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Fabrication of Sugar-Coated CoNi₂S₄/Ni₃P Nanostructure with Ultrahigh Electrochemical Performance for Supercapacitor Application

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Designing a novel hierarchically structured transition-metal sulfide and transition-metal phosphide composite electrode material is an effective way to improve the energy storage performance of supercapacitors (SCs). Herein, the CoNi₂S₄/Ni₃P (CNSP-500) nanocomposite material has been prepared via the two-step anion exchange method, in which the nanocomposite material of Ni₃P coated CoNi₂S₄ forms the unique sugar-coated nanostructure exhibiting excellent electrochemical performance as the electrode material. The optimized CNSP-500 electrode material achieves a superhigh area-specific capacitance of 8.86 F/cm² (mass-specific capacitance of 3100 F/g) at the current density of 3 A/g, which is approximately seven times higher than the precursor of Cobalt-Nickel carbonate hydroxides (CN). Moreover, the area-specific capacitance of 6.44 F/cm² can be obtained even at the high current density of 20 A/g, which indicates excellent rate capability of the CNSP-500 electrode material. This preparation strategy provides a fine method for designing high-performance SCs based on transition-metal sulfides and transition-metal phosphides.

Keywords: Electrode materials; Nanostructure; Capacitance; Energy storage; Supercapacitors

1. INTRODUCTION

The exploitation of portable and efficient electronic storage devices is an important research content to meet the needs of life. SCs have attracted more attention of many researchers due to their advantages of high power output, fast charging and discharging, long service life and high security [1-5]. The electrochemical performance of SCs will be affected by morphologies, structures and elements composition of the electrode materials [6]. At present, a variety of pseudocapacitors (PCs) electrode materials including transition-metal oxides [7-10]/ hydroxides [11-14] and transition-metal sulfides [15-

18] have been synthesized owing to their high theoretical capacity and high production on earth [19]. Unfortunately, the development of transition-metal compounds is constrained by their poor performance which is mainly reflected in low electronic conductivity, poor rate capability and poor cycling stability. Hence, introducing other ions or constructing hierarchically structured composites based on the transition-metal compounds will improve electrochemical performance of the electrode materials via increasing their conductivity and the active sites [20,21,22], which provides research ideas to enhance the energy storage performance of SCs effectively.

Transition-metal phosphides have been proved to be another excellent PCs materials [23]. For example, Zong et al. [24] reported that NiCo₂O₄/NiCoP nanoflake-nanowire arrays with a homogeneous hetero-structure grown on Nickel Foam (NF) achieve an ultrahigh mass-specific capacitance of 2288.8 F/g at the current density of 1 A/g. Lei et al. [25] illustrated that the composite material of Ni-Mo-S@Ni-P obtained by two-step method shows a remarkable mass-specific capacitance of 1770 F/g at 1 A/g. Jiang et al. [26] found ternary Ni-S-P nanoparticles on graphene nanosheets (G/Ni-S-P) using anionic P-substitution strategy, which can achieve an excellent specific capacitance of 1406 C/g at 1 A/g. Chang et al. [27] reported the core-shell nanocolumn arrays of the hierarchical NiCo₂S₄@NiCoP with a high area-specific capacitance of 5.98 F/cm² at 1 mA/cm². According to above researches, an optimized integration of transition-metal sulfides and transition-metal phosphides is considered as an efficient method to perfect the capacitance of SCs.

On the basis of above consideration, the composite material with sugar-coated nanostructure mainly composed of Ni, Co, S and P elements is prepared via the two-step anion exchange method. For the electrode material, the special nanostructure and elements composition are favorable for enhancing rapid redox reactions and ions/electrons transport by generating abundant active sites, metallization states and transmission channels. As the electrode material, it is superb for the CNSP-500 electrode material to achieve a high area-specific capacitance of 8.86 F/cm² (mass-specific capacitance of 3100 F/g) at the current density of 3A/g, and also can realize 6.44 F/cm² at a higher current density of 20A/g, indicating its excellent rate capability. We believe that the CNSP-500 electrode material with sugar-coated nanostructure is a promising candidate material for SCs and our developed strategy is an effective way to introduce unique electrode materials with better electrochemical performance in the future.

