



Electrochemical deposited high-crystallinity vertical platinum nanosheets onto the carbon nanotubes directly grown on carbon paper for methanol oxidation

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ABSTRACT

In this study, the high-crystallinity vertical platinum nanosheets (PtNSs) were deposited onto the carbon nanotubes (CNTs) directly grown on the carbon paper (CP) as the PtNSs/CNTs/CP hybrid nanostructure to promote the electrocatalytic performance of methanol oxidation reaction (MOR). CNTs were initially synthesized on the carbon fibers of CP as catalyst supporting material by chemical vapor deposition method. Subsequently, PtNSs electrocatalysts with high activity were synthesized onto the CNTs surface by electrodeposition method. Scanning electron microscopy, high-resolution transmission electron microscopy and X-ray diffraction were employed to investigate the morphology and structural features of PtNSs/CNTs/CP. The Pt loading was examined by inductively coupled plasma mass spectrometry. The electronic structures of PtNSs were examined by X-ray photoelectron spectroscopy. The electrocatalytic properties were examined by Cyclic Voltammetry method. Our work suggests that PtNSs/CNTs/CP electrode could provide higher surface area with a lower Pt content and show better crystalline than Pt Black. The catalytic efficiency of prepared PtNSs/CNTs/CP electrode, as determined by the electrochemical active surface area and the catalyst mass activity for the MOR, were 1.39 times and 2.95 times better than those of a commercial Pt-black catalyst, suggesting that PtNSs/CNTs/CP electrode might be a good candidate for catalyst of MOR.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention as promising energy devices due to a series of advantages, including simple construction, the high energy density at low temperature, the high durability, easy operation, and pollution-free production [1,2]. However, few obstacles were existed in realizing the commercialization of DMFCs, particularly the high expense of platinum (Pt) which is still recognized as the best catalyst for methanol oxidation reaction (MOR) [3]. Therefore, morphology controlled nanostructures of Pt were desired to achieve the high catalytic activities, such as Pt nanoparticles [4,5], Pt nanoflowers [6,7], Pt nanocubes [8,9], Pt nanowires [10,11], and Pt nanodendritic [12].

In addition, the supporting material of catalyst has been recognized as one of the important factors in determining the electrochemical performance of the catalysts. Various supporting materials of catalysts have

been studied, including conductive polymers [13–15], titanium oxide nanotubes [16–19], and carbon nanomaterials [20–22]. Among these supporting materials, carbon nanotubes (CNTs) have received a great deal of attention to replace conventional activated carbon black due to their structural tube features, superior electrical conductivity and high stability in electrochemical reaction [23–25]. In conventional process, the mixed catalyst bearing CNTs and polymer electrolytes were pasted onto diffusion layers such as carbon papers (CP) as a catalytic gas diffusion layer at the anode in fabricating a DMFC. However, the pasting process usually involved binder materials that induced the agglomerations, which not only decreased the active surface area but also provided a poor adhesion to the substrate.

Directly growing CNTs on CP could avoid undesirable effect stemmed from pasting process mentioned above and improve the electrical conductivity between the catalyst supports and the diffusion layer, related researches for low temperature fuel cells were studied [26,27]. Hence, in this work, the CNTs were directly grown on CP as catalyst supporting material and following vertical Pt nanosheets (PtNSs) were electrodeposited on. The activities of the prepared catalytic electrodes were examined by half-cell tests in mixed methanol (CH₃OH) and

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sulfuric acid (H_2SO_4) to learn the relationship between activity and catalyst morphology accompanying with several material analyses.

2. Experimental

2.1. Preparation of the PtNSs/CNTs on CP substrate

2.1.1. Synthesis of CNTs

In this study, CNTs were initially grown on the CP (EC-TP1-060, ElectroChem. Inc.) via a thermal chemical vapor deposition (CVD). Prior to the CVD process, a thin layer of 70 nm Ti followed by 12 nm Ni was deposited on CP by electron-gun evaporation (ULVAC, EBX-10C, Japan). The Ni layer acted as a catalyst for hydrocarbon decomposition and for the growth of CNTs, while the Ti thin film was acted as a buffer for enhancing the adhesion of Ni on the CP. In order to nucleate the Ni thin film into nanoparticles and reduce the catalysts, the as-prepared specimens were then loaded into the quartz tube of the home-made furnace and thermally pretreated at 850 °C under a mixed gas of 320 standard cubic centimeter per minute (sccm) Nitrogen (N_2) and 70 sccm Hydrogen (H_2) for 30 min. Subsequently, for CNTs growth, a 15 sccm Acetylene (C_2H_2) was added as a carbon source with the gas mixture of 320 sccm N_2 and 70 sccm H_2 for 30 min. The furnace was then cooled down to the room temperature under N_2 atmosphere. The furnace pressure was maintained at 2666 Pa throughout the process by using an advanced pressure control system (APC, MKS Instruments).

2.1.2. Electrodeposition of PtNSs

Prior to the electrodeposition of PtNSs, the specimens underwent a hydrophilic treatment in order to increase the number of PtNSs deposition sites on the CNTs surfaces, the details of the process were described in our previous work [28]. A three-electrode electrochemical configuration was used to deposit PtNSs at the applied potential of $-0.3 V_{\text{SCE}}$ (voltage vs. saturated calomel electrode, SCE) onto the specimens that served as the working electrode, a Pt mesh served as the counter electrode and a SCE was used as the reference electrode. The electrolyte consisted of the Argon (Ar) saturated mixed solution of 0.8 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, item #11,051, USA) and 0.1 M H_2SO_4 (96.8%, J.T. Baker, item # JT-9244-05, USA).

