Electrospun Hollow Carbon Nanofibers Decorated with CuCo$_2$O$_4$ Nanowires for Oxygen Evolution Reaction

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Abstract: In recent years, spinel-type structural cobalt salts (NiCo$_2$O$_4$, CuCo$_2$O$_4$, etc.) have been widely used electrocatalysis because of their superior properties such as large crustal reserves, low cost, environmental friendliness, high electrochemical activity, abundant oxidation valence, and stable chemical properties. In this paper, hollow carbon nanofibers loaded CuCo$_2$O$_4$ nanowires (CuCo$_2$O$_4$@CNFs) were prepared by electrospinning technique and solvothermal method. The CuCo$_2$O$_4$@CNFs exhibit enhanced electrocatalytic activity for oxygen evolution reaction (OER), requiring an overpotential of 273 mV in a 1.0 M KOH solution to achieve a current density of 10 mA cm$^{-2}$. In addition, the overpotential remained almost constant after 3000 cycles of voltammetry measurements. The enhanced electrocatalytic activity may be attributed to the unique one-dimensional hollow nanostructure of CNFs and high dispersion of CuCo$_2$O$_4$ nanowires, which enhanced the charge transfer and improved the diffusion of the electrolyte ions at the surface.

Keywords: CuCo$_2$O$_4$; OER; electrocatalysis; CNFs; electrospinning

1. Introduction

Currently, with the intensification of the global energy crisis and environmental pollution, the realization of efficient energy conversion and effective environmental governance has become an urgent problem to be solved [1,2]. Among them, clean energy, which can replace traditional fossil fuels, has a great research and application prospect. In much clean energy, hydrogen stands out from many substitutes of fossil fuel because of its high energy density, high combustion efficiency, green and clean, renewable, and other characteristics. Electrocatalytic water decomposition is an efficient and effective hydrogen production method. OER is a key component of water splitting. However, the complex four-electron transfer process and slow reaction kinetics of OER limits the smooth progress and reaction rate of OER at low overpotential. It is well-known that noble metal catalysts such as RuO$_2$ and IrO$_2$ are highly reactive catalysts for OER, but the wide application of such materials is limited because of high cost and low reserves [3]. Therefore, it has become a remarkable research direction to find OER's highly efficient non-precious metal catalysts [4–6].

Among many non-noble metal catalysts, AB$_2$O$_4$ spinel oxides with special physicochemical properties have attracted widespread attention in the field of electrochemistry due to the tunability of two unequal cations in the crystal lattice, such as MnCo$_2$O$_4$, CoFe$_2$O$_4$, CoAl$_2$O$_4$, and NiCo$_2$O$_4$ [7–9]. The crystal structure of spinel consists of oxygen anions and metal cations [10]. Oxygen anions are closed cubic stacks [11]. Trivalent cations usually occupy the position of an octahedron, while divalent cations usually occupy the position of a tetrahedron [12]. Experimental results and theoretical calculations show that redox-active octahedral plays a vital role in oxygen electrocatalysis [10]. During the OER process, adjacent octahedral loci coordinate with each other to promote reaction
From the perspective of crystal structure, spinel materials have good thermodynamic and chemical stability. In addition, due to the interface and synergy between metal cations, mixed transition metal oxides have good electronic conductivity and exhibit more promising properties than single metal oxides [13]. Therefore, spinel oxides have demonstrated attractive catalytic performance. In particular, nanostructured CuCo2O4 has become a promising OER electrocatalyst due to its environmental protection and low cost [14]. CuCo2O4 with spinel structure exhibits high catalytic activity by merit of its special electronic structure between copper ion and cobalt ion. Importantly, the structural flexibility and valence of spinel oxides offer great potential for fine-tuning their catalytic properties. Nevertheless, the main problem with this kind of material is its low conductivity, which limits the improvement of its catalytic performance and leads to poor cycling stability. According to previous reports, recombination of CuCo2O4 with materials with high conductivity is thought to improve the catalytic performance of this material [9].

