Ultrasmall NiFe layered double hydroxide strongly coupled on atomically dispersed FeCo-NC nanoflowers as efficient bifunctional catalyst for rechargeable Zn-air battery

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ABSTRACT An atomically dispersed FeCo-NC material with the 3D flower-like morphology was used as a unique substrate for the controllable deposition of ultrasmall NiFe layered double hydroxide nanodots (termed as NiFe-NDs) to simultaneously promote the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The size-limiting growth of NiFe-NDs (~4.0 nm in diameter) was realized *via* the confinement of the 3D flower-like mesoporous structure and the rich N/O functionality of FeCo-NC. Benefiting from the distinctive structure with the simultaneously maximum exposure of both OER and ORR active sites, the NiFe-ND/FeCo-NC composite showed an ORR half-wave potential of 0.85 V and an OER potential of 1.66 V in 0.1 mol L⁻¹ KOH at 10.0 mA cm⁻². *In-situ* Raman analysis suggested the activity of OER was derived from the Ni sites on NiFe-ND/FeCo-NC. Moreover, the NiFe-ND/FeCo-NC-assembled Zn-air battery (ZAB) exhibited a very small discharge-charge voltage gap of 0.87 V at 20 mA cm⁻² and robust cycling stability. Furthermore, the NiFe-ND/FeCo-NC composite was also applicable for fabricating all-solid-state ZAB to power wearable electronics with superior cycling stability under deformation. Our work could enlighten a new applicable branch of atomically dispersed metal-nitrogen-carbon materials as unique substrates for fabricating multifunctional electrocatalysts.

Keywords: atomically dispersed catalyst, NiFe layered double hydroxide, oxygen electrocatalyst, bifunctionality, zinc-air battery

INTRODUCTION

Carbon-based composites are a typical family of functional materials for electrochemical applications due to their low costs, high adjustability, high conductivity and compatibility with the secondary metallic components [1–5]. Carbon materials such as graphene/carbon nanotube (CNT) oxide, reduced/heteroatom-doped graphene/CNT oxide, and synthetic heteroatom-doped carbon are the most commonly used substrates for depositing metallic compounds [6–12]. In most cases, they act as templates or conductive substrates [13,14], while a few of them have been developed as co-catalysts [15–17]. Nowadays, integrating active components into delicately designed composites to enable multifunctionality and improve the utilization of both substrates and secondary components is an emerging trend [18], which is mainly credited by the developed synthetic technologies for carbon materials with atomic dopants. Normally, the atomic metal dopants are much more active than their non-metal counterparts due to their features of highly unsaturated coordination and strong metal-substrate interactions [2,19–21].

Currently, it is still rare to apply the newly developed atomically dispersed metal-nitrogen carbon (MNC) materials as substrates to support secondary catalytic components especially for the promotion of closely paired electrochemical reactions that demand largely different surface properties. For instance, the paired oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in aqueous metal-air batteries are theoretically reversible with O₂/OH⁻ conversions, but involve converse

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processes: ORR is gas-intaking and OER is gas-evolving, demanding catalysts to be hydrophobic and hydrophilic, respectively [22–24]. Consequently, most ORR catalysts require annealing while that of OER does not [25–27]. Many types of non-precious metal-based catalysts have been investigated to promote ORR and OER [28], among which, the atomically dispersed MNC and layered double hydroxides (LDH) represent two typical sorts of electrocatalysts for ORR and OER, respectively [2,20,21,9–31]. For instance, atomically dispersed Fe-NC, obtained *via* high-temperature treatments, exhibited extraordinary ORR performance showing half-wave potentials of 0.90 V which surpassed the commercially available Pt/C catalyst (58 mV) [2,25]; however, Fe-NC materials normally showed sluggish OER activity, making them not applicable as OER catalysts. On the contrary, the NiFe-LDH materials are normally synthesized at room temperature and exhibit extraordinarily low overpotentials in the range of 200–300 mV, and yet unfortunately they are not suitable for ORR due to insufficient conductivity and inappropriate surface wettability [26]. Therefore, efficient compositing of typical ORR-active components (such as atomically dispersed MNC) and OER-active components (such as NiFe-LDH) to achieve satisfactory bifunctionality for oxygen electrocatalysis and downstream alkaline metal-air batteries remains challenging [30].

In this work, ultrasmall NiFe-LDH nanodots (NiFe-NDs) were strongly coupled with a three-dimensional (3D) flower-like atomically dispersed FeCo-NC material and utilized as highly efficient catalyst to simultaneously promote the paired ORR/OER. The atomically dispersed FeCo-NC substrate was synthesized after modification on our previously reported method [21], possessing multiple features of 3D flower-like structure, large specific surface area, high N/Fe/Co contents, and excellent ORR performance. The 3D flower-like structure and N/O functionalities of FeCo-NC played critical roles in the size-limiting growth of NiFe-NDs. X-ray photoelectron spectroscopy (XPS) analyses revealed that the NiFe-NDs were controllably deposited on the N/O-containing sites rather than FeCo-N_x sites. The as-prepared composite, denoted as NiFe-ND/FeCo-NC, exhibited excellent bifunctional ORR and OER performance by showing an ORR half-wave potential of 0.85 V and an OER potential of 1.66 V at $j=10\text{ mA cm}^{-2}$, rendering NiFe-ND/FeCo-NC as promising candidate for alkaline rechargeable metal-air batteries. Besides, the NiFe-ND/FeCo-NC-assembled Zn-air battery (ZAB) delivered an impressive power density and cycle life, confirming the excellent bifunctional performance and strong coupling interaction between the NiFe-

NDs and FeCo-NC substrate. Impressively, when integrated into a all-solid-state ZAB, the NiFe-ND/FeCo-NC also showed a high open-circuit voltage (1.412 V), low charge-discharge gap, and excellent cycling durability under alternately folding and releasing, suggesting its promising application in wearable electronics.

