Anchoring MnCo$_2$O$_4$ Nanorods from Bimetal-Organic Framework on rGO for High-Performance Oxygen Evolution and Reduction Reaction

Hongxun Yang,*†‡∥ Miaomiao Zhu,†‡ Xingmei Guo,† Chao Yan,*§ and Shengling Lin*†

1School of Environmental & Chemical Engineering, ‡Marine Equipment and Technology Institute, and §School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China
∥Zhenjiang Borun New Materials, Co. Ltd., Zhenjiang 212050, Jiangsu, China

ABSTRACT: Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are important reactions of energy storage and conversion devices. Therefore, it is highly desirable to design efficient and dual electrocatalysts for replacing the traditional noble-metal-based catalysts. Herein, we have developed a high-efficiency and low-cost MnCo$_2$O$_4$-rGO nanocomposite derived from bimetal-organic frameworks. For OER, MnCo$_2$O$_4$-rGO showed an onset potential of 1.56 V (vs reversible hydrogen electrode (RHE)) and a current density of 14.16 mA/cm$^2$ at 1.83 V, being better than both pure MnCo$_2$O$_4$ and Pt/C. For ORR, MnCo$_2$O$_4$-rGO exhibited a half-wave potential ($E_{1/2}$) of 0.77 V (vs RHE), a current density of 3.33 mA/cm$^2$ at 0.36 V, a high electron transfer number $n$ (3.80), and long-term stability, being close to the performance of Pt/C. The high activity of MnCo$_2$O$_4$-rGO was attributed to the synergistic effect among rGO, manganese, and cobalt oxide. As a result, the resultant MnCo$_2$O$_4$-rGO has a great potential to be applied as a high-efficiency ORR and OER electrocatalyst.

1. INTRODUCTION

With the development of economy and society, there has been a growing demand for green energy because of the non-renewable fossil fuel energy sources.3–5 The metal–air battery has become the focus of research due to its higher energy density than the current state-of-the-art lithium-ion batteries, high conversion efficiency, environment friendliness, etc.6–8 The cathode reactions in the metal–air battery, namely, the oxygen reduction reaction (ORR) in the discharge process and the oxygen evolution reaction (OER) in the charging process, play a key role in the energy conversion efficiency.6–9 However, the kinetics of the ORR and OER are slow due to the high overpotential; therefore, the development of good bifunctional catalysts has become the key to improve the metal–air battery.10–13 It is well known that platinum, iridium, and ruthenium are excellent catalysts for the ORR and OER. However, the disadvantages of high cost, limited reserves, poor durability, and rapid inactivation seriously hamper their large-scale applications in the ORR and OER.14–20 Therefore, it is highly desirable to develop high-performance and inexpensive bifunctional non-noble-metal electrocatalysts.21

Cobalt-based binary spinel-type metal oxides as inexpensive bifunctional non-noble-metal electrocatalysts, such as MnCo$_2$O$_4$,22–26 CuCo$_2$O$_4$,27 NiCo$_2$O$_4$,28 etc., show excellent performance in the ORR and OER because of their redox stability, the complementation and synergy of two metals, and their variable valence state.22–28 Especially, MnCo$_2$O$_4$ has been widely utilized in metal–air battery, alkaline fuel cells, and solid oxide fuel cells.22–26 At the same time, graphene is a famous carbonaceous material with a single layer of carbon atoms tightly packed into a two-dimensional honeycomb lattice structure.27,28 Compared with other carbon materials, graphene has a larger specific surface area, excellent conductivity, and higher electrochemical stability, and produces a synergistic effect on binding with a metal oxide, which can improve the electrocatalytic activity of oxide and stability.30,31 For example, Dai et al. reported spinel manganese-cobalt oxide/graphene nanocomposites with advanced oxygen reduction electrocatalytic activity because of their synergistic effect between cobalt oxide, manganese oxide, and graphene.31 Despite these efforts, studies on MnCo$_2$O$_4$/graphene bifunctional catalysts for the ORR and OER are still scarce. Significant performance gaps remain unfilled to furnish bifunctional catalytic activity on a par with precious-metal-based catalysts.

On the other hand, metal-organic frameworks (MOFs) with various morphologies and architectures composed of metal ions and bridging ligands have been known as highly potential precursors or sacrificial templates to prepare a series of tailorable porous inorganic micro/nanomaterials,32–34 such as porous hollow metal oxides. Apart from the more specific surface area, which could increase the contact surface between...
electrode material and electrolyte, the porous microstructure could provide more catalytic active sites, resulting in enhanced electrochemical activities. However, there are less reports about MnCo2O4-rGO nanocomposites derived from bimetal-organic frameworks (MOFs)/graphene oxides.

