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Atomically ordered intermetallic PdZn coupled with Co Nanoparticles: as 10.28/DOTA06682F highly dispersed dual catalyst chemically bonded to N-doped carbon for boosting oxygen reduction reaction performance

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Abstract

In this work, a dual catalyst composed of atomically ordered intermetallic PdZn and Co nanoparticles was synthesized and chemically bonded to nitrogen-doped carbon by simultaneously modulating the lattice spacing of Pd nanoparticle guest and the metal centers of the zeolite imidazolate framework (ZIF) host through a one-step heating procedure. Results reveal that the ability of PdZn alloy to catalyze oxygen reduction reaction can be regulated by adjusting the lattice spacing between Pd-Pd through the formation of the ordered PdZn, resulting from Zn^{2+} in ZIF-8 host lattice diffusing into Pd phase. Meanwhile, the secondary active sites (Co nanoparticles) and N-doped carbon (particularly N-doped carbon nanotubes) carrier are obtained by doping Co^{2+} into ZIF-8 host lattice, which can further improve the catalytic activity. The characterization results show the existence of Pd-N and Co-N bonds between the dual catalyst and the carrier, which can be regulated by controlling the synthesis conditions, such as the atomic ratios of Pd guest to Zn in ZIF-8 host, pyrolysis

temperatures, and doping Co²⁺ into ZIF-8 host lattice. The dual catalyst bonded to view Article Online N-doped carbon exhibits high ORR catalytic activity with a desirable onset potential (0.916 V), and diffusion-limiting current density (~5.70 mA cm⁻²), superior to other reported Pd-based catalysts and comparable to commercial Pt/C. Moreover, the chemical bonds between the dual catalyst and the carrier results in the dual catalyst with a small size of 5.9 nm and prolonged electrochemically active duration (no obvious change of the half peak potential after 2000 cyclic voltammetry cycles and 90.6 % current retention after a 4 h chronoamperometric test). Thus, the highly dispersed ordered-PdZn/Co on N-doped carbon is a promising substitute to the commercial Pt/C for alkaline fuel cells.

Keywords: Atomically ordered intermetallic PdZn, Co nanoparticle, N-doped carbon, Zeolite imidazolate framework, Oxygen reduction reaction

1. Introduction

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Fuel cells, based on directly converting the chemical energy of fuels into electrical energy without the limitation imposed by the Carnot efficiency, are an ideal power source with high fuel conversion efficiency, high energy density, low emissions of CO₂ and other pollutants, and quiet operation.¹⁻³ Among various fuel cells, alkaline fuel cells exhibit easier electrode reactions and a higher efficiency at low temperatures.⁴ However, the performance of alkaline fuel cells is severely limited by oxygen reduction reaction (ORR) at the cathode, which has a sluggish kinetics, several orders of magnitude slower than that of fuel oxidation reaction at the anode.^{5,6} Therefore, many efforts have been devoted to improve the performance of ORR by rationally designing and synthesizing suitable electrocatalysts.

Nowadays, Pd-based catalysts have attracted extensive research interest because of their relatively low costs, excellent methanol-tolerance, and high catalytic activity in alkaline media, although the catalytic activity of pure Pd is not enough to replace Pt in fuel cells.⁷⁻⁹ According to the Sabatier principle,^{10,11} the catalytic performance of Pd-based catalysts for ORR can be regulated by altering the lattice spacing between Pd-Pd and thereby adjusting the binding affinity of the active sites of the catalysts to

the substrate (O₂).¹² Adding secondary metals (such as Zn, Cu, Fe, Co or Ni)¹² with PDDTA06682F different lattice constants has been proven an effective approach to modulate the lattice spacing between Pd-Pd, which plays a crucial role in the catalytic performance for ORR. Bampos et al. confirmed that PdZn/C had the most positive onset potential (0.80 V *vs.* reversible hydrogen electrode) and the highest catalytic activity for ORR among a series of carbon-supported Pd-M alloys (M=Ni, Ag, Co, Cu, Fe, Zn).¹⁶ However, in these alloy phases, the secondary metal atoms are generally randomly distributed in Pd phase to form disordered solid solutions without local preference.^{17,18}

Recently, several studies demonstrated that atomically ordered intermetallic nanoparticles with defined stoichiometry and crystal structures exhibited superior catalytic activity, long-term stability, and poison tolerance for ORR, compared to their disordered counterparts.¹⁹⁻²² The enhanced performance of the ordered intermetallic nanoparticles has been attributed to their atomically uniform active sites, more negative enthalpy of mixing and stronger heteroatomic bonding between Pd and the secondary metal atoms.¹⁷ One traditional method to prepare ordered intermetallic nanoparticles is to anneal alloy nanoparticles at high temperatures in order to facilitate inter-diffusion and equilibration of metal atoms.²³ However, during annealing procedure, nanoparticles inevitably aggregate and form large-size particles (>10 nm) with limited surface-exposed active sites.²⁴ Dispersing nanoparticles into different matrices prior to heating process is an effective approach to address the problem.²⁵ Lee and co-workers coated 2.7 nm PtFe alloy nanocrystals with silica shells to prevent the nanocrystals from sintering up to 850 °C. But the silica shells need to be removed after the heating process in order to expose the ordered alloyed nanoparticles.²⁶ Zeolite imidazolate frameworks (ZIFs) are now widely used as a support to disperse metal nanoparticles with controlled particle sizes by virtue of the confinement effect of the micropores in ZIFs.²⁷⁻²⁹ However, the uniform microporous structure of ZIFs blocks the diffusion of reactants near to the catalyst surface, and the high electrical resistivity of ZIFs indicates their poor electron transfer ability. Both of these factors impede the effective use of ZIFs in electrochemical catalysis. Therefore, to overcome these drawbacks, annealing ZIFs at high temperature to form porous carbon has

