Short communication

Electrocatalytic oxidation of formaldehyde on palladium nanoparticles supported on multi-walled carbon nanotubes

Guo-Yu Gao, Dao-Jun Guo, Hu-Lin Li *

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

Abstract

Palladium (Pd) nanoparticles were dispersed on iodinated multi-walled carbon nanotubes (I-MWNTs) by the aqueous solution reduction of $Pd(NO_3)_2$ with formaldehyde. The structure and nature of the resulting Pd-MWNT composites were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The electrocatalytic properties of the Pd-MWNT modified glassy carbon electrode (Pd-MWNT/GCE) for formaldehyde oxidation have been investigated by cyclic voltammetry; high electrocatalytic activity of the Pd-MWNT/GCE can be observed. This may be attributed to the high dispersion of palladium catalysts and the particular properties of MWNT supports. The results imply that the Pd-MWNT composite has good potential applications in fuel cells.
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Keywords: MWNTs; Palladium nanoparticles; Electrocatalytic; Formaldehyde

1. Introduction

Palladium (Pd) and palladium group metals are the most frequently employed catalyst materials on inert supports like carbon, for the electrochemical reactions in fuel cells operating with acid or alkaline electrolytes [1–4]. Attempts have been made to obtain high surface area catalysts in order to achieve high efficiencies. It is well known that the basic properties of the catalysts are strongly affected by the microstructure and the surface reactivity [5,6]. Among these factors, the morphology and nanostructure of supports are considered to be the main factors in obtaining high dispersion of nanoparticle catalysis. Carbon nanotubes (CNTs), as a new form of carbon, have become the focus of current research due to their special mechanical and electronic properties [7–10]. Due to their interesting properties, nanometer size and high surface area, CNTs are also of great interest for many applications, for example, batteries [11], flat panel displays [12], and chemical sensor [13]. Furthermore, high accessible surface area, low resistance, and high stability [14] suggest that CNTs are suitable materials for electrodes and catalyst supports in fuel cell applications [15–19].

HCHO, as one of the intermediate products of methanol oxidation as well as HCOOH, is important to investigate its electrochemical oxidation behavior. Several reports have been published on the oxidation of HCHO [20–25] but many of them were carried out on Pt electrodes. Villullas et al. [26] prepared Pt-modified SnO_2 thin film electrodes by a sol–gel method for the anodic oxidation of formaldehyde; Santos and Bulhões [27] reported the electrochemical and adsorptive behavior of formaldehyde at Pt electrodes in acidic media. Until now, no sufficient investigation has been made for HCHO using carbon nanotubes as the support materials compared to CH_3OH or HCOOH.

This paper reports spontaneous Pd nanoparticle formation on iodinated multi-walled carbon nanotubes (I-MWNTs) [28] by the aqueous solution reduction. The key idea is to combine Pd nanoparticles and I-MWNT to modify a GC electrode in order to improve their electroactivity for formaldehyde oxidation.

2. Experimental

2.1. Preparation and pretreatment of MWNTs

MWNTs used in this work were produced via the chemical vapor deposition method, and their purity was about 95%.

* Corresponding author. Tel.: +86 931 891 2517; fax: +86 931 891 2582.
  E-mail address: lihl@lzu.edu.cn (H.-L. Li).

MWNT samples are usually 10–25 nm in diameter. MWNT (100 mg) was dispersed in 100 cm^3 concentrated nitric acid heated and refluxed for 10 h [29,30]. Then the mixture solution was filtered with a PTFE membrane disc filter (1 μm pore size) under vacuum followed by washing several times with double-distilled water for neutralization. After the oxidation treatment, the sample was obtained in order to produce oxide functional groups (such as quinoid, carbonyl, and carboxylate) at the defect sites located at the ends and/or the sidewalls of the carbon nanotubes.

