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Fe_2P Nanoparticles Decorated Heteroatom-Doped Carbon Nanotubes as High-Performance Oxygen Reduction Catalysts

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Abstract. In this paper, a kind of hybrid oxygen reduction catalysts composed of Fe_2P nanoparticles and heteroatom-doped mesoporous carbon nanotubes (HCNTs) were prepared and used as a novel alternative to traditional noble metal-based catalysts. Polyphosphazene nanotubes (PZSNTs) were used as carbon matrix precursors, and PZSNTs absorbed ferric acetylacetonate were carbonized to obtain the hybrid catalysts, Fe_2P-CNTs. Fe_2P nanoparticles embedded in graphited carbon layers could be generated on the surface of HCNTs. Fe_2P-CNTs showed excellent catalytic activity, and their performance was even comparable to that of Pt/C catalysts. The synergistic effect between Fe_2P nanoparticles and HCNTs via electronic interaction could enhance the activity of the catalysts. These findings provide a facile approach for rational design heteroatom-doped carbon-based ORR catalysts with polyphosphazene acting as the precursor, and reveal a method to promote the activity of active centers by electronic interaction.

Keywords. Oxygen reduction, catalyst, Fe_2P, heteroatom-doped carbon, polyphosphazene

1. Introduction

The design of oxygen reduction (ORR) catalysts with low cost and high efficiency has drawn great interest in recent years [1, 2]. Heteroatom-doped carbon nanomaterials, characterized by high conductivity, excellent stability, and low cost, bring hope for the design of new efficient ORR catalysts. Over the past decade, a series of carbon-based catalysts have been designed, and their performance even exceeded that of Pt/C catalysts in some aspects [3, 4].

Electronic structure sets a great impact on the ORR activity of catalysts, as well as for carbon-based catalysts [5, 6]. By introducing transition metal compounds into carbon materials, electronic interactions between carbon materials and transition metal compounds could affect the outer electrons of the active centers, and can be utilized to regulate the activity of the catalysts [7]. Research involving the improvement of catalytic activity by combining transition metals and heteroatom-doped carbon has drawn great attention in recent years [8, 9]. DFT studies also focused on regulating the electronic structure of the active sites [10, 11]. The electronic structure of the carbon could be regulated by the electron-donating properties of transition metal compounds, and the

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activity of the active centers could be effectively regulated.

In this paper, novel ORR catalysts composed of heteroatom-doped mesoporous carbon and Fe_2P were designed based on ferric acetylacetonate and PZSNTs acting as the precursors. PZSNTs, a kind of hybrid nanotubes with highly cross-linked structures, are excellent precursors for carbon-based catalysts. In the carbonization process, PZSNTs can form heteroatom-doped porous carbon during carbonization and maintain a good tubular structure. Herein, by annealing PZSNTs and ferric acetylacetonate in the N_2 atmosphere, Fe_2P nanoparticles, embedded in a graphitized carbon shell, were formed and supported on the surface of HCNTs. Although Fe_2P nanoparticles could not directly contact the reactants and participate in the ORR process, they can effectively enhance the catalytic activity of the active centers on the surface of HCNTs through electronic interaction.

2. Experimental Section

2.1. Synthesis of PZSNTs Complexed with Ferric Acetylacetonate (PZSNTs-FeAc)

The synthesis of PZSNTs-FeAc consists of two major sections, synthesis of PZSNTs and the complexation process. PZSNTs were prepared by the method we reported in our previous work [12]. In the complexation process, 0.4 g PZSNTs were first dispersed in 30 mL of methanol. PZSNTs-FeAc could generate gradually by adding 0.6 mL of 0.2 M ferric acetylacetonate solution to the dispersion and magnetic stirring for 3 hours. By cleaning with deionized water three times and freeze-drying, PZSNTs-FeAc was obtained as an intermediate product.

2.2. Synthesis of Fe_2P-CNTs

Fe_2P-CNTs were obtained by direct carbonizing PZSNTs-FeAc in an inert atmosphere. For comparison, PZSNTs were calcined under similar conditions without transition metal nanoparticles. The typical process was conducted by referring to our previous work [13].

2.3. Characterization and Electrochemical Measurements

Characterization and Electrochemical measurements were conducted referring to our previous work [13].

