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ScienceDirect
Applied Surface Science 254 (2008) 2934–2940
applied surface science
www.elsevier.com/locate/apsusc

Functional multi-walled carbon nanotube/polyaniline composite films as supports of platinum for formic acid electrooxidation

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Received 7 September 2007; received in revised form 14 October 2007; accepted 15 October 2007
Available online 22 October 2007

Abstract

Embedding of carbon nanotubes in conducting polymeric matrices for various nanocomposites material is now a popular area. In this article, a concise chemical method has been described for the preparation of homogeneous nanocomposite of multi-walled carbon nanotube (MWNT)/polyaniline (PANI) by electrochemical codeposition. For this we functionalized the MWNTs via the diazotization reaction. This helped to disperse the nanotubes in aniline. The composite films were dispersed Pt by electrodeposition technique. The presence of MWNTs and platinum in the composite films was confirmed by XRD analysis and transmission electron microscopy (TEM). Four-point probe investigations revealed that the MWNT/PANI composite films exhibited a good conductivity. Cyclic voltammograms (CV) showed that Pt-modified MWNT/PANI composite films perform higher electrocatalytic activity and better long-term stability than Pt-modified pure PANI film toward formic acid oxidation. The results imply that the MWNT/PANI composite films as a promising support material improves the electrocatalytic activity for formic acid oxidation greatly.

PACS : 81.07.De; 82.35.Cd; 82.45.Yz

Keywords: Multi-walled carbon nanotubes; Polyaniline; Composite film; Formic acid electrooxidation; Electrocatalytic activity

1. Introduction

Since the discovery of carbon nanotubes (CNTs), extensive research in the fields of applied physics, chemistry, materials science and engineering has rapidly emerged [1–3]. CNTs, which possess unique topological hollow tubular structure, are the most typical one-dimensional nanomaterial in the order of micrometers in length and nanometers in diameter. Owing to their outstanding mechanical characteristics, good electronic conductivity, nanometer size and high-accessible surface area, CNTs can be used to prepare the multi-functional composites with excellent electronic and mechanical properties. Recently, many attempts have been conducted to deposit various metal particles onto the surface of CNTs for their application in the area of catalysis. Some metals and their compounds, such as Pt, Pd, Ag, Au, Ni, Fe, have been deposited on the CNTs successfully [4–9]. CNTs are considered as the potential supports for making heterogeneous catalysts [10–12]. However, there are difficulties in dispersing metal nanoparticles with uniform dispersion and regular sizes in the CNTs surfaces. Therefore to obtain the good highly dispersed nanoparticles, the surface carbon nanotubes must be modified via a proper functionalization.

On the other hand, many literatures have shown that conducting polymers with porous structure and high-surface area are usually used as matrix to incorporate noble metal catalyst [13]. Concurrently, the PANI is known to be one of the most technologically important conducting polymers because of its environmental stability, easiness and low cost of synthesis [14]. Extensive efforts have been made to prepare functional CNT/PANI composites, which are expected to exhibit useful electrical and optical properties and superior mechanical strength recently [15–20]. Philip et al. [21] covalently functionalized the multi-walled nanotubes with *p*-phenylene diamine and prepared

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doi:10.1016/j.apsusc.2007.10.033

homogeneous polyaniline/carbon nanotube composites by the in situ polymerization. In those composites, carbon nanotubes can be covalently functionalized or doped to PANI [22–24]. The combination of PANI with CNTs would offer an attractive composite support material for electrocatalyst to enhance its activity and stability based on morphological modification or electronic interaction between two components [25].

However, the insolubility and poor compatibility of CNTs with the polymer limited the feasibility of synthesizing this kind of composite film [26]. In this work, a novel method has been described for the preparation of homogeneous nanocomposite of MWNT/PANI by electrochemical codeposition. For this we functionalized the MWNTs via the diazotization reaction [27]. The 4-carboxylicbenzene group is modified on a MWNT surface via a C–C covalent bond which is strong and propitious to disperse them well in the aniline. The MWNT/PANI composite films modified by electrochemically depositing platinum subsequently shows much higher mass activity and long-term stability for formic acid oxidation than a pure PANI film. The procedure for the preparation of Pt-modified MWNT/PANI composite films was shown in Fig. 1. Until now, no sufficient investigation has been made for HCOOH using MWNT/PANI composite as the support materials compared to CH_3OH or HCHO.

