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Highly Active and Durable Iron-Cobalt Alloy Catalyst Encapsulated in N-doped Graphitic Carbon Nanotubes for Oxygen Reduction Reaction by Nanofiberous Dicyandiamine Template

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Exploring competitive electrocatalyst to replace Pt-based catalysts for oxygen reduction reaction (ORR) of fuel cells is one of the most hopeful strategies to confront the energy and environmental crisis. Herein, we highlight FeCo alloy catalyst encapsulated in N-doped graphitic carbon nanotubes (FeCo@N-GCNT-FD) as a greatly efficient non-precious electrocatalyst for ORR. The FeCo@N-GCNT-FD catalyst exhibits a positive onset (0.96 V vs RHE), half-wave potentials (0.88 V vs RHE) and 5.6 times specific activity of commercial Pt/C at 0.70 V in alkaline media. The excellent catalytic behavior of the FeCo@N-GCNT-FD is attributed to structural properties with a large surface area and the synergistic effect of FeCo alloy and N-GCNT, which guarantee a large number of accessible catalytic sites and rapid mass-transfer kinetics. Theoretical calculations further confirm that the strong synergetic and electronic effect, especially the FeCo-N_G sites, provides a favorable local coordination environment and electronic structure and lower oxygen absorbance energy. The improvement of ORR activity and durability of the catalyst by the synergetic and electronic effects between metal and carbon provides a versatile approach for tuning the catalytic performance of non-noble electrocatalysts.

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Introduction

With the demand for low emission or zero-emission, the low cost and high energy density battery and/or fuel cells are highly desirable to be developed to satisfy the requirement of the car. Currently, the largescale commercialization of the low-temperature proton-exchange membrane fuel cells (PEMFCs) is still hindered due to the sluggish kinetics of the oxygen reduction reaction (ORR), which requires expensive electrocatalyst with a high mass loading noble metal Pt to achieve adequate power and energy densities.¹⁻³ Even the state-of-theart platinum or Pt-based alloys exhibit good electrochemical performance toward ORR, their cost, scarcity, and long-time stability dramatically limit their practical application and commercialization.⁴⁻ ⁷ Alternatively, if Pt-free materials, so-called costless electrocatalysts, such as nonprecious catalyst, metal-free catalyst, with comparable ORR electrocatalytic activity to Pt-based catalysts, can be favorably expected to take the dominant place. Comparing with chemical inert Pt, although other transition metals such as Fe, Co, Ni also exhibit catalytic activity to some extent, the most critical issue is their stability

in the harsh environment because they can be dissolved into the acidic or basic solution.

To solve the problem of the metal dissolution, a variety of transition metal compounds, such as chalcogenides,⁸⁻¹⁰ oxides,¹¹⁻¹⁴ and carbides/nitrides,15-21 with considerable improvements in stability for ORR have been developed. However, it is hard to satisfy and take the place of Pt-based ORR catalysts due to the catalysts are unstable at the harsh environment of a PEMFCs cathode, especially in acidic solution.²² Recently, nanocomposites of iron carbides and carbon (Fe₃C/C, GL-Fe/Fe₅C₂/NG),^{15, 16, 23} anchoring cobalt nanocrystals through the plane of graphene,²⁴ the sole metal or metal alloy/nitrogen-doped carbon synthesized via pyrolysis of complex metal-organic framework,^{25, 26} the encapsulation of earth-abundant transition metals (such as Fe, Co, Cu, Ni)27-37 in N-doped carbons materials have been successfully developed to be stable ORR catalyst with enhanced catalytic activities due to the synergetic effects between metal and heteroatom-doped carbon. In addition, the outlayer carbon material effectively prevent from the metal dissolution issue even in the acidic media. That opens a door to develop high performance and durability electrocatalyst for ORR. Importantly, the intermetallic compounds with ordered structure exhibit excellent electrocatalytic activity and long-term stability.7, 38-40 Aim to this target, we propose that FeCo intermetallic wrapped with heteroatom doped carbon is expected to be a high performance and stability.

As a heterogeneous reaction, the ORR takes place on the surface of catalyst between liquid-solid interfaces. The catalytic activity of the catalyst strongly depends on the specific surface area of catalyst.⁴¹ To

