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Facile and scalable synthesis of coal tar-derived, nitrogen and sulphur-codoped carbon nanotubes with superior activity for O₂ reduction by employing an evocating agent

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Since heteroatom-doped carbon nanomaterials were proved to be one of the most promising alternatives to noble metal platinum-based cathode electrocatalysts in fuel cells over the past years, considerable efforts have been devoted to promoting their practical application. Although much progress has been made, the large-scale practical application of these heteroatom-doped carbon nanomaterials is presently inaccessible due to the lacks of facile synthesis method and low-cost heteroatom precursors with broad sources. Herein, we used the cost-effective, nitrogen (N) and sulphur (S)-containing coal tar which has abundant supply as N and S precursor to synthesize value-added N and S-codoped carbon electrocatalysts for the oxygen reduction reaction (ORR) by employing the evocating agent of dicyandiamide (DICY). The results demonstrated that DICY could effectively help coal tar to form N and S-codoped carbon nanotubes (NS-CNTs) on the surface of CoCl₂ nanoparticles. The as-synthesized NS-CNTs exhibited highly comparable ORR activities to commercial Pt-C catalyst both in acidic and alkaline media. This report not only provides a novel, facile and scalable approach for the preparation of low-cost CNT electrocatalysts with superior ORR activities but also offers a new and clean-utilizing path for the harmful N and S elements in coal tar and helps to reduce the environmental pollution.

1. Introduction

The development of cathode electrocatalysts has become one of the hottest topics due to its critical impact on the overall performance of fuel cells. Recently, as one of the most promising alternatives to noble metal platinum (Pt) catalysts, metal-free carbon materials doped or codoped with foreign atoms such as nitrogen (N),¹⁻⁴ phosphorus (P),^{5,6} sulphur (S),⁷ silicon (Si),^{8,9} boron (B),^{10,11} selenium (Se)¹² and halogen (F, Cl, Br, I),¹³⁻¹⁵ have drawn tremendous attentions because of their indisputable improved activities for the oxygen reduction reaction (ORR). Among them, heteroatom-codoped carbon nanomaterials, especially, N/S-codoped carbon nanomaterials,¹⁶⁻¹⁸ exhibited much higher ORR activity than the ones doped with unitary heteroatom owing to the synergistic coupling effect between these doped atoms. However, despite these great advances, the large-scale application of heteroatom-doped carbon nanomaterials is presently inaccessible mainly due to the following four reasons: (i) most of heteroatom precursors are synthetic chemicals with complicated and environmentally-unfriendly synthesis routes, (ii) most of heteroatom-containing chemicals are flammable, explosive and

toxic, (iii) the price of some employed precursors is still high although they are generally much cheaper than Pt-based catalysts, (iv) available synthesis methods for the heteroatom-doped carbon materials are complexity and high-energy consumption in general. Thus, exploring new heteroatom precursors with abundant sources and much low price, reducing the dependence on the hazardous and high-cost chemicals and establishing facile synthesis approaches are urgent and vital for the large-scale application of heteroatom-doped carbon nanomaterials in future fuel cells.

Coal tar, as one of main by-products of coal coking, has abundant supply (ca. 10 million tons a year in china now) and much low price. Most important of all, except aliphatic and aromatic hydrocarbons in coal tar, there also exist lots of N and S-containing heterocyclic chemicals such as pyridine, quinoline, thiophene and their derivatives.¹⁹ However, these N and S-containing chemicals in coal tar are extremely difficult to be removed or utilized and often cause serious environmental pollution during the utilization process of coal tar. In this work, we tried to employ the N and S-containing compounds in coal tar as cheap precursors to synthesize NS-codoped carbon nanotubes (NS-CNTs) and estimate their ORR activities in acidic and alkaline media. The results indicated that coal tar could be easily converted to NS-CNTs on the surface of CoCl₂ nanoparticles with the help of the evocating agent of low-cost dicyandiamide (DICY, C₂H₄N₄) (Fig. 1). More interestingly, the as-synthesized NS-CNTs exhibited much superior activities for the ORR both in acidic and alkaline electrolytes. Meanwhile, it is noted that, solid-state pyrolysis for the synthesis of CNTs, especially for the synthesis of heteroatom-codoped CNTs, was less developed over the past decades compared with the common gas- and liquid-phase

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pyrolysis methods.²⁰ Directly pyrolyzing the solid mixture of coal tar and DICY evocating agent to synthesize NS-CNTs with low argon (Ar) and energy consumption in this work would provide a novel, facile and effective approach for the large-scale synthesis of heteroatom-doped CNTs, showing a greatly promising application for cathode electrocatalyst in future fuel cells.

