BINARY METAL ORGANIC FRAMEWORKS DERIVED HIERARCHICAL
HOLLOW $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -DOPED CARBON COMPOSITE WITH SUPERIOR
SODIUM STORAGE PERFORMANCE

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ABSTRACT

Binary Ni/Co metal organic frameworks (Ni-Co-MOF) with a hollow-sphere structure that is decorated with cone-shaped protrusions were prepared via a facile solvothermal reaction. Carbonization and sulfurization of the Ni-Co-MOF produce a Ni₃S₂/Co₉S₈/N-doped carbon composite that retained the hierarchical structure. The final composite material presents exceptional electrochemical performance when used as anode in sodium-ion batteries. A reversible specific capacity of 419.9 mAh/g at a current density of 0.1 A/g was achieved after 100 cycles, with an exceptional capacity retention of 98.6%. Furthermore, superior rate capability was also demonstrated: an average capacity of 323.2 mAh/g at a current density of 2 A/g can be achieved. This exceptional performance can be attributed to the unique nano-architecture derived from the MOF precursor, as the resultant material possesses an ideal profile for an excellent anode material: ultrafine Ni₃S₂ and Co₉S₈ particles (< 7 nm), a hollow, porous structure, and an ultrathin N-doped carbon coating.

Keywords: Metal organic frameworks, Sodium-ion batteries, N-doped carbon

TABLE OF CONTENTS

	Page
LIST OF FIGURES	vi
CHAPTER	1
I. INTRODUCTION	1
1.1 Sodium ion battery	1
1.2 Anode	3
1.2.1 Metal Organic Framework	3
1.2.2 Ternary metal sulfide	5
1.3 Challenge and Solutions	5
1.4 Previous work	6
CHAPTER	9
II. EXPERIMENT	9
2.1 Chemicals and Solvents	9
2.2 Characterization and Instrument	9
2.3 Synthesis of Ni-Co-MOF precursor	10
2.4 Synthesis of Ni ₃ S ₂ /Co ₉ S ₈ /N-doped Carbon Composite	11

2.5. Battery Fabrication.....	11
CHAPTER	12
III. RESULT AND DISCUSSION	12
3.1 TEM	12
3.2 XRD	14
3.3 XPS	15
3.4 SEM	16
3.5 HRTEM.....	17
3.6 Long Cycle.....	19
3.7 Cyclic Voltammetry.....	21
3.8 BET	23
3.9 Thermogravimetric Analysis	24
3.10 Elemental Analysis	24
CHAPTER	27
IV. CONCLUSION.....	27

LIST OF FIGURES

Figure	Page
I-1	Synthetic route for Ni-Co-MOF precursor. 4
III-1	TEM images of Ni-Co-MOF prepared with different reaction time (A) 2 h (B) 3 h; (C) 6 h and (D) 10 h. (E) The schematic illustration of the structure evolution. 12
III-2	(A) XRD pattern of the product after carbonization and (B) after sulfurization. (C) Schematic Illustration of synthesis of Ni ₃ S ₂ /Co ₉ S ₈ /N-doped carbon composite..... 14
III-3	High-resolution XPS spectra for C 1s (A) and N 1s (B) 15
III-4	SEM images of Ni-Co-MOF (A) and products obtained after carbonization (B) and sulfurization (C). 16
III-5	TEM (A) of Ni ₃ S ₂ /Co ₉ S ₈ /N-doped carbon. HRTEM (B, C, D) of a single cone grown on the sphere. 17
III-6	STEM Z-contrast image (E) and the corresponding elemental EDX mapping images of Nickel (F), Cobalt (G), Sulfur (H), Carbon (I) and Nitrogen (J). . 17
III-7	(A) C-Rate performance tested under current densities ranging from 0.05 A/g to 2 A/g. (B) Long cycle test performance obtained with a current density of 0.1 A/g. (C) Long cycle test performance obtained with a current density of 1

	A/g.	19
III-8	Electrochemical performance for $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$: A) Cyclic voltammogram profiles obtained with a scan rate of 0.2 mV/s within the chemical window of 0.005-3V. (B) Charge/Discharge profile for the 1 st , 20 th , 50 th , and 100 th at a current density of 0.1 A/g. (C) Charge/discharge profile at different C-rates.	21
III-9	Nitrogen adsorption-desorption isotherm of the Ni-Co-MOF precursor for A and $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$ composite for B	23
III-10	TGA results for Ni-Co-MOFs (A) and $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$ composite (B).....	24
III-11	ICP results for $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$ composite testing the percentage of Ni (A) and Co(B).....	24
III-12	CHN analysis results for the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$ composite.....	25

