Research Article

Preparation and Study of Multi-Heteroatom Carbon Nanotube as Excellent Electrocatalyst for Oxygen Reduction Reaction Using Polydopamine Derivative

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F and other heteroatom codoped multiwalled carbon nanotubes as nonmetal electrocatalyst were developed through pyrolysis of polydopamine derivative under high temperature. The influence of the amount and type of heteroatom on the catalytic activity was investigated. Especially, N/S/F-codoped carbon nanotubes exhibit the most excellent electrocatalytic activity for oxygen reduction reaction and stability. The method afforded an excellent building block to universally design multi-heteroatom-doped or F-doped carbon materials for ORR or other energy-relevant applications.

1. Introduction

To date, Pt-based materials are preferably used as the electrocatalyst for fuel cell because of the low over potential and high current density [1–3], though Pt-based catalysts as precious metal are expensive and their kinetics of the oxygen reduction reaction (ORR) is sluggish.

To overcome the above problem, the nonmetal catalysts with similar activity of oxygen reduction reaction and superior long-time durability compared to Pt-C catalyst become the focus of proton exchange membrane fuel cell in recent years [4–6]. Among them, heteroatom-doped carbon has attracted intensive attention due to excellent catalytic performance, high stability, and low cost, such as nitrogen, sulfur, boron, phosphorus, fluorine, and so on [7–12]. These heteroatom-doped carbon materials emerged one after another for metal-free catalytic technology. Afterwards, dual or multiple doped carbon materials were studied for further enhancement in the catalytic activity due to the synergistic effect of different heteroatoms, such as N/S, N/B, N/P, N/I, N/B/P, and so on [13–17]. Meanwhile, researchers found

that F-doped carbon materials showed the promising ORR performance because F atom affected greatly the electronic properties of carbon materials [9]. Few literatures about F-doped or codoped carbon materials were reported because of the difficult preparing process.

Polydopamine as a carbon resource to form carbon-coated materials has been investigated in the previous work because of its strong molecule designability and easy deposition on substrates [18] such as CN_x electrocatalyst; N, S doped graphene; and so on [19, 20].

Based on these studies, we developed firstly a novel route to prepare F and other heteroatom codoped carbon-based catalyst and study the influence of the kind and the amount of heteroatom on the ORR activity.

2. Materials and Methods

First, carboxylic MWCNTs were dispersed uniformly in pH 8.5 Tris-HCl buffer solution through the ultrasonic method for 1 h. Then, the polydopamine was deposited on MWCNTs after the addition of 0.2 mg/mL of dopamine hydrochloride

- (1) N/S-CNTs $I_D/I_G = 1.07$ $\sigma = 1.10 \text{ S/cm}$
 (2) N/S/F-CNTs-2 $I_D/I_G = 0.93$ $\sigma = 0.56 \text{ S/cm}$
 (3) N/S/F-CNTs $I_D/I_G = 1.10$ $\sigma = 1.19 \text{ S/cm}$

FIGURE 1: Raman spectra of the catalysts.

(a)

(b)

(c)

FIGURE 2: F1s, N1s, and S2p XPS spectra of N/S/F-CNTs-2.

FIGURE 3: TEM of the samples: (a) carboxylic MWCNTs; (b) CNTs-Pdop-S(CF₂)₇CF₃; (c) N/S/F-CNTs; (d) N/S-CNTs. The inserted scale bar is 50 nm.

in the above solution under stirring continuously at room temperature for 24 h. Afterwards, CNTs-modified polydopamine, named PDA-CNTs, were obtained by centrifugation, washing, and drying in succession.

PDA-CNTs were dispersed uniformly into anhydrous CH₂Cl₂ through the ultrasonic method. Then, 1-octanethiol (or 1H, 1H', 2H, 2H'-perfluorooctanethiol) and anhydrous triethylamine were added to the solution under N₂ atmosphere for 24 h. The obtained CNT-PDA-S(CH₂)₇CH₃ or CNT-PDA-S(CF₂)₇CF₃ was centrifuged, rinsed, and dried. Finally, the sample was heated at 800°C under N₂ for 2 h to obtain N, S codoped CNTs or N, S, F codoped CNTs, named N/S-CNTs or N/S/F-CNTs. For the comparison of the electrocatalytic activity, PDA-CNTs were also heated under the same condition to prepare N-doped MWCNTs, named N-CNTs. Also, CNT-PDA-S(CF₂)₇CF₃ was pyrolyzed at 600°C under N₂ for 2 h, named N/S/F-CNTs-2.

