Electrochimica Acta 55 (2010) 2319–2324

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Using RTILs of EMIBF4 as "water" to prepare palladium nanoparticles onto MWCNTs by pyrolysis of $PdCl_2$

Keqiang Ding*, Guokai Yang

College of Chemistry and Materials Science, Hebei Normal University, Yuhua East Road No: 113, Shijiazhuang 050016, PR China

ARTICLE INFO

Article history:
Received 30 July 2009
Received in revised form
29 November 2009
Accepted 30 November 2009
Available online 3 December 2009

Keywords:
Pyrolysis
Palladium nanoparticle
RTILs
MWCNTs
Ethanol oxidation reaction (EOR)

ABSTRACT

For the first time, palladium nanoparticles supported on MWCNTs (multi-walled carbon nanotubes), denoted as Pd/MWCNTs, were prepared by a simple pyrolysis process of $PdCl_2$ dissolved in room temperature ionic liquids (RTILs) of 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) rather than water. X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were used to characterize the structure of Pd/MWCNTs, and the results showed that Pd nanoparticles with highly crystalline structure and a diameter of around 4 nm were prepared, and more importantly, except for carbon and palladium no other elements were detected. The results obtained from a pyrolysis process only containing $PdCl_2$ and EMIBF4 testified that in our developed pyrolysis process, EMIBF4 was used not only as ligands, to form a novel complex, but also as a reducing agent, to reduce Pd^{2+}. The electrocatalytic performance of Pd/MWCNTs-modified glassy carbon electrode towards ethanol oxidation reaction (EOR) was also probed by cycle voltammetry (CV), demonstrating that it was possible to utilize the obtained Pd/MWCNTs as anode materials in fuel cell. Initiating the application of RTILs in the pyrolysis process and finding that EMIBF4 could be employed as ligands and reducing agents are the main contributions of this preliminary work.

1. Introduction

Recently, room temperature ionic liquids (RTILs) have attracted much more attentions due to its excellent features, for example, low-volatility, non-toxicity, non-flame, higher conductivity compared to common organic solvent, and higher solubility for organic substances when comparing with aqueous solutions [1–5]. Summarily, RTILs are mainly applied in the following fields of chemistry (1) being used as solvents in organic synthesis [6]. (2) Being employed as electrolytes in electrochemistry [7]. However, to the best of our knowledge, the application of RTILs in pyrolysis process was not reported so far, though numerous papers concerning RTILs were published every year.

Meanwhile, carbon nanotubes (CNTs) has become an important research field especially since the work achieved by Iijima [8] was published. Many advantages of CNTs have been reported [9]. Of them, being employed as an ideal substrate to modify the electrode surface was thought as the main contribution of CNTs when used in electrochemistry [10,11]. Therefore, immobilizing metal nanoparticles onto CNTs has turned into a main task due to the key role of CNTs and metal nanoparticles in electrocatalysis, biosensor and so on [12,13].

Due to the advantages of CNTs, immobilizing metal nanoparticles (especially, platinum, gold and other transition metals) onto CNTs, has become an important task for electrochemistry researchers. Palladium nanoparticles, due to its potential applications in fuel cells, were also attached onto the surface of CNTs by many developed methods. So far, there are three typical methods to generate Pd nanoparticles onto a CNTs surface. (a) Chemical reduction. For example, Xing and co-workers [14] prepared carbon black-supported Pd nanoparticles by a conventional impregnation synthesis method, in which $PdCl_2$ and $NaBH_4$ were employed as the precursor of palladium and the reducing agent, respectively. Lin et al. immobilized Pd nanoparticles onto CNTs by the reduction of $Pd(hfa)_2{\cdot}xH_2O$ in a supercritical carbon dioxide, in which hydrogen gas was used as reducing agents [15]. (b) Thermal decomposition. For instance, Chen and co-workers synthesized the carbon nanotubes-supported Pd nanoparticles by a solid-state reaction, in which hydrogen gas was used as a reductive reagent and also $PdCl_2$ the precursors of palladium [16]. (c) Electrochemical reduction. For instance, Cui et al. [17] modified Pd nanoparticles onto the surface of CNTs by means of galvanostat method, in which a constant current of −5 mA was applied on a graphite electrode for 4 h in a 0.05 M H_2SO_4 solution having 2 mM $PdCl_2$.

In this work, we modified Pd nanoparticles onto the surface of MWCNTs through a very simple method of hydrolysis process in which no other reducing agents were introduced except for multi-walled carbon nanotubes (MWCNTs) and RTILs of EMIBF4. XRD,

* Corresponding author. Tel.: +86 311 86268311; fax: +86 311 86269217.
E-mail address: dkeqiang@263.net (K. Ding).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.11.094

TEM and EDS were employed to characterize the obtained samples, revealing that palladium nanoparticles were formed on MWCNTs. The electrocatalytic activities of Pd/MWCNTs towards EOR were examined by cyclic voltammograms (CVs) in a 1 M KOH solution, indicating that EOR could occur on this developed Pd-coated MWCNTs.

2. Experimental

2.1. Chemicals and materials

Multi-walled carbon nanotubes (MWCNTs, outer diameter: 10–20 nm, length: 0.5–500 μm) were purchased from Shenzhen Nanotech Port Co., Ltd. (China). RTILs of EMIBF4 with a purity of more than 99% were obtained from Hangzhou Chemer Chemical Co., Ltd. (China). A glassy carbon (Ø = 2 mm) electrode purchased from Tianjin Aida Co., Ltd. (China) was used as the working electrode.

