Carbon-Coupling Metallic Cobalt as Trifunctional Catalysis for Oxygen Reduction/Evolution and Hydrogen Evolution

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Abstract The next-generation energy storage focuses on sustainability and renewability, facilitating the process of metal-air batteries and fuel cells. Nevertheless, their performances are suffering from the tardy development of the elaborate design and large-scale synthesis strategy of cost-efficient electrocatalysts. In this work, a convenient strategy for facile synthesizing electroactive material is proposed. As a result, a trifunctional Co/C catalyst is fabricated *via* a convenient calcination process, utilizing the pyrolysis of cobalt acetate and melamine. The prepared Co/C sample delivers a positive half-wave potential of 0.75 V in oxygen reduction reaction (ORR). Furthermore, the low overpotentials at 10 mA cm⁻² are shown in alkaline conditions for oxygen evolution reaction (OER, 388 mV) and hydrogen evolution reaction (HER, 202 mV). The improved activity is mainly due to the interaction between Co and the in situ formed carbon carrier. The promising trifunctional activities endow the Co/C sample with a bright prospect in metal-air batteries and overall water splitting.

Keywords trifunctional catalyst, oxygen reduction, oxygen evolution, hydrogen evolution

Introduction

Renewable energy storage devices represented by metal-air batteries and fuel cells are obtaining much attention owing to the carbon neutrality policy and the transformation of energy structure. To some extent, the discharging and charging ability of these devices successively hinging on the oxygen reduction (ORR) and oxygen evolution (OER) properties of the electrocatalyst. In other words, these devices severely suffer from the sluggish kinetics and low energy conversion efficiency of ORR and OER.^[1] Therefore, the development of promising bifunctional ORR/OER catalysts is crucial to the commercialization of the devices. Unfortunately, the current commercial catalysts for fuel cells and metal-air batteries are mainly Pt-, Ir- and Ru-based precious metals materials, which are limited by their scarcity, high price, poor toxicity resistance, and unsatisfactory stability.^[2,3] As a result, it is imperative and urgent to explore earth-abundant, cost-effective, and stable non-noble metal electrocatalysts, especially bifunctional ORR/OER catalysts.

So far, carbon-supported metal materials, such as carbon-coupling metallic cobalt, are eye-catching due to their good electronic conductivity, favorable chemical and mechanical stability, and abundant nano-/micro-structures.^[4] Considering the chemical substitution reaction of the active metal atoms in catalysts and the H⁺ ions in acidic electrolytes, alkaline electrolytes are more suitable for such catalysts to provide a suitable working environment.^[5] In recent years, carbon-supported transition metal oxides/sulfides/hydroxides are proved to be good ORR/OER/HER catalysts.^[6-9] For example, Qiu and co-authors developed a flash Joule heating method for synthesizing Ag/Co/C hybrid ORR catalyst.^[5] Rasaki's group reported Pt-comparable carbon-supported cobalt (C@CoC_x) ORR catalyst.^[10] Furthermore, Chen's group designed a complex CoC_x-based compound with CoFe phosphide and carbon carrier, denoted as

CoC_x/(Co_{0.55}Fe_{1.945})₂P@C. The compound displayed excellent ORR and OER activity in 0.1 M KOH electrolyte and even in rechargeable zinc-air batteries.^[11] Zhang *et al.* synthesized a ternary Fe/Co/WC@NC ORR catalyst *via* a one-pot strategy. Interestingly, the methanol tolerance ability of Fe/Co/WC@NC endows prospects in fuel cells.^[12] Unfortunately, the complex elementary composition and hierarchical structure increase the cost and difficulty in manufacturing and thus hinder the large-scale preparation and application of these catalysts. Therefore, it is promising to develop a convenient and affordable strategy to produce carbon-coupling metallic cobalt multifunctional electrocatalyst.