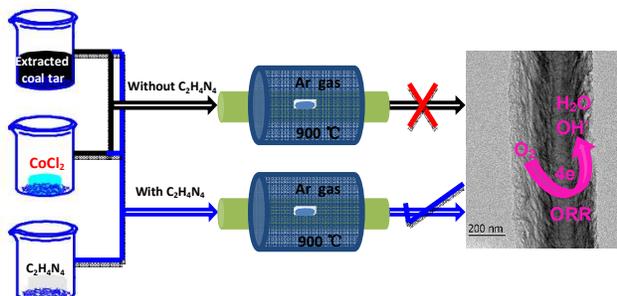


Fig. 1 Schematic illustration for the fabrication of NS-codoped CNTs with the extracted coal tar as N and S precursor and $C_2H_4N_4$ as the evocating agent.

2. Experimental section

2.1 Preparation of materials

The commercially available Pt-C (47.6 wt% on Vulcan XC-72) catalyst and coal tar were purchased from BASF Fuel Cell, Inc., USA and Zaozhuang mine company, China, respectively. The coal tar was extracted by ethanol to remove asphalt before utilization. Other chemicals were purchased and used without any further purification.

In a typical synthesis of N and S-containing carbon nanomaterials, 0.1 g of extracted coal tar were mixed with 0.02 g of $CoCl_2$. The quartz boat with the solid mixture was placed in the fore-end of a quartz tube which temperature had been raised to 900 °C. 100 ml min^{-1} of Ar was introduced to remove the air after two flanges at two ends of the quartz tube were fixed. Then, the quartz boat was pushed to the high temperature zone of quartz tube and heated with an Ar flow of 25 ml min^{-1} for half an hour. Afterward, the tubular furnace was cooled down to room temperature with an Ar flow rate of 15 ml min^{-1} . The resultant samples were collected from the quartz tube and denoted as NS-CNMs. The samples of NS-CNTs1, NS-CNTs2, NS-CNTs3 and N-CNTs were fabricated under the same conditions according to the mass ratio of 5: 40: 1, 5: 80: 1, 5: 120: 1 and 0: 80: 1 of the extracted coal tar, DICY and $CoCl_2$, respectively.

2.2 Electrode preparation and electrochemical measurements

The pretreatment procedures of glassy carbon electrodes (GC, 5.0 mm in diameter) were as follows: prior to use, the electrodes were polished mechanically with aluminite powder on an abrasive paper to obtain a mirror-like surface, washed with ethanol and de-ionized water by sonication for 5 min and dried in a desiccator. 1.5 mg of each grinded sample was dispersed in 0.5 ml of solvent mixture of Nafion (5%), de-ionized water and acetone (V: V: V = 15: 385: 100) by sonication. 10.0 μl suspension was dropped onto the glassy carbon electrode surface. And the electrode was dried at room temperature for 1 h in a desiccator before the electrochemical

measurements. Consequently, 0.31 mg cm^{-2} of each example was loaded onto the surface of bare glassy carbon electrode.

Electrochemical experiments were carried out at room temperature in a three-electrode cell connected to an electrochemical analyzer (Pine Research Instrumentation, USA). NS-CNMs/GC, NS-CNTs1/GC, NS-CNTs2/GC, NS-CNTs3/GC, N-CNTs/GC and Pt-C/GC were used as the working electrodes, an Ag/AgCl with saturated KCl as reference electrode, and a Pt or graphite electrode as counter electrode. All potentials were measured and reported vs the potential of Ag/AgCl electrode. The cyclic voltammetry (CV) experiments were conducted in an oxygen-saturated 0.1 M KOH or 1.0 M $HClO_4$ solution with or without 3.0 M CH_3OH at room temperature. The linear sweep voltammetry (LSV) measurements were performed in the oxygen-saturated 0.1 M KOH or 1.0 M $HClO_4$ solution at the scan rate of 10 mV s^{-1} .

