Iron encased organic networks with enhanced lithium storage properties

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Abstract
Developing promising electrode materials for next-generation high-performance lithium ion batteries (LIBs) becomes critically important. So far, a great number of transition metal (M)-based composites (e.g., oxides, sulfides, selenides, and M-carbon) as promising anodes have been intensively reported. Despite the huge progress achieved on the development of M-nitrogen-doped carbon (M-N-C) as catalysts in the field of electrocatalysis, the study of M-N coordination sites, and how they might affect the anode properties of M-N-C for LIBs, is still rare. Here, we designed and fabricated a series of Fe-N-C hybrids as anodes for LIBs, including iron (Fe) nanoparticles cores encapsulated in well-defined nitrogenated holey graphitic structures (Fe@C2N) and Fe encapsulated in a three-dimensional (3D) cage-like organic network (Fe@CON). Such hybrids display promising lithium ion storage properties. In particular, benefitting from its 3D-interconnected microporous structure and rich Fe-N-C species, one Fe@CON (e.g., HCF@3DP) exhibits a superb reversible capacity of 747.3 mAh g⁻¹ at 0.1 C, excellent rate capability (e.g., 320.8 mAh g⁻¹ at 10 C) and long cycling stability (over 400 cycles).

KEYWORDS
anode, carbon, iron-nitrogen, lithium ion batteries, Prussian blue

1 | INTRODUCTION

As one of leading energy storage technologies, lithium ion batteries (LIBs) have gained huge economic progress in portable and smart devices due to their immense energy and power densities, high cycling life, and minimal ecological impact. The rapid development of electric vehicles, however, requires LIBs with improved power...
and energy density in future.1 As a result, serious pursuits have been dedicated to developing promising electrode substances for high-performance LIBs.

So far, a great number of anode candidates for LIBs such as oxides of transition metals (MOx, M = Fe, Ni, Co, and Mn), carbon-originated materials (e.g., carbon nanotube, graphene, and three-dimensional [3D] carbon), and combinations have been explored.2,3 Similarly, transition metal (M)-based composites (e.g., oxides, sulfides, selenides, and M-C) as highly active catalysts have been also widely reported in the electrocatalysis field,4-6 specifically, for oxygen reduction reaction (ORR).5 Experimental and theoretical results both have uncovered the existence of M-nitrogen (M-N) coordination sites within M-nitrogen-doped carbon (M-N-C) enables the M-N-C catalytic performance, resulting in excellent ORR activity. This occurs because the interaction between M and N is energetically favorable to the adsorption and reduction of molecular O2 at M-N sites.7-9 As a result, several reports have also revealed that M-N-C as cathodes displayed the promising electrochemical performance in various metal-air batteries.10-14 Moreover, as conductive frameworks and sulfur host, the M-N-C could also significantly reduce the “shuttle effect” of polysulfide all along the discharge-charge process, thus induce the high capacity and stability of M-N-C/S hybrid for lithium sulfur batteries.15-17 This is primarily owing to improved electrical conductivity of the hybrid and robust adsorption ability of lithium polysulfides between Fe-N-C and sulfur. Nonetheless, despite the huge advances realized in the field of electrocatalysis as well as material for cathode host for lithium air/sulfur batteries, the study of M-N-C as anode materials for LIBs is yet not well established. As proposed, additional studies of M-N-C as anode substances for LIBs are highly desirable.

