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PtRu overlayers on Au nanoparticles for methanol electro-oxidation

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ABSTRACT

PtRu overlayer structures were deposited on the surface of carbon-supported Au nanoparticles with atomic-scale thicknesses and their activity for methanol electro-oxidation was examined. The results of transmission electron microscopy, X-ray diffraction, and cyclic voltammetry demonstrated that the PtRu deposited uniformly on Au nanoparticles. The peak potential in CO stripping analysis shifted to higher potentials with decreasing amounts of PtRu, indicating stronger Pt–CO and Ru–CO bonding. PtRu utilization was enhanced with decreasing PtRu, which might be attributed to the overlayer structures on Au substrates. In methanol electro-oxidation, a negative effect of the strengthened Pt–CO and Ru–CO bonding on surface specific activity and a positive effect of PtRu utilization on mass specific activity might contribute competitively to overall activity for methanol electro-oxidation.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been considered ideal power sources for potable electronic devices. A great deal of research on methanol electro-oxidation has been conducted so far on finding optimal materials for the catalyst, on effective surface structures, and on lowering the overall cost of DMFCs. However, DMFCs are still limited by high production costs due to heavy loading of Pt and its alloy materials. One major effort, nowadays, is on enhancing Pt utilization through modifying the surfaces of non-Pt nanoparticles [1–3]. The Pt utilization in catalysts can be defined as the dispersion or exposed percentage of Pt atoms in the catalyst [1].

Recently, we reported electrocatalytic activities of Pt-modified Au nanoparticles using a successive reduction process [3,4]. Pt-modified Au nanoparticles were synthesized using a highly dispersed Au substrate, resulting in high Pt utilization and greatly enhanced mass specific activities in methanol electro-oxidation. In addition to the high Pt utilization, it was reported, by Zhao and Xu [1], that Pt-modified Au nanoparticles showed high stability in methanol electro-oxidation. However, Pt cannot be used alone in real DMFC catalysts because CO species can be adsorbed on Pt surface during methanol electro-oxidation and can block further adsorption of methanol.

Pt-based bimetallic catalysts (including PtRu, PtSn, PtW, and PtOs) have been investigated, and PtRu electrode has shown the most promising results among them. The role of second metals in the catalysts has been known to be the supplying of OH species at low potentials and/or the weakening of the Pt–CO bond [5,6]. Therefore, it is desirable to modify Au nanoparticles with PtRu bimetallic overlayers.

In surface-modified catalysts, the intrinsic activities of active sites, in addition to the Pt utilization, are also worthy of consideration for the interaction between underlayer and overlayer materials (between Au and PtRu in this case). It is interesting that the Pt–CO bond on Pt-modified Au substrate becomes weaker or stronger than that on the surface with Pt alone. Zeng et al. [7] reported that the CO stripping peak of core-shell Au-Pt nanoparticles was located at potential more negative than that of Pt/C while Du and Tong [8] reported opposite results. In our previous publication [9], Pt-modified Au nanoparticles showed higher mass specific activity but lower area specific activity than Pt/C. We explained that the results can be attributed to (1) the strengthened Pt–CO bonding or the weakened ensemble effect and (2) the enhanced Pt utilization.

In this work, PtRu bimetallic species were deposited onto carbon-supported Au nanoparticles (Au/C) with atomic-scale thicknesses and were applied as catalysts for methanol electro-oxidation. Various amounts of PtRu were loaded onto Au nanoparticles and their surface structures and electrocatalytic activities were investigated.

2. Experimental

2.1. Catalyst preparation

All aqueous solutions were prepared with deionized (DI) water, which was further purified with a Milli-Q system (Millipore water,

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18.2 MΩ cm). The following chemicals were obtained from Aldrich: $HAuCl_4{\cdot}3H_2O$, $H_2PtCl_6{\cdot}xH_2O$, sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7{\cdot}2H_2O$), $NaBH_4$, and ethylene glycol (EG). All chemicals were of analytical grade and were used as received.

The details for preparing Au/C were presented in our previous reports [3,4]. The 30 wt% Au/C was prepared as follows: Au colloid nanoparticles were prepared by adding $HAuCl_4{\cdot}3H_2O$ to DI water, followed by the addition of aqueous sodium citrate. Then, $NaBH_4$ and sodium citrate dissolved solution were added quickly with vigorous stirring [10]. The solution was stirred for 30 min, and then carbon black (Vulcan XC-72R) was added. Au colloid particles were supported spontaneously on the surface of the carbon black particles during the 48 h stirring period. Finally, the solution was filtered and evaporated.

The PtRu overlayers on Au nanoparticles were prepared using a polyol reduction process and the procedure is as follows: Pt precursor ($H_2PtCl_6{\cdot}xH_2O$) and Ru precursor ($RuCl_3{\cdot}xH_2O$) were dissolved in EG and adequate amounts of the solutions were added to Au/C-dispersed EG solution. The total volume of the solution was 200 ml. The solution was refluxed in a three-neck flask at 80 °C for 12 h. After cooling at room temperature, the solution was filtered, washed with DI water and ethanol, and then evaporated. The amounts of Pt and Ru precursors were calculated to produce an atomic ratio of Pt:Ru = 2:1. The PtRu:Au ratio was adjusted to create samples with PtRu:Au atomic ratios of 0.25:1, 0.5:1, 0.75:1 and 1:1. Hereafter, the PtRu overlayers on Au/C samples are designated as SPR-[*x*] (*x* = the PtRu/Au atomic ratio). For comparison, 60 wt% Pt_2Ru_1/C was synthesized in EG at 160 °C for 3 h, which is designated as PtRu/C.

