Thin Solid Films 584 (2015) 98–102

Contents lists available at ScienceDirect

Thin Solid Films

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

Pulse electrodeposition of Pt and Pt–Ru methanol-oxidation nanocatalysts onto carbon nanotubes in citric acid aqueous solutions

Huei-Yu Chou [a], Chien-Kuo Hsieh [b], Ming-Chi Tsai [a], Yu-Hsuan Wei [a], Tsung-Kuang Yeh [a,*], Chuen-Horng Tsai [a,*]

[a] Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC
[b] Department of Materials Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan, ROC

ARTICLE INFO

Keywords:
Carbon nanotubes
Platinum
Platinum–ruthenium
Pulse electrodeposition
Citric acid
Sulfuric acid
Methanol oxidation

ABSTRACT

In this study, platinum nanoparticle/carbon nanotube (Pt NP/CNT) and platinum–ruthenium nanoparticle (Pt–Ru NP/CNT) hybrid nanocatalysts were prepared by the pulse-electrodeposition method in different aqueous solutions containing citric acid (CA) or sulfuric acid (SA). The electrocatalytic properties of the Pt NP/CNT and Pt–Ru NP/CNT electrodes prepared using different aqueous solutions were investigated for methanol oxidation. The results show that the electrochemical mass activities of these hybrid nanocatalysts prepared in the CA aqueous solution were increased by factors of 1.46 and 2.77 for Pt NPs and Pt–Ru NPs, respectively, compared with those prepared in SA aqueous solutions using the same procedure. These increased mass activities are attributed to the CA playing dual roles as both a stabilizing agent and a particle size reducing agent in the aqueous solutions. The approach developed in this work enables further reductions in the particle sizes of noble-metal nanocatalysts.

1. Introduction

Carbon nanotubes (CNTs) have potential applications in a wide variety of scientific areas. Because of their unique quasi-one-dimensional structural features, high specific surface area, high conductivity, and electrochemical stability, CNTs have been used as anchored templates to scale down the particle size to nanometer dimensions [1]. Researchers have readily considered platinum (Pt) and platinum–ruthenium (Pt–Ru) catalysts anchored on CNTs as hybrid nanocatalytic electrodes for low-temperature fuel cells [2–12], their goal was to increase the dispersion of the catalysts via the nanoscale surface curvature and higher specific surface area of the CNTS to improve the activities of the Pt and Pt–Ru catalysts. The electrochemical property of mass activity (M.A., the reaction current density normalized by the catalyst loading) of a catalyst is well known to be strongly related to its nanoparticle (NP) size and distribution. Researches have recently reported a number of approaches for preparing Pt and Pt–Ru catalyst NPs by electrodeposition methods [2,13,14]. The electrolytes most commonly used for the electrodeposition of Pt and Pt–Ru NPs are sulfuric acid (SA) aqueous solutions because of their excellent electrical conductivity. In addition, an electrode with Pt–Ru particles being simultaneously electrodeposited onto CNTs in an SA aqueous solution at a more negative potential exhibited a better efficiency in methanol oxidation (i.e., greater methanol oxidation current density at a lower potential and with better CO tolerance). However, the excellent electrical conductivities of the SA aqueous solutions result in high diffusional mass transport of metal ions during the electrodeposition process, which in turn leads to clustering or growth of the metal NPs. To control the size of nanocatalysts during electrodeposition, a stabilizer [15] and viscous additive [16] are added to the acid aqueous solutions to prevent agglomeration, which enables the electrodeposition of NPs with a desirable size and better dispersion.

Citric acid (CA) has been used for the electrodeposition of homogeneous alloys such as gold–cobalt [17], nickel–ferrite [18], rhenium–nickel [19], and nickel–tungsten [20]. Notably, CA serves dual roles as an electrolyte and a stabilizing agent. CA can adsorb onto the surface of NPs, where it exhibits hydrophobic and coulombic effects [21], which enable it to function as a stabilizer. In this paper, we use CA as a stabilizing agent and a reducing agent for the pulse-electrodeposition of Pt or Pt–Ru NPs on CNTs directly grown on carbon cloth to demonstrate that the particle sizes of Pt and Pt–Ru catalysts can be further reduced at the foregoing negative deposition potential.

