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Cobalt-Tannin-Framework Derived Amorphous Co-P/Co-N-C on N, P co-doped Porous Carbon with Abundant Active Moieties for Efficient Oxygen Reactions and Water Splitting

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Abstract: It is still a tremendous challenge to develop low-cost, earthabundant and efficient catalyst with multi-functional activities for hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Herein, a facile and scalable avenue was developed to prepare amorphous Co-P/Co-N-C supported on N, P co-doped porous carbon (Co-P/Co-N-C/NPC) with large specific surface area (1462.9 m² g⁻¹) and abundant reactive sites including Co-P, Co-N and NPC. Then the prepared electrocatalyst exhibits outstanding catalytic performance for HER (η =234 mV@10 mA cm⁻²), OER (η =374 mV@10 mA cm⁻²) and ORR ($E_{1/2}$ =0.89 V, *vs* RHE). Benefiting from the excellent HER performance and outstanding OER activity, the Co-P/Co-N-C/NPC delivers a current density of 10 mA cm⁻² for overall water-splitting at a cell voltage of 1.59 V which is comparable with the noble IrO₂ - Pt/C couple electrode.

Introduction

Ever-increasing environmental pollution and demand for sustainable energy have stimulated to explore eco-friendly and renewable energy and conversion system, such as hydrogen gas, fuel cells and metal-air batteries.^[1] Hydrogen has attracted extensive attentions due to the merits of high gravimetric energy density and environmental-friendly.^[2] Relative to the traditional technology, electrochemical water-splitting, composed by hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), is an efficient and pollution-free avenue to generate hydrogen gas.^[3] Apart from hydrogen gas, Zn-air batteries are considered as the most promising and appealing candidates to satisfy our requirement for power devices, because of the lowcost, high energy density, eco-friendly and great safety merits.^[4] For both water-splitting and Zn-air battery, electrocatalysts act as significant role to enhance the efficiency and reduce the energy consumption.^[5] At present, Pt-group based noble metals present the best catalytic performance for both oxygen reduction reaction (ORR) and HER, and IrO₂/RuO₂ exhibit the outstanding catalytic activity for OER.^[6] However, the high-cost, scarcity, poor durability

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and insufficient catalytic performance for HER, OER and ORR limited their large-scale applications and made these precious metals decreasingly attractive.^[7] To this end, it is urgent to develop low-cost, earth abundant, efficient and excellent stability non-noble electrocatalyst with trifunctional activity for HER, OER and ORR to accelerate the development and large-scale applications of water-splitting and Zn-air batteries.^[8]

Among the explored non-precious electrocatalyst, M-N (Fe/Co-N) based nanomaterials have been considered as appealing candidates for Pt due to the earth abundant properties and high catalytic performance in both acid and alkaline electrolytes for ORR.^[9] However, the obtained M-C catalysts possess poor catalytic activity for OER which result in sluggish charging performance in rechargeable metal-air batteries.^[10] Relative to M-N, M-P based compounds present excellent catalytic activity for both HER and OER due to the P species can trap protons by acting as a Lewis base for HER and benefiting the formation of peroxide during OER process.^[11] Furthermore, both experimental and theoretical results demonstrated that M-P can also act as promising active sites for ORR. For instance, Yu et al reported that Fe-P exhibits excellent catalytic performance for ORR in both acid and alkaline media.^[12] Zhao et al, using density functional theory (DFT), predicted that Fe- and Co-P₄ moieties can activate oxygen molecular which is benefit for ORR via an ideal four electrons avenue.^[13] Thus, the combination of M-N and M-P in the prepared catalysts can afford excellent trifunctional activities for ORR, HER and OER. Besides, the crystal structure is also a significant parameter to optimize the catalytic activity and amorphous structures can make themselves own outstanding performance in energy conversion benefiting of short-range structural ordering and abundant active sites.^[14] Apart from the above mentioned factors, the introduction of carbon matrix into the catalysts is also an important strategy to tune the catalytic performance by lower the resistance, enlarge the specific surface area and avoid the aggregation of metal species.[15] The in-situ formed carbon support via metal-ligand interactions could effectively avert metal species assemble and contact intimately which can expose abundant active sites and enhance the durability.[16]

In this contribution, a facile and easily scalable approach was developed to prepare highly active catalyst with abundant active moieties of amorphous Co-P and Co-N-C supported on N and P co-doped porous carbon matrix (Co-P/Co-N-C/NPC) for ORR, HER and OER (Scheme 1). Moreover, the in-situ prepared carbon support via cobalt-tannin-framework makes the metal species distributed uniformly and can contact with the carbon support intimately. Impressively, the prepared Co-P/Co-N-C/NPC presents excellent electrocatalytic for ORR, HER and OER. It also exhibits comparable catalytic performance with noble metals in

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full water-splitting which also possesses excellent long-term stability.



