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Exploring of efficient non-noble ORR catalysts alternative to Pt-based catalysts are highly demanded for fuel cells and rechargeable metal-air batteries. Herein, we demonstrate a rational design and synthesis of a N, P-doped carbon with encapsulated Co nanoparticles as efficient electrocatalyst for ORR. The catalyst is derived from a mixture of Co-MOF and triphenylphosphine with mass ratio of 3:1 by pyrolysis in N₂ atomsphere at 700 °C. The catalyst exhibits a superior ORR catalytic performance among its counterparts in 0.1 M KOH with onset and half-wave potentials of 0.88 and 0.80 V, much larger limiting current density of -5.93 mA cm⁻² that surpasses the commercial 20 % Pt/C, in addition to the durability and resistance to methanol. The enhanced ORR activity of the catalyst can be attributed to the synergistic effect between Co NPs and N, P atoms, the relative large contact surface, more exposed active sites and good electrical conductivity. This work would provide some new ideas for designing and constructing promising carbon based non-precious metal electrocatalysts for future practical fuel-cell applications.

Introduction

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Worldwide concern about the energy shortage and environmental issues stimulates the pursuit of clean and sustainable energy storage and conversion technologies, such as renewable fuel cells and rechargeable metal-air batteries.¹⁻⁶ As one of the electrochemical conversion reactions that can provide or store electrical energy efficiently, oxygen reduction reaction (ORR) is of the great importance in these batteries. However, the sluggish kinetics of ORR at the cathodes usually requires the use of electrocatalysts.^{7,8} Though platinum (Pt) and its alloys are known to be highly efficient catalysts in boosting ORR rate, commercialization of these catalysts is hindered by their prohibitive cost and low stability. Hence, exploration of cost-effective eletrocatalysts with competitive performance to replace Pt-based materials has been a foremost subject of this field.9-16

So far, great efforts have been devoted to exploring nonnoble catalysts for ORR, including transition-metal-coordinating macrocyclic compounds,^{17, 18} metal-nitrogen-doped carbon (M-N/C),^{4, 19-25} transition-metal carbides or nitrides,²⁶⁻²⁹ heteroatom doped metal-free carbon materials,³⁰⁻³³ and even conducting polymers,^{34, 35} etc. Among these materials, the M-N/C (M = Mn, Fe, Co, Ni) have been regarded as a very promising family of candidates for ORR, especially the Co-N/C materials.^{15,}

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To fabricate such M-N/C materials, the precursor method has been adopted followed by a pyrolysis process in specific atmosphere. A precursor can be the directly blended mixture (individual metal, carbon and nitrogen sources),^{23, 41, 42} the renewable biomass resources (such as peanut shell, soy milk, etc.)^{43, 44} or the metal-organic frameworks (MOFs).⁴⁵⁻⁵² Generally, the as-synthesized M-N/C materials are expected to inherit some structural characteristics from the precursors. Even the minimal retention of essential fragments sometimes can greatly affect the final performance of the material. In this respect, MOFs are more attractive candidates and efforts have been devoted to converting them into non-precious metal/carbon based materials. There are several advantages in using MOFs as precursors to fabricate the M-N/C materials: 1) there are numerous transition metal-centered MOFs to choose; 2) metal centers and organic ligands are highly dispersed in MOFs structure; 3) MOFs show great diversity in metal centers and functional groups; 4) heteroatoms, such as N, can be in situ doped into carbon matrix during pyrolysis; 5) MOFs possess high specific surface area and porosity that may be inherited by the carbon material. Though many carbon-based M-N/C materials have been derived from MOFs, substantial studies are still demanded dedicated to the design and synthesis of new M-N/C materials for catalyzing ORR.

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Herein, we report on the rational design and synthesis of a N, P-doped carbon with encapsulated Co nanoparticles (NPs) as efficient electrocatalyst for ORR. The catalyst was prepared from a facile strategy of pyrolysis of a Co-MOF and triphenylphosphine mixture with mass ratio of 3:1 in N_2 atomsphere at 700 °C (denoted as Co@NC-P(3-1)). The catalyst exhibits a superior ORR catalytic performance in 0.1 M KOH with onset and half-wave potentials of 0.88 and 0.80 V, limiting current density of -5.93 mA cm⁻², and excellent durability and resistance to methanol. The good ORR catalytic activity can be attributed to the fact that the as-synthesized catalyst inherits some original advantages of the Co-MOF in terms of homogeneous distribution of Co centers, N-rich ligands, and large surface area. Besides Co NPs, the heteroatoms (N, P) in carbon structure also act as exposed active sites. The synergistic effect generated between them facilitates the kinetics of ORR process. This work would provide some new ideas for designing and constructing promising carbon based non-precious metal electrocatalysts for future practical fuel-cell applications.

