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Functional Species Encapsulated in Nitrogen-doped Porous Carbon as a Highly Efficient Catalyst to Oxygen Reduction Reaction

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Abstract: The scarcity, high cost and poor stability of precious metal-based electrocatalysts have stimulat the development of novel non-precious metal catalysts to oxygen reduction reaction (ORR) for the use fuel cells and metal-air batteries. Here, we *in-situ* fabricated a hybrid material (Co-W-C/N) with functior species (tungsten carbide and cobalt nanoparticles) encapsulated in N-doped porous carbon framewor through a facile multi-constituents co-assembly method combined with subsequent annealing treatment. T unique structure is in favor of anchoring active nanoparticles and facilitating mass transfer steps. T homogenously distributed carbide nanoparticles and adjacent Co-N-C sites lead to the electrocataly synergism for ORR. The existence of Co and W can promote the graphitization of the carbon matri Benefiting from its structural and material superiority, the Co-W-C/N electrocatalyst exhibits excelle electrocatalytic activity (with a half-wave potential of 0.774 V vs. RHE), high stability (96.3% of the init current remaining after 9000 s of continuous operation) and prominent immunity against methanol alkaline media.

INTRODUCTION

Commercialization of new energy storage and conversion devices such as proton exchange membrane fuel

cells (PEMFCs) and metal-air batteries is of global significance for renewable and sustainable energy sources.^[1-3] Currently, the major performance-limiting factor for these devices is the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode.^[4] Traditionally, platinum-based materials are regarded as the most effective catalyst for the ORR, taking into consideration their high activity via the effective four-electron-transfer pathway leading oxygen to water. But the prohibitive cost, low abundance and poor durability severely hinder their large-scale application.^[5, 6] The development of non-precious metal catalyste (NPMCs) with both excellent activity and high stability, therefore, is pivotal to address this issue.^[7, 8] Ov the past several decades, tremendous efforts have been devoted to the rational design and synthesis NPMCs as alternatives to Pt-based materials, including heteroatom-doped (N, P or S) carbonaceo materials,^[9-12] non-precious metal oxides,^[13-15] carbides,^[16-18] and transition-metal-N/C composites.^{[19-} Among the several promising catalysts, transition-metal carbide materials are extremely attractive due their high durability, favorable conductivity and superior corrosion resistance.^[22, 23] Tungsten carbide (W was discovered by Levy and Boudart to exhibit similar electronic structure and catalytic properties platinum group metals for several chemical reactions and regarded as a possible ORR catalyst.^{[24,} Recently, great progress has been achieved in the exploration of the catalytic activity and stability WC-based materials. For example, an intermittent microwave heating assisted method was reported by Sh to synthesize palladium and iron on nanocrystalline tungsten carbide (Pd/Fe-WC/C) as an OF electrocatalyst, which shows comparable activity to Pt/C.^[16] In 2011, Liu et al. developed a new WC-bas catalyst via a molten solvent route with the high-surface-area WC as a noncarbon electrocatalyst support f nanosized Pt clusters.^[25] It was found that the activity of the Pt clusters is enhanced on WC compared wi... supported on carbon, and the most likely cause of this enhancement is electron transfer between the catalyst and support, leading to a rearrangement of the Pt d-band. In addition, WC shows extremely high stability and anti-poisoning effect on carbon monoxide (CO) in electrocatalysis.^[26] In spite of the intriguing characteristics, one limitation of previous studies is just utilizing WC as the electrocatalyst support of precious metals,^[16, 27] due to its inferior ORR performance in direct comparison to platinum. Non-precious transition metal (cobalt or iron) and nitrogen doped carbon (Me–N–C) catalysts are another group of promising NPMCs to ORR, whose active sites are generally speculated to be associated with N coordinated metal structures (Me-N_x) with average coordination number x from 2 to 4 by X-ray absorption techniques or Mössbauer spectroscopy.^[7, 28, 29] But still, these reported Me-N-C catalysts are easy to deactivation in t^ho harsh electrolyte causing insufficient endurance, which limited the wide applications.^[30]

One compromise is to integrate the two components WC and Me–N–C together. Herein, we report facile method to prepare a novel Co-W-C/N catalyst from the low-cost silicotungstic acid, cobalt nitra dicyandiamide and phenol-formaldehyde through an evaporation-induced self-assembly (EISA) process a subsequent thermal treatment. We use the highly volatile triblock copolymer Pluronic F127 (Mw =12 60 as the template to construct the 3D porous system, in which the N-doped graphited carbon framework decorated by uniformly distributed functional species carbide and cobalt nanoparticles. The resulti: Co-W-C/N catalyst generated high activity and superior stability to ORR, due to abundant binary active sit carbide nanoparticles and the adjacent Co-N-C species, the integrated synergism of porous structure, hij surface area and highly graphited conductive network.

