Interconnected N-doped carbon nanotubes enclosed with Co nanoparticles have been synthesized by a strategy of urea-assisted pyrolysis of bimetallic metal–organic framework (MOF) precursor. The modulation of Co/Zn ratio in bimetallic MOF precursors can not only regulate spatial dispersion and local structural disorder of Co cores, but also lead to the alterable proportion of the component nitrogen types in catalysts, which impacts the charge distribution of the carbon sheath and further ameliorates the charge transfer. Moreover, urea, an assisted nitrogen/carbon source, plays an active role in the formation and growth of N-doped carbon nanotubes. Such Co–N–C system results in more provided active sites (e.g., Co and Co–N, moieties), noncorrosive metal cores protected by carbon materials as well as short diffusion pathway of ions due to the synergetic effect of core–sheath structure. Benefiting from these controllable strategies, C121 (pyrolysis product of Co0.5Zn0.5-ZIF and urea precursor) embraces the current density of 10 mA cm−2 at the overpotential of 251 and 279 mV for hydrogen evolution reaction (HER) in acid and alkaline media, respectively, which enables it to be an efficient electrocatalyst for HER under both extreme pH conditions.

1. Introduction

Severe environmental threat and the impending global energy crisis are becoming one of the most urgent issues for most countries. Sustainable hydrogen production via electrochemical water splitting is one of the most favored methods for energy storage and conversion. Catalysts are aimed to boost hydrogen evolution reaction (HER) efficiency by minimizing reaction kinetic barriers and subsequently reducing the overpotential. Many metal-containing materials have proved to efficiently catalyze HER with negligible overpotential almost irrespective of pH, but their scarcity and high cost limit their practical applications. Developing cost-effective and competent electrocatalysts for HER in both acid and alkaline media is still a major challenge.

Recently, carbon materials containing noble-metal-free components and N coordination sites (M–N=C, M = Co, Fe, Ni, etc.) have been emerged as efficient HER catalysts. However, the detailed mechanism behind the activity of M–N=C composites remains elusive and is still an unresolved issue. Particular attention should be taken that the metal nanoparticles can effectively adjust the electronic environment of the interacted carbon regions by interfacial charge transfer, which has dramatically enhanced the electrocatalytic performances in HER. Furthermore, a large number of research results (including experimental and theoretical) show that the lower adsorption free energy of H* is beneficial to improving the HER activity, which could be achieved by constructing an N-doped carbon surface structure with metal nanoparticles sitting below. Thus, modulating the size, content, and dispersity of the metal nanoparticles in porous carbon composite is favorable to ameliorating the catalytic activity of M–N=C materials.

Metal–organic frameworks (MOFs) have been recognized as eye-catching precursors for the synthesis of M–N=C materials due to their tailorable morphologies and highly dispersed metal species. Zeolitic imidazolate frameworks (ZIFs), as a particularly interesting subcategory of MOFs, have been extensively explored as molecular separation, gas adsorption and catalysis. Given their versatile configurations of metal ions and N-containing organic ligands as well as the tunable structure, ZIFs have been considered as promising sacrificial
templates or precursors to fabricate M–N–C nanomaterials via pyrolysis treatment under inert atmospheres.\textsuperscript{[27,28]} Despite tremendous advances in the development of these catalysts, the high metal consumption, uncontrollable nitrogen doping level, severe fusion, and aggregation are still technical challenges to overcome. Moreover, the modulation of the metal centers and the nitrogen doping level by a straightforward carbonization of monometallic MOF is quite limited because of the settled MOF composition.

Inspired by the previous reports\textsuperscript{[29–32]} we presented a urea-assisted pyrolyze bimetallic MOF precursor synthetic strategy to produce the Co–N–C electrocatalysts with homogeneously distributed Co nanoparticles enclosed in interconnected N-doped carbon nanotubes for HER. It would be interesting to develop such a core–sheath structure with retention of rational N functionalities proportion and high dispersion of metal cores. Urea, as an extra nitrogen/carbon source, can be conducive to the growth of carbon nanotubes (CNTs) and the formation of the graphitic structure as well as optimize the N configuration of catalysts. The tunable nanostructures were easily synthesized by adjusting the Co/Zn ratios of the bimetallic precursor, which were favorable for various electrochemical applications.