Among the M-N-C hybrids, iron (Fe) based hybrids have been commonly investigated as energy storage and conversion materials (including electrocatalysts). This is mainly due to their abundant materials, high corrosion resistance, nontoxicity, and low cost. The current Fe-nitrogen-doped carbon (Fe-N-C) composites are simply catalogued as follows: (i) metal species (e.g., Fe, FeOx, and Fe4C0) encapsulated in nitrogenated carbon substrate, (ii) Fe-N embedded in N-C, and (iii) removal of bulk Fe species from (i) and (ii).18-20 Despite the debate over the center of M-N-C functional sites (ie, M-N or N-C), it has been commonly recognized that M is a key to enhancement and excellence electrocatalytic performance.21-24 In efforts to synthesize Fe-N-C, various efficient approaches have been developed. For instance, direct carbonization of Fe-N macrocycles (e.g., phthalocyanine-Fe25 and tetrakis (4-iodophenyl) porphyrin-Fe26) and metal organic frameworks (e.g., iron imidazolate27,28 and Prussian blue29,30) will preserve rich Fe-N coordination structures, which are homogeneously distributed in Fe-N-C hybrids. A typical but effective way to introduce high-level N doping to carbon (N-C) is to use inorganic (e.g., NH3,31,32 cyanamide,33 and melamine34) and organic (e.g., polypyrrole,35 polyaniline,36 and polydopamine37) nitrogen-containing resources as precursors. The resulting N-C is an ideal candidate to accommodate Fe species from Fe-based resources (e.g., FeCl3 and Prussian blue). Moreover, approaches have been developed to facilitate rapid mass transportation (e.g., electrolyte and O2) and maximize the number of functional sites, including the rational synthesis of the Fe-N-C hybrid with 3D hierarchically porous structures38-46 and conductive carbon (e.g., graphene, carbon nanotube, and carbon fiber).47-49 As expected, both the hybrid’s structure and the interaction between N-C and the Fe precursor largely affect electrochemical property of the Fe-N-C hybrid.

Herein, we devised and fabricated a set of Fe-N-C hybrids as anodes for LIBs. As shown in Scheme 1, the Fe-N-C hybrids include Fe particle centers encased in distinct nitrogenated holey structures (Fe@C2N, Scheme 1A), and Fe encapsulated in a 3D cage-like organic network50 (Fe@CON, Scheme 1B) using different Fe-based resources as raw materials (iron(III)hexacyanoferrate [FeHCF] for HCF@3DP and iron(III) chloride [FeCl3] for Fe@3DP). The Fe@CON (e.g., HCF@3DP) in particular, thanks to its rigid and highly microporous structure and rich Fe-N-C species, displays outstanding lithium-ion storage properties with a superb reversible capacity of 747.3 mAh g−1 at 0.1 C, magnificent rate capability (e.g., 320.8 mAh g−1 at 10 C), and expanded cycling steadiness (over 400 cycles).

2 | RESULTS AND DISCUSSION

Scheme 1B presents the fabrication of Fe encapsulated in the 3D Fe@CON and its lithiation-delithiation process. As can be seen, the 3D CON framework was constructed via the condensation reaction of hexaketocyclohexane (HKH) octahydrate and triptycene hexamine (THA) as the starting monomers.50 FeHCF and FeCl3 were taken as Fe precursors to encapsulate Fe nanoparticles in the CON (Fe@CON) and the resulting Fe@CON products were designated as HCF@3DP and Fe@3DP, respectively. For comparison, Fe nanoparticles were also encapsulated in the two-dimensional C2N framework (Fe@C2N, Scheme 1A)51 using FeCl3 as the Fe precursor. Detailed information about the synthesis of HCF@3DP, Fe@3DP and Fe@C2N is provided in Experimental Section.

X-ray diffraction (XRD) patterns of HCF@3DP, Fe@3DP, and Fe@C2N are displayed in Figure 1A. All samples have an expanded diffraction peak at ~25.5° and a region of 42°- 48°, which are well indexed to
SCHEME 1 Synthesis schemes of, A, Fe@C₂N and, B, Fe@CON, and their lithiation-delithiation processes