Many studies have shown that carbon materials not only have high electrical conductivity but also can accelerate the electron transfer rate. More extensive studies include emerging carbon nanotubes (CNTs) and graphene because of their excellent charge transport properties and unique physical and chemical stability [15]. However, CNTs are one-dimensional materials with smaller dimensions and exist interaction forces between nanotubes. Using CNTs as the carrier to prepare catalysts, it is often necessary to disperse the CNTs themselves before loading, and it is easier to form agglomeration after the reactions such as the precursor and heat treatment of the supported catalyst, resulting in a decrease in the specific surface area and the masking of the active site [16]. It is difficult to maximize the excellent inherent properties of the material. Although graphene is a two-dimensional material, due to its extremely thin sheet layer and a strong interaction force between the sheet layers, it is easy to curl into a zero-dimensional or short one-dimensional structure when using it as a carrier to prepare its composite material system [17]. Therefore, graphene will also encounter problems like those of CNTs. How to solve the above problems has become a hot topic.

Carbon nanofibers (CNFs) prepared by electrospinning technology may solve this problem. CNFs are usually the form of nanofiber mesh felt, and their fiber diameter is generally between tens to hundreds of nanometers. The length is generally more than a few hundred microns. Its specific surface area is large, and the degree of graphitization is high. At the same time, CNFs also combine the good electrical and thermal conductivity of other carbon nanomaterials, excellent mechanical properties, excellent physical and chemical stability, and special surface properties [18]. If the composite material is constructed with CNFs as the reaction source or support, its unique fiber mesh felt structure would provide an ideal structural framework for obtaining a nanostructure system with three-dimensional characteristics. The surface of CNFs has a large number of uniform unsaturated suspension bonds that may become the active site of the chemical reaction, realizing the in-situ growth of the catalyst material on its surface. In particular, the fibers of the one-dimensional hollow CNFs have many excellent characteristics: (1) The high specific surface area allows it to adsorb many chemicals, which is conducive to the necessary chemical reactions on its surface. (2) The hollow porous structure makes it more convenient for the transfer of substances [19].

In this paper, we used the solvothermal method to grow CuCo2O4 nanowires on the prepared hollow CNFs. The nanowires of CuCo2O4 combined with hollow CNFs have a large specific surface area and good electrocatalytic performance. They not only improve the conductivity but also provide a channel for particle migration on the electrode surface and accelerate the mass transfer efficiency [20,21]. The synergy between the two provides the possibility of improving the catalytic performance of the material.
2. Experimental Section

2.1. Preparation of the Hollow CNFs

The CuCo2O4 hollow CNFs were prepared by electrospinning methods. Initially, 476 mg of polyacrylonitrile (PAN) and 270 mg of polystyrene (PS) were placed in 6 mL DMF, and the mixture was stirred for 24 h under heating conditions of 65 °C to form a uniform, stable precursor liquid for electrospinning. Subsequently, the prepared solution was loaded into a plastic syringe filled with a nozzle. The electrospinning condition was a DC voltage of 7.5 kV, and the distance between the syringe and the collected tin foil was 12 cm. Finally, PAN/PS nanofibers were collected.

The PAN/PS nanofibers were heated at 270 °C for 1 h in a tube furnace under an air atmosphere for pre-oxidation. The heating rates were both 1 °C/min. Then the heating rate of the tube furnace was adjusted from 5 °C/min to 900 °C in the N2 atmosphere for 2 h. After that, the hollow CNFs were achieved after naturally cooling down. Finally, the hollow CNFs were soaked in a beaker containing concentrated nitric acid for 24 h, and then it was washed with deionized water until the pH was closed to neutral.