Herein, we propose a convenient strategy for large-scale synthesizing Co/C for ORR, OER, and HER catalysis. Briefly, this strategy bases on the pyrolytic reaction of melamine and the carbonation reaction of Co²⁺ in Co(Ac)₂·4H₂O precursor. Further, Co²⁺ is partially reduced to metallic Co by the reductive carbon species in Co(Ac)₂·4H₂O and/or melamine. In the presence of melamine, the produced metallic cobalt nanoparticles couple with carbon and uniformly disperse, and thus the product Co/C sample remains nano-scale morphology. In the absence of melamine, the produced metallic cobalt nanoparticles tend to agglomerate and form larger microparticles, denoted as the Co sample. For electrochemical properties, the Co/C sample displays a Pt-comparable half-wave potential of 0.75 V *versus* RHE for the ORR, and low overpotentials at 10 mA cm⁻² (η_{10}) of 388 and 202 mV respectively for OER and HER, which confirms it a trifunctional electrocatalyst, and endows it a bright prospect in metal-air batteries and fuel cells. Subsequently, we investigate the electrocatalytic properties of Co nanoparticles. As a result, the Co sample exhibits moderate activity of ORR ($E_{1/2}$ = 0.69 V), and high overpotentials of OER (η_{10} = 431 mV) and HER (η_{10} = 394 mV). With the professional characteristics of XRD, SEM, and XPS, we study the detailed structure of Co/C and Co, and

illuminate the relationship between structure and electrochemical performance.

Experimental

Synthesis of Co/C

The Co/C was synthesized *via* a pyrolysis reaction. To be specific, 4.0 g $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and 2.0 g melamine were added into a glass dish with ethanol, followed by ultrasonic dispersion to form a uniform suspension. The obtained suspension was dried at 80 °C overnight and then pulverized to obtain uniform violet powder as the precursor. The precursor was transferred to a corundum porcelain boat and placed in a tube furnace, subsequently heated at 550 °C for 2 h under N_2 with a heating rate of 5 °C min^{-1} . The obtained black powder was Co/C nanoparticles.

Synthesis of metallic Co

The manufacturing method of the Co sample was similar to the Co/C sample except for that only $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ was used as the precursor.

Materials characterization

The crystal structure and surface structure of three samples were successively studied by powder X-ray diffraction (XRD, PANalytical, X'Pert3, Cu target), scanning electron microscope (SEM, Hitachi, SU8220), Raman spectra (LabRAM HR, $\lambda = 633$ nm), transmission electron microscopy (TEM, Thermo, Talos F200S), and X-ray photoelectron diffraction (XPS, Escalab 250Xi, Al target). Moreover, the pyrolysis processes were analyzed by thermogravimetric and differential thermal analysis (NETZSCH, STA409PC, TGA-DTA) under the N_2 atmosphere with a rate of 5 °C min^{-1} .

Electrocatalytic measurements

The OER, HER, and ORR performances were examined by cyclic voltammetry (CV) curves and linear sweep voltammetry (LSV), finished in a CHI 760E electrochemical workstation. Unless otherwise noted, all electrochemical measurements mentioned were performed on a three-electrode system assembling with a working electrode, a graphite rod counter electrode, and an Ag/AgCl reference electrode containing a 3.5 M KCl internal reference solution. Unless otherwise specified, the potentials mentioned in this work are represented by the potentials versus RHE.

The OER and HER performances were measured in N_2 -saturated 1 M KOH solution, which working electrode was a carbon fiber paper (CFP) with surface coated catalyst with a mass loading of 0.86 ± 0.05 mg cm^{-2} . The catalyst ink was dripped onto the surface of CFP and then dried at 60 °C.

The ORR performance and electrochemical surface area (ECSA) were measured in O_2 -saturated 0.1 M KOH solution, which working electrode was respectively a rotating ring disk electrode (RRDE) and a rotating disk electrode (RDE) loading with catalyst on the ring with a mass loading of 0.135 ± 0.005 mg cm^{-2} . Especially, LSV curves of ORR were collected in a four-electrode system using an RRDE as a working electrode.

