycles. The Ragone plots of the CoHCF//AC hybrid device and some reported PBA-based-hybrid systems are shown in Fig. 6f. Remarkably, a high energy density of 43.89 W h kg^{-1} could be achieved at a power density of 1 kW kg^{-1} in this work. Also, even at a high power density of 3 kW kg^{-1} , the energy density of the device could still retain 27.78 W h kg^{-1} . Moreover, the electrochemical performance of the CoHCF//AC hybrid device compares favorably to those of many previously reported PBA-based-hybrid systems, such as CoHCF//carbon black modified reduced graphene oxide (mRGO) [34],

Figure 6 (a) CV curves of CoHCF and AC electrodes at a scan rate of 20 mV s^{-1} . (b) CV curves of the CoHCF//AC hybrid device at various scan rates. (c) GCD curves at different current densities. (d) The specific capacitance as a function of the current density. (e) Cycling stability and (f) Ragone plots of the CoHCF//AC hybrid devices.

CoHCF/reduced graphene oxide (rGO)//AC [35], MnHCF// Fe_3O_4 /rGO [36], CoHCF//carbon microspheres (CMS) [37], and CoHCF//AC [22].

Based on the mentioned discussion and analyses, the hierarchical CoHCF microtubes exhibited prominent electrochemical performance, which benefits from the unique hollow structure. First, the hollow structure with a high surface area could provide more active sites available for the energy storage interface. Moreover, the hollow structure could provide considerable channels/pathways, thereby shortening the ion/mass diffusion distance. Furthermore, the CoHCF microtubes were structurally stable during the ion insertion/extraction, which is critical to electrochemical stability.

CONCLUSIONS

In summary, hierarchical CoHCF microtubes were successfully fabricated by a self-templated method using electrospun nanofibers as precursors. Ascribed to the unique architecture, the CoHCF microtubes exhibited superior electrochemical performance with high specific capacitance (281.8 F g^{-1} at 1 A g^{-1}), good rate capability (64.6% of capacitance retention at 20 A g^{-1}) and long cycling stability (93% capacitance retention after 5,000 cycles). Furthermore, the hybrid supercapacitor assembled with CoHCF microtubes and AC also delivered high energy/power densities and long cycle life. More

significantly, this work provides a promising way to synthesize 1D hollow-structured PB/PBA varieties with tailored composition for a wide range of applications.

Received 3 December 2019; accepted 12 January 2020;
published online 17 March 2020

- Wang X, Feng J, Bai Y, *et al.* Synthesis, properties, and applications of hollow micro-/nanostructures. *Chem Rev*, 2016, 116: 10983–11060
- Lai X, Halpert JE, Wang D. Recent advances in micro-/nano-structured hollow spheres for energy applications: From simple to complex systems. *Energy Environ Sci*, 2012, 5: 5604–5618
- Yu L, Wu HB, Lou XWD. Self-templated formation of hollow structures for electrochemical energy applications. *Acc Chem Res*, 2017, 50: 293–301
- Zheng M, Xiao X, Li L, *et al.* Hierarchically nanostructured transition metal oxides for supercapacitors. *Sci China Mater*, 2018, 61: 185–209
- Liu J, Wu C, Xiao D, *et al.* MOF-derived hollow Co_9S_8 nanoparticles embedded in graphitic carbon nanocages with superior Li-ion storage. *Small*, 2016, 12: 2354–2364
- Zhu YP, Ma TY, Jaroniec M, *et al.* Self-templating synthesis of hollow Co_3O_4 microtube arrays for highly efficient water electrolysis. *Angew Chem Int Ed*, 2017, 56: 1324–1328
- Yin X, Li H, Han L, *et al.* Lightweight and flexible 3D graphene microtubes membrane for high-efficiency electromagnetic-interference shielding. *Chem Eng J*, 2020, 124025
- Kim C, Jung JW, Yoon KR, *et al.* A high-capacity and long-cycle-life lithium-ion battery anode architecture: Silver nanoparticle-decorated SnO_2/NiO nanotubes. *ACS Nano*, 2016, 10: 11317–11326