Herein, we report a MnCo2O4-reduced graphene oxide (rGO) nanocomposite derived from bimetal-organic frameworks (MOFs)/graphene oxides as a bifunctional non-noble-metal electrocatalyst. The ORR electrocatalytic activity of the MnCo2O4-rGO catalyst in a 0.1 M potassium hydroxide solution is close to 20% of the commercial Pt/C, and the OER electrocatalytic activity in a 1 M potassium hydroxide solution is better than that of Pt/C, in terms of onset voltage and diffusion-limited current density.

The high electrocatalytic activities of MnCo2O4-rGO for the OER and ORR are caused by its porous spherical structure, which promotes the transfer of electrons. The catalyst also shows excellent stability in alkaline media. The method not only provides a new route for synthesizing MnCo2O4-rGO but also has the advantages of low cost and high yield, and thus, it can be produced on a large scale and promote the development of metal–air battery.

2. RESULTS AND DISCUSSION

2.1. Characterizations of MnCo2O4-rGO. Figure 1 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the MnCo2O4-rGO nanocomposites. As shown in Figure 1a, the as-prepared product consists of reduced graphene oxides and nanorods with a diameter of 100 nm. These nanorods appear to be wrapped between the rGOs. Figure 1b shows the TEM images of the MnCo2O4-rGO nanocomposites. It can be seen that the as-prepared product consists of rGOs and MnCo2O4 nanorods, which is consistent with the results of the SEM images. The selected area electron diffraction pattern in Figure 1c suggests that the MnCo2O4-rGO nanocomposites are polycrystalline. The diffraction rings match well with the (311) and (400) planes of spinel-structured MnCo2O4, in a good agreement with the X-ray diffraction (XRD) results in the following part. To further probe the incorporation of the MnCo2O4/rGO nanocomposites, energy-dispersive system (EDS) spectroscopy was also used. Figure 1e–h displays the elemental mappings of Co (red), Mn (green), O (blue), and C (yellow), revealing the presence of the Co, Mn, O, and C elements in the MnCo2O4/rGO nanocomposites.

The Raman spectra of the MnCo2O4-rGO nanocomposites are shown in Figure 2a, which displays two prominent peaks around 1350 cm⁻¹ (D band) and 1580 cm⁻¹ (G band). It is well known that the intensity ratio of the D to G band (I_D/I_G) was used to probe the ordered and disordered crystal structures of carbon. The smaller the I_D/I_G ratio, the higher the degree of ordering in the carbon material. The I_D/I_G value of the MnCo2O4-rGO nanocomposites is 0.98. Hence, the Raman results correspond to the presence of rGOs in the MnCo2O4-rGO nanocomposites. Figure 1b presents the XRD pattern of the MnCo2O4-rGO nanocomposites. The characteristic peaks correspond to well-crystallized MnCo2O4 (JCPDS Card No. 30–0820) with the spinel structure of the (220), (311), (400), (422), (511), and (440) planes. The structure of the MnCo2O4-rGO nanocomposites is considered as a mixed valence oxide with a cubic spinel structure, in which manganese and cobalt are distributed over the positions of eight faces and tetrahedra.

To further determine the elemental composition and valence states, the MnCo2O4-rGO nanocomposites were investigated by the X-ray photoelectron spectroscopy (XPS). All of the binding energies were corrected for specimen charging by referring them to the C 1s peak (284.6 eV). Figure 3a shows the overall XPS spectra of the MnCo2O4-rGO nanocomposites, which clearly show the existence of C, O, Mn, and Co. The atom ratio between Mn and Co is determined to be 1:2, which is same as the theoretical value. The XPS spectrum of Co 2p can be fitted by considering two spin–orbit doublet characteristics of Co³⁺ and Co²⁺, indicating the existence of Co with different valence states (Co³⁺ and Co²⁺) (Figure 3b). The two peaks located at 780.2 (Co 2p₁/₂) and 795.6 eV (Co 2p₃/₂) could be ascribed to Co³⁺, while the peaks located at 780.9
(Co 2p3/2) and 795.5 eV (Co 2p1/2) could be ascribed to Co2+. Similarly, as exhibited in Figure 3c, the spectrum of Mn 2p also indicates the presence of Mn2+ and Mn3+. The main peaks locate at 654.2 eV (Mn 2p1/2) and 642.8 eV (Mn 2p3/2) belong to Mn3+, while the two peaks located at 641.8 eV (Mn 2p3/2) and 652.4 eV (Mn 2p1/2) could be ascribed to Mn2+.39 The existence of Mn3+/Mn2+ and Co3+/Co2+ solid-state redox couples could provide a notable electrochemical activity. The XPS spectrum of C 1s shows that three distinct C configurations coexist, including carbonyl carbon (C=O), carbon (C–O), and graphic carbon (C–C) (Figure 3d).27