Experimental

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Materials: 18-crown-6 was procured from Energy Chemical. KOH, Ni(NO₃)₂·6H₂O, Tetrafluoroboric acid (HBF₄) and N,Ndimethylacetamide (DMA) were purchased from Sinopharm Chemical Reagent Co. Ltd (China). Biphenyl-4,4'-dicarboxylate (H₂bpdc) was supplied by Chemsoon Co. Ltd. 4-cyanopyridine was obtained from Alfa Aesar. Methanol (CH₃OH) was procured from Tianjin Fuyu chemical reagent. The platinum on carbon (Pt/C, 20wt %) and Nafion solution (5wt %) were obtained from Sigma-Aldrich. All the chemicals were used as received without any further purification.

Synthesis of 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt): 1.0 g of 18-crown-6 and 0.224 g of KOH were dissolved into a beaker with 10 mL of CH₃OH. After stirred for 5 min, the solution was transferred into a 20 mL Teflon-lined stainless steel autoclave, which was opened and maintained at 323 K for 3 h. Then 8.32 g of 4-cyanopyridine was added into the above solution and stirred for another 5 min. Thereafter, the autoclave was sealed and kept at 473 K for 10 h. After cooling down to room temperature, the product was filtered, washed with water to neutral and dried at room temperature for 3 days. Finally, about 4.5 g of brown solid was received (54 % yield).

Preparation of Co-MOF [Co₃(\mu_3-OH)(bpdc)₃(tpt)]: The Co-MOF was synthesized according to the previous work.⁵³ Typically, certain amount of Co(NO₃)₂·6H₂O (0.058 g, 0.2 mmol), tpt (0.031 g, 0.1 mmol) and H₂bpdc (0.024 g, 0.1 mmol) were dispersed into a 10 mL solution of DMA/CH₃OH (v/v, 1:1) in 20 mL glass vial. Then, 100 μ L of HBF₄ (40% in water) was added into the solution. After sonicated for 30 min, the mixture was sealed and heated to 393K for 3 days. The red crystals were filtered, washed with DMA and CH₃OH, and dried at 333 K for 10 h.

Preparation of Co@NC catalyst:

The as-prepared Co-MOF (0.6 g) was placed in a crucible. Then, the crucible was transferred into the tube furnace and heated to 473 K for 1 h and 973 K for 3 h sequentially with a heating

speed of 5 °C min⁻¹ under N₂ atmosphere. After naturally cooling to ambient temperature, the sample Was ¹m PihSed^CWith⁴m Picf, washed with water to neutral and dried at 333 K for 10 h. The final sample was denoted as Co@NC.

Preparation of Co@NC-P catalysts:

The as-prepared Co-MOF (0.6 g) was firstly fully mixed with triphenylphosphine (0.2 g) and placed in a crucible. Then, the crucible was transferred into the tube furnace. The pyrolysis and sample treatment procedures were the same as Co@NC. The sample obtained at this mass ratio of Co-MOF and triphenylphosphine was denoted as Co@NC-P(3-1). The Co@NC-P(5-1) and Co@NC-P(1-1) catalysts were prepared in the same way but with different initial amount of triphenylphosphine of 0.12 g and 0.6 g, respectively.

Characterization:

Powder X-ray diffraction (PXRD) patterns were acquired at room temperature using a XPert Pro MPD diffractometer with Cu K α radiation (λ = 1.5418 Å). The morphology and structure of the samples were observed on field-emission scanning electron microscope (SEM, HITACHI S4800) and Transmission electron microscopy (TEM) images were collected on a FEI Tecnai F30 with an acceleration voltage of 300 kV. A SSA-4300 surface area and pore size distribution analyzer was applied to measure the Brunauer Emmett Teller (BET) surface area. Raman spectrum was recorded on a HORIBA Evolution Raman Microscope spectrometer with the excitation wavelength of 532 nm. X-ray photoelectron spectrum (XPS) measurements was carried out on a Thermo ESCALAB 250 Spectrometer and the binding energies were calibrated based on the graphite C 1s peak (284.6 eV). Inductively coupled plasma optical emission (ICP-OES) results were collected via a Varian 715 ICP optical emission spectrometer.

