

Construction of Nickel Oxide/Nitrogen-doped Carbon Nanotubes Catalysts with High Activity for Oxygen Reduction Reaction

Pinghua YANG & Jianping XU

College of Chemistry and Environment Engineering, Jiangxi Province Engineering Research Center of Ecological Chemical Industry, Jiujiang University, Jiujiang, China, 332005

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ABSTRACT: Nickel oxide/nitrogen-doped carbon nanotubes catalysts for the (ORR) were fabricated using a simple chemical plating method. Scanning electron microscopy (SEM) and Energy dispersive spectrometer (EDS) was used to characterize its structure. Electrochemical method studies show that the nickel oxide/nitrogen-doped carbon nanotubes could exhibit a high ORR activity.

INTRODUCTION

The commercial application of fuel cells has been hindered by the high cost and scarcity of the requisite noble metal materials (Winter M. & Brodd R. J. 2004). With high activity and practical durability, the non-noble metal catalysts has been viewed as a good substitute to promote the development of fuel cells (Alexey Serov & Chan Kwak. 2009). Various non-noble metal catalysts materials have been evaluated as potential substitutes for Pt-based catalysts (Kuanping Gong 2007). With their excellent electrocatalytic activities, nitrogen-doped carbon nanotubes have attracted attention (Yu D et al. 2010, Wang Z et al. 2011). The new way to prepare of metal-free catalyst for the ORR has opened. The doping of N atoms play a key role in their catalytic activity enhancement toward the ORR for that their change the electronic structure of carbon nanotubes (Kurak K A & Anderson A B 2009).

Herein, we have prepared a nickel oxide/ nitrogen-doped carbon nanotubes (NiO_x/N-CNTs) composite material via a simple chemical plating method. The NiO_x/N-CNTs exhibit excellent electrocatalytic activity toward the ORR in an alkaline medium.

EXPERIMENTAL SECTION

Apparatus

Scanning electron microscopy (SEM) images were obtained by using VEGA II LSU SEM (Czech TESCAN). All electrochemical experiments were carried out on a CHI660B electrochemical workstation (Chenhua Instrument Company of Shanghai, China) in a conventional three electrodes cell. The working electrode was a composite films electrode with a diameter of 3 mm, the auxiliary electrode consisted of a platinum wire, and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials reported in this paper are relative to SCE.

Reagents

Carbon nanotubes (CNTs, Shenzhen Nanotech Port Co. Ltd, China) have a typical diameter of 10-20 nm and length of 5-15 μm. The purity was more than 97%. Other chemicals were of analytical grade and were used as received. Double distilled water was used throughout the experiments. All the procedure was acted at room temperature. Oxygen was removed by purging with high-purity nitrogen for 10 minutes and a nitrogen atmosphere was kept over the solution during measurements.

Synthesizing of nickel oxide/nitrogen-doped carbon nanotubes

Firstly, their was synthesizing of nitrogen-doped carbon nanotubes. Take 100 mL 30% hydrazine hydrate, 100 mL water and 600 mg carbon nanotubes has imposed on the distillation flask. The mixture was heated to 60 °C and reflux for 6 h, then clean the filtration with water. The filtration solid was drying to 80 °C for 8 h.

Nickel oxide/nitrogen-doped carbon nanotubes were prepared by chemical plating method. Firstly, 0.6 g functionalized N-CNTs was mixed with 50 ml mixture solution of 5 g/L sodium hypophosphate,

1 g/L sodium acetate and sodium citrate. Secondly, appropriate proportion nickel sulfate was dropped one by one into the mixture and then water bath heating at 60°C for 50 min.

Electrode preparation

Prior to use, the glassy carbon electrode was carefully polished with chamois leather containing 0.05 μm Al_2O_3 slurry and then ordinal ultrasonically cleaned in ethanol and distilled water. 10.0 mg of NiOx/N-CNTs was dispersed with the aid of ultrasonic agitation in 10mL N,N-dimethylformamide to give a 1.0 mg/mL black suspension. The NiOx/N-CNTs /GC electrode was prepared by dropping 20 μL of the suspension on the clean GC electrode surface and then evaporating the solvent in air. The CNTs /GC and N-CNTs /GC electrodes were prepared by the similar method.

