Functionalization of multi-walled carbon nanotubes with iron phthalocyanine via a liquid chemical reaction for oxygen reduction in alkaline media

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HIGHLIGHTS

- A facile chemical route is provided to prepare FePc-modified CNTs as ORR catalyst.
- FePc-RCNTs exhibit better ORR activity and stability than Pt/C in alkaline media.
- The synergy effect of FePc and CNTs plays a key role in the catalysis for ORR.

GRAPHICAL ABSTRACT
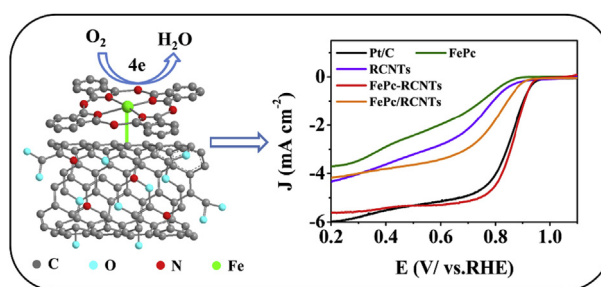
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ABSTRACT

Iron single-atom catalyst in form of iron-nitrogen-carbon structure possesses the excellent catalytic activity in various chemical reactions. However, exploring a sustainable and stable single-atom metal catalyst still faces a great challenge due to low yield and complicated synthesis. Here, we report a functional multi-wall carbon nanotubes modified with iron phthalocyanine molecules via a liquid chemical reaction and realize the performance of similar single-atom catalysis for oxygen reduction reaction. A serial of characterizations strongly imply the structure change of iron phthalocyanine molecule and its close recombination with multi-wall carbon nanotubes, which are in favor of ORR catalysis. Compared to commercial platinum-carbon catalyst, composites exhibit superior activity for oxygen reduction reaction with higher half-wave potential (0.86 V), lower Tafel slope (38 mV dec^{-1}), higher limiting current density and excellent electrochemical stability. The corresponding Zinc-air battery also presents higher maximum power density and discharge stability. Therefore, these findings provide a facile route to synthesize a highly efficient non-precious metal carbon-based catalyst.

1. Introduction

Recently, the single-atom catalysis has become a new research frontier in the field of heterogeneous catalysis. Because single-atom catalysts exhibit the lowest limit of metal size to obtain the maximum atom efficiency and expose the most active sites in catalysis [1–13], they have been widely studied and applied in various catalytic reactions such as CO_2 reduction [2,3], CO oxidation [4], hydrogen generation

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[5–9], C-H bond oxidation [10] and oxygen reduction reaction (ORR) [1,11–13] et al. At present, metal-N_4 materials supported on carbon matrix have increasingly emerged as one of the most promising single-atom catalysts [14–16]. However, it is still difficult to stabilize the active structure of metal centers during a catalytic reaction due to serious aggregation and migration of metal atom [14,16–20]. Therefore, the most important thing in the production of single-atom catalysts is to explore an appropriate strategy for stabilizing the metal atoms on the carbon matrix. Bao groups prepared a single-atom catalyst by embedding highly dispersed FeN_4 structure in the graphene matrix through high-energy ball milling method [17,18]. Xie et al. synthesized a symbolic high-performance single-atom ORR catalyst with abundant atomically dispersed Fe-N_x species after the high-temperature pyrolysis [19]. In addition, Li et al. also achieved an atomically dispersed Fe-N_4 catalyst for ORR, in which the iron atom was anchored on N-doped carbon support by utilizing an eliminable zeolitic imidazolate framework-8 (ZIF-8) template [20]. As a matter of fact, all of these atomically dispersed metal-N_4 catalysts were produced via the coordination of unsaturated metal atom with nitrogen atoms. Unfortunately, the above preparation methods not only are low efficient, but also easily generate a great deal of less-active Fe-based oxide nanoparticles (NPs).

For stabilizing the metal atom, an efficient route may be to form axially covalent bonds between carbon matrix and metal-N_4 macrocycles, where the central metal atom has been immobilized to nitrogen atoms in advance. By taking advantage of these features, metal atom can be effectively stabilized by highly planar π-π interactions and axially chemical covalent bonds. Actually, the ORR activity in Fe(Co)-N_4 macrocycles such as phthalocyanines, porphyrins have been widely investigated, among which iron phthalocyanine (FePc) holds the best ORR performance [21–31]. Nevertheless, their catalytic activity and stability are still poor owing to the formation of FePc aggregation and their poor electrical conductivity [25]. Cho et al. solved this problem through the functionalization of pyridine-modified multi-wall carbon nanotubes (MWCNTs) with axially-coordinated FePc molecules [26]. The formation of planar construction and strong covalent bonds could prevent FePc molecules from aggregating and enhance the conductivity and stability of catalytic system. Afterwards, Liu et al. also found that iron porphyrin (FeTPP) can be covalently grafted on the surface of MWCNTs through axially imidazole chains and used as a promising alternative to Pt/C catalyst [32]. However, these synthetic processes are too complicated to conveniently prepare the effective ORR catalysts. Recently, we have reported the synergistic ORR catalysis of four- and five-coordinated Fe atoms in Fe(II)Pc/Fe(III)Pc/graphene nanostructures due to the formation of axial Fe-O-C bond in a simple liquid chemical reaction between graphene oxide and FePc precursor [33]. It is believed that the simple reaction can be applied in the synthesis of other carbon-based ORR catalysts in order to achieve similar single-atom catalytic performance.