2. Results and Discussion

In a typical synthetic process, the fine homogeneous mixture of Co(Zn)–ZIF and urea is pyrolyzed together in a covered alumina boat at a high-temperature under an inert atmosphere (Figure 1). Inside the alumina boat, the assisted nitrogen source (urea) evaporated and decomposed. This approach is aimed at prolonging the residence time of volatile intermediates on the carbon, thus increasing the density of nitrogen-containing active sites. Then, the organic linkers (MeIm) and the assisted nitrogen source (urea) are converted into a carbon state, and the coexisting metal ions (Co\textsuperscript{II} and Zn\textsuperscript{II}) are thermally reduced to metallic metal nanoparticles, respectively. The N doping is acquired from the decomposition of urea and N-rich methylimidazole ligands of the ZIF precursor. On further increasing the pyrolysis temperature to 900 °C, the Zn atoms were evaporated. In particular, during the aforementioned pyrolysis process, the zinc atoms in the CoZn–ZIFs regularly separates from the cobalt atoms and stalls the excessive growth of cobalt nanoparticles, leading to abundant, highly dispersed, and catalytically active cobalt species generated.\textsuperscript{[33]} In the meantime, the as-formed cobalt species provided catalytically active sites to effectively catalyze the formation of N-doped carbon nanotubes. Moreover, the presence of Co–N\textsubscript{x} moieties present in the composites cannot be passed into silence as these are also considered as active sites for the HER.

The crystallographic structures of as-synthesized Co(Zn)–ZIFs were determined by powder X-ray diffraction (XRD) technique, which match well with the simulated one (Figure 2). ZIF-67 (Co-ZIF) and ZIF-8 (Zn-ZIF) are highly compatible in structure, and therefore the generated bimetallic ZIFs (BMZIFs) inherit the topology from both parent structural configurations. The XRD peak diffraction relative intensities increase with decreasing Co/Zn ratio in the bimetallic ZIF crystals, which can be explained by the fluorescent of Co elements induced by Cu radiation.\textsuperscript{[34]} XRD was measured to further identify the crystalline nature and compositions of the samples obtained from different pyrolysis precursors. In Figure 3a, the XRD patterns display broad diffraction peaks at ≈26°, corresponding to the (0 0 2) planes of graphitic structures. Three well-defined reflexes at about 44°, 52°, and 76° are consistent with the (1 1 1), (2 0 0), and (2 2 0) planes of face-centered cubic Co (JCPDS #15-0806), respectively.\textsuperscript{[35]}

Field-emission scanning electron microscopy (FESEM) images of Co-ZIF and CoZn-ZIF reveal typical rhombic dodecahedron shape with particle sizes of several hundred nanometers (Figure S1, Supporting Information). The chemical compositions of the as-synthesized ZIF crystals were analyzed by energy-dispersive X-ray spectroscopy (EDS). EDS mapping results indicated a homogeneous dispersion of Co, C, N, and Zn. Meanwhile, the experimental atomic ratio of Co and Zn was in excellent accordance with the nominal reactant ratio. After annealing hybrid precursors of the ZIF and urea under inert atmospheres, a large number of carbon nanotubes with length up to tens of micrometers could be observed.

![Figure 1. Schematic illustration of the preparation of Co–N–C electrocatalysts from bimetallic ZIFs and urea.](image1)

![Figure 2. XRD patterns of as-prepared ZIF precursors and the corresponding structures.](image2)
Moreover, Brunauer/C60.2, 400.2 fi

The intensity of all the samples presented higher 7712 eV corre-

7727 eV was attributed to the Co 1s 0.2, and 401.0 –

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a) XRD patterns of as-prepared electrocatalysts; scanning electron microscopy (SEM), transmission electron microscopy (TEM), and HRTEM

dispersity of Co cores after the evaporation of Zn elements.