Electrochemical Measurements

Cyclic voltammetry (CV) was performed at room temperature in 0.1 mol.L⁻¹ KOH solutions, which were purged with high purity nitrogen or oxygen for at least 10 min prior to each measurement. The modified electrode acted voltammetric cycles from 0.2 V to -1.2V at a scan rate of 50 mV.s⁻¹.

RESULTS AND DISCUSSION

Characterization of nickel oxide/ nitrogen-doped carbon nanotubes

Figure.1 shows the SEM images for the CNTs, N-CNTs and the NiOx/N-CNTs. It is clear from the SEM images in Figure 1 that the surface of CNTs has been coated with nickel oxide.

Figure 2 shows the Energy Dispersive Spectrometer (EDS) images for the N-CNTs and the NiOx/N-CNTs. It showed that the elemental composition of this material. The atomic ratio of nitrogen is 14% and that of oxygen is 86% (Fig. 2 A). The EDS image show that the NiOx/N-CNTs is composed of nitrogen, oxygen and *nickel* element (Figure 2 B).

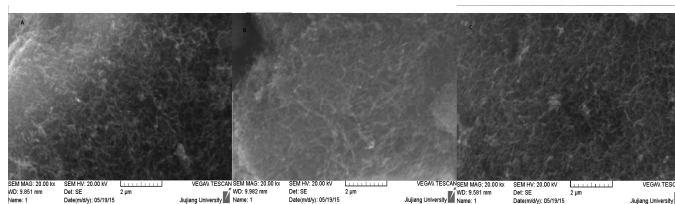


Figure 1. SEM image of the CNTs(A), N-CNTs(B) and the NiOx/N-CNTs(C)

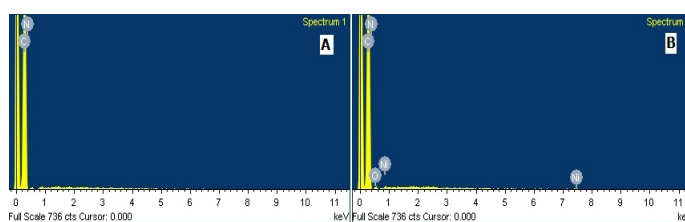


Figure 2. EDS image of the N-CNTs(A) and the NiOx/N-CNTs(B)

Figure 3 is a comparison of the infrared spectra of N-CNTs and CNTs. It showed that 1300-1100 cm^{-1} has C-C bond stretching vibration peaks, 2000-1500 cm^{-1} has the double bonds C=C stretching vibration peaks. The change of the peak of the 1300-1100 cm^{-1} and 2000-1500 cm^{-1} region showed the appearance of C-N bond and C=N bond.

Electrocatalytic Activity for Oxygen Reduction Reaction

Cyclic voltammetry was used to investigate the electrocatalytic activity of the nickel oxide/ nitrogen-doped carbon nanotubes. Figure 4 showed the cyclic voltammograms of the NiOx/N-CNTs in 0.1 mol.L⁻¹ KOH solutions, saturated with or without O₂. There have no obvious redox current peaks when the oxygen was removed (Fig. 4 a). However, there has a very large reductive current peak at -0.37 V in the air saturated 0.1mol.L⁻¹ KOH, which corresponds to the O₂ reduction reaction. (Fig. 4 b).

