Skillful Introduction of Urea during the Synthesis of MOF-Derived FeCoNi–CH/p-rGO with a Spindle-Shaped Substrate for Hybrid Supercapacitors

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Cite This: ACS Omega 2022, 7, 33019−33030

1. INTRODUCTION

The supercapacitors have been widely used in rail transit, electric buses, wind power, smart grid, and other emerging markets due to its excellent characteristics of high power density, quick charge and discharge, long cycle life, safety and reliability, and environmental friendliness.1 Supercapacitors can be classified into electric double-layer capacitors (EDLCs), pseudocapacitors (PCs), and hybrid capacitors (HSCs) according to the charge storage mechanism of electrode materials. The electrode material, one of the components of the supercapacitors, has great effects on charge storage. Hence, the design and development of high-performance electrode materials has become one of the research hotspots in the field of supercapacitors in recent years.2−5 The electrode materials used in EDLCs are mainly carbonaceous materials (for instance, graphene, activated carbon, etc.), but the whole bulk of the material is not fully utilized, which results in low and unsatisfactory energy density. Transition metal oxides,5 hydroxides,6 sulfides,6 phosphating compounds,7 and conductive polymers8 are common typical electrode materials of PCs. Meanwhile, HSCs consist of a EDLC anode and PC cathode with their synergy effect, which is conducive to the improvement of the energy density.8 Among many electrode materials, the transition metal carbonate hydroxide (CH) has become a potential pseudocapacitive electrode material because of its metal ion tunability and a large number of redox active sites.10 At present, these results are mainly focused on mono-metal or binary-metal CH, such as Co–CH,11 Zn–CH,12 NiCo–CH,13 NiCu–CH,14 NiFe–CH,15 CoFe–CH,16 and so forth. However, on account of the introduction of a third metal elements, the rarely reported ternary-metal CH (such as NiCoMn–CH17 and ZnNiCo–CH)18 should have a synergistic effect to raise the conductivity of the materials and provide more redox active sites.17 These previously reported M–CH was frequently prepared by the one-pot method, resulting in a single material shape, poor adjustability, and easy lamellae aggregation.

Furthermore, the morphology of electrode materials affects the electrochemical performance of composites significantly.19 Metal ion etching using metal–organic framework (MOF) materials with large specific surface area and pore size as well
as high porosity can be acted as self-templates,\textsuperscript{20} resulting in CH nanosheets distributed on the templates with various surface morphologies. However, the bottleneck problems of CH composites, such as poor conductivity and cycling stability, seriously restrict their further application. Therefore, it is necessary to design a novel CH-based composite with a combination of other special forms and other materials such as carbon nanotubes,\textsuperscript{21} carbon fiber,\textsuperscript{22} carbon cloth,\textsuperscript{23} graphene,\textsuperscript{24} and other carbon materials with good electrical conductivity. Graphene is the most widely used of these carbon materials. GO is commonly used as a precursor in graphene composites, which is subsequently chemically reduced to reduced graphene oxide (rGO). Chemical reductants such as sodium borohydride (NaBH\textsubscript{4}) as a self-template and urea as a precipitant and reducing agent were used in this study.\textsuperscript{88A} The ternary-metal composite (FeCoNi\textsubscript{2} CH) was fabricated by a self-template method. Herein, a novel chemical strategy was used to prepare a ternary-metal composite (FeCoNi\textsubscript{2} CH/p-rGO) using MIL-88A as a self-template and urea as a precipitant and reducing agent. The MIL-88A template’s original peculiar shape was kept, preventing lamellae aggregation. Meanwhile, it solved the problem of adding extra harmful reducing chemicals (such as NaBH\textsubscript{4}, H\textsubscript{2}O, and NaBH\textsubscript{4}) to traditional reduction methods. As a result, the as-prepared FeCoNi\textsubscript{2} CH/p-rGO composite exhibited high specific capacitance (1346 F g\textsuperscript{-1}) and rate capability (55.5% at 10 A g\textsuperscript{-1}). In addition, in order to obtain better electrochemical performance, we chose a FeOOH/activated carbon (AC) (m\textsubscript{FeOOH}/m\textsubscript{AC} = 1:2) mixture to substitute pure FeOOH or AC as the anode, which combines EDLC and PC charge storage mechanisms. The related self-assembling FeCoNi\textsubscript{2} CH/p-rGO/FeOOH/AC HSC displayed a high energy density of 46.93 W h kg\textsuperscript{-1} at 400 W kg\textsuperscript{-1} and cycle stability of 66.7% after 3000 cycles.

2. EXPERIMENTAL SECTION

2.1. Materials. Graphite oxide (GO) dispersion was bought from Jiangsu Hengqiu Technology Co., Ltd. (Jiangsu Province, China). All the other chemical reagents used in this experiment were analytically pure without further purification.

