One-pot synthesis of nitrogen and phosphorus-dual-doped carbon nanotube array as highly effective electrocatalyst for oxygen reduction reaction
One-pot synthesis of nitrogen and phosphorus-dual-doped carbon nanotube array as highly effective electrocatalyst for oxygen reduction reaction

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A nitrogen and phosphorus-dual-doped carbon nanotube (N, P-CNT) array has been successfully synthesized by a novel one-pot method, using aminophosphonic acid resin as the N, P and C sources. The N, P-CNTs are open with large inner channels, allowing oxygen molecules to access a large number of catalytically active sites on inner walls. The N, P-CNTs are not only comparable to Pt/C in electrocatalytic activity for oxygen reduction reaction (ORR) in 0.1M KOH, but are also highly stable and tolerant to methanol and CO poisoning. An onset potential of 0.95 V closing that of Pt/C and a well-defined limiting current plateau for the ORR are observed. Moreover, there is almost no visible current density decrease on N, P-CNTs after 5,000 cycles.

The N, P-dual-doped CNTs with a robust nano-structure has been synthesized by one-pot method and the material shows enhanced activities and durability for oxygen reduction reaction.
1 Introduction

Considerable efforts have been devoted to synthesize hollow nanostructured carbon materials such as fullerenes, carbon nanotubes, nanoshell, carbon nanocages and nanocone for their specific architectures and unique physical and chemical properties. Carbon nanotubes (CNTs), one of the most important hollow nanostructured carbon materials, exhibit potential applications in hydrogen storage, lithium-ion batteries (LIBs), supercapacitors, nanocantener and nanoreactor and fuel cells. It has been reported that doped carbon materials by heteroatoms such as nitrogen, boron, phosphorus, sulfur and fluorine have high electrocatalytic activity, high durability and high tolerance towards poisoning of the oxygen reduction reaction. Dai et al. showed that nitrogen-doped CNT (N-CNT) array has high electrocatalytic activity for the oxygen reduction reaction in alkaline solutions. Recently, Dai et al. exhibited that CNTs array co-doped with N and P has significantly enhanced electrocatalytic activity towards ORR compared with CNTs doped by N or P only due to the synergistic effect. Doping with heteroatoms can modulate the structure, electronic and physicochemical properties of carbon materials like CNTs. For example, the incorporation of nitrogen atoms into CNTs can activate the π electrons of carbon by the conjugation with the lone-pair electrons of N dopants and significantly increase active sites for the ORR. ORR at the cathode of fuel cells plays a key role in the performance of fuel cells.

Doping CNTs by N or P can be achieved via ‘in situ’ doping and ‘post-synthesis treatment’ methods. However, for in situ doping methods, such as arc-discharge, CVD and laser ablation, special instrumentation or rigorous condition control is often required. The method of post-synthesis treatment requires toxic nitrogen precursors (e.g., NH3). Moreover, the ORR activities of majority of reported N-CNTs are still not satisfactory as compared to Pt-based catalysts. Architecture or nano-structure of CNTs plays an important role in the electrocatalytic activity of N-CNTs. For example, CNTs having bamboo-like structure and nodes could reduce the catalytic active sites in inner walls by blocking their access to oxygen molecules. On the other hand, less catalytically active sites may lead to a two-electron oxygen reduction pathway, forming intermediate H2O2 species, which reduces the electrocatalytic efficiency as well as the stability of catalysts. Therefore, it is of scientific and technological importance to develop novel and facile strategies to synthesize N and P-doped CNTs with robust nano-structure for enhanced activities and durability for ORR.

Herein, for the first time, we report a facile and one-pot synthesis of nitrogen and phosphorus-dual-doped carbon nanotube (N, P-CNT) array with simultaneous nitrogen and phosphorus doping by pyrolysis of nitrogen and phosphorus-containing resin in the presence of nickel foam. Due to the available catalytic active sites in inner walls and the synergetic effect arising from co-doping CNTs with both P and N, the N, P-CNT array shows superior ORR activity with respect to bamboo-like N-CNTs. The N, P-CNTs catalyst provides sufficient catalytically active sites, therefore, an excellent electrocatalytic performance for ORR in terms of electrocatalytic activity and stability in an alkaline medium.

