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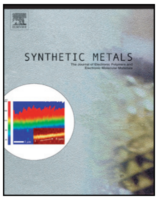

Pt-Au bimetallic nanoparticles decorated on reduced graphene oxide as an excellent electrocatalysts for methanol oxidation

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ABSTRACT

In this study, we report a general and simple strategy for the synthesis of platinum nanoparticles (PtNPs), highly dispersed on reduced graphene oxide (RGO) substrate with Au nanoparticles. The electrochemically active surface area (ECSA) of the Pt-Au-RGO electrocatalyst is found to be higher than the Pt-RGO electrocatalyst, which is more comparable to a commercial Pt/C catalyst. The obtained ratio of the voltammetric forward peak current to the reverse peak current for the Pt-Au-RGO electrocatalyst ($I_f/I_b = 2.33$) is much higher than that of the Pt-RGO electrocatalyst ($I_f/I_b = 1.16$). This phenomenon is attributed to the synergistic effects of the Au and the RGO substrate, which help to enhance the electrochemical activity of Pt nanoparticles for methanol oxidation and carbonaceous poisoning resistance. The reported methanol oxidation is found to exhibit excellent electrocatalytic performance, reliability, and stability, surpassing that of several reported modified electrodes that can also be used for platinum-based catalysts in fuel cell applications.

1. Introduction

In recent decades, the depletion of fossil fuel reserves and environmental pollution have been caused by increasing global energy demands, which has stimulated greater interest in developing different kinds of high-efficiency and low-cost renewable energy technologies [1–3]. The fuel cell is one alternative among various energy devices [4,5]. In particular, direct methanol fuel cells (DMFCs) are an attractive choice for energy-conversion devices to power portable electronics and electric vehicles, because methanol is an abundant and inexpensive liquid fuel with a high volumetric energy density, and it can be easily handled, stored, and transported [6]. Despite considerable advances in recent years, the practical application of DMFCs is still hindered by the high cost of the Pt catalyst and the sluggish methanol oxidation reaction [7,8]. A novel approach is aimed at synthesizing a new type of Pt-based catalyst with improved Pt utilization and catalytic activity, which has become the main issue for DMFCs [9]. Several strategies have been explored to achieve this goal, including modulating the size and shape of the Pt nanoparticles and preparing Pt catalysts in various forms, such as mesoporous Pt, highly ordered Pt nanotube arrays, and 3D dendritic Pt nanostructures, among others [10].

Two main aspects have become the focus of a large number of studies on the enhancement of catalytic performance [11]. These are the fabrication of Pt-based bimetallic catalysts (using a transition metal such as Cr, Mn, Fe, Co, Ni, Cu, or Zn, or a noble metal such as Ru, Pd, Ag, or Au) based on a bi-functional mechanism and their synergistic or electronic effects [12,13]. It is well-known that Au plays an important role in enhancing the catalytic performance of catalysts and is special in view of its inertness in the bulk state. Therefore, Pt-Au nanocatalysts can be expected to provide synergistic electrocatalytic activity for CO oxidation [14]. Furthermore, the use of bimetallic Pt-Au significantly increases the electrochemical active surface area (ECSA) of Pt, which is an essential factor in improving the catalytic performance and utilization efficiency of Pt catalysts [15]. In addition, the incorporation of bimetallic Pt-Au could address the problem of poisoning due to the CO-like species in Pt catalysts by changing the electronic band structure of Pt and modifying the

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strength of surface adsorption [16,17]. Recently, carbon based materials (carbon black, carbon nanotubes, mesoporous carbon, or graphene) have attracted great attention as the electrocatalyst support in methanol oxidation for fuel cell application [18,19]. This can strengthen the dispersion and stability of the metal nanoparticles, which enhances the catalytic stability, activity, and selectivity [20,21]. Among various supports, carbon materials have attracted great attention as catalyst supports in fuel cells due to their unique electrical, thermal, and micro/mesoporous properties [22,23].

Among these, graphene-based nanocomposites are the best in terms of all electrochemical energy aspects [24]. These materials have been demonstrated to be promising candidates as catalyst supports for application in fuel cells due to their unique properties, such as low cost, large surface area ($>2600\,m^2\,g^{-1}$), superior mechanical strength and elasticity, excellent electrical and thermal conductivity, and ease of modification [25,26]. These carbon materials provide high mass transport of reactants to the electrocatalyst and significantly enhance the availability through the ECSA of electrocatalysts for electron transfer [27]. Moreover, the presence of the oxygen-containing groups (epoxy, hydroxyl, and carboxyl groups) on the graphene surface can improve the poisoning-tolerance of the catalyst in a DMFC [28].

Herein, we report an efficient Au-RGO architecture using an effective strategy to enhance the loading of Au nanoparticles into RGO. The as-prepared Au-RGO serves as a platform to support and markedly enhance the electrocatalytic activity of Pt nanoparticles in forming the Au-RGO composites. Interestingly, the Pt-Au-RGO composite showed excellent electrocatalytic performance during methanol electro-oxidation in an acidic medium. In addition, the electrocatalytic performance of the Pt-Au-RGO composites for methanol oxidation and CO tolerance in fuel cell application was also systematically investigated. The obtained results showed that the Pt-Au-RGO-modified electrode demonstrated an effective and stable performance in the oxidation of methanol compared with the Pt-RGO and Pt/C composites.

