Interface Decoration Of N-Doped Carbon Nanotube with Fe For Enhancing Oxygen Catalytic Activity

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Abstract. Oxygen electrocatalytic reactions, including oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are extremely important in energy storage and conversion technology. The ORR is happened in cathode electrode in fuel cells or metal air batteries when discharging, the OER is occurred in anode electrode in water splitting or rechargeable metal air batteries when charging. Currently, the high-performance catalyst developed for ORR still relies on platinum (Pt) and its alloys. On the other hand, ruthenium (Ru) oxides were demonstrated to be high performance electrocatalysts for OER. However, their scarcity, limited stability, and aggregation limited the development of electrochemistry energy storage and conversion. Herein, we synthesize a series of transition metal nanoparticles embedded in nitrogen doped carbon nanotubes (M-CNT) and further decorating the interface of N-CNT with Fe element for enhancing oxygen catalytic activities. The results show that the type of transition metal determine the morphologies of N-CNT and the catalytic performance in ORR and OER. After further modification by introducing Fe element, the Fe-CNT based catalyst displays a superior ORR activity, even surpasses that of Pt/C, the Ni-CNT based catalyst with Fe decoration also showes a significant enhancement in OER. This work provides a feasible strategy to develop highly efficient oxygen catalysts with low-cost, earth-abundant transition metal elements via further decoration.

1. Introduction

Currently, fossil fuel is not enough to satisfy the demand of peoples’ life for its pollution to environment and non-renewable resource. [1-3] Exploiting renewable energy to replace the fossil fuel is a major challenge in nowadays. Electrochemical energy storage and conversion technology has attracted mush attentions for its high efficiency and zero carbon emissions. In the electrochemical energy storage and conversion process, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the most important electrode reactions, especial in fuel cell, metal-air battery or water splitting. [4] However, all of mentioned devices are restricted for the inherently sluggish reaction kinetics of oxygen catalytic reaction. Pt and Pt based alloy catalyst shows best ORR performance, and Ru or Ir oxides are the best OER catalysts with lowest overpotential. These noble metal-based catalysts limit the large-scale application for their prohibitive cost and scarcity in nature.
and low stability. [5] Therefore, it is extremely imperative to search low-cost oxygen catalysts with comparable or even superior performance, which consist of earth abundant elements.

Recently, transition metal-based catalysts and carbon-based catalysts have been emerging as a class of appealing alternatives due to their earth abundance, tunable chemical composition and large surface area. [6-9] The Fe, Co and Ni are favourite elements in oxygen catalytic reaction. The Fe based catalysts display excellent ORR performance in acidic and alkaline solution, the Co based catalysts exhibit outstanding ORR and OER performance in alkaline solution. When doping and alloying, the NiFe, CoFe or CoNi based catalysts show robust ORR or OER catalytic activities compared to bare Fe (or Co, or Ni) based catalysts. Carbon materials are also famous for their abundant organic carbon sources, variable precursor design, tunable dopants, large surface area, outstanding conductivity and chemical stability. [10-12] For example, carbon nanotube is verified to be an effective oxygen catalyst when doping or modified by heteroatoms (N, B, S, P or other metal atoms) in many publications[13-15].

In our research, we synthesized a series of N doped CNT with transition metal (Fe, Co, Ni) nanoparticles embedded in the CNT via pyrolyzing transition metal salt and dicyandiamide in Ar atmosphere. After acidic etching, the obtained samples (M-CNT) display ordinary ORR or OER catalytic activities. When further decorating M-CNT with Fe element by introducing hemin and oxide graphene, the pyrolyzed sample Fe-CNT@Fe/G exhibits best ORR performance with more positive onset potential, larger limited diffusion current density (5.3 mA cm⁻²) and half-wave potential (0.835V vs.RHE). Interestingly, the Ni-CNT@Fe/G displays a significant enhancement in OER performance. This result indicate that interface decoration is an effective approach to tune or improve the oxygen catalytic activities in transition metal and carbon-based catalysts.