2 Experimental section

2.1 Synthesis of N, P-CNT array

The as-received aminophosphonic acid resin (APAR, Sunresin New Materials Co. Ltd., China) was cleaned with deionized water and then dried before using. The treated resin (1.5 g) was placed in a clean quartz boat and the boat was capped with a nickel foil. The boat was then heated to 850 °C at a heating rate of 3 °C min⁻¹ and held for 30 min in a tube furnace in N2 atmosphere. After cooling down to room temperature, the nickel foil was treated with diluted hydrochloric acid to remove nickel substrates and then the N, P-CNTs were collected. The N-doped CNTs (N-CNTs) were also synthesized for comparison. Commercial carbon nanotubes (CNTs) with purity of > 95 % (Shenzhen Nanotech Co., Ltd., China) and Pt/C (46.7 wt% Pt, TKK, Japan) catalysts were used as received.

2.2 Physical characterization

The Raman spectroscopic measurements were carried out on a Raman spectrometer (Renishaw Corp., UK) using a He–Ne laser with a wavelength of 514.5 nm. The X-ray photoelectron spectroscopy (XPS) measurements were performed in an ESCALAB 250 spectrometer under vacuum (about 2×10⁻⁹ mbar). Monochromatic Al Kα (150 W, 1486.6 eV) was used as the excitation source. All the binding energies were calibrated with respect to C1s peak at 284.8 eV. The morphology characterizations were performed on a scanning electron microscopy (SEM) (Quanta 400 FEG, FEI Company). The transmission electron microscopy (TEM) and element mapping investigations were carried out on a JEOL JEM-2010 (JEOL Ltd.) operating at 200 kV and FEI Tecnai G2 F30.

2.3 Electrochemical characterization

The performance of the N, P-CNTs for ORR was measured on a rotating ring-disk electrode (RRDE) with a bipotentiostat (Pine Instrument Co., USA) in a three-electrode cell by using a reversible hydrogen electrode (RHE) as the reference electrode, and a graphite electrode as the counter electrode. The working electrode was a rotating ring/disk electrode with a glassy carbon disk (5.61 mm in diameter). 5.0 mg of N, P-CNTs (N-CNTs or CNTs) was added into 1.9 mL ethanol and 0.1 mL Nafion solution (5 wt%, DuPont, USA) and ultrasonicated for 30 min to form a well-dispersed ink. The ink (100 μL) was transferred onto the surface of the glass carbon electrode and then dried under infrared lamp for 5 min to obtain a catalyst thin film. The total Pt loadings were controlled at 0.0101 mg cm⁻². The ORR tests were performed with a scan rate of 5 mV s⁻¹ in an O2-saturated 0.1 mol L⁻¹ KOH solution at 25 °C. The rotating speed was controlled at 1600 rpm. In the RRDE tests, the ring potential was set to 1.2 V vs. RHE.

3 Results and Discussion

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Fig. 1 Schematic illustration of the growth process of N, P-CNT array and SEM images of growing N, P-CNTs at different stages (a, arrangement of the APAR and Ni foam as substrate, b, initial Ni foam substrate, c, Ni foam at 850 °C for 1 min and d, Ni foam at 850 °C for 15 min).

Fig. 1 and Fig. S1 (Supporting Information) show the principle of the growth process of the N, P-CNT array, using aminophosphonic acid resin (APAR) precursor. The APAR precursor was decomposed in N₂ at 325 °C, providing nitrogen, phosphorus and hydrocarbon sources for the growth of N, P-CNT array (Fig. 1a). As temperature arises, the released phosphorus species reacted with clean nickel foam (Fig. 1b), forming rod-like Ni₂P particles²⁹,³⁰ on the surface of nickel foam (Fig. 1c). The rod-like Ni₂P particles served as seeds to catalyze the growth of carbon nanotubes (Fig. 1d). As the Ni₂P catalyst particles are most likely located at the tip of carbon tubes, the growth process may follow the ‘adsorption-diffusion-precipitation model’ in CVD method using metal particles as catalysts.³¹,³² The hydrocarbons released by the resin would adsorbed on the surface of Ni₂P particles and the carbon diffusion and consequent precipitation would lead to the growth of carbon nanotubes with simultaneously doping of N and P. Such simultaneous growth mechanism of N, P-CNTs is further confirmed by the element mapping investigations (Fig. 2). Ni and P are mainly accumulated at the tip of the tube (Fig. 2), indicating that nickel was pulled away from the Ni foam substrate by the formation of Ni₂P seeds, which is confirmed by XRD in Fig. S2. The uniform distribution of N and in less degree of P along the carbon tubes confirms the simultaneously doping of N and P during the growth of carbon tubes.