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attracted increasing attention.³⁰⁻³³ Wang et al. used Co-incorporated ZIF-8 topprepare/DOTA06682F Co-doped porous carbon through a calcination process, and then utilized the Co-doped porous carbon as the support to prepare 5-nm intermetallic Pt₃Co nanoparticles through an additional calcination procress.³⁴ Hu et al. employed porous carbon derived from ZIF-8 to disperse Pd precursors and then prepared uniform intermetallic PdZn nanoparticles through a heat treatment at 400 °C under H₂ atmosphere.²⁴ All these intermetallic nanoparticles supported on ZIF-derived porous carbons exhibit an enhanced electro-catalytic performance in ORR. However, most of these synthetic processes involved porous carbon as a carrier, which had been synthesized during extra calcination process, resulting in higher cost and tedious operations. Furthermore, the interaction between the intermetallic nanoparticles and their carriers is usually under relatively weak control, thus the nanoparticles are prone to migration and aggregation during the calcination procedure, leading to the loss of surface area and electrochemical activity.³⁴⁻³⁶ Therefore, to date, it still remains a great challenge to fabricate ultra-small (< 10 nm) intermetallic nanoparticles with enhanced bonding with their carriers through a one-step heating process.

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Herein, a dual catalyst containing ordered PdZn (o-PdZn) and Co nanoparticles was synthesized with an average particle size of 5.9 nm through a one-step heating process of Pd nanoparticles hosted in Co²⁺-doped ZIF-8. As described in Scheme 1, starting from Pd nanoparticles hosted in ZIF-8 with a Pd to Zn molar ratio of 0.05, PdZn nanoparticles loaded on NC were prepared with the modulated lattice spacings by adjusting the Pd to Zn molar ratios and heating temperatures. During the heating treatment, the atomically dispersed Zn²⁺ ions from ZIF-8 diffuse into Pd phase to form o-PdZn nanoparticles with regulated lattice spacing between Pd-Pd. Simultaneously, from the starting material, Co²⁺ was introduced into ZIF-8 lattice to produce Co nanoparticles as secondary active sites. At the same time, the Co species catalyze the carbonization process of the nitrogen-containing organic linkers in ZIF-8 host to produce various N-doped carbon materials (NC), especially N-doped carbon nanotubes (CNTs), as the carrier of the dual catalyst. Finally, in the optimized conditions, a highly dispersed dual catalyst supported on NC (referred to as

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o-PdZn/Co/NC) was synthesized. Results show that there are chemical bonds between/DOTAGGB2F N atoms in the NC carrier and metal atoms (Pd and Co), which yields a dual catalyst with an ultra-small particle size of 5.9 nm. The as-prepared catalyst exhibits high ORR performance, such as a desirable onset potential (0.916 V), excellent diffusion-limiting current density (~ 5.70 mA cm⁻²) and long-term durability (essentially no change in $E_{1/2}$ after 2000 cyclic voltammetry (CV) cycles and 90.6% current density retention after a 4-h chronoamperometric test). The excellent performance on ORR makes this catalyst a promising substitute to the Pt/C for alkaline fuel cells.

2. Experimental Section

2.1 Chemicals

Zn(NO₃)₂·6H₂O (99.0%), Co(NO₃)₂·6H₂O (99.0%), 2-methylimidazole (98.0%), and Na₂PdCl₄ (>98%) were purchased from Aladdin Chemistry Co. Ltd. NaBH₄ (96%), and methanol (\geq 99.5%) from Sinopharm Chemical Reagent Co. Ltd. Commercial 20 wt% Pt/C (HiSPECTM 3000) was obtained from Johnson Matthey. All the other chemicals were of analytical grade (AR) and used as received. Ultrapure water (18.2 MΩ·cm) was prepared from a Thermal Smart2 water purification system (USA).

2.2 Synthesis of electrocatalysts

For ZIF-8 synthesis, 2.453 g Zn(NO₃)₂·6H₂O and 5.419 g 2-methylimidazole were separately dissolved in 50 mL of methanol, and then were mixed up and stirred at room temperature for 2 h. After centrifugation, ZIF-8, the powdery product, was washed with methanol three times, and dried at 80 °C overnight. The Co-centered ZIF, denoted as ZIF-67, was synthesized through the same steps as above except that Zn(NO₃)₂·6H₂O was replaced with Co(NO₃)₂·6H₂O, while bimetallic ZIF (BiM-ZIF) containing Co and Zn was synthesized by changing Zn(NO₃)₂·6H₂O to a mixture of Zn(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O with different molar ratios of Co to Zn.