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achieve high activity, it is highly desirable to prepare the catalyst high surface area. Dicyandiamide, as a principal source of graphitic-C₃N₄ (g-C₃N₄), can also be served as N-doped graphitic carbon nanotube precursor because it has abundant C and N.42-44 In this report, we developed a simple and facile synthesis route to prepare alloy nanoparticles wrapped with in N-doped graphitic carbon nanotube (N-GCNT) by pyrolyzing transition metal salts and dicyandiamine mixture. Nanofibrous dicyandiamine can form by self-assembly with freeze-drying technique, and can be further used as template for the formation of N-GCNT in the presence of transition metal salt in the thermal pyrolysis process. The resulting FeCo nanoparticles encapsulated in N-GCNT (FeCo@N-GCNT-FD) catalyst features a bamboo-like morphology with FeCo alloy inside of N-GCNT. It exhibits high surface area of 317.9 m²/g and a suitable wall thickness (2~2.5 nm) of N-GCNT, which contribute to more catalytic active sites and lower oxygen absorbance energy through the synergetic and electronic effects. In addition, the N-GCNT effectively prevent the alloy nanoparticles from the dissolution in both acidic and basic environment, which endow high durability for the FeCo@N-GCNT-FD. This method provides a versatile strategy to fabricate low-cost and high-performance nonprecious catalysts with controllable metal species and heteroatom-doped carbon-based materials.

Experimental

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Sample preparation.

1. Pretreatment of dicyandiamide.

Dicyandiamide was dissolved into a certain amount of deionized water and the mixture was continually stirred for 30 min to form a homogeneous 2 wt% solution. The solution was frozen in liquid nitrogen to induce the freezing assistant assembly. Then the freezing dicyandiamide was placed into the lyophilizer to keep above 48 h under vacuum. The freeze-drying treated and commercial dicyandiamide was denoted as DCDA-FD, DCDA, respectively.

2. Preparation of the FeCo@N-GCNT-FD and FeCo@N-GCNT.

In a typical synthesis, 8 mmol FeAc₂, 8 mmol CoAc₂·4H₂O, and 32 mmol nanofibrous DCDA-FD were fully ground. Then the mixture was heated to 800 °C at 10 °C min⁻¹ and kept for 2 h in an Ar atmosphere. After cooling down, the residue was collected and washed with 0.5 M $\rm H_2SO_4$ at 85 oC for 8 h to remove metal unwrapped with N-GCNT, which is denoted as FeCo@N-GCNT-FD. And then, the samples were washed by deionized water till neutral and dried at 80 °C overnight, respectively. For comparison, FeCo alloy nanoparticles wrapped in the N-doped graphite carbon nanotube was also synthesized by a similar process except that the commercial dicyandiamide takes the place of nanofibrous dicyandiamide and denoted as FeCo@N-GCNT. In order to check the effect of temperature on the phase transformation, the different annealed temperature (600~800 °C) samples were also synthesized. Notably, this work refers to FeCo@N-GCNT-FD and FeCo@N-GCNT annealed at 800 °C except for special instructions. In addition, the graphitic C₃N₄ (g-C₃N₄) is synthesized by the thermal treatment of DCDA in a crucible with a cover and heated at 550 °C for 2 h in static air at a ramp rate of 2.3 °C min⁻¹.

Materials Characterizations.

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The structures of electrocatalysts are characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer, Cu K α). The morphology of the samples was examined by scanning (SEM, Hitachi-SU-8010) and transmission electron microscopy (TEM, TECNAI-F20), respectively. The detailed chemical composition of the electrocatalysts was carried out by XPS (AXIS-Ultra instrument from Kratos Analytical, Al K α radiation, $h\nu$ =1486.6 eV). The micro-Raman spectra were recorded on Raman microscope (L2BRAM ARAMIS) with 532 nm line of an Ar ion laser as an excitation source. The specific surface area of the catalysts was measured by nitrogen adsorption-desorption isotherm curve at 77 K. XAFS spectra were recorded at beamline 1W1B of the Beijing Synchrotron Radiation Facility. The pretreatment of the dicyandiamide was used by the Lyophilizer (LGJ-10).

Electrochemical measurements.

All the electrochemical measurements were carried out with BioLogic VMP3 electrochemical workstation in a conventional three-electrode configuration controlled at room temperature. A three-electrode cell was employed using a rotating ring-disk electrode (RRDE, 5mm in diameter from Pine Instrument) as working electrode, a Hg/HgO (0.1 M KOH) electrode as the reference electrode, and a GC film as the counter electrode. All the potentials in the present study were referred to the reversible hydrogen electrode (RHE), as reported previously in conversion method ($E_{(RHE)} = E_{(Hg|HgO, 0.1M KOH)} + 0.933$ V). The Hg/HgO (0.1 M KOH) reference electrode is 0.164 V versus NHE. To prepare catalyst inks, the working electrodes were prepared as following: 4.7 mg of the electrocatalysts and one drop 2% Nafion solution were dispersed in 1 mL isopropyl alcohol by sonication for 30 min to form a homogeneous ink. Then 20 µL of ink was loaded onto the polished RRDE, and the electrode was dried at room temperature.