2.2. Electrochemical Properties. To investigate the ORR performance of the as-prepared samples, the prepared working electrode was first placed in a N2-saturated and O2-saturated 0.1 M KOH solution for CV test. As can be seen in Figure 4a, the MnCo2O4-rGO nanocomposites exhibited a superior ORR

Figure 3. (a) XPS survey scan of MnCo2O4-rGO nanocomposites. (b) High-resolution XPS spectra of the Co 2p peak. (c) High-resolution XPS spectra of the Mn 2p peak. (d) High-resolution XPS spectra of the C 1s peak.

Figure 4. (a) CV curves of MnCo2O4, MnCo2O4-rGO, and Pt/C in O2-saturated (solid lines) and N2-saturated (dashed lines) 0.1 M KOH electrolyte solution at a scan rate of 50 mV/s. (b) Linear sweep voltammograms (LSV) curves of MnCo2O4-rGO in O2-saturated 0.1 M KOH at a scan rate of 10 mV/s at different rotating-disk electrode (RDE) rotation rates (rpm). (c) LSV curves of MnCo2O4, MnCo2O4-rGO, and Pt/C in O2-saturated 0.1 M KOH with a sweep rate of 10 mV/s at 1600 rpm and (d) the corresponding Tafel slopes.
activity, showing a more positive onset potential (≈0.89 V vs reversible hydrogen electrode (RHE)) and peak potential (≈−0.72 V vs RHE) and a much higher peak current density (2.58 mA cm⁻²) than MnCo₂O₄ (~0.83, 0.60 V, and 1.32 mA cm⁻², respectively). The onset potential for the Pt/C catalyst (20 wt % Pt on Vulcan HCA-PT20) is located at 0.93 V vs RHE, only ≈40 mV more positive than that of the MnCo₂O₄-rGO nanocomposites, but the peak current density of the Pt/C catalyst (2.26 mA cm⁻²) is lower than that of the MnCo₂O₄-rGO nanocomposites. This indicates that the addition of graphene in MnCo₂O₄ can increase the ORR catalytic activity to close to commercial Pt/C in 0.1 M KOH. It should be noted that the electrocatalytic performance of pure rGO is limited according to previous reports. Hence, pure rGO is not considered in further ORR study.

The rotating disk electrode (RDE) measurements were usually employed to delve into the ORR kinetics and mechanism of the MnCo₂O₄-RGO nanocomposites, and LSV polarization curves were recorded at different rotation rates in an O₂-saturated 0.1 M KOH solution (Figure 4b), which exhibits an increase in the limiting current density with an increase in the rotation rate. The Koutecky–Levich (K–L) plots extracted from the above LSV polarization curves (between 0.6 and 0.4 V) (Figure 4b inset) exhibit a linear relationship between J⁻¹ and ω⁻¹/². The fitting lines are almost parallel, indicating that the first-order reaction kinetics is related to the concentration of dissolved oxygen and has a similar electron transfer number (n) at different voltages of ORR. It is reported that the mechanism of electron transfer in the ORR is a direct and effective four-electron reduction reaction [eq 1] or two-electron reduction reaction [eq 2], and the electron transfer number (n) can be calculated on the basis of the Koutecky–Levich (K–L) equations [eqs 3–5], the average electron transfer number (n) of MnCo₂O₄-rGO was calculated as 3.8 on the basis of the Koutecky–Levich (K–L) equations, indicating a four-electron transfer process. Thus, H₂O is directly formed as an intermediate product from oxygen by consuming four electrons according to the previous literature. The four-electron reduction reaction pathway is favorable for increasing the reaction rate, so it has important applications in metal–air batteries.