Electrochemical measurements:

All electrochemical measurements were performed on a Gamry electrochemical work station (INTERFACE 1000 T) with a rotating electrode system (RDE710 Rotating Electrode) at room temperature. A three-electrode cell configuration was employed by using a glassy carbon rotating disk (RED, 5.0 mm in diameter) as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The potentials were converted to its potential vs. the reversible hydrogen electrode (RHE) by using the equation $E_{RHE} = E_{SCE} + 0.059 \text{pH} + E_{SCE}^{\theta}$ in 0.1 M KOH. The catalyst inks were prepared by dispersing 4 mg of sample and 40 µL of 5 wt % Nafion solution in a mixture solvent of 800 uL water and 200 uL ethanol by 1 h sonication. Then 15 μ L of the catalyst ink was pipetted onto the pre-cleaned glassy carbon electrode with a loading equivalent to 0.294 mg cm⁻². The linear sweep voltammograms (LSVs) were collected at a scan rate of 10 mV s⁻¹. Cyclic voltammetry (CV) measurements were conducted in a N₂-saturated or O₂-saturated 0.1 M KOH with a scan rate of 10 mV s⁻¹. The catalytic durability for ORR was investigated by chronoamperometry at 0.812 V vs. RHE for 10 h with a rotating speed of 400 rpm. The kinetic parameters were calculated using the Koutecky–Levich (K–L) equation:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}$$

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Scheme 1. Schematic representation of the synthesis of Co@NC-P materials.

$$B = 0.62 n F C_0 D_0^{2/3} v^{-1/6}$$

where *j* is the measured current density, j_k is the kinetic-limiting current density, ω is the angular velocity of the disk, *n* is the electron transfer number, *F* is the Faraday constant (*F* = 96485 C mol⁻¹), C_0 is the bulk concentration of O_2 ($C_0 = 1.2 \times 10^{-6}$ mol cm⁻³ in 0.1 M KOH), D_0 is the diffusion coefficient of O_2 ($D_0 = 1.9 \times 10^{-5}$ cm s⁻¹ in 0.1 M KOH), and υ is the kinematic viscosity of the electrolyte ($\upsilon = 0.01$ cm² s⁻¹ in 0.1 M KOH).

Results and discussion

The synthesis of Co@NC-P materials is illustrated in Scheme 1. Red octahedral crystals of Co-MOF with good crystallinity were obtained via solvothermal reaction of Co(NO₃)₂·6H₂O, tpt and H₂bpdc in a mixed solvent of DMA/methanol (Figure S1 and S2). This Co-MOF was chosen as the precursor owing to its Co center, N-containing ligands and the open structure, which are considered as important factors to derive efficient ORR electrocatalysts with hierarchical structures. To in situ dope P atoms in the final structure, the Co-MOF was throughly mixed with triphenylphosphine before the subsequent pyrolysis, which was performed at 700 °C under N₂ atmosphere by using a tube furnace. The hybird materials obtained from different amount of triphenylphosphine were further treated with HCl to remove the accessible Co species, giving Co@NC-P composites.

The morphology and microstructure of the sample derived from the mixture of Co-MOF and triphenylphosphine with a mass ratio of 3:1 (Co@NC-P(3-1)) were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From the SEM images (Figure S3a and 3b), it can be observed that the original crystal outline was not firmly preserved after HCl treatment and it presents no particular morphology. More details of the structure is revealed by TEM images (Figure 1a, 1b and S3c, 3d). As shown, the organic ligands of tpt and H₂bpdc and the Co center in Co-MOF has been successfully transformed into nanosheet-like carbon matrix and Co NPs respectively in Co@NC-P(3-1). The Co NPs are wrapped by graphitic carbon and highly dispersed in the carbon material with an average diameter of around 12.3 nm (Figure 1d and S3e), suggesting the ability of Co metal in promoting the graphitization degree of carbon. High-resolution TEM image of the Co NPs presents the lattice fringes with an interplanar distance of 0.200 nm that can be ascribed to the lattice distance of the (111) plane of Co metal (Figure 1e). The lattice spacing of around 0.344 nm is corresponding to the (002) planes of carbon



Figure 1. TEM images (a, b), selected-area electron diffraction pattern (c), high-resolution TEM images (d-f), HAADF-STEM image (g) and corresponding EDX elemental mappings of C (h), N (i), Co (j) and P (k) respectively of Co@NC-P(3-1).