For the cyclic voltammetry (CV) experiments and polarization tests, the working electrodes were conducted in a N₂ and O₂-saturate 0.1 mol L⁻¹ KOH in the potential range of 0.2~1.2 V (*vs* RHE), with a scan rate of 50 mV s⁻¹, 10 mV s⁻¹ with varying rotating speed from 400 rpm to 2500 rpm, respectively. The kinetics of the ORR for FeCo@N-GCNT-FD, FeCo@N-GCNT and commercial Pt/C catalysts were studied by the RDE method. The electron transfer number of the catalyzed ORR was calculated by the Koutecky–Levich equation at various potentials as follows:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

B = 0.62nFC₀(D₀)^{2/3}v^{-1/6}
 $J_K = nFkC_0$

where J is the measured current density, J_L and J_K are the diffusion limiting and kinetic current densities, respectively. ω is the angular velocity, n is electron transfer number, F is the Faraday constant (96485 C mol-1), C₀ is the bulk concentration of O₂ (1.2 × 10⁻³ mol L⁻¹), D₀ is the diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm² s⁻¹), v is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹), and k is the electron-transfer rate constant. For the Tafel plot, the kinetic current was calculated from the mass-transport correction of RDE by: Published on 05 March 2018. Downloaded by University of New England on 05/03/2018 06:22:38

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$$J_K = \frac{J \times J_L}{J_L - J}$$

All RRDE measurements were performed on a Pine Instrument device in O₂ saturated 0.1 M KOH solution at a scan rate of 5 mV s⁻¹ at 1600 rpm and the ring potential was kept at 1.4 V vs. RHE. Hydrogen peroxide yields and the electron transfer number (n) could be determined by following the equations^{45, 46}

$$H_2O_2(\%) = 200 \times \frac{I_R/N}{\frac{I_R}{N} + I_E}$$
$$n = 4 \times \frac{I_D}{I_D + \frac{I_D}{N}}$$

Herein, I_D and I_R are the disk and ring currents, respectively. N is the ring collection efficiency and the measured N value was 0.37. Accelerated durability tests for the working electrode was performed by running 30000 cycles between 0.6 and 1.2 V (*vs.* RHE) in O₂-saturated 0.1 M KOH, with a scan rate of 200 mV s⁻¹. The measurements of the chronoamperometric response were performed in the O₂-saturated electrolyte for 12 h by constantly bubbling O₂. In the methanol crossover tests, 1 M methanol was introduced into O₂-saturate 0.1 mol L⁻¹KOH. Commercial 20 wt% Pt/C (Pt/C's loading 20 µg cm⁻²) was also used to compare their catalytic activities.

The electrochemically active surface area (ECSA) was estimated from the electrochemical double-layer capacitance according to a previously published report.⁴⁷ The electrochemical capacitance determined from was cyclic voltammograms measured in a non-Faradaic region at different scan rates. Electrochemical impedance spectroscopy (EIS) measurement was carried out at 0.75 V vs RHE of 5 mV in the frequency range from 0.01 Hz to 100 kHz using an Autolab electrochemical workstation (Autolab PGSTAT302N).

Density function theory (DFT) calculation.

All spin-polarized DFT calculations were performed by using the Vienna Ab-initio Simulation Package (VASP)⁴⁸ ⁴⁹with the generalized gradient approximation PBE (Perdew-Burk-Ernzerhof) functional.⁵⁰ The plane wave basis (kinetic energy cutoff values was 520 eV) and PAW (projector-augmented wave) pseudopotential were employed.⁵¹ The atomic positions were fully optimized until the Hellmann-Feynman force less than 0.05 eV/Å and total energy convergence criteria was set to 1×10^{-4} eV.

Our calculation employed a (6, 6) metallic carbon nanotube (CNT), and about 10 Å vacuum layer were set to the direction of perpendicular to the CNT axis. The metal@N-doped CNT supercell has a lattice with x, y = 18.0 Å and z=9.73 Å. The Monkhorst-Pack k-point grid 1×1×3 was set in all calculations. The calculations of Gibbs free energy of ORR intermediates was followed the Nørskov's method⁵² and the work potential U_{work} was defined as U_{work} = min{- ΔG_i }.

Results and discussion

Dicyandiamide, which is considered to be a principal source of graphitic-C₃N₄, also can be served as N-doped carbon nanotube precursor.^{42, 43} As shown in Figure S1 and S2, compared with the pristine dicyandiamide (DCDA), the freeze-drying self-assembled

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dicyandiamide (DCDA-FD) exhibits a fluffy condition, with floecule morphology, which is significantly different 1fron 19/the Apristine dicyandiamide (Figure S1a, b). Figure S1a, b showed that pristine DCDA shows massive and bulk morphology in millimeter or micrometer size. However, DCDA-FD displays nanofibrous morphology due to the rapid self-assembly of DCDA molecules in the aqueous solution during the frozen process.42 The evolution of such a well-ordered architecture is attributed to the fast nucleation and the oriented growth of dicyandiamide within liquid nitrogen at the undercooling temperature that is far below the freezing point of the solution,^{42, 43} illustrating a vital influence on the morphology and performance of the nanostructural precursor. Importantly, this fibrous morphology is also beneficial to the formation of N-GCNT in thermolysis process. Although both bulk and fibrous DCDA can form N-GCNT in the presence of transition metal, fibrous DCDA-FD could form large-scale N-GCNT with a small diameter and uniform and thin wall thickness.