- 9 Yin X, Li H, Wang H, *et al.* Self-templating synthesis of cobalt hexacyanoferrate hollow structures with superior performance for Na-ion hybrid supercapacitors. *ACS Appl Mater Interfaces*, 2018, 10: 29496–29504
- 10 Lou XWD, Archer LA, Yang Z. Hollow micro-/nanostructures: Synthesis and applications. *Adv Mater*, 2008, 20: 3987–4019
- 11 Jia R, Li L, Ai Y, *et al.* Self-healable wire-shaped supercapacitors with two twisted NiCo₂O₄ coated polyvinyl alcohol hydrogel fibers. *Sci China Mater*, 2018, 61: 254–262
- 12 Wang Z, Zhou L, David Lou XW. Metal oxide hollow nanostructures for lithium-ion batteries. *Adv Mater*, 2012, 24: 1903–1911
- 13 Li Z, Wu HB, (David) Lou XW. Rational designs and engineering of hollow micro-/nanostructures as sulfur hosts for advanced lithium-sulfur batteries. *Energy Environ Sci*, 2016, 9: 3061–3070
- 14 Peng S, Li L, Hu Y, *et al.* Fabrication of spinel one-dimensional architectures by single-spinneret electrospinning for energy storage applications. *ACS Nano*, 2015, 9: 1945–1954
- 15 Liu J, Qiao SZ, Budi Hartono S, *et al.* Monodisperse yolk-shell nanoparticles with a hierarchical porous structure for delivery vehicles and nanoreactors. *Angew Chem Int Ed*, 2010, 49: 4981–4985
- 16 Zhang L, Wu HB, Madhavi S, *et al.* Formation of Fe₂O₃ microboxes with hierarchical shell structures from metal-organic frameworks and their lithium storage properties. *J Am Chem Soc*, 2012, 134: 17388–17391
- 17 Kong B, Selomulya C, Zheng G, *et al.* New faces of porous Prussian blue: Interfacial assembly of integrated hetero-structures for sensing applications. *Chem Soc Rev*, 2015, 44: 7997–8018
- 18 Hu M, Belik AA, Imura M, *et al.* Synthesis of superparamagnetic nanoporous iron oxide particles with hollow interiors by using Prussian blue coordination polymers. *Chem Mater*, 2012, 24: 2698–2707
- 19 Zhang M, Hou C, Halder A, *et al.* Interlocked graphene-Prussian blue hybrid composites enable multifunctional electrochemical applications. *Biosens Bioelectron*, 2017, 89: 570–577
- 20 Nossol E, Zarbin AJG. A simple and innovative route to prepare a novel carbon nanotube/Prussian blue electrode and its utilization as a highly sensitive H₂O₂ amperometric sensor. *Adv Funct Mater*, 2009, 19: 3980–3986
- 21 Xu Y, Zheng S, Tang H, *et al.* Prussian blue and its derivatives as electrode materials for electrochemical energy storage. *Energy Storage Mater*, 2017, 9: 11–30
- 22 Wang JG, Zhang Z, Zhang X, *et al.* Cation exchange formation of Prussian blue analogue submicroboxes for high-performance Na-ion hybrid supercapacitors. *Nano Energy*, 2017, 39: 647–653
- 23 Zhao Y, Liu J, Horn M, *et al.* Recent advancements in metal organic framework based electrodes for supercapacitors. *Sci China Mater*, 2018, 61: 159–184
- 24 Jiang Y, Yu S, Wang B, *et al.* Prussian blue@C composite as an ultrahigh-rate and long-life sodium-ion battery cathode. *Adv Funct Mater*, 2016, 26: 5315–5321
- 25 You Y, Wu XL, Yin YX, *et al.* High-quality Prussian blue crystals as superior cathode materials for room-temperature sodium-ion batteries. *Energy Environ Sci*, 2014, 7: 1643–1647
- 26 Xue L, Li Y, Gao H, *et al.* Low-cost high-energy potassium cathode. *J Am Chem Soc*, 2017, 139: 2164–2167
- 27 Wessells CD, McDowell MT, Peddada SV, *et al.* Tunable reaction potentials in open framework nanoparticle battery electrodes for grid-scale energy storage. *ACS Nano*, 2012, 6: 1688–1694
- 28 Ren W, Qin M, Zhu Z, *et al.* Activation of sodium storage sites in Prussian blue analogues *via* surface etching. *Nano Lett*, 2017, 17: 4713–4718
- 29 Jia H, Wang Z, Zheng X, *et al.* Interlaced Ni-Co LDH nanosheets wrapped Co₉S₈ nanotube with hierarchical structure toward high performance supercapacitors. *Chem Eng J*, 2018, 351: 348–355
- 30 Qiu X, Liu Y, Wang L, *et al.* Reverse microemulsion synthesis of nickel-cobalt hexacyanoferrate/reduced graphene oxide nanocomposites for high-performance supercapacitors and sodium ion batteries. *Appl Surf Sci*, 2018, 434: 1285–1292
- 31 Augustyn V, Come J, Lowe MA, *et al.* High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nat Mater*, 2013, 12: 518–522
- 32 Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ Sci*, 2014, 7: 1597–1614
- 33 Jia H, Wang Z, Li C, *et al.* Designing oxygen bonding between reduced graphene oxide and multishelled Mn₃O₄ hollow spheres for enhanced performance of supercapacitors. *J Mater Chem A*, 2019, 7: 6686–6694
- 34 Zhao F, Wang Y, Xu X, *et al.* Cobalt hexacyanoferrate nanoparticles as a high-rate and ultra-stable supercapacitor electrode material. *ACS Appl Mater Interfaces*, 2014, 6: 11007–11012
- 35 Wang JG, Zhang Z, Liu X, *et al.* Facile synthesis of cobalt hexacyanoferrate/graphene nanocomposites for high-performance supercapacitor. *Electrochim Acta*, 2017, 235: 114–121
- 36 Lu K, Li D, Gao X, *et al.* An advanced aqueous sodium-ion supercapacitor with a manganous hexacyanoferrate cathode and a Fe₃O₄/rGO anode. *J Mater Chem A*, 2015, 3: 16013–16019
- 37 Lu K, Song B, Gao X, *et al.* High-energy cobalt hexacyanoferrate and carbon micro-spheres aqueous sodium-ion capacitors. *J Power Sources*, 2016, 303: 347–353