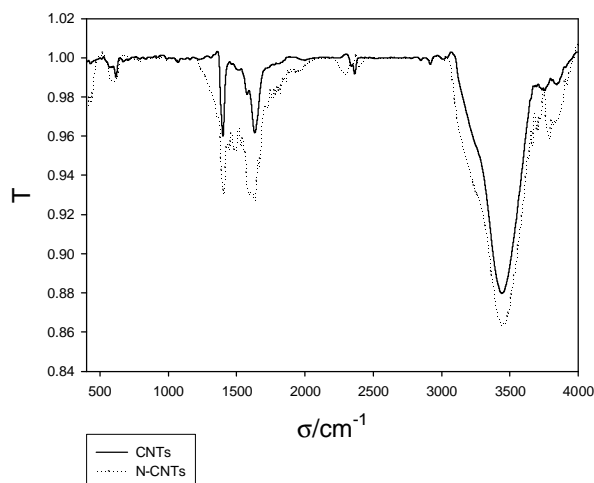


Figure 3. IR image of the CNTs and N-CNTs

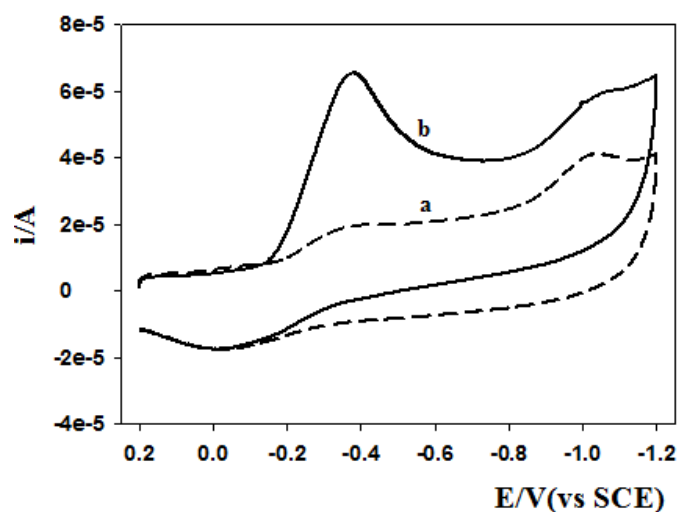


Figure 4. Cyclic voltammograms of NiO/N-CNTs, for the oxygen reduction reaction in 0.1 mol.L⁻¹ KOH solutions with (b) or without O₂(a)

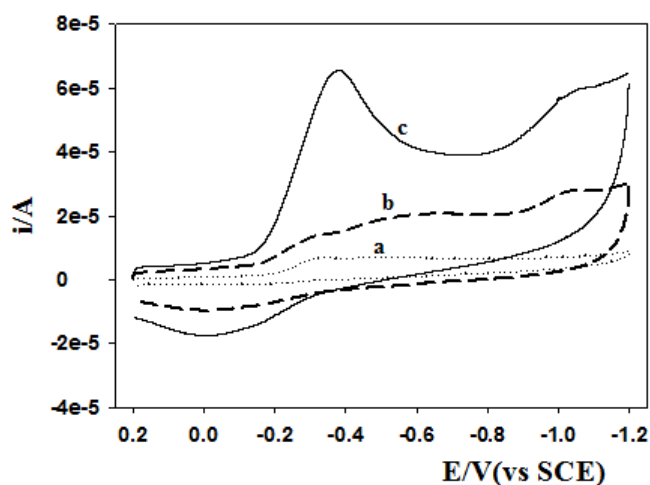


Figure 5. Cyclic voltammograms of (a) CNTs, (b) N-CNTs and (c) NiOx/N-CNTs, for the oxygen reduction reaction in 0.1 mol.L⁻¹ KOH solutions saturated with O₂.

Figure 5 showed the cyclic voltammograms of the CNTs, N-CNTs and the NiOx/N-CNTs in 0.1 mol.L⁻¹ KOH solutions, saturated with O₂. Equal amounts of each catalyst were loaded on a glassy-

carbon electrode. As shown in Figure 5, the current of the bare glassy carbon electrode (Fig. 5 a) is very low and that of the nitrogen doped carbon nanotube (Fig. 5 b) is higher. After modification of nickel oxide, the electric current is higher than the nitrogen doped carbon nanotubes (Fig. 5 c). The reduction current of NiO_x/N-CNTs (58 μA, Fig. 5 c) is five times larger than that of N-CNTs catalyst (Fig. 5 b) and nine times larger than that of CNTs. The nickel oxide/ nitrogen-doped carbon nanotubes boasts a greater electrocatalytic activity to ORR and will be a potential catalytic material.

CONCLUSIONS

In this paper, we have reported a nickel oxide/ nitrogen-doped carbon nanotubes composite material via a simple chemical plating method. The electrochemical behaviour of the composite material for ORR has studied. The nickel oxide/ nitrogen-doped carbon nanotubes show electrocatalytic activity to ORR and may be a potential cathode material of the air battery.

Acknowledgements

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