The rechargeable zinc-air batteries measurements

The rechargeable zinc-air battery was assembled by a polished zinc plate, a stainless-steel mesh coated with a catalyst, a membrane separator, and a set of metal-air battery molds (OMS-T1). The 6 M KOH electrolyte is with an additive of 0.2 M $\text{Zn}(\text{Ac})_2$. The measurements of zinc-air batteries were conducted on a LAND CT3001A 1U system and a CHI 760E electrochemical workstation.

Results and Discussion

Structural and morphological properties

The crystal phases of the samples are detected by XRD (Figure 1). Briefly, the XRD pattern of both Co and Co/C samples show diffraction peaks at around 44.4°, 51.7°, and 75.9°, which matches well with the (111), (200), and (220) facets of cubic Fm-3m structure of metallic Co (PDF# 15-0806). Moreover, no impure diffraction signal could be detected, indicating the successful formation of metallic Co *via* calcination. In other words, $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ dehydrates and decomposes into well-crystalline metallic Co nanoparticles with or without melamine. Interestingly, the XRD pattern of the Co/C sample displays a weaker intensity of diffraction peaks than that of the Co sample, suggesting that the partial lattice distortion is caused by the coupling of metallic cobalt and the carbon derived from melamine. No obvious signals indexing to carbon species are detected, indicating that the C atoms are highly dispersed in the cobalt phase instead of producing $\text{g-C}_3\text{N}_4$.^[13,14]

Figure 1 XRD patterns of Co/C and Co sample.

Raman spectra roughly offer surface information of Co/C and Co samples. Figure 2 shows Raman scattering modes assign to the F_{2g} , E_g , and A_{1g} vibration peaks of Co_3O_4 , the peaks in which at ~ 190 and 670 cm^{-1} are indexed to the stretching modes of Co-O bonds in octahedron and tetrahedron, respectively.^[15] The detection of Co-O implies the surface oxidation of metallic Co, possibly due to the oxidation of atmosphere, and the heat effect of the Raman testing process and consistent with the active reducibility of Co. Additionally, the signals at ~ 1350 for the D band and ~ 1580 cm^{-1} for the G band are the typical Raman scattering of carbon.^[16] Unfortunately, no distinct peaks corresponding to the C-C bonds are detected, probably due to the strong signal of Co, and the weak crystallinity of carbon in Co/C and Co samples.

The differences in morphology and elementary composition of the two samples were observed by SEM. Figure 3a demonstrates the nanosphere morphology of the Co/C sample with a diameter in the range of 20–80 nm. On the contrary, Figure 3b shows the bulk morphology on the micron scale of the Co sample, implying the agglomeration of products during pyrolysis in the absence of melamine. The carbon nanoparticles derived from the pyrolysis of melamine might promote the dispersion of Co species.

Figure 2 Raman spectra of Co/C and Co sample.

Figure 3 SEM images and element mapping of (a, c) Co/C and (b, d) Co sample.

Table 1 Quantitative analysis of element via EDS

Samples	Co (atom%)	C (atom%)	Co (w%)	C (w%)
Co/C	68.00	32.00	91.25	8.75
Co	99.15	0.88	99.82	0.18

The difference in elementary composition is certified by energy disperse spectroscopy (EDS) as shown in Figures 3c, 3d, and Table 1. Dominant Co atoms (99.12 atom%) and negligible C atoms (0.88 atom%) are detected. The probable resources of C atoms in the Co sample include that the pyrolysis of residual acetate, the carbon pollutants on silicon wafers, and the carbon in conductive adhesives. On the contrary, abundant C atoms (32.00 atom%) are present in the Co/C sample owing to the pyrolysis of melamine. The atomic ratio of Co and C in the Co/C sample reaches 2.1 : 1. Herein, the C atoms promote the dispersion of Co atoms, which explains the morphological advantage of the Co/C sample.

