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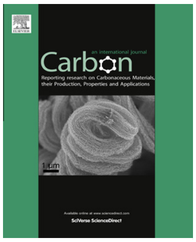

A co-pyrolysis route to synthesize nitrogen doped multiwall carbon nanotubes for oxygen reduction reaction

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ABSTRACT

Nitrogen-doped multiwall carbon nanotubes (N-MWCNTs) have been synthesized by a co-pyrolysis route of iron(II) phthalocyanine (FePc) loaded and PEO_{20}–PPO_{70}–PEO_{20} retained in mesoporous silica. In this process, FePc was used as both Fe-catalyst, carbon and nitrogen sources, and P123-containing mesoporous silica was employed as both the substrate and carbon seeds/source for the growth of N-MWCNTs. The obtained samples have well-defined morphology and graphitic structure, and show high electrochemical catalytic activity and stability for oxygen reduction reaction, attributing to the highly graphitic structure and the pyridinic-type nitrogen in the N-MWCNTs. The power density of a single fuel cell using N-MWCNT as cathodic catalyst was measured to be 67.7% of that of a standard single cell using 40% Pt/C as cathodic catalyst.

1. Introduction

Carbon nanotubes (CNTs) are now well-known for their distinguished features, such as high surface area and excellent electrical conductivity, which make them very promising in various applications, such as chemical sensors, energy-storage media, molecular reinforcements in composites, catalysts, and so on [1–3]. Moreover, the structural and morphological characters of CNTs make them also highly suitable as a kind of support materials in catalysis. The doping of CNTs with nitrogen has drawn much attention because of the conjugation effect between the nitrogen lone-pair electrons and the graphene Π-system [4,5], which may create new nanomaterials with tailored electronic and mechanical properties. In the last few years, nitrogen-doped CNTs came into a research focus as potential catalysts for oxygen reduction reaction (ORR) [6–10], and it has been established that the nitrogen-doped CNTs demonstrate high electrocatalytic activity for ORR in basic, neutral and acidic electrolyte media [11–16]. To further enhance the electrocatalytic properties of CNTs and promote their potential application, it will be of great significance to develop a rapid and simple approach to synthesize the CNTs doped with various heteroatoms.

Great efforts have been made to synthesize CNTs with the desired performance since the first study of CNTs by Iijima [17]. Most of these methods start with the deposition of a metal catalyst (Fe, Co or Ni) on a support (SiO_2 or Al_2O_3) followed by various pretreatments of the catalyst before the growth of

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CNTs [18–24]. Among them, chemical vapor depositon is the most promising method to synthesize high quality CNTs with different gaseous carbon sources (such as methane, acetylene, ethylene and benzene, and so on) [23,25–28]. However, up to now, these methods of synthesizing carbon nanotubes highly rely on high temperature, catalysts on various substrate, and the following etching or thermal annealing processes, which are rather complicated and costly. Though several basic steps are generally acknowledged in the chemical CNTs production, yet the growth mechanism needs further investigation.

Recently, there have been a few reports on the simple growth technique of CNTs by the pyrolysis of FePc (iron(II) phthalocyanine) in a quartz reactor [29–34]. These techniques need two heating zones where FePc molecules were sublimated in the first zone at low-temperature and carried by gas flow to the second one of higher temperature where FePc decomposed and was used as carbon and nitrogen sources and Fe catalysts for preparing N-MWCNTs. This process is also complicated and less productive. To simplify the process, in the present work, FePc was mixed with PEO_{20}–PPO_{70}–PEO_{20} (P123) retained mesoporous silica, which was used as the structure-directing agent in mesoporous silica synthesis and then the mixture was directly used for the co-pyrolysis of FePc and P123 to produce N-MWCNTs. In this synthesis strategy, the mesopore framework of the silica template acts as the substrate. P123 and FePc are the carbon source and Fe nanoparticles derived from the FePc pyrolysis are the catalysts for the formation of nanotubes, and meanwhile, N-doping is achieved by FePc pyrolysis. No additional catalysts, substrates, and N sources are needed in the synthesis, therefore the present technique is featured with distinctive controllability, large quantity of production and short time duration of fabrication. After the purification of the pyrolysis products, the N-MWCNTs with high quality and quantity can be obtained. Hereafter, the electrochemical catalytic property for ORR of the obtained N-MWCNT catalyst is examined, and the results show that the as synthesized N-MWCNTs can be used as an alternative for the cathodic catalyst in the proton exchange membrane fuel cells (PEMFCs).