FIGURE 1 Structural characterizations: A, XRD patterns; B, Raman spectra; C, nitrogen adsorption-desorption isotherms; D, TGA curves of HCF@3DP, Fe@3DP and Fe@C₂N obtained in air condition at a ramping rate of 10°C min⁻¹. Inset in C: the pore size distributions. TGA, thermogravimetric analysis; XRD, X-ray diffraction
carbon,\textsuperscript{52} and cubic Fe (ICSD \#52258) and orthorhombic Fe\textsubscript{3}C (ICSD \#16593),\textsuperscript{53,54} respectively. It should be noted that the HCF@3DP displays a broader carbon peak at $\approx 26.5^\circ$ than the other two samples, which can probably be attributed to the rigid and shape persistent framework of the HCF@3DP. Raman spectra (Figure 1B) of all samples have two characteristic bands of carbon materials at $\approx 1350$ cm\textsuperscript{-1} (D band) and $\approx 1595$ cm\textsuperscript{-1} (G band). The D band is attributed to defects/disorder, while the G band is associated with the graphitic lattice vibration mode with $E_{2g}$ symmetry. The intensity ratios ($I_D/I_G$) of D and G bands for the HCF@3DP, Fe@3DP, and Fe@C\textsubscript{2}N are 1.15, 1.09, and 0.92, respectively. The relatively higher $I_D/I_G$ of HCF@3DP and Fe@3DP than Fe@C\textsubscript{2}N is mainly due to the presence of more defects in HCF@3DP and Fe@3DP. Nitrogen adsorption-desorption isotherms characterization (Figure 1C) suggests that the surface areas of the HCF@3DP (476.2 cm\textsuperscript{2} g\textsuperscript{-1}) and Fe@3DP (336.9 cm\textsuperscript{2} g\textsuperscript{-1}) are much larger than that of Fe@C\textsubscript{2}N (287.7 cm\textsuperscript{2} g\textsuperscript{-1}). The average pore diameter, specific surface area, and pore volume of HCF@3DP, Fe@3DP, and Fe@C\textsubscript{2}N are summed up in Table S1.

To estimate the Fe content in the samples, thermogravimetric analysis (TGA) was performed (Figure 1D). According to the assumed residual product of Fe\textsubscript{2}O\textsubscript{3}, the Fe contents of the HCF@3DP, Fe@3DP, and Fe@C\textsubscript{2}N are estimated to be 14.1, 26.9, and 25.4 wt\%, respectively.

In order to probe the chemical structure and the oxidation states of HCF@3DP, Fe@3DP, and Fe@C\textsubscript{2}N, X-ray photoelectron spectroscopy (XPS) was carried out. As presented in Figure S1, all of the XPS surveys reveal the characteristic peaks of C 1s, N 1s, O 1s and Fe centered at $\approx 285, \approx 398, \approx 532$, and $\approx 718$ eV, respectively. From the XPS analysis (Figure S1), the Fe contents in HCF@3DP, Fe@3DP, and Fe@C\textsubscript{2}N are determined to be 1.0%, 0.1%, and 0.4%, respectively. The relatively low Fe content shown in all samples is mainly associated with the XPS technique, which only detects the element content at the surface. Moreover, the samples were vigorously washed with strong acids, leading to leaching of the unencapsulated Fe species in the materials. The detailed atomic compositions are compiled in Table S2. Figure 2 exhibits the deconvoluted XPS spectra of the HCF@3DP, Fe@3DP, and Fe@C\textsubscript{2}N. As disclosed in Figure 2A,E,I, the C 1s spectra are resolved into C=C, C=N, C=N, and C=O at 287.4, 285.2, 287.0, and 289.2 eV, respectively. As for the N 1s spectra (Figure 2B,F,J), they are split into pyridinic N at 398.6 eV, pyrrolic N at 400.9 eV, and graphitic N at 401.9 eV. The fitted peaks in the high O 1s spectra

\begin{figure}[h]
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\caption{Deconvoluted high resolution XPS spectra of samples: A,E,I, C 1s; B,F,J, N 1s; C,G,K, O 1s; D,H,L, Fe 2p peaks of, A-D, HCF@3DP; E-H, Fe@3DP; I-L, Fe@C\textsubscript{2}N. XPS, X-ray photoelectron spectroscopy.}
\end{figure}
(Figure 2C,G,K) are assignable to C=O (531.5 eV), and moisture and oxygen (533.2 eV), respectively. Despite the low Fe content on the surfaces of samples, the resolved XPS spectra of Fe 2p (Figure 2D,H,L) indicate the formation of Fe$_3$C interfaces and zerovalent Fe (Fe$^0$) particle cores, as evidenced by Fe$^{3+}$ 2p$_{1/2}$ (722.4 eV) and 2p$_{3/2}$ (709.9 eV), and Fe$^0$ (720.2, 708.4 eV), respectively.