2. EXPERIMENTAL

2.1 Materials

In our experiments, the main chemical reagents containing glucose ($C_6H_{12}O_6$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), ammonium fluoride (NH_4F), urea (CON_2H_4), sodium sulfide ($Na_2S \cdot 9H_2O$) and sodium hypophosphite (NaH_2PO_2) are analytical grade and are used without further purification. Prior to synthesizing, the NFs (3.0 cm×1.0 cm) were cleaned by 3 M hydrochloric acid, acetone, ethanol and deionized (DI) water to remove oxide layer from the surface, and then put them in the vacuum drying box overnight at 60°C.

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2.1.1 Preparation of the Cobalt-Nickel carbonate hydroxides precursor:

 $C_6H_{12}O_6$ (0.036 g, 0.2 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.29 g, 1 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.145 g, 0.5 mmol), NH_4F (0.11 g, 3 mmol) and $CO(NH_2)_2$ (0.6 g, 10 mmol) were dissolved in 40ml DI water to form a evenly mixed pink solution under continuous magnetic agitation. Subsequently, the pink solution and the pretreated NF were transferred into a 50ml Teflon-lined stainless-steel autoclave, which was heated and reacted at 120°C for 8h, and then cooled down to room temperature naturally. To remove the residual chemical reagents adsorbed on the surface, the obtained product was cleaned with DI water and ethanol repeatedly and then put it in the vacuum drying box overnight at 60°C. The prepared sample was recorded briefly as CN. The calculated mass loading of the CN electrode material was 0.94 mg/cm².

2.1.2 Preparation of the CoNi₂S₄ sample:

 $0.2 \text{ mmol} (0.48 \text{ g}) \text{ Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was dispersed into 40ml DI water and mixed well by continuous magnetic stirring. Then, the prepared CN sample and the mixed solution were transferred into 50ml Teflon-lined stainless-steel autoclave, which was maintained at 120 °C for 4 h in a heating oven. When the reactor cooled down to room temperature naturally, the product was repeatedly cleaned with DI water and ethanol (3-5 mins), and put it in the vacuum drying box overnight at 60°C. The prepared material was recorded briefly as CNS. The mass loading of the CNS electrode material was 1.22 mg/cm².

2.1.3 Preparation of the CoNi₂S₄/Ni₃P sample:

In this section, the CNS electrode material prepared above was used as the substrate for the subsequent phosphorization treatment. Different amounts of NaH₂PO₂ powder (100mg, 500mg and 1000mg) and the prepared CNS electrode material were placed on the upstream and the downstream of the Al₂O₃ porcelain boat respectively, which was heated to 350°C and reacted for 2 h with a ramping temperature rate of 1°C/min at an atmosphere of nitrogen. When cooled down to room temperature, the synthesized electrodes were recorded as CNSP-X (X=100, 500, 1000). The mass loading of the optimized CNSP-500 electrode material was 2.86 mg/cm², compared with the CNSP-100 electrode material (1.84 mg/cm²) and the CNSP-1000 electrode material (3.11 mg/cm²), respectively.

2.2 Materials Characterization

Scanning Electron Microscope (SEM, Hitachi S4800) and Transmission Electron Microscope (TEM, FEI Tecnai G2F20) were used to observe and analyze the morphologies and nanostructures of the obtained samples in our experiments. The structures and the crystallinity of the prepared materials were characterized by X-ray diffraction (XRD, Rigaku SmartLab D/max 2500 PC), operating at 40 kV and using Cu Ka radiation from 10° to 80°. Meanwhile, the elemental components and valence states about the synthetic compounds were analyzed by X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250Xi).

2.3 Electrochemical measurements

The conventional three-electrode test system was used to measure the electrochemical performance of the synthesized electrode materials which were soaked in 2M KOH aqueous solution. The obtained samples (1.0 cm×1.0 cm), platinum electrode (1.0 cm×1.0 cm) and the Hg/HgO electrode were served as the working electrodes, counter electrode and reference electrode, respectively. The performance parameters of the working electrochemical impedance spectroscopy (EIS) were studied in an Autolab PGSTAT 302N electrochemical working station. The mass-specific capacitance C_m (F/g) can be calculated using equation (1):

$$C_m = I \,\Delta t / m \,\Delta V \tag{1}$$

The area-specific capacitance C_a (F/cm²) can be calculated using equation (2):

 $C_a = I \,\Delta t / S \,\Delta V \tag{2}$

where *I* corresponds to the discharge current (A), Δt represents the discharge time (s), *m* is the mass loading (g), ΔV refers to the working voltage window (V) during the charge-discharge process and S is the area (1.0 cm²) of the working electrode.