2.2. Preparation of MIL-88A and MIL-88A/GO. MIL-88A was prepared according to the previous preparation protocol.\textsuperscript{28} MIL-88A/GO was prepared by a hydrothermal method, which involved the following processes. First, a certain amount of graphite oxide at a concentration of 5 mg/mL (0.25, 0.5, 1, or 2 mL) was dispersed by ultrasound in 15 mL of ultrapure water for 15 min, and the resulting solution was stirred magnetically for 30 min to obtain solution A. Moreover, different ratios of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (300/0.200/100:150/100:200:0/300 mg) were mixed and stirred for 10 min to obtain solution B. Then, solution A and solution B were mixed and stirred for 30 min and transferred to a 100 mL Teflon-lined stainless steel reactor for 5.0 h at 90 °C. When cooled to room temperature, the samples were dried overnight in a 60 °C vacuum oven after regular washing by centrifugation to obtain FeCoNi\textsubscript{2} CH with different molar ratios of Co/Ni. The fabrication process of FeCoNi\textsubscript{2} CH with different etching times was similar to that of FeCoNi\textsubscript{2} CH with different molar ratios of Co/Ni, with the difference being 150 mg of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O as well as Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and a reacting time of 2.5/5.0/7.5/10.0/12.5 h, respectively. The fabrication process of FeCoNi\textsubscript{2} CH/p-rGO was similar to that of FeCoNi\textsubscript{2} CH with different etching time, except that MIL-88A was replaced by MIL-88A/GO with different GO contents, and the reaction time was 10 h.

2.3. Fabrication of FeCoNi\textsubscript{2} CH and FeCoNi\textsubscript{2} CH/p-rGO. FeCoNi\textsubscript{2} CH was fabricated using a hydrothermal method, which involved the following processes. First, 22 mg of MIL-88A was dissolved in 12 mL of anhydrous ethanol and stirred magnetically for 10 min to obtain solution A. Moreover, different ratios of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (300/0.200/100:150/100:200:0/300 mg) were added to solution A. Then, the mixture was stirred for 10 min to obtain solution B. Then, solution A and solution B were mixed and stirred for 30 min and transferred to a 100 mL Teflon-lined stainless steel reactor for 5.0 h at 90 °C. After cooling to room temperature, the samples were dried overnight in a 60 °C vacuum oven after regular washing by centrifugation to obtain FeCoNi\textsubscript{2} CH with different molar ratios of Co/Ni. The fabrication process of FeCoNi\textsubscript{2} CH with different etching times was similar to that of FeCoNi\textsubscript{2} CH with different molar ratios of Co/Ni, with the difference being 150 mg of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O as well as Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and a reacting time of 2.5/5.0/7.5/10.0/12.5 h, respectively. The fabrication process of FeCoNi\textsubscript{2} CH/p-rGO was similar to that of FeCoNi\textsubscript{2} CH with different etching time, except that MIL-88A was replaced by MIL-88A/GO with different GO contents, and the reaction time was 10 h. In addition, in order to study the effect of different molar ratios of Co/Ni, we chose MIL-88A/GO with a mass ratio of the cathode and anode is ascertained on the basis of the charge storage balance rule by the following formula

\[
\frac{I \times \Delta t}{m \times \Delta V} = \frac{C}{\Delta V}\]  

where \(I\) (A), \(\Delta t\) (s), \(m\) (g), and \(\Delta V\) (V) denote discharge current, discharge time, mass of active substance on electrode, and potential window, respectively.

2.4. Synthesis of FeOOH. FeOOH was synthesized by a hydrothermal strategy previously reported.\textsuperscript{29} The hydrothermal strategy previously reported.

2.5. Material Characterization. X-ray diffraction (XRD) diagrams were obtained using a XPert PRO MPD X-ray diffractometer with Cu Ka radiation (\(\lambda = 1.5406\) Å) at a scan speed of 2° min\textsuperscript{-1}. The morphology and size of the products were examined by scanning electron microscopy (SEM, Hitachi S4800). The element contents and chemical composition of the products were confirmed by energy-dispersive X-ray spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). All XPS spectra were corrected using the C 1s line at 284.6 eV. Raman spectra were recorded using a Horiba Scientific LabRAM HR Evolution with a 532 nm laser source. The micromorphology and structure were further characterized by transmission electron microscopy (TEM, TECNAI F20). Fourier transform infrared (FT-IR) spectra were recorded on an IRAffinity-1 spectrometer with KBr pellets. The N\textsubscript{2} adsorption and desorption isotherms were measured using a Micromeritics TriStar 3020 instrument in the static mode to get the results of specific surface area and pore structure.

2.6. Electrochemical Characterization and Tests. All electrochemical tests were achieved at room temperature with a three-electrode system using CHI 660E (Chenhua Instrument, Shanghai, China). The platinum plate and Hg/HgO electrode acts as counter electrodes and reference electrodes, respectively. The working electrode was fabricated by compounding the active substance, acetylene black, and polyvinylidene fluoride (PVDF) conductive adhesive uniformly at a mass ratio of 8:1:1 and pressing it into nickel foam (1 × 1 cm\textsuperscript{2}) using a pressing machine. The nickel foam was then dried overnight in a vacuum oven at 60 °C. Furthermore, the electrochemical performance parameters of cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were tested in a 2 M KOH aqueous electrolyte to assess the electrochemical properties of electrode materials. The specific capacitance (C, F g\textsuperscript{-1}) can be computed by the following equation

\[
C = \frac{I \times \Delta t}{m \times \Delta V}
\]  

where \(I\) (A), \(\Delta t\) (s), \(m\) (g), and \(\Delta V\) (V) denote discharge current, discharge time, mass of active substance on electrode, and potential window, respectively.