To synthesize of Pd nanoparticles supported on ZIFs, 10 mL Na₂PdCl₄ aqueous solution with different concentrations was added into 20 mL aqueous dispersion containing 150 mg ZIF-8, ZIF-67 or BiM-ZIF. The mixture was stirred under a

vacuum environment for 1 h, filtered and washed with ultrapure water for three times/DOTA06682F

to get rid of the $PdCl_4^{2-}$ unabsorbed on the ZIF. Then, the obtained powder was re-dispersed into 20 mL water, in which a certain volume of 1.5 mg mL⁻¹ NaBH₄ aqueous solution was quickly added. The molar amount of NaBH₄ was at least three times larger than that of Pd²⁺. The reaction lasted for 2 h under stirring. After filtration and washing with water for three times, Pd nanoparticles supported on ZIF-8, ZIF-67 and BiM-ZIF (Pd@ZIF-8, Pd@ZIF-67 and Pd@BiM-ZIF, respectively) were obtained by vacuum drying at 60 °C for 12 h. Then, the harvested powders were carbonized in a tube furnace (CTF 12/65/550, Carbolite Gero Ltd., United Kingdom) under N₂ flow at a heating rate of 5 °C min⁻¹ to reach a carbonization temperature in the range from 700 to 1100 °C and held for 3 h to obtain electrocatalysts denoted as PdZn/NC, Pd/Co/NC and PdZn/Co/NC, respectively.

2.3 Material characterizations

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The morphology and the structure of the as-prepared nanostructured materials were studied by using field-emission scanning electron microscopy (SEM, Ultra Plus, Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). Atomic resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images, elemental mapping, and high-resolution TEM (HRTEM), were acquired with 300 KV high-resolution TEM (Theims Z, FEI, USA). Structural information was obtained using X-ray diffraction (XRD) via a high-speed detector (D/teX-Ultra, Rigaku, Japan) with graphite-monochromated Cu K_{α} radiation sources. Nitrogen adsorption-desorption isotherms were measured at 77 K with the one-station adsorption instrument (Autosorb iQ, Quantachrome, USA). Samples were degassed at 150 °C for 24 h at reduced pressure before measurement. The total surface areas were calculated through the Brunauer-Emmett-Teller (BET) method. Raman spectra were recorded on a spectrometer (DXR 532, Thermo, USA) with a 532 nm laser excitation. Chemical information was obtained using X-ray photoelectron spectroscopy (XPS, ESCALAB Xi⁺, Thermo Fisher, USA) with an Al K_{α} X-ray monochromator.

2.4 Electrochemical measurements

The electrochemical characteristics were investigated in a standard three-electrode system on a CHI700E electrochemical workstation (CH Instruments, USA), comprising a reference electrode (Ag/AgCl saturated with KCl), a counter electrode (Pt wire), and catalyst modified working electrode (glassy carbon or rotating ring-disk electrode with disk electrode diameters of 3 mm and 4 mm, respectively). Carbon rod was also used as counter electrode to eliminate the possible interference of platinum wire as a counter electrode. To modify the working electrode, 2 mg electrocatalyst was dispersed into 1 mL ultrapure water through sonication to form a uniform suspension, and 10 μ L of the suspension was drop-casted onto the working electrodes. After the catalyst was dried in a desiccator, 5 µL Nafion solution (0.05 wt%) was drop-casted on the catalyst surface. Polarization curves were obtained by using rotating ring-disk electrode (RRDE-3A, BAS, Japan) in O₂-saturated 0.1 M KOH and nitrogen background at a scan rate of 10 mV s⁻¹, while the ring potential was constant at 0.5 V vs. Ag/AgCl. The electrochemical surface areas (ECSA) were determined, based on the electrochemical double layer capacitance (Cdl) in non-Faradaic potential region of CV measurements, which were carried out in a potential range from 0.36 to 0.46 V vs. Ag/AgCl at different scan rates.³⁷ The chronoamperometric measurement was carried out at 0.7 V. Accelerated durability tests were conducted by CV in a potential range from 0.55 to 0.97 V, at a scan rate of 250 mV s⁻¹. All the potentials in this article were referred to reversible hydrogen electrode (RHE) unless stated otherwise.

3. Results and discussion

3.1 Characterization of electrocatalysts

Zn-centered ZIF-8 with a rhombic dodecahedral morphology was firstly synthesized by sedimentation method, which possesses a large specific surface area of 1663.740 m² g⁻¹ and uniform microporous structure with pore volume of 0.617 cm³ g⁻¹ (Fig. S1a and Fig. 1a). When ZIF-8 was impregnated in Na₂PdCl₄ precursor solution, the existing capillary pressure in the MOFs can cause the solution to spontaneously penetrate the interior voids of the MOFs.²⁷⁻²⁹ Moreover, during the impregnation procedure, another protocol, a vacuum environment, was adopted to make the channet/DOTA06682F full of the precursor solution. After NaBH₄ aqueous solution was quickly added, Pd nanoparticles is loaded in the channels of ZIF-8 via a wet-chemical reduction process. The as-prepared Pd@ZIF-8 shows a same morphology to that of ZIF-8 with a statistical average particle size of about 150 nm (Fig. 1b). TEM analyses indicate that Pd nanoparticles are uniformly dispersed in the porous structure of ZIF-8 with average sizes of about 1.6 nm (Fig. 1c). BET measurement indicates that both the microporous surface area and volume of Pd@ZIF-8 decrease with the increase of the molar ratio of Pd guest to Zn in ZIF-8 host (r), indicating that Pd nanoparticles are confined in the micropores of ZIF-8 (Table S1). However, the surface area and volume of Pd@ZIF-8 are as high as $1277 \pm 2 \text{ m}^2 \text{ g}^{-1}$ and $0.46 \pm 0.03 \text{ cm}^3 \text{ g}^{-1}$, respectively, for r = 0.35. The XRD patterns of Pd@ZIF-8 are identical to that of the pristine ZIF-8 and no characteristic diffraction peaks of metal Pd are observed (Fig. 1d, Fig. S1b and Fig. S1c) when the Pd to Zn molar ratios in the range from 0 to 0.35. This may be caused by the relatively low loadings and small sizes of the Pd nanoparticles with high dispersity.^{25,38} While when the Pd to Zn molar ratios increase to 0.40, a crystal diffraction peak of Pd (111) at 40° appears. This means that only if the amount of Pd is not excessive (the Pd to Zn molar ratios ≤ 0.35), the Pd nanoparticles with small sizes can be distributed homogeneously in ZIF-8, which is beneficial for the formation of o-PdZn during calcination. When a certain proportion of Zn is replaced with Co, the resulting BiM-ZIF has the same rhombic dodecahedral morphology as ZIF-8 and Pd@ZIF-8 (Fig. S1d). The XRD patterns support that BiM-ZIF possesses the same high crystallinity and similar unit cells as well as crystal lattices as ZIF-8 and ZIF-67 alone (Fig. S2a).³⁹ After Pd nanoparticles loaded, Pd@BiM-ZIF reveals a similar XRD pattern, verifying that the Pd nanoparticles are well-confined in the BiM-ZIF crystalline structure, which is consistent with the TEM image of Pd@BiM-ZIF (Fig. S2b).