(Figure 1f). To demonstrate the distribution of participating elements, elemental mappings were also recorded for Co@NC-P(3-1) (Figure 1g-k). As reaveled, the retained Co element cluster around where the Co NPs are found. A considerable amount of N atoms is detected to be preserved and distributed homogeneously through out the carbon matrix, in which, the P atoms have also been confirmed to be successfully doped. Although the doping amount of P atoms is low, they also play an important role in regulating the local electron configuration of carbon and enhancing the catalytic performance.

The structural crystallinity and composition of Co@NC-P materials were also characterized by powder X-ray diffraction (PXRD) measurement. As shown in Figure 2a, the broad peak appears around 24 ~ 25.8° can be ascribed to the characteristic diffraction peak of carbon ((JCPDS 41-1487). The four diffraction peaks presented at 44.3°, 51.5°, 75.9° and 92.4° match well with the (111), (200), (220) and (311) crystal planes of Co metal (JCPDS 15-0806), respectively, which confirms that the Co element preserved mainly exists in the form of Co metal. Raman spectra were further measured to analyze the structural defects and disordered graphitic structures of carbon in Co@NC-P composites (Figure 2b). Two sharp characteristic peaks appearing at around 1333 (D band) and 1583 cm⁻¹ (G band) correspond to the disordered carbon and graphitic sp² hybridized carbon. The intensity ratio of the D band to G band (I_D / I_G) for Co@NC, Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(1-1) are calculated to be 1.00, 1.02, 1.35, and 0.98, respectively. The Co@NC-P(3-1) sample presents the highest I_D/I_G value, suggesting more defects are generated in the structure. It is believed to be caused by more heteroatoms incorporation into the carbon structure at a initial mass ratio of 3:1 for Co-MOF and triphenylphosphine, which is also supported by XPS data in Table S1. The accurate Co contents in

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Figure 2. (a) PXRD patterns, (b) Raman spectra, (c) N_2 adsorption-desorption isotherms (inset: pore-size distributions), (d) C1s XPS spectra, (e) N1s XPS spectra, (f) $Co2p_{3/2}$ XPS spectra of Co@NC, Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(1-1); (g) P2p XPS spectra of Co@NC-P(5-1), Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(3-1), and Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(1-1); (h) different kinds of doping N species in Co@NC, Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(1-1).

these materials were further confirmed by ICP-OES (Table S2). It is 32.08 %, 9.18 %, 16.36 % and 33.12 % for Co@NC, Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(1-1), respectively. The Co@NC-P(5-1) sample shows the lowest Co content. That is because the electron donating effect of triphenylphosphine induced more severe collapse of the MOF structure during the pyrolysis. More Co centers escaped from the carbon matrix and were washed away by HCl treatment. As the amount of triphenylphosphine increases, the MOF crystals were protected better by the benzene rings of triphenylphosphine, and less Co centers could escape during the pyrolysis, leading to incremental increasement of Co conten in Co@NC-P(3-1), and Co@NC-P(1-1). The N₂ adsorption- desorption isotherms and pore-size distributions (Fig. 2c) of the resulting samples show that all the samples display a type IV isotherm with hysteresis. The total BET surface areas are calculated to be 256, 179, 225 and 211 m² g⁻¹, respectively. The higher heteroatoms doping and larger surface area of Co@NC-P(3-1) are favorable for catalyzing the ORR process.