To characterize the morphologies of HCF@3DP, scanning electron microscopy (SEM, Figure 3A) and transmission electron microscopy (TEM, Figure 3B-E) were employed. The samples consisted of uniform fine nanoparticles (e.g., Fe@3DP, Figure S2A,E), and spheres with diameters ranging from 1 to 1.5 μm for Fe@C$_2$N (Figure S3A) and 600-800 nm for HCF@3DP (Figure 3A,B). Fe@C$_2$N nanospheres were formed after heat treatment in which the precursor were reduced into Fe$^0$ nanoparticle cores and simultaneously coated by the well-defined nitrogenated graphitic carbon from the conversion of C$_2$N.$^{53}$

The formation mechanism of the HCF@3DP sphere is similar to the case of Fe@C$_2$N because the CON structure is an open and large 3D cage-like organic network. However, the larger-size HCF used as a Fe-based precursor is more likely prone to form large particles (i.e., HCF@3DP) than small particles (i.e., Fe@3DP). High-resolution TEM (HR-TEM) and scanning TEM (STEM) images of HCF@3DP (Figure 3B,C) and Fe@3DP (Figure S2E,F) indicate that highly crystalline Fe nanoparticle cores with well-defined lattice fringe were encapsulated in graphitic shells with a thickness of 2.0-3.0 nm.

**FIGURE 3** Morphological characterization of samples: A, SEM morphology. Scale bar: 2 μm. B, STEM image. Scale bar: 100 nm. C, HR-TEM images of HCF@3DP. Scale bar: 10 nm. D, STEM image of HCF@3DP. Scale bar: 500 nm. E, Corresponding elemental mappings of C, N, Fe, and O. SEM, scanning electron microscopy; HR-TEM, high resolution transmission electron microscopy; STEM, scanning transmission electron microscopy.
Despite the differences in morphologies and sizes, energy-dispersive X-ray spectrometry elemental mappings indicate that C, N, and Fe elements are homogeneously dispersed through all the samples (Figures 3E, S2B-D, and S3B-D).

Figures 4A and S4 display the discharge/charge profiles of HCF@3DP, Fe@3DP, and Fe@C₂N at different C-rates from 0.1 to 10 C (namely, 1 C = 372 mAh g⁻¹). All electrodes display the classic electrochemical performance of carbonaceous materials.⁵⁶ Cyclic voltammetry (CV) measurements of HCF@3DP, Fe@3DP, and Fe@C₂N for the initial five cycles at 0.1 mV s⁻¹ are shown in Figures 4B and S5. As can be seen, all electrodes show a clear reduction peak at ~0.7 V vs Li⁺/Li in the initial cathodic scan, corresponding to the development of solid electrolyte interfaces (SEI).⁵⁷ Li⁺ storage in the electrode mainly occurs below 0.5 V. In the following initial anodic scan, the double oxidation peaks at ~0.1 and 1.05 V are attributed to the release of Li⁺ from the host structures. Compared to HCF@3DP and Fe@3DP, Fe@C₂N displays stronger reversibility at ~0.1 V than ~1.05 V. This result indicates that the Li⁺ out of the lithiated Fe@C₂N structures mainly occurred at ~0.1 V, which is analogous to that of commercial graphite used as an anode for LIBs.⁵⁸ In the following cathodic-anodic scans, the disappearance of the reduction peak at ~0.7 V and the high overlapping oxidation peaks at ~1.05 and 0.1 V for all electrodes indicate the formation of strong and stable SEI in the initial cycle and desirable reversibility of electrochemical reactions during cycles.
The CV features were also indicated in the charge-discharge sketches of electrodes assessed at 0.1 C between 0.02 and 3 V (Figure 4B). The CV results also confirm the lack of Fe oxides and the presence of stable Fe-N-C species in the electrodes. This is because Fe oxides used as anodes for LIBs repeatedly have distinct reduction peaks of Fe$^{3+/2+}$/$\text{Fe}^0$ at −0.7 V, which are coupled with the formation of Li$_2$O, as well as reversible oxidation peaks at 1.5-1.8 V related to the oxidation of Fe$^0$/Fe$^{2+}$ and Fe$^{2+}$/Fe$^{3+}$.