2. Experiment

2.1. Materials

Dicyandiamide (DCDA), ferric chloride (FeCl₃), cobalt dichloride (CoCl₂), nickel chloride (NiCl₂), potassium hydroxide (KOH) were purchased from Adamas-beta. The alcohol and sulfuric acid were obtained from Aladdin. Commercial Pt/C (20wt%) catalyst and Nafion solution (5%) were supplied by Johnson Matthey company and Sigma-Aldrich respectively. All the chemicals were directly used as received without further treatment.

2.2. Synthesis of M-CNT

Synthesis of Fe-CNT, Co-CNT, and Ni-CNT: the synthesis of transition metal embedded in nitrogen doped carbon nanotube (M-CNT) was carried out by a facile pyrolysis process. Typically, the FeCl₃ salt (0.73g) and DCDA (3.0g) were dissolved in 50mL deionized water. After magnetic stirring for 30min, the mixture solution was heated to 80°C for evaporating water. The obtained dried mixture was ground and then pyrolyzed at 800°C for 2h with a heating rate of 5°C min⁻¹ in argon atmosphere. The synthesized CNTs were etched by 0.5M H₂SO₄ to remove the exposed metal clusters for 8h at 80°C. Finally, the Fe-CNT was procured by rinsed with deionized water and ethanol. The Co-CNT and Ni-CNT were synthesized as the same procedure.

Synthesis of Fe-CNT@Fe/G, Co-CNT@Fe/G and Ni-CNT@Fe/G: typically, 20mg of Fe-CNT, 20mg of hemin were dissolved in 20ml deionized water, then added 5mL of GO (2mg/ml) in referred solution. After subjecting ultrasonic treatment and freeze-drying, the obtained precursor (Fe-CNT/Hemin/GO) was placed in tube furnace for pyrolysis as the same process of Fe-CNT. Then the obtained sample was denoted as Fe-CNT@Fe/G. The Co-CNT@Fe/G and Ni-CNT@Fe/G were also prepared with similar process.

2.3. Physical and electrochemical characterization

Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with CuKα1 radiation (λ=0.15406 nm). The morphologies and the structures of the
samples were characterized using field-emission scanning electron microscopy (FESEM; Hitachi SU-8010) and transmission electron microscopy (TEM; JEOL-2100F). Raman spectra measurements were conducted using a multichannel modular triple Raman system, with confocal microscopy at room temperature and an excitation wavelength of 532 nm. The Brunauer-Emmett-Teller (BET) specific surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (NOVA 2200e). XPS measurements were carried out on an X-ray photoelectron spectrometer (Thermo ESCALAB 250).

2.4. electrochemical measurements
The ORR performances were evaluated in a typical three-electrode system by an electrochemical workstation (CHI760E), which connected a rotator machine (MSR, Pine Instruments). The working electrode was prepared by coating catalyst layer on the surface of rotating disk electrode (RDE, 5mm of diameter). The counter electrode was Pt wire, the reference electrode was an Ag/AgCl electrode (saturated KCl solution). The electrolyte was 0.1 M KOH (pH=13.0) aqueous solution. Before electrochemical measurements, the electrolyte was saturated with O\textsubscript{2} or N\textsubscript{2} by injecting O\textsubscript{2} or N\textsubscript{2} gas in the solution continuously. The cyclic voltammograms and LSV curves were collected at 10mV s\textsuperscript{-1} form 1.2V to 0.1V (vs. RHE).

Preparation of the working electrode: Typically, 5 mg of catalyst was added into 1.0 mL mixture solution with 760uL of DI water, 200uL of ethanol, and 40uL of Nafion (5%) solution. After ultrasonic treatment with one hour, the uniform catalyst inks were obtained. 20 uL of catalyst ink was stepwise added into the clear surface of glassy carbon of RDE by Eppendoff. Then the working electrode was natural dried at room temperature. For comparison, a commercial Pt/C catalyst ink was prepared as the same procedure and the loaded on working electrode as above-mentioned.