EXPERIMENTAL SECTION

Materials

Cobaltous chloride (CoCl_2), ferric chloride (FeCl_3), zinc chloride (ZnCl_2), and zinc acetate ($\text{Zn}(\text{OAc})_2$) were purchased from Aladdin Reagent Co., LTD. Formamide (FA) was purchased from Xilong Chemical Co., Ltd. Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel nitrate hexahydrate ($(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. The commercial RuO_2 and Pt/C catalyst (20 wt.%, ~3 nm Pt nanoparticles on Vulcan XC-72 carbon support) were purchased from Sigma-Aldrich Co., LTD. All chemicals were analytical reagent grade (AR grade) and used as received without further purification.

Preparation methods

Synthesis of atomically dispersed FeCo-NC

The precursors for atomically dispersed FeCo-NC was synthesized according to a previous report [21], with the synthetic method described in brief below. Anhydrous FeCl_3 (0.005 mol L^{-1}), CoCl_2 (0.005 mol L^{-1}), and ZnCl_2 (0.090 mol L^{-1}) in 30 mL FA were sonicated for 30 min to form a homogeneous solution at room temperature. Then the uniform solution was transferred into a 50 mL-packed Teflon-lined stainless autoclave and heated at 180°C for 12 h. The resulting black product was collected by centrifugation, washed with deionized water and ethanol for thrice, respectively, and dried in oven at 80°C for 6 h. In the subsequent pyrolysis procedure, the dried precursor was placed in a porcelain boat and then placed into a flow-through tube furnace, kept at 900°C for 1 h with a heating rate of 5°C min^{-1} under nitrogen atmosphere. After being naturally cooled to room temperature, the typical FeCo-NC was obtained, the as-obtained sample was used without any further treatment.

Synthesis of NiFe-ND/FeCo-NC composite

The NiFe-ND/FeCo-NC was prepared by a precipitation method. Firstly, 50 mL of solution composed of

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8.1 mg) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.7 mg) was added dropwise to the dispersed FeCo-NC (100 mg) in 100 mL deionized water with ultrasonic treatment at room temperature (25°C). Then the aqueous solution containing NaOH (0.15 mol L⁻¹) and Na₂CO₃ (0.15 mol L⁻¹) was added drop by drop to maintain the pH value of the system at ca. 8. After magnetic stirring for 12 h at room temperature (25°C), the solution was centrifuged at 5000 rpm and washed with deionized water and ethanol for thrice. The NiFe-ND/FeCo-NC was obtained after drying for 6 h at 60°C, with a FeCo-NC:NiFe-ND/FeCo-NC weight ratio of ~4:5. Reference NiFe-LDH sample was prepared under identical conditions to NiFe-ND/FeCo-NC, but without adding the FeCo-NC.

Characterizations

The crystal structures of the samples were analyzed by powder X-ray diffraction (X' pert PRO MPD, PANalytical, Almelo, the Netherlands) with Cu K α radiation ($\lambda=1.5418$ Å). The morphologies of the samples were observed by field-emission scanning electron microscopy (SEM, JSM-7900F, JEOL, Japan) and high-resolution transmission electron microscopy (HRTEM, JEM-2100UHR, JEOL, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS). XPS (ESCALAB 250, Thermo Fisher Scientific, USA) with an Al K α X-ray source was used to study the surface chemical composition and valence state of the elements. The single atom catalysts were characterized by high-angle annular dark-field scanning TEM (HAADF-STEM) using a scanning/transmission electron microscope (Titan 80-300, FEI, USA), equipped with a probe spherical aberration corrector. Raman spectra were recorded using a Raman spectrometer (DXR2, ThermoFisher, USA) at excitation laser wavelength of 532 nm. Nitrogen adsorption/desorption analyses were performed at 77 K using a surface analyzer (ASAP 2460, Micromeritics, USA). Prior to the measurement, the samples were degassed at 300°C. The specific surface areas (SSAs) of the samples were calculated according to the Brunauer-Emmett-Teller (BET) method. The pore size distribution plot was made by applying the Barrett-Joyner-Halenda (BJH) method on the adsorption branch. The bubble contact angle (BCA) was measured by the captive bubble method underwater and the behaviors of bubbles were recorded by a microscope (SZX 16, OLYMPUS) mounted on a high-speed CCD camera (i-SPEED3, AOS Technologies). The resulting catalyst was uniformly dispersed onto the carbon paper and the illumination was achieved by a fiber optically illuminator system (CEL-TCX 250).

