

Nitrogen-Promoted Self-Assembly of N-Doped Carbon Nanotubes and Their Intrinsic Catalysis for Oxygen Reduction in Fuel Cells

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Carbon nanotubes (CNTs) have attracted great attention because of their excellent properties in a variety of applications.^{1–4} Their perfect hollow structures have excited chemists to renovate traditional adsorption and catalysis materials and, actually, it has been proved that they could significantly promote the adsorption of energy molecules^{5–7} and modulate molecular reactivity and selectivity.^{8,9} Such responses are usually generated by structural defects, especially those concerned with bond cleavage, whereas, the bond-saturated carbon atoms in an exact hexagonal structure make less contribution due to their chemical inertness. To further tune and improve the reactivity and catalytic ability of CNTs, researchers tend to modify the crystalline nanotube by controllably placing foreign active atoms into carbon frameworks or surfaces.^{10–12} As reported, the introduction of nitrogen atoms into sp²-hybridized carbon frameworks (called N-doping) seems generally effective in modulating their electrical property and chemical reactivity. The lone electron pair in nitrogen can provide additional negative charges into the delocalized π system and thus leads to a significant improvement of the interaction between carbon structures and foreign molecules,^{13,14} which is of central importance in catalysis. For example, NCNTs and other N-doped carbon structures have been reported to exhibit excellent electrocatalytic performance for oxygen reduction reaction (ORR) in fuel cells,^{15–19} which brings along tremendous technological implications due to the potential replacement of traditional expensive platinum catalysts.

ABSTRACT Nitrogen atoms were found to exhibit a strong ability to promote the self-assembly of nitrogen-doped carbon nanotubes (NCNTs) from gaseous carbons, without an assistance of metal atoms. On the basis of this discovery, pure metal-free CNTs with a nitrogen-doping level as high as 20 atom % can be directly synthesized using melamine as a C/N precursor. This offers a novel pathway for carbon nanotube synthesis. Furthermore, the metal-free and intact characteristics of the NCNT samples facilitate a clear verification of the intrinsic catalytic ability of NCNTs. The results show that the NCNTs intrinsically display excellent catalytic activity for oxygen reduction in fuel cells, comparable to traditional platinum-based catalysts. More notably, they exhibit outstanding stability, selectivity, and resistance to CO poisoning, much superior to the platinum-based catalysts.

KEYWORDS: nitrogen catalysis · self-assembly · nitrogen-doped carbon nanotubes · fuel cells · oxygen reduction

Despite the great attention given to the catalytic functions of NCNTs for ORR, many basic issues are still in debate,^{16,19,20} including the identification of actual working sites involved in the employed samples. This question emerges because most of NCNTs previously used for ORR tests possibly contain a small amount of metal impurities, as estimated from their metal-involved synthesis processes.^{15,20,21} A possible contribution of metal impurities to the ORR catalysis cannot be excluded completely. It greatly disturbs the characterization and understanding of the intrinsic catalytic function of NCNTs and the mechanism details. Indeed, early reports have shown that metal-N₄ macrocycles are active for ORR^{22,23} and, more recently, the groups of Dodelet and Liu^{24,25} reported that the coordination of iron ions with nitrogen atoms incorporated in carbon frameworks can create active sites

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for ORR. These events emphasize the necessity to investigate into the intrinsic catalysis of NCNTs by employing exactly metal-free samples. Strictly speaking, the employed samples should additionally keep their structure intact; any severe post-treatment should be avoided because the local nitrogen structures are easily destroyed due to their relatively high reactivity.