2.2. Synthesis of the Hollow CNFs Immobilizing CuCo2O4 Nanowires (CuCo2O4@CNFs) Composite Structure

Firstly, the 2 mmol Cu(NO3)2·3H2O, 4 mmol Co(NO3)2·6H2O, and 9 mmol urea were dissolved in 15 mL ethanol and stirred vigorously for 30 min. Secondly, the hollow CNFs and the prepared mixed solution were put into a 20 mL Teflon-lined stainless autoclave. The autoclave was sealed and kept in an electric oven at 130 °C for 6 h. When the sample was cooled to room temperature, it was slightly sonicated in alcohol for 3 min and dried at 60 °C. Finally, the sample was placed in a tube furnace to adjust the heating rate from 1 °C/min to 270 °C and maintained for 2 h in air. When the sample was cooled to room temperature, a CuCo2O4@CNFs composite structure sample was obtained. Furthermore, for comparative experiments, CuCo2O4 without the hollow CNFs was synthesized by the same solvothermal method.

2.3. Characterizations

We used scanning electron microscopy (SEM, Hitachi SU 70), transmission electron microscopy (TEM, Tecnai-TF-20-FEI), and X-ray diffractometer (XRD, Tokyo, Japan, Japan Institute of Technology, D/max-2600/pc) to characterize the morphology, size, and crystal structures of the samples. The sample elements were qualitatively analyzed by X photoelectron spectroscopy (XPS) and were analyzed the bonding between atoms.

2.4. Electrochemical Measurements

Electrochemical catalytic properties OER was carried out on the electrochemical workstation (VMP3, Paris, France) with a standard three-electrode system, including the sample as the working electrode and a saturated calomel electrode as the reference electrode, and a platinum electrode as the counter electrode. The electrolyte was a KOH solution of 1.0 M. All potentials were set with reference to the reversible hydrogen electrode (RHE). The conversion formula is as follows: \( E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{pH} + 0.2415 \text{V} \). The linear sweep voltammetry (LSV) tests were performed at a scan rate of 5 mV s\(^{-1}\) and a voltage range of 0-0.9 V, and all LSV curves were corrected with 95% iR compensation. At different sweep rates (20, 40, 60, 80, and 100 mV s\(^{-1}\)), cyclic voltammetry (CV) is used to test electrically dual-layer capacitors (Cdl). In the frequency range of 0.01 Hz–105 Hz, we performed electrochemical impedance spectroscopy (EIS) at 10 mV. The stability of the materials was tested by chronopotentiometry (CP) under the condition of a current density of 10 mA cm\(^{-2}\) and was tested CV with a sweep speed of 100 mV s\(^{-1}\).
3. Results and Discussion

The phase structure of the prepared sample was analyzed with XRD. The XRD spectra of pure carbon nanofibers, CuCo2O4@CNFs and CuCo2O4, are shown in Figure 1. From the XRD patterns of the pure CNFs, the broad peaks centered at around 25° and 44° are attributed to the (002) and (100) planes of the carbon structure in the CNFs. In comparison with the pure CNFs, we can see that the CuCo2O4@CNFs correspond with the CuCo2O4 standard map peaks of the cubic phase from the picture. The characteristic peaks are at 19.1°, 31.3°, 37.0°, 39.0°, 45.1°, 56.1°, 59.6°, 65.7°, corresponding to (111), (220), (311), (222), (400), (422), (511), (440) crystal surface of CuCo2O4 (JCPDS 01-1155). The results show that the above CuCo2O4 have a cubic spinel structure [22].

