Controllable synthesis of N-doped carbon nanohorns: tip from closed to half-closed, used as efficient electrocatalysts for oxygen evolution reaction

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The development of efficient, cost-effective and stable N-doped carbon material with catalytic activity as an excellent catalyst for the oxygen evolution reaction (OER) is critical for renewable energy systems. In this study, the unique tip-half-closed N-doped carbon nanohorns (THC-N-CNHs) were firstly produced by the positive pressure-assisted arc discharge method using N2 as the nitrogen source. Benefitting from the novel tip-half-closed structure and sufficient porosity, the specific surface area (SSA) of THC-N-CNHs is calculated to be 670 m2 g−1 without any further treatment, which is three times larger than that of traditional tip-closed CNHs. More importantly, the content of nitrogen can achieve ~1.98 at% with noticeable pyridinic-N enrichment, increasing the number of active sites for the OER. Furthermore, the three-dimensional spherical feature and the unique pore structure for THC-N-CNHs lead to the fast transportation of electrons, and facile release of the evolved O2 bubbles during the OER process. Therefore, THC-N-CNHs exhibit excellent electrocatalytic activity toward the OER, with an overpotential of 328 mV at 10 mA cm−2, which is superior to that of most N-doped carbon material-based electrocatalysts. Meanwhile, the resulting catalyst also shows excellent durability after long-term cycling. Finally, we emphasize that THC-N-CNHs can be promising candidates as cheap, industrially scalable catalytic scaffolds for OER application.

1. Introduction

Oxygen evolution reaction (OER) catalysis constitutes the bottleneck for water splitting, solar cells, metal-air batteries, fuel cells and other renewable energy systems due to the sluggish kinetics of the OER, which involves a complex four-electron/proton transfer process. Although noble metal oxides like IrO2 and RuO2 show excellent catalytic performance for the OER, their widespread development is restricted by their high cost and scarcity. However, considerable research efforts have been devoted to the development of efficient OER catalysts based on transition metal sulfides and transition metal oxides, such as NiS2, FeS2, NiO and so on. However, the inherently low conductivity and easy reuniting at the nano-scale after cycling limited their applications for the OER. To solve those problems, the nanoparticles of transition metal sulfides and transition metal oxides are usually supported on conductive substrates such as graphene and carbon nanotubes (CNTs) to enhance the conductivity. Previous research also showed that the conductivity of carbon nanomaterials can be improved obviously when adding N atoms into the carbon nanomaterials. Moreover, the N atoms can contribute to the catalytic sites and play synergistic effects between N atoms and metal nanoparticles. However, N-doped graphene is inclined to aggregate or stack hindering the utilization of the active sites and enhancing the transfer resistance after a long-term OER process. In addition, the long length N-doped CNTs enhance the barriers for O2 releasing and transfer resistance. Based on those considerations, new structure carbon materials should be exploited urgently, which can prevent the aggregation for the nanoparticle catalyst after several cycling, as well as including favorable porosity and N atom doping.

Carbon nanohorns (CNHs) have attracted extensively attention in many research field due to their superior electrical conductivity, the high specific surface area (SSA) after oxidation-treatments, and the optimized nanoporous characteristics. However, studies on N-doped CNHs-based catalysts used for OER are rare, probably limited by the morphological characteristics of the traditional CNHs. Traditional CNHs are constructed by thousands of individual CNH through self-assembling mechanism to form the spherical aggregates with 80–100 nm in diameter. The individual CNH tube exhibits the cone-shaped tips presenting closed structure with 40–50 nm in length and 2–3 nm in diameter, distributing pentagonal and heptagonal defects on the tips. In generally, CNHs are formed...
2. Experimental

2.1 Synthesis the CNHs

CNHs were prepared by direct-current arc discharge in positive pressure as reported in previous research. In this work, the reaction conditions are set up at 0.15 MPa in N₂ and Ar atmosphere and 100 A electric current. In detail, an anode and a rod-shaped graphite cathode were set horizontally with 6 and 20 cm in length, respectively. The polarization curve was obtained by consecutive linear sweep voltammetry (LSV) at 5 mV s⁻¹ until there is no obvious variation. The 100 mL of 1 M KOH solutions at atmospheric environment is used as the electrolyte solution. According to the LSV curves by plotting overpotential against log(current density), Tafel slopes can be calculated. Electrochemical impedance spectroscopy (EIS) was carried out at 5 mV between 0.01 Hz and 100 kHz. By taking continuous cyclic voltammetry curve (CV) for 2000 cycles, the long-term stability can be evaluated by comparing value of LSV curves before and after cycling at same density current. 80% iR-corrected was applied for all polarization curves.