As depicted in the Scheme 1, a facile solid-state reaction method was demonstrated to synthesize the FeCo alloy catalyst wrapped in N-doped graphitic carbon nanotubes (denoted as FeCo@N-GCNT-FD) simply utilizing nanofibrous dicyandiamide and metal salt (Co(CH₃COO)₂ and Fe(CH₃COO)₂) as the precursors. Firstly, DCDA-FD mechanically mixed with metal salts to obtained mixture, followed by heating treatment in Ar atmosphere at high temperature 600-800 °C for 3 hours. In the pyrolysis, graphitic carbon nitride forms at low temperature stage and further converted to graphitic carbon nanotube with the presence of the FeCo alloy particles produced from the decomposition of metal salts.



Scheme 1. Schematic illustration of the formation of FeCo@N-GCNT-FD electrocatalyst.

Figure 1a shows the XRD patterns of FeCo@N-GCNT-FD and FeCo@N-GCNT. The peaks at around 45°, 65.5°, and 83° can be assigned to the FeCo alloy body-centered cubic crystal structure (JCPDS, No. 65-4131), corresponding to its (110), (200), and (211) planes, respectively, indicating that the product contains FeCo alloy nanoparticles. Another diffraction peak located at 26.4° is the characteristic (002) diffraction peaks of graphitic carbon. Comparing with FeCo@N-GCNT, the (002) diffraction peak is weaker and broader, indicating that its domain size of (002) direction turns small. To understand the formation of FeCo@N-GCNT-FD, the FeCo@N-GCNT-FD samples were also synthesized at various temperatures and denoted as FeCo@N-GCNT-FD-x, where x represents carbonization temperature of 400, 500, 600, 700 and 800 °C. Figure S3 illustrates X-ray diffraction (XRD) pattern of FeCo@N-GCNT-400 and 500, and g-C₃N₄, indicating the DCDA converts into layered graphitic carbon nitride at 400 °C. The sample displays yellowish brown due to the presence of the metal salt. Raising up the temperature to 500 °C, the

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sample turns into carbon black, the XRD diffraction peak broadens owing to carbonization. However, there is no metal signal is observed. Graphite carbon and FeCo alloy characteristic peaks formed in the high temperature (600-800 °C) treated samples (Figure S4), indicating FeCo alloy nanoparticles form in the high temperature stage. Figure S5 shows SEM images of FeCo@N-GCNT-FD-600~800 °C. As known, Fe and Co nanoparticles can be served as catalyst for the formation of carbon tube.53,54 Only carbon particles are observed in the FeCo@N-GCNT-600 sample. That indicates that carbon nanotube does not form at this stage although FeCo alloy nanoparticles have been formed. When the thermal treatment temperature reaches 700 °C and above, the nanotube structures are presented in the samples. Thus, we propose that the metal salts convert into FeCo alloy nanoparticles at 600 °C, which further work as a catalyst to promote the carbon nitride into the carbon nanotube. And the FeCo alloy nanoparticles are wrapped by in situ formed carbon nanotube. Figure 1b shows N2 adsorption-desorption isothermal of FeCo@N-GCNT-FD and FeCo@N-GCNT. Both of them belong to type IV nitrogen adsorptiondesorption isotherm. The loops are observed and range from the relative pressure of 0.4 to 1.0 indicating that mesopores and macropores coexist in the samples. The Brunauer-Emmett-Teller (BET) result reveals that the unique structure endows FeCo@N-GCNT-FD catalyst with a large specific surface area of 317.9 m² g⁻¹, which is 2.6 times higher than the FeCo@N-GCNT (122.8 $m^2 g^{-1}$). With such high BET specific surface area, more active sites and more favorable mass transport of ORR relevant species can be expected during the electrocatalytic ORR.



Fig. 1 (a) Powder XRD patterns of FeCo@N-GCNT–FD and FeCo@N-GCNT annealed at 800 °C under Ar atmosphere after acid etching. (b) N_2 adsorption/desorption isotherms of FeCo@NGCNT-FD and FeCo@N-GCNT. (c, d) STEM images of FeCo@N-GCNT-FD (inset HRTEM images) and FeCo@N-GCNT (inset HRTEM images), respectively.