![Figure 1. XRD patterns of pure CNFs and CuCo2O4@CNFs.](image)

The morphological features of the as-obtained CuCo2O4@CNFs and CuCo2O4 are revealed by SEM. SEM image of the hollow CNFs obtained by electrospinning and calcination in Figure 2a. It can be clearly seen that the surface of the nanofiber is smooth and has a large aspect ratio, without obvious secondary structure. There is no accumulation and crosslinking between the fibers. Furthermore, Figure 2b is a side SEM image of synthetic hollow CNFs at large magnifications. Due to the polystyrene after high-temperature separation from PAN to form a carbon fiber with a hollow structure, this structure has a large specific surface area relative to the solid fiber and can provide a fast channel for electron transfer on its surface, which is conducive to the improvement of the electrochemical properties of the entire system. Figure 2c,d shows an SEM image of CuCo2O4@CNFs. As can be seen from the image, the wire-like CuCo2O4 nanostructures are uniformly immobilized to the surface of the hollow CNFs. The synergistic effect between the hollow CNFs and the nanowires of CuCo2O4 can increase the number of active sites on the surface of the catalyst, provide a new electron transfer path, enhance the mass transfer efficiency and gas dissipation, accelerate the reaction kinetics [23,24] and thus improve the OER performance of the CuCo2O4 electrode material [25]. Correspondingly, the EDX results demonstrate that the CuCo2O4@CNFs nanofibers consist of Cu (12.61 at.%), O (61.82 at.%), and Co (25.57 at.%). (Figure 3).
By transmission electron microscopy (TEM), the microstructure of the prepared samples was further observed. The TEM image of CuCo$_2$O$_4$@CNFs is shown in Figure 4. From Figure 4a, we can see that the hollow CNFs in the composite structure have a diameter of about 500 nm, and the surface grows needle-like CuCo$_2$O$_4$, which is consistent with the results observed by the SEM. At the same time, it can be clearly seen that there is a clear gap between the CuCo$_2$O$_4$ needle-like structure stacked by small particles (Figure 4b). CuCo$_2$O$_4$ lattice fringes can be clearly observed from high-resolution transmission electron microscopy (HRTEM) images in Figure 4c with a crystal plane spacing of 0.24, 0.28, 0.47 nm, which are in agreement with the crystal plane spacing of the (311), (220), (111) crystal planes of the spinel-type CuCo$_2$O$_4$, and it respectively demonstrates the successful formation of the secondary structure and its immobilization on the surface of the hollow CNFs.
We used the X-ray photoelectron spectroscopy (XPS) technique to analyze the elemental composition and chemical valence of CuCo$_2$O$_4$@CNFs. As shown in Figure 5a, it can be seen from the full spectrum of the sample that the types of elements are consistent with the feeding during the preparation process. The XPS spectrum shown in Figure 5b is C 1s region. The binding energy peak at 284.6 eV can be attributed to C–C bonds and is identified as originating from the amorphous carbon phase or from adventitious carbon. The peak at 286.3 eV is characteristic of the combination of C–O groups. Moreover, the peak of the carboxyl carbon (O–C=O) is located at 288.2 eV. The XPS spectrum shown in Figure 5c is Cu 2p, and the peaks located at 934.1 and 954.0 eV are assigned to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively. After fitting the two satellite peaks, the XPS spectra of the Cu 2p can be fitted to four peaks, where the characteristic peaks with peaks of 941.8 and 962.2 eV are assigned to Cu$^{3+}$. The characteristic satellite peaks with peaks of 781.1 and 796.4 eV belong to Cu$^{2+}$. Figure 5d shows three peaks at 789.9, 779.6, and 795.3 eV, belonging to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively. Moreover, the existence of spinel structures is proved by two satellite peaks at the binding energies of 787.6 eV and 804.4 eV. The XPS spectrum in Figure 5e is O 1s, the wide and asymmetric peak of the O 1s spectrum indicates that there may be more than one chemical state according to the binding energy. The peaks at 529.7, 531.3, and 533.1 eV relate to metal-oxygen bond (lattice O), surface hydroxyl groups, (O–H) and oxygen doubly bonded to carbon (C=O), respectively. This is consistent with the XPS results of previously reported CuCo$_2$O$_4$ [26].
Figure 5. X-ray photoelectron spectra of CuCo2O4@CNFs, (a) survey scan, (b) C 1s (c) Cu 2p, (d) Co 2p, (e) O 1s.