CHAPTER I

INTRODUCTION

The global concerns regarding depletion of fossil-based resources, global warming and environmental pollution address most of the attention nowadays. Renewable clean energy has been studied to mitigate the issue. Due to the intermittent nature of geographic and climatic environment, the availability of the renewable clean energy is seriously influenced. In succeeding for renewable energy, energy storage attracts attention. Lithium-ion batteries (LIBs) with high energy densities, for example, have become a dominant energy storage. There are many portable electronic and applications in stationary or electrical vehicles (EVs). For the global market, there is an increasingly large demand. In this way, lithium resources are too limited. Availability (0.006 wt% abundance on earth) and cost are two main reason causing the challenge for the large-scale applications of LIBs.

1.1 Sodium ion battery

Lithium-ion batteries (LIBs) have garnered great attention as a technology whereby much focus is set forth in exploring high energy density materials to boost performance¹⁻⁴. Although lithium-ion batteries have been successfully applied in mobile electronic devices and electronic vehicles (EVs), the limited lithium abundance is a difficult problem to

address for large-scale applications that are driven predominately by cost. Therefore, alternative batteries with reasonable energy density, but very low cost are necessary. Sodium-ion batteries (SIBs) have been considered as one of the ideal choices as it possesses similar chemistry to lithium-ion batteries but has the potential for cells with much lower cost.

Na-ion batteries with the widespread availability of sodium (4th most abundant element, 2.64wt% on earth) and lower cost are considered as potential alternatives for the future energy storage. The ionic radius of Na⁺ ion (1.02 Å) is much larger than that of Li⁺ ion (0.59 Å) causing lower Na⁺ ion diffusion coefficient, larger volume expansion and inducing more sluggish electrochemical reaction for sodium storage. Recently, significant progress has been made in advancing ambient temperature sodium-ion batteries as a large variety of electrode materials can be directly transferred from LIBs to SIBs⁵⁻⁷. With rapid and reversible Na ion insertion and extraction, difficulty exists in identifying stable electrode materials, especially the anode materials. Graphite is the mostly used commercial anode material for the Li-ion batteries. Due to the interlayer distance of graphite being too small to accommodate graphite, it is not suitable candidate for NIBs. Therefore, in order to achieve a NIBs with a better performance it is urgent to develop other anodes.

Therefore, it is challenging for SIBs to reach the same specific capacity, even when normalizing for the high mass/charge ratio of Na⁺, and stability as LIBs, in order to achieve widespread adoption.

For a sodium-ion battery, it usually contains 4 components: Anode, Cathode, Electrolyte and Separator. Graphite is the most commonly used anode materials and sodium oxide is the most commonly used cathode materials. Imagine in the discharge process, the sodium oxide releases electron to transfer through the electrolyte and the separator to react with the anode materials. The chemical reaction releases electron which delivers the battery capacity.

1.2 Anode

Transition metal oxides/sulfides, which have been successfully used in LIBs as conversion-reaction type electrodes, show promise in the application of SIBs⁷⁻¹¹, but the major challenges regarding these conversion-reaction type electrodes are the huge volume change during the cycling and inferior intrinsic conductivity. Researches upon different anode material for the sodium-ion battery can be classified into 5 types: (1) carbon based materials, (2) alloy- based materials, (3) metal oxides or sulfides, (4) titanium-based composites, and (5) organic composites. Among these, we can see from the graph below. Metal oxides or sulfides possess great capacitance.¹²

1.2.1 Metal Organic Framework

To combat this, designing a specially structured material, which can not only buffer/restrain the volume variation but also enhance the overall conductivity, behooves significant consideration. One of the most effective strategies to address the aforementioned challenges could be nano-engineering combined with carbon hybridization. Recently, metal-organic frameworks (MOF) have been intensively investigated as

precursors for preparing such carbon-coated metal-oxides due to their tunable composition and nano-structural hierarchy^{13–16}. The homogeneous distribution of metal ions and organic ligands lead to well-organized nanostructures on carbonization of the MOF; for instance, ZnO Quantum Dots embedded in a carbon matrix derived from MOF-5 exhibited excellent lithium storage performance.¹⁷ Similar strategies have been reported as an effective way to fabricate high performance anode materials for LIBs,^{11,15,18} but the use of these MOF-derived materials in SIBs has been limited.