3. RESULTS AND DISCUSSION

The detailed growth processes associated with the synthesized compounds can be described as follows: First, the CN precursor with nanowire structure is prepared by one-step hydrothermal method and the hydrolysis of urea is the source of CO_3^{2-} and OH⁻ during this process. With the increase of reaction temperature and reaction time, the carbonate hydroxides are gradually synthesized by reactions between metal cations and hydrolyzed anions [28,29]. Moreover, NH₄F is not only a kind of reaction reagent and also plays a crucial role in activating the NF substrate, which makes the obtained compounds attach to the substrate steadily [29]. Next, the precursor of CN is put into the Na₂S solution as a substrate to prepare the second material: CoNi₂S₄. In this whole process, we take full use of anion exchange reactions between CO_3^{2-} , OH⁻ and S²⁻ and the mechanisms are as follows [30,31,32,33]:

$$CO(NH_{2})_{2} + H_{2}O \rightarrow 2NH_{3} + CO_{2} \qquad (3)$$

$$CO_{2} + H_{2}O \rightarrow CO_{3}^{2^{-}} + 2H^{+} \qquad (4)$$

$$NH_{3} + H_{2}O \rightarrow NH_{4}^{+} + OH^{-} \qquad (5)$$

$$2Ni^{2^{+}} + CO_{3}^{2^{-}} + 2OH^{-} + H_{2}O \leftrightarrows Ni_{2}CO_{3}(OH)_{2}.H_{2}O \qquad (6)$$

$$2Co^{2^{+}} + CO_{3}^{2^{-}} + 2OH^{-} \leftrightarrows Co_{2}CO_{3}(OH)_{2} \qquad (7)$$

$$Co^{2^{+}} + 2Ni^{2^{+}} + 4S^{2^{-}} \leftrightarrows CoNi_{2}S_{4} \qquad (8)$$

In the end, the CNS electrode material is treated with NaH_2PO_2 as a P source. At high temperature, NaH_2PO_2 will decompose PH₃ [34], and then reacts with the CNS compound to systhesis the CNSP-500 electrode material.



Figure 1. SEM images of the obtained materials at different magnifications. (a-b) CN; (c-d) CNS; (e-f) CNSP-500.

In Fig. 1, SEM images of the obtained materials are well represented. The morphology of CN with different magnifications is shown in the Fig. 1a-b. The pointed tops of smooth nanowires can be clearly seen and are basically in a state of aggregation. Different from smooth nanowire structure of the CN precursor, the multi-dimensional nanostructure of CNS is synthesized by sulfurizing the CN precursor. The top of the CNS nanowire array shows the aggregation of many interconnected nanosheets, exposing more ion transport channels (Fig. 1c-d). From the view of CNSP-500 sample (Fig. 1e-f), the morphology of CNS sample further evolves into an unique structure of abundant interconnected nanospheres being wrapped by nanosheets after phosphating, which is similar to the structure of "sugarcoated". The in-depth morphology of the obtained samples is analyzed by combining TEM and HRTEM measurements. The nanostructure of CN precursor is displayed in Fig. 2a-2b. The structure of a large amount of smooth and thin nanowires with the diameter of 30-80nm and the length of nanowires is about 1.0 µm can be observed. In Fig. 2c, the HRTEM shows a crystal lattice spacing of 0.237 nm, which can be ascribed to the (440) lattice plane of Ni₂CO₃(OH)₂!H₂O. Notably, rough nanowires of the CNS electrode material with a higher average diameter of 60-100 nm are wrapped by the interconnected nanosheets (Fig. 2d-e). The interplanar spacing of 0.284 nm is contributed to the (300) lattice plane of CoNi₂S₄ (Fig. 2f). Under the phosphorization treatment of CNS sample (Fig. 2g-i), the (311) lattice plane of CoNi₂S₄ and the (132) lattice plane of Ni₃P can be confirmed by the interplanar distances of 0.285nm and 0.173nm, respectively. These results indicate that the prepared CNSP-500 electrode is a composite material which contains both transition-metal sulfides and transition-metal phosphides.



Figure 2. TEM and HRTEM images of the three obtained materials. (a-c) CN; (d-f) CNS; (g-i) CNSP-500.