Acknowledgements This work was supported by the National Natural Science Foundation of China (51821091 and 51872233), and the Natural Science Foundation of Shaanxi Province (2018JM5044). We would like to thank the Analytical & Testing Center of Northwestern Polytechnical University for the morphology characterizations.

Author contributions Yin X, Li H and Lu J designed the experiments. Yin X and Yuan R performed the material characterizations. Yin X wrote the paper with support from Zhang L. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Xuemin Yin is currently a PhD student at the School of Materials Science and Engineering, Northwestern Polytechnical University. His research focuses on the nanomaterials for electrochemical energy storage.

Hejun Li is a professor at the School of Materials Science and Engineering, Northwestern Polytechnical University. He received his PhD degree from Harbin Institute of Technology in 1991. His current research interests include advanced carbon/carbon composites, anti-oxidation coatings, paper based friction materials and nanomaterials.

Jinhua Lu is an associate professor at the School of Materials Science and Engineering, Northwestern Polytechnical University. Her current research interests include carbon/carbon composites and nanomaterials.

类普鲁士蓝空心微米管的通用性制备及其作为高性能非对称超级电容器的研究

殷学民, 李贺军*, 袁瑞梅, 张磊磊, 卢锦花*

摘要 在电化学储能领域, 具有可控组成的一维空心结构纳米材料引起了人们的极大关注. 本文以静电纺丝制备的聚丙烯腈(PAN)-醋酸钴($\text{Co}(\text{Ac})_2$)纳米纤维为模板, 首次采用简易的自模板法制备了一维铁氰化钴(CoHCF)空心微米管. PAN- $\text{Co}(\text{Ac})_2$ 纳米纤维模板与铁氰化钾溶液反应, 合成了核壳结构的PAN- $\text{Co}(\text{Ac})_2$ @ CoHCF 纳米纤维; 随后, 选择性溶解去除PAN- $\text{Co}(\text{Ac})_2$ 芯部, 从而得到 CoHCF 空心微米管. 得益于其独特的结构优势, CoHCF 空心微米管电极在 Na_2SO_4 电解液中表现出优异的电化学性能, 如高比电容(281.8 F g^{-1} @ 1 A g^{-1}), 良好的速率性能和长时间循环稳定性(5000次循环后电容保持率为93%). 由 CoHCF 为正极和活性炭(AC)为负极组装的非对称超级电容器, 具有 43.9 W h kg^{-1} 的高能量密度、 20 kW kg^{-1} 的功率密度以及长的循环寿命. 更重要的是, 这种通用性的自模板合成策略可以推广到其他组成可控的一维空心普鲁士蓝(PB)及其类似物(PBA)材料, 因而在很多领域具有广泛的应用前景.