The Koutecky–Levich plots were obtained by $i^{-1} = i_k^{-1} + (0.62nFD^{2/3}\nu^{-1/6}\omega^{1/2})^{-1}$, where i_k^{-1} is the kinetic limiting current density, ω is the rotational speed, n is the number of electron transferred, F is the Faraday constant ($F = 96485 C mol^{-1}$), C is the bulk concentration of O_2 ($C = 1.2 \times 10^{-3} mol L^{-1}$ for 0.1 M KOH; $C = 1.6 \times 10^{-3} mol L^{-1}$ for 1.0 M $HClO_4$), D is the diffusion coefficient of O_2 ($D = 1.9 \times 10^{-5} cm^2 s^{-1}$ for 0.1 M KOH; $D = 1.1 \times 10^{-5} cm^2 s^{-1}$ for 1.0 M $HClO_4$), ν is the kinetic viscosity of the electrolyte (0.01 $cm^2 s^{-1}$ for both 0.1 M KOH and 1.0 M $HClO_4$), ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed).

2.3 Characterizations

The morphologies of the samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (MERLIN compact). Elemental compositions were carried out on a vario MACRO cube CHNS elemental analyzer. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Thermo Scientific ESCALAB 250XI using Al K α radiation, and the C1s peak at 284.8 eV was taken as internal standard.

3. Results and Discussion

3.1. Structure Characterization

SEM and TEM images illustrated that the sample synthesized by the extracted coal tar was graphene-like three-dimensional carbon materials (Figs. 2A and B), demonstrating that the extracted coal tar was not easily converted to CNTs directly with $CoCl_2$ as catalyst probably because massive coal tar sticking on the catalyst surface produced a super-saturation carbon atoms during the rapid pyrolysis process and did not favour the nucleation of CNTs.²¹ However, the samples synthesized by different proportions of the extracted coal tar and DICY were mainly composed of carbon nanotubes (Figs. 2C–J), indicating that DICY would reduce the sticking of coal tar on the surface of $CoCl_2$ nanoparticles and promote the nucleation of NS-CNTs. It is interesting to note that, the morphologies of the synthesized NS-CNTs and N-CNTs were quite different from the reported bamboo-like N-containing ones.^{8,18} Relative to CNTs only with one layer tube wall prepared by traditional gas- and liquid-phase synthesis methods, there existed two layer tube walls in NS-CNTs and N-CNTs (Fig.S1). The formation mechanism of these CNTs with two layer tube walls on the surface of $CoCl_2$ nanoparticles was a typical top-growth,²² evidenced by

Fig.S1C. The possible formation details of NS-CNTs were described in supporting information (Fig. S2). Compared to the average tube diameter of N-CNTs (332 nm), the tube diameters of three coal tar-derived NS-CNTs1 (82 nm), NS-CNTs2 (75 nm) and NS-CNTs3 (91 nm) all significantly became much smaller. The smaller average diameter and wider diameter distribution for three NS-CNTs were probably caused by the complicated components in coal tar. These interesting results indicated that some heteroatom-containing substances which could not directly form heteroatom-doped CNTs could be led to form the desired CNTs by employing some selected evocating agents, suggesting a facile method for the synthesis of heteroatom-doped CNTs. The main elemental compositions in the synthesized samples were analyzed by the elemental analyzer. Table 1 showed that the sample synthesized by the extracted coal tar (NS-CNMs) contained a certain amount of N (0.62 wt.%) and S (0.30 wt.%), meaning that N and S in coal tar could be used as N and S precursors to fabricate N and S-codoped carbon materials. Meanwhile, from Table 1, it also could be found that with the addition of DICY into the extracted coal tar, N content in NS-CNTs1, NS-CNTs2 and NS-CNTs3 increased drastically to 3.59, 6.07 and 4.93 wt.% while S content decreased to 0.23, 0.21 and 0.18 wt.%, respectively, indicating that DICY as N-containing precursor also could effectively increase the N doping content in NS-CNTs. The decrease of S doping content with the increase of DICY is most probably due to the loss of some S-containing compounds such as thiophene and its derivatives in coal tar caused by the gases from the pyrolysis of DICY. The N and S doping contents mainly depended on the mixing ratio of coal tar and DICY. The successful doping of N and S into the framework of samples was further confirmed by XPS analysis. N 1s peaks in XPS spectra (Figs. 3A and B) could be assigned to pyridine-like N (ca. 398.7 eV), graphite-like N (ca. 400.9 eV) and pyridine N-oxide (ca. 402.4 eV),⁸ and weak S 2p peaks appearing at 163.6 and 168.5 eV were attributed to –C–S–C– and –C–SOx–C– bonds, respectively (Fig. 3C).¹⁸