The XRD analysis of CN, CNS and CNSP-500 samples are shown in Fig. 3. The three strong diffraction peaks at 44.5°, 51.8° and 76.4° are matched well with the NF (JCPDS Card No. 04-0850) marked as "#" in the picture. The XRD diffraction peaks of CN centered at 2θ =21.7°, 37.9°, 50.3°, and 55.7° can be considered as the (240), (440), (570) and (640) planes of Ni₂CO₃(OH)₂!H₂O (JCPDS Card No. 29-0868), respectively [30]. The diffraction peaks of the cobalt compound are not obvious owing to its low crystallinity and the adjacent atomic radius between cobalt and nickel elements. Hence, the precursor of CN can be ascribed to the Cobalt-Nickel carbonate hydroxides. After sulfurizing the CN precursor for 8h, the prepared CNS electrode material can be turned out to be CoNi₂S₄ (JCPDS Card No. 24-0334), which is based on its diffraction peaks located at 31.4°, 38.1°, 47.2°, 50.2° and 55.0° of (311), (400), (422), (511) and (440) planes [28,35]. After further phosphorization of the CNS sample, except the peaks of CNS, new peaks centered at 36.4°, 41.7°, 42.8°, 43.6°, 45.2°, 46.6° and 52.7° are matched well with (031), (231), (330), (112), (240), (141) and (132) planes of Ni₃P (JCPDS card No. 34-0501), respectively [36,37]. This result indicates that CoNi₂S₄ and Ni₃P compounds coexist in the CNSP-500 electrode material, which is consistent with TEM results.



Figure 3. XRD images of the CN, CNS and CNSP-500 electrode materials.

The detailed elements information on the prepared CNSP-500 electrode material surface can be analyzed by XPS measurements (Fig. 4). The survey spectrums of CN, CNS and CNSP-500 are described in Fig. 4a, which show all elements in the prepared materials. The information about valence states of the CN and CNS compounds elements is displayed in Fig. S1 and Fig. S2. From these spectra, the nature of CN precursor and CNS compound can be verified. For the CNSP-500 electrode material, the spin-orbit splitting values of Co $2p_{3/2}$ and Co $2p_{1/2}$ situated at 781.2 eV and 797.0 eV confirm the coexistence of Co^{3+} and Co^{2+} in Fig. 4b [38,39]. The peaks of Ni 2p (Figure. 4c) show the binding energy centered at 852.8 eV (Ni $2p_{3/2}$) and 870.1 eV (Ni $2p_{1/2}$), which are matched with Ni^{$\delta+$} (0 < δ < 2) in Ni-P bond, and the peaks at 855.9 eV and 873.6 eV are ascribed to Ni²⁺[31,34]. The remaining peaks at 861.3 eV and 879.3 eV are the two satellites of Ni 2p. Fig. 4d reveals the peaks information of P 2p. Two distinct peaks at 129.6 eV and 130.4 eV are attributed to P 2p_{3/2} and P 2p_{1/2} of P-M in metal phosphide, and the binding energy at 133.4 eV is ascribed to PO_4^{3-} on account of oxidation of the phosphide in the air [40,41]. In Fig. 4e, the spin-orbit peaks of S $2p_{3/2}$ and S $2p_{1/2}$ can be confirmed by peaks centered at 161.2 eV and 162.7 eV, respectively. Besides, another peak (169.4 eV) indicates the satellite peak of S 2p [42,43]. Compared the S 2p spectrum of CNS (Fig. S3), the peak intensity of CNSP-500 is obviously weak, which indicates the smaller content of sulfide on the CNSP-500 electrode surface. In fact, at a high temperature, the partial S elements will release from the CNS compound, creating a lot of vacancies [44]. Meanwhile, there are partial atomic substitution between S atoms and P atoms in the synthetic process of CNSP-500.

In our experiment, glucose is involved in the synthesis of compounds as a carbon source. Fig. 4f displays the C 1s spectrum of CN, CNS and CNSP-500. From the fitting data, the peak intensity (O-C=O) representing carbonate hydroxides becomes more and more weak for different materials. For the C-C bond situated at 284.7 eV, there are no significant changes in peak intensity. The common peak of C-C bond appearing together in all prepared compounds confirms the truth of C-doping in all prepared samples, which is helpful for the prepared materials to improve their whole performance. Regrettably,

the unconspicuous characterization of carbon in XRD and TEM is mainly due to its poor crystallinity. Moreover, the oxygen contribution of the CN, CNS and CNSP-500 electrodes is different. The O 1s contribution of the CN precursor is resulting from the carbonate hydroxides (Fig. S1c). The co-existence of O in the CNS and CNSP-500 electrode materials is closely related to oxidation of the materials surface in the air (Fig. S3).