In the MOF synthesis, nickel nitrate and cobalt nitrate were used as a metal ion source, while trimesic acid was used as the organic ligand. After solvothermal reaction, a supramolecular complex with metal ions and organic ligands was formed. Our previous work indicates that PVP can be used as a stabilizer to help the formation of a regular spherical structure.¹⁷ An optimized amount (1.5 g) of PVP was employed, and the resulting MOF was characterized by transmission electron microscopy (TEM).

Figure I-1 Synthetic route for Ni-Co-MOF precursor.

1.2.2 Ternary metal sulfide

In the past decades, researches in science and engineering communities have been carried out intensively on various transition metal oxides (or sulfides, nitrides, and phosphides). Among these promising anode materials, metal sulfides, such as cobalt sulfides, nickel sulfides, and molybdenum sulfides, have been considered as highly applicable for Na-ion batteries. Compared to their corresponding metal oxide, they possess higher electrical conductivity, better mechanical and thermal stability, and richer redox chemistry giving them high specific capacity for several times higher than those of carbon/graphite-based materials. In particular, there are 2 reasons for the ternary nickel cobalt sulfides demonstrating to be more attractive compared to binary metal sulfides and ternary metal oxides, ternary nickel cobalt sulfides: (1) they can offer richer redox reaction sites than binary cobalt sulfides and nickel sulfides due to the contributions from both nickel and cobalt ions. (2) they possess a great advantage over ternary metal oxides in terms of electronic conductivity due to the low band gap. These characteristics make them promising candidates for the anode material of Na-ion batteries with high energy density and power density.^{19–21}

1.3 Challenge and Solutions

However, there are several obstacles like low electro-utilization and short lifetime for metal sulfides because of the large volumetric expansion. There are approaches to mitigate these issues, (i) increase the contact area a per unit mass between the electrode and electrolyte permitting a higher sodium-ion flux achieving higher charge/discharge rates and more ion adsorption sites for charge transfer possessing higher specific capacitances; (ii) shorter path

for ionic and electronic transport, resulting in a faster diffusion rate reaching higher power;
 (iii) better accommodation of the mechanical strain and structural distortion causing by the ion insertion and extraction and other reactions getting longer cycle life.¹²

Thus, for high-rate and durable sodium storage, to achieve engineering efficient nanostructures is vital. The nanostructures reduce the particle size shortening the Na⁺ ion diffusion path resulting in a faster diffusion rate reaching higher power. Also, carbon matrixes like graphene with superior conductivity, large surface area, and excellent mechanical flexibility have been added or coated at the surface of metal sulfides with the

1.4 Previous work

The comparison of Sodium storage performance between our work and previous results have been listed below:

Reference	Active Materials	Current Density (A/g)	Capacity (mAh/g)	Cycles	Retention
Wang et al. ²²	NiS ₂ -GNS	0.08 1.6	314 168	200	77%
Shang et al. ²³	Ni ₃ S ₂ -PEDOT	0.6 1.2	280 310	30	88%
Pan et al. ²⁴	NiS-20rGO	Charge 0.2 Discharge 0.05	160	10	88%

Song et al. ²⁵	Rod-like Ni₃S₂-Ni	0.05 0.8	315.3 230	100	90.6%
Kim et al. ²⁶	Ni₃S₂	0.05	342	16	81%
Qin et al. ²⁷	NS-RGO	0.1 1	391.6 346	50	77.1%
Zhang et al. ⁹	csCo_xS_y-DPC	0.5	300	50	77%
Du et al. ²⁸	Co₃S₄-PNS/GS	0.5 2	329 307	50	71
Zhou et al. ²⁹	Co₃S₄@PANI	0.2 2	252.5 189.3	100	44%
Ko et al. ³⁰	Co₉S₈-carbon	0.5 1.5	404 326	50	80%
This work	Ni₃S₂-Co₉S₈-Graphene	0.1 2	419.9 323.2	100	98.6%
* GNS: graphene nanosheets; PEDOT: poly(3,4-ethylenedioxythiophene); rGO: reduced graphene oxide; NS: nickel sulfide; csCo _x S _y -DPC: core-shell cobalt sulfides-dodecahedral porous carbon; Co ₃ S ₄ -PNS/GS: Co ₃ S ₄ porous nanosheets/graphene sheets ; PANI: polyanilin					