The OER performances of CuCo2O4@CNFs, CuCo2O4, and RuO2 were tested in a 1.0 M KOH electrolyte using a typical three-electrode system under room temperature. Figure 6a shows the polarization curves after 95% compensation with a scan rate of 5 mV s\(^{-1}\), and the voltage window is 0–0.9 mV. The linear sweep volt-ampere (LSV) curve shows that CuCo2O4@CNFs requires a lower over-potential of 273 mV to achieve a current density of 10 mA cm\(^{-2}\), which is significantly less than the over-potential of CuCo2O4 (358 mV). In addition, when driving the current density of 50 mA cm\(^{-2}\), the CuCo2O4@CNFs needs only 336 mV overpotential, which is much smaller than CuCo2O4 (447 mV). At the same current density, the overpotential of CuCo2O4@CNFs nanofibers is close to the level of RuO2. The Tafel slope in Figure 6b can be used to further evaluate the rate of OER reactions [27,28]. It can be seen from the figure that the Tafel slope of the CuCo2O4@CNFs is 82.8 mV dec\(^{-1}\), which is smaller than the Tafel slope of pure CuCo2O4 powder at 133.1 mV dec\(^{-1}\). The results show that the hollow CNFs improve the conductivity efficiency and ion transport efficiency of the composite system. Therefore, the rate of oxygen production in the OER reaction of CuCo2O4@CNFs is obviously higher than that of pure CuCo2O4 powder. At the same time, we evaluated some recent works and compared the electrochemical properties of various related catalysts with the prepared CuCo2O4@CNFs to show that CuCo2O4@CNFs has a strong OER activity under alkaline conditions (Table 1).
To demonstrate the high electrocatalytic performance of CuCo2O4@CNFs against OER, we measured the double-layer capacitance (C_{dl}) of the CuCo2O4@CNFs to estimate its electrochemical surface area (ECSA) \([16]\). We performed cyclic voltammetry (CV) tests at the voltage window (1.16–1.26 V vs. RHE) and different scanning rates (20, 40, 60, 80, and 100 mV s\(^{-1}\)), respectively (Figure 7a,b). The active area of metal oxides can be calculated by the CV method to obtain the double layer capacitance, as shown in Figure 7c. The number of active sites on the surface of the sample can be roughly estimated by analyzing the ECSA. According to Figure 7a, the C_{dl} value of CuCo2O4@CNFs is 99.4 mF cm\(^{-2}\), which is 4 times the C_{dl} value of pure CuCo2O4 (23.7 mF cm\(^{-2}\)). It is well known that C_{dl} values are closely related to the ECSA. Larger ECSA also favors the adsorption and decomposition of water molecules and provides more active sites to accelerate the transfer of electrolyte electrons during the OER reaction process. Stability is also another effective reference for evaluating the efficiency of materials. As shown in Figure 7d–f, the retention rate of the sample is still considerable after 12 h. Moreover, we evaluated the stability of CuCo2O4@CNFs electrodes by CV at 100 mV s\(^{-1}\) sweep speeds. The LSV curves almost