3. Results and discussion

3.1 The nanostructures of N-doped CNHs

The traditional morphology of the as-grown CNHs with a diameter ~100 nm is shown in Fig. 1(a), which are synthesized in 0.15 MPa Ar by positive pressure assisted arc discharge. The CNHs consist of tubular CNH structures with cone-closed caps observed by HRTEM in Fig. 1(b), also named as tip-closed CNHs at here, which is consistent with the structure of previous reported dahlia-like CNHs. Noticeably, the pentagon and heptagon are the necessary condition to form the cone-cape structure. The model diagrams for overall structure of CNHs, the top view and front view of the individual CNH are illustrated in Fig. 1(c), (g) and (l). The pentagon and heptagon are marked by the orange color in Fig. 1(g) and (l). Interesting, adding a little amount N₂ (0.05 MPa) into the arc furnace cavity, the
morphology of the produced has a significant diversification compared to the tip-closed CNHs as illustrated in Fig. 1(d) and (e). The periphery of CNH exhibits half curled state at tips, which is similar to the few-layer graphene structure confirmed by the interlayer spacing (~0.35 nm) for the graphene layer as depicted in Fig. 1(f). Herein, this production is referred to as the tip half-closed N-doped CNHs (THC-N-CNHs). It should be emphasized that the structure for the rest body of THC-N-CNHs is similar to the tip-closed CNHs. The schematic diagram in Fig. 1(i) makes a vivid description for the individual THC-N-CNH. From the SEM image in Fig. 1(h), we can see that the THC-N-CNHs is also a typical spherical aggregate. The elements of C, O and N are consistently appeared in the THC-N-CNHs (Fig. 1(i–k)) obtained via EDX. However, when the arc furnace is fully filled with 0.15 MPa N₂, the production become the carbon mixture, including amorphous carbon, few CNHs as depicted in Fig. 1(j).

Two markedly peaks referred to as D and G bands at ~1351 and ~1582 cm⁻¹ are appeared simultaneously for tip-closed CNHs and THC-N-CNHs as depicted in Fig. 2. The G band represents the phonon vibrations in sp² carbon materials caused by a normal first-order Raman scattering process. The intensity of D band can be affected by the structural defects. 31 On the basis of the empirical law named Tuinstra and Koenig equation, the nanocrystalline size or defect density for graphitic nanostructures can be obtained by the ratio of I_D and I_G. 32,33 As illustrated in Fig. 2, with increased the N-doping amount, the ratio of I_D and I_G decreases from 1.2 to 0.9, suggesting that the less defects exist on the THC-N-CNH. It should be noted that the result is against to the common scene, the more hetero-atoms doping the more defect degree. It is well known that pentagonal and heptagonal defects are the essential condition to form the cone-shaped cap for CNHs. This result suggests that with increased the N-doping content, the cone-shaped cap structure for CNHs tends to transform the plane structure, which is in agreement with the HRTEM observation. Moreover, the 2D peak become protruding for THC-N-CNHs in contrast to tip-closed CNHs, revealing that the part structure of THC-N-CNH is similar to the graphene sheets. 34

The N-doping amount and chemical bonding types of the radical composition for all samples can be measured by XPS. In this experiment, three major peaks appearing at ~284.5, ~399.5 and ~533 eV can be denoted as C 1s, N 1s and O 1s as shown in Fig. 3(a), respectively. The content of N atom from THC-N-CNH is calculated to be 1.98 at%. As depicted in Fig. 3(b), the N peak can be divided into three peaks, the peaks at 401.1 eV, 399.4 eV and 397.9 eV correspond to the graphitic-N, pyrrolic-N and pyridinic-N structures. Interestingly, in our case the pyridinic-N content is predominant holding 57%, suggesting that N atoms are linked with two coordinated C atoms at the defect and edge on CNHs. 22% N atoms are connected with two C atoms to form the five-membered ring, and the graphitic-N only occupy 19%. Although the N-doping amount is less than 2 at%, electrocatalytic performance can be significantly improved, attributing to the unique distribution of N-configuration, which will be discussed later in detail. The peak of O 1s can be fitted only one single peak at 532.5 eV as shown in Fig. 3(c), which is attributed to oxygen adsorbed on the surface aroused by exposure in air for THC-N-CNHs and Tip-closed CNHs. 35,36