2.7. Fabrication of the Hybrid Supercapacitor. The mass ratio of the cathode and anode is ascertain by the basis of the charge storage balance rule by the following formula
\[ \frac{m_+}{m_-} = \frac{C_+ \times \Delta V_+}{C_- \times \Delta V_-} \]  

(2)

where \( m_+ \) and \( m_- \) are the loading mass (g); \( C_+ \) and \( C_- \) are the specific capacitance (F g\(^{-1}\)); and \( \Delta V_+ \) and \( \Delta V_- \) are the voltage range (V); the plus and minus signs are the cathode and anode electrodes, respectively.

The electrochemical performance parameters of CV and GCD of HSC were measured in a 6 M KOH aqueous electrolyte. The energy density \( (E, \text{W h kg}^{-1}) \) and power density \( (P, \text{W kg}^{-1}) \) of the HSC are calculated according to the following equations

\[ E = \frac{1}{2} C \times \Delta V^2 \]  

(3)

\[ P = \frac{E}{\Delta t} \]  

(4)

where \( C \) (F g\(^{-1}\)), \( \Delta V \) (V), and \( \Delta t \) (s) are electrochemical performance parameters of HSC, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Fabrication of the FeCoNi−CH/p-rGO Composite.

The possible synthetic mechanism of the FeCoNi−CH/p-rGO composites with a spindle-shaped substrate is shown in Scheme 1. First, the GO reacts with Fe\(^{3+}\) and fumaric acid to form MIL-88A/GO with the hydrothermal method. Moreover, the adscititious urea, Ni(NO\(_3\))\(_2\)·6H\(_2\)O, and Co(NO\(_3\))\(_2\)·6H\(_2\)O are mixed in the solution, and the sacrificial template MIL-88A is continuously etched during the hydrolysis reaction. When Fe\(^{3+}\) is released, FeCoNi−CH is formed by the coprecipitation of Fe\(^{3+}\), Ni\(^{2+}\), Co\(^{2+}\), OH\(^-\), and CO\(_3^{2-}\) generated by the hydrolysis of urea as a precipitant. Meanwhile, urea can also work as the reducing agent to partially reduce GO to rGO, resulting in FeCoNi−CH/p-rGO composites. The reduction of GO is facilitated through the reducing species originated from the decomposition of urea. The underlying mechanism could be as follows: a prior investigation of GO reduction using NaOH or KOH reveals that an alkaline environment can promote the reduction of GO to rGO. It so happened that one of the hydrolysis products of urea, OH\(^-\), can provide an alkaline environment and it just so occurred. Furthermore, investigations have revealed that after reducing GO to rGO with urea, there are nitrogen-containing functional groups on rGO, which could be owing to the action of NH\(_4^+\), another urea hydrolysis product, in the reduction process. The partial reduction of GO in this case is due to a shorter reaction period than the literature-recommended 30 h, so we can encourage GO reduction further by prolonging the reaction time or increasing the amount of urea used. During the synthetic process, the factors (Co/Ni ratios, etching and coprecipitation times, and the amount of GO) were accordingly regulated to optimize the electrochemical properties of the composite.

#### 3.2. Structural, Morphological, and Composition Characterization.

XRD is used to characterize the phases of the as-prepared materials. Four characteristic diffraction
peaks at 2θ values of 7.7, 10.2, 12.8, and 15.1° are displayed in Figure 1a, which can be indexed to the (010), (011), (002), and (012) planes of the spindle-shaped MIL-88A phase. For the MIL-88A/GO, the diffraction peaks at 10.7° are indexed to the (001) of GO. Meanwhile, the disappearance of diffraction peaks at 7.7 and 12.8° and the appearance of some new diffraction peaks at 20–30° show that GO participates in coordination and forms new phases in the formation process of MIL-88A/GO. The diffraction peaks of FeCoNi−CH and FeCoNi−CH/p-rGO (Figure 1b) at 21.1, 30.2, 33.8, 35.7, 37.2, 39.1, and 60.0° are in good accordance with the Ni$_6$Fe$_2$(CO$_3$)(OH)$_{16}$·H$_2$O phase (JCPDS no. 26-1286). Moreover, the peaks of 8.3, 11.6, 12.3, and 16.4° shift to a higher or lower angle than the simulated NiFe−CH, demonstrating that Co$^{2+}$ has been successfully inset into the crystal lattice of FeNi−CH to cause a slight lattice expansion and shrinkage. Meanwhile, the diffraction peaks at 21.7, 24.4, 27.6, 32.7, 35.0, 37.9, and 40.2° can be indexed to the Ni$_6$(CO$_3$)(OH)$_2$·H$_2$O phase (JCPDS no. 29-0868), indicating successful preparation of FeCoNi−CH. In addition, the characteristic peaks at 22.3 and 28.9° come from residual fumaric acid (JCPDS no. 47-2118) during the reaction. The XRD patterns of materials synthesized in different conditions, including Co/Ni ratios, etching and coprecipitation times, and the amount of GO, are shown in Figures S1–S3.

Figure 2. SEM images of MIL-88A (a) and FeCoNi−CH (b) and partial enlargement higher-resolution of FeCoNi−CH (c), MIL-88A/GO (d), and FeCoNi−CH/p-rGO (e) and partial enlargement higher-resolution of FeCoNi−CH/p-rGO (f).