Figure 4C reproduces rate capability of the HCF@3DP, Fe@3DP, and Fe@C$_2$N electrodes. The Fe@CON before impregnation of Fe to 3D CON was also tested. As exhibited in Figure S6, the 3D CON shows a very low initial capacity of 41.2 mAh g$^{-1}$ at 0.1 C, due to its poor conductivity. At 0.1 C, however, the HCF@3DP, Fe@3DP, and Fe@C$_2$N electrodes deliver immense first discharge capacities of 1243.9, 1477.3, and 746.7 mAh g$^{-1}$ with primary Coulombic efficiencies (CEs) of 60.1%, 52.4%, and 45.0%, respectively. Such large irrevocable capacity of the electrodes is because of the formation of SEI. When the C-rate was increased from 0.2 to 5 C, the HCF@3DP electrode exhibits the leading rate capability among all electrodes, with high average specific capacities of 680.7 (0.2 C), 594.4 (0.5 C), 532.9 (1 C), 475.8 (2 C), and 391.8 (5 C) mAh g$^{-1}$ respectively, which are much greater than Fe@C$_2$N electrodes also deliver much higher capacity and Fe@3DP electrodes. The relatively long-term cycling stability of the HCF@3DP and Fe@3DP, and Fe@C$_2$N electrodes were further evaluated between 0.02 and 3 V for 400 cycles (Figure 4D). At 1 C, the HCF@3DP and Fe@3DP exhibit primary discharge capacities of 968.6 and 1177.0 mAh g$^{-1}$, respectively, which are much greater than Fe@C$_2$N (497.6 mAh g$^{-1}$). Over the entire 400 cycles, the HCF@3DP and Fe@3DP electrodes also deliver much higher capacity than the reference Fe@C$_2$N. It is worth noting that the Fe@3DP electrode displays a bigger primary reversible capacity, 774.3 mAh g$^{-1}$, than HCF@3DP (747.3 mAh g$^{-1}$) at 0.1 C. Despite the fact that Fe@g3DP (836.1 mAh g$^{-1}$) has a superior initial discharge capacity than HCF@3DP (817.1 mAh g$^{-1}$) at 5 C, HCF@3DP exhibits a higher capacity retention of 47.7% after 400 cycles compared to Fe@3DP (31.7%). The higher capacity retention of HCF@3DP is primarily due to bigger surface area and the more defects of HCF@3DP than Fe@3DP, leading to the stronger rate capability of HCF@3DP.

Electrochemical impedance spectroscopy (EIS) analysis determined that the electrodes measured at 5 C after 400 cycles had different calculated charge transfer resistances ($R_{ct}$), in the order of Fe@C$_2$N > HCF@3DP > Fe@3DP (Figure S7). The EIS results suggest that the 3D CON structure together with rich Fe-N-C active sites enhance the transfer rate of charges and provide strong kinetics for Li$^+$ insertion and extraction. The excellent rate capability of HCF@3DP and cycling stability of Fe@3DP can be attributed to their rare 3D CON structures with complementary microporous structure and rich Fe-N-C active sites. The structural characteristics are advantageous for the brisk penetration of electrolyte, fast dissemination and greater storage of Li$^+$, and alleviation of the big volume fluctuation during the Li$^+$ insertion/extraction. Moreover, the average CEs of the electrodes following the first few cycles (Figure 4D) could be maintained, approaching 99.5%, indicating the strong cycling stability of the electrodes. Figure S8 shows the representative discharge/charge profiles of HCF@3DP, Fe@3DP, and Fe@C$_2$N electrodes measured at 5 C. These profiles, showing retained relative stability after 100, 400 cycles are symbolic of the electrochemical nature of carbonaceous structures, further indicating the stability of the electrodes.