The Pd@ZIF-8 and Pd@BiM-ZIF were carbonized through a thermal treatment at different temperatures under N_2 atmosphere to obtain PdZn/NC and PdZn/Co/NC, respectively. TEM analysis shows that PdZn/NC has an overall hexagon projection

similar to Pd@ZIF-8, but the Pd nanoparticles are enlarged to about 5.3 nm (Fig.12a)?/DOTA06682F HAADF-STEM image and the corresponding elemental mapping for C, N, Pd, and Zn demonstrate that Pd and Zn are distributed synchronously and homogeneously on the NC matrix (Fig. 2b). Interestingly, after the Zn in the ZIF matrix was partly replaced with Co, the TEM image of PdZn/Co/NC indicates the formation of tubular antennas acting as a bridge to connect the carbon carriers, which demonstrates that the doping of Co can catalyze the N-containing organic linkers to form N-doped CNTs (Fig. 2c). Along with the formation of N-doped CNT, the metal nanoparticles grow to about 5.9 nm, slightly larger than those of PdZn/NC. XRD pattern of the PdZn/NC exhibits characteristic peaks at 26.8°, 30.8°, 41.2°, 44.1°, 54.4°, 64.2°, 72.7°, and 79.2° (PDF card 06-0620), suggesting the formation of ordered PdZn instead of the initial Pd nanoparticles (Fig. 3a). Consistent with the XRD result, HRTEM analysis of PdZn/NC displays the lattice fringes of o-PdZn (111) and (200) plane with an inter-planar spacing of 0.22 nm and 0.21 nm, respectively (Fig. 3b).⁴⁰ To observe the crystal structure of PdZn/NC on the atomic scale. STEM operated at 300 KV was carried out. As shown in Fig. 3c, along the (010) direction, the ordered crystal structure of PdZn is visualized from the atomic resolution HAADF-STEM image. It can be observed that the lattice spacings of 2.9 Å and 3.3 Å indicate the (100) and (001) planes of o-PdZn, which are consistent with the theoretical values of 2.9 and 3.4 Å (o-PdZn, PDF No. 01-072-2936), respectively.¹⁷ Because the light intensity (I) of the atomic resolution HAADF-STEM image is proportional to the atomic number (Z), $I \propto Z^{1.7}$, the bright spots represent Pd atoms and the grey spots represent Zn atoms. It can be seen that Pd atoms are piled into a periodic square array and each Zn atom packs into the center of the square composed of four Pd atoms (Inset of Fig. 3c). Therefore, it is reasonable to infer that the o-PdZn has a body-centered cubic crystalline structure with a stoichiometric ratio of Pd to Zn at 1:1 as shown in Fig. 3d. The line-scan profile for the PdZn nanoparticle (Fig. 3e, dash line) indicates that Pd and Zn uniformly distributed in the same single crystal (Fig. 3f). This uniform intermetallic structure may be due to the fact that the atomically dispersed Zn in ZIF-8 matrix diffuses into Pd nanoparticles. Similar to those in PdZn/NC, the PdZn

nanoparticles in PdZn/Co/NC are also observed with highly crystalline natureDand the/DOTA06682F

lattice spacing of 0.22 nm for o-PdZn alloy (111) (Fig. S3a). In addition, Co nanoparticles and nanostructured carbon present lattice spacing of 0.20 and 0.34 nm in HRTEM of PdZn/Co/NC (Fig. 3d and Fig. S3a), representing the planes of Co (111) and graphitic C (002), respectively. Furthermore, line-scan of one PdZn nanoparticle (Fig. S3b, dash line) indicates that Pd and Zn are also synchronously distributed in the same single crystal (Fig. S3b). Therefore, the doping of Co into ZIF-8 matrix maintains the atomically order intermetallic structure of PdZn alloy.⁴¹ The formation of graphitic C is affirmed by the Raman measurements (Fig. S4). Because of the D band at 1350 cm⁻¹ corresponding to the edge defects and the G band at 1580 cm⁻¹ assigned to the *sp*²-bonded graphitic carbon,⁴² the lower intensity ratio of the D band to G band (I_D/I_G) for the PdZn/Co/NC suggests a higher graphitization of its NC carrier, comparing with the PdZn/NC without Co component.