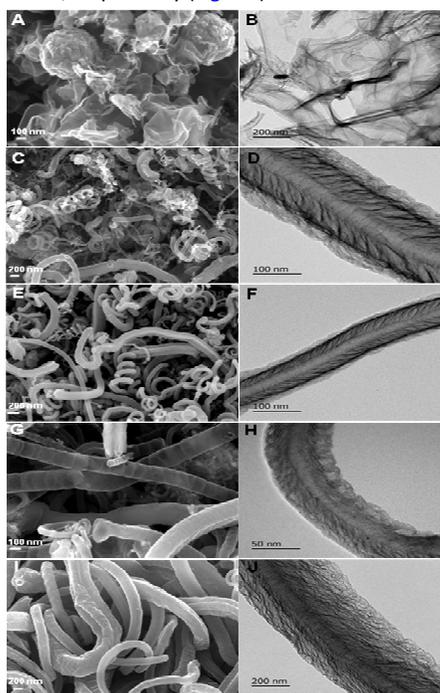


Fig. 2 SEM and TEM images of the NS-CNMs (A, B), NS-CNTs1 (C, D), NS-CNTs2 (E, F), NS-CNTs3 (G, H) and N-CNTs (I, J).

Table 1 Main elemental composition of synthesized samples analyzed by the elemental determinator.

Samples	C (wt. %)	N (wt. %)	S (wt. %)	H (wt. %)
N-CNTs	78.63	5.54	-	0.72
NS-CNMs	58.6	0.62	0.30	0.75
NS-CNTs1	76.65	3.59	0.23	0.73
NS-CNTs2	80.72	6.07	0.21	0.76
NS-CNTs3	77.61	4.93	0.18	0.77

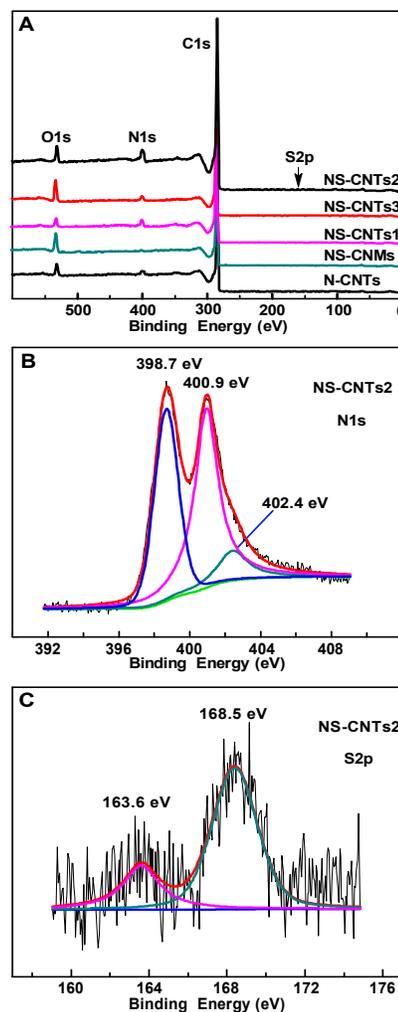


Fig. 3 (A) XPS surveys of NS-CNMs, NS-CNTs1, NS-CNTs2, NS-CNTs3 and N-CNTs and (B) N 1s and S 2p (C) spectra of the NS-CNTs2.