X-ray photoelectron spectrum (XPS) measurements were further performed to provide insights into the detailed chemical composition and bonding configuration of the as-synthesized composites. The XPS spectra of the composites verify the presence of elemental C, N, Co, P and O. Figure 2d shows the high-resolution C 1s spectra, which can be deconvoluted into C-C (284.6 eV), C=N (285.5 eV), C=O (286.5 eV), and O-C=O (289.1 eV). Fittings of the N 1s spectra of Co@NC-P materials (Figure 2e) show four peaks that are assigned to the pyridinic N (398.3 eV), Co-N (399.1 eV), pyrrolic N (400.0 eV), and graphitic N (400.8 eV). The total nitrogen contents in Co@NC, Co@NC-P(5-1), Co@NC-P(3-1), and Co@NC-P(1-1) are 5.16, 3.71, 5.88 and 4.91 at %, respectively (Figure 2h). The nitrogen doping efficiency of Co@NC-P(3-1) is enhanced compared with Co@NC due to the introduction of appropriate amount of triphenylphosphine. Co@NC-P(3-1) shows the highest total content of the two major nitrogen components in all the samples: pyridinic N and graphitic N, which are regarded as effcient actives sites for ORR.23, 54-56 For the Co 2p3/2 spectra (Figure 2f), the peaks at 778.3, 780.6, and 784.5 eV correspond to the binding energies of metallic Co, CoO_x/CoC_xN_x , and $Co-N_y$ species, respectively. By the XPS measurements, the P element is comfirmed to be low in content (Figure 2g). Three peaks are deconvoluted corresponding to the binding energies of P 2p_{3/2} orbital (128.1 eV), P $2p_{1/2}$ orbital (129.1 eV) and oxidized P (133.2 eV). In addition to N atoms, the P-doping also can induce defects in the carbon framework and increase the electron delocalization due to its good electron donating properties, promoting active sites towards ORR.57,58

The ORR kinetic processes in the as-synthesized composites were evaluated by using the rotating disk electrode (RDE) measurements in 0.1 M KOH electrolyte. Cyclic voltammograms(CV) were recorded to verify their ORR



Figure 3. (a) CV curves in N_2 and O_2 -saturated 0.1 M KOH electrolyte, (b) LSV curves and (c) Tafel slopes of Co@NC, Co@NC-P(5-1), Co@NC-P(3-1), Co@NC-P(1-1) and 20 % Pt/C, respectively; (d) LSV curves of Co@NC-P(3-1) at different rotation rates (inset: corresponding K-L plots of J⁻¹ vs. ω^{-1} at different potentials); (e) Chronoamperometric responses of Co@NC-P(3-1) and 20 wt % Pt/C at + 0.812 V vs. RHE in an O2-Μ кон solution (400 saturated 0.1 rpm): (f) Chronoamperometric responses of Co@NC-P(3-1) and 20 wt % Pt/C at + 0.812 V vs. RHE in an O₂-saturated 0.1 M KOH solution with the addition of 0.2 mol dm⁻³ methanol (400 rpm).

response in N₂- and O₂-saturated electrolyte (Figure 3a). As shown, all the samples present featureless slopes for cathodiccurrent within the entire potential range when the electrolyte is N2-saturated, while well-defined cathodic peak are observed in O₂-saturated electrolyte. The Co@NC-P(3-1) shows the largest current density and most positive oxygen reduction peak centered around 0.82 V vs. reversible hydrogen electrode (RHE), indicating its superior ORR activity among all the as-synthesized samples. Figure 3b compares the linear sweep voltammetry (LSV) curves recorded for these materials and that of the commercial 20 % Pt/C under the same mass loading in O₂-saturated 0.1 M KOH at 1600 rpm. Notably, Co@NC-P(3-1) exhibits prominent ORR activity, surpassing its counterparts, with more positive values of onset potential of 0.88 V and half-wave potential of 0.80 V. The diffusion-limited current density of -5.93 mA cm⁻² is larger than that of the commercial 20 % Pt/C (-5.46 mA cm⁻²). The small Tafel slope of Co@NC-P(3-1) (66 mV dec⁻¹) also demonstrates that the Co@NC-P(3-1) catalyst possesses a faster electron transfer rate compared to that of 20 % Pt/C (88 mV dec⁻¹) (Figure 3c). From the Nyquist plots recorded at -150 mV vs. SCE (Figure S7), Co@NC-P(3-1) shows the smallest charge-transfer resistance, suggesting its good electrical conductivity, which is one of the ARTICLE

key factors contributing to its good ORR performance its Vs of the samples at different rotating speeds from 400 to 2500 fpm were also investigated (Figure 3d and S4-6). The corresponding Koutecky-Levich (K-L) plots of Co@NC-P(3-1) show a good linear relationship between J⁻¹ and $\omega^{-1/2}$. The number of electrons transferred (n) per oxygen molecule (at 0.39 V) derived from the slopes indicates that Co@NC-P(3-1) (n = 3.97) participates in an efficient 4-electron pathway resulting in the direct reduction of O₂ to HO⁻ in 0.1 M KOH solution.