2. Experimental

2.1. Preparation of MWNT/PANI solutions

Aniline was distilled under reduced pressure and stored under nitrogen gas. All other reagents were used as received. All the solutions were prepared using twice distilled water. MWNTs used in this work were produced via the chemical vapor deposition method, and their purity was about 95%. The process of preparation and purification are described in detail elsewhere [27]. Sixteen milligrams of MWNTs were devoted into 20 ml 1,2-dichlorobenzene (ODCB) under sonication for 10 min. The suspension was added a solution of the 0.72 g 4-aminobenzoic acid in 10 ml acetonitrile, then bubbled with nitrogen for 10 min. After that, 1.71 ml isoamyl nitrite was quickly added via syringe. The mixed suspension was vigorous magnetic stirred at 60 °C for 24 h in an inert atmosphere. After cooling to room temperature, the suspension was diluted with dimethylformamide (DMF), filtered with a PTFE membrane disc filter (0.45 μm pore size) under vacuum followed by washing extensively with DMF until the filtrate became colorless [28]. Excess unreacted 4-aminothiophenol and isoamyl nitrite must be removed efficiently. DMF were removed by washing with sufficient absolute ethanol.

After then, the functional multi-walled carbon nanotubes were added to 50 ml aniline with content 0.8 wt% (weight percent with respect to aniline monomer) [29]. The mixture was heated at reflux for 3 h in the dark. After being cooled to room temperature, MWNTs-aniline solution was obtained by filtration through a ∅0.1 μm Super Membrane disc filters (German) under vacuum.

2.2. Preparation of Pt-modified MWNT/PANI composite films

MWNT/PANI composite films were prepared by a protocol modified from Wang's method [30]. The deposition was carried in a solution of 1 M H_2SO_4 containing 0.1 M aniline dissolved MWNTs in 0.8 wt % in a three-electrode cell. The electrochemical deposition MWNT/PANI composite films were carried out in the cycling potential range of −0.2 to +1.2 V at a sweep rate 50 mV/s for 25 cycles using a CHI660A. A platinum sheet (geometric surface area = 2 cm^2) was used as the working electrode, another platinum sheet and a saturated calomel electrode (SCE) were used as the counter and reference

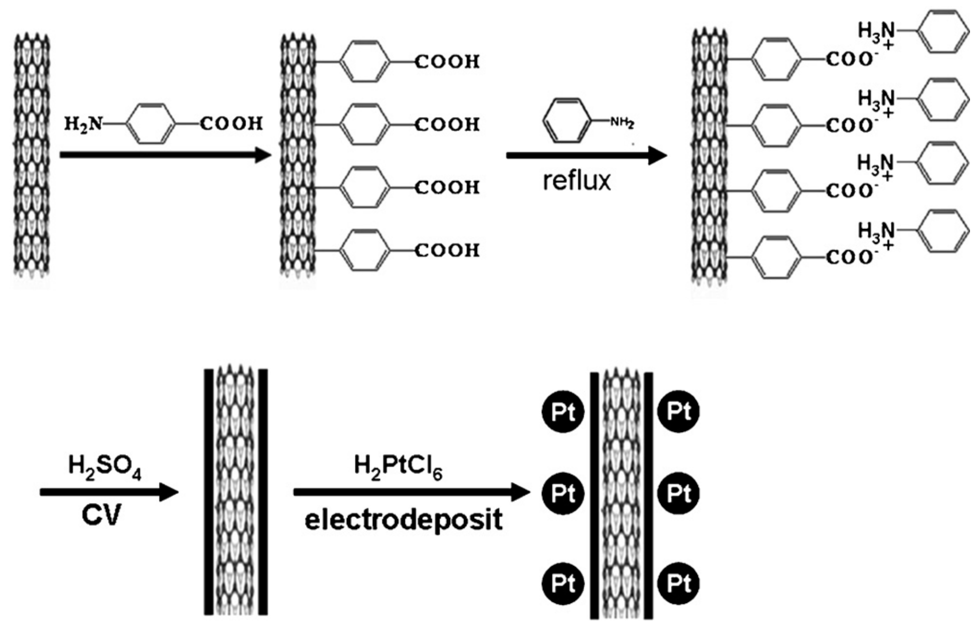

Fig. 1. Schematic procedure for the preparation of Pt-modified MWNT/PANI composite films.