The ZIF and urea are carbonized together accompanying with
direct introduction of Co and N into the carbon matrix as the
components of the catalysts. It is generally accepted that nitrogen
doping occurs at different locations in carbon lattice, which are
often crucial for electrochemical performance. For further
insight into the catalyst surface, X-ray photoelectron spectroscopy
(XPS) measurements were recorded to elucidate the chemical
binding characteristics of the N and Co elements present in
the electrocatalysts (Figure 4a–d). Deconvolution of the core-level
XPS N 1s spectrum of the composites resulted in a combination
of pyridinic, pyrrolic, and graphitic nitrogen species with max-
ima located at 398.4 ± 0.2, 400.2 ± 0.2, and 401.0 ± 0.2 eV,
respectively. As shown in Figure 4e, the graphitic N proportion
gradually increased from 33.88% to 65.68%, whereas the
pyridinic N proportion gradually decreased from 56.60% to
15.02% and pyrrolic N proportion remained almost unchanged
in the bimetallic MOF as the precursor. The XPS analysis con-

firmed that Zn incorporation positively impacts the graphitic
nitrogen retention. In addition, the major nitrogen components
in both samples are pyridinic N and graphitic N, which are also
treated as important catalytic sites for HER.[38] These results
indicated that the proportion of surface N species could be fine-tuned
by altering the Co and Zn ratio in the ZIF precursors.

To further illuminate the local atomic structure of Co species,
X-ray absorption fine structure (XAFS) measurements were car-
ried out. As shown in X-ray absorption near-edge structure
(XANES) spectrum, the curves were similar as that of Co foil,
demonstrating that the Co valence of the samples is close to
metallic cobalt (Figure 4f). After onset peak position, the peak
distribution gradually deviates from the referenced Co foil, which
is on account of altered coordination environment of metal cores
that leads to the different structures and scattering paths. After
onset peak position, a pre-edge feature at ≈7712 eV corre-
sponded to the electronic transition of Co from 1s to 3d. The
main peak located at ≈7727 eV was attributed to the Co 1s–4p
transition.[39,40] The intensity of all the samples presented higher
energy relative to Co foil, demonstrating that Co atoms was strongly
influenced by N-doped carbon nanotubes and carried the positive
charges. In addition, higher Zn/Co ratio in bimetallic precursors
could contribute to more intense interaction between Co and N.
As shown in the extended X-ray absorption fine structure

Figure 3. a) XRD patterns of as-prepared electrocatalysts; scanning electron microscopy (SEM), transmission electron microscopy (TEM), and HRTEM images of various hybrids: b,f,j) C1; c,g,k) C2Z1; d,h,l) C1Z1, and e,i,m) C1Z2.
(EXAFS) spectrum, the peak at \( \approx 1.65 \) and \( \approx 2.2 \) Å was assigned to the Co─C/N and Co─Co bonds, respectively (Figure 4g).\(^{[41,42]}\)

Along with the growth of Zn/Co ratio, the coordination number of Co─Co was decreased, due to the adjustment of the distances among Co by Zn element, which could deliver more N sites to suppress the agglomeration of Co after the Zn evaporation. In other words, the changed Zn/Co ratio can modulate the disorder degree of Co species, promoting the electrochemical activity of the catalysts.

As shown in Figure 5a, the polarization curves obtained through linear sweep voltammetry (LSV) electrochemical mode at a scan rate of 5 mV s\(^{-1}\) in 0.5 M \( \text{H}_2\text{SO}_4 \) electrolyte saturated with \( \text{N}_2 \). The C1Z1 sample presents an overpotential \( (\eta_{10}) \) of 251 mV at the current density of 10 mA cm\(^{-2}\), which is smaller than those of C1, C2Z1, and C1Z2 samples. Moreover, for a high current density of 40 mA cm\(^{-2}\), the overpotential of C1Z1 sample is still stay ahead of the others (Figure S4b, Supporting Information). The intrinsic catalytic activity is also assessed by Tafel slopes to gain deeper insights into the hydrogen evolution mechanism. Based on the corresponding LSV data, the Tafel slope of C1Z1 is 84.9 mV dec\(^{-1}\), relatively lower than that of C1 (90.5 mV dec\(^{-1}\)), C2Z1 (105.5 mV dec\(^{-1}\)), and C1Z2 (102.1 mV dec\(^{-1}\)), indicating a beneficial HER kinetics of C1Z1 sample (Figure 5b). From the experimental results, it was established that the local disorder degree of the cobalt center was closely associated to the electron transfer kinetics of the electrocatalytically active sites and the electrochemical performance.