2.2. Catalyst characterization

High resolution-transmission electron micrographs (HR-TEM) were obtained on a JEOL 2010 operated at 200 kV. Samples were prepared by placing a drop of catalyst solution onto a carbon-coated copper grid and then drying. Analysis of X-ray diffraction (XRD) was performed using a Rigaku D/MAX 2500 operated with a Cu Kα source (λ = 1.541 Å) at 40 kV and 200 mA. The samples were scanned from 30° to 55° (2θ) with a scan rate of 2°/min. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 220I XL (Thermo Electron) photoelectron spectrometer. The X-ray source was Al Kα operating at 10 kV and 120 W. Samples were prepared by depositing the catalysts on an Si wafer using double-sided tape. Energy dispersive X-ray (EDX) analysis was carried out using an SEM-EDX system (JEOL, JSM-7000F).

Cyclic voltammogram was obtained in a conventional three-electrode electrochemical cell using a glassy carbon (GC) electrode (6 mm diameter) as a working electrode, and Pt wire and saturated calomel electrode as a counter and a reference electrode, respectively [11–16]. Electrochemical measurements were all recorded and reported vs. normal hydrogen electrode (NHE). The GC electrode was polished with 1, 0.3, 0.05 μm-Al_2O_3 slurry and washed ultrasonically with DI water before use. The ink slurry was prepared by mixing carbon-supported nanoparticles, a 5 wt%

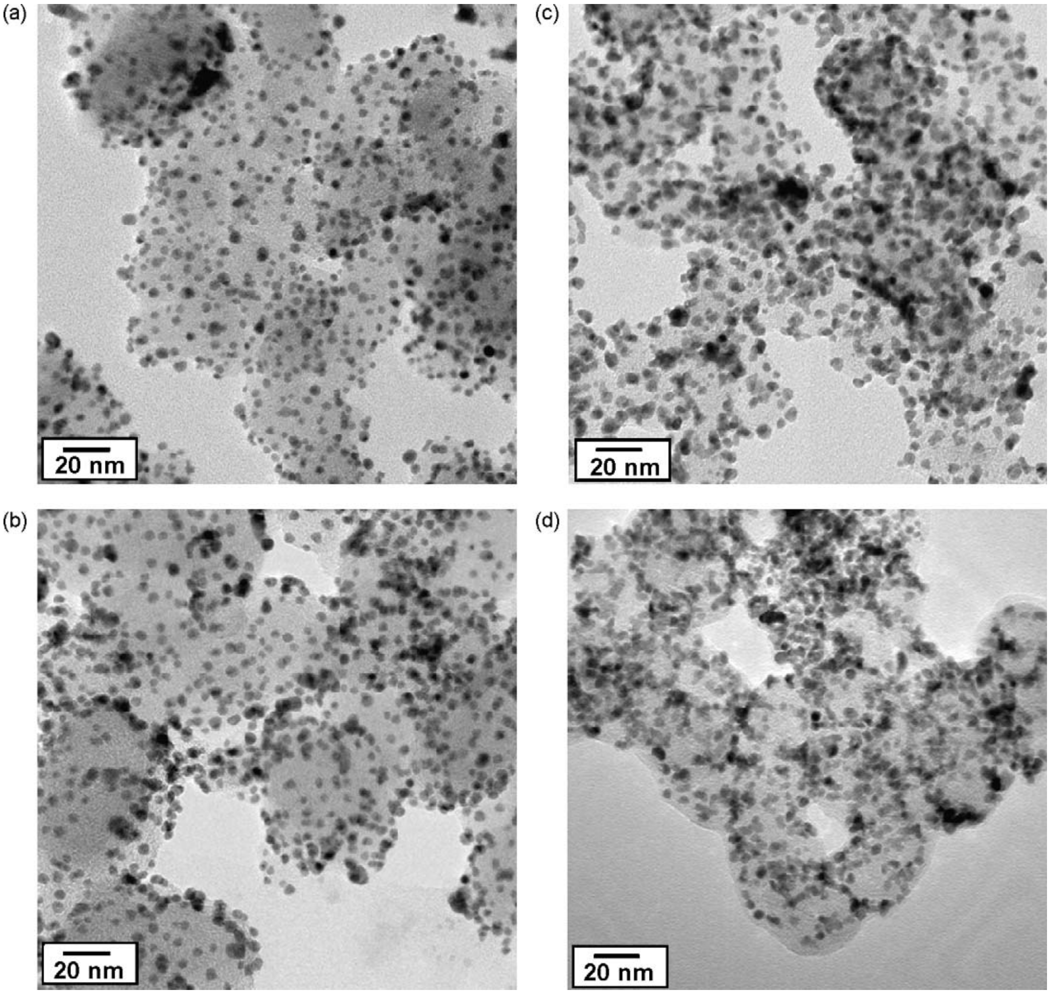

Fig. 1. TEM images of the Au and PtRu overlayers on Au nanoparticles: (a) Au/C, (b) SPR-[0.5], (c) SPR-[1], and (d) PtRu/C.

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