3 | CONCLUSIONS

In summary, we reported an efficient strategy for the synthesis of Fe encapsulated in 3D CON structures (Fe@CON, such as HCF@3DP and Fe@3DP) and evaluated them as anodes for LIBs. The fabricated Fe@CON has unique structural features, including a 3D cage-like microporous structure and rich Fe-N-C species. The 3D cage-like microporous structure not only effectively provides a grand surface area and sufficient transporting channels for the Li$^+$ diffusion and storage, but also significantly alleviates volume adjustments during the charge-discharge process. Moreover, rich Fe-M-C uniformly distributed through the entire CON structure provides increased active sites for Li$^+$ storage. The combination of the CON network with rich Fe-N-C species give the HCF@3DP outstanding lithium storage properties, with a lofty reversible capacity of 747.3 mAh g$^{-1}$ at 0.1 C, superb rate capability (e.g., 320.8 mAh g$^{-1}$ at 10 C), and prolonged cycling stability (over 400 cycles). Such outstanding lithium storage properties not only make HCF@3DP a great potential anode for LIBs, but also highlight the importance of other transitional metal (M)-N-C materials as anodes for LIBs.

4 | EXPERIMENTAL SECTION

4.1 | Synthesis of CON

THA hexahydrochloride (500 mg, 0.887 mmol) solution in N-methyl-2-pyrrolidine (NMP) was charged with
several droplets of sulfuric acid ($\text{H}_2\text{SO}_4$) into a 200 mL flask (three-necked) round bottom under nitrogen condition. Then, the flask was shifted to an ice bath. Under vigorous stirring, HKH octahydrate (0.277 g, 0.887 mmol) was added into the reaction flask. After stirring the mixture on the ice bath for 2 hours, the temperature was slowly raised to 175°C and maintained for 6 hours in reflux condition. After the culmination of the reaction, the reaction mixture was decanted into the distilled water. The precipitates of were obtained by filtration on polytetrafluoroethylene (PTFE) membrane. The precipitates were secured by filtration on a PTFE (0.5 μm) membrane. The product was washed by Soxhlet extraction with water and methanol for 3 days each. The obtained precipitates after Soxhlet extraction were desiccated under reduced pressure (0.01 mmHg) overnight to give a bright brown powder of quantitative yield.

4.2 | Synthesis of HCF@3DP

THA (1 g, 1.77 mmol), HKH octahydrate (0.554 g, 1.77 mmol), HCF (0.50 g, 0.58 mmol), and NMP (60 mL) were placed into a round bottom flask (three necked) on the ice bath under inert condition (nitrogen). The temperature was gradually increased to 175°C and the reaction mixture was agitated using magnetic stirring bar for 6 hours. After finishing of the reaction, the system was allowed to cool down to ambient condition and precipitated in distilled water. The brownish fluffy precipitates were secured by filtration on a PTFE (0.5 μm) membrane. The resulting material was washed by Soxhlet extraction for 3 days each with methanol and water, respectively, and then freeze-dried at −120°C under decreased pressure. Furthermore, the sample was heat treated at 700°C for 3 hours under inert atmosphere (argon). Eventually, the obtained materials were treated with 4 M HCl to get rid of poorly encased iron leftover if any.

4.3 | Synthesis of Fe@3DP

In a round bottom flask (three necked) on the ice bath, HKH octahydrate (0.554 g, 1.77 mmol), THA (1 g, 1.77 mmol), and iron chloride (0.80 g, 4.93 mmol) were taken. Then, under the nitrogen flow, NMP (60 mL) was slowly added to the flask. After mixing the temperature of reaction was gradually increased to 175°C and continued the stirring at this temperature for 6 hours. Then the reaction temperature was cooled to 80°C and sodium borohydride NaBH₄ (40 mL, 10% solution in NMP) was added to the reaction mixture and then the reaction was refluxed again at 175°C for additional 2 hours. The reaction was permitted to cool down to ambient condition after the completion of reaction and decanted into distilled water. The black product was procured by vacuum filtration through a PTFE (0.5 μm) membrane. The resulting materials were further washed by Soxhlet extraction with methanol and water for 3 days each, respectively, and freeze dried at −120°C under decreased pressure. The sample was then heat treated at 700°C for 3 hours under inert condition (argon). Subsequently, the material was washed away with 4 M HCl solution to get rid of defectively encased excess iron if present.