2.2. Electrocatalytic Analysis

To investigate the electrocatalytic activities of three NS-CNTs for the ORR, the cyclic voltammetry (CV) measurements were performed in an aqueous solution of N₂-protected or O₂ saturated 0.1 M KOH or 1.0 M HClO₄ solution with a flow rate of 25 ml min⁻¹ in comparison with NS-CNMs, N-CNTs and GC. As shown in Fig. 4A, in alkaline medium, the ORR peak potential (-0.28 V) and current density (1.5 mA cm⁻²) of NS-CNMs were much higher than those (-

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0.48 V, 0.5 mA cm^{-2}) of the bare GC and a bit lower than those (-0.27 V , 2.59 mA cm^{-2}) of N-CNTs, indicating that the N and S-containing coal tar could be used as N and S precursor to prepare NS-codoped carbon catalysts for the ORR. For NS-CNTs1, NS-CNTs2 and NS-CNTs3, their ORR peak potentials (-0.29 , -0.27 and -0.24 V) all were much more positive than that of GC and similar to those of N-CNTs and NS-CNMs. However, their peak current densities (3.0 , 5.60 and 3.02 mA cm^{-2}) all were much significantly larger than those of NS-CNMs and N-CNTs, confirming that coal tar could be served as precious useful N and S precursor to fabricate highly active electrocatalysts for the ORR in alkaline medium. Among three NS-CNTs, NS-CNTs2 with the peak potential at about -0.27 V and peak current density of 5.60 mA cm^{-2} showed the highest ORR activity. Similarly, in acidic medium, three coal tar-derived NS-CNTs also exhibited much higher electrocatalytic activity towards the ORR than NS-CNMs, N-CNTs and GC, as shown in Fig. 4B. And NS-CNTs2 with the highest peak potential ($+0.33 \text{ V}$) and largest peak current density (ca. 5.2 mA cm^{-2}) among three NS-CNTs even showed a highly comparable electrocatalytic activity to Pt-based catalysts (Pt, ca. 1.0 wt. %) reported in our previous works.^{23,24} These superior ORR activities of NS-CNTs2 in acidic and alkaline media were probably mainly caused by its larger N content and smaller diameter compared with those of NS-CNTs1 and NS-CNTs3 (Fig. 5A).

In order to better understand the ORR activities of these three NS-CNTs, the linear sweep voltammetry (LSV) tests were also carried out in an oxygen-saturated 0.1 M KOH or 1.0 M HClO_4 solution with a flow rate of 25 ml min^{-1} at a rotation speed of 1600 rpm . In alkaline medium, from Fig. 4C, it could be found that the onset potential (-0.16 V) and diffusion current densities (3.0 mA cm^{-2}) of NS-CNMs at -0.6 V was much higher than those (-0.34 V , 1.0 mA cm^{-2}) of bare GC and a bit lower than those (-0.11 V , 3.74 mA cm^{-2}) of N-CNTs. However, the onset potentials (-0.13 , -0.09 and -0.08 V) of NS-CNTs1, NS-CNTs2 and NS-CNTs3 all were obviously higher than that of NS-CNMs. And the diffusion currents (4.60 , 7.22 and 5.19 mA cm^{-2}) of these three NS-CNTs at -0.6 V were even much considerably larger than those of NS-CNMs and N-CNTs. More surprisingly, the diffusion currents of NS-CNTs2 and NS-CNTs3 at the potential range from -0.27 to -1.0 V remarkably exceeded those of the commercial Pt-C catalyst (47.6 wt. %). In acidic medium, as shown in Fig. 4D, the onset potentials of three NS-CNTs at about $+0.47 \text{ V}$ were also much higher than those (about $+0.12$, $+0.25$ and $+0.45 \text{ V}$) of GC, NS-CNMs and N-CNTs. And their diffusion current densities all indicated comparable ORR activities to the reported Pt-based catalysts (Pt, ca. 1.0 wt. %) as well^{23,24} although they were inferior to those of the commercial Pt/C catalyst (Fig. 4D). These LSV test results were in a good agreement with the data from CV measurements both in alkaline and acidic media, further confirming the superior ORR activity of NS-CNTs and demonstrating the feasibility of resource utilization of N and S in coal tar for the preparation of low-cost and effective cathode electrocatalysts. The higher reaction currents on three NS-CNTs than those on N-CNTs both in acidic and alkaline media were mainly caused by synergistic effects between N and S (i.e. the dual doping of N and S could introduce asymmetrical spin and charge density and lead to the increase of active sites), as evidenced by density functional theory calculations in previous reported NS-codoped carbon materials.¹⁷