Figure 4c displays the linear sweep voltammograms (LSV) of the MnCo₂O₄, MnCo₂O₄-rGO, and Pt/C at a rotating rate of 1600 rpm in O₂-saturated 0.1 M KOH. It can be seen that the pure MnCo₂O₄ material exhibits poor electrocatalytic activity toward ORR in an alkaline solution, while MnCo₂O₄-rGO represents a higher electrocatalytic activity (onset potential of 1.11 V, current density of −3.33 mA/cm² at 0.36 V) than MnCo₂O₄ (onset potential of 1.12 V, current density of −2.30 mA/cm² at 0.36 V). Therefore, the combination of graphene and MnCo₂O₄ is essential to improve the electrochemical activity of ORR. On the other hand, the E₁/₂ value of MnCo₂O₄-rGO is 0.77 V, similar to that of Pt/C at 0.80 V and more positive than that of pure MnCo₂O₄ at 0.66 V, as shown in Figure 4c. The slope of the Tafel plots of MnCo₂O₄-rGO was −150.1 mV/dec, better than the ones of MnCo₂O₄ (~142.2 mV/dec) and Pt/C (~120.2 mV/dec) (Figure 4d). These results further confirmed that the MnCo₂O₄-rGO nanocomposite is an efficient electrochemical catalyst for the ORR and had very good kinetic processes.

As a bifunctional catalyst, excellent ORR and OER activities are both required. Therefore, the OER catalytic activity of MnCo₂O₄-rGO was also evaluated. Linear sweep voltammetry (LSV) was carried out in a N₂-saturated 1 M KOH solution at a rotating rate of 1600 rpm for MnCo₂O₄, MnCo₂O₄-rGO, and Pt/C (Figure 5a). The onset potential and the current density are the main parameters to evaluate the catalytic activity of the sample on OER. The onset potential of MnCo₂O₄ is 1.63 V, and the current density is 6.12 mA/cm² at 1.83 V. Furthermore, the onset potential of MnCo₂O₄-rGO is 1.56 V, and the current density reached 14.16 mA/cm² at 1.83 V. The results showed that the addition of graphene could enhance the OER performance. It should be noted that the onset potential of MnCo₂O₄-rGO is lower than that of Pt/C.
showed a higher activity than MnCo2O4 for both the ORR and OER due to a synergistic effect of the graphene and MnCo2O4. It should be noted that the OER activity of MnCo2O4-rGO has structural and chemical stabilities after long-term stability for electrocatalytic activity, indicating that MnCo2O4-rGO is also better than that of commercial Pt/C. In addition, the current does not decline. It could be concluded that the MnCo2O4-rGO composite has a long-term stability for electrocatalytic activity, indicating that MnCo2O4-rGO has structural and chemical stabilities after stability test.

3. CONCLUSIONS

In this work, a new bifunctional electrocatalyst with excellent ORR and OER activities was designed and synthesized by the combination of MnCo2O4 and graphene. MnCo2O4-rGO showed a higher activity than MnCo2O4 for both the ORR and OER due to a synergistic effect of the graphene and MnCo2O4. It should be noted that the OER activity of MnCo2O4-rGO is also better than that of the commercial Pt/C catalyst. On the whole, the MnCo2O4-rGO nanocomposite is an excellent bifunctional electrocatalyst for the OER and ORR, and is expected to be a good bifunctional oxygen electrode for metal-air batteries.

4. EXPERIMENTAL SECTION

4.1. Materials. All of the chemicals were directly used after purchase without further purification. Deionized water was used for the preparation of all solutions.

4.2. Synthesis of MnCo2O4/rGO Composite. Graphene oxide (GO) was synthesized from graphite by a modified Hummers’ method, similar to our previous reports.49−51 In a typical synthesis, 0.414 g of manganese acetate and 0.881 g of cobalt acetate were dispersed in 30 mL of deionized water, then 50 mL of a GO solution (1 mg/mL) was added in it as solution A, and 0.752 g of fumaric acid was dispersed into 30 mL of ethanol as solution B. Then, solution B was added into solution A under continuous stirring for 30 min, and the reaction mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave. The hydrothermal reaction was carried out at 200 °C for 6 h. The product was collected by centrifugation and washed three times with water and ethanol before drying. Finally, the dried powder was put in a tubular furnace at 600 °C for 3 h at a 4 °C/min heating rate in nitrogen. For comparison, MnCo2O4 was synthesized under a similar condition without the presence of GO.

4.3. Material Characterizations. The crystal structures of the as-prepared products were determined by X-ray diffraction (XRD, XRD-6000) using the Cu Ka radiation (0.15406 nm). The microstructures and morphologies of the products were characterized using scanning electron microscopy (SEM, JEOL, JSM 6480) and transmission electron microscopy (TEM, Philips Tecnai 12) with energy-dispersive X-ray analysis (EDX). The Raman spectra of the as-prepared products were obtained by a Renishaw Raman spectrometer.