Electrochemical evaluation

All the electrochemical measurements were carried out in a standard three-electrode setup on an electrochemical workstation (760E, CH Instruments, Shanghai) using a rotating disk electrode (RDE, Pine Research Instrumentation) at room temperature (25°C). The Pt electrode, saturated calomel electrode (SCE), and polished glassy carbon (GC) electrode ($S \sim 0.196$ cm²) were employed as the counter electrode, reference electrode, and the substrate for the working electrode, respectively. For the preparation of the working electrode, 5.0 mg of the catalyst was dispersed in a mixed solution containing 500 μL of ethanol and 10 μL of Nafion (DuPont, 5.0 wt.%) solution with the assistance of sonication for at least 1 h. Then, the ink was loaded onto the surface of GC and dried at room temperature with ~ 0.20 mg cm⁻² catalyst loading for all samples. The commercial 20 wt.% Pt/C ink and RuO₂ ink were prepared under the same protocol. All electrochemical measurements including cyclic voltammograms (CVs), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry were performed in 0.1 mol L⁻¹ KOH aqueous solution (pH 12.8) at room temperature. Prior to the test, the electrolyte was pre-saturated with high-purity N₂ or O₂ flow for at least 30 min, and a constant gas flow was kept during the measurements. The potentials *versus* the SCE were converted to the reversible hydrogen electrode (RHE) scale based on the following Nernst equation

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \times \text{pH} + 0.241. \quad (1)$$

For ORR measurements, CV curves were collected at the scan rate of 40 mV s⁻¹, and LSVs were recorded at a scan rate of 5 mV s⁻¹. Chronoamperometry tests were conducted in O₂-saturated 0.1 mol L⁻¹ KOH at 0.55 V (*vs.* RHE) with a rotation rate of 1600 rpm. The electron transfer number (n) was calculated by the Koutecky-Levich equation (2) and (3) as follows

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K}, \quad (2)$$

$$B = 0.2nFC_{\text{O}_2}D_{\text{O}_2}^{\frac{2}{3}}\nu^{-\frac{1}{6}}, \quad (3)$$

where J , J_L and J_K are the measured current density, limiting current density and kinetic current density, respectively. ω is the angular velocity of the disk, n is the electron transfer number. F (96,485 C mol⁻¹), C_{O_2} (1.2×10^{-6} mol cm⁻³) and D_{O_2} (1.9×10^{-5} cm² s⁻¹) are the Faraday constant, the bulk concentration of O₂, and the diffusion coefficient of O₂ in 0.1 mol L⁻¹ KOH, respectively. ν (0.01 cm² s⁻¹) is the kinematic viscosity of the

electrolyte. The constant of 0.2 is employed when the rotation rate is expressed in rpm.

Liquid ZAB assembly

The rechargeable liquid ZAB measurements were assembled with a custom mold. For fabrication of the gas-diffusion cathode, the catalyst ink with a certain volume was coated on the carbon paper and then dried at room temperature. Polished Zn foil was used as the anode. The gas diffusion area was controlled at 1.0 cm^2 to allow O_2 penetration. The catalyst loading was about 1.0 mg cm^{-2} and 6.0 mol L^{-1} KOH aqueous solution containing 0.2 mol L^{-1} $\text{Zn}(\text{OAc})_2$ was used as the electrolyte. The long-term cycling test was carried out with 10-min charging and 10-min discharging at different current densities by using a Land-CT2001A testing system. The red light-emitting diodes (LED, 2.7 V) panel is commercially available.

Flexible solid-state ZAB assembly

The flexible solid-state ZAB was fabricated in a sandwich structure. The outermost layer air cathode was fabricated by dropping a certain volume of catalyst ink onto a cleaned carbon cloth ($2 \times 2.5\text{ cm}^2$, W1S 1005, CeTech) with a catalyst loading of 1 mg cm^{-2} . The solid electrolyte was prepared as follows: 1 g polyvinyl acetate (PVA) powder (molecular weight $\sim 195,000$) was dissolved in 10.0 mL deionized water at 95°C for 2 h with continuous stirring. Then 1.0 mL of 18.0 mol L^{-1} KOH containing 0.02 mol L^{-1} zinc acetate was added dropwise. After being stirred for 0.5 h, the transparent gel was poured into a container and frozen at -20°C for 2 h. The solid electrolyte was obtained after thawing at room temperature.

Then the air electrode was directly coated on the surface of the electrolyte wrapped Zn-spring anode. The test for the wearable ZAB was performed using recurrent galvanostatic pulses for 5-min of discharge followed by 5-min of charge. The red LED light (1.7 V) is commercially available.

RESULTS AND DISCUSSION

The synthesis of NiFe-ND/FeCo-NC composite is illustrated in Scheme 1. The atomically dispersed FeCo-NC material was firstly obtained *via* stepwise solvothermal treatment/pyrolysis by modifying our previous method [21], with heavily loaded N species and atomically dispersed Fe and Co components in the N-doped carbon materials, and 3D flower-like mesoporous structure (Fig. 1a). As shown in Fig. 1b, no obvious particulate metal aggregates are in FeCo-NC. HAADF-STEM confirms the atomic dispersion of Fe/Co components in FeCo-NC, as indicated by the dense isolated bright dots in Fig. 1c. The 3D flower-like mesoporous structure and rich N/O functionality can benefit the confinement of ion adsorption and tunable nucleation of NiFe-NDs [13].

To obtain strongly coupled NiFe-ND/FeCo-NC composite, FeCo-NC was suspended in $\text{Ni}^{2+}/\text{Fe}^{3+}$ solution, and afterwards, the NiFe-NDs were *in-situ* grown on the FeCo-NC upon the dropwise addition of alkaline solution. As revealed in Fig. 1d, e, the NiFe-NDs are decorated on the petals of flower-like FeCo-NC. The particle-size histogram was drawn based on 50 nanodots (Fig. 1e, inset), and the average diameter was calculated to be 3.7 nm based on the Gaussian distribution result. Whereas the directly prepared NiFe-LDH without FeCo-NC substrate shows bulk stacking structure (Fig. S1),

Scheme 1 Schematic diagram for preparing the NiFe-ND/FeCo-NC composite.