RESULTS AND DISCUSSION

Figure 1 schematically illustrates the overall fabrication procedure of Co-W-C/N composite. It synthesized on the base of an EISA method using F127 as the scaffold template and resol as the carb... source, which were co-mixed with silicotungstic acid, cobalt nitrate and dicyandiamide as the precursors. Owing to the multiple phenolic hydroxyl groups, resol molecules can serve as a bridge to connect the template F127 and the other precursors via hydrogen bonding and electrostatic interactions, which makes the

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three components co-assemble into ordered mesostructure during the EISA process.^[31] During thermosetting at 100 °C for formation of the rigid phenolic resin and subsequent thermal treatment at 350 °C for the pyrolysis of the F127 template, dicyandiamide provides closed N species while resol can form a stable framework. With this method, the metal ions and nitrogenous ligand would be *in-situ* incorporated into the resultant carbon matrix, which would cause an electronic connection between the carbon framework and metals.^[32] After the carbonization at 750 °C, the porous Co-W-C/N catalyst was successfully obtained wi^{+th} the tungsten carbide and cobalt nanoparticles uniformly anchored in the 3D porous N-doped carb framework.



Figure 1. Schematics showing the formation of porous Co-W-C/N.



Figure 2. (a) XRD patterns of Co-W-C/N as well as Co-N/C and W-C as references. The deconvoluted (b) W, (c) N 1s a (d) C 1s spectra of the Co-W-C/N catalyst.

In order to identify the nature of the composites, XRD patterns of the three samples were recorded as show in Figure 2a. Several distinct diffraction peaks at 31.5°, 35.6°, 48.3°, 64.0°, 77.1° and 84.1° in the XR pattern of W-C can be indexed to (001), (100), (101), (110), (102) and (201) planes of WC (JCPDS N 51-093) and four diffraction peaks at 40.2°, 58.2°, 73.1° and 87.0° are indexed to (110), (200), (211) at (220) planes of metallic W (JCPDS No. 04-0806). The XRD pattern of Co-N-C sample shows the typic diffraction peaks corresponding to metallic Co (JCPDS No. 15-0806), in which the diffraction peaks around 44° and 51° were assigned to the (111) and (200) facets of face-centered-cubic Co crystal. This resu indicates the conversion from Co²⁺ cations to metallic Co⁰ due to the carbothermal reduction, in gouaccordance with the previous reports where Co nanoparticles was wrapped by the porous N-doped carbon matrices under high temperature treatment.^[33-36] The XRD pattern for Co-W-C/N exhibits the diffraction peaks for both WC and metallic Co, as well as the peak of tiny amounts of W. Compared with the diffraction peaks in W-C and Co-N-C, the corresponding diffraction peaks in Co-W-C/N shows larger peak width at half height, indicating the fine grain size. A broad diffraction peak is found in the XRD pattern of Co-W-C/N at about 23°, which can be indexed to (002) plane of amorphous carbon framework.^[33, 37] In addition, the XRD pattern for Co-W-C/N shows a small diffraction peak of graphitic carbon at about 26°, demonstrating the formation of graphitic structure,^[38] which is ascribed to the effect of catalytic graphitization on amorphous carbon by the transition metals.^[34, 39, 40] One important thing to note is that we successfully obta^{im} WC at a relative low temperature of 750 °C, which is generally synthesized either by carbothermic reduction at a high temperature above 1000 °C or at the assistance of reducing ambient.^[25, 41] Actually the simil result can be also observed for Co-W-C (Figure S1). So we can conclude that Co can accelerate t formation of tungsten carbide.

