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Growing Platinum-Ruthenium-Tin ternary alloy nanoparticles on reduced graphene oxide for strong ligand effect toward enhanced ethanol oxidation reaction

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GRAPHICAL ABSTRACT

Growing $Pt_1Ru_{0.5}Sn_{0.5}$ ternary alloy nanoparticles on reduced graphene oxide for strong ligand effect of Ru and Sn to greatly promote Pt-catalyzed ethanol oxidation reaction.
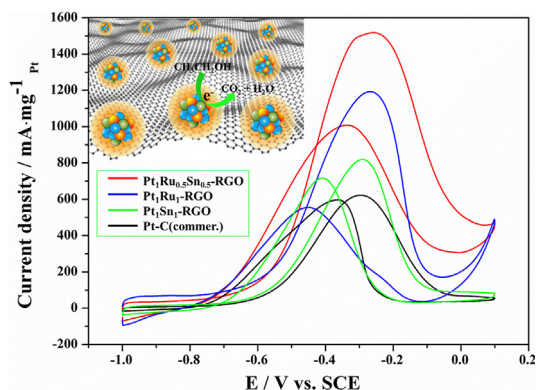
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ABSTRACT

Uniform $Pt_1Ru_{0.5}Sn_{0.5}$ ternary alloy nanoparticles are *in situ* deposited on reduced graphene oxide ($Pt_1Ru_{0.5}Sn_{0.5}$-RGO) through its functional groups and defects as nucleation sites to greatly electrocatalyze ethanol oxidation reaction for much higher mass current densities, larger apparent specific current densities and better stability than commercial Pt-C catalyst (Pt-C(commer)). Mechanistic studies indicate that the excellent electrocatalytic activity and anti-poisoning are resulted from a strong ligand effect of the ternary alloy components, in which the charge transfer is boosted while decreasing the density of states close to the Fermi level of Pt to reduce bond energy between Pt and CO-like adsorbates for greatly improved anti-poisoning ability. This work holds a great promise to fabricate a high performance anode catalyst with a low Pt loading for direct ethanol fuel cells.

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1. Introduction

Reduced graphene oxide (RGO), a single-atom-thick sheet of hexagonally arrayed sp²-bonded carbon atoms [1], has been used

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as an excellent supporting material for catalysts in electrochemical energy storage and conversion systems such as fuel cells [2–7] due to its high specific surface area and superior electrical conductivity [8–11]. Currently, direct ethanol fuel cells (DEFCs) have been recognized as a promising power source of portable electronic devices and automotive vehicles [12] because of their low toxicity and low operating temperature, while its liquid fuel nature is easy to adopt the conventional fuel transportation/storages. Additionally, ethanol is renewable and could be produced in large scales from biomass fermentation [13,14]. It is known that noble metal platinum (Pt) is the commonly used catalyst for ethanol electro-oxidation [15]. Nevertheless, plain Pt suffers from low efficiency, poor stability, high cost and easy poison by reaction intermediates [16]. Thus, it is a great demand to develop a low Pt loading electrocatalyst while having high activity and excellent stability toward ethanol oxidation reaction.

One promising strategy to enhance the catalytic activity of a low-loading Pt for ethanol electro-oxidation is to alloy Pt with some translation metals such as Ru [17–19], Sn [20–22], Pd [23–25], and Cu [26,27]. PtRu binary alloy catalyst has been report to catalyze ethanol electro-oxidation, in which the presence of Ru could produce Ru-OH species on Ru surface while activating water molecules to remove the poisonous intermediates on Pt surface at a lower potential [28–30]. Previous researches have revealed that the presence of Sn in Pt-based alloy catalysts could modify the electronic structure of Pt [31–33], and promoted the dissociative adsorption of ethanol to break the C—C bond at a lower potential [34,35].

Herein, for the first time $Pt_1Ru_{0.5}Sn_{0.5}$ ternary alloy nanoparticles were directly grown on RGO ($Pt_1Ru_{0.5}Sn_{0.5}$-RGO) to deliver much higher electrocatalytic activity and stability than the known commercial Pt-C(commer.), thus renders a great potential as a high active low-Pt anode electrocatalyst for DEFCs. For comparison, Pt_1Ru_1-RGO and Pt_1Sn_1-RGO as well as Pt-C(commer.) were investigated under the same experimental conditions.