Figure 1 (a) SEM, (b) TEM, and (c) HADDF-STEM images of the atomically dispersed FeCo-NC. (d–f) HRTEM images of the NiFe-ND/FeCo-NC composite. The inset in panel (e) shows the size histogram of nanodots diameters. (g) XRD patterns of FeCo-NC, NiFe-ND/FeCo-NC, and reference sample NiFe-LDH. (h) Dark-field TEM image and corresponding element mapping images of NiFe-ND/FeCo-NC.

confirming the critical role of FeCo-NC in the size-limiting growth of NiFe-NDs. HRTEM (Fig. 1f) reveals that the fringe spacing of NiFe-NDs is ~ 0.25 nm, which is consistent with the (012) lattice spacing of NiFe-LDH [32], confirming the formation of NiFe-NDs on FeCo-NC. The broad peak at around 26.5° can be assigned to the (002) reflection of graphitic carbon in FeCo-NC [21], with no metallic component for FeCo-NC (Fig. 1g). A new set of hydrotalcite-like characteristic (003), (006), (012), and (110) peaks for NiFe-LDH are consistent with previous literatures [33].

The dark-field TEM and EDS mapping results in Fig. 1h indicate the homogeneous distribution of Ni, Fe, Co, C, O and N, implying the uniform growth and high dispersion of NiFe-NDs on the atomically dispersed FeCo-NC substrate. Besides, the SEM image in Fig. S2 further confirms that the morphology of FeCo-NC is well-kept after grafting NiFe-NDs. Raman spectroscopy

(Fig. 2a) further reveals the typical D and G bands for graphitic carbon in both samples before and after the deposition of NiFe-NDs. The D band (~ 1360 cm^{-1}) and G band (~ 1600 cm^{-1}) respectively correspond to the disorder vibration mode of structural defects and the well-ordered scattering of graphitic carbon [1,34]. As can be seen, the intensity ratio of the distorted carbon to graphitic carbon (I_D/I_G) in FeCo-NC is 1.22, indicating the FeCo-NC contains plenty of structural defects. The alien functionalities especially the N-/O-containing groups can serve as anchoring sites for the adsorption of $\text{Ni}^{2+}/\text{Fe}^{3+}$ and also the fast nucleation sites for NiFe-ND growth, which can enable strongly coupled interfacial junctions [35]. The pore structures of NiFe-ND/FeCo-NC and FeCo-NC were examined using N_2 adsorption-desorption isotherms (Fig. 2b). The typical type-IV isotherm with hysteric loops indicates the presence of various pore types ranging from meso- to micropores [36]. Further-

more, the BET SSA of FeCo-NC decreases to 220 from $280 \text{ m}^2 \text{ g}^{-1}$ after NiFe-ND growth. As indicated by the pore size distribution curves in Fig. 2b inset, the NiFe-NDs were likely grown in the mesopores, resulting in the decrease of SSA and mesopore volume [37].

XPS measurements were conducted to gain further insight into the elemental composition in the NiFe-ND/FeCo-NC. As shown in Fig. S3a, the XPS element survey corroborates the co-existence of Ni, Fe, Co, C, N, and O. Fig. S3b indicates that the total non-metal content in FeCo-NC approaches 99.40 at.%, and the Fe and Co contents are 0.35 and 0.24 at.%, respectively. The Ni and Fe contents in NiFe-LDH/FeCo-NC increase to 2.46 and 1.51 at.%, respectively. The feature of high N content in both NiFe-ND/FeCo-NC and FeCo-NC is also confirmed by the C 1s spectra and their deconvolution. As shown in Fig. S3d, considerable C–N bonding is observed at 285.6 eV. Meanwhile, the surface O content of NiFe-ND/FeCo-NC increases from 7.31 to 17.77 at.% after NiFe-ND growth [34]. The core level N 1s region (Fig. S3c) can be deconvoluted into four types of N species in both

NiFe-ND/FeCo-NC and FeCo-NC: pyridinic N ($\sim 398.2 \text{ eV}$), pyrrolic N ($\sim 399.3 \text{ eV}$), graphitic N ($\sim 400.5 \text{ eV}$) and oxidized N ($\sim 403.0 \text{ eV}$) [38]. The pyridinic N takes more than 50% in both NiFe-ND/FeCo-NC and FeCo-NC, and the high content of anchorable pyridinic and pyrrolic N is beneficial for stabilizing more Co and Fe in isolation state [39].

The high-resolution Ni 2p XPS spectrum of NiFe-ND/FeCo-NC in Fig. 2c exhibits four main peaks, corresponding to Ni $2p_{3/2}$ (856.5 eV) and Ni $2p_{1/2}$ (874.0 eV) of Ni^{2+} and two other shake-up satellites. Interestingly, a 0.6 eV binding energy shift of Ni 2p to higher position is detected for NiFe-ND/FeCo-NC compared with NiFe-LDH, indicating the Ni in NiFe-NDs is in electron depletion state after being deposited on FeCo-NC [36]. For Co 2p spectrum, the characteristic peaks at ~ 780.8 and $\sim 795.6 \text{ eV}$ in FeCo-NC are ascribed to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively, no obvious variation appears after grafting NiFe-NDs (Fig. 2d), suggesting the NiFe-NDs are probably anchored on the N-/O-containing sites [40]. Similarly, the peaks centered at ~ 710.4 and $\sim 712.4 \text{ eV}$ are