Figure 3. XPS spectra of the FeCoNi−CH/p-rGO composite: survey spectrum (a), Ni 2p (b), Co 2p (c), and Fe 2p (d); C 1s of MIL-88A (e), MIL-88A/GO (f), and FeCoNi−CH/p-rGO (g).
and the concentration of Co is lower than that of Ni. There may be two reasons for the analysis: one is that the $K_{sp}$ values of Co(OH)$_2$ and Ni(OH)$_2$ at the same temperature are different, resulting in different precipitation sequences, with Ni(OH)$_2$ taking precedence over Co(OH)$_2$. The other is that the nucleation rate of each ion in the reaction system is different during the formation of FeCoNi–CH, leading to a high content of metal elements with a fast nucleation rate in the FeCoNi–CH phase.

The chemical composition and valence state of the material surfaces of the MIL-88A, MIL-88A/GO, and FeCoNi–CH/p-rGO composites are characterized by XPS. In Figure 3a, the XPS survey spectrum of the FeCoNi–CH/p-rGO composite shows the Ni 2p, Co 2p, Fe 2p, O 1s, and C 1s peaks, which are very much in accord with the composition of FeCoNi–CH/p-rGO. As shown in Figure 3b, two main peaks representing Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ at 855.7 and 873.2 eV are separated by fitting. The gap in binding energy of 17.5 eV shows that the valence state of Ni is “+2”.

In the same way, the spectrum of Co 2p (Figure 3c) can also be divided into two major peaks, standing for Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively, at 780.98 and 796.83 eV and two satellite peaks, which indicates the valence state of Co is “+2”. Meanwhile, the two main peaks located at 713.0 and 725.3 eV in the Fe 2p spectrum (Figure 3d) demonstrate that the valence state of Fe is “+3”. As displayed in Figure 3e–g, the appearance of the oxygen-containing bond C=O in MIL-88A/GO proves the successful introduction of GO. The decrease in the intensity of C=O and the carboxyl peak of FeCoNi–CH/p-rGO indicates that GO is partially reduced to rGO by urea at 90 °C because the carboxyl and C=O groups do not disappear completely. This result may be caused by residual fumarate C$_2$H$_4$O$_4^{2-}$ and unreduced GO. Also, the offset of the binding energy position shows the presence of CO$_3^{2-}$ from FeCoNi–CH. The XPS spectra of MIL-88A and MIL-88A/GO are shown in Figure S5.

Raman spectroscopy is an effective characterization for analyzing the structural characteristics of carbonaceous materials, which can reflect the degree of reduction from GO to rGO. As shown in Figure 4a, the peak at 1661 cm$^{-1}$ is caused by the stretching vibration of C=C in fumaric acid. In addition, the same high wavenumber peak also appears in the spectrum of FeCoNi–CH, which is attributed to the fumarate C$_2$H$_4$O$_4^{2-}$ isolated from MIL-88A during the etching process. This is exactly consistent with the XRD result, and it is necessary for C$_2$H$_4$O$_4^{2-}$ to balance the extra cationic charge in the layered CH. For MIL-88A/GO and FeCoNi–CH/p-rGO, two distinct main peaks are located at 1350 and 1598 cm$^{-1}$, representing the D and G peaks of the carbonaceous material, respectively. The D peak is caused by the disorder and structural defect of sp$^3$ carbon, while the G peak is caused by the plane vibration of ideal sp$^3$ hybrid carbon. The relative strength ratio of peak D and peak G ($I_D/I_G$) is commonly used to measure the degree of graphitization and defect of the sample. The $I_D/I_G$ values of MIL-88A/GO and FeCoNi–CH/p-rGO were 1.39 and 1.90, respectively, indicating a larger degree of defects in rGO nanosheets despite the partial reduction of GO. On the one hand, when GO is reduced to rGO, the oxygen-containing functional groups of GO are removed, and the sp$^3$ hybrid carbon-conjugated graphene can be rebuilt, which usually results in an increase in $I_D/I_G$ values. On the other hand, the increasing of the defect degree is also due to the interaction between rGO and FeCoNi–CH. Moreover, the peaks at 450, 537, 666, and 290 cm$^{-1}$ in the FeCoNi–CH/p-rGO spectrum are attributed to CO–O, Ni–O, as well as Fe–O stretching vibration in CH and E-type, respectively. Moreover, the widening of the peak at 450 cm$^{-1}$ arises from the defect and disordered structure of CH,
Figure 5. TEM images of FeCoNi−CH/p-rGO (a), partial enlargement of FeCoNi−CH/p-rGO (illustration is the selected area electron diffraction diagram) (b), HRTEM images of p-rGO (c) and FeCoNi−CH/p-rGO (d), and elemental mapping of FeCoNi−CH/p-rGO for C, O, Fe, Co, and Ni (e).