In our work, the Ni₃S₂/Co₉S₈/N-doped carbon composite exhibited impressive sodium storage capability both in merits of cyclic and rate performance. Such performance can be attributed to careful design of materials, in which the Ni₃S₂/Co₉S₈/N-doped carbon composite developed several properties favorable for facile sodium storage: First, it is

known that the kinetics of sodium storage are more sluggish than that of lithium storage. Thereby it is highly desirable to build ultrafine nanostructures that can combat reaction area limitations. The uniformly distributed metal ions and organic ligands in the MOF leads to the growth of metal particles during MOF pyrolysis that can be limited by the carbon layer, leading to the desired nanostructure. Second, to maintain the electrode integrity, it is necessary to mitigate the volume expansion of conversion reaction type electrode. In this respect, the hollow structure provides a buffer void-space for inevitable volume expansion. Moreover, the pores that exist between the carbon coated metal sulfides subunits impart a large interface between the electrolyte and the electrode, facilitating the metal-ion diffusion. Finally, the carbon layers coated on the surface of metal sulfides form an interconnected conducting network, significantly enhancing the electrical conductivity of the electrode.

CHAPTER II

EXPERIMENT

2.1 Chemicals and Solvents.

N,N-dimethylformamide (DMF, ACS grade, EMD), ethanol (Decon Laboratories, Inc.), thiourea ($\text{CH}_4\text{N}_2\text{S}$, >99%, Acros), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >99.9%, STREM CHEMICAL), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 99.999% Sigma-Aldrich), trimesic acid (95%, Sigma-Aldrich), sodium perchlorate (NaClO_4 , 98%, Sigma Aldrich), polyvinylpyrrolidone (PVP, $M_w = 40000$, Scientific Polymer Products), ethylene carbonate (EC, 99.9%, Sigma-Aldrich), diethyl carbonate (DEC, 99%, Sigma-Aldrich), fluoroethylene carbonate (FEC, 98%, Alfa Aesar), carbon black (Super P, Timcal), poly(acrylic acid) (PAA, $M_w = 450000$, Scientific Polymer Products), N-methyl-2-pyrrolidone (NMP, 99.5% Sigma-Aldrich), sodium (99.8% Acros) were used without further purification.

2.2 Characterization and Instrument

The XRD patterns were measured by using a Rigaku Ultima IV X-ray diffractometer using Cu K_α radiation ($\lambda = 1.541 \text{ \AA}$). The SEM images were acquired using either FEI Quanta 450 or JEOL JSM-7401F operating at 10 kV. TGA analyses were conducted using a Q500

(TA Instruments) under N₂ with a temperature ramp rate of 10 °C/min. TEM images were taken by JEOL 1203 or FEI Tecnai G2 F20. HRTEM images, and corresponding EDX maps were collected by FEI Tecnai G2 F20 equipped with an EDAX SUTW (super ultrathin window) energy-dispersive X-ray spectrometer (EDAX). The surface area was determined from gas adsorption measurements using a Micromeritics TriStar II instrument. The sample was degassed (Micromeritics VacPrep 061) at 80 °C for 12 h prior to obtaining nitrogen adsorption/desorption isotherms at 77 K. ICP test was carried out on a Agilent 730 Axial ICP-OES and carbon and nitrogen contents were determined by Perkin Elmer Series II CHNS/O analyzer model 2400. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area from the adsorption isotherm using a relative vapor pressure range of 0.04 - 0.27. Galvanostatic discharge/charge tests were conducted by using a battery analyzer (MTI BST-8A, 1 mA) within the voltage window of 0.005-3 V (vs. Na/Na⁺). Cyclic voltammetry (CV) was accomplished by using an electrochemical workstation (CHI608E) at a scan rate of 0.2 mV/s.

2.3 Synthesis of Ni-Co-MOF precursor.

In a typical procedure, 1.5 g PVP was dissolved into the solvent with mixed distilled water, ethanol, and DMF at a volumetric ratio of 1:1:1. Then 432 mg of Ni(NO₃)₂·6H₂O, 72 mg Co(NO₃)₂·6H₂O, and 150 mg trimesic acid were added under vigorous stirring for 30 min before transferring into a 50 mL Teflon-lined solvothermal reactor. The mixture was heated at 150 °C for 10 h inside of the sealed reactor. The final light purple products were collected and washed with ethanol for several times with a centrifuge (Eppendorf 5702). The final product was dried in an oven at 80 °C for 8 h.