Figure 2 (a) Raman spectra of NiFe-ND/FeCo-NC and FeCo-NC. (b) N_2 adsorption/desorption isotherms of FeCo-NC and NiFe-ND/FeCo-NC, the inset shows their pore size distribution curves. (c) High resolution Ni 2p spectra, (d) Co 2p spectra, and (e) Fe 2p spectra of FeCo-NC, NiFe-ND/FeCo-NC, and NiFe-LDH. (f) Gas BCA measurement of NiFe-ND/FeCo-NC and FeCo-NC under water.

respectively assigned to the Fe 2p_{3/2} of Fe²⁺ and Fe³⁺ branches (Fig. 2e) [41,42]. Since Ni and Fe occupy divalent and trivalent cation sites with a ratio of 3:1 in the crystalized NiFe-LDH, respectively, only trivalent Fe³⁺ other than Fe²⁺ is deconvoluted in NiFe-LDH [43]. After NiFe-ND deposition, the Fe³⁺/Fe²⁺ ratio significantly increases to 0.82 compared with the original FeCo-NC (0.36). The above-confirmed binding energy shifts of Ni and the significantly altered Fe³⁺/Fe²⁺ ratio confirm the successful loading of NiFe-NDs on FeCo, and strong coupling interaction between the NiFe-NDs and FeCo-NC [18,36], therefore leading to the Co-N and Fe-N coordinations in FeCo-NC undisturbed [21]. Besides, BCAs of FeCo-NC before and after loading NiFe-NDs were measured to evaluate their aerophilicity [44,45]. Digital images in Fig. 2f show that the NiFe-ND/FeCo-NC exhibits a larger BCA of 135.8° ± 2.2° than that of FeCo-NC (130.2° ± 2.1°), confirming its higher aerophilicity, which may benefit the efficient utilization of gaseous oxygen and facilitate high-rate ORR kinetics [46]. While the lower aerophilicity of NiFe-ND/FeCo-NC resulted from grafting NiFe-NDs renders reduced adhesion force to O₂ bubbles, which could contribute to the OER [24,47].

To further study the electrocatalytic performance of NiFe-ND/FeCo-NC composite, CV measurements were initially carried out using a conventional three-electrode setup in O₂- or N₂-saturated 0.1 mol L⁻¹ KOH solution. Fig. S4 features FeCo-NC with a typical rectangular double-layer capacitor profile in N₂-saturated electrolyte, whereas a well-defined reduction peak centered at ~0.85 V in O₂-saturated 0.1 mol L⁻¹ KOH can be observed, suggesting its pronounced electrocatalytic ORR activity [48]. The performance of NiFe-ND/FeCo-NC was also evaluated against the individual component based on the LSV with RDE equipment, a mechanical mixture of NiFe-LDH and FeCo-NC (denoted as NiFe-LDH+FeCo-NC, with weight ratio of 1:4) and the commercial Pt/C catalyst (Fig. 3a). The NiFe-ND/FeCo-NC manifests excellent ORR activity with a high onset potential (E_{onset}) and half-wave potential ($E_{1/2}$) of ~0.93 and ~0.85 V, respectively, which are comparable to that of Pt/C (~0.94 and 0.85 V, respectively) and better than that of the mechanical mixture of NiFe-LDH+FeCo-NC (~0.91 and 0.83 V, respectively), while NiFe-LDH exhibits the worst ORR performance [49].

As previously studied by our group, the superior ORR activity of atomically dispersed binary FeCo-NC mainly originated from the cooperative Fe(N₃)-Co(N₃) sites in the N-doped carbonaceous material [21], and additionally

due to the ultrasmall sizes of NiFe-NDs that avoid severely blocking of the Fe/Co-based active sites [50,51]. RDE measurements with rotation speeds ranging from 400 to 2025 rpm were conducted to further investigate the ORR reaction kinetics (Fig. 3b and Fig. S5). The limiting current density increases with the acceleration of rotation speed, as the oxygen flux diffuses faster to the electrode surface under higher rotation speed [52]. The Koutecky-Levich (K-L) curves derived from the corresponding polarization curves at different potentials are further plotted, and reflect good linearity with parallelism from 0.3 to 0.7 V. The electron transfer number n values calculated from the K-L plots indicate 4-e⁻ reduction pathways on both NiFe-ND/FeCo-NC and FeCo-NC. Meanwhile, the Tafel slope values calculated using 1600-rpm LSV curves are 87, 90, 98, and 92 mV dec⁻¹ for FeCo-NC, NiFe-ND/FeCo-NC, NiFe-LDH+FeCo-NC, and Pt/C, respectively (Fig. S6), indicating faster kinetics of NiFe-ND/FeCo-NC compared with the NiFe-LDH+FeCo-NC mixture. The improvement of ORR activity could be explained by the strong coupling interaction between the NiFe-NDs and FeCo-NC substrate, as evidenced by the XPS results.

EIS was further conducted, as shown in Fig. 3c, the arc in the high-frequency region is related to the charge-transfer resistance (R_{ct}) correlating with electrochemical kinetics at the catalyst interface, and the smaller radius is associated with faster mass/electron exchange behavior [40,53]. As can be seen, the semicircular diameter of NiFe-ND/FeCo-NC is smaller compared with that of NiFe-LDH+FeCo-NC, indicating the faster reaction kinetics with a higher electron transfer rate, which is in good agreement with the catalytic activity measured by LSV [38,43]. Owing to the high graphitization degree and the 3D flower-like structure of FeCo-NC substrate, the catalysts exhibit very good long-term stability in O₂-saturated electrolyte [54], showing limited variation in E_{onset} and $E_{1/2}$, and very high current retention of 91% after 10,000 s continuous working at 0.6 V (vs. RHE), while the commercial Pt/C exhibits 23% current degradation, as compared in Fig. 3d.