Figure 4. XPS spectra of the CNSP-500 electrode material. (a) Survey spectrum of the CN, CNS and CNSP-500 electrode materials; (b) Co 2p; (c) Ni 2p; (d) P 2p; (e) S 2p; (f) C 1s spectrum of the CN, CNS and CNSP-500 electrode materials.



Figure 5. (a) CV curves (b) GCD curves of the CN, CNS and CNSP-500 electrode materials; (c) CV curves under various scan rates (d) GCD curves under various current densities of the CNSP-500 electrode material.

In a three-electrode system, the performance parameters of the obtained electrodes are tested in 2M KOH solution. Fig. 5a shows CV curves about the CN, CNS and CNSP-500 electrodes at the scan rate of 5 mV/s in the voltage window of -0.1-0.7V. A pair of apparent redox peaks indicate the pseudocapacitance character of the synthesized electrodes in the process of energy storage. The related reversible and fast faradaic redox reactions are described below [30,35,37]:

$$\begin{split} Ni_{2}(CO_{3})(OH)_{2} + 4OH^{-} &\rightarrow 2NiOOH + 2CO_{3}^{2-} + 2H_{2}O + 2e^{-} \quad (8) \\ Co_{2}(CO_{3})(OH)_{2} + 4OH^{-} &\rightarrow 2CoOOH + 2CO_{3}^{2-} + 2H_{2}O + 2e^{-} \quad (9) \\ NiOOH + H_{2}O + e^{-} &\leftrightarrow Ni(OH)_{2} + OH^{-} \quad (10) \\ CoNi_{2}S_{4} + 2OH^{-} &\leftrightarrow CoS_{x}OH + Ni_{2}S_{4-x}OH + 2e^{-} \quad (11) \\ CoS_{2x}OH + OH^{-} &\leftrightarrow CoS_{2x}O + H_{2}O + e^{-} \quad (12) \\ Ni_{3}P &\leftrightarrow 3Ni^{2+} + P^{6-} \quad (13) \\ Ni^{2+} + 2OH^{-} &\leftrightarrow Ni(OH)_{2} \quad (14) \\ Ni(OH)_{2} + OH^{-} &\leftrightarrow NiOOH + H_{2}O + e^{-} \quad (15) \end{split}$$

There are abundant valence states of ions providing rich redox reactions for the prepared CNSP-500 compound.



Figure 6. (a) Mass-specific capacitance of CN, CNS and CNSP-500; (b) Area-specific capacitance of CN, CNS and CNSP-500; (c) Nyquist plots of CN, CNS and CNSP-500; (d) Cyclic performance of CNSP-500.

The CV curves of the CNSP-500, CN and CNS electrodes at different scan rates are displayed in Fig. 5c and Fig. S4a-b, respectively. As the scan rate increases, the current density rises gradually and the position of a pair of redox peaks changes. The location of anodic peaks shifts towards a higher voltage and the location of cathodic peaks shifts towards a lower voltage, which illustrates the fact of fast redox reactions on the electrode/electrolyte surface. Meanwhile, the shape of the oxidation peaks begins to

change with the scan rates increasing, which is mainly attributed to the polarization phenomenon in the process of energy storage.

The GCD curves of the CN, CNS and CNSP-500 electrodes at the current density of 3A/g in a voltage window of -0.1-0.55V are displayed in Fig. 5b. The visible voltage platforms of GCD curves also confirm the pseudocapacitance character of the prepared electrode materials, which are same with the CV analyses. Fig. 5d and Fig. S4c-d display GCD curves of the CNSP-500, CN and CNS electrodes at various current densities (3 A/g-20 A/g), respectively. It is important that the symmetrical GCD graphs indicate highly reversible faradaic redox reactions of the synthetic materials in the storage process [38].