3. Organization of the Text

Scheme 1. Schematic of synthesizing M-CNT and further interface decoration with Fe element
As shown in Scheme 1, the synthesis of M-CNT is directly pyrolyzing transition metal salt and DCDA mixture in Ar atmosphere. [16, 17] Subsequently, the achieved M-CNT is decorated with hemin as Fe source and GO via adsorption or hybrid. Followed by further carbonization at 800°C, the interface decorated M-CNT@Fe/G samples are obtained. The morphologies of as-synthesized samples are measured by SEM and shown in Figure 1. The Figure 1a, 1b and 1c display the SEM images of Fe-CNT, Co-CNT and Ni-CNT, respectively. The shapes of CNT are affected by the type of transition metal. The diameter of Fe-CNT (50–100 nm) is smaller than that of Co-CNT (100~200nm), but larger than that of Ni-CNT. Meanwhile, Fe-CNT presents micron order length as well as smooth surface compared with Co-CNT. The Ni-CNT are composed of abundant small CNTs with a tumour-liked shape in the terminal. This tumour-liked shape is most probable the Ni nanoparticles encapsulated by graphitic layers. The morphologies for Fe-CNT, Co-CNT and Ni-CNT are determined by the initial
shape of metal nanoparticles, which are formed in the thermal reduction in high temperature. Based on the obtained samples, the interface decoration with Fe element is performed by introducing hemin and GO with Fe-CNT, or Co-CNT, or Ni-CNT. The Figure 1d is the SEM image of Fe-CNT/Hemin/GO, which is obvious different from that of Fe-CNT. The CNTs are wrapped with hemin and GO nanosheets on their surface, clearly indicating the good dispersion of CNTs in the hemin and GO mixtures. After pyrolysis at 800°C and acid etching, the obtained Fe-CNT@Fe/G are also tested by SEM. As shown in Figure 1e and 1f, the Fe-CNT are also coated with other carbon materials, derived from hemin and GO.

![Figure 1](image_url)

**Figure 1.** SEM images of Fe-CNT (a), Co-CNT (b), Ni-CNT (c), (d) Fe-CNT/Hemin/GO, (e) and (f) the Fe-CNT@Fe/G and corresponding magnified image.

In order to further verify the structure and interface decoration, the TEM measurement is performed. As shown in Figure 2a, the Fe-CNT is a bamboo-like structure with Fe nanoparticles (the dark dot) embedded in the carbon layers. This result also can be confirmed by the magnified TEM image in Figure 2b and 2c that the outer is graphitic layer with 0.340 nm of lattice spacing and the inner is the Fe metal with 0.210 nm of lattice spacing, corresponding to (311) plane. Figure 2d is the TEM image of Ni-CNT@Fe/G, that a lot of metal alloy are encapsulated by graphitic layer with the diameter of about 50nm. Additionally, the STEM dark field image and corresponding element mapping based on energy dispersive spectroscopy (EDS) for Ni-CNT@Fe/G reveals the spatial distribution of C, N, Ni and Fe in Figure 2e-2i, indicating the successful introducing of Fe element in the Ni-CNT catalysts.