The morphologies of the samples were observed by field emission transmission electron microscopes (FEI Tecnai G2 F20). The component of the carbon material was analyzed on Raman microscope (Renishaw InVia). X-ray photoelectron spectra (XPS) were recorded on ESCALAB 250Xi (Thermo Fisher Scientific) to analyze the compositions of the support and the electrocatalyst, and all the binding energies were calibrated to C1s peak at 284.8 eV. Electrochemical tests were carried out by CHI 660E electrochemical workstation in a standard three-electrode system. The working electrode was prepared by pasting electrocatalyst inks on a glassy carbon rotating disk electrode with the diameter of 3 mm. The ink contained 5 mg of catalysts, 30 μL of 5 wt.% Nafion solution, and 1 mL ethanol. 5 μL ink was dropped on the surface of the glassy carbon electrode. The counter electrode

was a platinum wire with the diameter of 0.5 mm, and the SCE electrode was served as a reference electrode. Cyclic voltammetry was performed from 0.1 to -0.5 V at 5 mV/s in O₂-saturated or N₂-saturated 0.1 M KOH solution. Using the rotating ring disk electrode with the diameter of 3 mm, linear sweep voltammetry was performed from 0.1 to -0.5 V at a scan rate of 10 mV/s with the rotational speed from 400 to 2000 rpm in the O₂-saturated 0.1 M KOH solution.

3. Results and Discussions

There were two typical peaks measured at 1350 cm⁻¹ and 1590 cm⁻¹ in all the Raman spectra corresponding to D and G bands, respectively (Figure 1). The intensity of D band and G band ratio (I_D/I_G) can be used to assess the defect quantity and disorder of the structure. The I_D/I_G value increased from N/S-CNTs to N/S/F-CNTs obtained at the same temperature, which means that the heteroatom increased the disorder. In addition, I_D/I_G of N/S/F-CNTs-2 (0.93) is lower than that of the catalyst N/S/F-CNTs obtained at 800°C. It indicated that higher temperature made the heteroatom decomposed sharply, resulting in more defects and more active sites.

Figure 2 shows the XPS spectra of N, S, and F of N/S/F-CNTs-2. There was an obvious peak at 689.4 eV in the F1s peak of the catalyst, corresponding to the semi-ionic characteristic peak of C-F [9]. As shown in Figure 2, the N1s spectrum was deconvoluted to four peaks at 398.7, 399.6, 400.7, and 402.7 eV, belonging to pyridinic, pyrrolic, graphitic, and NO_x, respectively. The S2p characteristic peak can be deconvoluted to three peaks located at 162.2, 163.8, and 168.9 eV, assigned to S2p_{3/2} and S2p_{1/2} of C-S-C

FIGURE 4: Electrochemical measurement of support and catalysts. (a) CV in O_2 or N_2 -saturated 0.1 M KOH solution with a scan rate of $5 \text{ mV} \cdot \text{s}^{-1}$: (1) N/S-CNTs; (2) N/S/F-CNTs-2; (3) N/S/F-CNTs; (4) N/S/F-CNTs in N_2 ; (5) 20% Pt/C; (6) MWCNTs; (7) N-CNTs. (b) LSV in O_2 -saturated 0.1 M KOH solution at the rotation rate of 1600 rpm with a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$: (1) 20% Pt/C; (2) N/S/F-CNTs-2; (3) N/S-CNTs; (4) N/S/F-CNTs. (c) The current–time chronoamperometric response of catalysts: (1) 20% Pt/C; (2) N/S/F-CNTs.

(thiophene-S) and $C-SO_x-C$, respectively [21]. Among them, semi-ionic C-F, pyridinic N, and thiophene-S were beneficial to improve the ORR performance. Besides, the multi-heteroatoms in the carbon material can form some non-electron-neutral sites because of the synergic effect [22, 23].