Apart from the outstanding ORR activity, the NiFe-ND/FeCo-NC also exhibits significantly improved activity towards OER compared with FeCo-NC. As shown in Fig. 3e, the potential required to reach $j=10 \text{ mA cm}^{-2}$ for NiFe-ND/FeCo-NC is ~1.66 V, which is significantly lower than that of FeCo-NC (~1.80 V) and NiFe-LDH+FeCo-NC (~1.73 V). It should be noted that the redox peaks locating at ~1.5 V are detectable in NiFe-LDH, NiFe-ND/FeCo-NC, and NiFe-LDH+FeCo-NC, which

Figure 3 Electrochemical measurements on FeCo-NC, NiFe-ND/FeCo-NC, NiFe-LDH+FeCo-NC, NiFe-LDH, and reference sample (Pt/C and/or RuO₂): (a) ORR LSV curves, (b) LSV curves of NiFe-ND/FeCo-NC at different rotation speeds (inset shows their corresponding K-L plots). (c) Nyquist plots of the catalysts in 0.1 mol L⁻¹ KOH. (d) The durability tests of NiFe-ND/FeCo-NC and reference sample Pt/C. The inset shows the LSV curves before and after durability test for 10,000-second long working at 0.6 V (vs. RHE). (e) OER LSV curves and (f) the corresponding Tafel plots. (g) Potential gaps between the ORR $E_{1/2}$ (half-wave potential) and the OER at 10 mA cm⁻². (h) *In-situ* Raman spectra of NiFe-ND/FeCo-NC at different potentials during anodic and cathodic sweep in a CV cycle and (i) Raman spectra of NiFe-ND/FeCo-NC and NiFe-LDH+FeCo-NC at potential=1.5 V (vs. RHE) holding for 10 min.

can be assigned to the Ni²⁺/Ni³⁺ redox reaction. The most obvious redox peak for NiFe-ND/FeCo-NC suggests its intense charge transfer relating to Ni²⁺/Ni³⁺ transformation [34]. Meanwhile, the corresponding Tafel slope of NiFe-ND/FeCo-NC is ~92 mV dec⁻¹, lower than those of NiFe-LDH+FeCo-NC (~122 mV dec⁻¹) and NiFe-LDH (~100 mV dec⁻¹), as shown in Fig. 3f.

Compared with NiFe-LDH and NiFe-LDH+FeCo-NC, the excellent OER activity of NiFe-ND/FeCo-NC composite can be ascribed to the high activity of NiFe-NDs,

high conductivity of FeCo-NC substrate and the strong coupling effect between NiFe-NDs and FeCo-NC (Fig. 2c). Besides, the NiFe-NDs anchored on FeCo-NC are expected to expose more active sites compared with bare NiFe-LDH due to nanosize effects [55]. The stability tests reveal that the LSV profile of NiFe-ND/FeCo-NC is retainable after 3000 cycles (Fig. S7a) [34]. Besides, the SEM image reveals that the morphology of the catalyst is well maintained after durability tests (Fig. S7b). Fig. 3g displays the comparison of bifunctional ORR/OER ac-

tivity of NiFe-ND/FeCo-NC with other materials studied in this work. The NiFe-ND/FeCo-NC exhibits the smallest potential gap (ΔE) of 0.81 V between E_{j10} (the potential at a current density of 10.0 mA cm^{-2}) and $E_{1/2}$ (ORR half-wave potential), which is much smaller than that of FeCo-NC (0.95 V) and NiFe-LDH+FeCo-NC (0.90 V).

In-situ Raman analyses were performed to investigate the underneath OER mechanism on NiFe-ND/FeCo-NC by monitoring the distribution of the key reaction intermediates during OER process, and the digital image of a custom mold *in-situ* electrochemical cell is shown in Fig. S8. A series of Raman spectra for NiFe-ND/FeCo-NC act as a functional of applied potential during the CV sweep from 1.3 to 1.5 V then to 1.3 V, as shown in Fig. 3h. The peaks at 460 and 532 cm^{-1} can be assigned to the Ni–O vibration mode in NiFe-LDH during the sweep from 1.30 to 1.40 V [56,57]. As the applied potential increases to 1.50 V, where the OER of NiFe-ND/FeCo-NC occurs, the primary two peaks disappear and the pair of new peaks at 477 and 553 cm^{-1} appear. These two peaks are probably attributed to the characteristic Ni–O vibration in NiOOH, indicating the generated oxyhydroxides under the oxygen evolution potential. Meanwhile, the spectral features of NiFe-ND/FeCo-NC and NiFe-LDH+FeCo-NC physical mixture were further collected after activation at 1.50 V for 10 min. As shown in Fig. 3i, a series of peaks assigned to NiOOH and FeOOH ($\sim 689 \text{ cm}^{-1}$) can be observed. It could be found that the peak relative intensity I_{553}/I_{477} of NiFe-ND/FeCo-NC after activation is higher than that of the physical mixture, indicating that more NiOOH active sites are generated in NiFe-ND/FeCo-NC, and a stronger peak of FeOOH appears. The above results clearly evidence that more Ni and Fe ions are oxidized to NiOOH and FeOOH active sites in NiFe-ND/FeCo-NC under OER conditions compared with NiFe-LDH+FeCo-NC physical mixture [58], suggesting the beneficial effect of FeCo-NC substrate. The aforementioned results further suggest that the NiFe-ND/FeCo-NC can serve as efficient non-precious metal bifunctional ORR/OER electrocatalyst for alkaline metal-air batteries.