Current technologies for NCNT synthesis are based on two strategies, direct synthesis and post-treatment.^{13,25–37} The direct synthesis of NCNTs is characterized as a simultaneous occurrence of tube formation and N-doping, usually performed in a stream containing NH_3 or N_2 ^{25–29} or by employing nitrogen-containing carbon precursor.^{30–33} In this way, metal catalysts, such as iron, cobalt, and nickel, were often required to promote the decomposition of carbon precursors and formation of tubular structures.^{25–33} The post-treatment technology for NCNT synthesis is often carried out by treating presynthesized CNTs with NH_3 (or nitrogen ions) to implant nitrogen atoms into carbon networks^{34–37} or by coating CNT surfaces with nitrogen-containing substrates (e.g., polyaniline).³⁸ The NCNTs obtained from the direct metal-catalyzed synthesis contain a large amount of metal catalysts. The metals are required to be removed completely for ORR catalysis studies. However, as shown by numerous researches, a complete removal of the metal catalysts is quite difficult,^{39–42} and the rigorous oxidative conditions required easily destroy the original local structure of nitrogen–carbon. The NCNTs obtained from the postimplantation methods seem more suitable for ORR catalysis studies but still suffer from a query that the synthesis of original CNTs are normally catalyzed by metals.

In this paper, we described a discovery that nitrogen atoms themselves exhibit a strong peculiar promotion for the self-assembly of NCNTs from gaseous carbons, without any help from metal catalysts. Based on this new knowledge, pure metal-free CNTs with an N-doping level as high as 20 atom % can be directly synthesized by employing melamine as a C/N precursor, in which any post-treatment is unnecessary. More importantly, such intact samples allow us to check the intrinsic catalytic ability of NCNTs more clearly, and the results show that NCNTs indeed exhibit excellent electrocatalytic performance for oxygen reduction.

The nitrogen-promoted assembly of NCNTs was initially discovered when we attempted to directly synthesize metal-free NCNTs through a carbon self-catalysis process.⁴³ Contrary to previous knowledge that metal catalysts are required for the formation of CNTs under relative mild conditions of chemical vapor deposition (CVD),⁴⁴ recent findings showed that proper anisotropic carbon structures exhibit a self-assembly and/or self-catalysis function for CNT formation, in which any metal catalyst is unnecessary.^{43,45–47} In this light, we strived to synthesize metal-free NCNTs by the

previously employed detonation-assisted CVD (DACVD) method,^{48–51} using a quaternary reaction system. Briefly, 2,4,6-trinitrophenol (TNP) was used as an explosive for the creation of a high-temperature reaction environment, metal-removed CNTs as a catalyst, cyclohexane (C_6H_{12}) as carbon source, and urea ($\text{CO}(\text{NH}_2)_2$) as nitrogen source. The proportions used are given in Supporting Information, Table S1. This reaction system readily resulted in the formation of NCNTs (Supporting Information, Figure S1) after detonation. Interestingly, when the CNT catalysts were excluded from the quaternary system, tubular structures were still evident in the products (Figure S2), although the tube yield ($\sim 20\%$) was lower than the quaternary system ($\sim 70\%$). Since the detonation-induced decomposition of hydrocarbons (e.g., C_6H_{12} and benzene) always results in amorphous granular nanoparticles under similar reaction conditions (Figure 1a and Supporting Information, Figure S3), we supposed that the formation of nanotubes in the TNP- C_6H_{12} - $\text{CO}(\text{NH}_2)_2$ ternary system is promoted by $\text{CO}(\text{NH}_2)_2$, most likely in association with the nitrogen atoms involved. This further motivated us to investigate the reaction system and the possibility of efficiency improvement. We employed more than 10 N-containing compounds, such as pyridine, aniline, *p*-phenylenediamine, triazine, and melamine as united C/N sources. All of the compounds used gave positive results to support the viewpoint of the promotion effect of nitrogen atoms on nanotube formation, although there was a large difference in nanotube yield. The current data showed no visible correlation between the chemical situation and nanotube yield, likely due to their complex decomposition and transformation in the detonation-generated high-temperature and high-pressure environments. In contrast, the effect of the nitrogen content in precursors on nanotube formation was quite evident (Table S1). For instance, *p*-phenylenediamine (N/C atomic ratio, 1:3) was more effective than aniline (N/C atomic ratio, 1:6), with CNT yields of about 40% and 10%, respectively (Figure S4). Triazine, with an N/C atomic ratio of 1:1, led to higher CNT yield of larger than 80% (Figure S5). More interestingly, melamine, a common compound with an N/C atomic ratio as high as 2:1, resulted in nearly pure CNTs (Figure 1b), in which only a trace amount of particle impurity was present. These results clearly indicate the strong promotion ability of nitrogen atoms for nanotube formation, without helps from metal atoms.