The chemical environment of the catalyst was carefully investigated by the XPS. The XPS surves spectrum is exhibited in Figure S2, clearly demonstrating the presences of W, Co, C, N and O elemen Figure 2b shows the enlarged W spectrum of Co-W-C/N, which is deconvoluted into five major componer According to previous reports, the three peaks located at 31.6, 33.7, and 37.7 are corresponding to W 4f; W 4f_{5/2} and W 5p_{3/2} peaks of tungsten carbide. The relatively higher ones at 35.8 and 38.3 eV should assigned to W 4f_{7/2} and W 4f_{5/2} orbits of W⁶⁺, respectively.^[42-44] The formation of W oxide characterist peak can be ascribed to unavoidable oxidation in air atmosphere. The high-resolution N1s spectrum (Figu 2c) of the samples can be mainly fitted by three peaks centered at 398.6, 400.1 and 401.6 eV, which a assignable to pyridinic-N, pyrrolic-N and graphitic-N in the pyrolyzed products.^[36, 45] There exists lar amount of pyridinic-N and graphitic-N in Co-W-C/N, which are reported to play a crucial role in OK., performance.^[30, 46, 47] Pyridinic N can serve as metal-coordination sites due to the lone-pair electrons, forming metal-N/C configurations.^[48,50] The high-resolution spectrum C1s spectrum of Co-W-C/N (Figure 2d) centers at 284.8 eV with an asymmetric tail at the higher binding energies, which demonstrates that the

carbon atoms are connected with N or O heteroatoms. The deconvolutions of the C1s spectrum are corresponding to four peaks at 284.7, 285.2, 286.2 and 288.1 eV, which are associated with sp² graphitic lattice C=C&C-C, C-N&C-O, C=N&C=O and O-C=O, respectively.^[51, 52] The XPS spectra are consistent with the result of XRD, not only revealing the successful doping of N into the carbon framework but also indicating the rich WC and Co-N-C active species in the catalyst.

SEM and TEM images in Figure 3a, 3b and S2a clearly disclose the well-dispersed nanoparticles in the carbon matrix with the parallel cylindrical nanopores. Figure 3c illustrates the N2 adsorption-desorptiv isotherm of Co-W-C/N composite and the corresponding pore size distribution in the inset. It exhibits type-IV curve and a H_1 -type hysteresis loop, suggesting the existence of typical cylindrical mesopores.^{[53,} The pore size distribution plot demonstrates that Co-W-C/N possesses a narrow pore size distribution centered at around 4.6 nm. The mesopores in the carbon framework endows the catalyst with his accessibility to electrolyte infiltration and feasible diffusion path for reactants.^[55] The BET surface area a total pore volume are determined to be 558 m² g⁻¹ and 0.47 cm³ g⁻¹ as shown in Table S1. From Figure 3 we can conclude that most of the nanoparticles are in the range of 5~20 nm. A deep look at the catalyst in Figu 3e, S2b and S2c demonstrates that the catalyst consists of the flocculent carbon (or quasi-nano-rin nanostructure, which is similar to the results of the relative researches.^[56, 57] The bright-field high-resoluti TEM (HRTEM) image in the inset of Figure 3e reveals that the carbon atom layers are closely compacted with well-ordered arrangement, forming the graphite shells, in keeping with the results of XRD. Figure 3f shows th Co nanoparticles are well crystallized with the interlayer spacing of 0.198 nm, in accordance with t theoretical value of the (111) plane, and surrounded by the graphite layers with a lattice distance of 0.331 n.... The formation of the crystalline graphite shells structure was thought to remarkably improve the electrical conductivity, being of importance for electrocatalytic activity.^[34, 45, 58] Figure S3d and S3e clearly exhibits the lattice overlap of WC (101) with a lattice distance of 0.187 nm and Co (200) with an interlayer spacing value of 0.178 nm. The high-angle annular dark-field scanning TEM (HAADF-STEM) images and EDX elemental mappings in Figure 3g shows that the Co, W and N elements were homogeneously distributed over the carbon framework. The successful incorporation of N into the carbon framework would not only ameliorates the surface wettability but also constitutes the Co-N-C configuration combined with the Co crystals.^[34, 48] Thus, we endow the porous carbon with rich WC and Co-N-C active species and unique structure with these nanoparticles encapsulated by the graphitic carbon shell.