4.4. Electrochemical Measurements. All electrochemical tests were carried out on an electrochemical workstation (CHI 760E, Chenhua Ltd. Co., China) with a conventional three-electrode cell. A Pt foil and a saturated calomel electrode (SCE) were applied as the counter and reference electrodes, respectively. The working electrode was prepared by loading the catalysts on a glassy carbon electrode with a disk diameter of 5 mm (disk area = 0.1963 cm2) and as the rotating disk electrode. The sample ink was prepared by mixing 4.12 mg of material, 50 μL of 5 wt% Nafion solution, 200 μL of ethanol, and 800 μL of deionized water followed by 30 min of sonication, forming a homogeneous catalyst ink. Then, 20 μL of the homogeneous ink was dropped onto the glassy carbon with the corresponding mass loading and dried slowly in air. Similarly, 2.06 mg of 20 wt % Pt was used to prepare the ink and 20 μL was dropped onto the glassy carbon electrode with a mass loading of 0.20 mg/cm2.

Before test, a N2 or O2 flow was introduced into the electrolyte in the cell for 30 min to give a saturation state. The working electrode was cycled with a scan rate of 20 mV/s for at least 50 times before the data collection. Cyclic voltammetry (CV) experiments were done at a scan rate of 50 mV/s in a N2- or O2-saturated KOH solution (0.1 mol/L). The linear sweep voltammetry (LSV) experiments were conducted in an O2-saturated KOH (0.1 M) solution at different speed rates (400, 625, 900, 1225, 1600, 2025, 2500 rpm) at a scan rate of 10 mV/s. As for OER, the LSV experiments were different with ORR. They were conducted in a N2-saturated KOH (1.0 M) solution at a scan rate of 10 mV/s, and the data were collected after stabilization. The stability tests for ORR were carried out at 0.4 V in an O2-saturated 0.1 M KOH solution (ω = 1600 rpm) by the chronoamperometric method. The recorded potentials all use a negative scan pattern, and the potentials were referenced to the reversible hydrogen electrode (RHE) through RHE calibration (E(RHE) = E(Ag/AgCl) + 0.0951pH + 0.197). Furthermore, to ensure O2 saturation, the gas was bubbled into the electrolyte prior to the start of each experiment and maintained over the electrolyte during each measurement.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02362.

Synthesis and characterization of materials; XPS; electrochemical properties (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: yhongxun@126.com (H.Y.).
*E-mail: linshl5757@sina.com (S.L.)
ORCID
Hongxun Yang: 0000-0003-1445-3468
Chao Yan: 0000-0002-6008-9452

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was financially supported by the National Natural Science Foundation of China (S1672114), the Foundation from Marine Equipment and Technology Institute for Jiangsu University of Science and Technology, China (HZZ20190004), and the Modern Agricultural Projects of Zhenjiang (NY2017022).

REFERENCES

(1) Xu, X. F.; Chen, Y.; Wang, S. B.; Gao, S. Y.; Lou, X. W. Interfacial manganese oxide and cobalt in porous graphite carbon polyhedrons boosts oxygen electrocatalysis for Zn-Air batteries. Adv. Mater. 2019, 29, 1902339.

(2) Chen, Y.; Zhu, Y.; Tian, M.; Chen, C.; Jia, X.; Gao, S. Y. Sustainable self-powered electro-fenton degradation of organic pollutants in wastewater using carbon catalyst with controllable pore activated by EDTA-2Na. Nano Energy 2019, 59, 346–353.

(3) Gao, S. Y.; Zhu, Y.; Chen, Y.; Tian, M.; Yang, Y.; Jiang, T.; Wang, Z. Self-power electroreduction of N2 into NH3 by 3D printed triblock electric nanogenerators. Mater. Today 2019, 28, 17–24.

(4) Han, M.; Shi, M.; Wang, J.; Zhang, M.; Yan, C.; Jiang, J.; Guo, S.; Sun, Z.; Guo, Z. Efficient Bifunctional Co/N-doped Carbon Electro catalysts for Oxygen Reduction and Evolution Reactions. Carbon 2019, 153, 575–584.

(5) Hao, Y.; Xu, Y.; Liu, J.; Sun, X. Nickel–cobalt oxides supported on Co/N decorated graphene as an excellent bifunctional oxygen catalyst. J. Mater. Chem. A 2017, 5, 5954–5960.