To further gain a better understanding of the electrode kinetics for the as-prepared catalysts, electrochemical impedance spectroscopy (EIS) measurements were investigated at different overpotentials in the initial region of HER. Figure 5c,d,g,h shows the Nyquist plots for the impedance data collected in acidic electrolyte. With increasing overpotentials, the depressed semicircles diameter takes an apparent shrinking tendency, which indicates that the electron transfer capability becomes faster under incremental cathodic bias. Figure 5e,f,i,j shows Bode plots for the electrocatalytic materials. As shown in the phase Bode plots, the region at middle and low frequencies could be attributed to the charge transfer among the electrocatalyst–electrolyte interfaces, which is closely related to the HER kinetics process.\(^{[43,44]}\) The high-frequency response between 1 and 100 kHz associated with the ohmic contact between the glassy carbon substrate and the catalyst. This component presents a largely potential-independent process and could be related to the porous properties of catalysts. The aforementioned EIS data can be fit using an equivalent circuit (Figure 5k) consists of the uncompensated
solution resistance ($R_s$) in series with two parallel units of resistor and capacitor. Previous studies have been postulated that the high-frequency range with potential-independent properties described by $R_{\text{contact}}$ and CPE2, which is related to the electrode porosity, with the contact between the catalysts and the glassy carbon substrate. Another low-frequency time constant ($R_{\text{ct}}$ and CPE1) is attributed to the HER kinetic process. The Tafel slope was analyzed by impedance data as well, which was derived from the plot of the logarithmic reciprocal of $R_{\text{ct}}$ versus overpotentials. In this approach, a Tafel slope of 99.7 mV dec$^{-1}$ was found for C1Z1 from EIS data. The slope values are basically accorded with those obtained from LSV results (Figure 5l), suggesting that the Volmer–Heyrovsky mechanism is the main route of HER on C1Z1. The difference between the Tafel slopes assessed by the LSV and EIS approaches is within the acceptable range (Figure S4a, Supporting Information).

Figure 5. HER evaluation in 0.5 M H$_2$SO$_4$. a) LSV polarization curves of the C1, C2Z1, C1Z1, and C1Z2 samples; b) Tafel slopes from LSV curves; c,d,g,h) Nyquist plots and e,f,i,j) Bode plots of all samples; k) the fitted equivalent electrical circuit from EIS data; l) the corresponding Tafel slopes from impedance data.
The HER performance of the as-prepared electrocatalysts in alkaline media (1.0 M KOH) was also investigated. As shown in Figure 6a, the C1Z2 presented an overpotential of 268 mV at the current density of 10 mA cm$^{-2}$, which was lower than that of C1 (363 mV), C2Z1 (325 mV), and C1Z1 (279 mV). It is noteworthy that, at higher current density (40 mA cm$^{-2}$), the C1Z1 exhibit a better electrocatalytic HER activity ($\eta = 339$ mV) than C1Z2 ($\eta = 345$ mV) (Figure S5b, Supporting Information). The Tafel slopes obtained from voltammetry data (Figure 6b) reveal values of 98, 141.5, 104.2, and 119.6 mV dec$^{-1}$ for C1, C2Z1, C1Z1, and C1Z2, respectively. The Faradaic efficiency (FE) was assessed by comparing the theoretical and experimental value of the amounts of generated H2. The amounts were in good agreement with the calculated values, and the FE is calculated to be 95.50%, indicating a good current efficiency during HER (Figure S6, Supporting Information). In alkaline media,

![Figure 6. HER evaluation in 1.0 M KOH. a) LSV polarization curves of the C1, C2Z1, C1Z1, and C1Z2 samples; b) Tafel slopes from LSV curves; c,d,g,h) Nyquist plots and e,f,i,j) Bode plots of all samples; k) the fitted equivalent electrical circuit from EIS data; l) the corresponding Tafel slopes from impedance data.](image-url)
similar impedance properties and identical trends can be observed and indicates that the similar electrochemical processes carried out at various overpotentials (Figure 6c–l). Meanwhile, Tafel slopes from both LSV and EIS data are also assessed, and the results are basically accordant (Figure S5a, Supporting Information).