To examine the binding nature of PdZn/NC and PdZn/Co/NC, XPS measurements were carried out. As depicted in Fig. 4a, for PdZn/NC, the Pd 3d region of the spectra shows binding energies at 335.2, 335.7 and 337.9 eV corresponding to metal Pd, PdZn alloy and highly oxidized Pd respectively.^{43,44} Meanwhile, the high-resolution N 1s region of the spectrum in Fig. 4b presents five peaks centering at 398.5 ± 0.2 , $399.2, 400.5 \pm 0.3, 401.1 \pm 0.3$ and 405.6 eV, corresponding to pyridinic N (42.09%), Pd-N (17.4%), pyrrolic N (19.73%), graphitic N (8.72%) and oxidized N (12.06%), respectively.45 Both the highly oxidized Pd and the peak of Pd-N indicate the formation of chemical bonds between PdZn alloys and their NC carriers, which is attributed to the electron transfer from Pd 3d to N 2p, thus resulting in highly oxidized Pd.⁴⁰ Similar to the PdZn/NC, the chemical bonds between PdZn and N in carrier also exist in PdZn/Co/NC according to its high-resolution Pd 3d and N 1s spectral regions (Fig. 4a,b). It is interesting to note that graphitic N (32.68%) and metal-N (30.91%) are the major N species in PdZn/Co/NC, and the atomic contents of graphitic N and metal-N in PdZn/Co/NC are larger than those of PdZn/NC (Fig. 4c). This implies that the doping of Co into the host lattice has a positive effect on increasing the amount of metal-N and graphitic N species during pyrolysis. Furthermore, the high-resolution

Co 2p region of the spectrum reveals peaks of metallic Co (778.5 eV), $\mathbb{CON}_{x} - \mathbb{C}_{y}^{\text{View Article Online}}$ (780.5 eV), and Co-N_x (782.5 eV) species (Fig. 4d),⁴⁵ indicating the formation of chemical bonds between Co nanoparticles and C, N atoms in carbon matrix. All these results demonstrate that the electrocatalysts with PdZn nanoparticles (around 5 nm)

and Co nanoparticles are assembled on NC carrier through chemical bonds.

3.2 Electrochemical activity of PdZn/Co/NC towards ORR

The electrochemical characteristics of the as-prepared nanomaterials were examined by cyclic voltammetry. Besides Pt wire counter electrode, carbon rod counter electrode was also applied in case of the possible interference. As shown in Fig. S5a, LSV curves with carbon rod counter electrode is identical to that with Pt counter electrode, which means that the Pt counter electrode is as effective as carbon one. Therefore, the Pt wire counter electrode were used in the following electrochemical tests. Well-defined cathodic peaks are observed in O₂-saturated 0.1 M KOH. The peak potentials are located at 0.861, 0.795, 0.806, 0.663, 0.574, 0.604 and 0.567 V for PdZn/Co/NC, Co/NC, PdZn/NC, Pd@BiM-ZIF, BiM-ZIF, Pd@ZIF-8, and ZIF-8, respectively (Fig. 5a). Thus, either the introduction of Pd nanoparticle guest or the doping of Co into host lattice can improve the ORR performance of ZIF-8, and after heating treatment the PdZn/Co/NC and PdZn/NC achieve even better electrocatalytic activity towards ORR. This might be caused by the formation of highly dispersed o-PdZn supported on N-doped graphitic carrier. Therefore, introducing Co ions into ZIF-8 host skeleton before the Pd loading and thermal treatment can yield a more effective electrocatalyst (PdZn/Co/NC). Briefly, the excellent electrocatalytic activity of PdZn/Co/NC is due to (1) the formation of highly dispersed o-PdZn alloy on N-doped carbon carrier; (2) Co nanoparticles acting as active sites for ORR; and (3) the formation of N-doped carbon nanotubes and the graphitic C possessing superior charge mobility in their atomic matrix.⁴⁶ The ORR polarization curves show that PdZn/Co/NC has an onset potential (E_{onset}) of 0.916 V, much higher than those of PdZn/NC, Co/NC, Pd@BiM-ZIF, BiM-ZIF, Pd@ZIF-8, and ZIF-8, which are 0.849, 0.849, 0.725, 0.676, 0.662, 0.648 V, respectively (Fig. Moreover, a high diffusion-limiting current density of 5.70 mA cm⁻² is obtained 5b).

for PdZn/Co/NC, which is slightly higher than that of 5.20 mA cm⁻² for PdZn/NC⁰and^{1/D0TA06682F}

about 1.3, 3.3, 4.6, 4.2, 6.1-fold higher than those of Co/NC, Pd@BiM-ZIF, BiM-ZIF, Pd@ZIF-8, and ZIF-8, respectively (Table S2). Interestingly, PdZn/Co/NC with Pd weight of 11.42% exhibits comparable ORR performance to the commercial 20% Pt/C with similar E_{onset} , half-wave potential ($E_{1/2}$) and diffusion-limiting current density. In addition, PdZn/Co/NC has a similar Tafel slope (~60 mV dec⁻¹) to commercial Pt/C, but the overpotential is lower than that of Pt/C under the same kinetic current density (Fig. S5b). Based on Koutecky-Levich Equation, a 4-electron reduction process of oxygen is verified for PdZn/Co/NC (Fig. S6). Normalized based on the ECSA, the kinetic current of PdZn/Co/NC is calculated to 1.19 mA cm⁻² (0.75 V), which is 4.1, 2.6, 1.2-fold larger than those of Co/NC, PdZn/NC, and Pt/C, respectively (Fig. S7). All these results confirm that the ORR performance of PdZn/Co/NC is better than those of Pd-based and Co-based metal catalysts in literature,⁴⁴⁻⁴⁹ which were not supported or loaded on supports, like reduced graphene oxide (rGO) and TiO₂, through simple wet impregnation reduction method (Table S3).