2.4 Synthesis of $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped Carbon Composite

The MOF precursor was heated in an Ar-filled tube furnace to 500 °C at a ramp rate of 2 °C/min for carbonization. The resulting black powder was collected and mixed thoroughly with thiourea at a mass ratio of 1:2. The mixture was heated to 350 °C for 2 h in the tube furnace at a ramp rate of 1 °C/min in an Ar atmosphere for the sulfurization process. The furnace was subsequently cooled down to room temperature under Ar flow to obtain the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite.

2.5. Battery Fabrication

The slurry was prepared by mixing the active material ($\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite), carbon black, and PAA in NMP with a mass ratio of 7:2:1. The slurry was then casted on a copper foil by use of a doctor blade. Afterwards, the coated electrode was dried at 80 °C overnight and the dry electrode was then punched into disks for coin cell fabrication. The mass loading of active materials was $\sim 0.7\text{--}0.8\text{ mg/cm}^2$. Sodium metal was used as the counter electrode and the separator was a glass fiber membrane (WhatmannTM, GF/B Cat. No. 1821 090). The electrolyte was 1 M NaClO_4 in EC and DEC (1:1 v/v) with 10 wt % fluoroethylene carbonate. Battery assembly was carried out in an Ar-filled

CHAPTER III

RESULT AND DISCUSSION

3.1 TEM

Figure III-1 TEM images of Ni-Co-MOF prepared with different reaction time (A) 2 h; (B) 3 h; (C) 6 h and (D) 10 h. (E) The schematic illustration of the structure evolution: ball-in-ball structure with smooth surface was formed initially. Then the interior part began to dissolve and diffuse to the surface for recrystallization; finally, hollow spheres with cone-shaped structure on the surface were generated.

The Ni-Co-MOFs precursors are prepared through a facile hydrothermal reaction. The nickel nitrate, cobalt nitrate and trimesic acid provide the metal ions and organic molecules respectively, while PVP (Polyvinylpyrrolidone)^{31–33} work as the surfactant to stabilize the

formation of the sphere structure, altogether forming the metal organic framework. It has been studied that the suitable amount of PVP is of great importance to form a uniform structure.¹⁸ By controlling the amount, figure D has shown the sphere with cone-shaped materials on the surface was formed with a diameter of around 1.5 μm . The corresponding TEM (transmission electron microscopy) image were shown in figure D confirming and further indicating the hollow spherical structure with cone-shaped materials on the surface.²¹

During the hydrothermal reaction, the metal ions (Ni^{2+} , Co^{2+}) are consisting with the organic link (trimesic acid) at the presence of the PVP surfactant. Firstly, the Ni-Co-contained precursors are formed as ball in ball structure with smooth surface as shown in figure A after 2h of solvothermal reaction. Then as the increasing of the reaction time, figure B and figure C show that the inner ball of the precursors dissolved and diffused to the surface while cone-shaped materials are formed on the surface making it more and more rugged. When the reaction time reaches 10h, the inner ball disappeared leaving the structure being hollow sphere with cone-shaped materials to form the rugged surface (figure D). To better present the evolution of the Ni-Co-MOFs precursors, the corresponding process of figure 1E is drawn in detail.

3.2 XRD

Figure III-2 (A) XRD pattern of the product after carbonization indicates the formation of metallic Ni and Co. The (111) diffraction peaks of Ni and Co are overlapped. (B) XRD pattern of the product after sulfurization showed the generation of metal sulfides. (C) Schematic Illustration of synthesis of $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$ composite

To have the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{Graphene}$ composite, successive carbonization and sulfurization were carried on. The Ni-Co-MOF firstly goes through thermal annealing under Ar at 500°C for 30 min. The hollow spherical structure with cone-shaped materials on the surface can be retained confirmed by the SEM results of figure 2E. Then the X-ray diffraction (XRD) from figure 2B reveals every peak can be assigned to every

diffraction peak indicating the precursors having been reduced to achieve metallic particles Ni and Co. Thiourea was mixed with the Ni/Co/ Graphene composite at the mass ratio of 2:1 under thermal annealing of 350 °C for 2h under Ar to obtain the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{Graphene}$ composite. The XRD results in figure 2C further shows that the every peak can be assigned perfectly to every diffraction peak indicating the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{Graphene}$ composite was obtained with the retained structure shown from the SEM image in figure 2F. The diffraction peak from both XRD tests suggest the nanocomposites being highly crystallined were obtained for both stages while the possessed broad peak from 20–30° is ascribed to carbon.^{34,35}

3.3 XPS

Figure III-3 High-resolution XPS spectra for C 1s (A) and N 1s (B) confirmed the nitrogen doping of carbon.