Figure 6. CV graphs of FeCoNi−CH and FeCoNi−CH/p-rGO at a sweep speed of 5 mV s\(^{-1}\) (a), CV graphs of FeCoNi−CH/p-rGO at different sweep speeds (b), image of linear fitting relationship between anode and cathode peak current and sweep speeds (c), relative contributions between these two charge storage mechanisms of capacitive and diffusion-controlled at different scan rates: FeCoNi−CH (d) and FeCoNi−CH/p-rGO (e), GCD graphs for FeCoNi−CH and FeCoNi−CH/p-rGO tested at a current density of 0.5 A g\(^{-1}\) (f), GCD graphs of FeCoNi−CH/p-rGO at various current densities (g), specific capacitance vs various current densities for FeCoNi−CH and FeCoNi−CH/p-rGO (h), and Nyquist curves of FeCoNi−CH and FeCoNi−CH/p-rGO with the inset of partial enlargement of high frequency region of the impedance spectrum (i).
indicates the triumphant synthesis of the FeCoNi−CH/p-rGO composite.

The FT-IR spectra of MIL-88A, MIL-88A/GO, FeCoNi−CH, and FeCoNi−CH/p-rGO are exhibited in Figure 4b,c. The two similar wavenumbers of 1605 and 1396 cm\(^{-1}\) in MIL-88A and MIL-88A/GO represent the symmetric and asymmetric stretching vibrations of the carboxyl groups, respectively, and the wavenumber of 571 cm\(^{-1}\) represents the stretching vibration of Fe−O in MIL-88A. The wide peak at 3416 cm\(^{-1}\) wavenumber may be caused by residual water during the preparation of MIL-88A by hydrothermal method or water in the test environment,\(^{34}\) and the peak at 2350 cm\(^{-1}\) wavenumber is due to CO\(_2\) in the test environment.\(^{35}\) For FeCoNi−CH and FeCoNi−CH/p-rGO (Figure 4c), the wavenumbers at 1616, 1557, 1462, and 1395 cm\(^{-1}\) illustrate the existence of CO\(_3^{2−}\). Therein, the bands at 1616 and 1557 cm\(^{-1}\) are attributed to the C=O and those at 1462 and 1395 cm\(^{-1}\) indicate the C−O. The CO\(_3^{2−}\) is made up of one C=O and two C−O. Therefore, the wavenumber at 1115 cm\(^{-1}\) can be ascribed to the bending vibration of CO\(_2^{−}\). The wavenumber at 621 cm\(^{-1}\) is due to the overlapping of the asymmetric vibration of CO\(_3^{2−}\) and to M−O stretching vibration.\(^{46}\)

The type IV isotherms that come from N\(_2\) adsorption and desorption isotherms (Figure S6) depict mesoporous material, and the usual IV-H3 hysteresis indicates that the materials have a layered hollow structure, which is consistent with SEM images.\(^{48}\) The calculated Brunauer−Emmett−Teller (BET) specific surface areas of FeCoNi−CH and FeCoNi−CH/p-rGO composite are 30 and 27 m\(^2\) g\(^{-1}\), respectively, which demonstrates there are many active sites. The result of a slight decrease after compositing p-rGO is within the margin of test error and similar to the phenomenon reported in previous literature.\(^{49}\) The pore volumes of FeCoNi−CH and FeCoNi−CH/p-rGO composite calculated from Barrett−Joyner−Halenda (BJH) are 0.16 and 0.11 cm\(^3\) g\(^{-1}\) and the BJH pore diameters (Figure S6 inset) are within the range of 4 to 50 nm and 4 to 60 nm, respectively. The hierarchical porous structure allows more hydroxide ions to come into contact with the active substances and promotes electrochemical performance further.\(^{50}\)

The TEM images of FeCoNi−CH/p-rGO are shown in Figure 5. It can be seen that the MOF template is etched, and FeCoNi−CH nanosheets are grown on the MOF substrates by self-assembly. Furthermore, the folding of the edges of the nanosheets demonstrates their ultrathin characteristics. As can be seen from Figure 5d, surface spacings of 0.20, 0.23, 0.24, 0.25, 0.26, and 0.29 nm are well corresponding to the (2, 0, 14), (2, 0, 10), (2, 0, 8), (1, 0, 16), (2, 0, 2), and (1, 1, 4) crystallographic planes of the FeCoNi−CH phase, respectively. The selection of electron diffraction in the illustration further proves the existence of the FeCoNi−CH phase. Meanwhile, the 0.21 nm crystal plane spacing corresponds to the GO (101) crystal plane in Figure 5c,\(^{40}\) indicating that GO has not been completely reduced. The mapping results (Figure 5e) exhibit that Fe, Co, and Ni elements are uniformly distributed, and the image of the C element indicates the existence of some fumarate C\(_6\)H\(_8\)O\(_4^{2−}\) isolated from MOFs and CO\(_3^{2−}\) in FeCoNi−CH layers.

### 3.3. Electrochemical Properties of the FeCoNi−CH and FeCoNi−CH/p-rGO Composite

The Co/Ni ratios and etching times are crucial to influence the electrochemical performance of FeCoNi−CH. Therefore, we regulate these factors to find that the optimal conditions for the electrochemical performance of the as-synthesized materials are a Co/Ni ratio of 1:1 and an etching time of 10 h (Figures S7 and S8). On this basis, the addition amount of GO is further regulated to 0.5 wt % to optimize the electrochemical performance of the FeCoNi−CH/p-rGO composites (Figure S9).