ZABs were assembled with NiFe-ND/FeCo-NC as the cathode material to demonstrate its application potentials (Fig. 4a). Reference ZAB cells were also assembled using FeCo-NC, NiFe-LDH+FeCo-NC, and Pt/C+RuO₂ (with a mass ratio of 1:1). As shown in Fig. S9, the ZAB assembled with NiFe-ND/FeCo-NC exhibits a higher open-circuit voltage (1.465 V) than that with NiFe-LDH+FeCo-NC (1.461 V) and Pt/C+RuO₂ (1.455 V), which is very

close to that of FeCo-NC (1.470 V). Two NiFe-ND/FeCo-NC-assembled ZABs in series manage to power a 2.7 V LED panel (Fig. 4a). At 10.0 mA cm^{-2} , the NiFe-ND/FeCo-NC composite is able to promote the ZAB device with a specific capacity of $629 \text{ mA h g}_{\text{Zn}}^{-1}$ ($\sim 77\%$ of theoretical capacity), which is close to that of FeCo-NC ($650 \text{ mA h g}_{\text{Zn}}^{-1}$) and outperforms that of NiFe-LDH+FeCo-NC mixture ($\sim 600 \text{ mA h g}_{\text{Zn}}^{-1}$, Fig. 4b). Fig. 4c displays the discharge and charge curves of rechargeable ZAB assembled using different samples with a scan rate of 10 mV s^{-1} . The NiFe-ND/FeCo-NC ZAB shows the lowest charge voltage compared with other catalysts and similarly high discharge voltage as FeCo-NC. The maximum power density of NiFe-ND/FeCo-NC ZAB can reach up to 141.0 mW cm^{-2} at 247 mA cm^{-2} , which is almost 1.5 times of that using Pt/C+RuO₂.

The charge-discharge voltage gaps of different samples versus different current densities are summarized in Fig. 4d. All the samples follow the trend of enlarged charge-discharge voltage gap along with the increase of current density, which is governed by the electrochemical polarization rules [5]. The gap-enlarging rates for different samples show large variations: among all samples, the NiFe-ND/FeCo-NC shows the least tendency of gap broadening, FeCo-NC and NiFe-LDH+FeCo-NC follow, while Pt/C+RuO₂ shows the worst capability of maintaining high performance at large current rates. At a high current rate of 20.0 mA cm^{-2} , the charge voltage for Pt/C+RuO₂ increases to 2.30 V and its discharge voltage touches down to 0.93 V, while the NiFe-ND/FeCo-NC can still supply a 2.03-V charge plateau and a 1.11-V discharge plateau. Galvanostatic discharge and charge measurements were carried out with selected current densities with 10-min charge/10-min discharge intervals to investigate their long-term cycling stability. At the current density of 5.0 mA cm^{-2} , the NiFe-LDH/FeCo-NC-assembled ZAB supplies a 1.94-V charge plateau and 1.23-V discharge plateau, delivering a very small voltage gap of 0.71 V (Fig. S10), which is 40 mV smaller than that of FeCo-NC.

Particularly, the NiFe-ND/FeCo-NC-assembled ZAB possesses superior charge performance compared with both FeCo-NC and NiFe-LDH+FeCo-NC, which can be attributed to the well-dispersed NiFe-NDs on the FeCo-NC support. As shown in Fig. 4e, at large current density of 20.0 mA cm^{-2} , the Pt/C+RuO₂ encounters quick fading after the 30th cycle, while NiFe-ND/FeCo-NC is still able to operate with stable charge/discharge profile for more than 480 cycles and supply a 2.01-V charge plateau and 1.14 V discharge plateau at 300th cycle. In comparison,

Figure 4 (a) A photograph of LED panel (2.7 V) powered by two series connected NiFe-ND/FeCo-NC-based liquid ZABs. (b) Galvanostatic discharge curves at a current density of 10.0 mA cm^{-2} . (c) Polarization curves and power density curves. (d) Charge-discharge voltage gaps *versus* different current densities. (e) Galvanostatic charge-discharge cycling curves at 20.0 mA cm^{-2} .

the NiFe-LDH+FeCo-NC mixture delivers a continuously enlarged gap and provides a 2.27 V charge plateau and 0.97-V discharge plateau at the 300th cycle. Table S1 summarizes the performances of ZABs based on NiFe-ND/FeCo-NC and other materials studied in this work and the results reported in previous literatures. As compared, the NiFe-ND/FeCo-NC exhibits very small charge-discharge voltage gap at very large current density of

20.0 mA cm^{-2} , with better durability and stability.

Moreover, to meet the increasing demand for flexible electronics, all-solid state ZABs were fabricated, as schemed in Fig. 5a, NiFe-ND/FeCo-NC is loaded on the carbon cloth and used as the air cathode. Alkaline PVA hydrogel and zinc spring act as the solid-state electrolyte and anode, respectively. As shown in Fig. 5b, c, a high open-circuit potential of 1.412 V is delivered by using

Figure 5 (a) Scheme of a rechargeable solid-state flexible ZAB using NiFe-ND/FeCo-NC as the cathode catalyst. (b) Photograph of the solid ZAB with an open-circuit voltage of 1.412 V. (c) Polarization curves and power density curves of flexible ZABs (10 mV s⁻¹ scan rate). (d) Digital photo shows the application of wearable ZABs. (e) The charge-discharge curves of the NiFe-ND/FeCo-NC-based solid-state ZAB under alternately folding and releasing conditions.