The ORR activity of as-synthesized materials is dependent on the molar ratios of Pd and Zn (r), Co doping percentage and pyrolysis temperature during the preparation of electrocatalysts. Polarization curves are presented in Fig. 6a to evaluate the ORR activity of as-synthesized materials. Based on the polarization curves, the kinetic current densities, $J_{\rm K}$, are calculated, based on the polarization curves according to Koutecky-Levich Equation, as shown in Fig. 6b. It can be seen that when r = 0, the as-prepared electrocatalyst without Pd component exhibits an unsatisfactory ORR performance ($E_{\rm onset} = 0.761$ V and $J_{\rm K} = 0.56$ mA cm⁻²). With the increase in Pd loading, the limited diffusion current densities of the PdZn/NC with r = 0.35 exhibits the highest kinetic current density of 7.78 mA cm⁻², which is 13.9, 4.8, 1.9, 1.6, 2.7, 11.1-fold those of PdZn/NC with r = 0, 0.05, 0.20, 0.30, 0.40, and 0.50, respectively. The onset potentials of PdZn/NC show the same trend as the limited diffusion current densities, but the onset potentials of

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PdZn/NC vary over a very small range. At r = 0.50, the onset potential is the /DOTADGEREF minimum and negatively shifts about 45 mV from the highest onset potential for r = 0.35. The half-wave potentials follow the same trend as that of onset potential, in which half-wave potentials increase from 0.614 to 0.766 V in the range from r = 0 to r = 0.35, and negatively shifts 45 and 80 mV for r values of 0.40 and 0.50, respectively. Tafel plots of PdZn/NC with different r values (Fig. 6c) show that the Tafel slopes decrease to 57.6 mV dec⁻¹ with the increase of Pd loading to 0.35, and then increase by raising Pd loading from to 0.50.

The effect of pyrolysis temperatures on the electrochemical properties of the PdZn/NC was also investigated. It can be seen from Figs. 6d, 6e and 6f that the onset potentials and half-wave potentials of PdZn/NC obtained from 700 to 900 °C exhibit a dramatically positive shift. At the same time, kinetic current densities increase from 0.01 to 7.78 mA cm⁻² and Tafel slopes decrease from 121.4 to 57.6 mV dec⁻¹ (Fig. 5e). At higher temperatures, the onset potential, half-wave potential, and Tafel slope tend to reach their limits, while the kinetic current density decreases to 7.22 and 4.24 mA cm⁻² for 1000 and 1100 °C, respectively. From all these electrochemical measurements, it can be concluded that the PdZn/NC at r = 0.35 and pyrolysis temperature of 900 °C displays the most positive E_{onset} (0.849 V) and $E_{1/2}$ (0.766 V), the largest kinetic current density (7.78 mA cm⁻²), and the smallest Tafel slope of 57.6 mV dec⁻¹ in the low overpotential zone, indicating an enhanced catalytic activity and the least polarization in the same potential window for ORR.53,54 Besides, for all the PdZn/Co/NC prepared using BiM-ZIF as the matrix, the sample with Co to Zn molar ratio of 0.4 displays the most positive onset potential and half-wave potential, which are slightly higher than those of its analogues with different Co contents. All the PdZn/Co/NC catalysts show higher onset potentials and half-wave potentials than those of catalysts prepared with single metal (Zn or Co) in the ZIF matrix (Fig. S8). When Co is doped in catalysts, its onset potential positively shifts by 70 mV compared with PdZn/NC, and 20 mV compared with the catalyst derived from the Pd nanoparticles hosted in ZIF-67 (only containing Co metal atoms) (Fig. S8). The high onset potential and half-wave potential of PdZn/Co/NC can be attributed to the

formation of Co nanoparticles and carbon tubular antennas during the carbonized/DOTA06682F process (Fig. S9).