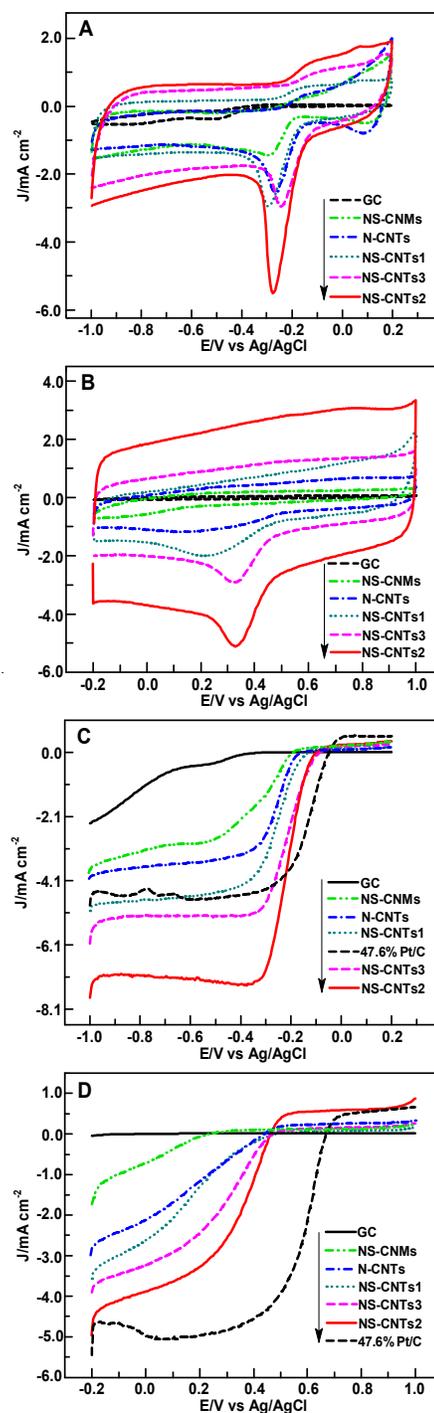


Fig. 4 Typical CVs of GC, NS-CNMs, NS-CNTs1, NS-CNTs2, NS-CNTs3 and N-CNTs in O_2 -saturated 0.1 M KOH (A) or 1.0 M HClO_4 (B) aqueous solution at a scan rate 100 mV/s . The LSV curves of GC, NS-CNMs, NS-CNTs1, NS-CNTs2, NS-CNTs3, N-CNTs and commercial Pt-C in O_2 -saturated 0.1 M KOH (C) or 1.0 M HClO_4 (D) aqueous solution at a rotation speed of 1600 rpm and scan rate of 10 mV/s .

To get further insight into the ORR behaviour of NS-CNTs2 with the highest activity, the Koutecky-Levich plots (i^{-1} vs $\omega^{-1/2}$) were

calculated at -0.6 and -0.1 V in alkaline and acidic media (Figs. 5A and B) on the basis of LSVs at different rotation rates (Figs. S5A-L) together with those of NS-CNTs1, NS-CNTs3, NS-CNMs, N-CNTs and commercial Pt-C catalyst, respectively. From Figs. 5A and B, it could be found that all K-L plots displayed good linearity. Based on the slopes of K-L plots, the transferred electron number (n) per oxygen molecule during the electrochemical process of each catalyst was calculated. As shown in Fig. 5C, the n values (3.8, 4.0, 3.8 and 3.7 in alkaline medium and 3.1, 3.2, 3.2 and 3.0 in acidic medium) for NS-CNTs1, NS-CNTs2, NS-CNTs3 and N-CNTs were a bit smaller than those (4, 4) of the commercial Pt-C catalyst and much larger than those (3.4, 2.0) of NS-CNMs, meaning that the efficient 4-electron reduction dominated the electrocatalytic process on the surface of NS-CNTs both in acidic and alkaline media.