The electrochemical surface area (ECSA) and the roughness factor (RF) were further assessed in acid and alkaline electrolytes by calculations from the double-layer capacitance ($C_{dl}$) that was measured by the cyclic voltammograms (CVs) technique at different scan rates (Figure S7 and S9, Supporting Information). Obviously, C1Z1 displayed the great $C_{dl}$ whether in acid or alkaline electrolyte (9.26 and 7.83 mF cm$^{-2}$, respectively) (Figure S8 and S10, Supporting Information). The corresponding ECSA and RF values were calculated and shown in Table S1 and S2, Supporting Information, which suggests the larger active surface areas and more active sites of C1Z1.

The electrochemical stability of C1Z1 in both acid and alkaline electrolytes was evaluated by chronopotentiometry measurement at the current density of 10 mA cm$^{-2}$ (Figure 7). C1Z1 maintained great duration for up to 20 h without significant increase in the overpotential. Such the excellent electrochemical activity can be clarified by the regulation of Zn element, leading to the proper spatial dispersion of Co cores to prevent the aggregation, which facilitate the exposure of active sites and avoid the excessive destruction of structures for catalysts during the HER process. As a whole, the aforementioned results reveal that C1Z1 can function as a highly efficient and robust HER catalyst under both extreme pH conditions.

As suggested earlier, the regulation of Co/Zn ratio for bimetallic MOF precursor not only allows the controllable local disorder degree of the cobalt center that endows the catalysts with superior electron transfer kinetics, but also leads to the formation of effective carbon defects by the removal of Zn during the pyrolysis that provides more active sites for HER.$^{[46]}$ Moreover, the electron transfer relies a lot on the nitrogen content and types due to the closed work function of Co and N-doped carbon, thus nitrogen-rich carbon nanotubes with the relatively higher flat band potential are beneficial to adjust the electron density of metal centers by accepting electrons from Co nanoparticles, which further enhanced the electrochemical activity. Meanwhile, with the nitrogen dopants, the carbon structure can also be regulated via lowering the valence band and elevating the conduction band, leading to more favorable electronic structure.$^{[47,48]}$ Such boosted interaction between N-doped carbon nanotubes and Co nanoparticles facilitates the HER process resulting from faster electronic mobility and short diffusion length.

3. Conclusions

In summary, we reported a Co–N–C nanostructure with evenly dispersed Co nanoparticles fenced in interconnected N-doped carbon nanotubes for HER by a urea-assisted pyrolyze bimetallic MOF precursor synthetic strategy. Co centers deliver more exposed electrochemical active sites due to the stimulated chemical interaction with nearby carbon materials, whereas N-doped CNTs not only protect metallic Co from the corrosion of acid/alkaline environment but also possess more structural defects that can act as decisive active sites for electrocatalysis because of the heteroatom doping. Appropriate regulation of Co/Zn ratio for bimetallic MOF precursor leads to rational construction of the nanostructures through adjusting the spatial distribution, the Co–Co bond strength and the types of doped N. Meanwhile, urea, an assisted nitrogen/carbon source, is conducive to the growth of N-doped CNTs and the favorable interfacial electronic structure. C1Z1 as the optimal HER catalyst impressively exhibits low overpotentials at 10 mA cm$^{-2}$ (251 mV in acid media and 279 mV in alkaline media), faster charge transfer rate as well as superior long-term stability under both extreme pH conditions. Such controllable structure and synthetic strategy in this study can give more inspiration in developing efficient pH-universal electrocatalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.
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