The electrochemical performances of the CN, CNS and CNSP-500 electrodes are displayed in Fig. 6 and all of the calculated capacitance are based on the formulas (1) and (2) which are related to mass-specific capacitance and area-specific capacitance, respectively. In Fig. 6a, the optimized electrode of CNSP-500 realizes a series of mass-specific capacitance of 3100.0, 2992.3, 2843.1, 2718.5, 2471.5 and 2252.3 F/g at various current densities of 3, 5, 8, 10, 15 and 20 A/g, respectively. For comparsion, the mass-specific capacitance of 1330.2 and 5292.5 F/g can be achieved at the current density of 3 A/g for the CN and CNS electrodes, respectively. Area-specific capacitance as a comprehensive electrochemical parameter is also a significant indicator to measure the performance for the electrode materials in energy storage. Compared with the CN and CNS electrode materials, the CNSP-500 electrode material with a high mass-specific capacitance and higher mass loading has achieved an ultrahigh area-specific capacitance.

At the current density of 3 A/g, the area-specific capacitance of the obtained CN and CNS electrodes are only 1.25 F/cm^2 and 6.45 F/cm^2 in Fig. 6b, respectively. The optimized CNSP-500 electrode has the ultrahigh area-specific capacitance of 8.86 F/cm^2 at 3 A/g which is approximately seven times higher than the precursor of CN, and the area-specific capacitance of 6.44 F/cm^2 at the high current density of 20 A/g implying excellent rate performance of the CNSP-500 sample. In addition, the lower capacitance of CNSP-100 (6.18 F/cm^2) and CNSP-1000 (6.99 F/cm^2) at the current density of 3 A/g also indicate that the electrode material synthesized at the condition of 500mg NaH₂PO₂ as a P source is the best sample with an ultrahigh area-specific capacitance (Fig. S5-S6).

To better verify the performance of prepared electrodes, the EIS datas of the CN, CNS and CNSP-500 electrodes are measured at the potential of 5 mV in the frequency range from 100 kHz to 0.01 Hz (Fig. 6c), and the corresponding inset image is the equivalent circuit diagram for fitting the EIS data which are mainly containing four parts: the equivalent series resistance (R_s), the charge transfer resistance (R_{ct}), a capacitor element (C_p) referring to the pseudo-capacitance and a constant phase element (CPE) standing for the double-layer capacitance [45]. The R_s represents the internal resistance resulting from the electrolyte, the electrode and the interface of electrode and electrolyte, which is calculated by the intercept between the semicircle and the axis. The R_{ct} caused by the electrons diffusion is the diameter of the semicircle in the high frequency [46]. From the EIS analyses, the smallest internal resistance R_s of the CNSP-500 electrode is 0.39 Ω compared with the CN electrode (0.86 Ω) and the CNS electrode (0.44 Ω), which implies excellent electrical conductivity of the CNSP-500 electrode material. Moreover, the smallest semicircle of the CNSP-500 electrode confirms its lower Ret (0.73 Ω) compared with the CN (2.76 Ω) and CNS (1.35 Ω) electrodes, indicating an easier electrons transport for the CNSP-500 electrode material. The CNSP-500 electrode material possessing lower resistances of

 R_s and R_{ct} promotes rapid redox reactions at the electrolyte/electrode interface. As a result, the CNSP-500 electrode is proved to be a potential material in energy storage, which is same with the CV and GCD results. The cycling performance is an important parameter in measuring structural stability of the material. Fig. 6d displays the cyclic stability of the CNSP-500 electrode material at the scan rate of 30 mV/s and the capacitance retention is 63% after 2,000 cycles, which indicate a good stability owing to its unique nanostructure.

Electrode	Capacitance	Rate capability	Ref.
NiCo ₂ O ₄ /NiCoP	2288.8 F/g at 1 A/g	71.8% (from 1 A/g to 20 A/g)	[24]
Ni-Mo-S@Ni-P	1770 F/g at 1 A/g	51.4% (from 1 A/g to 20 A/g)	[25]
NiCo ₂ S ₄ @NiCoP	5.98 F/cm ² at 1 mA/cm ²	70.29% (from 1 mA/cm ² to 50 mA/cm ²)	[27]
P-CSs@Ni ₁ -Co ₂ -P	1040.3 F/g at 1 A/g	49.2% (from 1 A/g to 30 A/g)	[48]
NiCoP@NiCoP	1125 C/g at 1 A/g	78% (from 1 A/g to 10 A/g)	[49]
CoP@NiCoP	1911.6 F/g at 2 A/g	61.68% (from 2 A/g to 25 A/g)	[50]
NiMoO4@NiS2/MoS2	970 F/g at 5 A/g	73.2% (from 5 A/g to 20 A/g)	[51]
CoNi ₂ S ₄ /Ni ₃ P	3100 F/g at 3 A/g (8.86 F/cm ²)	72.6% (from 3 A/g to 20 A/g)	This work

Table 1. The electrochemical performance comparison about the synthesized CNSP-500 electrode material and some relevant materials reported in recent years.