NiFe-ND/FeCo-NC as the air cathode, and it also delivers a high maximum power density of $\sim 121.1 \text{ mW cm}^{-2}$, outperforming Pt/C-RuO₂ ($\sim 77.6 \text{ mW cm}^{-2}$). Meanwhile, the two in-series NiFe-ND/FeCo-NC-based wearable ZABs assembled using rubber glove as flexible substrate, can continuously light up a commercial red LED light

(Fig. 5d). Typically, the mechanical flexibility and stability tests of NiFe-ND/FeCo-NC-assembled solid-state ZAB were performed by alternately folding (120°) and releasing for every two charge-discharge cycles. As shown in Fig. 5e, with the cycling test carried out for more than 100 min, there is no obvious variation in charge ($\sim 1.93 \text{ V}$)

and discharge (~ 1.28 V) voltage platforms at a current density of 1.0 mA cm^{-2} , indicating the robust cycling stability under deformation of the solid-state ZAB.

CONCLUSIONS

In summary, a feasible approach was developed to design bifunctional electrocatalysts using atomically dispersed MNC as a new type of active substrate. HRTEM reveals that the ultrasmall sized NiFe-NDs are sparsely deposited on the 3D flower-like FeCo-NC, which is critical to avoid the blocking of ORR-active FeCo sites. XPS analyses reveal that the Ni species in NiFe-NDs are more electron-depleted. Taken together, strong coupling interactions between the NiFe-NDs and FeCo-NC substrate are successfully achieved. Electrochemical measurements confirm that the controllable compositing of ultrasmall OER-active NiFe-NDs and ORR-active FeCo-NC substrate render exceptional bifunctional performance towards ORR and OER. Remarkably, the NiFe-ND/FeCo-NC composites exhibit the smallest potential gap of 0.81 V consisting of a 0.85 V ORR half-wave potential and a 1.66 V potential at a current density of 10.0 mA cm^{-2} in 0.1 mol L^{-1} KOH. Meanwhile, under OER conditions, the more Ni(Fe)OOH active sites are observed in NiFe-ND/FeCo-NC compared with their physical mixture, further confirming the OER enhancement of FeCo-NC substrate. Moreover, rechargeable liquid-state ZABs assembled using NiFe-ND/FeCo-NC as cathode possess a very small charge-discharge voltage gap, high rate capability, and highly robust cycling stability. Furthermore, the NiFe-ND/FeCo-NC could be applicable for fabricating all-solid-state ZAB to power wearable electronics, delivering a high open-circuit voltage and a stable charge-discharge voltage platform under repeatedly bending condition. Our work may enlighten the N-doped carbon materials with atomic decoration of metal components as a new type of unique substrate for fabricating integrated composites with multifunctionalities.

Received 12 January 2020; accepted 23 February 2020;
published online 7 April 2020

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Acknowledgements This work was financially supported by the National Natural Science Foundation of China (21701101), the National Key Research and Development Project, Key Projects of Intergovernmental International Innovation Cooperation (2018YFE0118200 and 2016YFF0204402), the Fundamental Research Funds for the Central Universities (18CX06063A), the Key Research and Development Project of Shandong Province (2019JZZY010506), the Scientific Research Awards Foundation for Outstanding Young Scientists of Shandong Province (ZR2018JL010), the Joint Fund of Outstanding Young Talents of Shandong Province (ZR2017BB018), and the Program of Qingdao Scientific and Technological Innovation High-level Talents Project (17-2-1-1-zhc).

Author contributions Wang Y and Zhang G designed and engineered the samples; Wang Y, Ma M, and Ma Y performed the experiments; Huang J, Chen C and Zhang Y helped analyze and discuss the data; Wang Y and Zhang G wrote and revised the paper with support from Sun X and Yan Z. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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超小NiFe水滑石耦合单原子FeCo-NC纳米花用于可充电锌空气电池

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摘要 单原子分散的FeCo-NC材料, 具有特殊的花状结构和原子级分散Fe/Co位点, 适用于可控沉积超小NiFe水滑石纳米点(NiFe-ND), 从而制备具有优异氧还原(ORR)和氧析出(OER)性能的双功能催化材料. FeCo-NC材料本身具有三维立体花状介孔结构和丰富的N/O功能位点, 可以实现对NiFe-ND尺寸的有效控制(直径约4 nm), 使得制备的特殊复合材料的OER和ORR活性位暴露度达最大值. 电化学测试表明在0.1 mol L⁻¹ KOH电解液中NiFe-ND/FeCo-NC的ORR半波电势为0.85 V, 当电流密度为10 mA cm⁻²时的OER电势为1.66 V. 原位拉曼结果进一步证实了NiFe-ND/FeCo-NC材料优良的OER活性来源于电化学过程中产生的丰富Ni(Fe)OOH活性相. 采用NiFe-ND/FeCo-NC组装的锌空气电池具有较小的充放电电压差(0.87 V, 20 mA cm⁻²)和持久的循环稳定性. 同时, NiFe-ND/FeCo-NC也可以应用于全固态锌空气电池, 即使在形变的情况下仍然具有良好的循环稳定性. 本工作可为单原子金属氮碳催化剂作为特殊基底材料应用于新型多功能催化剂的研发提供指导.