3. Results and Discussion

The TEM technique was applied to characterize the morphology of Fe_2P-CNTs. As revealed in Figure 1a, the synthesized Fe_2P-CNTs have the characteristic of a one-dimensional structure with 60 nm-80 nm in diameter. Nanoparticles with diameters ca. 15 nm-25 nm were generated and uniformly distributed on the surface of the carbon matrix. Figure 1b displays the magnified TEM image of the nanoparticles on Fe_2P-CNTs. As shown in the image, a graphitized carbon layer with a thickness ca. 3 nm-6 nm was formed on the surface of the nanoparticle, and forming a core-shell structure with the nanoparticle.

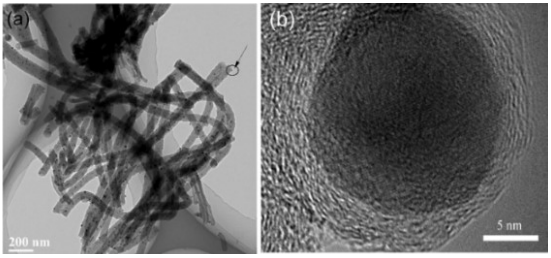

Figure 1. TEM images of Fe_2P-CNTs at different magnifications.

The structure of Fe_2P-CNTs was identified using XRD. Three diffraction peaks at 2θ= 40.3°, 44.2° and 47.3° are shown in Figure 2a, which are in accordance with the (111), (201) and (210) planes of Fe_2P (PDF 85-1227). The diffraction peak at 2θ=22°-25° is weak and broad, suggesting the turbostratic carbon structure of the carbon nanotubes. Raman spectra were used to characterize the regularity of the carbon matrix (Figure 2b), and the results also indicate the amorphous structure of the carbon matrix.

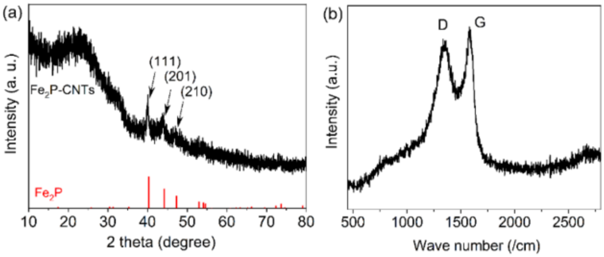

Figure 2. (a) XRD patterns of Fe_2P-CNTs; (b) Raman patterns of Fe_2P-CNTs.

XPS results show that Fe_2P-CNTs are mainly composed of carbon. A considerable level of heteroatoms including N, O, P and Fe were retained after the carbonization process. The quantities of each atom of Fe_2P-CNTs are shown in Table 1. Figure 3a shows that the N peaks can be fitted into two peaks, 400.7 and 402.3 eV, corresponding to pyrrole nitrogen and tetravalent nitrogen, respectively [14]. The spectrum of P 2p peak could be deconvoluted into two peaks: the remarkable peak at ca. 129.8 eV corresponding to the P species of Fe_2P nanoparticles, and the peak at 133.0 eV to P-C or P-O in the carbon nanotubes (Figure 3b). Apart from part of the P atoms formed Fe_2P with Fe atoms, heteroatoms such as N and P were linked to the framework carbon nanotubes by covalent bonding. Heteroatoms not only improve the surface wettability, but also endow the materials with active sites for ORR catalysis. Figure 3c shows the XPS spectrum of Fe_2P peaks, and the peaks at ca 707.2 eV and 720.1 eV could be ascribed to $Fe_2P_{3/2}$ and $Fe_2P_{1/2}$. The binding energy of Fe in this paper is lower than that of many other reports, indicating an increased energy level of the d orbital for Fe. The increasing of d orbital energy level would set a positive effect on the adsorption of intermediates in the ORR process [15].

Table 1. XPS results and structural properties of Fe_2P-CNTs.