The active materials always come across a tough issue of having high mass-specific capacitance with a low mass loading and resulting in a poor area-specific capacitance in the synthesis of electrode materials, which further limits its application in the storage process. In general, it is a challenge to meet the condition that both having an outstanding capacitance and a high mass loading for the synthesized electrode materials. Clearly, although the mass-specific capacitance of the CNS electrode is much higher than the CNSP-500 and CN electrodes, which is mainly due to the fact that the tridimensional nanostructure of the CNS electrode material can expose more ion transport channels and the synthesized sulfur vacancies can facilitate redox reactions in the experiment [44,47], the CNSP-500 electrode material with ultrahigh mass-specific capacitance and area-specific capacitance balances the mass loading and the electrochemical performance reasonably. The electrochemical performance comparison of different phosphides which were synthesized in recent years is shown in Tab. 1. In our work, the favourable electrochemical performance of the CNSP-500 electrode material could be summed up the following reasons: (1) In our experiments, the prepared CNSP-500 electrode material is taking the conductive sulfide of CoNi₂S₄ grown on NF as the substrate to synthesize another composite material of CoNi₂S₄/Ni₃P with high theoretical capacity and conductivity, which can accelerate the process of electrolyte ions diffusion and make the electrode material be fully used. (2) Having a high-efficiency structure is the key point to achieve higher electrochemical performance for the electrode materials. The special sugar-coated nanostructure of the CNSP-500 electrode exposes more active sites and makes the electron/ion transport paths shorten effectively, which contributes to rapid redox reactions at the interface between the electrode and the electrolyte. (3) Moreover, the strong synergistic effects provided by the abundant valence states of ions on the composite material surface promote richer redox reactions [40]. In short, the excellent electrochemical performance of the CNSP-500 composite electrode is connected with its chemical composition and unique sugar-coated nanostructure.

4. CONCLUSIONS

In conclusion, the special sugar-coated nanostructure of the CNSP-500 electrode material is synthesized by hydrothermal and one-step phosphorization method. Based on its unique nanostructure and abundant elements composition, lots of active sites and valence states of ions on the CNSP-500 electrode material surface further facilitate the contact between electrolyte ions and electrodes and promote rich redox reactions, and then realize a superb electrochemical performance. The optimized CNSP-500 electrode material with an excellent rate capability achieves ultrahigh area-specific capacitance of 8.86 F/cm² (mass-specific capacitance of 3100 F/g) and 6.44 F/cm² (mass-specific capacitance of 2252.3 F/g) at the current density of 3 A/g and 20 A/g, respectively. Moreover, the capacitance retention of 63% after 2,000 cycles proves all-right structural stability of the CNSP-500 electrode material. In brief, preparation of the CNSP-500 electrode material with special nanostructure and ultrahigh capacitance has the reference value in the energy storage for future SCs.

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SUPPORTING INFORMATION

Fig. S1. XPS spectra of the CN electrode material. (a) Co 2p; (b) Ni 2p; (c) O 1s; (d) C 1s.

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As is shown in Fig. S1a-1d, the CN compound is mainly constituted by four main elements: Co, Ni, C, and O. In addition, all of the spectras are individually fitted by Gaussian method in terms of spinorbit doublets and shake-up satellites (marked as "Sat"). In Fig. S1a, the spectrum peaks of Co 2p are located at 781.4 eV, 785.4 eV, 797.5 eV, and 802.9 eV, among which the binding energy at 781.4 eV and 797.5 eV are ascribed to Co $2p_{3/2}$ and Co $2p_{1/2}$ of Co²⁺, and 785.4 eV and 802.9 eV are the two shakeup satellites, respectively [1,2]. Ni 2p (Fig. S1b) spectrum can also be matched with two spin-orbit doublets and two shake-up satellites, which the peaks situated at 856.3 eV and 874.0 eV can be contributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ of Ni²⁺, and the other two peaks (861.9 eV and 879.4 eV) are the two shake-up satellites, respectively [2,3]. It is worth mentioning that the peak splitting energy of 17.7 eV between Ni 2p_{3/2} and Ni 2p_{1/2} corresponds to the spin-orbit coupling [4]. The spectrum of O 1s (Fig. S1c) are mainly made up of three peaks (530.7 eV, 531.4 eV, and 532.3 eV) which are indexed to M-O-H (hydroxide group), O-C=O (carbonate groups), and the adsorbed H₂O by the active materials, respectively [5]. Fig. S1d displays the spectrum of C 1s. The peaks at 284.6 eV, 285.8 eV, and 289.2 eV correspond to the non-oxygenated carbon (C-C), C-O and O-C=O [6]. The spectrum results indicate the nature of the nickel-cobalt carbonate hydroxide of the CN precursor, which are consistent with XRD and TEM measurements.