To highlight the effect of GO on the electrochemical properties of composites, we performed the comparison between the FeCoNi−CH/p-rGO and FeCoNi−CH. As shown in Figure 6a, the CV curves of FeCoNi−CH and FeCoNi−CH/p-rGO at 5 mV s\(^{-1}\) have two similar pairs of distinct redox peaks, indicating that they are typical pseudocapacitive electrode materials. When the peak current increases (Figure 6b), the corresponding electrode potential also continuously shifts from the equilibrium potential and the polarization phenomenon occurs. The potential offset is linearly correlated with the peak current, so the polarization is mainly caused by the Ohm internal resistance in the electrode system.\(^{51}\) The CV curve (Figure 6a) also shows that the integral area of FeCoNi−CH/p-rGO is larger than that of FeCoNi−CH, manifesting that the specific capacitance of FeCoNi−CH/p-rGO is well improved.

Based on the analysis of CV curves, we further explore the charge storage mechanism of electrode materials with the reaction kinetic theory, which was first proposed by Simon et al.\(^{52}\) Reaction kinetics is used to express the relationship between peak current \(i\) and sweeping speed \(v\)

\[
i = a v^b
\]

where \(a\) and \(b\) are constants, and the value of \(b\) can be obtained by linear fitting of \(\log(i)\) and \(\log(v)\). In general, \(b = 0.5\) demonstrates that a diffusion controlled battery-like mechanism is leading, and \(b = 1\) demonstrates that capacitive behavior is dominant, here including electric double-layer capacitance and pseudocapacitance,\(^{53}\) and \(b = 0.5−1\) manifests both the above processes.\(^{54}\) For FeCoNi−CH/p-rGO electrode materials, we label two pairs of redox peaks as peaks I, II, III, and IV (Figure 6b), and the corresponding \(b\) value is 0.54, 0.61, 0.60, and 0.59, respectively (Figure 6c). These results show that the diffusion-controlled battery-like behavior is dominant.\(^{55}\) The contribution proportion of both mechanisms can be quantified by the following two formulas

\[
i(V) = k_1 v + k_2 v^{1/2}
\]

\[
i(V)/v^{1/2} = k_1 v^{1/2} + k_2
\]

where \(i(V)\) is the response current at different potentials (A) and \(k_1\) and \(k_2\) correspond to capacitance process and diffusion control process, respectively. The values of \(k_1\) and \(k_2\) can be derived from the numerical relationship between \(i(V)/v^{1/2}\) and \(v^{1/2}\). For the composites FeCoNi−CH and FeCoNi−CH/p-rGO, the contribution ratios of the two mechanisms at varied scan rates are shown in Figure 6d,e, respectively. The similarity is that the proportion of the diffusion-controlled mechanism process decreases gradually with sweep speed increasing. Because the time of ion diffusion is shortened due to the rise in sweep speed, the number of ions inserted into the lattice is limited. On the contrary, the capacitance contribution will increase.\(^{54}\) The difference is that the capacitive contribution ratio of FeCoNi−CH/p-rGO is lower than that of FeCoNi−CH at the same scan rate. This may be due to the accelerated ion migration rate after rGO combination, which
contributes to the occurrence of the diffusion-controlled mechanism process. Therefore, the proportion of the diffusion-controlled mechanism process is higher, and the capacitance contribution becomes low accordingly.

Based on the GCD curves shown in Figure 6f, the specific capacitance of the FeCoNi−CH and FeCoNi−CH/p-rGO composites are calculated to be 1110 and 1346 F g⁻¹ at 0.5 A g⁻¹, respectively. According to the GCD curves (Figure 6g), the specific capacitance of the FeCoNi−CH/p-rGO composites is calculated to be 1346, 1307, 1199, 978, 747, and 427 F g⁻¹ at 0.5, 1, 2, 5, 10, and 20 A g⁻¹, respectively. The capacitance retention rate (Figure 6h) of the FeCoNi−CH/p-rGO composites at 1−10 A g⁻¹ is 55.5%, which is higher than that of FeCoNi−CH (32.1%). The reason for the high rate capability of FeCoNi−CH/p-rGO is that p-rGO can improve its electrical conductivity and facilitate rapid charge transfer.

In order to study the speed of electron migration and ion diffusion in the Faraday redox process in an electrochemical system, EIS tests are implemented on the FeCoNi−CH and FeCoNi−CH/p-rGO composites. Figure 6i shows that the two curves consist of an arc in the high-frequency scope and an inclined straight line in the low-frequency scope, which is exactly similar to the AC impedance spectrum of the electrochemical system composed of pseudocapacitive electrode materials. In the high-frequency region, the intercept between the curve and the X-axis stands for $R_s$, including the inherent resistance, electrolyte resistance, and interface contact resistance. The FeCoNi−CH/p-rGO exhibits the lower $R_s$ value 0.63 Ω due to its higher conductivity than that of FeCoNi−CH (0.66 Ω). The semi-arc diameter of the high frequency scope stands for the electron transfer resistance $R_{ct}$. According to the fitting result, the $R_{ct}$ of FeCoNi−CH and FeCoNi−CH/p-rGO is 1.00 and 0.53 Ω, respectively, which means the electrical conductivity of the FeCoNi−CH/p-rGO is better. The low-frequency inclined straight line reflects the Warburg resistance of OH⁻ diffusing from the electrolyte to the surface of the electrode material. Moreover, the higher the slope is, the lower the ion diffusion resistance is. The fitting result is that the line slope of FeCoNi−CH/p-rGO is larger than that of FeCoNi−CH, which illustrates that the ion
diffusion resistance is low and the ions are easy to diffuse and move in the electrolyte for FeCoNi–CH/p-rGO. The EIS analysis results show that FeCoNi–CH composed with p-rGO can improve the conductivity of the electrode material, and further promote the optimization of electrochemical properties. In addition, there is no obvious difference between the BET specific surface area and pore structure change. The specific surface area and pore structure in FeCoNi–CH and FeCoNi–CH/p-rGO according to the above analysis, so the influence of improved conductivity after compositing p-rGO on the electrochemical properties is greater than that of the specific surface area and pore structure change.