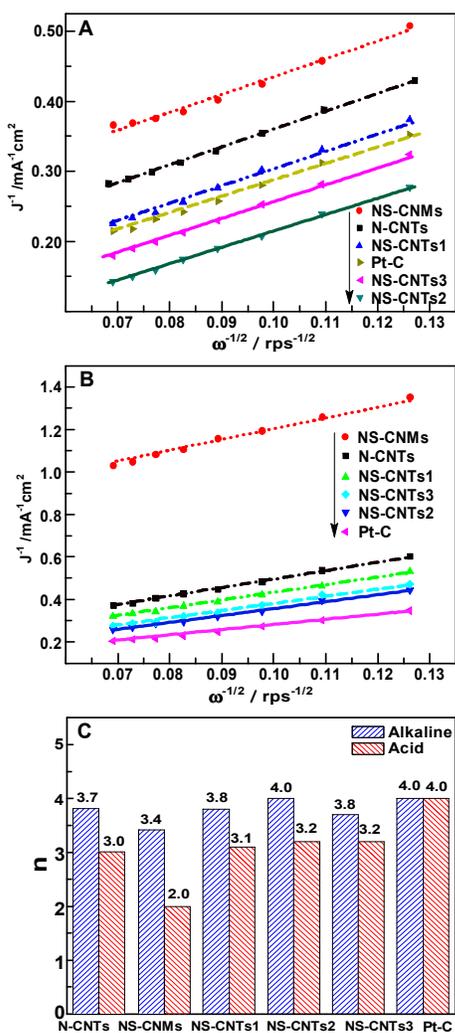


Fig. 5 The Koutecky-Levich plots (J^{-1} vs $\omega^{-1/2}$) at -0.6 or -0.1 V in an O₂-saturated 0.1 M KOH (A) or 1.0 M HClO₄ (B) solution and the electrons transferred numbers of NS-CNMs, N-CNTs, NS-CNTs1, NS-CNTs2, NS-CNTs3 and commercial Pt-C in alkaline and acidic media (C).

