Co$_2$P Embedded into P and N Dual-Doped Carbon Nanotubes and Graphene as a Bifunctional Oxygen Electrocatalyst

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Abstract. The reasonable design of inexpensive and efficient bifunctional electrocatalyst towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is still challenging for Zn-air batteries. Herein, a novel and effective design is proposed to fabricate Co$_2$P nanoparticles encapsulated in doped carbon nanotubes and rGO sheets (Co$_2$P/NPCNTs-rGO) through a direct self-catalyzed growth procedure. That is, cobalt phthalocyanine derivatives as the cobalt sources are not only employed to form Co$_2$P nanoparticles, but also used to catalyze the formation of CNTs and rGO. Benefiting from the unique structure and composition, the Co$_2$P/NPCNTs-rGO-800 shows significant OER (overpotential of 420 mV) and ORR (half-wave potential of 0.73 V) properties. Most importantly, the activity parameter of Co$_2$P/NPCNTs-rGO-800 ($\Delta E$=0.92 V) is comparable to that of RuO$_2$ (0.91 V) and lower than that of Pt/C (1.05 V), indicating that Co$_2$P/NPCNTs-rGO-800 is of a good comprehensive ORR/OER bifunctional performance. This work provides an effective strategy for the synthesis of outstanding multifunctional catalysts for wider practical applications.

1. Introduction

Recently, rechargeable Zn-air batteries have become one of the most promising energy conversion/storage technologies, because of their safety, high theoretical energy density and environment-friendliness [1-3]. As for Zn-air batteries, the actual properties are mainly dominated by the essential electrochemical reaction including oxygen evolution reaction (OER) and oxygen reduction (ORR) in the cathode [4]. Up to now, Pt/C materials are considered as excellent catalysts for ORR, whereas Ir and Ru are efficient for OER [5]. Nevertheless, widespread promotion of these precious-metal-based catalysts has largely impeded, owing to their scarce sources, high costs, single function and poor durability. So that, developing efficient, cheap and good durability bifunctional electrocatalysts for Zn-air batteries is of great significance [6]. In this regard, Co$_2$P has received increased attention due to its multiple advantages of nature abundance, environment-friendliness, and efficient redox reactivity [7,8]. Unfortunately, the single Co$_2$P exhibits unsatisfactory electrical conductivity during the catalytic processes, which has certainly impacted electrocatalytic performance of Co$_2$P.

To overcome the above shortcomings, it is a good idea to encapsulate Co$_2$P nanoparticles into carbon materials, which can endow the compound with high electrical conductivity. Nevertheless, the simple encapsulation through the direct carbonization of organics can easily suffer from the significant aggregation, thus hindering the exposure of the active sites. So that, it is urgent to use a suitable carbon matrix to anchor the Co$_2$P. Among them, graphene interconnected with carbon nanotubes (CNTs-rGO) seems to be an effective matrix [9]. The Co$_2$P nanoparticles can be encapsulated in CNTs and rGO, which effectively prevents aggregation and facilitates electrons transport for both OER and ORR [10].
In this report, we synthesized Co$_2$P encapsulated in doped carbon nanotubes and rGO sheets via solvothermal and pyrolysis processes. During the pyrolysis process, Co from cobalt tetraniitrophthalocyanine (CoPc(NO$_2$)$_4$) can catalyse the production of carbon nanotubes on graphene sheets and then combine with P from chloride trimer (Cl$_6$N$_3$P$_3$) to form Co$_2$P nanoparticles. Benefiting from unique design, the obtained electrocatalyst shows significant properties for both OER and ORR.

2. Experiment

2.1. Electrocatalyst Synthesis:
Typically, 0.40 g CoPc(NO$_2$)$_4$, 0.75 g melamine, 0.025 g Cl$_6$N$_3$P$_3$, and 2 g graphene oxide (GO) suspension (2.50 wt%) were added in 25 mL N, N-Dimethylformamide (DMF). After being homogenized by ultrasound, the mixture was heated to 180 ℃ for 24 h in Teflon-lined autoclave. Following that, the product was washed for three times with deionized water and freeze-dried with the vacuum. After that, the as-prepared precipitate was pyrolyzed to 800 ℃ for 2 h, which was named as Co$_2$P/NPCNTs-rGO-800.

2.2. Electrochemical characterizations:
To prepare the working electrode, 5 mg catalyst was added into 1 mL ethanol containing 50 μL Nafion solution and ultrasonically dispersed to form the electrocatalyst ink. After that, 10 μL electrocatalyst ink was deposited on a rotating disk electrode (RDE) and then dried naturally. The ORR/OER activities were evaluated with a three-electrode cell containing RDE as working electrode, graphene rod as reference electrode and saturated calomel electrode (SCE) as the counter electrode.