Figure 3. (a) SEM and (b) TEM images of Co-W-C/N. (c) N₂ adsorption-desorption isotherms of Co-W-C/N. The inset (c) exhibits the corresponding pore size distribution. (d) The corresponding particle size distribution of the nanocrystals in (b). (e, f) HRTEM images of Co-W-C/N. The fast Fourier transform (FFT) patterns taken from selected area in (f) is employed to verify the crystalline structure. (g) HAADF STEM image and EDX mapping of Co-W-C/N.

To evaluate the electrocatalytic properties toward ORR, cyclic voltammetry (CV) measurements (Figure

4a) were first performed for Co-W-C/N and commercial 20 % Pt/C catalysts in O₂- and N₂-saturated 0.1 M KOH solution. Both the catalysts exhibit a pronounced cathodic peak in O₂-saturated 0.1 M KOH solution, while no peaks can be observed at the presence of N₂, confirming a substantial ORR process. Shown in Figure 4b are the steady-state linear sweep voltammetric (LSV) curves of W-C, Co-W-C, Co-N/C, Co-W-C/N, Co-W-C/N-acid (Co-W-C/N after etching of 1 M hydrochloric acid)and Pt/C catalysts under a same rotation rate of 1600 rpm in O₂-saturated 0.1 M KOH solution. Among the investigated samples Co-W-C/N exhibits significantly enhanced ORR activity compared to those control catalysts W-C, Co-W-Co-N/C and Co-W-C/N-acid. The values of onset potential Eonset and half-wave potential E1/2 for Co-W-C/ are 0.960 V and 0.774 V, which are close to those of Pt/C. Note that the current density Co-W-C/ outperforms that of Pt/C at high overpotential, which is due to the large specific surface area of Co-W-C/. W-C exhibits very poor ORR activity in terms of E_{onset} and $E_{1/2}$, similar to the results of the relative researches.^[42, 44] On introducing cobalt nitrate, the ORR electrocatalytic performance of the corresponding catalyst can be greatly improved. It is noteworthy that while both cobalt and nitrogen were introduced in the catalyst, the ORR activity of the catalyst Co-W-C/N tremendously leaped forward in terms of remarkably positively shifted $E_{1/2}$, which is 94 and 63 mV positive than that of the catalysts W-C at Co-N/C, respectively. This is ascribed to the coexistence of rich Co-N/C active sites and carbide specie Combined with the results of XRD, we can conclude that the strong synergetic coupled effect of carbide a Co-N-C active sites endows the catalyst higher activity than either of the single configuration. What interesting is that the ORR activity of Co-W-N/C after etching of 1 M hydrochloric acid is significant degraded. This can be explained the loss of the most Co species, with only WC remained, according t... XRD pattern (Figure S4). The comparison of electrocatalytic ORR activity, including E_{onset} and $E_{1/2}$ for Co-W-C/N and other reported nonprecious electrocatalysts, are also shown in Table S2. The Tafel plots (Figure S5) can be constructed from the RDE polarization curves by taking the logarithm of the kinetic current density. The corresponding Tafel slope of Co-W-C/N is calculated to be 86 mV dec⁻¹ and close to that of Pt/C (69 mV dec⁻¹), indicating that Co-W-C/N undergoes an analogous ORR mechanism to Pt/C.^[59] The lower Tafel slope given by the cobaltic samples compared to W-C should be due to the catalytic graphitization effect of Co, which would lead to enhanced electrical conductivity.^[34, 60, 61] The low Tafel slope makes the ORR overpotential rise slowly with current density increasing, suggesting that oxygen is easily adsorbed and activated at its surface.^[15] To gain deep insights into the ORR mechanism of Co-W-C/N rotating ring-disc electrode (RRDE) measurements were conducted at room temperature in O2-saturated (M KOH solution. The ring current (i_r) (the oxidation of H_2O_2) of Co-W-C/N is negligible in comparison the disc current (i_d), indicating the strikingly suppressed H₂O₂ evolution during the ORR process (Figure 4 The H₂O₂ yield and the electron transfer number (n) of Co-W-C/N and Pt/C are derived from the ring a disc current according to Eqs. (5) and (6), as presented in Figure 4e and 4f. It is revealed that the H₂O₂ yie on Co-W-C/N were below 16% over the scanned potential range. The corresponding electron transf number n during the reaction is almost constant at 3.91 from 0.9 to 0.6 V and gradually decreases to ~3.64 potentials higher than 0.4 V. Specifically, the H_2O_2 yield on Co-W-C/N was ~4% at $E_{1/2}$, compared with 1. on Pt/C. The low H₂O₂ yield and near optimal four electron pathway are close to the RRDE results of Pt/ suggesting a near 4-electron reaction dominant pathway.

