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Two-step pyrolysis process to synthesize highly dispersed Pt–Ru/carbon nanotube catalysts for methanol electrooxidation

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Abstract

Highly dispersed Pt–Ru particles with different atomic ratios supported on carbon nanotubes were synthesized using an easy two-step synthesis method including adsorption and pyrolysis. In this method, the functionalized carbon nanotubes act as adsorption sites for metallic ions and subsequently act as nucleation center for catalyst deposition in the pyrolysis process. The deposited Pt–Ru nanoparticles disperse on the carbon nanotubes surface uniformly, and the bulk composition of the Pt–Ru particles can be adjusted simply by changing atomic ratios of the metallic solution for adsorption. Finally, the electrocatalytic activity of the as-prepared catalysts supported on carbon nanotubes toward oxidation of methanol was studied. Results showed that their electrocatalytic activity, having long-term stability, strongly depends on the atomic ratio of Pt to Ru. The higher the concentration of Pt in the binary system is, the greater the electrocatalytic activity will be.

Keywords: Carbon nanotubes; Pyrolysis; Electrodes; Catalyst; Catalytic properties

1. Introduction

Direct methanol fuel cell (DFMC) attracts increasing attention for its potential as clean power sources for portable devices and vehicles or small stationary [1,2]. Although many efforts have been devoted to the DMFC development in recent years, problems are still remained to be overcome in terms of performance efficiency and power density. One of the problems is the relative sluggish kinetics of methanol oxidation at the platinum-based catalysts, resulting in high overpotentials [3,4]. Catalysts of highly dispersed platinum-based nanoparticles supported on porous carbon are routinely used in DMFC. However, many platinum-based particles are trapped in the pores of the carbon electrodes, resulting in less utilization of the catalysts due to their inaccessible to the reactants [5]. Carbon nanotubes (CNTs), due to their unique structural of nanometer size and high surface area, mechanical and electrical properties, have been proposed to be an alternative metal catalysts support. Several papers have reported the application of carbon nanotubes in fuel cells as catalysts support and electrode materials [6–14]. Up to now, successful supporting platinum-based catalysts on the carbon nanotubes is usually achieved by using chemical modification [6], chemical reduction [7–10], electrochemical reduction [11,12], chemical vapor deposition [13], and supercritical fluid fabrication [14]. Herein, we report on an easy method to fabricate platinum-based catalysts nanoparticles supported on CNTs simply by using a two-step method including adsorption and pyrolysis processes. In the first step, the surface functional groups of CNTs provide active sites for interaction with metal

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ions, i.e., the oxygen atom of the functional group serve as one of the two axial ligands of the complexes of Pt(IV) and Ru(III). In the second step, the adsorbed Pt(IV) and Ru(III) complexes are precursors which are subsequently converted to Pt–Ru particles via pyrolysis process. These functional groups on CNTs hence contribute to a well-dispersed deposition of Pt–Ru particles on the surface of CNTs [15]. Although the Pt–Ru alloy is considered to be the best catalysts for the methanol oxidation, its electrocatalytic activity is determined by the atomic ratio of Pt to Ru in the alloys. Therefore, Pt–Ru catalysts supported on CNTs with different Pt–Ru atomic ratios were synthesized and their electrocatalytic activities toward the electrooxidation of methanol were investigated.

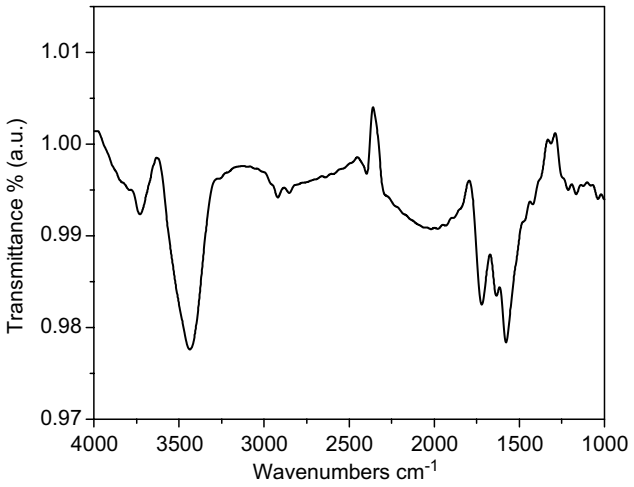

Fig. 1. FTIR spectrum of functionalized CNTs.