The adsorption/desorption isotherms of N₂ at 77 K for the tip-closed CNHs and THC-N-CNHs are depicted in Fig. 4(a). In this surface area analysis, the values of SSA for the tip-closed CNHs and THC-N-CNHs are calculated to be 139 m² g⁻¹, and 663 m² g⁻¹, respectively. SSA of the THC-N-CNHs is significantly larger than that the tip-closed CNHs increased by 476%. It should be noted that the tip-half closed structure significantly enhance the SSA, which is comparable to the oxidized CNHs at 550 °C in air as reported in previous research. 37

The pore size distributions of the micropore and mesopore are calculated by the method proposed by Dollimore and Heal 37 on the tip-closed CNHs and THC-N-CNHs, respectively, as illustrated in Fig. 4(b). The main-peak position of micropore of THC-N-CNHs is similar to the tip-closed CNHs, which locates at ~0.6 nm being consistent with the width of interstitial spaces. It can be inferred that the internal spaces of the CNH tubes with tip half-closed structure is the major contributor for SSA, but interstitial micropore plays a relatively small contributor for SSA. There is no obviously peak for tip-closed CNHs range from 2–5 nm as depicted in Fig. 4(c). It should be recognized that the protruding peak at 3–4 nm for THC-N-CNHs are identical to the diameter of the individual CNH owning to the half-closed structure at tips distributing on the periphery for CNHs.

### 3.2 The formation mechanism of THC-N-CNHs

As previous reported, the arc temperature field during arc discharge process can be distributed from 500–5500 K as shown in Fig. 5(a) and the growth mechanism for the traditional CNHs can be summarized as following. 29 The graphite of anode can be sublimated into the C atoms and small carbon clusters above 5500 K; during 3000–5000 K, the small carbon clusters and carbon atoms get together to form the graphene sheets; then CNHs are formed by the curled graphene sheets into the during 2000–3000 K. The result confirmed that by controlling the duration of graphene sheets and carbon clusters at 2000–3000 K is the critical parameter for synthesis the traditional tip-closed CNHs.

In this experiment, by introducing positive pressure and a little amount of N₂ during arc discharge process, the periphery of CNHs with tip-closed structure turns into the tip-half-closed structure. Moreover, N atoms contents can be obtained to be 1.98 at%. In comparison with the previous reports, Sano et al. 38 reported that CNHs can be synthesized by arc-in-water method in N₂, whereas the CNHs have no nitrogen doping. Although Qi et al. 39 reported that the large-scale nitrogen doped CNHs can be achieved by arc discharge method in flowing nitrogen at atmospheric pressure, the obtained production is the traditional tip-closed N-doped CNHs. Hence, one can see that N₂ and positive pressure are the essential conditions to form the tip-half closed structure and to involve abundant N atoms doping.

After observation the process of arc discharge, we found that the rate for the evaporation the anode in N₂ (0.05 MPa) and Ar (0.10 MPa) mixture gas is nearly three times faster than that the purity Ar (0.15 MPa). It is to say that the process of arc discharge
last shorter time than that purity Ar when burn same length anode. As results, the diffusion rate graphene sheets and carbon clusters increase sharply at the region of 2000–3000 K, causing their duration and reaction time become shorter. Therefore, there is no enough time to curl the tube structure into the half-closed structure. Notably, N₂ can be decomposed into N atoms above 5000 K, but retain nitrogen molecules at 2000–3000 K. Namely, N atom and C atom only can be combined at region near 5000 K. Therefore, the half-closed structure for the CNH tubes induced the larger amount of N atoms exposing on the edges to form the pyridinic-N as shown in Fig. 5(b). The enrichment of pyridinic-N is consistent with the results of XPS results. To confirm this speculation, the comparison experiment is established, decreasing the gas pressure can increase the diffusion rate based on the previous report.²⁹ Whereas, in 0.1 MPa Ar atmosphere the prepared production mainly focuses on the amorphous carbon, only retained a few tip-half closed CNHs as depicted in Fig. 2(h). Known from this, N₂ is
indispensable condition to synthesize the THC-N-CNHs for positive pressures assisted arc discharge. When the buffer gas is all instead by N2, a consideration number of the production are changed to the amorphous carbon, and other carbon materials as shown in Fig. 1(h). In other words, sufficient reaction time is another vital parameter to form the tip-half closed N-doped CNHs.