The production of high density rod-like Ni₂P particles with uniform size is critical to grow such N, P-CNT array. Very different from bamboo-like N-CNTs, where asymmetric metal catalyst particles would lead to the accumulation of carbon at graphite-catalyst edges and consequently the formation of nodes³³-³⁵, the cylindrical Ni₂P rod catalysts avoid the formation of nodes. This is indicated by the growth of very uniform and hollow N, P-CNTs (Fig. 1g). The one-pot synthesis strategy designed for the growth of N, P-CNT arrays has significant advantages over conventional in-situ doping or post-synthesis methods. First, the use of APAR provides a low cost and environmentally friendly way for the carbon, nitrogen and phosphorus resource, and requires no special instruments or rigorous conditions. Second, the rod-like Ni₂P particles as catalyst seeds are formed in situ and high density and uniform formation of such rod-like seeds prevent formation of bamboo-like structure and nodes. Third, P and N atoms are simultaneously incorporated into the CNTs during the tube growth, eliminating the post-synthesis or extra doping processes.

Fig. 2 TEM image (the bar is 100 nm) and corresponding element mappings of a growing N, P-CNT.

As shown in the inset of Fig. 3a, the overall view of the nickel foam substrates covered with compact and uniform N, P-CNTs,
and formed coral-like array. The magnified SEM images show that the N, P-CNTs have noodle-like shape and a length of 20-30 micrometers (Fig. S3). The N, P-CNTs are vertically aligned, and some adjacent N, P-CNTs may be in contact along the length of the array. The N, P-CNTs show bigger tube with diameter of about 100-200 nm (Fig. 3a and 3c), as compared to the conventional multi walled carbon nanotubes (MWCNTs). The N, P-CNT formed by the one-pot synthesis method is also characterized by open end structure (Fig. 3c). It can be observed that defects and distortions in the carbon lattice of the wall, as shown in Fig. 3d. The wall thickness of the tube is about 4.5 nm and ratio of internal diameter to wall thickness can be as high as 20. In contrast, the synthesized N-CNTs show typical bamboo-like structure as shown in Fig. 4. From the SEM image of the N-CNTs, the N-CNTs grow randomly. Thick wall and nodes can be clearly observed in the TEM image of a single N-CNT.

**Fig. 4** SEM and TEM images of the N-CNTs.

![TEM image](image_url)

**Fig. 5** (a) Raman spectra of the N, P-CNTs and N-CNTs, (b) XPS-N1s spectrum of the N-CNTs, (c) XPS-P2p and (d) XPS-N1s spectrum of the N, P-CNTs.

![Raman spectra](image_url)

**Table 1** XPS analysis of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrogen (at. %)</th>
<th>Phosphorus (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-CNTs</td>
<td>4.90</td>
<td>0</td>
</tr>
<tr>
<td>N, P-CNTs</td>
<td>4.17</td>
<td>4.28</td>
</tr>
</tbody>
</table>

The electrocatalytic activities of as-synthesized N, P-CNTs for oxygen reduction reaction are shown in Fig. 6 and Fig. S4. For the purpose of comparison, the performances of N-CNTs, commercial CNTs and Pt/C (46.7 wt% Pt, TKK, Japan) catalysts for ORR are also given. The ring current increases dramatically on CNTs at the oxygen reduction potential region (Fig. 6a), which indicates more HO\textsubscript{2} generated by a two-electron reduction of oxygen. However, the ring current is negligible for the ORR on N, P-CNTs. The onset potential on N, P-CNTs is 0.95 V vs. RHE, very close to 0.80 V, the onset potential of the Pt/C catalyst. Most importantly, the half wave potential of the reaction on the N, P-CNTs is 0.79 V vs. RHE, almost the same as that on the Pt/C catalyst (0.795 V). The remarkable electrocatalytic activity of N, P-CNTs for ORR is not only attributed to N, P-dual doping which can change the net charge of adjacent carbon atoms to facilitate the ORR but also its unique architecture. The open-end N, P-CNT has large amount of the hollow channels and inner walls, which increase the active sites compared with bamboo-shaped N-doped CNT.
Fig. 6 (a) The linear sweep curves (down) of the catalysts on RDE for ORR and corresponding ring currents (up) at 1600 rpm in O$_2$-saturated 0.1 mol L$^{-1}$ KOH at 25 °C with a sweep rate of 5 mV s$^{-1}$, (b) electron-transfer number $n$ of the catalysts at different potentials, (c) calculated H$_2$O$_2$ production yields of the catalysts, (d) constant potential polarization curves of the N, P-CNTs and Pt/C at constant potential of 0.7 V vs. RHE and (e, f) ORR performance of the N, P-CNTs and Pt/C before and after 5,000 cycles in 0.1 mol L$^{-1}$ KOH.