For commercialization, the electrocatalytic durability of the catalyst and its resistance to methanol crossover effect are two very important aspects to be considered. To probe the durability of Co@NC-P(3-1) in constant ORR process, chronoamperometry at 0.812 V vs. RHE was conducted for 10 h. The time-dependent current density curve is shown in Figure 3e in comparison with 20 % Pt/C, which reveals better electrochemical durability of Co@NC-P(3-1) with a decrement of 9.4 % over 10 h, while the 20 % Pt/C presents a more obvious degraded ORR performance with a current density drop of 29.4 %. To discuss the reasons of the durability reduction of the catalyst, PXRD and TEM was used to characterize the morphology and structure of the catalyst after chronoamperometry test (Figure S8). From the TEM images we can see that the structures of carbon was well maintained without any obvious changes. However, a certain degree of agglomeration of the encapsulated Co nanoparticles and the lattice fringes with an interplanar distance of 0.238 nm that can be ascribed to the (311) plane of Co_3O_4 phase are found in the catalyst after the chronoamperometry test. To acquire the PXRD pattern of the tested catalyst, we deposited the catalyst ink on a piece of titanium plate with the same loading density as the glassy carbon electrode. In the PXRD pattern, diffraction peaks of Co metal are preserved, and small new peaks that can be attributed to the Co₃O₄ phase also show up. From these results, we can conclude that the agglomeration and oxidation of the encapsulated Co nanoparticles is the cause of the 9.4 % reduction of the ORR performance of the catalyst after 10 h chronoamperometry test.

The influence of methanol crossover on Co@NC-P(3-1) and 20 % Pt/C was investigated by injecting equivalent of 0.2 mol dm⁻³ methanol into the 0.1 M KOH solution. As shown in Figure 3f, the addition of methanol triggers a drastic and sharp surge of current density of 20 % Pt/C that cannot be recovered to the initial level. By contrast, the Co@NC-P(3-1) exhibits much stronger tolerance against chemical corrosion as compared to 20 % Pt/C since no obvious decay in current density has been observed. The graphitic carbon shells of Co NPs protect them from corrosion in the alkaline solution, providing promising potential for future commercial applications.

The above results suggest that the as-synthesized Co@NC-P(3-1) material is an efficient electrocatalyst for ORR. The good ORR performance can be attributed to the following three aspects: 1) The appropriate amount of encapsulated Co NPs could facilitate the protonation of O_2 and enable the full fourelectron reduction pathway on the outer metal-free active sites;³⁶ 2) N- and P-doping induces defects and increases the electron delocalization, promoting active sites towards ORR; 3)

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Relative large contact surface and good electrical conductivity also boosts the electrocatalytic performance. Compared with Co@NC, the P atoms doping in Co@NC-P(3-1) increases the exposed active sites and induces synergistic effect between N and P atoms, enhancing its ORR activity. As for Co@NC-P(5-1) and Co@NC-P(1-1), the limited N- and P-doping affects their kinetic processes of ORR.

Conclusions

In summary, a N, P-doped carbon with encapsulated Co NPs was synthesized as efficient ORR catalyst from pyrolysis of a mixture of Co-MOF and triphenylphosphine with mass ratio of 3:1. In this catalyst, Co NPs are wrapped by graphitic carbon shell, free from corrosion in the alkaline solution. The N and P atoms were in situ doped into the carbon matrix, promoting active sites towards ORR. Compared with its counterparts, the catalyst shows a superior ORR performance with more positive onset and half-wave potentials of 0.88 and 0.80 V and much larger limiting current density of -5.93 mA cm⁻², which surpasses the commercial 20 % Pt/C, in addition to the durability and resistance to methanol in 0.1 M KOH. The enhanced ORR activity of Co@NC-P(3-1) can be attributed to the synergistic effect between Co NPs and N, P atoms, the larger contact surface, more exposed active sites and good electrical conductivity. This work would provide some new ideas for designing and constructing promising carbon based nonprecious metal electrocatalysts for future practical fuel-cell applications.

Conflicts of interest

There are no conflicts to declare.

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