The RDE polarization curves of the Co-W-C/N at various rotation speeds from 400 to 2025 rpm were al measured to get more information about the ORR kinetics and to further validate whether it catalyzes t ORR *via* a four electron ORR process. Figure S6 shows that the voltammetric profiles for both Co-W-C, and Pt/C exhibit obvious diffusion-limiting currents after a mixed kinetic diffusion region and an increas... current intensity with increasing rotating rate due to the shortened diffusion distance.^[62] The good linearity between J⁻¹ and $\omega^{-1/2}$ and the nice parallelism of the fitting lines of the Koutecky-Levich (*K-L*) plots for Co-W-C/N suggest the first-order reaction kinetics toward the concentration of dissolved O₂ and similar

values of electron transfer number over the potential range. On the basis of K-L equations, described in the supporting information in detail, the average electron transfer number (n) for Pt/C and Co-W-C/N at 0.3-0.6 V can be determined from the fitting slopes of the *K-L* plots to be about 4.01 and 3.89, respectively, approximate to 4. This conclusion is in agreement with the calculated results of RRDE measurements, further confirming the outstanding ORR activity of Co-W-C/N.



Figure 4. (a) CV curves of Co-W-C/N and 20 wt% Pt/C at a scan rate of 20 mV s⁻¹ in O₂-saturated (solid line) or N₂-saturated (dash line) 0.1 M KOH solution. (b) Steady-state ORR polarization curves of different catalysts at 1600 rpm with a sweep rate of 5 mV s-1 in O₂-saturated 0.1 M KOH solution. RRDE voltammograms for (c) Co-W-C/N and (d) 20 wt%

Pt/C. Hydrogen peroxide yield and corresponding electron transfer number during ORR for (e) Co-W-C/N and (f) 20 wt% Pt/C.

Chronoamperometry was performed by holding the electrodes for 9 000 s at a constant potential of 0.2 V in O₂-saturated 0.1 M KOH solution to evaluate the stability of the catalysts. Figure 5a shows that about 96.3% relative current for Co-W-C/N still remains in comparison with up to 16.4% loss of its initial current over Pt/C catalyst, demonstrating a much better stability of Co-W-C/N than Pt/C. An accelerated durability test was carried out to further testify the long-term stability of Co-W-C/N in catalyzing ORR by cycling t potential over the range 1.0-0.4 V in O₂-saturated 0.1 M KOH at a scan rate of 50 mV s⁻¹ for 5 0 continuous cycles. As shown in Figure 5b, Pt/C exhibited 81 mV negative shift of $E_{1/2}$ and significa attenuation in diffusion-limited current density, which is commonly observed in Pt/C caused by t dissolution of Pt nanoparticles.^[30, 63] However, Co-W-C/N shows almost no changes of Eonset and only ve slight shift of $E_{1/2}$ (9 mV) after 5 000 cycles. The slight shift for E_{onset} and $E_{1/2}$ indicates the superior stabili of the active sites in Co-W-C/N. The small decrease of limited current density can be found for Co-W-C/ which should be attributed to the unavoidable oxidation of the carbon matrix.^[30] These results are we consistent to the features of the I-t plots and confirm the superior durability of Co-W-C/N to that of Pt/ Methanol tolerance is one of the major concerns for the potential application in direct methanol fuel cel where methanol may cross over the membrane and deteriorate the ORR. Figure 5d shows the influence methanol addition into O₂-saturated 0.1 M KOH solution on the instant current curves of Co-W-C/N as Pt/C catalysts under identical experimental conditions. With the injection of 3 M methanol at 500 s, t current slightly decreases over the Co-W-C/N while a rapid current falloff is observed in the ORR current ... the Pt/C electrode, suggesting that Co-W-C/N demonstrates a much stronger tolerance to methanol crossover.



Figure 5. (a) I–t chronoamperometric stability measurements (at 0.2 V) of Co-W-C/N and 20 wt% Pt/C in O₂-saturat 0.1 M KOH solution at a rotating speed of 1600 rpm. Polarization curves at 1600 rpm for (b) Pt/C and (c) Co-W-C/N befor and after 5000 cycles. (d) Methanol crossover tests for Co-W-C/N and Pt/C catalysts performed on the RDE (1600 rpm by injecting of 3 M methanol into the electrolyte.