TEM images of PdZn/NC show that the particle size is enlarged with increasing of Pd loading (Fig. S10). With excessive Pd in precursor (r = 0.50), a severe agglomeration of nanoparticles with a wide distribution is observed, which is disadvantageous to the catalyst activity.^{24,34} XRD measurements were also performed to explore the relation between ORR performance of PdZn/NC and Pd to Zn molar ratio as well as pyrolysis temperature (Fig. 7a). When r is less than 0.35, no diffraction peaks at 40.2°, 46.8°, and 68.3° are observed for PdZn/NC, demonstrating that no pure Pd phase is formed during the carbonization process. Instead, all the Pd nanoparticles transform into disordered PdZn (d-PdZn) and o-PdZn with ordered intermetallic PdZn structure (PDF card 06-0620). Due to the smaller diameter of the doped Zn atoms than that of Pd atoms, the crystal plane spacing of d-PdZn contracts by 1.23% compared to the pure Pd phase. Therefore, the (111) peak of d-PdZn emerges at higher angle (40.7°) than that of Pd (40.2°) in accordance with Bragg's law.¹⁹ In contrast, the crystal plane spacing of the o-PdZn contracts by 11.0% in the c direction and expands by 5.45% in the a and b directions due to its atomically order intermetallic structure. As a result, the (111) peak of o-PdZn appears at the highest angle (41.2°), verifying the smallest crystal plane spacing in the (111) orientation. When r reaches 0.35, the peaks associated with d-PdZn disappear and only the peaks from o-PdZn are observed. When the Pd guest is excessive (r > 0.35), both pure Pd phase and o-PdZn co-exist. Thus, the PdZn/NC with r = 0.35 has only o-PdZn component with the smallest lattice spacing of Pd-Pd, showing the best catalytic activity. Hence, the formation of PdZn alloy with atomically order intermetallic structure is the key player for the excellent ORR of PdZn/NC by weakening the O₂ affinity to Pd surface and enhancing its ORR activity.¹² On the other hand, PdZn/NC prepared by heating at low pyrolysis temperatures of 700 and 800 °C show a poor crystallinity of the metal phase with a broad XRD peak around 40°, indicating the coexistence of the Pd, d-PdZn and o-PdZn (Fig. 7b). On the contrary, when the heating temperature reaches 900 °C, the pure Pd phase is completely converted to

o-PdZn with good crystallinity indicated by the sharp XRD peaks. Neverthetess, the/DOTA06682F

PdZn/NC synthesized at a higher temperature (1100 °C) exhibits a new alloy with different stoichiometry (Pd_{3.9}Zn_{6.1}, PDF card 06-0630) along with pure Pd phase, which may be attributed to the Zn atoms rapidly and heterogeneously doped into Pd at high temperature. It also confirms the crucial function of o-PdZn component on the catalyst activity.

The corresponding capacitance measurements show that the $C_{\rm dl}$ values (based on charging currents in non-Faradaic potential region of CV curves) of PdZn/NC increase from 0.63 mF cm⁻² to 14.21 mF cm⁻² in the range of r from 0 to 0.35 and then dramatically decrease to 5.14 mF cm⁻² for r = 0.50 (Fig. S11a). A similar trend is observed by increasing carbonization temperature and the largest C_{dl} value is obtained at 900 °C (Fig. S11b). The high C_{dl} value of PdZn/NC at r = 0.35 and prepared at 900 °C indicates a large electrochemical active surface area, which also makes an important contribution high electrocatalytic to its activity. The N_2 adsorption-desorption measurements confirm the change of surface areas and pore volumes of PdZn/NC with different r and pyrolysis temperature (Fig. S12). It can be observed from Table S4 that the macro-/mesopores volume of as-prepared PdZn/NC increases relative to their corresponding precursors, and PdZn/NC with r = 0.35reaches the largest value of 1.264 cm³ g⁻¹ although the surface area decreases with the increase of Pd loading. Thus, the calcination process of Pd@ZIF-8 promotes the transformation of pore structure from micropores to macro/mesopores, which in turn enhances the diffusion of reactants into the catalyst layers and leads to the good catalyst activity in ORR.⁴⁶ Notably, when r = 0.50, PdZn/NC is severely agglomerated, which leads to a small surface area and pore volume, and weak activity for ORR. On the other hand, both the surface areas and the macro-/mesopores of PdZn/NC increase with the increasing pyrolysis temperature from 700 to 900 °C, and then decrease at 1000 °C. Therefore, when PdZn/NC is prepared at r = 0.35 and at 900 °C, the largest surface area and pore volume corresponding to the highest ORR activity is achieved.

The lifetime of the PdZn/Co/NC is tested by using chronoamperometric

experiments and accelerated durability tests. As shown in Fig. 8a, PdZn/Co/NC/Co/NC/CO/ROG/SEPF maintains 90.62% of its initial current after continuous running for 4 h, while Pt/C and PdZn/NC (r = 0.35) maintain only 90.59% and 91.73% of their initial currents after running 2 h, respectively. When r changes to 0.30 or 0.50, PdZn/NC keep only 86.32% or 55.09% of their initial currents after running 2 h. Therefore, the longtime stability of PdZn/Co/NC could be attributed to the chemical bonds between PdZn, Co and their NC carriers, and the formation of atomically ordered intermetallic structure, which has stronger heteroatomic bonding between Pd and the secondary metal atoms than its disordered counterpart. Moreover, the accelerated durability tests were implemented through scanning the potential between 0.97 and 0.55 V for 2000 cycles at a scan rate of 250 mV s⁻¹ by using RRDE. The PdZn/Co/NC exhibits almost no change in $E_{1/2}$ and 2.3% loss of limiting current density (J_L). In contrast, commercial Pt/C suffers a negative $E_{1/2}$ shift of 15 mV and 11.7% loss of limiting current density at 0.7 V, respectively (Fig. S13). Thus, the as-prepared PdZn/Co/NC (11.42% Pd) possesses much better stability than that of the commercial Pt/C (20% Pt) catalyst.