2. Experimental methods

The processes for the synthesis and subsequent hydrophilic treatment of CNTs were similar to those reported previously [22], except that an acetylene gas stream was used as a carbon source. In a three-electrode electrochemical cell, Pt and Pt–Ru NPs were electrodeposited onto the prepared specimens (CNTs directly grown on carbon cloth that acted as working electrodes). A Pt mesh served as the counter electrode,

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* Corresponding author.
E-mail address: tsai@aec.gov.tw (C.-H. Tsai).

http://dx.doi.org/10.1016/j.tsf.2014.12.016
0040-6090/

and a saturated calomel electrode (SCE) was used as the reference electrode. A potential of $-1.20\ V_{SCE}$ was therefore chosen in this study. For the electrodeposition of Pt–Ru and Pt, 0.2 mM $H_2PtCl_6 \cdot 6H_2O$ (Alfa Aesar, item #11051) with and without 0.8 mM $RuCl_3 \cdot xH_2O$ (Alfa Aesar, item #43364) were formulated in CA or SA aqueous solutions as precursors. Two different electrolytes—0.15 M CA and 0.01 M SA—were used to control the pH values of all of the electrolytes in the range between 1.9 and 2.2. The electrolytes were saturated with Ar gas during the deposition processes conducted under ambient pressure and magnetic stirring and at a controlled temperature of 30 °C. The Pt/CNTs and Pt–Ru/CNTs prepared in the CA electrolyte were denoted as CA-Pt and CA-PtRu, respectively, whereas those prepared in the SA electrolyte were denoted as SA-Pt and SA-PtRu, respectively. After the electrodeposition process (20 min), the catalytic electrodes (Pt/CNTs and Pt–Ru/CNTs) were thoroughly cleansed with distilled water. Before the tests in Ar-saturated 1 M CH_3OH + 0.5 M H_2SO_4 aqueous solutions, each specimen was activated by cyclic voltammetry (CV) at a scan rate of 50 mV s^{-1} in the potential range between -0.25 and $+1.0\ V_{SCE}$ for 5 cycles in an Ar-saturated 0.5 M H_2SO_4 aqueous solution. The CV analyses for evaluating the methanol oxidation efficiency of the specimens were conducted at a scan rate of 20 mV s^{-1} in the potential range between -0.2 and $+0.9\ V_{SCE}$ for 5 cycles. An Autolab PGSTAT302N potentiostat was used for all of the electrochemical operations. The morphologies and structures of the specimens were analyzed by scanning electron microscopy at 10–15 kV (SEM, JEOL JSM-6330F), transmission electron microscopy at 200 kV (TEM, JEM-2100F), and X-ray diffraction scan at 20 kV and scanning angle from 10°–2θ to 90°–2θ with a scanning rate of 1.6° min^{-1} (XRD, Rigaku, Cu-Kα source ($\lambda = 1.54056$ Å) with a Ni filter). The loadings of Pt and Pt–Ru in 1 cm^2 sample were ultrasonicaly dissolved into 4 mL aqua regia and 1 mL hydrofluoric acid. Its diluted solution of 50 mL from initial was estimated on the basis of data measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce) with parameters 1.5 kW frequency power, 15 L min^{-1} plasma gas flow and 2 mL sampling solution.

3. Results and discussion

3.1. Characterization of the CNT-supported Pt and Pt–Ru electrodes

SEM micrographs of the prepared specimens are shown in Fig. 1. Well-dispersed Pt and Pt–Ru NPs were observed on the CA-Pt and CA-PtRu specimens (Fig. 1(a) and (c)). Small areas of accumulated Pt clusters of approximately 150 to 200 nm in diameter, along with petal-shaped agglomerations, were typically observed on the SA-Pt specimen, as shown in Fig. 1(b). Compared with the results in our previous work [22], where catalysts were prepared in 0.5 M SA aqueous solutions by electrodeposition, the use of CA during the electrodeposition process had a distinct positive effect on the dispersion of the Pt and Pt–Ru catalysts and on the reduction of their particle sizes at the more negative deposition potential. According to the TEM micrographs shown in Fig. 2, the particle sizes of CA-Pt and CA-PtRu were 2–6 and 2–3 nm, respectively, consistent with the SEM observations. Accordingly, we speculated that CA provided an adequate ionic conductivity during the deposition processes, reduced the particle sizes of the Pt and Pt–Ru catalysts, and prevented them from serious agglomerating.