2.2. Catalyst preparation

Twenty milligrams of surface-oxidized MWNTs prepared as described above was suspended in ethanol with ultrasonic treatment. Iodinated MWNT (I-MWNT) were synthesized according to the chloramines-T (N-chloro-P-toluenesulfonamide) method, in brief, a mixture of 20 mg of surface-oxidized MWNTs, 20 mL of 40 mmol L^{-1} NaI solution and 20 mL of 5 mg L^{-1} chloramines-T was reacted in deionized water for 3 min at room temperature. Then the reaction was terminated with 40 mL of 8 mg L^{-1} Na$_2$S$_2$O$_5$. After that the solution was filtered till it was neutralized. Some Pd(NO$_3$)$_2$ solution was added to the I-MWNT, so that it had the desired Pd loading. Pd attached to the I-MWNT by adding formaldehyde (37%) to the solution at 20 °C for 20 h. The solid was filtered and washed with deionized water and then dried at 80 °C for 6 h. For comparison, Pd nanocatalyst supported on Vulcan-72 (Pd/C), and their electrodes were also prepared under the same preparation conditions.

2.3. Preparation of Pd-MWNT catalyst electrode

Five milligrams of Pd-MWNT catalyst, 50 μL of Nafion solution (5 wt.%, Aldrich) and 1.0 mL of alcohol were mixed. A measured volume (ca. 25 μL) of this mixture was transferred via a syringe onto a glassy carbon electrode and heated under an infrared lamp to remove the solvent.

2.4. Characterization

The morphology of synthesized nanoparticles was observed on a Hitachi 600 transmission electron microscopy (TEM). The samples were prepared by dipping the Pd-MWNT ethanol solution on the Cu grids and observed at 100 kV.

X-ray diffraction (XRD) data from the samples were collected using a Rigaku D/MAX 24000 diffractometer with Cu Kα radiation.

Electrochemical measurements were performed with BAS100B electrochemical analyzer (USA), a conventional cell with a three-electrode configuration was used throughout this work. The working electrode is a Pd-MWNT/GCE (glassy carbon electrode), platinum foil was used as counter electrode, saturated calomel electrode (SCE) was reference electrode, and all potentials were measured and reported with respect to SCE in this paper. All measurements were performed at room temperature.

3. Results and discussion

3.1. TEM analysis of the Pd-MWNT catalyst

It is well known that the MWNTs prepared by the chemical vapor deposition method are accompanied with many metal catalysts, support materials and amorphous carbon. Therefore, it is necessary to use some surface treatment procedures to purify the raw MWNTs to ensure the Pd particles are well deposited onto the MWNTs. Fig. 1(a) shows the TEM image of the purified MWNTs treated with concentrated nitric acid, showing a very clean surface for all the tubes. It can also be seen that the MWNTs are very long and present as a highly entangled
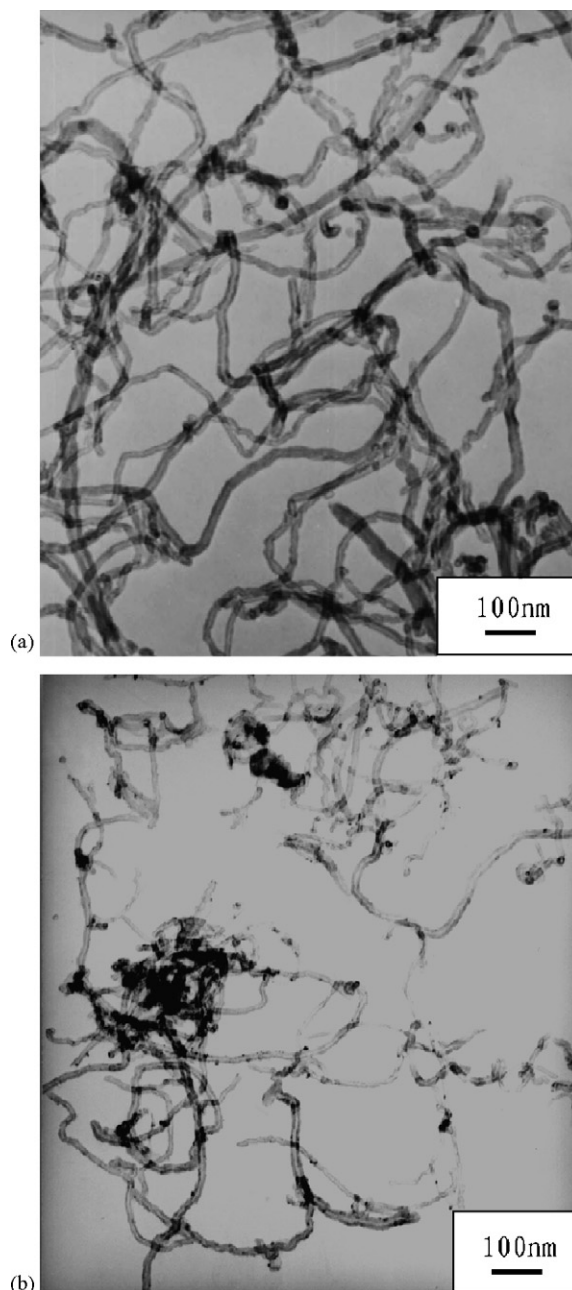