2.2. Characterization

The microstructures of the specimens were characterized by applying high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100F) and scanning electron microscopy (SEM, JEOL, JSM-6330F). The crystal structures of the specimens were revealed by using X-ray diffraction (XRD, PANalytical X'Pert PRO MPD, Netherlands) operated with $\text{Cu-K}\alpha_1$ (1.54187 Å). In order to study the surface chemical states of the specimens, X-ray photoelectron spectroscopy (XPS) was conducted by using a PHI Quantera SXM/AES 650 (ULVAC-PHI Inc., Japan.) with a hemispherical electron analyzer and a scanning monochromated Al $\text{K}\alpha$ ($h\nu = 1486.6$ eV) X-ray source. The XPS peak deconvolution and assignment of binding energies were corrected by the C1 s peak at 284.6 eV. For spectral analysis, curve fitting was performed using the Gaussian–Lorentzian method after applying the Shirley background correction. The Pt content of each specimen was determined by inductively coupled plasma-mass spectrometer (ICPMS, Agilent 7500ce, USA). The electrochemical activity studies were performed by the method of cyclic voltammetry (CV) in a three-electrode configuration in the solution consisted of 0.5 M H_2SO_4 with or without 1 M CH_3OH , the specimen served as the working electrode, a Pt mesh and a SCE were used as counter electrode and reference electrode, respectively.

All the electrochemical measurements, the hydrophilic treatment of CNTs and the electrodeposition of PtNSs on CNTs were performed by using a potentiostat station (CHI1140B, CH Instruments, Inc., USA). In addition, in order to examine the enhancement of the prepared PtNSs/

CNTs/CP electrode, the commercial Pt Black catalyst with 40 wt.% Pt which purchased from Premetek was used as a reference catalyst.

3. Result and discussion

3.1. Characterizations

Fig. 1(a) and (b) showed the low-magnification SEM images of CP and CNTs/CP specimens, respectively. As we can see from Fig. 1(b), well distribution and high density CNTs with the 100 nm in mean diameter and 2–3 μm in length were grown vertically on the CP. The as-prepared CNTs with the larger space between each of CNTs could provide enough diffusion channel to exchange reactants and products in the chemical solution for further either electrodeposition of PtNSs or methanol oxidation reaction on the catalyst of PtNSs of the inner CNTs. Fig. 1(c) and (d) showed the high-magnification SEM images of CNTs/CP and PtNSs/CNTs/CP specimens, respectively. As we can see from Fig. 1(d), the SEM image of PtNSs/CNTs/CP electrode displayed that the CNTs were well covered by PtNSs, we herein suggest this phenomenon might attribute to the process of hydrophilic pretreatment of CNTs. According to our previous report [28], the morphologies of the reduced Pt nanomaterials would be affected by the hydrogen-bubble adsorption on the electrode surface during the electrodeposition. Therefore, PtNSs in this study were electrodeposited via a potentiostatic approach at the applied potential of $-0.3 V_{\text{SCE}}$, which was lower than the standard hydrogen reduction reaction potential of $-0.241 V_{\text{SCE}}$, thus the hydrogen bubbles were expected to be generated for the assistance to synthesize the specific morphology of Pt nanomaterials.

Fig. 1(e) showed the TEM image of PtNSs/CNTs/CP electrode, similar observation could also be confirmed by the SEM depicted in Fig. 1(d), showing that the CNTs were well covered by PtNSs. Fig. 1(f) showed HRTEM image of PtNSs, the inter-fringe distances of Pt were ~ 0.23 nm and ~ 0.19 nm which were ascribed to Pt (111) and Pt (200), respectively [29]. The results of HRTEM image suggested that the as-prepared PtNSs retained high crystallinity with minimum defects.

Crystallinities of the prepared specimens were further investigated by XRD in the scan range from a 2θ of 30° to 80°. Fig. 2 showed the XRD patterns of the prepared specimens. The bottom curve and the middle curve were the XRD pattern of CP and CNTs/CP specimens, respectively, and the diffraction peaks shown at $2\theta = 42.3^\circ, 44.5^\circ, 54.7^\circ$, and 77.4° correspond to (100), (101), (004), and (110) planes of carbon (JCPDS, No. 89-7213). The top curve was the XRD pattern of PtNSs/CNTs/CP electrode, and the diffraction peaks shown at $2\theta = 39.8^\circ, 46.3^\circ$, and 67.5° correspond to (111), (200), and (220) planes of Pt (JCPDS, No. 87-0646), respectively.

Fig. 3 showed the XPS spectrum which were used to define the oxidation state of the as-prepare PtNSs. The Pt 4f signal consisted of three pairs of the doublets. The first doublet (71.3 and 74.6 eV) was assigned to the metallic state Pt^0 [30], the second set of doublets (75.3 and 72 eV) was caused by the Pt^{2+} chemical state as PtO or $\text{Pt}(\text{OH})_2$ [30], and the third doublet of Pt was the weakest in intensity at even higher binding energies (74.5 and 77.8 eV) of Pt^{4+} such as PtO_2 [30,31]. All the doublets were fit with 4:3 peak area ratio and 3.3 eV peak separation [32]. With measuring the relative peak areas ratio, the percentage of Pt^0 species in PtNSs was higher than that of the Pt Black. According to the previous reports [33,34], the activity of Pt might be higher as the amount of oxidized Pt lower since the oxygen would block the active sites of Pt during the MOR. Hence, based on the result of XPS in this study, we herein suggest that our prepared PtNSs might possess higher activity than that of Pt Black. The binding energy values and the corresponding peak area ratios obtained from Fig. 3 were also given in Table 1.

3.2. Electrochemical analysis

The electrochemical activities were studied by the method of CV. Fig. 4 showed the effect of different scan rate on the MOR of the

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