The morphology and structure of FeCo@N-GCNT-FD are investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1 and Figure S6 show the typical TEM and SEM images of FeCo@N-GCNT-FD and FeCo@N-GCNT. Both of them exhibit bamboo-like tube loaded with alloy nanoparticles inside. In the case of FeCo@N-GCNT-FD, average tube diameter ranges from 50 to 100 nm and the wall thickness is 2.0±0.5 nm. The high-resolution TEM (HRTEM)

investigation reveals that the lattice fringe spacing of FeCo allow nanoparticles is 0.202 nm, corresponding to the (140) GP/stal plane of FeCo phase. This result agrees with XRD results. The similar morphology and structure are also observed in the case of FeCo@N-GCNT sample, as shown in Figure 1d and Figure S6d-f. However, the N-GCNT display a larger diameter (200~300 nm) in FeCo@N-GCNT. And the HRTEM illustrate that FeCo alloy nanoparticles are enclosed with a ~5.5 nm thickness graphene layers, which is thicker than that in FeCo@N-GCNT-FD. Additionally, Figure S6 and S7 clearly illustrate more FeCo alloy nanoparticles encapsulated in the tube in the case of FeCo@N-GCNT-FD due to nanofibrous produced in the DCDA-FD.

To further analyze the local atomic structure of Co, Fe species in the catalysts, extended X-ray absorption fine structure (EXAFS) absorption spectra were recorded for both FeCo@N-GCNT-FD and FeCo@N-GCNT, respectively. As seen in Figure 2a, the overall spectrum of Co K-edge EXAFS of both samples can be distinguished from the reference Co foil. Fourier transform (FT) is a fundamental step in the data extraction and interpretation of EXAFS spectra.55 The coordination environments of the Co atoms in both catalysts were further corroborated using FT k³-weighted EXAFS spectrum at the Co K-edge (Figure 2b, c). We found that the two samples exhibited one obvious FT peak located at 2.2 Å, which were mainly attributed to the scattering of metal-metal bonding (eg, Co-Co, Co-Fe, Fe-Fe), in comparison with the reference Co foil. Besides, the Fe K-edge EXAFS and FT-EXAFS spectra of the two samples show the similar curves to that of the reference Fe foil (Figure 2d-f), also indicating that the metal-metal bonding could be the main contributor in the asobtained FeCo@N-GCNT-FD and FeCo@N-GCNT. Specifically, FeCo alloy remains after 8 h of harsh acid washing with 0.5 M H₂SO₄ at 85 °C, revealing the high chemical durability of the FeCo alloy encapsulated with doped carbon nanotube, and in turn, preventing the FeCo alloy from oxidation. The result also agrees with the XRD measurement owing to the standard FeCo alloy (JCPDS, No. 65-4131).



Fig. 2 (a, d) Co, Fe K-edges from FeCo@N-GCT-FD and FeCo@N-GNT as well as Co, Fe foils, respectively. (b, c and e, f) Fourier transformed magnitudes of the k³-weighted Co, Fe K-edge EXAFS data and first-shell fit for FeCo@N-GCNT-FD and FeCo@N-GCNT, respectively.

The surface chemical composition and binding energy of the FeCo@NGCT-FD were performed by X-ray photoelectron

Journal Name

Journal Name

spectroscopy (XPS) as shown in Figure 3. The high-resolution Co 2p_{3/2} spectra shown in Figure 3a is deconvoluted into three peaks centered at 779.3 eV, 782.2 and 787.3 eV, which can be attributed to the existence of metallic Co, CoC_xN_y , and $Co-N_y$, Co-O, respectively.^{32, 56, 57} Similarly, the deconvoluted Fe 2p spectrum shows the existence of three different peaks as shown in Figure 3b. The peak located at 707.9 eV is corresponding to the iron with zero state (Fe⁰), which emphasizes the existence of metallic Fe. The broad peaks at 710.5 and 714.2 eV can be assigned to the $2p_{3/2}$ orbitals of Fe²⁺ and Fe^{3+} species, respectively. Interestingly, the peak at 714.2 eV represents an indication of the Fe2+-N bonding. 25, 35, 46, 58, 59 According to the XPS results of the Co and Fe, it can further confirm the presence of the chemical bonding between metal-metal and metal-N in the FeCo@NGCT-FD, respectively. Furthermore, the high-resolution N 1s spectrum (Figure 2c) was divided into two dominant peaks at 398.6 and 401.0 eV, which can be assigned to pyridinic-N (20%) and quaternary-N (53%), and a minor peak at 404.4 eV, which can be attributed to pyridine N-oxides (27%).46, 60, 61 The graphitic N was reported to play a crucial role in oxygen reduction reaction.^{46, 62} Besides, pyridinic N, due to its electron-donating properties, can serve as metal anchoring sites for Fe, Co atoms.⁴⁶ Moreover, in this work, the in situ synthesized N-GCNT can not only provide strong support for the N-coordinated Co, Fe atoms but also regulate the surface electron structure between metal and N-GCNT, which are favorable for ORR catalytic activity (DFT calculation will be discussed in detail).