(6) Dong, Y.; Deng, Y.; Zeng, J.; Song, H.; Liao, S. A high-performance composite ORR catalyst based on the synergy between binary transition metal nitride and nitrogen-doped reduced graphene oxide. J. Mater. Chem. A 2017, 5, 5829–5837.

(7) Gao, S. Y.; Geng, K. R.; Liu, H. Y.; Wei, X. J.; Zhang, M.; Wang, P.; Wang, J. J. Transforming organic-rich amaranthus waste into Nitrogen-doped carbon with superior performance of the oxygen reduction reaction. Energy Environ. Sci. 2015, 8, 221–229.

(8) Li, X.; Zhao, Y.; Yang, Y.; Gao, S. Y. A universal strategy for carbon–based ORR-active electrocatalyst: One porogen, two pore–creating mechanisms, three pore types. Nano Energy 2019, 62, 628–637.

(9) Li, X.; Guan, B.; Gao, S. Y.; Lou, X. W. A general dual-templating approach to biomass-derived hierarchically porous heteroatom-doped carbon materials for enhanced electrocatalytic oxygen reduction. Energy Environ. Sci. 2019, 12, 648–655.

(10) Gao, S. Y.; Li, L.; Geng, K. R.; Wei, X. J.; Zhang, S. Recycling the biowaste to produce nitrogen and sulfur self-doped porous carbon as an efficient catalyst for oxygen reduction reaction. Nano Energy 2015, 16, 408–418.

(11) Gao, S. Y.; Wei, X.; Fan, H.; Li, L.; Geng, K. R.; Wang, J. Nitrogen-doped carbon shell structure derived from natural leaves as a potential catalyst for oxygen reduction reaction. Nano Energy 2015, 13, 518–526.

(12) Gao, S. Y.; Li, X.; Li, L.; Jianjun Wei, X. J. A versatile biomass derived carbon material for oxygen reduction reaction, supercapacitors and oil/water separation. Nano Energy 2017, 33, 334–342.

(13) Zhao, Y.; Li, X.; Jia, X.; Gao, S. Y. Why and how to tailor the vertical coordinate of pore size distribution to construct ORR-active carbon materials? Nano Energy 2019, 58, 384–391.

(14) Gao, S. Y.; Liu, H. Y.; Geng, K. R.; Wei, X. J. Honeysuckle-derived porous nitrogen, sulfur, dual-doped carbon as high-performance metal-free oxygen electroreduction catalyst. Nano Energy 2015, 12, 785–793.

(15) Qiu, L.; Liu, Y.; Baek, J.; Dai, L. Nitrogen-Doped Graphene as Efficient Metal-Free Electro catalyst for Oxygen Reduction in Fuel Cells. ACS Nano 2010, 4, 1321–1326.

(16) Yu, X.; Feng, Y.; Guan, B.; Lou, X.; Paik, U. Carbon coated porous nickel phosphides nanoflakes for highly efficient oxygen evolution reaction. Energy Environ. Sci. 2016, 9, 1246–1250.

(17) Liu, G.; Li, W.; Bi, R.; Atangana, E. C.; Yu, X.; Zhang, L. Cation-Assisted Formation of Porous TiO2−x Nanoboxes with High Grain Boundary Density as Efficient Electrocatalysts for Lithium-Oxygen Batteries. ACS Catal. 2018, 8, 1720–1727.

(18) Doan-Nguyen, V.; Zhang, S.; Trigg, E.; Agarwal, R.; Li, J.; Su, D.; et al. Synthesis and X-ray Characterization of Cobalt Phosphide (Co3P) Nanorods for the Oxygen Reduction Reaction. ACS Nano 2015, 9, 8108–8115.

(19) Abidat, I.; Bouchenafa-Saïb, N.; Habrioux, A.; Comminges, C.; Canaff, C.; Rousseau, J.; et al. Electrochemically induced surface modifications of mesoporous spinels (Co3O4−x MnCo2O4−y NiCo2O4−z) as the origin of the OER activity and stability in alkaline medium. J. Mater. Chem. A 2015, 3, 17433–17444.

(20) Gao, S. Y.; Wei, X. J.; Liu, H. Y.; Geng, K. R.; Wang, H. Q.; Moehwald, H.; Shchukin, D. Transformation of worst weed into N-, S-, and P-tridoped carbon nanorings as metal-free electrocatalysts for the oxygen reduction reaction. J. Mater. Chem. A 2015, 3, 23376–23384.