The majority of the nanotubes produced by the nitrogen promotion exhibit a bamboo-like morphology (Figure 2a) because rich nitrogen atoms were incorporated into the carbon networks, similar to N-doped tubules synthesized by other methods.^{52,53} Elemental mapping along the bamboo-like tubules (Figure 2b) reveals that nitrogen atoms are relatively rare at the straight sections and instead concentrated at the curved joints between different compartments.

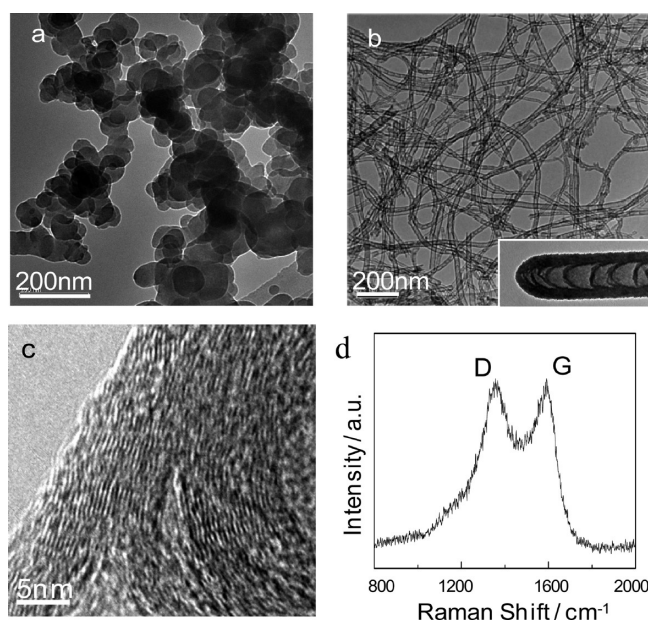


Figure 1. (a) TEM image of products obtained from detonation of the TNP- C_6H_{12} mixture. (b) TEM and (c) HRTEM of the tubes obtained from the TNP-melamine mixture. Inset of panel b shows a typical closed tube end with a hollow core. (d) Raman spectrum of the tubes obtained from the TNP-melamine mixture, in which the strong G-band indicates a graphitic structure, whereas the D-band suggests the presence of structural defects.

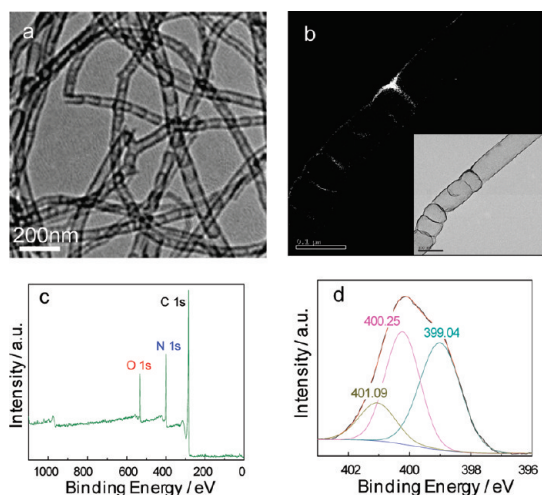


Figure 2. NCNTs produced from melamine: (a) bamboo-like morphology of the tubes; (b) N-mapping of the individual tube shown in the inset; (c) survey XPS spectrum; (d) high-resolution N1s XPS spectrum.