| Catalysts                        | Overpotential | Electrolyte | Ref. |
|---------------------------------|---------------|-------------|------|
| Co-PN carbon nanofibers         | 285 mV        | 1.0 M KOH   | [21] |
| FeCo carbon nanofibers          | 377 mV        | 1.0 M KOH   | [29] |
| NiCo@C nanofibers               | 290 mV        | 1.0 M KOH   | [30] |
| CoCuPx carbon nanofibers        | 288 mV        | 1.0 M KOH   | [31] |
| CoNC/NCNTs@ carbon nanofibers   | 330 mV        | 1.0 M KOH   | [32] |
| Co-ZIF-350-air micro-fibers     | 370 mV        | 1.0 M KOH   | [33] |
| Ni/NiP@N carbon nanofibers      | 285 mV        | 1.0 M KOH   | [34] |
| NiFe@N carbon nanofibers        | 294 mV        | 1.0 M KOH   | [35] |
| FeOx/NiFeOx@ carbon nanofibers  | 350 mV        | 1.0 M KOH   | [36] |
| FeNiP@N carbon nanofibers       | 300 mV        | 1.0 M KOH   | [37] |
| CoOx/CoOx@N carbon nanofibers   | 310 mV        | 1.0 M KOH   | [38] |
| NiP/MnOx nanofibers             | 280 mV        | 1.0 M KOH   | [39] |
| RuNi-N carbon nanofibers        | 290 mV        | 1.0 M KOH   | [40] |
| CoNC@MoS: carbon nanofibers     | 350 mV        | 1.0 M KOH   | [41] |
| Zn/Co-ZIFs/PAN-CS-800 nanofibers| 367 mV        | 1.0 M KOH   | [42] |
| Co/P carbon nanofibers          | 288 mV        | 1.0 M KOH   | [43] |
| Fe doped CoO/C nanofibers       | 362 mV        | 1.0 M KOH   | [44] |
| This work                       | 273 mV        | 1.0 M KOH   |      |

Figure 6. (a) OER polarization curves of RuO\(_2\), CuCo2O4@CNFs, and CuCo2O4 at a scan rate of 5 mV s\(^{-1}\), (b) Tafel plots of CuCo2O4@CNFs and CuCo2O4.
coincide with the original curves of the CuCo2O4@CNFs after 3000 cycles. The above results show that CuCo2O4@C exhibits remarkable catalytic performance and stability in OER.

![Figure 7](image)

**Figure 7.** (a) The double-layer capacitance of the CuCo2O4@CNFs, (b) the double-layer capacitance of the CuCo2O4@CNFs, (c) the electrochemical double-layered capacitance measurements linear fitting of the capacitive currents of the catalysts against the scan rate to fit a liner regression, (d) stability of the CuCo2O4@CNFs electrode at 10 mA cm$^{-2}$, (e) CV curves of CuCo2O4@CNFs electrode before and after 3000 cycles at the scan rate of 100 mV s$^{-1}$ in the range of 1.06–1.56 V vs. RHE, (f) polarization curves of CuCo2O4@CNFs electrode and CuCo2O4 electrode before and after 3000 cycles at the scan rate of 5 mV s$^{-1}$. SEM image of CuCo2O4@CNFs electrode after 3000 cycles (inset).

We used AC impedance spectroscopy (EIS) tests to further explore CuCo2O4@CNFs electrode-related properties (Figure 8). The electrolyte is 1 M KOH, and the frequency is 105 to 0.01 Hz with a perturbation amplitude of 10 mV. The CuCo2O4@CNFs electrode has a faster electron transfer rate in the OER process compared with the pure CuCo2O4 electrode. The electron transfer resistance of CuCo2O4@CNFs is small, and the small electron transfer resistance indicates that the special structure of the composite material can improve the chemisorption rate and the redox kinetics of the process [25].
4. Conclusions

In conclusion, hollow carbon nanofibers decorated with CuCo$_2$O$_4$ nanowires was synthesized by electrospinning and solvothermal method, and the OER properties of the composite structure were studied. Benefited from the 1D hollow nanostructure, the highly dispersed CuCo$_2$O$_4$ nanowires, the smallest transmission impedance for iron and electron, the CuCo$_2$O$_4$@CNFs obtained the most excellent OER activity in our cases. As a result, it needs only 273 and 336 mV to drive the current density of 10 and 50 mA cm$^{-2}$ and superior structural stability. As we all know, the conductivity of carbon material as catalyst support will greatly affect the performance of the catalyst. The conductivity of hollow carbon nanofiber prepared in this paper is lower than that of commercial carbon cloth or carbon paper, which will be improved in future work.

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