Scheme 1. Schematic illustration for the fabrication of Co-P/Co-N-C/NPC.

Results and Discussion

Coordination effects act as important role to form gel and the FT-IR results (Figure S1) demonstrated the interaction between TA and Co2+ due to the blue shift of -OH which can efficient avert the aggregation of metal species. The morphology and nanostructure of the prepared electrocatalysts were measured scanning electron microscopy (SEM). As shown in Figure 1a, the obtained Co-P/Co-N-C/NPC exhibits abundant pores relative to without acid and NH₃ treatment (Figure S2a). The porous structure in the obtained catalyst can expose abundant active sites and benefit the release of produced gas during HER and OER due to the adhered bubbles would hinder the diffusion of electrolyte and electron transfer which degrade the catalytic activity.^[17] Elements of C, N, Co and P contained in the prepared Co-P/Co-N-C/NPC before and after acid/NH₃ treatment (Figure 1b-e and Figure S2be). X-ray photoelectron spectroscopy (XPS) survey spectrum in Figure 1f also confirmed the elements in the obtained catalysts. The X-Ray diffraction (XRD, Figure S3a) of the obtained Co-P/Co-N-C/NPC was mainly composed by amorphous structure. Two typical peaks, G and D band, were observed in the obtained Raman spectra (Figure S3b) which also demonstrated the existence



Figure 1. SEM image of Co-P/Co-N-C/NPC (a) and corresponding elemental mappings of C (b), N (c), Co (d) and P (e). (f) XPS survey spectrum of Co-P/Co-N-C/NPC. (g) TEM (g) and S-TEM (h) images of Co-P/Co-N-C/NPC. (i) N_2 adsorption/desorption isotherm of Co-P/Co-N-C/NPC.

of carbon matrix. TEM was further conducted to investigate the microstructure of the prepared Co-P/Co-N-C/NPC (Figure 1h) which no nanoparticles can be observed on the porous carbon. N₂ adsorption/desorption results in Figure 1i demonstrate the obtained catalyst with large specific surface area (1462.9 m² g⁻¹) which is in line with the SEM and TEM results. The elemental mappings from Figure S4 further demonstrated the distribution of C, Co, N, and P in the obtained catalyst.

High-resolution XPS spectra of C, N, P and Co were further analyzed to determine the chemical valence in the prepared Co-P/Co-N-C/NPC. For C 1s in Figure 2a, the peaks located at 284.5 eV, 285.4 eV and 286.6 eV are ascribed to C-C, C-P and C-N, respectively, indicating N and P doped into the carbon matrix successfully.^[18] The peaks at 398.2 eV, 399.8 eV, 401.1 eV and 402.2 eV in N 1s are ascribed to pyridinic-N, pyrrolic-N, graphitic-N and oxidized-N, respectively.^[19] Graphitic-N and pyridinic-N, act as active sites for ORR, possess lone-pair electrons which can coordinate with metals to form M-N species.^[20] As shown in Figure 2c, the spectrum of P 2p confirmed the existence of Co-P (129.8 eV), oxidized P (131.9 eV), P-C (132.7 eV) and Co-O-P (133.9 eV),^[15b, 21] indicating the existence of Co-P and P doped into the carbon matrix successfully. Moreover, in the Co 2p range, the peaks located at 781.6 eV and 796.5 eV are ascribed to ionic state Co with shakeup satellites (785.8 eV and 802.2 eV). Thus, the prepared Co-P/Co-N-C/NPC exhibits Co-N, Co-P and NPC active moieties which acts as significant role during catalytic process.



Figure 2. High-resolution XPS spectra of C 1s (a), N 1s (b), P 2p (c) and Co 2p (d) in the prepared Co-P/Co-N-C/NPC.