Above all, we propose that the morphology of THC-N-CNHs can be constructed by introducing the heterogeneous atoms and controlling the reaction time at the region of 2000–3000 K.

3.3 The electrocatalytic activity for THC-N-CNHs

The electrocatalytic activity towards OER for tip-closed CNHs, THC-N-CNHs and RuO2 was evaluated by a three-electrode chemical station. As summarized in Fig. 6(a), a low overpotential of 328 mV can drive the current density of 10 mA cm⁻², slightly higher than that of RuO2. In contrast, the undoped tip-closed CNHs hardly have catalytic activity, indicating that N-doping in CNHs significantly improve the OER activity. Compared to the behaviors of other nano-carbon catalysts like N-doped CNTs, N-doped graphene, this overpotential is more favorable. Contributing to the unique spherical construction, high conductivity and N-doping for THC-N-CNHs, the reaction at electrolyte/electrode interface can be accelerated and the charge transport capability can be improved significantly during the OER process. Specially, the N introduced in the CNHs was predominantly pyridinic-N, which could donate the electron to the π-bond, attracting electrons acted as electrocatalytic active sites.

Based on the LSV curves, the Tafel slopes can be evaluated to investigate the OER kinetics for all samples. The much lower Tafel slope for THC-N-CNHs (101.5 mV dec⁻¹) slightly larger...
than that RuO$_2$ ($91.0$ mV dec$^{-1}$) reveals appropriate kinetic and superior catalytic activity (Fig. 6(b)).

The electron transfer rate between the catalyst/electrolyte interface can be analyzed by EIS measurements.$^{43,44}$ In generally, the diameter of Nyquist plot with a semicircle characteristic indicates the value of charge-transfer resistance ($R_{ct}$), the smaller $R_{ct}$, the more favorable electrocatalytic kinetics. The $R_{ct}$ value of THC-N-CNHS is $9$ $\Omega$, which is much smaller than that of tip-closed CNHS ($16$ $\Omega$), suggesting THC-N-CNHS holds much more efficient electron transfer and better catalytic activity during OER process than that of tip-closed CNHS, as shown in Fig. 6(c).

To evaluate the long-term durability, 2000 cycles CV scanning tests were carried out. The value of the overpotential become slight larger than that the initial LSV curve after 2000 CV cycles, which exhibit outstanding electrocatalytic durability for OER, as displayed in Fig. 6(d). From Fig. 6(e), we can see that the structure of most THC-N-CNHS can’t be damaged, but a small part of THC-N-CNHS was broken up to a small carbon sheet, indicating that THC-N-CNHS have excellent structural stability.

4. Conclusion

In summary, the catalyst-free and cost-effective synthesis of N-doped CNHS with novel tip half-closed structure and high SSAs in naturally were successfully fabricated via arc discharge by employing positive pressure and N$_2$. The experimental results show that the growth mechanisms for THC-N-CNHS is not only related to the reaction time at 2000–3000 K, but also the composition of the gas above 5000 K for arc temperature. The N atom contents can be achieved to 1.98 at% with enrichment of pyridinic-N. Under 1 M KOH solution, the THC-N-CNHS acquired a low overpotential of 328 mV at 10 mA cm$^{-2}$ and Tafel slope of 101.5 mV dec$^{-1}$, slightly larger than that the precious metals RuO$_2$. THC-N-CNHS rendered the promising electrocatalytic activity, attributing to the large SSAs, adequate porosity, N-doping, structural stability and unique tip half-
closed structure. Those result indicate that THC-N-CNH can be a potential candidate as catalyst and a supporting carrier for metal nanoparticles during OER process.

Conflicts of interest

There are no conflicts to declare.

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