High energy density and power density are the prerequisites for the practical application of supercapacitors. On the basis of previous studies, we constructed the composite FeCoNi–CH/p-rGO//FeOOH/AC HSC (Figure 7a). Compared to pure FeOOH or AC electrodes, assembling HSC with using FeCoNi–CH/p-rGO and FeOOH/AC as cathode and anode materials obtains better overall electrochemical performances. The CV (Figure 7b) and GCD (Figure 7c) curves under the voltage window of −1.1 to 0 V with varied scan rates reveal a pair of redox peaks and a potential platform in the low potential window, as well as a rectangular shape and an inclined straight shape, respectively, in the high potential window, which demonstrate that FeOOH/AC is a typical pseudocapacitance and electric double-layer capacitance binding electrode. At 1, 2, 3, 5, 8, 10, and 15 A g⁻¹, the specific capacitance of FeOOH/AC is calculated to be 289, 201, 168, 136, 109, 91, and 68 F g⁻¹, respectively. Calculated by eq 2, the optimized mass ratio of FeCoNi–CH/p-rGO to FeOOH/AC is 1:2. To determine the suitable voltage window for FeCoNi–CH/p-rGO//FeOOH/AC HSC, we perform the test for FeCoNi–CH/p-rGO and FeOOH/AC at 5 mV s⁻¹. As displayed in Figure 7d, the wider voltage windows at 0–0.6 and −1.1 to 0 V are observed, which exceed the limiting voltage of hydrosil (1.23 V). The CV curves (Figure 7e) of FeCoNi–CH/p-rGO//FeOOH/AC HSC at various voltage windows show the stable shape between 1.0 and 1.6 V. The slightly prominent redox peak in the curve indicates that the capacitance contribution of FeCoNi–CH/p-rGO/FeOOH/AC HSC is attributed to the pseudocapacitance of the cathode electrode and the electric double-layer capacitance as well as the pseudocapacitance of the anode electrode. When the voltage window rises above 1.7 V, polarization occurs, which illustrates that severe hydrosil has occurred. Therefore, the optimal potential window is 1.6 V. With the rise of sweep speed, the CV curves still remain rectangular in shape (Figure 7f), and the polarization phenomenon is not obvious (Figure S10d,g). The GCD curves are triangular on the whole window with a few platforms (Figure 7g), which further proves that the electrochemical performance of the HSC comes from the pseudocapacitance characteristic of the cathode material and the electric double-layer as well as the pseudocapacitance characteristic of the anode material. At 0.5, 1, 2, 3, 5, 8, and 10 A g⁻¹, the specific capacitance is calculated to be 132, 121, 98, 81, 65, 48, and 40 F g⁻¹, respectively. Furthermore, the cycling stability of the FeCoNi–CH/p-rGO/FeOOH/AC HSC is detected at 5 A g⁻¹ (Figure 7h). A high cycling stability of 66.7% is clearly exhibited, which falls between the 50% of FeCoNi–CH/p-rGO/FeOOH (shown in Figure S10i) and the 75% of FeCoNi–CH/p-rGO//AC (shown in Figure S10k) specific capacitance retention after cycling 3000 cycles. Step-like capacitance degradation in alkali environments may involve microstructure collapse caused by expansion and shrinkage, loss of available active sites, and resistance increase during charge–discharge processes. Therefore, the assembling of HSC using FeCoNi–CH/p-rGO and FeOOH/AC as cathode and anode materials can improve the overall electrochemical performance due to the synergy of pseudocapacitive material FeOOH and electric double-layer material AC.

According to eqs 3 and 4, the energy density and power density of the FeCoNi–CH/p-rGO//FeOOH/AC HSC device are computed, and the Ragone plot is shown in Figure 7i. The maximum energy density of 46.93 W h kg⁻¹ of the device is delivered, which is between 59.73 W h kg⁻¹ (FeCoNi–CH/p-rGO/FeOOH) and 41.33 W h kg⁻¹ (FeCoNi–CH/p-rGO//AC), and the corresponding power density is 400 W kg⁻¹. When the power density rises to 8000 W kg⁻¹, the energy density can still be 14.30 W h kg⁻¹. This result illustrates that the FeCoNi–CH/p-rGO//FeOOH/AC HSC device can maintain a high level of energy density under high current density and can achieve efficient, safe, and stable operation. Meanwhile, the FeCoNi–CH/p-rGO//FeOOH/AC HSC in this work precedes most of the other transition metal hydroxide-type HSCs reported previously, such as CoNiFe-LDH@CNFs//AC [P = 800 (8000) W kg⁻¹, E = 30.2 (22.04) W h kg⁻¹], NiCo-LDH on ZnSnO₄//AC [P = 283.4 (5817.2) W kg⁻¹, E = 23.0 (9.7) W h kg⁻¹], Ni–Co LDH/NG@AC [P = 354 (10 800) W kg⁻¹, E = 31.2 (9.9) W h kg⁻¹], CoMn-LDH/carbon fiber paper//AC [P = 400 (6400) W kg⁻¹, E = 19.1 (12.8) W h kg⁻¹], and rGO/NiMn-LDH/NF//AC [P = 700 (3425) W kg⁻¹, E = 22.5 (16.2) W h kg⁻¹]. Table 1 shows the comparisons of electrochemical performance intuitively.