The nitrogen doping was quantified by high-resolution XPS spectra of C1s and N1s, which

can be observed in Figure 3-3. The N1s spectrum was fit with two peaks at 397 eV and 398.1 eV, which correspond to $(C)_3-N(sp^3)$ and $N-H(sp^3)$, respectively.³⁶ For the N-doped carbon, the C1s peak can be deconvoluted into four peaks: C-C (282.5 eV), C-OH (283.1 eV), C-N-C (283.9 eV) and C=O (286.3 eV).³⁷ The N content in carbon was about 17 atom % from XPS. Such a high nitrogen content in the carbon can provide a plethora of defects that promote enhanced conductivity.³⁸

3.4 SEM

Figure III-4 SEM images of Ni-Co-MOF (A) and products obtained after carbonization (B) and sulfurization (C). The hollow sphere structure is well maintained after both annealing steps.

The SEM image (Figure 1c) indicated that the diameter of the spherical Ni-MOFs is around 1 μm and small crystalline needles covered the surfaces of MOFs. After successive carbonization, oxidation and sulfuration treatments, hierarchical Ni_9S_8 / Co_3S_2 nanocrystals covered with a graphene shell were obtained with the same intact.

3.5 HRTEM

Figure III-5 TEM (A) further confirmed the hollow feature of Ni₃S₂/Co₉S₈/N-doped carbon. HRTEM (B, C, D) of a single cone grown on the sphere surface illustrated an average particle size around 5 nm with a uniform ultrathin carbon layer (2-3 nm) on the particle.

Figure III-6 STEM Z-contrast image (E) and the corresponding elemental EDX mapping images of Nickel (F), Cobalt (G), Sulfur (H), Carbon (I) and Nitrogen (J) indicate that all the elements are homogeneously distributed.

The $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{Graphene}$ composite was further characterized by both low magnification TEM and high resolution TEM. The latter (figure 3-1D) confirmed the retained hollow spherical structure compared to the Ni-Co-MOFs precursors before the sulfurization and carbonization process. The latter (figure 3-5A) exhibits the size of the nanocrystalline particles are around 7nm. The detailed image PI is presented and the covered graphene surface with an average

As demonstrated in Figure 3.5A-D, the sphere structure with hollow feature of the initial MOF is nearly perfectly preserved after carbonization and sulfurization. High-resolution TEM of a single cone structure from the surface of the sphere, as depicted in Figure 3.5A, demonstrates ultrafine nanocrystals with diameter of ~5 nm. The detailed HRTEM image (Figure 3.5 C) presents obvious lattice fringes, in which the 3.0 Å spacing can be ascribed to the (311) interplane spacing of Co_9S_8 . The N-doped carbon shell is visible in Figure 3D. The STEM image in Figure 3E reveals the structure of hollow sphere in more detail. Energy dispersive X-ray spectroscopy (EDS) mapping illustrates the elemental distribution of $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N-doped carbon}$ composite in Figure 3F-3J to demonstrate the homogenous distribution of nickel, cobalt, sulfur, nitrogen, carbon within the composite. In addition, the strong signal of nitrogen demonstrates the high content of nitrogen, which is consistent with the XPS result.

3.6 Long Cycle

Figure III-7 (A) C-Rate performance tested under current densities ranging from 0.05 A/g to 2 A/g. An average capacity of 323 mAh/g was obtained at 2 A/g. (B) Long cycle test performance obtained with a current density of 0.1 A/g. The capacity retention is about 98.6% after 100 cycles. (c) Long cycle test performance obtained with a current density of 1 A/g. The capacity retention is about 93% after 300 cycles.