The morphology and elementary distribution of the two samples were further tested via TEM. In terms of morphology, the TEM patterns in Figures 4a and 4b demonstrate that the nanoparticles in the Co/C sample are dispersed, while the particles in the Co sample are seriously agglomerated. Furthermore, the high-resolution image in Figures 4c and 4d displays a lattice fringe with a distance of 0.247 nm indexed to the (111) facet of metallic Co (PDF# 15-0806). In the Co sample, the crystal area is larger and the crystal fringe is clearer, indicating its higher crystallinity than the Co/C sample, which is in good agreement with XRD results. Compared with the

Figure 4 TEM images and elementary mapping of (a, c, e) Co/C and (b, d, f) Co samples.

elementary distribution in the Co sample, the Co atoms are evenly dispersed between the C atoms in the Co/C nanoparticles. It can be concluded that the addition of melamine can inhibit the growth of particles and thus control the particle size.

The XPS were carried out to analyze the surface natures of two samples. The binding energy of the C–C bond (284.8 eV) in the C 1s region was used as the reference standard for calibrating Co 2p and O 1s regions. According to Figure 5a, Co atoms in the Co/C sample display five deconvolution peaks located at around 777.8, 779.6, 781.1, 784.8, and 786.4 eV, which could be separately indexed to metallic Co⁰, Co³⁺ ions, Co²⁺ ions, and the satellite signal reflected the spin-orbit splitting of Co^{2+/3+}.^[17,18] Due to the active chemical properties of metallic Co⁰, the Co²⁺ and Co³⁺ ions are probably generated via a spontaneous oxidation reaction of metallic Co⁰ by the oxygen from the air, which agrees with the Raman test, and such phenomenon has been reported.^[19,20] Interestingly, the peak on behalf of metallic Co⁰ in Figure 5b is more intense in the Co sample rather than that in the Co/C sample, indicating that cobalt atoms tend to be in elemental form in absence of carbon particles. Therefore, it could be inferred that the carbon particles derived from melamine could: accelerate the oxidation of metallic cobalt atoms and create more Co^{2+/3+} species, which optimize the electronic structure of the Co/C sample. For the O 1s region of Co/C sample, Figure 5c, three peaks appeared at around 529.4, 531.6, and 533.5 eV indicate the existence of lattice oxygen, surface chemisorbed oxygen (hydroxyl), and adhering water,^[21] which evidence the oxidation of metallic Co⁰. The O 1s spectrum of the Co sample in Figure 5d shows deconvolution peaks similar to that of the Co/C sample.

Figure 5 XPS spectra of Co 2p and O 1s spectra of (a, c) Co/C and (b, d) Co sample.

Figure 6 TGA-DTA curves of the pyrolysis processes of (a) the mixture of melamine and $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and (b) the pure $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$.

The pyrolysis processes of Co/C and Co samples were analyzed via TGA and DTA. As can be seen in Figure 6b, a typical TGA curve of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ is collected. The rapid weight losses of 28.9%, 41.5%, and 70.8% successively reflect the processes of the melting of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and the dehydration of water molecules, the generation of basic cobalt acetate, and the further pyrolysis to form dominant metallic Co and minor carbon residue.^[22] However, in the presence of melamine, the TGA curve changed significantly, as shown in Figure 6a, probably because melamine affected the dehydration of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and the formation of basic cobalt acetate.^[23] Briefly, the residual mass of the mixture of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and melamine is 27.1% after TGA, similar to that of 29.2% of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$.