The XRD patterns of as-synthesized CNT in Figure 3a further reveal the structure of CNT and metal nanoparticles. A peak at approximately 26.3° is ascribed to (002) plane of graphitized carbon, in accordance with the graphitic degree of carbon nanotube. The weak peak at about 42.3° is assigned to (100) plane of carbon. Meanwhile, the diffraction peaks for metallic Fe (or Co, or Ni) are also observed in Figure 2a, revealing the crystalline structure of the embedded metals in CNT. The Raman spectrum is also measured to further verify the structure of Fe-CNT. As shown in Figure 3b, the peaks at 1350 cm⁻¹ (D band), 2680 cm⁻¹ (2D band), 1580 cm⁻¹ (G band) represent the defect and graphitic degree, respectively. The defect is probable due to the N doping and Fe wrapping, the high graphitic degree is attributed to CNT, which reflects better conductivity of Fe-CNT. The additional peaks at 472 and 797 cm⁻¹ are associated with different vibrational modes of metallic Fe and oxides. The surface area and pore structure of catalyst are very important in the electrocatalysis. Large surface area of catalyst is good for exposing abundant active sites, and appropriate pore structure is conducive to adsorption/desorption and transfer of reactant/product. Therefore, the surface and pore diameter
distribution of Fe-CNT was obtained by nitrogen adsorption-desorption isotherms measurements. As shown in Figure 3c, Fe-CNT displays type IV with visible hysteresis loop, suggesting its mesoporous characteristic. The BET specific surface area of Fe-CNT is calculated with 195.3 m$^2$g$^{-1}$, and the corresponding total pore volume is 0.612 cm$^3$g$^{-1}$. Meanwhile, The Barrett-Joyner-Halenda (BJH) analysis of Fe-CNT (inset in Figure 3c) shows a sharp peak at 4 nm, indicating amount of mesopores around 4 nm of diameter, which derived from the decomposition or leaving of small molecules during pyrolysis process.

Figure 2. (a-c) TEM images of Fe-CNT with different magnification; (d-i) TEM and STEM dark field image of Ni-CNT@Fe/G and corresponding EDS mappings.

Figure 3. (a) XRD pattern of M-CNT, (b-c) Raman spectra of Fe-CNT and corresponding BET plot, the inset is the pore diameter distribution of Fe-CNT

The element species and corresponding chemical state of as-synthesized samples were characterized by XPS. As shown in Figure 4a, the full survey scan of XPS analysis present C (89.86 at%), N (4.13 at%), O (5.02 at%) and Fe (1.0 at%) elements for Fe-CNT@Fe/G, suggesting high contents of N and Fe dopants. The high resolution C1s spectrum in Figure 4b exhibits two peaks at 284.8 eV and 285.8eV, assigned to C-C/C=C and C-N, respectively. To clarify the forms of existing N species, the high resolution N1s is deconvoluted into three peaks at 398.6 eV, 399.9 eV and 401.2 eV (shown in Figure 4c), which are ascribed to pyridinic N (44.8%), pyrrollic N (19.8%) and graphitic N (35.4%), respectively. The dominated pyridinic N and graphitic N would generate more active sites and enhance the conductivity. [18, 19] The high-resolution Fe 2p XPS spectrum in Figure 4d exhibited characteristic peaks of the Fe$^{II}$ oxidation states located at 709.7 eV (Fe 2p$_{3/2}$ peak) and 722.3
eV (Fe 2p\(_{1/2}\) peak), Fe\(^{\text{III}}\) oxidation states located at 711.8 eV (Fe 2p\(_{3/2}\) peak) and 724.9 eV (Fe 2p\(_{1/2}\) peak).

![Figure 4](image1.png)

**Figure 4.** XPS analysis of Fe-CNT@Fe/G (a) full XPS spectrum indicating the presence of Fe, N, C, O; high-resolution XPS spectra of C1s (b); N1s (c) and Fe2p (d).

![Figure 5](image2.png)