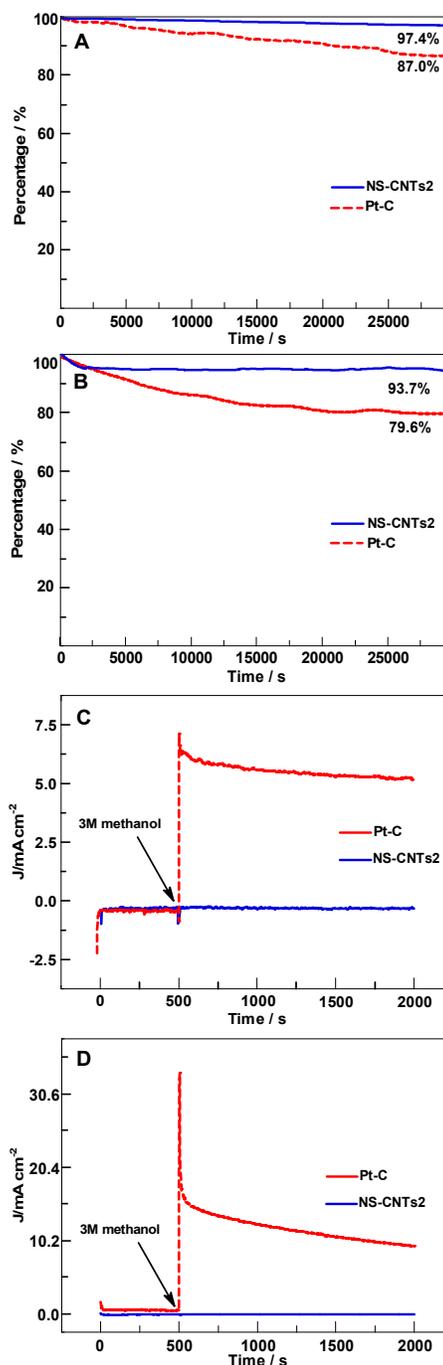


Fig. 6 The chronoamperometric responses of NS-CNTs2 and Pt-C in an oxygen-saturated 0.1 M KOH (A) or 1.0 M HClO₄ (B) solution with a flow rate of 25 ml min⁻¹ and graphite as counter electrode at -0.3 or +0.4 V for 30000 s, and I-t chronoamperometric responses for NS-CNTs2 and Pt-C upon the addition of 3.0 M methanol into an oxygen-saturated 0.1 M KOH solution at -0.3 V (C) or 1.0 M HClO₄ solution at +0.4 V (D) for 2000 s. The arrow indicates the introduction of methanol.

Since the stability is a major concern for all developed electrocatalysts, the stability of NS-CNTs2 with highest ORR activity was investigated by chronoamperometric response for 30000 s at -0.3 or +0.4 V in an oxygen-saturated 0.1 M KOH or 1.0 M HClO₄ solution with a flow rate of 25 ml min⁻¹ compared with commercial Pt-C catalyst, respectively. Figs. 6A and B showed that NS-CNTs2 only underwent a loss of 2.6 or 6.3 % in alkaline or acidic medium after 30000 s while the commercial Pt-C catalyst lost almost 13.0 or 20.4 % of initial current after the same time. Additionally, it is worthwhile to note that the NS-CNTs2 also exhibited remarkably excellent methanol tolerance when it was tested by chronoamperometry at a constant voltage of -0.30 and +0.40 V for 2000 s compared with the commercial Pt-C catalyst in alkaline and acidic media. As can be seen from Figs. 6C and D, the current density of NS-CNTs2 almost remained unchanged after the addition of 3.0 M methanol into the oxygen-saturated 0.1 M KOH or 1.0 M HClO₄ solution, indicating a remarkable tolerance to methanol crossover effects. In contrast, the corresponding I-t chronoamperometric response of the Pt-C catalyst showed a sharp decrease in the current with the addition of 3.0 M methanol (Figs. 6C and D). The outstanding stability as well as excellent methanol tolerance of NS-CNTs2 showed a better application prospect in the future direct methanol fuel cells.

4. Conclusions

In summary, we have successfully synthesized a series of coal tar-derived NS-CNTs with DICY as evocating agent and CoCl₂ as catalyst, indicating that the two environment-unfriendly N and S elements in coal tar could be used as useful and cheap precursors to fabricate value-added NS-CNTs on a large scale. DICY acting as evocating agent promoted coal tar to form NS-CNTs in this work, which would present a new approach to converting some heteroatom-containing substances into heteroatom-doped CNTs easily. Electrochemical tests showed that the coal tar-derived NS-CNTs exhibited superior ORR activity, longer-term stability and better methanol tolerance both in acidic and alkaline media, showing a greatly promising application for the preparation of much lower-cost and more efficient cathode catalysts in future fuel cells. Meanwhile, this work presented a novel clean-utilizing way for N and S-containing coal tar as well.

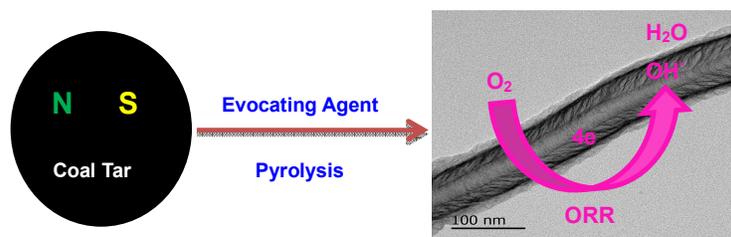
Acknowledgements

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Graphical abstract



Nitrogen and sulfur-codoped carbon nanotubes were synthesized with coal tar as nitrogen and sulfur precursor by a facile and scalable method of employing the evocating agent of dicyandiamide. Electrochemical test results indicate the synthesized coal tar-derived nitrogen and sulfur-codoped carbon nanotubes exhibit superior activities for the oxygen reduction reaction both in acidic and alkaline media.