Sample	**C (at. %)**	**N (at. %)**	**O (at. %)**	**P (at. %)**	**Fe (at. %)**	**S_{BET} (m^2/g)**	**V_{pore} (cm^3/g)**
Fe_2P-CNTs	90.3	1.54	5.82	1.16	0.46	397.0	0.23

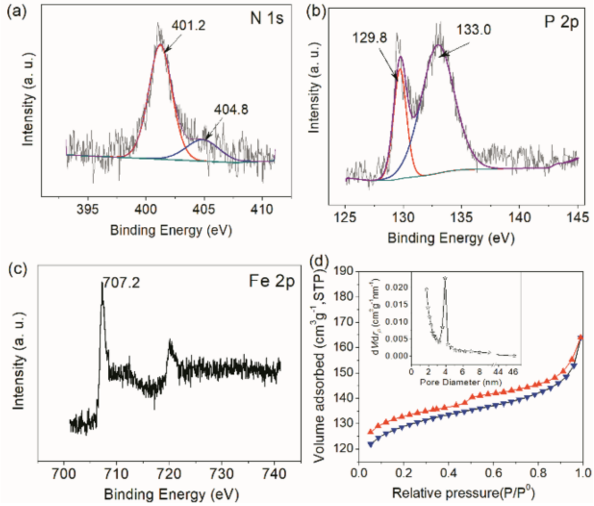

Figure 3. (a): XPS spectra of N1s; (b): XPS spectra of P_2P; (c): XPS spectra of Fe_2P; (d): Nitrogen adsorption-desorption isotherms of Fe_2P-CNTs; the inset in (d) shows the pore size distribution of Fe_2P-CNTs.

The specific BET surface area (S_{BET}) and pore volume (V_{pore}) are critical to the catalytic performance of the catalysts. S_{BET} and V_{pore} of Fe_2P-CNTs were calculated to be ca. 397.0 m^2/g and ca. 0.23 cm^3/g, respectively. The curve inserted in Figure 3d shows the pore size distribution of Fe_2P-CNTs, and a sharp peak at ca. 4 nm could be observed, indicating abundant mesopore with a pore size of about 4 nm distributed in Fe_2P-CNTs. The large S_{BET} and mesoporous structure will facilitate the exposure of the active centers and promote electrolyte diffusion in the ORR process.

In order to assess the influence of Fe_2P nanoparticles on the ORR activity of the HCNTs, CV and LSV measurements were conducted, and the results are shown in Figure 4. Figure 4a shows the CV curve of Fe_2P-CNTs with no obvious redox peaks in N_2-saturated electrolyte, indicating that no oxygen reduction process occurs. However, when the electrolyte was saturated with oxygen, the oxygen reduction process at ca. 0.81 V vs. RHE could be observed, suggesting obvious ORR catalytic activity of Fe_2P-CNTs.

LSV measurements were conducted with a series of RDE rates in O_2-saturated electrolytes for getting further insight into the ORR process that occurred with Fe_2P-CNTs. As shown in Figure 4b, Fe_2P-CNTs exhibit a more positive catalytic onset potential (ca. 0.92 V vs. RHE), which is obviously higher than that of HCNTs without the introduction of Fe (ca. 0.80 V vs. RHE). Furthermore, the catalytic performance of Fe_2P-CNTs is compared to that of commercial Pt/C. Fe_2P-CNTs show a similar LSV profile to Pt/C involving the onset potential and half-wave potential (ca. 0.80 V vs. RHE). In order to gain a deeper understanding of the catalytic process, Koutecky-Levich (*K-L*) plots, as well as the kinetic current (JK), were calculated based on the LSV data. The calculation process refers to the literature for details [16]. Figure 4c shows the *K-L* plots of Fe_2P-CNTs at potential ranging from 0.2 V to 0.6 V. Good linearity and parallel characteristic of the *K-L* plots indicated a first-order dependence of O_2 kinetics and similar electron transfer number (n) per O_2 molecule. The values of n per O_2 molecule for Fe_2P-CNTs are calculated to be 3.85 to 4.0 (inset in Figure 4c), suggesting that most O_2 molecules could be directly reduced to OH^-. For HCNTs, the ORR process shows a two-plateau peroxide pathway (i: 0.8 V-0.4 V; ii: 0.4 V to-0.05 V, vs. RHE). The n values for HCNTs are 2.89 to 3.37, lower than that of Fe_2P-CNTs (Figure 4f). The above results suggest that although Fe_2P nanoparticles are embedded in the carbon shell and cannot directly participate in the catalysis process, they have an important impact on the activity of the catalyst.