Electrocatalytic performances

To investigate the ORR performances of two samples, CV was firstly carried out. Figure 7a shows the CV curves separately collected in 0.1 M KOH O_2 -saturated solution. Especially, the CV curve of the Co sample displays an identifiable oxygen reduction peak is detected at around 0.68 V (versus RHE) in O_2 -saturated solution. For the Co/C sample, the reduction peak shifts to a positive potential, which is 69 mV higher than the Co sample. To further evaluate the ORR properties, LSV curves were measured and illustrated in Figure 7b. In terms of activity, the Co/C sample displays a positive half-wave potential of 0.75 V at 2.49 mA cm^{-2} surpassing the Co sample (0.69 V at 1.99 mA cm^{-2}), manifesting that the Co/C sample is more active than the Co sample. For reaction kinetics, the Co/C sample exhibits a larger diffusion-limited current density (j_L) of 4.97 mA cm^{-2} , suggesting its rapid reaction kinetics. On the contrary, the j_L of the Co sample is relatively

Figure 7 ORR performance of the two samples: (a) CV curves and (b) LSV curves; (c) Tafel plots; (d) the number of transferred electrons (n) and the yield of peroxide (y_{peroxide}); and (e, f) LSV curves before and after the accelerated aging tests.

moderate (3.97 mA cm^{-2}), hinting at its sluggish kinetic response. The Tafel plots were drawn in Figure 7c for a rough understanding of the reaction mechanism. The Co/C sample possesses a promising Tafel slope of 53.5 mV dec^{-1} , attributed to the Temkin-type oxygen adsorption mode.^[24] In contrast, the Tafel slope of the Co sample exhibits a moderate Tafel slope of 64.7 mV dec^{-1} , suggesting its relatively sluggish reaction kinetics.

For a deeper sight into the reaction mechanism, the number of transferred electrons (n) and the yield of peroxide (y_{peroxide}) were calculated based on the relative relationship between the ring current and the disk current, illustrated in Figure 7d. Compared with the Co sample, the reaction mechanism of the Co/C sample is closer to the four-electron transfer pathway than that of the Co sample. To be specific, the Co/C sample exhibits an average electron transfer number (n) of 3.49 per oxygen molecule, and an average yield of peroxide (y_{peroxide}) of 25.5% in the potential range of 0.3 to 0.7 V. In stark contrast, the n of Co sample is 2.66 per oxygen molecule, signifying the sluggish two-electron transfer pathway occurred. As a consequence, the y_{peroxide} of the Co sample is approached 75.6%, which is much higher than that of the Co/C sample.

Stability was evaluated by the accelerated aging test (ADT). ADT was conducted in the potential range of 0.57 to 0.77 V for 1000 cycling with a scan rate of 100 mV s^{-1} . According to Figures 7e and 7f, the Co/C sample demonstrates an inappreciable $E_{1/2}$ decay of a few millivolts and a mildly decrease of j_L from 4.97 to 4.88 mA cm^{-2} . However, the j_L of the Co sample is sharply declined from 3.97 to 3.64 mA cm^{-2} during ADT, suggesting its poor electrochemical stability.

OER and HER were measured to further explore the electrochemical properties of the Co/C sample, which results were drawn in Figure 8. For OER, Co/C sample and Co sample display comparable activity in N_2 -saturated 1 M KOH solution. Briefly, the overpotential at 10 mA cm^{-2} (η_{10}) of the Co/C sample

Figure 8 CV curves, LSV curves, and Tafel plots of (a–c) OER and (d–f) HER.

is 388 mV, which is 43 mV lower than that of the Co sample, indicating the better OER activity of the Co/C sample. Moreover, the Co/C sample affords a smaller Tafel slope of 80.2 mV dec⁻¹ than the Co sample (96.8 mV dec⁻¹), confirming its rapid reaction kinetics. For HER, the current density of the Co/C sample increases with the increase of overpotential. The coupling of carbon endows Co/C sample an excellent HER activity with a low η_{10} of 202 mV. Moreover, the Co/C sample possesses a large current density over 100 mA cm⁻² at -0.45 V. However, the Co sample fails to reach a comparable current density, which is approached to one-fifth that of the Co/C sample at -0.45 V.