2. Experimental

2.1. Material and instrumentation

The graphite (powder, $<20\,\mu m$), $H_2PtCl_6{\cdot}6H_2O$, 1 M $HClO_4$, $HAuCl_4$, methanol, and commercial Pt/C (20 wt%) used in this study were all purchased from Sigma-Aldrich. All of the aqueous solutions were prepared with double-distilled water (with a resistivity of 18.25 MΩ cm). All other chemicals were of analytical reagent grade and used without further purification.

Electrochemical measurements were performed on a CH Instrument 405A electrochemical workstation (Shanghai Chen Hua Co., China). A conventional three-electrode system was employed, including Pt-Au-RGO electrocatalyst-modified working electrode (glassy carbon electrode (GCE, $0.072\,cm^2$ geometrical surface area), an Ag/AgCl reference electrode, and a platinum wire used as a counter electrode. Transmission electron microscopy (TEM) images were collected using a Philips TECNAI 20 microscope (200 kV). SEM images captured with a Hitachi S-3000 were used to investigate the surface morphology and microstructure of the electrodes. The EDX were recorded using a HORIBA EMAX X-ACT Model 51-ADD0009. The XPS spectra were obtained using a PHI 5000 Versa Probe equipped with an Al Kalpha X-ray source (1486.6 eV). Raman spectra were measured with a Raman spectrometer (Dong Woo 500i, Korea) equipped with a charge-coupled detector. EIS was carried out at a frequency range of 100 kHz to 1.0 Hz with a ZAHNER instrument (Kroanch, Germany). XPS analysis was carried out using a PHI 5000 Versa Probe equipped with an Al Kalpha X-ray source (1486.6 eV). XRD analysis was carried out on an XPERT-PRO diffractometer (PANalytical B.V., the Netherlands) using Cu Kα radiation (k = 1.54 Å).

2.2. Fabrication of Pt-Au-RGO-modified electrode

The graphene oxide was synthesized using a modified Hummers method [29]. Briefly, graphite powder (1 g) was added to 150 mL of cooled (0 °C), concentrated H_2SO_4 and then 25 g of $KMnO_4$ was slowly added under ice-cooling. The mixture was then stirred at 35 °C for 30 min. Next, 600 mL of deionized water was slowly added to cause an increase in temperature to 50 °C, and the mixture was maintained at this temperature for 15 min. The reaction was terminated by adding 250 mL of water, and 6 mL of H_2O_2 (30 wt%) was subsequently added to reduce the residual $KMnO_4$ solution. The solid product was separated by centrifugation, washed using 2 M HCl solution, then washed 3–4 times with ethanol and dried overnight in a vacuum at 60 °C. Furthermore, in a typical procedure, 60 mg of graphite oxide was first dispersed in 300 mL ultra-pure water by sonication for 30 min to make the graphene disperse equally. Then, 1 mL of 0.01 M $HAuCl_4$ and 1 mL of 0.01 M K_2PtCl_4 (metal precursors in the case of Pt/Au = 1/1) were mixed with 48 mL of pure water. Next, the resulting solution was mixed with the above dispersion, followed by the addition of 5 mL of fresh $NaBH_4$ aqueous solution (200 μM) as the reductant. After 1 h of treating, the obtained black dispersion was separated by centrifugation (13,000 rpm) and washed four times with ultrapure water. Finally, the solid powders collected via centrifugation were sequentially washed with double-distilled water and ethanol several times before being dried at 60 °C in a vacuum oven for 12 h to obtain the Pt-Au-RGO composite. The Au-RGO and Pt-RGO composites with various Au and Pt ratios were synthesized using the same procedure but with the application of different nominal Au and Pt ratios in the metal precursors.

Prior to modification, the bare electrode was successively polished with 0.05 μm α-Al_2O_3 power slurries until a shiny mirror-like surface was achieved and was then sonicated in 1:1 acetone: double-distilled water for 5 min and dried at room temperature in a vacuum oven for 1 h. Then, 6 mg of the Pt-Au-RGO composite was dispersed in 1 mL of DMF using ultrasonic treatment to form a homogeneous black suspension. Next, 5 μL of the electrocatalyst suspension was carefully pipetted onto the surface of the GCE. Finally, 15 μL of 0.5 wt% Nafion was transferred evenly onto the surface of the dry Pt-Au-RGO and dried at room temperature to form a layer that prevented the catalyst particles from detaching. The Pt-RGO working electrodes were prepared using the same procedure described above. The electrocatalytic oxidation of methanol on the Pt-RGO, Pt/C, and Pt-Au-RGO electrocatalysts was investigated in a 1 M $HClO_4$ + 1.0 M CH_3OH aqueous solution by CV in the range of −0.0 to 0.8 V at a scan rate of 50 mV/s. The electrolyte solution was deaerated with ultrahigh-purity N_2 for 30 min before and throughout the test to remove trapped air. On the other hand, the ECSAs of the Pt-RGO, Pt/C, and Pt-Au-RGO electrocatalysts were calculated from CVs, which were recorded in 1 M $HClO_4$ between −0.2 to 1.2 V with a scan rate of $50\,mV\,s^{-1}$. In addition, the stability of the Pt-RGO, Pt/C, and Pt-Au-RGO electrocatalysts was evaluated by examining the chronoamperometry curves obtained at a given potential of 0.5 V versus that of Ag/AgCl. The process pathway of the Pt-Au-RGO electrocatalysts toward methanol oxidation is shown in Scheme 1.

3. Results and discussion

3.1. Morphology and characterization of the Pt-Au-RGO composites

The morphology and structure of the Pt-RGO, Au-RGO, and Pt-Au-RGO electrocatalysts were studied by SEM analysis. Fig. 1A