The electrocatalytic performance and reaction kinetics for ORR of the prepared catalysts were conducted in 0.1 M KOH first using linear sweeping voltammograms (LSVs). An excellent electrocatalyst for ORR should possess positive half-wave potential ($E_{1/2}$) and ideal four-electron reaction pathway.^[22] We first investigated the effects of pyrolysis temperature on the catalytic activities (Figure S5) and the catalyst prepared at 800 °C delivers the largest $E_{1/2}$ and limiting current density, thus all the samples are prepared at this condition. Figure 3a shows the ring and disc current density collected using a RRDE at 1600 rpm with

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a sweeping rate of 5 mV s⁻¹ of NPC, Co-P/PC, Co-N/NC, Co- $\ensuremath{\mathsf{P/Co-N-C/NPC}}$ and $\ensuremath{\mathsf{Pt/C}}$ in O_2 saturated electrolyte. As shown in Figure 3a and 3c, Co-P/Co-N-C/NPC exhibits the highest halfwave potential (0.89 V) relative to NPC (0.82 V), Co-N (0.82 V) and Co-P (0.68 V) which is even better than Pt/C (0.83 V) and comparable with the reported values (Table S1), indicating that the coexistence of cobalt species and heteroatoms act as significant role on enhancing the catalytic performance.^[7c, 23] The ring current of Co-P/Co-N-C/NPC is negligible compare with disk current, indicating the low yield of H2O2 during ORR process. The electron transfer number and H2O2 yield were obtained via equations 3 and 4 (see the experimental section). It can be observed in Figure 3b that the H₂O₂ yields are lower than 10% and the electron transfer numbers nearly 4 in the potential range of 0.3-0.8 V except Co-P/PC, demonstrating the prepared catalyst mainly through 4 electrons for ORR. Koutecky-Levich (K-L) equations (see the experimental section) also can be used to calculate the electron transfer numbers of the prepared catalysts. As shown in Figure 3d and Figure S 6a, 7a and 8a, the current density increased with the increasing of rotating speed due to the accelerating mass transport at the electrode surface. From the slope of K-L plot (inset in Figure 3d and Figure S6b, 7b), except Figure S8b, whose electron transfer number is 3.04, the electron transfer numbers of Co-P/Co-N-C/NPC is around 4 at various potentials, indicating a predominantly four electrons reaction avenue to generate water as the dominate product which is in line with the RRDE results.



Figure 3. RRDE voltammograms for Co-P/Co-N-C/NPC, Co-N/NC, Co-P/PC, NPC, Pt/C (a) and corresponding electron transfer number and H_2O_2 yield (b) in 0.1 M KOH. (c) Half-wave potential of the prepared catalysts. (d) LSVs of Co-P/Co-N-C/NPC at different rotation speeds of 400, 800, 1200 and 1600 rpm and K-L plots at different potentials (inset). (d) Methanol resistance measurement of Co-P/Co-N-C/NPC and Pt/C. (e) I-t curves of Pt/C and Co-P/Co-N-C/NPC in O_2 saturated electrolyte with a rotating speed of 1600 rpm.

Except the catalytic performance for ORR, the resistance of methanol crossover and long-term durability are also significant parameters for the prepared catalysts in the practical applications. The methanol tolerance of the obtained Co-P/Co-N-C/NPC was measured in O₂ saturated 0.1 M KOH with a rotating speed of 1600 rpm. It can be observed that Pt/C exhibits stark current decline after the addition of methanol at 300 s. On contrast, the obtained Co-P/Co-N-C/NPC presents negligible current loss at the same condition, suggesting its superior methanol resistance. The long-term stability of the prepared Co-P/Co-N-C/NPC was measured using current time (i-t) chronoamperometric strategy in O₂ saturated 0.1 M KOH at a constant potential of 0.7 V. It can be clearly observed that the obtained catalyst exhibits negligible current loss for 24 h relative to Pt/C. As above discussed, the prepared Co-P/Co-N-C/NPC possesses excellent catalytic performance via four electrons pathway, outstanding methanol tolerance and predominant long-term stability in alkaline medium.

Apart from alkaline electrolyte, we also measured the electrocatalytic performance for ORR in O₂ saturated 0.5 M H_2SO_4 , due to the proton exchange membrane fuel cells (PEMFC) operated at acid electrolyte which own high energy conversion efficiency, eco-friendly and low operating temperature.^[24] However, most of the non-precious catalysts present poorer catalytic activity in acid medium relative to alkaline electrolyte due to the low reaction kinetics. As shown in Figure 4a, the prepared Co-P/Co-N-C/NPC presents the most positive $E_{1/2}$ (0.7 V) relative to PC, Co-P/PC and Co-N/NC except the reference of Pt/C, indicating the best catalytic performance for ORR in 0.5 M H₂SO₄. The reaction pathway was calculated via K-L plots and the obtained electron transfer number is 3.99, demonstrating the prepared Co-P/Co-N-C/NPC goes through an ideal four electrons