Compared with other carbon materials, N-doped MWCNTs can efficiently recombine with FePc molecules as ORR catalyst owing to their unique structure and electronic properties, [26,29,34,35]. In addition, acidification [36] and Hummer methods [37] have hitherto been used to pretreat CNTs. The exterior of MWCNTs can be unzipped into layer structure via Hummer method, while it only becomes rougher after acidification. In this work, the N-doped MWCNTs are firstly oxidized through Hummer method to load more FePc molecules. Afterwards, the carbon-based FePc composite is synthesized through the recombination of FePc precursor and oxidized MWCNTs under ambient temperature. The as-obtained catalyst exhibits more positive half-wave potential, higher limiting current density, better stability and methanol tolerance than those of commercial Pt/C catalyst in alkaline solution, and the corresponding Zn-air battery also display higher power density and discharge stability.

2. Experimental section

2.1. Chemicals and materials

N-doped MWCNTs and iron phthalocyanine (FePc) were purchased from Chengdu Organic Chemicals Co. Ltd and J&K Chemicals Co. Ltd, respectively. Nafion (5 wt%) and Pt/C (20 wt%) were obtained from Shanghai Hesen Electric Co. Ltd. All other chemical reagents were from Sinopharm Chemical Reagent Co. Ltd and used as received without further purification. Milli-Q ultrapure water was used for all experiments with a resistivity of $18.25 \, M\Omega \, cm^{-1}$.

2.2. Synthesis of FePc precursor

FePc precursor was synthesized according to the chemical reaction (1).

$$2FePc + 2AgClO_4 + I_2 = 2FePc^+ \cdot ClO_4^- + 2AgI \downarrow \qquad (1)$$
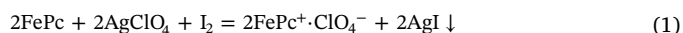
1.0 mmol silver perchlorate ($AgClO_4$) in 5.0 mL anhydrous acetonitrile (CH_3CN) and 0.5 mmol iodine (I_2) in 8.0 mL anhydrous dichloromethane (CH_2Cl_2) were added into 50 mL anhydrous CH_2Cl_2 solution including 1.0 mmol FePc. After vigorous stirring for 3 h and then aging for 3 h, silver iodide (AgI) was removed by centrifuging at 10,000 rpm for 10 min. Then the filtrate was poured into 200 mL petroleum and sealed for 2 h. The mixture was centrifuged at 10,000 rpm for 10 min again. The precipitation was dried under vacuum condition for 12 h for further use.

2.3. Synthesis of oxidized carbon nanotubes (OCNTs)

N-doped MWCNTs were firstly heated to 500 °C in a tube furnace at 5.0 °C min^{-1} and annealed for 1 h under high purity argon. Afterwards, 0.5 g N-doped MWCNTs were moved to 500 mL beaker containing 50 mL concentrated sulfuric acid (H_2SO_4) and stirred for 2 h and then ultrasonicated for 1 h at room temperature. 0.2 g sodium nitrate ($NaNO_3$) were added into the mixture and ultrasonicated for another 30 min. Subsequently, 1.25 g potassium permanganate ($KMnO_4$) was slowly added under continuous stirring condition. The reaction beaker was heated to 40 °C in an oil bath for 1 h. Then, 100 mL ultrapure water and 10 mL hydrogen peroxide (H_2O_2, 30 wt%) were slowly added to terminate the reaction. The dispersion was finally filtered and washed with abundant deionized water until the pH reached to neutral. The collected solid was dried at 60 °C under vacuum condition for 12 h, affording OCNTs.

2.4. Synthesis of the catalysts

In a typical experiment, 30 mL of 1.0 mM $FePc^+ \cdot ClO_4^-$ solution in anhydrous CH_3CN was quickly poured into 100 mL of 1 mg mL^{-1} OCNTs aqueous dispersed system. The system was stirred for 2 h, and then aged for 3 h. Afterwards, the composite was collected via the centrifugation of mixture at 10,000 rpm for 10 min and washed with ultrapure water for twice. As-obtained solid powder was named as FePc-OCNTs. The as-collected precipitation was transferred into 100 mL autoclave and treated at 120 °C for 2 h. The product was obtained by centrifuging at 10,000 rpm for 10 min and subsequently dried under freeze-drying condition. The final solid powder was labelled as FePc-RCNTs. Here, the RCNTs were also prepared through the hydrothermal treatment of OCNTs at 120 °C for 2 h. The FePc/OCNTs and FePc/RCNTs were obtained by a simple physical mixing method.

2.5. Physical characterizations

Scanning electron microscope (SEM, Hitachi SU8010) was firstly used to characterize the morphology of all samples. The morphology, composition and structure were further investigated by transmission