The survey X-ray photoelectron spectrum (XPS) of the nanotubes obtained from melamine (Figure 2c) displays a strong signal relative to N1s photoelectron excitation peak, corresponding to an atomic percent of 19.88%, comparable to the highest N-doping level reported previously.^{32,54} In view of the nonuniform distribution of nitrogen atoms in the bamboo-like tubular structure, the nitrogen content at the curved joints between different compartments should be higher than 20%. The high-resolution N1s XPS spectrum of the N-doped tubes is broad and asymmetric (Figure 2d), indicating that there are different binding configurations. From a curve deconvolution, the

spectrum can be well-fitted to three peaks with binding energies at 399.04, 400.25, and 401.09 eV, assigned to pyridinic-, pyrrolic-, and graphitic-like nitrogen species, respectively.⁵⁵ These data indicate that nitrogen atoms can be comfortably incorporated into a carbon network at a high N/C atomic ratio. It is likely associated with the triple-coordination characteristic of nitrogen atoms, which can well match with the sp^2 -hybridized carbon bonding structure; that is, the geometrical structure of sp^2 -carbon networks will not change greatly when nitrogen atoms are incorporated. In fact, nitrogen and carbon atoms can be well bonded as stable carbon nitride structure such as C_3N_4 .^{56,57}

The mechanism of the nitrogen-promoted tube evolution undoubtedly does not follow the widely known adsorption–diffusion–precipitation growth mode^{58,59} because no metal catalyst is involved and the closed tube ends have hollow cores (Figure 1b inset). To gain insight into the real mechanism, we froze possible intermediates at their evolution stage by quickly releasing the high-pressure hot gases from the reactor just behind the detonation wave, within 30 s. Such an operation effectively reduced the system temperature quickly and forcefully stopped the further evolution of intermediates. Typical intermediate objects are shown in Figure 3a–c and Supporting Information, Figures S6, and S7. Most of the intermediates collected exhibit one-dimensional nanowires, which are visibly assembled by nanoparticles. Some intermediates, as those shown in Figure 3c and Supporting Information, Figure S7, clearly reflect a subsequent structural transformation of nanowires into bamboo-like tubes. Such situations suggest that the nitrogen-promoted tube evolution

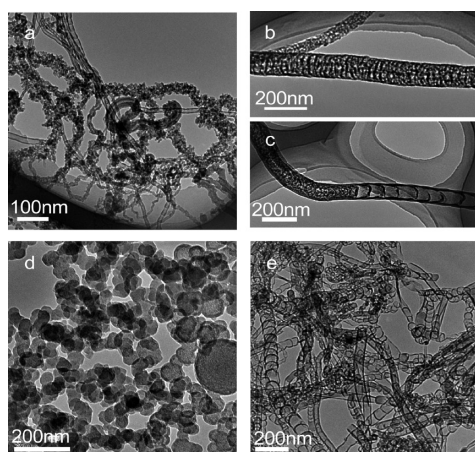


Figure 3. (a–c) Typical intermediates collected by freezing tube evolution in the TNP–melamine system. The freezing was carried out by releasing high-pressure hot gases within 30 s after the detonation; (d) nanoparticles obtained from a TNP–melamine mixture with a TNP loading of 6.6 mmol; (e) nanotubes transformed from the nanoparticles shown in panel d by additional detonation annealing with a TNP loading of 11 mmol.

likely follows a self-assembly mechanism, similar to the recently proposed particle–wire–tube stepwise evolution model.⁵⁰ To give a confirmation for the evolution mechanism, we designed and performed a special experiment, in which the nanoparticles (Figure 3d) produced from melamine at a low TNP loading of 6.6 mmol (corresponding to a low temperature, ~ 500 °C) were further annealed with the detonation system at a higher TNP loading of 11 mmol (corresponding to a higher temperature, ~ 1000 °C). As expected, the majority of the nanoparticles are assembled and transformed into nanotubes (Figure 3e), and wire-like objects assembled by nanoparticles are also present in the annealed samples (Figure S8). This result provides a strong support for the particle–wire–tube evolution model.