Furthermore, structural insights were verified by Raman spectra (Figure 3d). Note that well-defined D band (1350 cm⁻¹) and G band (1577 cm⁻¹) can provide information on the disorder and crystallinity of sp² carbon materials, respectively.^{19, 63} On the other hand, the extent of defects in catalysts can be quantified by estimating the relative intensities of ID/IG ratio. The higher ID/IG ratio of 0.84 was obtained when the annealed temperature arrived at 800 °C, implying that the degree of graphitization become higher with annealed temperature increased. The same results of XPS and Raman were obtained in the sample of FeCo@N-GCT as shown in Figure S8.



Fig. 3 High-resolution XPS spectra of a) Co 2p, b) Fe 2p and c) N 1s core levels in FeCo@N-GCNT-FD; (d) Raman spectrum of FeCo@N-GCNT-FD annealed at 600~800 °C.

The electrocatalytic activities of the obtained FeCo@N-GCNT-FD and FeCo@N-GCNT toward ORR were assessed in both 0.1 M KOH

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and 0.5 M H₂SO₄ media. As shown in Figure S9a and Figure S10a, there was no obvious characteristic peak for Feelo@N-GCNT4PD and FeCo@N-GCNT in the N2-saturated 0.1 M KOH media, while a welldefined cathodic peak (FeCo@N-GCNT-FD at around 0.8 V and FeCo@N-GCNT at about 0.78 V) toward ORR was obviously enhanced in O2-saturated KOH solution, indicating a pronounced ORR electrocatalytic activity. Figure 4a shows the linear sweep voltammetry (LSV) of FeCo@N-GCNT-FD, FeCo@N-GCNT, and commercial Pt/C catalysts. Obviously, a great advantage in terms of ORR limiting current (6.8 mA cm⁻²) is observed on FeCo@N-GCNT-FD electrocatalyst. Moreover, FeCo@N-GCNT-FD catalyst displays a positive onset potential (0.96 V vs reversible hydrogen electrode, RHE) than that of FeCo@N-GCNT (0.92 V vs RHE) and Pt/C (0.91 V vs RHE), and the value of the half-wave potential of the FeCo@N-GCNT-FD (0.88 V vs RHE) was 70 mV and 50 mV more positive than that of FeCo@N-GCNT (0.83 V vs RHE) and Pt/C (0.81 V vs RHE), respectively. Importantly, the kinetic current (J_K) , normalized against the electrode geometric area, was calculated from the LSV curve (Figure 4b). The FeCo@N-GCNT-FD calculated electrochemical JK value of 284.7 mA cm⁻² at 0.7 V, which is a typical half-cell cathode potential in an operating fuel cell, is 3.4 times that of FeCo@N-GCNT (84.5 mA cm⁻²) and 5.6 times that of Pt/C (50.6 mA cm⁻²), and exhibited a superior or comparable ORR performance to other nonnoble reference catalysts (Table S1), confirming a satisfied electrocatalytic activity of FeCo@N-GCNT-FD for ORR. In addition, the electrochemically active surface area (ESCA) of the FeCo@N-GCNT-FD and FeCo@N-GCNT were also evaluated by the double-layer capacitances (Cdl) (Figure S9). Obviously, the slope is much higher for the FeCo@N-GCNT-FD than the FeCo@N-GCNT, indicating that the FeCo@N-GCNT-FD have larger active surface areas and thus confirming its high intrinsic activity. Moreover, the electrochemical impedance spectra (EIS) characterization presented in Figure S10 confirmed the overall resistance of FeCo@N-GCNT-FD is much lower than that of FeCo@N-GCNT, benefitting for the charge transfer and mass transfer in the process of ORR.