2. Experimental

2.1. *Synthesis of silica template and N-MWCNTs*

Mesoporous silica with P123 ($Ia\bar{3}d$ symmetry) was prepared following the procedure reported by Ryoo et al. [35]. Typically, 6 g of surfactant P_{123} and 6 g of *n*-butanol was dissolved in a solution of 217 g distilled water and 11.4 g HCl (37 wt.%). To this homogeneous solution, 12.9 g of tetraethylorthosilicate (TEOS) was added under stirring at 311 K and continuously stirred at 311 K for additional 24 h. The mixture was heated for 24 h at 373 K under static conditions for the hydrothermal treatment followed by filtration, washing, drying at 353 K in air.

The as-prepared mesoporous silica with P123 was then used as a template for the preparation of N-MWCNTs. The typical synthesis procedure is as follows: FePc (0.5 g) and mesoporous silica with P123 (0.5 g) were mechanically mixed and then the mixture was heated at 900 °C for 10 h in a tube furnace under N_2 (99.9%) flow. The silica template was removed by treating in a 2 M NaOH solution at 80 °C, and Fe catalysts were etched away by 2.6 M HNO_3 solution. This purification product was collected by centrifugation and washed with distilled water and ethanol, and then dried at 353 K.

2.2. *Characterisation*

The powder X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a Rigaku D/Max-2550 V X-ray diffractometer with a Cu Kα radiation target (40 kV, 40 mA), and the scanning rate was 4°/min for the wide-angle measurement. The chemical composition of the samples was determined using an X-ray photoelectron spectroscope (XPS, ESCAlab250), and the binding energy of C (285 eV) was used as the charge-up correction. Fourier transform infrared (FTIR) spectra were obtained in the range of $\nu = 400$–$4000\ cm^{-1}$ by using Nicolet 7000-C spectrometer with a resolution of $8\ cm^{-1}$. The surface morphology of the sample was examined using a transmission electron microscopic (TEM) (a JEOL 200CX electron microscope operating at 160 kV). Energy dispersion spectrum (EDS) was obtained from an attached Oxford Link ISIS energy-dispersive spectrometer fixed on a JEM-2010 electron microscope operated at 200 kV. The graphitic degree of the sample is analyzed by selected area electron diffraction (SAED). Raman spectra were recorded on Micro-Raman spectrometer (Jobin Yvon HR800 UV) using an Ar ion laser (excitation wavelength: 514.5 nm). The N_2 sorption measurements were performed using Micromeritics Tristar 3000 at 77 K, and the specific surface area and pore size distributions were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

Electrochemical tests were performed on CHI 660A electrochemical workstation (CH Instrument, Inc.) with a standard three-electrode cell. Glassy carbon disks of 6 mm diameter ($0.283\ cm^2$) served as substrate for the catalyst materials. Catalyst ink with $5\ mg\ mL^{-1}$ (ethanol:water = 1:1, volume scale) and 25 μL Nafion solution (5%) was dispersed ultrasonically, and 20 μL aliqot was transferred onto the glassy carbon substrate, yielding a catalyst loading level of $0.35\ mg\ cm^{-2}$. A platinum wire and Ag/AgCl (3 M KCl) were used as counter and reference electrodes, respectively. 0.5 M H_2SO_4 solution was used as electrolyte for electrochemical measurements. High purity O_2 was used prior to the measurements to deaerate the electrolyte. The catalysts were characterized by cyclic voltammetry (CV) test at room temperature. An electrode tip (Pine Research Instrumentation) was used for the rotating disk electrode (RDE) measurements, and glassy carbon disks of 5 mm diameter served as substrate for the catalyst materials. 15 μL aliqot was transferred onto the glassy carbon substrate, yielding a catalyst loading level of $0.38\ mg\ cm^{-2}$. The kinetic parameters can be analyzed on the basis of the Koutecky–Levich equations [36]:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K} \tag{1}$$

$$B = 0.62nFC_0(D_0)^{2/3_\nu -1/6} \tag{2}$$