It is difficult to obtain direct evidence of the way nitrogen atoms work during their promotion for tube formation, but some experimental data allow us to get indirect insights into the system. In the particle–wire–tube model of CNT evolution, graphitic anisotropic carbon nanoparticles first form from a condensation of gaseous carbon species and then self-assemble into nanowires driven by an anisotropic interaction, and the nanowires finally develop into nanotubes as a consequence of particle coalescence and further structural reorganization (crystallization).⁵⁰ Unlike hydrocarbons, which always lead to amorphous nanoparticles under employed conditions (Figure 1a and Supporting Information, Figure S9), nitrogen-rich compounds (*e.g.*, melamine) result in orderly graphitic structures, as suggested by HRTEM (Figure 1c) and Raman (Figure 1d) analyses of the tubes produced. The carbon particles produced from *p*-phenylenediamine and triazine were imaged by HRTEM, they visibly exhibit a layered anisotropic

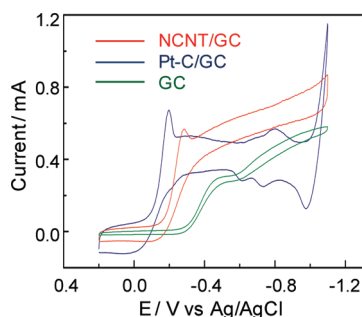


Figure 4. CV curves of different electrodes in an O_2 -saturated 0.1 M KOH aqueous solution. Scan rate, 100 mV s^{-1} .

structure (Supporting Information, Figure S10). These data clearly indicate that nitrogen atoms have a significant promotion effect on the formation of graphitic anisotropic structure, which is of central importance in the one-dimensionally oriented assembly of nanoparticles.⁵⁰ The nitrogen promotion possibly works through a transient formation of $-C\equiv N$ terminal groups at the peripheral dangling bonds of carbon species, which would kinetically stabilize carbon species and allow them to assemble into more stable sp^2 -hybrid structures under thermodynamic control. A similar process for C–H bonds was proposed by Chang *et al.*⁶⁰ to explain the promotion role of hydrogen in the formation of graphitic structure. In addition, the present nanotube evolution is actually accompanied with a partial breakage of carbon–nitrogen bonds because nitrogen content in the nanotubes produced is much lower than that in the precursor employed (*e.g.*, N/C atomic ratio/melamine, 2:1; nanotubes produced, about 1:4). It can be imagined that the breakage of the relatively weak carbon–nitrogen bonds (*vs* carbon–carbon bonds) could facilitate the generation of active reaction sites, which are beneficial to the interparticle anisotropic interaction and subsequent structural reorganization.

As described above, the promotion effect of nitrogen atoms could easily produce pure NCNTs in one step. The tubules obtained do not need any postpurification or modulation treatments, retaining intact nitrogen configurations. Thus, the intrinsic catalytic ability of NCNTs for ORR can be probed without possible influence from foreign factors, such as metals and post-treatment-induced structural alteration.

The electrocatalytic properties of the NCNTs for ORR were tested using a glassy carbon (GC) as working electrode modified with NCNTs (NCNT/GC) and compared with an electrode modified with commercial Pt–C catalyst (Pt–C/GC). Figure 4 shows the cyclic voltammogram (CV) curves of different electrodes in an O_2 -saturated aqueous solution of 0.1 M KOH. The ORR potential is about -0.48 V for the bare GC electrode, -0.20 V for the Pt–C/GC electrode, and -0.27 V for the NCNT/GC electrode, indicating significant catalytic activities of both Pt–C and NCNTs. The ORR