(21) Huang, Y.; Zhang, M.; Liu, P.; Cheng, F.; Wang, L. Co3O4 supported on N,P-doped carbon as a bifunctional electrocatalyst for oxygen reduction and evolution reactions. Chin. J. Catal. 2016, 37, 1249–1256.

(22) Parvez, K.; Yang, S.; Hernandez, Y.; Winter, A.; Turchanin, A.; Feng, X.; Muller, K. Nitrogen-Doped Graphene and Its Iron-Based Composite As Efficient Electrocatalysts for Oxygen Reduction Reaction. ACS Nano 2012, 7, 9541–9550.

(23) Wang, H.; Yang, Y.; Liang, Y.; Zheng, G.; Li, G.; Cui, Y.; Dai, H. Rechargeable Li-O2 batteries with a covalently coupled MnCo2O4/graphene hybrid as an oxygen cathode catalyst. Energy Environ. Sci. 2012, 5, 7931–7935.

(24) Liu, H.; Zhu, X.; Cheng, M.; Cong, Y.; Yang, W. Electrochemical performances of spinel oxides as cathodes for intermediate temperature solid oxide fuel cells. Int. J. Hydrogen Energy 2013, 08, 1052–1057.

(25) Liang, Y.; Wang, H.; Zhou, J.; Li, Y.; Wang, J.; Regier, T.; Gai, H. Covalent Hybrid of Spinel Manganese–Cobalt Oxide and Graphene as Advanced Oxygen Reduction Electrocatalysts. J. Am. Chem. Soc. 2012, 6, 3517–3523.

(26) Xu, C.; Lu, M.; Zhan, Y.; Lee, J. A bifunctional oxygen electrocatalyst from monodisperse MnCo2O4 nanoparticles on nitrogen enriched carbon nanofibers. RSC Adv. 2014, 4, 25089–25092.

(27) Ning, R.; Tian, J.; Asiri, A.; Qusti, A.; Al-Youbi, A.; Sun, X. Spinel CuCo2O4 Nanoparticles Supported on N-Doped Reduced Graphene Oxide: A Highly Active and Stable Hybrid Electrocatalyst for the Oxygen Reduction Reaction. Langmuir 2013, 29, 13146–13151.

(28) Lee, D. U.; Kim, B. J.; Chen, Z. One-pot synthesis of a mesoporous NiCo2O4 nanoplatelet and graphene hybrid and its oxygen reduction and evolution activities as an efficient bi-functional electrocatalyst. J. Mater. Chem. A 2013, 1, 4754–4762.

(29) Zhang, J. X.; Zhang, Z. Z.; Jiao, Y. T.; Yang, H. X.; Li, Y. Q.; Zhang, J.; Gao, P. The graphene/lanthanum oxide nanocomposites as electrode materials of supercapacitors. J. Power Sources 2019, 419, 99–105.
(30) Sheng, Z.-H.; Shao, L.; Chen, J.-J.; Bao, W.-J.; Wang, F.-B.; Xia, X.-H. Catalysis-Free Synthesis of Nitrogen-Doped Graphene via Thermal Annealing Graphite Oxide with Melamine and Its Excellent Electrochemical Activity. *ACS Nano* 2011, *S*, 4350–4358.

(31) Yin, H.; Tang, H.; Wang, D.; Gao, Y.; Tang, Z. Facile Synthesis of Surfactant-Free Au Cluster/Graphene Hybrids for High-Performance Oxygen Reduction Reaction. *ACS Nano* 2012, *6*, 8288–8297.

(32) Gao, S. Y.; Fan, B.; Feng, R.; Ye, C.; Wei, X.; Liu, J.; Bu, X. N-doped-carbon-coated Fe$_2$O$_3$ from metal-organic framework as efficient electrocatalyst for ORR. *Nano Energy* 2017, *40*, 462–470.

(33) Xie, Y.; Fang, Z.; Li, L.; Yang, H. X.; Liu, T. Creating Chemisorption Sites for Enhanced CO$_2$ Photoelectroduction Activity through Alkylamine Modification of MIL-101-Cr. *ACS Appl. Mater. Interfaces* 2019, *11*, 27017–27023.

(34) Yang, H. X.; Gao, X.; Wang, Z.; Li, M.; Wu, B.; Wang, Y.; Yang, C.; Yuan, A.; Yang, H. X. Controlled pyrolysis of MIL-88A to Fe$_2$O$_3$@C nanocomposites with varied morphologies and phases for advanced lithium storage. *J. Mater. Chem. A* 2017, *5*, 25562–25573.