Figure 4. (a) LSVs of Co-P/Co-N-C/NPC, Co-N/NC, Co-P/PC, NPC and Pt/C in O₂ saturated 0.5 M H₂SO₄ with a scanning rate of 5 mV s⁻¹ at a rotating speed of 1600 rpm. (b) LSVs of Co-P/Co-N-C/NPC with different rotating speed and K-L plots at various potentials (inset). (c) Methanol durability test of Co-P/Co-N-C/NPC and Pt/C in O₂ saturated acid electrolyte with a rotating speed of 1600 rpm. (d) I-t curves of Co-P/Co-N-C/NPC and Pt/C with a rotating speed of 1600 rpm in O₂ saturated electrolyte.

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reaction pathway for ORR in 0.5 M H₂SO₄. Similarly, the methanol tolerance and long-term stability in acid electrolyte are also vital parameters for the prepared nanomaterials. As shown in Figure 4c, Pt/C exhibits evident current loss after methanol addition but not detected of the prepared Co-P/Co-N-C/NPC, indicating the excellent methanol tolerance. The obtained Co-P/Co-N-C/NPC delivers poorer stability in acid electrolyte relative to alkaline medium due to the severe corrosion situation.^[25] Thus, the prepared nanomaterial possesses excellent catalytic activity, outstanding methanol resistance in acid electrolyte.

The OER performances of the obtained catalysts and IrO₂ were evaluated in 1 M KOH with RDE setup. As illustrated in Figure 5a, IrO₂ supported on Ni foam, act as reference, presents the best catalytic performance with an overpotential of 370 mV to deliver the current density of 10 mA cm⁻². Evidently, the prepared Co-P/Co-N-C/NPC possesses the lowest overpotential (374 mV) relative to other composites, except IrO2, including Co-N/NC (378 mV), NPC (406 mV) and Co-P/PC (450 mV), demonstrating its excellent catalytic performance for OER which is comparable with the reported materials (Table S2). It can be observed that the overpotential of NPC is lower than Co-P/PC, demonstrating the co-doping of different heteroatoms also can optimize the catalytic performance efficiently.^[26] The outstanding catalytic performance of Co-P/Co-N-C/NPC can be attributed to its abundant active moieties, such as Co-N, Co-P and NPC and the porous nanostructure with high specific surface area. Tafel slope is a significant means to investigate the kinetics of the prepared catalysts and the smallest value means the fastest current density promoting with the overpotential increased. Apart from IrO2 (75 mV dec⁻¹, Figure 5b), the obtained Co-P/Co-N-C/NPC possesses the lowest Tafel slope of 92 mV dec⁻¹ compared with Co-N (98 mV dec⁻¹), NPC (107 mV dec⁻¹) and Co-P/PC (142 mV dec⁻¹), further demonstrating its superiority for OER.



Figure 5. LSVs of Co-P/Co-N-C/NPC, Co-P/PC, NPC, Co-N/NC, IrO_2 and Ni foam for OER in 1 M KOH (a) and corresponding Tafel slopes (b). (c) Overpotentials and Tafel slopes of the prepared catalysts. (d) I-t curves for IrO_2 and Co-P/Co-N-C/NPC.

Besides, the long-term stability is an indispensable feature for an outstanding catalyst in practical applications. The long-term stability measurement of Co-P/Co-N-C/NPC and IrO₂ were collected at the constant overpotential for 10 mA cm⁻². The current-time curve of Co-P/Co-N-C/NPC presents negligible current density loss relative to IrO₂ after 50000 s, indicating its excellent stability. Thus, the prepared catalyst exhibits outstanding electrocatalytic performance and predominant stability in 1 M KOH for OER.

The electrocatalytic performance of the prepared Co-P/Co-N-C/NPC and other comparison nanomaterials for HER were measured using a typical three-electrode setup with RDE in 0.5 M H₂SO₄. As shown in Figure 6a, Pt/C, as the reference, exhibits the best electrocatalytic performance with the lowest overpotential to deliver the same specific current density. It can be observed that Co-P/Co-N-C/NPC needed the smallest overpotential (234 mV) to drive 10 mA cm⁻², which is an important parameter for the prepared catalyst, relative to Co-P/PC (278 mV), Co-N/NC (243 mV), NPC (241 mV) and Ni foam (297 mV), indicating its best catalytic performance for HER due to the abundant active moieties. The electrocatalytic activity enhanced evidently after acid and NH₃ treatment (Figure S9), due to the enlarged specific surface area and rich pores.^[27] It can be clearly observed that Co-P/Co-N-C/NPC presents the lowest Tafel slope (139 mV dec⁻¹), except Pt/C (33 mV dec⁻¹), relative to Co-P/PC (171 mV dec⁻¹), Co-N/NC (145 mV dec⁻¹), NPC (152 mV dec⁻¹) and Ni foam (173 mV dec⁻¹), indicating its excellent catalytic performance (Figure 6b). The HER stability of the prepared Co-P/Co-N-C/NPC was shown in Figure 6d. It can be clearly observed that the current density exhibits negligible loss after long-term test for 70000 s at a constant potential of 234 mV, demonstrating its outstanding stability in alkaline electrolyte.