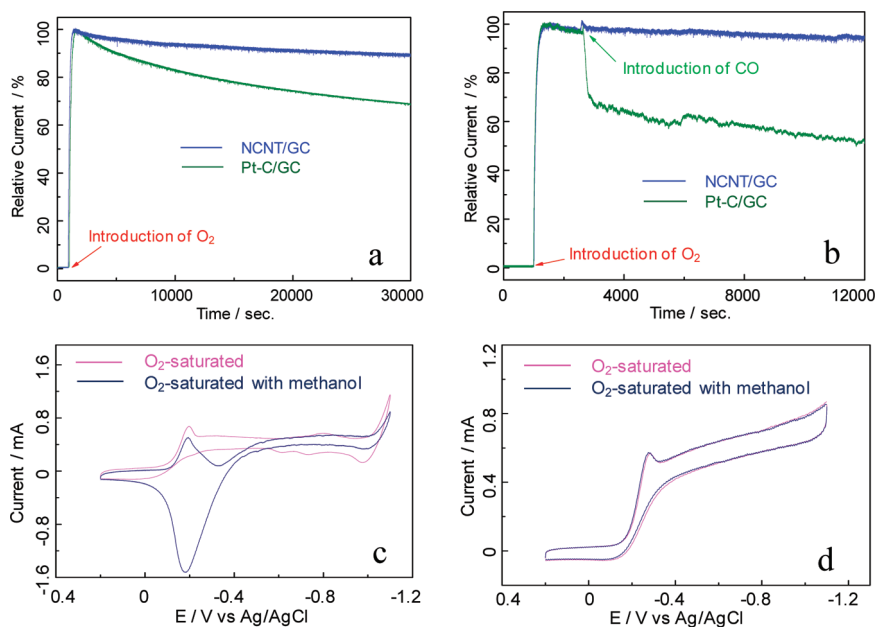


Figure 5. (a) The $i-t$ chronoamperometric responses of NCNT/GC and Pt-C/GC electrodes in O₂-saturated 0.1 M KOH at -0.27 and -0.20 V, respectively; (b) $i-t$ responses to the introduction of 10% CO. CV curves of (c) Pt/GC and (d) NCNT/GC electrodes in O₂-saturated 0.1 M KOH, with and without 3 M methanol.

potential of the NCNT/GC electrode is slightly lower than that of Pt-C electrode, while the current density is comparable for the two electrodes. The electrode modified with nitrogen-free CNTs was also tested, it displays an ORR potential of about -0.33 V (Supporting Information, Figure S11). Although the nitrogen-free CNTs are also somewhat active, its activity is significantly lower than that of the NCNTs, indicating the role of the doped nitrogen atoms in the creation of active sites. These data are in well agreement with the results obtained by Müllen *et al.*¹⁹ who studied the ORR electrocatalytic property of metal-free porous N-doped carbon materials. It should be noted that although the present NCNT sample contains nitrogen as high as 20 atom %, our result is somewhat different from that of Dai *et al.*¹⁵ who reported that the catalytic activity of NCNTs is much higher than that of the platinum catalyst. It is possibly derived from the differences in nitrogen configuration of NCNT samples and in the employed synthesis method. The NCNTs samples of Dai were synthesized by employing iron(II) phthalocyanine as precursor; pyrrolic and pyridinic nitrogen configurations are dominant. In addition, although the authors removed iron from NCNT samples by electrochemical purification, the contribution of a small amount of residual iron to ORR activity could not be completely excluded.

The electron transfers involved in the ORR process catalyzed by NCNTs were studied using a rotating ring disk electrode (RRDE) to detect possible intermediates (HO₂⁻) under steady-state conditions. The transferred electron numbers (n) per oxygen molecule, calculated from the experimental results (Supporting Information, Figure S12), is about 2.6, suggesting a four- and

two-electron combined pathway. This result is analogous to the data of Star *et al.*²⁰ obtained from the NCNTs synthesized by ferrocene-catalyzed chemical vapor deposition of MeCN and EtOH. However, it is different from the data of Dai *et al.*,¹⁵ who reported that their NCNT samples, synthesized by the pyrolysis of iron(II) phthalocyanine, exhibit a four-electron reaction process. The reason of this difference is still unclear and waits a further clarification.

Durability tests display that the NCNTs are quite stable within the test period. After 30000 s of reaction, 90% of the current could remain (Figure 5a). In contrast, after the same reaction duration, the Pt-C catalyst loses its activity greatly, with a current loss of 31%, likely caused by the aggregation of platinum particles.⁶¹ More importantly, as revealed by the current-time ($i-t$) chronoamperometric responses (Figure 5b), the NCNTs exhibit an exceptional resistance to CO poisoning, with a nearly constant activity upon the introduction of CO into the reaction system. On the contrary, the Pt-C catalyst is quite easily deactivated by CO.