As shown in Fig. 6b and 6c, the electron-transfer number $n$ and H$_2$O$_2$ production yields of the CNTs, N-CNTs, N, P-CNTs and Pt/C during the ORR can be calculated according to the following equations$^{49}$:

$$n = \frac{4I_D}{I_D + (I_R/N)}$$

$$\%H_2O_2 = 100\left(\frac{4-n}{2}\right)$$

where $n$ is the apparent electron-transfer number and $\%$H$_2$O$_2$ is the percentage of the electron used to generate the H$_2$O$_2$ during the ORR, $I_D$ the absolute value of the Faradaic current at the disk, $I_R$ the absolute value of the ring current and $N$ the collection efficiency. Obviously, the $n$ value was calculated to be from 3.95 to 3.97 and the H$_2$O$_2$ produced is below 3 % at potentials from 0.1 V to 0.85 V vs. RHE, indicating a high selectivity of O$_2$ reduction to H$_2$O through a four-electron route on the N, P-CNTs, similar to that on Pt/C catalysts. The CNTs and N-CNTs catalysts showed more H$_2$O$_2$ generated especially at high potentials. The stability of the N, P-CNTs and Pt/C catalysts were evaluated by chronoamperometric experiments at 0.7 V vs. RHE (Fig. 6d).

Based on the normalized current plots, the loss in the current density for the ORR on N, P-CNTs is only 4.2 % after 3 h polarization, while, in the case of the Pt/C lost 31.3%. After continuous potential cycling, there is no visible current density decrease on N, P-CNTs after 5,000 cycles (Fig. 6e), indicating the high durability of N, P-CNTs as ORR catalysts. However, significant decrease in current density and obvious shift in half wave potential (Fig. 6f) are observed on the Pt/C catalyst. It further indicates that N, P-CNTs has superior ORR stability compared with Pt/C catalyst.

We further evaluate the stability of the N, P-CNTs catalyst by an accelerated test in same media. After 2500 pulse potential cycles (30-60 s alternatively at 0.65 and 1.05 V/RHE) in 0.1 mol/L KOH, very little decrease in current density and almost no shift in half wave potential were observed on the N, P-CNT catalyst, indicating that the N, P-CNTs is very stable for ORR.

Fig. 7 The stability test of the N, P-CNTs catalyst.

Fig. 8 (a) Constant potential polarization curves of the N, P-CNTs and Pt/C at 0.7 V vs. RHE in O$_2$-saturated 0.1 mol L$^{-1}$ KOH solution with addition of N$_2$ (black line) and CO (red line) and (b) with addition of 1.0 mol methanol.

The N, P-CNTs catalyst also shows remarkable resistance and tolerance towards methanol and poisoning species of CO for ORR compared to Pt/C (Fig. 8). The Pt/C shows a significant current decay with the addition of CO into the electrolyte. However, in the case of N, P-CNTs, the effect of addition of CO on the polarization current is negligible (Fig. 8a). Similar results are observed for the introduction of methanol into the solution for ORR. Upon addition of 1.0 mol methanol to the O$_2$-saturated
solution, a sharp positive current increase occurs on Pt/C catalysts, indicating a rapid decay in activity (Fig. 8b). However, the change in the current density is negligible for the ORR on the N, P-CNTs after the introduction of methanol.

4 Conclusions

In summary, we have successfully demonstrated a novel one-pot approach to synthesize N, P-dual-doped CNT array as highly active electrocatalyst for ORR. The N, P-CNTs with open ends and large hollow channels provide a large number of catalytic active sites in inner walls allowing the access of oxygen molecules, such as a significant advantageous architecture is superior as compared with conventional bamboo-shape N-CNT and bamboo-shaped N, P-dual-doped CNTs. The comparable activity and much better methanol and CO tolerance for ORR as compared to Pt/C catalyst can be attributed to both the synergistic effect of N and P doping and unique architecture of the N, P-CNT array. This construction of robust CNTs nanostructure for the designed electrocatalytic application and other potential application will find a broad interest in scientific and industrial fields.

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Notes and references

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The N, P-dual-doped CNTs with a robust nano-structure has been synthesized by one-pot method and the material shows enhanced activities and durability for oxygen reduction reaction.