Crystallinities of the Pt and Pt–Ru catalysts were further investigated by XRD. Fig. 3 shows that the 2θ peaks at ca. 44.5° were signals from Ni (111). The 2θ peaks of Pt (111) at ca. 39.7° were observed in the patterns of the prepared specimens in which pure Pt was deposited, whereas the 2θ peaks of Pt (200) at ca. 46.2° were only observed in the SA-Pt specimen. The Pt (111) peak was observed to slightly shift to ca. 40.5° in the patterns of specimens with Pt–Ru catalysts (CA-PtRu and SA-PtRu), indicating that the Pt and Ru atoms had formed Pt–Ru bimetallic alloy [23]. Theoretically, the average size of crystallized particles is proportional to the reciprocal of the half-peak width (HPW) of a 2θ-peak, as described by the Scherrer formula [24]. Fig. 3 shows that the HPW of the Pt (111) peak in the pattern of CA-Pt (approximately 1.24) is broader than that in the pattern of SA-Pt (approximately 0.71), indicating that the mean particle size of the specimen prepared

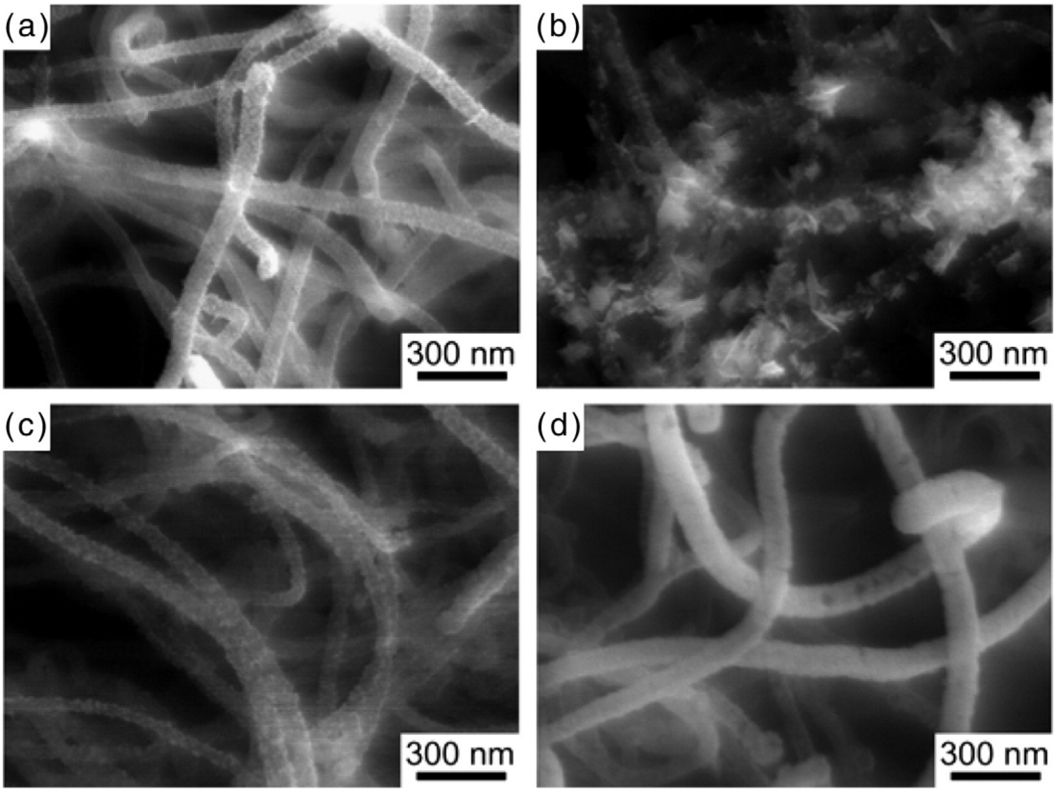

Fig. 1. SEM micrographs of prepared specimens: (a) CA-Pt, (b) SA-Pt, (c) CA-PtRu, and (d) SA-PtRu.