Fig. 1. Transmission electron micrograph (TEM) images of MWNT (a) and Pd-MWNT composites (b).
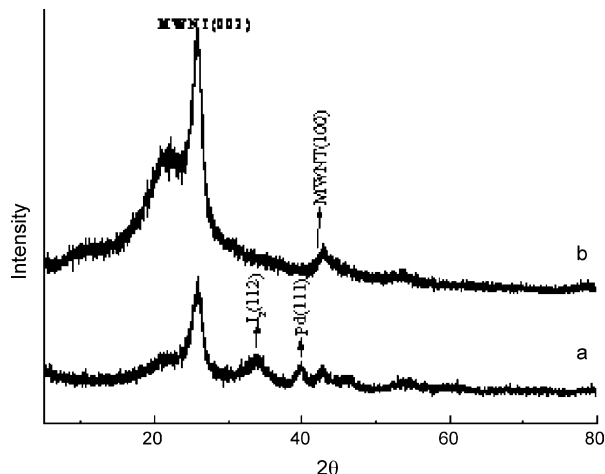
Fig. 2. XRD patterns of the Pd-MWNT catalyst (a) and MWNT (b).

Fig. 3. Cyclic voltammograms of 0.3 M HCHO in 0.1 M NaOH solution at MWNT (A), Pd/C (B), and Pd-MWNT (C) modified glassy carbon electrodes (50 mV s^{-1}).

network structure. The direct evidence of the formation of Pd nanoparticles on the surface of MWNTs is given by Fig. 1(b). It can be seen that well-dispersed, spherical particles are anchored onto the external walls of MWNTs, and the size range of these particles is about 5–10 nm.

3.2. XRD analysis of MWNT and Pd-MWNT catalyst

X-ray power diffraction spectrum of Pd-MWNT composites is shown in Fig. 2(a). It clearly shows one main characteristic peak of Pd(1 1 1) at 39.9, which indicates the successful reduction of metal salt to Pd. The peak of Pd looks so broad due to the small size of Pd nanopaticles. Thus, the average size of the Pd particles is 6.3 nm calculated by the Scherrer formula, in good agreement with the results by the TEM image. The diffraction peak at 33.9 is the diffraction of I_2(1 1 2), which comes forth during the synthesizing process. The same X-ray diffraction peaks appear at 25.9 and 42.8 (Fig. 2(b)) can be attributed to the hexagonal graphite structure (0 0 2) and (1 0 0), respectively, which demonstrates that oxidized MWNTs have a high electrical conductivity, and thus, could be fine supporting materials.