**Figure 5.** Electrochemical performance of as-synthesized M-CNT@Fe/G and M-CNT. (a) CV curves measured in N\(_2\) or O\(_2\) saturated 0.1 M KOH solution; (b) the LSV curves for ORR at 1600 r.p.m in O\(_2\) saturated solution by RDE method; (c) LSV curves for OER in O\(_2\) saturated solution; (d) the \(E_{\text{gap}}\) difference of M-CNT@Fe/G.
Based on the structure and morphology characterizations, it can be concluded that the samples including M-CNT and corresponding decorated samples M-CNT@Fe/G would exhibit interesting ORR and OER performance. Subsequently, the ORR and OER performances are primarily investigated on the rotating disk electrode. As shown in Figure 5a, the cyclic voltammetry (CV) curves of samples were first performed in O2 or N2 saturated 0.1 M KOH solution. All the CV curves display an obvious cathodic peak in O2 saturated solution, compared with those in N2 saturated solution, suggesting their significant ORR performance. [4] The peak potential is also affected by the transition metals that the Fe-CNT shows a more positive potential at 0.75V (vs. RHE) than that of Co-CNT (0.73V) or Ni-CNT (0.69V). Notably, the samples of M-CNT@Fe/G further exhibit positive shift after interface decorating with Fe element. For example, the oxygen reduction peak of Fe-CNT@Fe/G is 0.82V, about 70mV positive shift from 0.75V. When these samples are carried out by LSV measurement in O2 saturated solution, the curves are shown in Figure 4b. Further interface decoration with Fe, the onset potential (E onset), half wave potential (E1/2) and limited diffusion current density (JL) of M-CNT@Fe/G samples are positive shifted, in according with those of CV curves. Meanwhile, the sample Fe-CNT@Fe/G displays a Pt/C-like ORR performance, compared with commercial Pt/C catalyst in alkaline environment. The E1/2 of Fe-CNT@Fe/G is 0.835V, more positive that those of Pt/C and other samples. These results indicate that the Fe embedded CNT catalyst and corresponding further Fe decorated catalyst are deat at ORR. The other Co-CNT or Ni-CNT can be improved by interface modified with Fe element for ORR. The OER is also crucial reaction in water splitting and rechargeable metal-air fuel cell. Therefore, the OER performance are also measured by RDE. As shown in Figure 5c, the precious RuO2 catalyst exhibits outstanding OER performance with smallest overpotential (360 mV) vs. 1.23V RHE at 10mA cm-2. The prepared sample M-CNT are showing catalytic activity for OER with obvious anodic current density. However, the overpotential of those M-CNT catalyst are too high at 10mA cm-2. After interface decoration with Fe element, the OER performance of Fe-CNT@Fe/G and Co-CNT@Fe/G are not significantly improved except that of Ni-CNT@Fe/G, the sample Ni-CNT@Fe/G displays an obvious negative shift after introducing Fe heteroatom with a potential at 1.63V vs.RHE at 10mA cm-2. This significant enhancement is probable due to the synergistic effect of Ni and Fe with N-doped CNT. Figure 5d shows the potential gap (AE gap) of M-CNT@Fe/G samples between the E1/2 of ORR and E10 (current density at 10mA cm-2) of OER. The Ni-CNT@Fe/G presents a smallest AE gap with 0.86V, compared with Fe-CNT@Fe/G (0.89V) and Co-CNT@Fe/G (0.92V), indicating the favorable discharge and charge abilities for rechargeable metal-air fuel cells.

4. Conclusion

In summary, a series of transition metal nanoparticles embedded in nitrogen doped carbon nanotube (M-CNT) was synthesized by pyrolyzing transition metal (Fe, Co, or Ni) salts and dicyandiamide. The type of transition metal affected the morphology of M-CNT, including diameter, surface and shape of CNT. The obtained Fe-CNT, Co-CNT and Ni-CNT displayed different ORR and OER performances, whereas their catalytic activities would not satisfy the application of catalyst in ORR or OER. Therefore, an approach was carried out by decorating the interface of M-CNT with Fe element. The ORR measurement presented that the Fe-CNT@Fe/G showed a superior catalytic activity with positive E1/2 (0.835V vs.RHE) and large J1 (5.3 mA cm-2). The sample Ni-CNT@Fe/G displayed a significant improvement in OER test, which only need about 370mV overpotential to obtain 10mA cm-2. This result suggested the well synergistic effect of Ni and Fe in N-doped CNT. It can be concluded that interface decoration with special transition metal element is an effect way to further improve the catalytic activity for electrocatalysis.
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