As mentioned above, the obtained Co-P/Co-N-C/NPC nanomaterial shows satisfactory catalytic performance for both HER and OER in alkaline electrolyte. Therefore, an electrolyzer with a two-electrode setup with Co-P/Co-N-C/NPC as both anode and cathode was measured in alkaline electrolyte. Electrons transferred from anode to cathode during the full-water electrolysis which provide electrical power to generate O₂ at the anode and H₂ at the cathode. As shown in Figure 6e and the photograph of the water splitting (inset), the Co-P/Co-N-C/NPC || Co-P/Co-N-C/NPC couple electrode is capable to drive the full water-splitting with a cell voltage of 1.59 V which is comparable with the noble metals of IrO₂ || Pt/C and superior to the Ni foam || Ni foam and superior to the reported values (Table S3). Moreover, the obtained Co-P/Co-N-C/NPC || Co-P/Co-N-C/NPC also presented excellent stability for the overall water-splitting in the alkaline medium. Figure 6f shows that there is no evident loss of current density after long-term water-splitting reaction, suggesting its tremendous potential in practical applications as alternative to substitute precious metal catalyst for over-all water-splitting. The outstanding catalytic performance of the prepared Co-P/Co-N-C/NPC can be attributed to the following factors: the obtained nanomaterial possesses large specific surface area of 1462.9 m² g⁻¹ which can expose abundant active sites and the release of generated gas during HER and OER; the abundant active moieties act as significant role on enhancing the catalytic activity; the amorphous property of the catalyst can provide rich reaction sites; the co-doping of different heteroatoms can also benefit the catalytic process.

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Figure 6. LSVs of Co-P/Co-N-C/NPC, Co-N/NC, Co-P/PC, NPC, Pt/C and Ni foam for HER in 1 M KOH (a) and corresponding Tafel slopes (b). (c) Overpotentials and Tafel slopes of the prepared catalysts. (d) I-t curves of Co-P/Co-N-C/NPC. (e) Polarization curves of Co-P/Co-N-C/NPC || Co-P/Co-N-C/NPC, Ni foam || Ni foam and IrO₂ || Pt/C couples for full water-splitting. (f) I-t curves of Co-P/Co-N-C/NPC || Co-P/Co-N-C/NPC and IrO₂ || Pt/C.

Conclusions

In summary, an efficient tri-functional electrocatalyst of Co-P/Co-N-C/NPC was developed via cobalt-tannin-framework strategy which holds several merits: the catalyst possesses large specific surface area of 1462.9 m² g⁻¹ which can provide abundant active sites and benefit the release of produced gas; the rich active sites including Co-P, Co-N and NPC is benefiting on enhancing the catalytic performance; the amorphous properties endow the catalyst excellent activity benefiting of short-range structural ordering and abundant active sites. Then the obtained catalyst exhibits outstanding catalytic performance for HER, OER, ORR and full water-splitting. This work paves a facile and scalable strategy to develop efficient and low cost non-noble catalysts with multifunctional catalytic effects.

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Keywords: porous carbon • oxygen reduction reaction • nonnoble catalysts • multi-functional activities• water splitting

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A facile and scalable avenue was developed to prepare amorphous Co-P/Co-N-C supported on N, P codoped porous carbon (Co-P/Co-N-C/NPC) with large specific surface area (1462.9 m² g⁻¹) and abundant reactive sites including Co-P, Co-N and NPC, which exhibits outstanding catalytic performance for HER (η =234 mV@10 mA cm⁻²), OER (η =374 mV@10 mA cm⁻²) and ORR (E_{1/2}=0.89 V, vs RHE).



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Cobalt-Tannin-Framework Derived Amorphous Co-P/Co-N-C on N, P codoped Porous Carbon with Abundant Active Moieties for Efficient Oxygen Reactions and Water Splitting