To further investigate the ORR reaction kinetics and pathways of FeCo@N-GCNT-FD and FeCo@N-GCNT catalysts in 0.1 M KOH solution, rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurement were performed. The FeCo@N-GCNT-FD catalyst percentage of the formed peroxide species during the ORR process and the electron transfer number (n) were calculated from RRDE data (Figure 4c, d). The peroxide species yield (%) of FeCo@N-GCNT-FD is below 15% in the potential range from 0.1 to 0.8 V vs RHE and the average electronic transfer number n is \sim 3.96. Meanwhile, analysis of K-L plots at potentials of 0.48-0.63V vs. RHE for FeCo@N-GCNT-FD and FeCo@N-GCNT catalysts suggest that a four-electron pathway is the dominant catalytic mechanism (Figure S11, Figure S12). To compare the influence of annealed temperature, the ORR activity of FeCo@N-GCNT-FD-x in 0.1 M KOH was measured. As shown in Figures S11, the values of n were calculated about 3.8 and 3.85 for FeCo@N-GCNT-FD-600 °C and FeCo@N-GCNT-FD-700 °C over the potential range of 0.1 to 0.8 V, respectively, suggesting a near-four-electron oxygen reduction process. However, FeCo@N-GCNT-FD-800 °C displays an excellent ORR activity with more positive onset potential, half-wave potential and higher limiting current density (Figure S14) relative to FeCo@N-GCNT-FD-600 °C

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and FeCo@N-GCNT-FD-700 °C. It shows that improvement catalytic activity of FeCo@N-GCNT-FD catalyst not only depends on the morphology but also the degree of graphitization on the sample.

The methanol crossover effect and long-term ORR durability of the electrocatalysts were evaluated through LSV, chronoamperometric measurement at 0.75 V and accelerated durability tests (ADT). As shown in Figure 4e, upon the injection of 1 M methanol into the electrolyte, the FeCo@N-GCNT-FD electrocatalyst exhibits a strong tolerance to methanol, whereas the commercial Pt/C catalyst instantaneously led to a sharp drop of the current density due to the introduction of methanol oxidation reaction on the surface.64 Furthermore, the results shown in Figure 4f reveal that FeCo@N-GCNT-FD electrocatalyst exhibit excellent stability, retaining ca. 93% of the original current density after 12 h continuously running, while the commercial Pt/C retains only ca. 60% of the initial current. Meanwhile, the LSV curves of FeCo@N-GCNT-FD and FeCo@N-GCNT before and after ADT measurement also exhibited a bit degradation in the onset potential and half-wave potential with 30,000 continuous cycles between 0.6 and 1.2 V vs RHE at 200 mV s⁻¹ (Figure S11d, Figure S12d). More importantly, the TEM results (Figure S15) indicate that the morphology of FeCo@N-GCNT-FD, especially the stable thickness of N-GCNT-FD, remains intact after ADT, further confirming the remarkable durability of the FeCo@N-GCNT-FD electrocatalyst, while the N-GCNT thickness of the FeCo@N-GCNT catalyst has slightly changed, which may be attributed to the more suitable thickness between N-GCNT-FD and FeCo than the N-GCNT and FeCo, facilitating the charge transfer between them and further intact strongly²⁸.

In addition, FeCo@N-GCNT-FD catalyst exhibits high activity and excellent stability for ORR not only in 0.1M KOH but also in 0.5 M H2SO4 solution. As shown in Figure S16 and Figure S17, similarly, no obvious featured peak for FeCo@N-GCNT-FD in the N2-saturated 0.5 M H2SO4 solution, whereas a well-defined cathodic peak (FeCo@N-GCNT-FD at around 0.6 V and FeCo@N-GCNT at about 0.53 V) toward ORR was enhanced in O2-saturated 0.5 M H2SO4 solution, indicating a pronounced ORR electrocatalytic activity in acidic media. The ORR polarization curve of FeCo@N-GCNT-FD exhibits onset potential (ca. 0.82 V), but lower than that of the Pt/C catalyst. However, the H2O2 yield on the FeCo@N-GCNT-FD catalyst is below 15% in the potential range of 0.1-0.6 V vs RHE investigated (Figure S17c), also revealing a direct 4-electron-pathway dominated ORR process in acid medium. Moreover, the LSV curves of FeCo@N-GCNT-FD before and after ADT measurement were evaluated. After 10000 CV cycles between 0.6 and 1.2 V vs RHE at 200 mV s⁻¹ (Figure S17d), the onset potential and half-wave potential for FeCo@N-GCNT-FD exhibited only a small negative shift, demonstrating that the FeCo@N-GCNT-FD electrocatalyst also possesses high durability for ORR in 0.5 M H₂SO₄ medium. However, it is a great challenge to enhance the acidic catalytic activity compared with current references, especially the single atomic catalyst (Table S2).

Fig. 4 The electrocatalytic activities of FeCo@N-GCNT-FD and FeCo@N-GCNT. (a) RDE polarization curves of the FeCo@N-GCNT-FD, FeCo@N-GCNT and commercial Pt/C electrocatalysts in O₂-saturated 0.1 M KOH at 1600 rpm. (b) Histogram of the specific activity of FeCo@N-GCNT-FD, FeCo@N-GCNT and commercial Pt/C at different potentials. (c) RRDE curves of FeCo@N-GCT-FD at 1600 rpm. (d) Peroxide percentage and electron transfer number (n) of FeCo@N-GCNT-FD within the potential range of 0.1 V to 0.8 V. (e) RDE voltammetric responses to injection of 1 M methanol into O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ for FeCo@N-GCNT-FD catalyst. (f) Chronoamperometric responses of FeCo@N-GCNT-FD and commercial Pt/C electrocatalysts at 0.75 V in O₂-saturated 0.1 M KOH, which are normalized to the initial current responses.