Fig. S2. XPS spectra of the CNS electrode material. (a) Co 2p; (b) Ni 2p; (c) S 2p; (d) C 1s.

The XPS spectrum of CNS is shown in Fig. S2. The first doublet peaks at 778.5 eV, and 792.8 eV are indexed to Co^{3+} and the second doublet peaks at 781.4 eV and 796.7 eV are ascribed to Co^{2+} . The peaks at 785.9 eV and 802.7 eV are the two shake-up satellites of Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively (Fig. S2a) [7]. The binding energy at around 855.3 eV and 873.1 eV corresponding to Ni²⁺, and the peaks

at 856.3 eV and 874.3 eV corresponding to Ni³⁺ of the Ni 2p spin-orbit doublets are displayed in Fig. S2b [8,9]. Meanwhile, the another two peaks of 861.7 eV and 879.4 eV are the two satellites of Ni 2p (marked as Sat.). In Fig. S2c, the three peaks located at 161.5 eV, 162.7 eV and 168.3 eV correspond to S $2p_{3/2}$ (S²⁻) attributing to the low coordination of sulfur ions related to sulfur vacancies on the surface, S $2p_{1/2}$ (S²⁻) ascribing to the metal-sulfur bond, and a satellite peak of S 2p, respectively [7]. The C 1s spectrum is consisted of three peaks (284.8 eV, 286.1 eV and 289.2 eV) corresponding to C-C, C-O, and O-C=O valence bond in Fig. S2d [10]. According to the peak table of CNS, the content of Nickel element is much larger than Cobalt element on the surface of materials, which further confirms the existence of CoNi₂S₄.



Fig. S3. All O 1s spectrums of the CN, CNS and CNSP-500 electrode materials.



Fig. S4. CV curves of the (a) CN electrode (b) CNS electrode at various scan rates; GCD curves of the (c) CN electrode (d) CNS electrode at various current densities.



Fig. S5. (a) CV curves; (b) GCD curves; (c) Mass-specific capacitance comparison; (d) Area-specific capacitance comparison of the CNSP-100, CNSP-500 and CNSP-1000 electrodes.

To optimize the electrochemical performance of the electrode material, the samples of CNSP-100 and CNSP-1000 are synthesized using the same way with CNSP-500. The mass loading of CNSP-100 and CNSP-1000 are 1.84 mg/cm² and 3.11 mg/cm², respectively. The performance comparison of the CNSP-100, CNSP-500 and CNSP-1000 electrodes are displayed in Fig. S5. CV curves of the three phosphides electrodes at the scan rate of 5 mV/s in the voltage window of -0.1-0.7V are displayed in Fig. S5a, and GCD curves at the current density of 3 A/g in the voltage window of -0.1-0.55V are displayed in Fig. S5b. What's more, the capacity of the corresponding electrodes are shown in Fig. S5c-5d. Compared the area-specific capacitance of CNSP-100 (6.18 F/cm²) and CNSP-1000 (6.99 F/cm²), the material of CNSP-500 (8.86 F/cm²) achieves the highest area-specific capacitance among them. The detailed CV and GCD curves of the CNSP-100 and CNSP-1000 electrodes are presented in Fig. S6a-S6d, respectively. The visible redox peaks and the voltage plateaus reveal the pseudocapacitance character of the prepared phosphides in energy storage process.



Fig. S6. (a) CV curves at various scan rates; (b) GCD curves at various current densities of the CNSP-100 electrode; (c) CV curves at various scan rates; (d) GCD curves at various current densities of the CNSP-1000 electrode .

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