4.4 | Synthesis of Fe@C₂N

In a round bottom flask (three necked) on the ice bath, FeCl₃ (1.168 g) was completely dissolved in NMP (35 mL). Then hexaaminobenzene trihydrochloride (1.00 g, 3.603 mmol) was charged under inert condition (nitrogen) followed by the addition of HKH octahydrate (1.125 g, 3.603 mmol). Over the next 2 hours time, the reaction was allowed to reach to room temperature. The ice bath was then switched with an oil bath, and increased the temperature to 175°C refluxed for 8 hours. The reaction mixture was permitted to cool down to 80°C and added NaBH₄ (40 mL, 10% solution). The reaction mixture was refluxed again for 3 hours at 175°C. The flask was then cool down to room temperature and poured into distilled water. The black material was obtained by suction filtration using a PTFE (0.5 μm) membrane. The dark material was washed with methanol and water by Soxhlet extraction, respectively, and freeze-dried below −120°C under reduced pressure. After freeze drying, the materials were heat treated at 700°C for 2 hours in inert condition (argon). After treatment, the product was washed with 4 M HCl for 4 hours to eliminate unbound metallic residues, if present.

4.5 | Materials characterizations

Powder XRD data of the samples were collected from an X-ray diffractometer (Bruker D8 advance) with Cu-Kα radiation ($\lambda = 1.5406 \text{ Å}$). The microstructure and morphologies of the samples were characterized by field-emission SEM (FEI Nova NanoSEM450) and high-resolution HR-TEM (JEM-2100F, JEOL, Japan). The surface area was measured on a Micromeritics Tristar II Plus surface area analyzer and calculated by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller method. TGA was acquired by a STA-449-F3 Thermal Analyzer (NETZSCH, Germany) at a temperature range from 35°C to 900°C with a ramping rate of 10°C min⁻¹ under air atmosphere. XPS were
performed on a Kratos Axis Ultra spectrometer. The C 1s (BE = 284.6 eV) was used as a reference. Raman spectrometer (Horiba) with an excitation wavelength of 633 nm was used to record Raman spectra.

4.6 | Electrochemical measurements

The electrochemical measurements of the electrodes were performed using coin-type cells. The electrodes were fabricated by blending the active materials (i.e., HCF@3DP, Fe@3DP, Fe@C2N, and CON, 80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (i.e., HCF@3DP, Fe@3DP, Fe@C2N, and CON, 80 wt%) binder. The N-methyl-2-pyrrolidone was used blending solvent. The resulting slurries were uniformly coated on Cu foil and then dried at 90°C in vacuum oven overnight. Then, the as-prepared electrode was punched into round species with a mass loading of ~1.5 mg cm−2. The cells were fabricated in an argon-filled glove box (Mikrouna, H2O, O2 < 0.1 ppm) using the electrolyte (ethylene carbonate/diethyl carbonate (1:2 vol/vol), acetylene black (10 wt%), and polyvinylidene fluoride binder). The N-methyl-2-pyrrolidone was used blending solvent. The resulting slurries were uniformly coated on Cu foil and then dried at 90°C in vacuum oven overnight. Then, the as-prepared electrode was punched into round species with a mass loading of ~1.5 mg cm−2. The electrochemical measurements of the electrodes were performed using coin-type cells. The electrodes were fabricated by blending the active materials (i.e., HCF@3DP, Fe@3DP, Fe@C2N, and CON, 80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (i.e., HCF@3DP, Fe@3DP, Fe@C2N, and CON, 80 wt%) binder. The N-methyl-2-pyrrolidone was used blending solvent. The resulting slurries were uniformly coated on Cu foil and then dried at 90°C in vacuum oven overnight. Then, the as-prepared electrode was punched into round species with a mass loading of ~1.5 mg cm−2. The cells were fabricated in an argon-filled glove box (Mikrouna, H2O, O2 < 0.1 ppm) using the electrolyte (ethylene carbonate/diethyl carbonate (1:2 vol/vol), acetylene black (10 wt%), and polyvinylidene fluoride binder). The N-methyl-2-pyrrolidone was used blending solvent. The resulting slurries were uniformly coated on Cu foil and then dried at 90°C in vacuum oven overnight. Then, the as-prepared electrode was punched into round species with a mass loading of ~1.5 mg cm−2.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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