4. Conclusions

In summary, we have developed a strategy to synthesize high-performance o-PdZn/Co dual catalyst with a particle size of 5.9 nm assembled on nitrogen-doped carbon carrier for ORR through simultaneously modulating the lattice spacing of Pd guest and the metal center in ZIF-8 host. Through one-step annealing treatment, the atomically dispersed Zn in ZIF-8 host diffuses into Pd nanoparticle guest to form highly ordered PdZn with reduced lattice spacing between Pd-Pd. Simultaneously, Co nanoparticles and N-doped carbon nanotubes formed as secondary active sites and electron transfer channel, respectively, by the virtue of the Co²⁺ doped ZIF-8 host. Results reveal that the N-doped carbon chemically bonds to the dual active sites, which inhibits the migration and aggregation of the metal nanoparticles, consequently making the nanoparticle catalysts more durable. The o-PdZn/Co dual catalyst supported on N-doped carbon exhibits high ORR performance with a desirable onset potential (~0.916 V) and an excellent diffusion-limiting current density (~5.70 mA cm⁻²), superior to reported Pd-based catalysts and comparable to commercial Pt/C.

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Moreover, compared with commercial Pt/C, it exhibits an advantageous long-termp/DOTA06682F durability. Therefore, this study suggests that o-PdZn/Co/N-doped carbon is a promising substitute to the Pt/C for alkaline fuel cells.

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Scheme 1. Schematic illustration of the procedures to simultaneously modulate the/DOTA06682F ZIF-8 host and Pd guest for the synthesis of o-PdZn/Co/NC.

Fig. 1 (a) N_2 adsorption-desorption isotherms of ZIF-8 and Pd@ZIF-8, the inset showing the corresponding pore size distribution; (b) SEM image of Pd@ZIF-8; (c) TEM image of Pd@ZIF-8, inset displaying the corresponding size distribution of Pd nanoparticles; and (d) XRD patterns of ZIF-8 and Pd@ZIF-8.

Fig. 2 (a) TEM image of PdZn/NC, inset showing the corresponding particle size distribution of metal catalyst nanoparticles (i.e., o-PdZn). (b) HAADF-STEM image of PdZn/NC and the corresponding element mapping of C, N, Zn, and Pd. (c) TEM image of PdZn/Co/NC, inset showing the corresponding particle size distribution of metal catalyst nanoparticles (i.e., o-PdZn and Co).

Fig. 3 (a) XRD patterns of PdZn/NC and PdZn/Co/NC. (b) HRTEM of PdZn/NC. (c) Atomic resolution HAADF-STEM image of PdZn nanoparticles on the (010) direction, inset showing the crop of the superlattice feature from the red box. (d) Simulated HAADF-STEM images of o-PdZn stacks along (010) plane. (e) HAADF-STEM image and elemental mappings for o-PdZn nanoparticles. (f) Line scan profile extracted from the dash line in (e).

Fig. 4 X-ray photoelectron analyses: (a) Pd 3d and (b) N 1s regions for PdZn/NC and PdZn/Co/NC. (c) Atomic composition (%) of different N species determined by XPS analysis, in which N1-5 belong to pyridinic N (398.5 \pm 0.2 eV), Co-N_x (or Pd-N) (399.2 \pm 0.1 eV), pyrrolic N (400.5 \pm 0.3 eV), graphitic N (401.1 \pm 0.3 eV) and oxidized N (405.6 \pm 0.3 eV), respectively. The total N contents of PdZn/NC and PdZn/Co/NC are estimated to 8.76% and 5.67% (atomic composition) based on XPS, respectively. (d) Co 2p region for PdZn/Co/NC.

Fig. 5 (a) CV curves of ZIF-8, Pd@ZIF-8, BiM-ZIF, Pd@BiM-ZIF, Co/NC, PdZn/NC, and PdZn/Co/NC in N₂ (dash line) or O₂ (solid line) saturated 0.1 M KOH solution. Scan rate: 10 mV s⁻¹. The curves are displaced for clarity. (b) ORR polarization curves of ZIF-8, Pd@ZIF-8, BiM-ZIF, Pd@BiM-ZIF, Co/NC, PdZn/NC, PdZn/Co/NC and commercial Pt/C measured at 1600 rpm.

Fig. 6 (a) ORR polarization curves, (b) $J_{\rm K}$ at 0.75 V and $E_{1/2}$, and (c) corresponding/DOTA06682F Tafel plots of the PdZn/NC with different Pd to Zn molar ratios (*r*); (d) ORR polarization curves, (e) $J_{\rm K}$ at 0.75 V and $E_{1/2}$, and (f) corresponding Tafel plots of the PdZn/NC prepared at different pyrolysis temperatures. Polarization curves were recorded at 1600 rpm in O₂-saturated 0.1 M KOH.

Fig.7 XRD patterns of (a) PdZn/NC with different r, and (b) PdZn/NC with r at 0.35 and prepared at different temperatures.

Fig. 8 Chronoamperometric curves of PdZn/Co/NC, commercial Pt/C, and PdZn/NC with r = 0.35, 0.50 and 0.30.



Scheme 1. Schematic illustration of the procedures to simultaneously modulate the ZIF-8 host and Pd guest for the synthesis of o-PdZn/Co/NC.

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Fig. 8 Chronoamperometric curves of PdZn/Co/NC, commercial Pt/C, and PdZn/NC with r = 0.35, 0.50 and 0.30.

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Graphic abstract

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NaBH4 Solution impregnation 2-methylimidazole 80 O Pd NPs Na2PdCl4 Т Guest content N2 3h 🔍 Zn 🔘 Pd O-PdZn/NC Host center regulation O-PdZn/Co dual catalyst Zn^{2+} • O-PdZn • Co NCNT Zn^{2+}