The relationship between the recorded potential versus SCE was converted to an RHE scale according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.059pH$$

The ORR measurements were carried out in a 0.1 M KOH O$_2$-saturated solution, with a scan rate of 50 mV s$^{-1}$ for CV and 10 mV s$^{-1}$ for LSV. The electron transfer number (n) could be calculated according to the LSV curves at different potentials using the Koutecky-Levich (K-L) equations:

$$\frac{1}{J} = \frac{1}{J_D} + \frac{1}{J_k} = \frac{1}{B\omega^{3/2} + \frac{1}{nFkC_{O_2}}}$$

$$B = 0.62nFC_{O_2}(D_{O_2})^{2/3}v^{-1/6}$$

For OER measurements, the LSV curves were obtained at scan rate of 5 mV s$^{-1}$ in 1 M KOH O$_2$-saturated solution, which have been $iR$-corrected.

3. Results and discussion

The morphologies of Co$_2$P/NPCNTs-rGO-800 are investigated using scanning electron microscopy (SEM). It can be seen that lots of CNTs are distributed on the rGO sheets (Figure 1a). The overall morphology is evenly distributed without obvious aggregation. The magnified SEM image further displays that well-formed carbon nanotubes are distributed on graphene sheets (Figure 1b). It's worth mentioning that the 3D structure formed by the entanglement of CNTs and rGO can enhance the transport of electrons and the exposure of active sites, thus improving electrocatalytic activity of composite.
Figure 1. SEM images of Co$_2$P/NPCNTs-rGO-800.

The phase compositions for the Co$_2$P/NPCNTs-rGO-800 are further investigated by the XRD pattern (Figure 2). The XRD pattern displays the peak at around 26°, which is assigned to (002) planes of graphene. Moreover, the specific diffraction peaks can also be observed at 41.0°, 43.3°, 44.1°, 48.7, 52.0° and 56.2°, corresponding to (201), (211), (130), (031) (002) and (320) planes of Co$_2$P (JCPDS card No.32-0306), respectively. The XRD results confirm the successful synthesis of Co$_2$P nanoparticles in graphene.

Figure 2. XRD pattern of Co$_2$P/NPCNTs-rGO-800.

The ORR electrochemical behaviors of Co$_2$P/NPCNTs-rGO-800 are assessed. As presented in Figure 3a, linear sweep voltammetry (LSV) curves are first investigated. It can be found that Pt/C LSV curve shows a limited current density of 5.08 mA cm$^{-2}$, onset potential of 0.96 V and a half-wave potential of 0.75 V. As for Co$_2$P/NPCNTs-rGO-800, the LSV curve exhibits a limited current density of 2.78 mA cm$^{-2}$, onset potential of 0.86 V and a half-wave potential of 0.73 V. In addition, as for the Tafel plots, Co$_2$P/NPCNTs-rGO-800 shows smaller Tafel slope (55.3 mV dec$^{-1}$) than that of Pt/C (64.5 mV dec$^{-1}$) (Figure 3b), demonstrating the faster kinetic process of Co$_2$P/NPCNTs-rGO-800 catalyst for ORR [11].
The OER electrochemical behaviors of Co$_2$P/NPCNTs-rGO-800 are assessed. As presented in Figure 4a, LSV curves are first investigated. To afford current density of 10 mA cm$^{-2}$, the Co$_2$P/NPCNTs-rGO-800 shows overpotential (420 mV), which is a little bit higher than that of commercial RuO$_2$ (230 mV). In addition, as for the Tafel plots, Co$_2$P/NPCNTs-rGO-800 shows comparable Tafel slope (86.5 mV dec$^{-1}$) than that of RuO$_2$ (77.2 mV dec$^{-1}$) (Figure 4b), demonstrating the fast-kinetic process of Co$_2$P/NPCNTs-rGO-800 catalyst for OER.

In addition, the bifunctional OER/ORR properties of Co$_2$P/NPCNTs-rGO-800 are evaluated by a potential difference ($\Delta E$) between half-wave potential ($E_{1/2}$) for ORR and potential at 10 mA cm$^{-2}$ ($E_{j=10}$) for OER ($\Delta E= E_{j=10}-E_{1/2}$) (Figure 5). And it can be seen that $\Delta E$ value of Co$_2$P/NPCNTs-rGO-800 is calculated to be 0.92 V, which is comparable to that of RuO$_2$ (0.91 V) and much lower than that of Pt/C (1.05 V). This result indicates that the Co$_2$P/NPCNTs-rGO-800 shows a good comprehensive ORR/OER bifunctional performance, which has great potential to be the excellent air-cathode catalyst for rechargeable Zn-air batteries.
4. Conclusions
In summary, we have developed a universal, green and facile strategy to form in-situ Co$_2$P nanoparticles encapsulated in doped carbon nanotubes and rGO sheets through a self-catalyzed growth procedure. The obtained unique 3D structure endows the Co$_2$P-based electrocatalyst with highly electrons transport and diffusion kinetics capacities. Thanks to the effective strategies for design, the Co$_2$P/NPCNTs-rGO exhibits excellent catalytic activity for both ORR and ORR. Therefore, we believe that our present work not only provides a deeper investigation of 3D structure catalyst for ORR/OER, but also motivates the enthusiasm to synthesize more electrocatalysts for wider practical applications.

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