2. Experimental

2.1. Functionalization of carbon nanotubes

Multiwalled carbon nanotubes (Shenzhen Nanotech Co. Ltd.) were refluxed in 5 M HNO_3 for 5 h, and filtrated through a 220 nm membrane and washed with deionized water for several times. 0.5 g purified CNT was refluxed twice in a mixture of nitric acid and concentrated sulfuric acid for 2 h and then filtrated and washed with deionized water for several times, giving black powder of functionalized CNT. FTIR characterization on a Tensor-27 Fourier IR spectrometer equipped with a MCT detector (Bruker, USA) of the functionalized CNTs in KBr discs (Fig. 1) shows that the CNTs surfaces have functional groups such as phenol, carbonyl, and carboxyl groups located at ca. 1720 and 3440 cm^{-1}, respectively. The bands at 2920 and 2850 cm^{-1} are due to the C–H stretching modes in the CH_3 and CH_2 groups on CNT surface. The up-going band located at ca. 2350 cm^{-1} is due to the unbalanced CO_2 in the measuring chamber.

2.2. Preparation of multiwall carbon nanotubes supported Pt–Ru catalysts

The functionalized CNTs were respectively stirred in solutions of $PtCl_4 + RuCl_3$ with 3:1, 1:1 and 1:3 molar ratios of Pt to Ru for several hours and kept still overnight, and then filtrated and washed with deionized water for many time until the solution pHs approached 7.0. Pyrolysis of the functionalized CNTs adsorbed with platinum and ruthenium salts were carried out in a self-made furnace at 500 °C under N_2 atmosphere for 1 h to form black powder of Pt–Ru/CNTs hybrid composites. The whole process carried out under N_2 atmosphere, which could avoid induction of oxygen in the hybrid materials and at the same time remove the gaseous side-product such as chlorine engendering in the pyrolysis process.

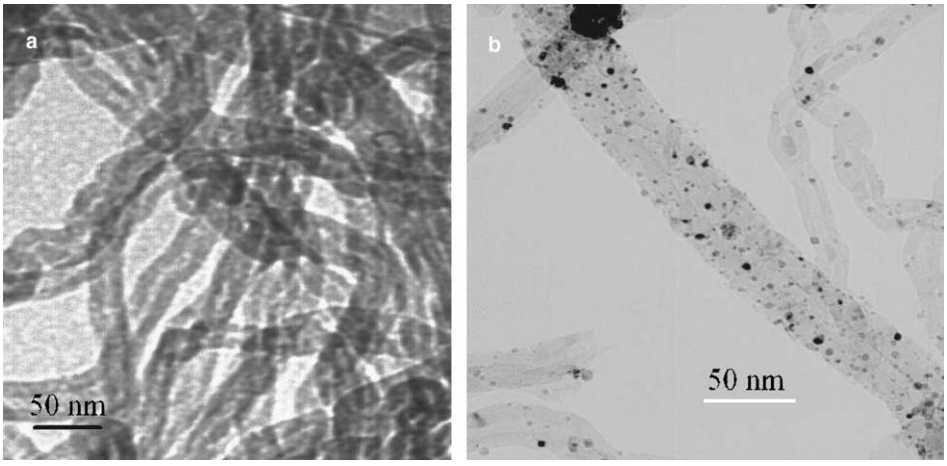

Fig. 2. TEM images of CNTs (a) and Pt–Ru/CNT (b).