3.3. Electrochemical properties of Pd-MWNT composites

In order to elucidate the catalytic function of Pd-MWNT composites in the oxidation of formaldehyde, we first investigated the voltammetric behavior of formaldehyde at the surface of MWNT, Pd/C and Pd-MWNT modified glassy carbon electrodes under identical conditions. Fig. 3(A) shows the typical cyclic voltammograms of 0.3 M HCHO in 0.1 M NaOH solution at MWNT/GCE, no current peaks of methanol oxidation are observed except the typical redox peaks of MWNT, which indicates that the MWNT have no electrocatalytic activity for methanol oxidation. From curve (C) in Fig. 3, on the scan to positive potentials from −0.8 V, the onset of the formaldehyde oxidation was around −0.20 V and a large formaldehyde oxidation peak was observed at +0.38 V and another acute peak of methanol oxidation was seen at +0.08 V on the reverse scan. The catalyst using MWNT give a larger peak than that of XC-72
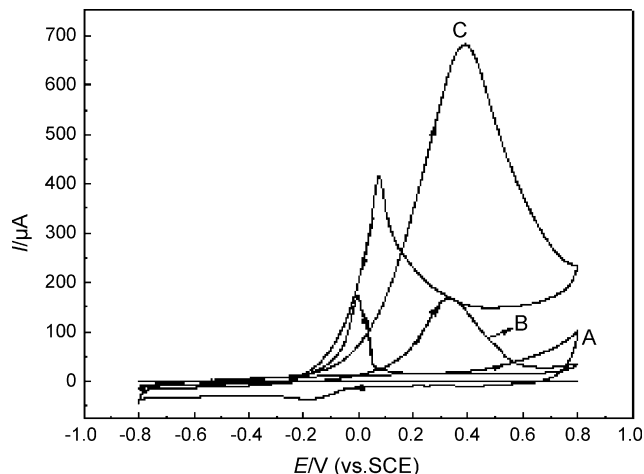
(curve (B)), which indicates a higher electrocatalytic activity in the formaldehyde oxidation reaction. This may be attributed to various causes, including that: (1) the special frame and properties of carbon nanotube make against the production of poisonous intermediates [31,32]; (2) the interaction between Pd and MWNT may change the Gibbs energy of reaction products or byproducts; and (3) highly dispersed Pd nanoparticles on the modified MWNTs.

Fig. 4 shows the CVs of 0.3 M HCHO in 0.1 M NaOH solution at various scan rates. The current of peak 1 was linearly proportional to the square root of scan rate within some range, which indicates that oxidation may be controlled by a diffusion process in a range of scan rates. Additionally, the peak 1 shifts negatively with the increasing scan rates while peak 2 almost remains the same, this demonstrates that the oxidation of HCHO become much easier and is completely an irreversible process [33].

CVs of 0.3 M HCHO in 0.1 M NaOH solution at Pd-MWNT/GCE with different scan upper limits is shown in Fig. 5. The fixed lower limit is −0.8 V. It can be observed that the
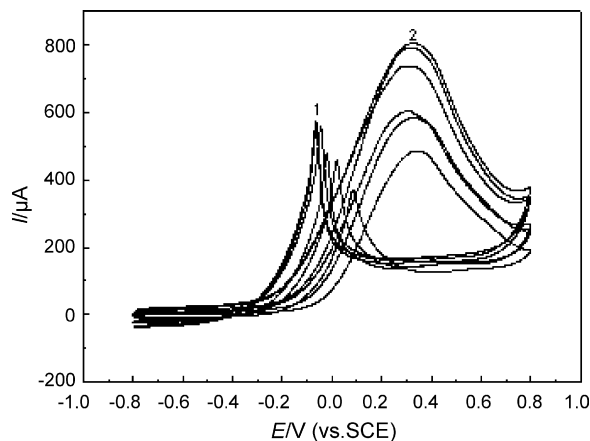