(35) Sun, M. C.; Sun, M.; Yang, H. X.; Song, W.; Nie, Y.; Sun, S. Porous Fe$_2$O$_3$ nanotubes as advanced anode for high performance lithium ion batteries. *Ceram. Int.* 2017, *43*, 363–367.

(36) Chen, Y. Y.; Yang, W.; Yang, H. X.; Guo, X.; Cai, X.; Guo, X.; Xu, B.; Li, M.; Yuan, A. Facile synthesis of porous hollow Co$_3$O$_4$ microfibers derived from metal-organic frameworks as an advanced anode for lithium ion batteries. *Ceram. Int.* 2017, *43*, 9945–9950.

(37) Wang, Z. K.; Zhang, Z. R.; Xia, J.; Wang, W.; Sun, S.; Liu, L.; Yang, H. X. Fe$_2$O$_3$@C core-shell nanotubes: Porous Fe$_2$O$_3$ nanotubes derived from MIL-88A as cores and carbon as shells for high power lithium ion batteries. *J. Alloys Compd.* 2018, *769*, 969–976.

(38) Wu, B.; Xie, Y.; Meng, Y.; Qian, C.; Chen, Y.; Yuan, A.; Guo, X.; Yang, H.; Wan, S.; Lin, S. Construction of unique heterogeneous cobalt-manganese oxide porous microspheres for the assembly of long-cycle and high-rate lithium ion battery anodes. *J. Mater. Chem. A* 2019, *7*, 6149–6160.

(39) Ge, X. M.; Liu, Y. Y.; Thomas Goh, F. W.; Andy Hor, T. S.; Zhang, K.; Ye, C.; Wei, X.; Yang, H. X.; Lin, S. L. Improvement of the Photocatalytic Activity and Electrochemical Property of Graphene-Grated Carbon Nitride Nanosheets with Enhanced Li-Storage Performance. *ACS Nano* 2018, *12*, 4350–4358.

(40) Yang, H. X.; Xie, Y.; Zhou, M.; Liu, Y.; Wang, Z.; Xu, M.; Lin, S. Hierarchical porous MnCo$_2$O$_4$ yolk-shell microspheres from MOFs as secondary nanomaterials for high power lithium ion batteries. *Dalton Trans.* 2019, *48*, 9205–9213.

(41) Zhang, K.; Yang, H. X.; Cai, X.; Ye, S.; Yan, C.; Wu, H.; Yuan, A.; Lin, S. Porous MoO$_2$-Cu/C/Graphene nano-octahedrons quadruple nanocomposites as an advanced anode for lithium ion batteries with enhanced rate capability. *J. Alloys Compd.* 2018, *731*, 646–654.

(42) Yang, H. X.; Zhang, K.; Wang, Y.; Yan, C.; Lin, S. CoFe$_2$O$_4$ derived from bi-metal organic frameworks wrapped with graphene nanosheets as advanced anode for high-performance lithium ion batteries. *J. Phys. Chem. Solids* 2018, *115*, 317–321.

(43) Yang, H. X.; Liu, X. Y.; Sun, S. N.; Nie, Y.; Wu, H. P.; Yang, T. Y.; Zheng, S. J.; Lin, S. L. Green and facile synthesis of Nanostructured CoO Nanoparticles Grown on Nitrogen-Doped Hollow Graphene Microspheres for Oxygen Reduction and Evolution Reactions. *Carbon* 2013, *53*, 130–136.

(44) Chakrabarty, S.; Mukherjee, A.; Wei-Nien Su, W. N.; Basu, S. Improved bi-functional ORR and OER catalytic activity of reduced graphene oxide supported ZnCo$_2$O$_4$ microsphere. *Int. J. Hydrogen Energy* 2019, *44*, 1565–1578.

(45) Lin, Z.; Waller, G. H.; Liu, Y.; Liu, M.; Wong, C. P. Simple preparation of nanoporous few-layer nitrogen-doped graphene for use as an efficient electrocatalyst for oxygen reduction and oxygen evolution reactions. *Carbon* 2013, *53*, 130–136.

(46) Jiang, Z.; Jiang, Z. Interaction Induced High Catalytic Activities of CoO Nanoparticles Grown on Nitrogen-Doped Hollow Graphene Microspheres for Oxygen Reduction and Evolution Reactions. *Sci Rep.* 2016, *6*, No. 27081.