To further clarify the mechanism of the enhanced activity for ORR, DFT theoretical calculations were performed. According to the results of N 1s XPS spectra only containing pyridinic-N (Nprid) and graphic N (N_G), the structures of FeCo@N_G-GCNT and FeCo@N_{prid}-GCNT were modeled and optimized, respectively, by a Fe₂Co₂ cluster and a Fe2Co2 cluster encapsulated in NG-or Nprid-doped (6, 6) single-walled GCNT (Figure 5a-d), which have been utilized as validated geometries in the previous study.^{27, 35} Figure 5c and 5d illustrate the isosurface plots of charge density of the Fe₂Co₂ cluster interfacing with NG-GCNT and N_{prid}-GCNT, respectively. It is evident that the significant charge redistribution occurs between the FeCo alloy cluster and N-GCNT interface, which induces amounts of electron transfers from the FeCo alloy clusters to N-GCNT and thus further enhances the catalysts' activity. However, the FeCo@NG-GCNT structure possesses an obvious more suitable electrostatic charge than the compound of FeCo@Nprid-GCNT, which is more beneficial for the adsorption of oxygen species.

Page 6 of 9



Journal Name



Fig. 5 (a, b) The optimized geometry of bare N_G-GCNT and N_{Pyrid}-GCNT, respectively. (c, d) The isosurface of charge density variation in FeCo@N_G-GCNT and FeCo@N_{Pyrid}-GCNT, respectively. Green area denotes charge density decrease and yellow area denotes charge density increase. e) DFT-calculated free-energy diagram for ORR on bare N_G-GCNT, FeCo@N_G-GCNT and FeCo@N_{Pyrid}-GCNT catalyst surfaces. The above diagrams show the adsorption geometry of O₂, *OOH, *O, and *OH on the electrocatalysts.

The mechanistic details are shown in Figure 5e, which exhibits free-energy paths obtained using DFT calculations for the relevant adsorbed reaction intermediates involved in ORR on bare NG-GCNT, FeCo@Ng-GCNT, and FeCo@Nprid-GCNT. Obviously, the free energy diagram illustrates that the three structures occur decline tendency, confirming all electron transfer steps to be exothermic in ORR.^{35, 65} For N_G-GCNT, the smallest Gibbs free energy change ΔG_1 of four reaction steps indicates that the most sluggish reaction step is the hydrogenation of adsorbed O2 that represents the rate-limiting step for ORR, which is agreement with the previously reported heteroatom-doped carbon-based materials.⁶⁶ The smallest ΔG_4 , as a significant benchmark to estimate the kinetics of the ORR, demonstrates that the fourth electron transfer reaction is the ratelimiting step. Specifically, for FeCo@NG-GCNT and FeCo@Nprid-GCNT, the calculated Uwork(ORR) values are 0.26 V (N-GCNT), 0.56 V (FeCo@Nprid-GCNT), and 0.64 V (FeCo@NG-GCNT), respectively, leading to a higher catalytic ORR performance increasing in the order of N-GCNT < FeCo@Nprid-GCNT < FeCo@NG-GCNT. Therefore, DFT calculations, well consist with the XPS fitting results and the above isosurface of charge density variation, highlight the synergetic and electronic effects between FeCo alloy and N-GCNT in producing suitable surface electronic environment and in turn enhancing the catalytic activity toward ORR.

Conclusions

In conclusion, we have synthesized FeCo alloy catalyst encapsulated in N-doped graphitic carbon nanotubes with a high surface area, which was fabricated by freeze-drying assembled dicyandiamide nanostructure precursor as N and C sources, in the role of greatly efficient non-precious electrocatalysts for ORR. The electrocatalytic measurements showed that FeCo@N-GCNT-FD displayed superior electrocatalytic activity, durability and methanol tolerance in alkaline solution, suggesting the potential of their fuel cell practical applications. Theoretical investigations demonstrated that the strong synergetic and electronic effects caused by FeCo alloy and N-doped carbon nanotubes played a vital role in the high ORR activity of FeCo@N-GCNT-FD. This work can broaden the design strategies for low-cost and high-performance view Apprecients catalysts with controllable metal species of the the controllable carbon-based materials.

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The catalytic performance of FeCo@N-GCNT-FD catalyst exhibits enhanced intrinsic activities and excellent durability for oxygen reduction reaction.