Long cycle galvanostatic charge/discharge tests were conducted at the current density of 0.1 A/g at the voltage range of 0.005–3 V. The cycling performance and the corresponding coulombic efficiency were presented in figure 3-6B. The initial specific capacity is 554 mAh/g during discharge. When charged to 3V, the reverse capacity appears to be 425 mAh/g resulting from some irreversible reaction and the formation of SEI layer. The initial coulombic efficiency is 76.7%. In this work, the nanocomposite with the ultrafine hollow structure and the size of Ni₃S₂/Co₉S₈ particles less than 8nm works to improve the cycling kinetics. Thus the coulombic efficiency promotes very fast and is almost 100% after the 3rd cycle. Even after 100 cycles, the Ni₃S₂/Co₉S₈/Graphene nanocomposite still delivered a capacity of 419.87 mAh/g with outstanding coulombic efficiency which is

almost 100%. The fading rate is about 0.01% per cycle indicating exceptional cycle stability.

Rate capability in Figure 4C was presented while enlarging the charging/discharging rate. When the higher and higher current density was applied to the battery at 0.05 A/g, 0.1 A/g, 0.25 A/g, 0.5 A/g, 1 A/g, 2 A/g successively, there is a slight decreasing of the average capacities being 416.7 mAh/g, 405.2 mAh/g, 385.3 mAh/g, 364.8 mAh/g, 347.8 mAh/g, 323.2 mAh/g due to the limitation of the Na⁺ ion diffusion. Even under a high current density of 2 A/g which means the charge/discharge process only took 15 min, the battery still delivered an average capacity of 323.2 mAh/g. Significantly, when the Na-ion battery was charged back to 0.05 A/g, the average capacity almost remained the same being 401.3 mAh/g which confirmed the great rate capability of the Ni₃S₂/Co₉S₈/Graphene nanocomposite. The outstanding mobility performance of sodium ion and electron assigned to the ultrafine nanostructure originated from the metal organic framework. As far as we know, this material presents the best electrochemical performance ever reported on the nickel sulfide or the cobalt sulfide.

3.7 Cyclic Voltammetry

Figure III-8 Electrochemical performance for Ni₃S₂/Co₉S₈/N-doped carbon : A) Cyclic voltammogram profiles obtained with a scan rate of 0.2 mV/s within the chemical window of 0.005-3V. (B) Charge/Discharge profile for the 1st, 20th, 50th, and 100th at a current density of 0.1 A/g. (C) Charge/discharge profile at different C-rates.

The cycle voltammetry was studied to elucidate the reduction and oxidation for sodium storage and evaluate the formation of SEI layer. CV was tested with 0.2 mV/s scan rate under the chemical window of 0.005–3 V versus Na/Na⁺. Figure 3-7B is the galvanostatic charge/discharge profiles collected at different current density from 0.05 A/g to 2 A/g corresponding to the c-rate results.

As shown in figure 3-7A, one enhanced reduction peak at 0.75V accompanied with a shoulder peak at 1.3V can be observed in the first anionic scan, while it then moved to 0.85 along with the shoulder peak 1.3 V for the second cycle. There is a huge loss in current density for the reduction peak in the first two cycle ascribed to some

irreversible reactions and the formation of the SEI layer. The oxidation peak at 1.37 and 1.75 V almost remained at the same voltage.^{12,39,22}

Learnt from the previous reports^{40,41}, the mechanism for M_aS_b ($M = \text{Co or Ni}$)/Graphene composite being two step reaction. During discharge process, the intercalation firstly happened when Na^+ intercalates into M_aS_b to form the intermediate $\text{Na}_xM_aS_b$ corresponding to the reduction peak at 1.3V for the second cycle. Then through a conversion reaction, $\text{Na}_xM_aS_b$ reduces to M particles impregnated in Na_2S matrix corresponding to the reduction peak at 0.85V for the second cycle.. The volumetric expansion during cycles is mainly caused by the conversion reaction. The mechanism can be written as below:

For the charge process, the oxidation peak at 1.37 and 1.75 V can be explained as the reversed formation of intermediate $\text{Na}_x M_aS_b$ and the formation of M_aS_b . The peaks are perfectly overlapped with each other for the third and forth cycle indicating outstanding reversibility of the cycle reaction for $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8$ /Graphene nanocomposite electrode. Figure X is galvanostatic charge/discharge profiles collected from different cycles at current density of 0.05mAh/g which can be perfectly matched with the the CV results form the figure 3-7A.