It is reported that the surface electroneutrality of the carbon structure could be disturbed by doping with heteroatoms, resulting reduced surface adsorption barrier. In the ORR process, the doped structure could efficiently facilitate the oxygen adsorption process. Herein, the doped structure within the carbon nanotubes could disturb the electroneutrality of the Fe_2P-CNTs effectively, and endows Fe_2P-CNTs ORR activity. On a deeper level, Fe_2P nanoparticles embedded in carbon layers have an important impact on the ORR activity of the doped carbon via host-guest electronic interaction. The π electrons of the doped carbon would be pushed to a higher HOMO level by Fe_2P nanoparticles, making the active centers on the HCNTs surface more sensitive to oxidization [10].

Methanol tolerance ability and the durability of Fe_2P-CNTs were studied. As shown in Figures 4e and 4f, in comparison with commercial Pt/C catalysts, Fe_2P-CNTs show more excellent catalytic durability and methanol tolerance.

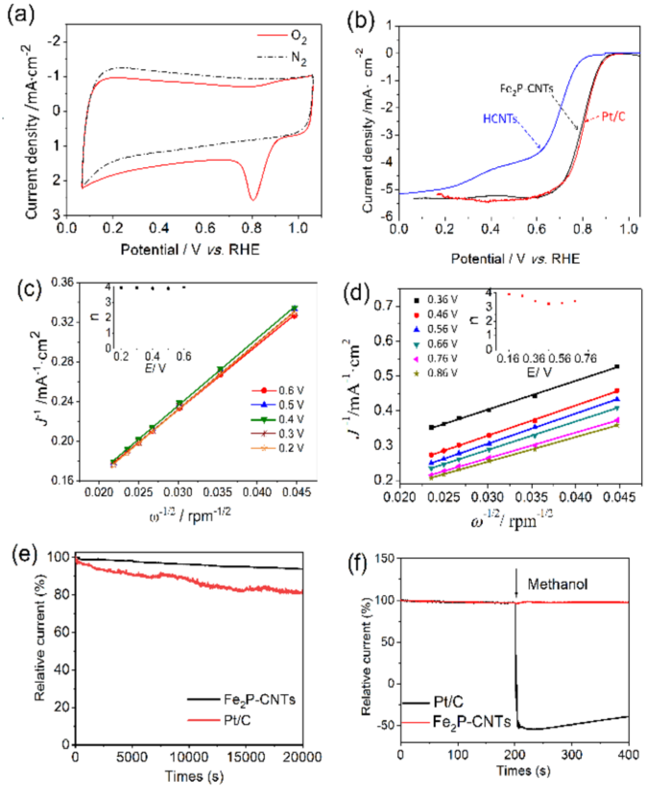

Figure 4. (a): CV curves of Fe_2P-CNTs in O_2-saturated and N_2-saturated electrolyte. (b): LSV curves of different catalysts at 1600 rpm. (c): *K-L* plots at selected potentials corresponding to Fe_2P-CNT recorded at selected potentials; (d): *K-L* plots at selected potentials corresponding to HCNTs recorded at selected potentials. (e): Durability of Fe_2P-CNTs; (f): Methanol tolerance ability of Fe_2P-CNTs.

Note: The insets in Figures 4c and 4d show the dependence of *n* on the potentials.

4. Conclusions

ORR catalysts (Fe_2P-CNTs) composed of Fe_2P nanoparticles and HCNTs were fabricated with PZSNTs and ferric acetylacetonate acting as the precursors. Electrochemical tests indicated highly efficient ORR catalytic performance of Fe_2P-CNTs involving high onset potential, $4e^-$ dominated pathway and high limited current density. In comparison with commercial Pt/C catalysts, Fe_2P-CNTs showed superior methanol tolerance ability and durability. The electronic structure of the active centers on HCNTs could be regulated by the Fe_2P nanoparticles via electronic interaction, and leading to prompted performance of the catalysts. This paper not only provides a strategy for rational designing carbon-based ORR catalysts with polyphosphazene acting as the precursor, but also reveals a practicable method to enhance the ORR activity by electronic interaction.

Acknowledgments

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