Considering that the accessible surface area of catalysts is generally very different in N₂-adsorption/desorption test and the electrochemical processes in the alkaline electrolyte. In this work, the electrochemically active surface area (ECSA) is used to determine the accessible surface area.^[25] In general, the larger the C_{dl}, the larger the ECSA.^[26] Therefore, the ECSA of two samples is assessed by C_{dl}. Figures 9a and 9b show CV curves of two samples measured in a non-faradic range from 0.87 to 0.97 V. Interestingly, the Co sample possesses a C_{dl} of 2.00 mF cm⁻² twice as large as that of the Co/C sample (0.99 mF cm⁻²), which reveals the higher specific activities of Co/C sample probably derived from optimizing of the electron structure of cobalt by coupling with carbon.

Brief discussion. The Co/C catalyst displayed a better activity than its counterpart, and this can be understood by the following reasons: 1) the Co/C catalyst has a relatively smaller size and good dispersion, this could favor for the expose and application of active sites; 2) the Co/C catalyst has relatively more carbon, and carbon play three key roles, one is for the dispersion of Co, and the other is its electrochemical activity, as carbon is one of most reported catalysts for ORR/OER; moreover, the interaction between carbon and Co could also help for the improvement of the activity.

Figure 9 (a, b) The CV curves collected in 0.1 M KOH under N₂ with scan rate ranging from 10 to 50 mV s⁻¹, and (c, d) the plots of current density against scan rate.

Figure 10 The rechargeable zinc-air battery performances of Co/C sample: (a) open-circuit voltage (V_{oc}), (b) polarization curve and power density, and (c) discharge curves under different current densities.

3.3 The rechargeable zinc-air batteries performances

In the respect of availability, measurements in the rechargeable zinc-air batteries were required for the Co/C sample. Figure 10a shows that the rechargeable zinc-air battery with Co/C demonstrates a horizontal V_{oc} of ~1.36 V (vs. Zn) during the 6-hour open-circuit voltage test, which difference is about 0.29 V from the theoretical V_{oc} (1.65 V vs. Zn).^[27] After 6 hours of standing, the V_{oc} of the battery increased by 37 mV. The charging and discharging polarization curve of the battery was measured to deliver the information of power density. According to Figure 10b, the battery displays a promising peak power density of 66.0 mW cm⁻² at 124.5 mA cm⁻². The battery was sequentially discharged at a series of current densities of 2, 5, 10, 20, 50, 5 mA cm⁻² for 1 h each to estimate the discharging rate performance, which results is illustrated in Figure 10c. The output voltage in the second segment drops by only 14 mV compared to that of the first segment of the discharging curve at 5 mA cm⁻², evidencing the extraordinary rate of performance of the Co/C sample. Herein, the promising power density and stability of the Co/C sample render strong proof of its practicability in the rechargeable zinc-air battery. Additionally, the good HER and OER properties could provide the Co/C sample a bright prospect in overall water splitting, which does not further study in this work. The electrochemical performance of Co-based materials in recent reports is listed in supporting information (Table S1), which shows that the Co/C sample is a promising trifunctional catalyst in the contemporary.

Conclusions

In summary, an efficient trifunctional Co/C catalyst with moderate ORR, OER, and HER activity was successfully prepared. Briefly, the Co/C sample displays promising ORR activity with the half-wave potential of 0.75 V, and OER and HER performances with low potentials of 388 and 202 mV at 10

mA cm^{-2} , respectively, which overperforms Co sample. The electrochemical properties of Co/C catalyst indicate the feasibility of the proposed convenient strategy for large-scale preparing Co/C trifunctional electrocatalyst. Compared with the Co 2p spectrum of Co sample, that Co/C sample displays a weaker peak of metallic cobalt. As a result, more $\text{Co}^{2+/3+}$ active species are generated in the Co/C sample accompanied by the introduction of carbon particles, which explains the higher activities of Co/C than the Co sample. In conclusion, the proposed strategy provides a feasible and convenient method for large-scale synthesizing trifunctional carbides-based catalysts used for energy storage and conversion.

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Supporting Information

Supporting information for this article is available on the WWW under www.genchemistry.org/EN/10.21127/yaoyigc20210013.

Conflict of Interest

The authors declare no conflict of interest.

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