The formation process of catalysts was observed by TEM. The diameter of carboxylic MWCNT distribution is about 10–20 nm, and its surface is flat (Figure 3(a)). However, the surface turned rough after deposition of the polydopamine nanofilm followed by the secondary reaction with 1H, 1H', 2H, 2H'-perfluorooctanethiol, and the thickness of the uneven surface is within the range of 5–13 nm (Figure 3(b)). Figure 3(c) shows that the thickness of the polymer film became thinner through pyrolysis to form N/S/F-CNTs, which is similar to that of N/S-CNTs (Figure 3(d)) and N-CNTs.

The cyclic voltammogram was measured to study the catalytic activity of electrocatalysts for ORR. It can be seen in Figure 4(a) that the reduction potential of MWCNTs was -0.30 V with the current density of $-0.90 \text{ mA} \cdot \text{cm}^{-2}$.

The reduction potential of N-CNTs shifted positively to -0.26 V , and the current density increased. The reduction potential of N/S-CNTs (-0.24 V) was a little more positive than that of N-CNTs. The doped S would increase the electron density of carbon materials, and its electronegativity (2.58) was a little higher than that of C (2.55), which induced C atom containing a few positive charge to improve the activity of ORR. However, the thiophene-S content of PDCN was low, indicating that the activity of ORR did not improve greatly. In surprise, the reduction potential of N/S/F-CNTs shifted hugely up to -0.16 V , and the current increased to $-1.45 \text{ mA} \cdot \text{cm}^{-2}$. Compared with commercial 20% Pt/C, it contained slightly lower reduction potential and higher current density. Electronegativity of F atom (3.98) was much higher than that of C atom, and the semi-ionic C-F bond in N/S/F-CNTs presented higher activity than the C-F covalent bond [9]. The doped F improved the electron structure of carbon and increased the active site. As a result, the catalytic activity greatly improved, and it was even superior to that of N/S/F-CNTs-2, although the content of S and F in N/S/F-CNTs-2

was twice higher than that of N/S/F-CNTs. Compared with polydopamine treated under 800°C, maybe sp^2 of C in N/S/F-CNTs-2 was much less likely to lead to poorer electrical conductivity, less defect, and lower activity [24]. Meanwhile, the reduction current of N/S/F-CNTs was weak in N_2 -saturated 0.1 M KOH solution. All the results showed that N/S/F-CNTs exhibited the highest catalytic activity.

Linear sweep voltammetry was carried out on the rotating disk electrode to analyze the reaction kinetics and catalytic mechanism for ORR. Figure 4(b) shows LSV of the catalysts under the rotating speed of 1600 rpm. Among the as-prepared catalysts, N/S/F-CNTs exhibited the highest onset potential (−0.11 V) that was more negative than that of 20% Pt/C (−0.07 V), but its $E_{1/2}$ (half-wave potential, −0.19 V) was higher than that of 20% Pt/C (−0.21 V). In addition, the LSV curve of N/S/F-CNTs showed wide current plateaus that started from −0.25 V and highest current density in the diffusion-controlled region. Compared with N/S/F-CNTs, the other two catalysts exhibited evidently worse catalytic activity. The value of electron transfer number for N/S/F-CNTs was close to 4.0, which was calculated from Koutecky–Levich curves with a potential range of −0.4 V to −0.5 V [25–27]. The four electron pathway was preferred due to a fast rate of oxygen reduction [28, 29]. Excellent stability of the electrocatalyst is very important for practical application [30]. Figure 4(c) shows the stability of N/S/F-CNTs and 20% Pt/C. Both the current values decreased with the increase of time; however, the current attenuation of the catalyst N/S/F-CNTs displayed a slight current attenuation. I/I_0 of Pt/C decreased to 86.5%, while N/S/F-CNTs maintained 94.6% of the initial value in the same period. Clearly, the results showed that N/S/F-CNTs contained remarkable electrochemical stability.

4. Conclusions

In conclusion, F and other heteroatom codoped carbon-based catalysts for ORR were prepared successfully through polydopamine derivative followed by pyrolysis. Among the catalysts, N/S/F-CNTs exhibit excellent activity for ORR and remarkable electrochemical stability, which is comparable with commercially expensive 20% Pt/C. In addition, PDA can be deposited on any substrate surface and react with organic molecules through Schiff base or Michael addition reactions or coordinate with metal ions. So, PDA is a good building block for designing multi-heteroatom-doped or metal-nitrogen-carbon materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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