2.2. Pyrolysis of $PdCl_2$ to form Pd nanoparticles onto MWCNTs in EMIBF4

MWCNTs supported Pd catalysts were synthesized by a simple pyrolysis process. Firstly, 2 ml EMIBF4 containing 5×10^{-3} M $PdCl_2$ and 10 mg MWCNTs were mixed together to yield a suspension solution, and then this resultant solution was ultrasonicated for 30 min. Secondly, the obtained suspension solution was placed in a home-made autoclave at room temperature, and the well sealed autoclave was transferred to a box-type furnace. Lastly, the temperature of the box-type furnace was increased to 230 °C within 20 min, and then it was kept for 3 h to fulfill the pyrolysis process. The resultant solution was filtered, and the obtained samples were washed with redistilled water thoroughly, and dried at ambient to generate the Pd-coated MWCNTs (denoted as Pd/MWCNTs).

2.3. Preparation of Pd/MWCNTs-coated glassy carbon electrode

Prior to each experiment, the working electrode of a glassy carbon (GC) electrode with a diameter of 2 mm was successively polished with 1 and 0.06 μm alumina powder on a microcloth wetted with doubly distilled water, leading to a electrode with a mirror like surface. For the preparation of Pd/MWCNTs-coated electrode, 4.6 mg of the resultant Pd/MWCNTs materials was added into a 1 ml aqueous solution of sodium lauryl sulfate (SDS) (the content of SDS is 1.5 mg/ml), and then the mixture was treated for 30 min with ultrasonication to form a uniform suspension. 5 μL of this mixture was dropped onto the surface of a well-treated GC electrode. Finally, the resultant Pd/MWCNTs-modified GC electrode was dried with hot air prior to the following electrochemical experiments.

2.4. Characterization

X-ray diffraction (XRD) analysis of the catalyst was carried out on a Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu Kα source (λ = 0.154 nm) at 40 kV and 30 mA. The 2θ angular region between 10° and 90°was explored at a scan rate of 1°/step. The obtained samples were characterized using transmission electron microscopy (TEM, HITACHI, H-7650, Japan). EDS spectrum analysis was carried out on a X-ray energy instrument (EDAX, PV-9900, USA). UV–vis spectra were obtained on a spectrophotometer V-500 (JASCO, Japan). Pyrolysis was implemented in a SRJX-8-13 box-type furnace equipped with KSY 12-16 furnace temperature controller.

Electrochemical experiments were conducted on a model CHI660B electrochemical workstation (Shanghai Chenhua Apparatus, China). A conventional three-electrode system was employed, in which a Pd/MWCNTs-modified GC electrode and platinum wire was used as the working electrode and counter electrode, respectively. It should be noted that the reference electrode is a saturated calomel electrode (SCE). All potentials in this paper were reported with respect to SCE. Experiments were carried out at room temperature.

3. Results and discussion

3.1. XRD analysis

The typical XRD patterns of the obtained samples are shown in Fig. 1. For the pattern (a) in Fig. 1, the diffraction peaks at 2θ of 26.1° and 43.2° are indexed to (0 0 2) and (1 0 1) planes of carbon nanotubes (CNTs), respectively, based on the data of JCPDS card 26-1077, according with the previous report very well [18]. After the pyrolysis process, the diffraction peaks corresponding to CNTs are still clearly exhibited, suggesting that the pyrolysis process did not destroy the crystal structure of MWCNTs. Also, some novel peaks were exhibited, and they can be assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face-centered cubic (fcc) palladium (JCPDS card, 89-4897), consistent with the former report [19] very well, and no impurity phases can be detected, indicating the formation of pure Pd and they are highly crystalline. Since no other diffraction peaks were found, Fig. 1 strongly demonstrates that only Pd particles are formed on the surface of MWCNTs. The particle average size was estimated using the Debye–Scherer formula, $t = 0.89\lambda/(\beta \cos\theta_B)$, where λ is the X-ray wavelength (1.5406 Å), θ_B is the Bragg diffraction angle, and β is the peak width at half-maximum. The average size was 4.5 nm and 4.8 nm as calculated from the Debye–Scherer formula on the (1 1 1) and (2 0 0) peak, respectively [20]. Also, the calculated particles size is very close to that measured by TEM studied, as shown below.

Fig. 2a is the TEM images of obtained samples. It can be seen that after the pyrolysis process, as shown by image (b), some black nanoparticles were exhibited on the surface of MWCNTs, which is

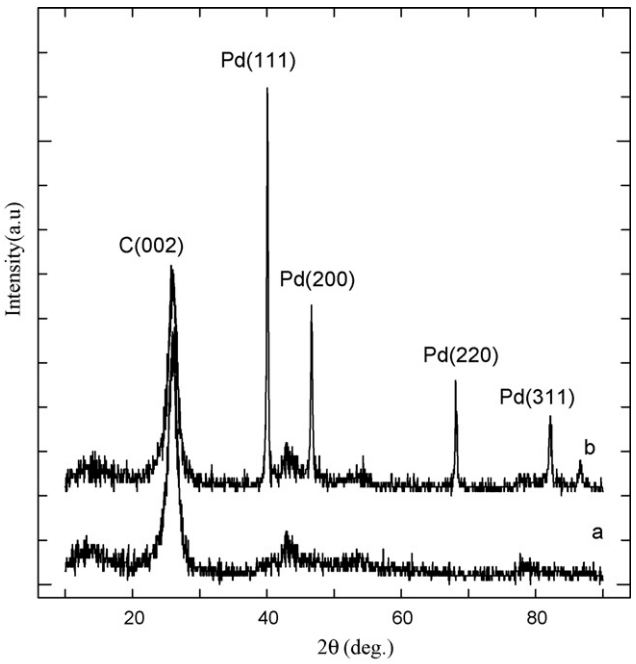

Fig. 1. XRD patterns for MWCNTs (a) and Pd/MWCNTs (b).