3.8 BET

Figure III-9 Nitrogen adsorption-desorption isotherm of the Ni-Co-MOF precursor for A and $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite for B

The Brunauer–Emmett–Teller (BET) surface area are tested for both the Ni-Co-MOF precursor and the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite. The hollow sphere $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon of Figure 3-8B composite possesses a relatively high Brunauer–Emmett–Teller (BET) surface area. The large surface area and porous structure provide significant contact between the electrolyte and the active material, which can effectively shorten the sodium-ion diffusion pathway, enhancing the electrochemical performance.

3.9 Thermogravimetric Analysis

Figure III-10 TGA results for Ni-Co-MOFs (A) under N₂ with a temperature ramp-rate of 10 °C/min and Ni₃S₂/Co₉S₈/N-doped carbon composite (B) with a temperature ramp-rate of 10 °C/min.

The TGA results for Ni-Co-MOF show that about 10% of the weight consists of residual water and DMF, and 35% was the organic ligand. Then the rest 55% are the metal-related complex. The carbon matrix for the Ni₃S₂/Co₉S₈/N-doped carbon composite can be calculated to be 23%.

3.10 Elemental Analysis

Figure III-11 ICP results for Ni₃S₂/Co₉S₈/N-doped carbon composite testing the percentage of Ni (A) and Co (B).

ICP-OES test is carried on to test the percentage of Ni and Co in $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite. Standard solution was prepared with the concentration of 0ppm, 1ppm, 2.5ppm, 5ppm, 10ppm, 20ppm, 30ppm, 40ppm, 50ppm. After fitting, the variance can be controlled to be above 0.999. The solution prepared has a concentration of 100 ppm. From the tests, we can see that the percentage of Ni is 35.6% and the percentage of Co is 5.4ppm.

```

DATE 08 02 17    TIME 11 15 58    OPERATOR ID QUICK
RUN 1    ID MSNC1    WEIGHT 1.974

                                SIGNALS

CARBON 19.24%        ZR 8451
HYDROGEN .41%        NR 9485
NITROGEN 9.19%       CR 15420
                                HR 15906

BLANKS 6 133 23
KFACTORS 15.614 43.562 5.572

OXFILL COMB BOOST1 BOOST2
 3      10      1      0

FILL TIME 22 SECONDS

DATE 08 02 17    TIME 11 20 56    OPERATOR ID QUICK
RUN 2    ID MSNC2    WEIGHT 1.610

                                SIGNALS

CARBON 19.34%        ZR 8449
HYDROGEN .37%        NR 9307
NITROGEN 9.31%       CR 14174
                                HR 14567

BLANKS 6 133 23
KFACTORS 15.614 43.562 5.572

OXFILL COMB BOOST1 BOOST2
 3      10      1      0

FILL TIME 22 SECONDS

```

Figure III-12 CHN analysis results for the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite

CHN analysis is carried on to test the percentage of carbon and nitrogen. From the results, we can see that approximately 19.3% carbon and 9.3% nitrogen are contained in

Ni₃S₂/Co₉S₈/N-doped carbon composite. The N content was about 9.25 wt % from CHN analysis. Such a high nitrogen content in the carbon can provide a plethora of defects that promote enhanced conductivity. The carbon content was measured to be ~19.30 wt%, which is reasonable for the composite anode material.

CHAPTER IV

CONCLUSION

In summary, the $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon composite was obtained by using a binary Ni-Co-MOF as the precursor. The structure and the composition of the MOF precursor naturally fit the desired properties of ideal sodium-ion battery electrode active materials: large surface area, hierarchical hollow structure, and carbon hybridization. Additionally, N-rich thiourea was introduced as a sulfurization reagent, which simultaneously sulfurized the metals into corresponding metal sulfides and doped carbon layers with nitrogen, providing increased capacity and boosted conductive surface coating. With those merits, the novel electrode materials have enhanced sodium storage kinetics, improved volume expansion mitigation capability, and high electrical conductivity to enable high rate performance. The sodium ion batteries with $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8/\text{N}$ -doped carbon anode materials demonstrated superior reversible capacity (419.87 mAh/g at 0.1 A/g after 100 cycles) and exceptional cycle stability (98.6% capacity retention) as well as outstanding rate capability (323.2 mAh/g at 2 A/g). The synthesis of Ni-CO-MOF and the corresponding $\text{Ni}_3\text{S}_2/\text{Co}_9\text{S}_8$ -/N-doped carbon composite is facile, cost-efficient, and scalable. The success of this strategy provides a host of possible routes for developing novel electrode materials for sodium-ion batteries.

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