Fig. 4. Cyclic voltammograms of 0.3 M HCHO in 0.1 M NaOH solution at the Pd-MWNT/GCE (scan rate 20, 40, 50, 70, 90, 100 mV s^{-1}).
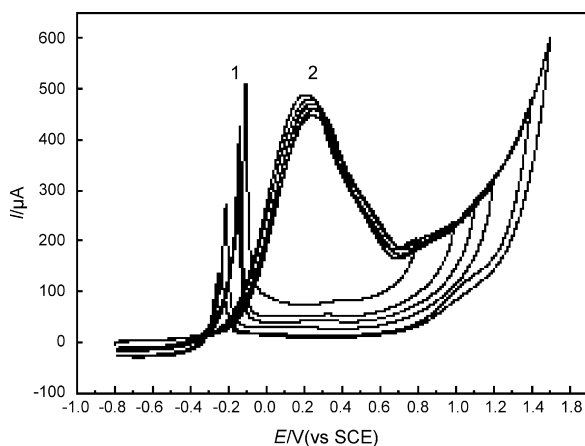
Fig. 5. Cyclic voltammograms of 0.3 M HCHO in 0.1 M NaOH solution at the Pd-MWNT/GCE with different scan upper limits (50 mV s^{-1}).

potential of peak 1 shifts negatively with the increasing scan upper limit while peak 2 almost remains the same, this demonstrates that the oxidation of HCHO becomes much easier to occur. So the oxidation of HCHO is through two approaches, the adsorptive productions and reaction intermediates. With the positive shift of the scan upper limit, the adsorptive byproducts are oxidized sufficiently, this can reduce the poisoning of catalysts. On the clean electrode surface, the oxidation process through intermediate becomes much easier, which can be seen from the negative shift of peak 1.

3.4. Long-term stability of Pd-MWNT composites

The long-term stability of Pd-MWNT composites was also investigated in 0.3 M HCHO + 0.1 M NaOH solution. The results are shown in Fig. 6. It can be observed that the peak current decreases gradually with the successive scans. The loss may result from the consumption of HCHO during the CV scan. It also may be due to the poisoning organic compound [31,32].
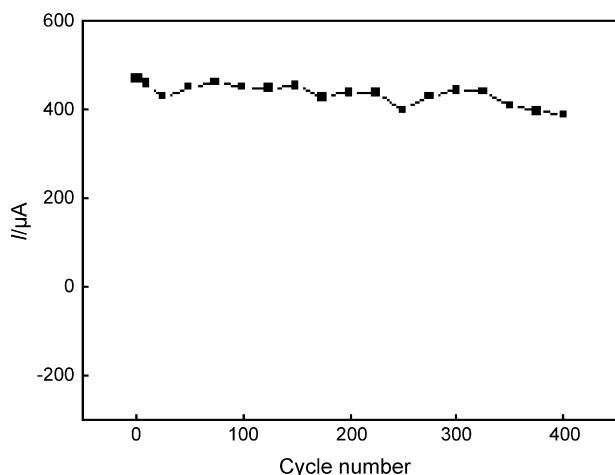

Fig. 6. Long-term stability of Pd-MWNT composites in 0.3 M HCHO + 0.1 M NaOH solution (50 mV s^{-1}).

4. Conclusions

In the present work, Pd-MWNT catalysts were prepared by a typical aqueous solution reduction of Pd(NO$_3$)$_2$ on iodinated multi-walled carbon nanotubes (HCHO reduction). TEM studies show that well-dispersed, spherical particles were anchored onto the external walls of MWNTs, and the size range of these particles was about 5–10 nm. The electrocatalytic properties of Pd-MWNT/GCE for formaldehyde oxidation have been investigated and high electrocatalytic activity is observed. This may be attributed to the high dispersion of nanoscale platinum catalysts and the particular properties of carbon nanotubes.

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