All the elctrocatalytic measurements indicate that Co-W-C/N is a promising candidate to Pt/C as t ORR catalyst. Such excellent properties can be ascribed to the rational design of Co-W-C/N: (1) Both W nanoparticles and Co-N-C species are uniformly distributed in the interior of rigid porous carbon matri This unique structure on the one hand improves the transportation of the reactants, intermediates, produc and on the other hand inhibits the self-aggregation during the catalysis process, thus preventing the loss ... available active sites. (2) The synergistic effect between the stable WC nanoparticles and the active Co-N-C species accelerates the ORR. (3) Highly graphitized carbon shell outside the active species can provide the fast electron-transport pathway. (4) The introduced heteroatom N would cause the polarized distribution of spin and charge density, which is considered as the one of the reasons for the high activity.^[64] The synergistic effect between lone electron pairs of N and the π -conjugated system of graphite would cause a unique electronic properties: the replacement of the carbon (C) atom with n-type dopant in graphitized carbon results in the donation of electrons to O₂, leading to the improvement of ORR activity.^[65] Figure 6 described the schematic microstructure and ORR process on the Co-W-C/N, in which WC and Co-N-C species are firmly anchored inside the N-doped porous carbon channel and well protected by the graphitiz^{-,1} carbon shell. The integral porous system provides the thorough route for the infiltration of electrolyte a transportation of reactants. The metal nanocrystal encased in graphitized carbon layers (M@C) structure h been confirmed to be an efficient design for electrocatalysis.^[45, 66] The special structure usually shows hi chemical durability because the outer carbon layers can protect the inner active species from direct conta with external environment. It can avoid the oxidization and corrosion of the active nanoparticles during t long-time ORR process, and furthermore prevent agglomeration with the adjacent nanoparticles.



Figure 6. Schematic illustration of the microstructure and ORR process on the Co-W-C/N.

CONCLUSION

In summary, a hybrid ORR catalyst was successfully fabricated through a simple procedure involving the process of multi-constituents co-assembly and the subsequent carbonization process. The resultant catalyst (Co-W-C/N) consists of tungsten carbide and Co-N-C species, which decorate the porous N-doped carbon

framework together. Benefiting from the high active sites yield and enhanced electron transfer capacity, this catalyst exhibits excellent electrocatalytic performance for ORR and superior durability to Pt/C. Co-W-C/N also shows better tolerance against methanol than Pt/C. The strong synergetic coupled effect between tungsten carbide and Co-N-C species was testified to enhance the ORR activity. These results lead us to firmly believe that Co-W-C/N hybrid catalyst is a promising non-precious metal electrocatalyst for fuel cells and metal–air batteries.

Experimental

Fabrication of porous Co-W-C/N

The porous Co-W-C/N nanocomposite was synthesized through a multi-component co-assembly pathway. typical synthetic process is shown as follows: 1.0 g of F127 was dissolved in 10 mL ethanol to form a cle solution. Simultaneously, a certain amount of silicotungstic acid (H₄SiW₁₂O₄₀), cobalt nitrate (Co(NO: 9H₂O) and dicyandiamide (C₂H₄N₄) were dissolved into ethanol to form uniform solutions, respectivel After 30 min, 5.0 g of soluble resol solution (20 wt% in ethanol) was added dropwise into the F127 solution and vigorously stirred for 10 min. Subsequently, the other precursor solutions were added into the abo mixture in turns. The obtained mixture solution was further stirred for 1 h and cast onto Petri dishes evaporate ethanol at room temperature for 12 h. Then, the obtained sticky membrane was subjected thermo-polymerization in an oven at 100 °C for 24 h. At last, the as-prepared orange membrane was scrap off and pyrolyzed in tube furnace at nitrogen atmosphere. The membrane was calcined at 350 °C for 3 h at then at 750 °C for 3 h. In order to better understand the catalytic performances and reveal the active sites ... the catalyst Co-W-C/N, three control catalysts were prepared under the similar procedures as Co-W-C/N except for no addition of dicyandiamide, silicotungstic acid, both cobalt nitrate and dicyandiamide, noted as Co-W-C, Co-N/C and W-C, respectively.