For direct methanol fuel cells, the crossover effect of methanol should be considered because methanol molecules fed to the anode sometimes permeate through the membrane to the cathode and seriously affect the performance of the cathode catalyst.^{19,62,63} Good ORR catalysts should be inert for methanol oxidation; however, traditional Pt-C catalysts are highly active undesirably. As shown in Figure 5c, a strong oxidation peak appears at -0.18 V when methanol is introduced into the ORR system. In contrast, the NCNTs exhibit excellent selectivity in ORR, with no visible response to methanol oxidation (Figure 5d), similar to

the previous reports.^{15,19} For methanol oxidation, metal catalysts are normally required to activate methanol and, actually, platinum is also employed frequently as anode catalysts in methanol fuel cells.⁶⁴

In conclusion, nitrogen atoms display a strong ability in promoting the self-assembly of tubular carbon nanostructures. This discovery offers a novel pathway for the synthesis of CNTs, especially NCNTs, and might provide valuable information for the understanding of the basic mechanism of CNT evolution. Nitrogen atoms

incorporated in carbon networks can indeed create highly active sites for oxygen reduction, which is comparable to traditional platinum-based catalysts. Combining their high activity, outstanding stability, selectivity, and resistance to CO poisoning, NCNTs represent a potential low-cost, robust ORR catalyst for fuel cell applications. Understanding of the mechanisms of the versatile catalytic functions of nitrogen atoms is necessary for further catalyst design and property modulation.

EXPERIMENTAL SECTION

Synthesis and Characterization. Mixtures of TNP and C/N precursors were employed to investigate the promotion effect of nitrogen atoms on CNT assembly and to synthesize NCNTs using the DACVD process. Supporting Information, Table S1 details the amounts of the compounds used in the experiments. The detonation experiments were performed in a sealed stainless steel pressure vessel (14 cm³) and initiated by quick heating (20 °C min⁻¹) the vessel to 320 °C. The detonation created a unique environment inside the vessel, with a temperature of about 1000 °C and pressure of about 15 MPa, which supported nanotube assembly. After the detonation, the vessel was allowed to stay in the heating furnace for 10 min before it was air-cooled at room temperature. The gaseous products were finally emptied and the solid products were collected for further analysis.

TEM images were taken on a JEM-2010 electron microscope, operated at 200 kV. All samples were prepared by suspension in ethanol and drop-casted on a carbon-coated copper TEM grid. The elemental mapping was achieved from electron energy loss spectroscopy (EELS) equipped on TEM. XPS analyses were performed using a Thermo ESCALAB 250 spectrometer, employing an Al-K α X-ray source with a 500 μ m electron beam spot. Raman measurements were performed by a Jobin-Yvon HR-800 Raman system, using the 514 nm line of an Ar laser as excitation source.

Electrocatalytic Tests. A GC electrode was carefully polished with gamma alumina powder until a mirror finish was obtained. Then the electrode was rinsed and fully sonicated with double distilled water to remove alumina residues. Finally, it was dried in vacuum. The NCNTs synthesized from TNP-melamine were used for catalysis tests and compared with a commercial Pt-C catalyst (20% Pt on Vulcan XC-72R, Johnson Matthey, UK). In a mixture of 5% Nafion (50 μ L) and ethanol (1 mL), the catalysts (5 mg) were dissolved by sonication. Then, the solution (20 μ L) was drop-casted on the GC electrode surface (0.2475 cm²) and air-dried with an infrared lamp. CV, *i*-*t* chronoamperometric measurement, and RRDE voltammetry were all performed using a CHI 760D electrochemical analyzer and a MSR electrode rotator at a rotation rate of 1500 rpm.

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Supporting Information Available: A table of experiment details, TEM images of experimental products, CV curves for CNT/GC electrode, and RRDE voltammograms for NCNT/GC electrode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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