| material                  | capacitance (F g⁻¹) | current density (A g⁻¹) | energy density (W h kg⁻¹) | power density (W kg⁻¹) | cycle performance | references |
|---------------------------|---------------------|------------------------|--------------------------|------------------------|-------------------|------------|
| CoNiFe-LDH@CNFs           | 1203                | 1                      | 30.2 (22.04)             | 800 (8000)             | 82.7%, 2000 cycle | 62         |
| NiCo-LDH/ZnSnO₄           | 1805                | 0.5                    | 23.7 (9.7)               | 283 (5817)             | 92.7%, 5000 cycle | 63         |
| Ni–Co LDH/NG              | 1720                | 3                      | 31.2 (9.9)               | 354 (10 800)           | 83%, 10 000 cycle | 64         |
| CoMn-LDH/CFP              | 980                 | 2                      | 19.1 (12.8)              | 400 (6400)             |                   | 65         |
| rGO/NiMn-LDH/NF           | 1696                | 1                      | 22.5 (16.2)              | 700 (3425)             | 91%, 1000 cycle  | 66         |
| FeCoNi–CH/p-rGO           | 1346                | 0.5                    | 46.9 (14.3)              | 400 (8000)             | 66.7%, 3000 cycle | this work  |
h kg$^{-1}$ at 400 W kg$^{-1}$ and cycle stability of 66.7% after 3000 cycles. This research provided a method for making MOF-derived ternary-metal CH/p-rGO electrode materials with various compositions and matrix morphologies, and the controllable synthesis materials could be able to expand their applications in the fields of electric energy storage, electrocatalysis, adsorption, and so forth. As a prospective research topic, the internal mechanisms impacting the electrochemical characteristics of the resultant materials under various preparation circumstances might be investigated further.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02712.

- XRD patterns of FeCoNi–CH with different molar ratios of Co/Ni; XRD patterns of FeCoNi–CH with different etching times; XRD patterns of FeCoNi–CH/p-rGO with different ratios of GO; EDS spectra of FeCoNi–CH and FeCoNi–CH/p-rGO; XPS spectra of MIL-88A: survey spectra, Fe 2p, and O 1s, and MIL-88A/GO: survey spectra, Fe 2p, and O 1s; N$_2$ adsorption and desorption isotherms and pore size distribution of the FeCoNi–CH and FeCoNi–CH/p-rGO; CV curves of FeCoNi–CH with different ratios of Co/Ni at a scan rate of 5 mV s$^{-1}$; GCD curves for FeCoNi–CH with different ratios of Co/Ni tested at a current density of 0.5 A g$^{-1}$; CV curves of FeCoNi–CH with Co/Ni ratio of 1:1 at different scan rates; GCD curves of FeCoNi–CH with Co/Ni ratio of 1:1 at different current densities; CV curves of FeCoNi–CH with different etching times at a scan rate of 5 mV s$^{-1}$; GCD curves for FeCoNi–CH with different etching times at a current density of 0.5 A g$^{-1}$; CV curves of FeCoNi–CH with etching time of 10 h at different scan rates; GCD curves of FeCoNi–CH with an etching time of 10 h at different current densities; CV curves of FeCoNi–CH/p-rGO with different ratios of GO at a scan rate of 5 mV s$^{-1}$; GCD curves for FeCoNi–CH/p-rGO with different ratios of GO at a current density of 0.5 A g$^{-1}$; CV curves of FeCoNi–CH/p-rGO with a GO content of 0.5 wt % at different scan rates; GCD curves of FeCoNi–CH/p-rGO with GO content of 0.5 wt % at different current densities; CV curves at a scan rate of 5 mV s$^{-1}$; GCD curves at current density of 1 A g$^{-1}$, and GCD curves at different current densities of AC, FeOOH, and FeOOH/AC; electrochemical performance of the FeCoNi–CH/p-rGO/AC HSC: CV curves at different scan rates, GCD curves at various current densities, and cycling performance at a current density of 5 A g$^{-1}$; and electrochemical performance of the FeCoNi–CH/p-rGO/FeOOH HSC: CV curves at different scan rates, GCD curves at various current densities, and cycling performance at a current density of 5 A g$^{-1}$ (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This project was financially supported by the National Natural Science Foundation of China (51972049 and 52073010) and the Projects of the Science and Technology Department of Jilin Province (JJKH2022123K). The authors would like to thank Shiyanjia Lab (www.shiyanjia.com) for the XRD and Raman measurements.

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