Structural and morphological characterization

The crystalline phases of Co-W-C/N were identified by Powder X-ray diffraction (XRD) using a Bruker D8 advance diffractometer with a Cu K α radiation (λ = 0.154056 nm) at 40 kV and 40 mA, operated at a scan rate of 6° min⁻¹. Transmission electron microscope (TEM, FEI Tecnai G2 at 200 kV) was used to analyze the distribution and size of the nanoparticles involved in the N-doped ordered mesoporous carbon matrix. STEM-EDX mapping was performed to qualitatively investigate the local element composition of t^ho catalysts through the energy dispersive X-ray spectrum attached to the FEI Tecnai G2 system. Nitrog adsorption-desorption isotherms (Micromeritics ASAP 2020, 77 K) were measured to confirm the poro morphology. The surface areas were estimated utilizing the Brunauer-Emmett-Teller (BET) method bas on the adsorption data. The pore size distributions derived from the adsorption branche of isotherms we estimated based on the Barrett-Joyner-Halenda (BJH) model and the total pore volumes (V_{total}) we calculated from the adsorbed amount at a relative pressure P/P₀ of 0.993. X-ray photoelectron spectrosco₁ (XPS) spectra were recorded on a PHI Quantera SXM surface analyzer (ULVAC-PHI Inc., Japan) with Al Ka source.

Electrochemical measurements

All electrochemical measurements were performed on a CHI760D potentiostat with a typical three-electro cell. The three-electrode system consists of a glassy carbon (GC) electrode (Pine Instrumentation, 5 mm f RDE and 5.6 mm for RRDE) coated with the catalyst ink as the working electrode, a saturated calor electrode (SCE) as the reference and a Pt foil as the counter electrodes, respectively. All potentials report in this work have been converted to the RHE scale. Catalysts were loaded on the GC electrode by dropwi... casting the catalyst ethanol suspension, which consists of catalyst powder, conductive carbon black (Vulcan XC-72), 5 wt.% Nafion ethanol solution and absolute ethanol, and dried at 50 °C to form a thin layer. The loading is controlled at 0.625 mg cm⁻². Vulcan XC-72-supported 20 wt.% Pt catalyst with a loading of 25 µg

Pt cm⁻² was also measured for comparison. All the electrochemical measurements were carried out in N₂- or O₂-saturated 0.1 M KOH at room temperature. The cyclic voltammetry measurements (CVs) were scanned between 1.2 and 0.4 V with a scan rate of 20 mV s⁻¹. The linear sweep voltammetrys (LSVs) was performed via RDE technique to collect the polarization curves at a scan rate of 5 mV s⁻¹ from 1.2 to 0.1 V at various rotating speeds from 400 to 2025 rpm. In chronoamperometric responses (*I*-*t* plots), the potential was set to 0.2 V in O₂-saturated 0.1 mol L⁻¹ KOH for 9000 s. The stability tests were carried out in the O₂-saturate-⁴ electrolyte for 5000 CV cycles in the potential range from 1 to 0.4 V and the RDE polarization curves befc and after 5000 CV cycles were recorded to test the durability of Co-W-C/N catalyst. Methanol resistan tests were performed through the chronoamperometric response by adding 3 M methanol into the electroly For RRDE tests, the disk electrode was scanned at a rate of 5 mV s⁻¹ and the ring electrode potential was set to 1.4 V. The hydrogen peroxide yield [H₂O₂(%)] and the electron transfer number (n) were determin from the following equations:

$$\begin{split} H_2O_2(\%) &= 200 \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \\ n &= 4 \frac{I_d}{I_d + \frac{I_r}{N}} \end{split}$$

where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt rin which was determined to be 0.40 from the reduction of K_3 Fe[CN]₆.

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Keywords: Tungsten carbide, nitrogen-doping, oxygen reduction reaction, non-noble metal catalysts

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Graphical Abstract



This structure with functional species encapsulated in nitrogen-doped porous carbon is in favor of anchoring active nanoparticles and facilitating mass transfer steps. The homogenously distributed tungsten carbide nanoparticles and the adjacent Co-N-C sites lead to the electrocatalytic synergism for ORR. Benefiting from its structural and material superiority, the Co-W-C/N electrocatalyst exhibits excellent electrocatalytic activity, high stability and prominent immunity against methanol.