2. Experimental sections

2.1. Synthesis of catalysts

Graphene oxide (GO) was obtained from graphite powders (<20 μm, Sigma-Aldrich) through a modification of Hummers and Offeman's method [36,37]. In a typical reaction, 0.7 g of graphite, 0.7 g of $NaNO_3$, and 32 mL of concentrated sulfuric acid were added when stirred vigorously in an ice bath, retaining the temperature between 10 °C to 20 °C. Followed, 4 g of $KMnO_4$ was slowly added within 30 min. After that, the reaction solution was transferred to a 35 ± 3 °C water bath and stirred for about 1.5 h, forming a thick paste. Next, 56 mL of deionized water was added very slowly while at rapid agitation, and temperature of the water bath was quickly raised to 98 ± 3 °C. After 1 h, 4 mL of H_2O_2 (30%, V/V) was gradually added with the color of the solution from dark brown to yellow. After a few minutes of mixing, transferred the solution to a 1000 mL beaker filled with 500 mL deionized water, precipitating for one day. The next day, poured the supernatant out, then added 60 mL of 50 °C warm water. After 5 min, the warm solution was centrifuged at low-speed centrifugation at 1000 rpm for 3 min. It was repeated until all visible particles were removed (about 2–3-times). The supernatant then underwent high-speed centrifugation steps at 14,000 rpm for 15 min with 5% HCl for 7–10 times and then deionized water for 7–10 times, respectively. It was continued until the pH of the solution closed to 7. The final sediment was redispersed in deionized water by ultrasonication, giving a solution of exfoliated GO, and centrifuged this solution again at 14,000 rpm for 15 min to collect the supernatant. Finally, the GO solution was gained at the concentration of 8.67 mg·mL^{-1}, which was ready for subsequent experiments.

The catalysts were prepared by a facile modified polyol reduction method [31,38–40]. Briefly, 21 mg GO (2.422 mL) was uniformly dispersed in 9 mL of ethylene glycol (EG) under ultrasonication for 10 min. While vigorous magnetic stirring, a certain amount of chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$, Aladdin), ruthenium (III) chloride hydrate ($RuCl_3·xH_2O$, Sigma-Aldrich) and tin chloride dihydrate ($SnCl_2·2H_2O$, Aladdin) were added into the above solution, respectively. Subsequently, the mixture was continued stirring for 3 h, followed 3 mL ethanol into rapidly. Then, the mixture after 20 min of N_2 saturation was sealed in a Telfonlined autoclave and was hydrothermally treated at 200 °C for 6 h. The resulting colloid solution with $Pt_1Ru_{0.5}Sn_{0.5}$, Pt_1Ru_1 and Pt_1Sn_1 alloy nanoparticles (NPs) supported on reduced graphene oxide that were respectively simplified as $Pt_1Ru_{0.5}Sn_{0.5}$-RGO, Pt_1Ru_1-RGO and Pt_1Sn_1-RGO was cooled down to room temperature. The products were separated by centrifuge and thoroughly washed with ethanol and deionized water. Finally, freeze dried, and got the reserve catalysts. The compositions of the catalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), of which the Pt loading is 21.3%, 20.1% and 23.4% in $Pt_1Ru_{0.5}Sn_{0.5}$-RGO, Pt_1Ru_1-RGO and Pt_1Sn_1-RGO, respectively.

2.2. Characterization

TEM (JEM-2100, JEOL, Japan) was used to characterize the morphologies of the acquired catalysts. Energy Dispersive Spectroscopy (EDS) analysis was tested on the SEM (JSM-6510LV, Japan) to analyze the composition of the catalysts. X-ray powder diffraction (XRD) patterns of the samples were collected by Shimadzu XRD-7000 X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). The X-ray Photoelectron Spectroscopy (XPS) were performed by an ESCALAB 250 Xi XPS system.

2.3. Electrochemical behaviour

The electrochemical properties of the prepared catalysts were measured on CHI 660E electrochemical work station (Shanghai Chenhua Instrument Company, China) in a standard three-electrode cell [41] when Glassy carbon electrode (GCE, diameter 4.0 mm) modified with the prepared catalysts used as a working electrode, a platinum sheet and saturated calomel electrode (SCE) were used as the counter and reference electrode. The electrolyte was 0.5 moL·L^{-1} (0.5 M) H_2SO_4, or 1 mol·L^{-1} (1 M) KOH prepared by using deionized water (18.2 MΩ cm) and KOH (90%, Sigma-Aldrich). All measurements were collected under N_2 (ordinary-grade purity, Sanxia) saturation. Generally, appropriate amount of the prepared catalysts and Pt-C(commer.) (30 wt%) were ultrasonically mixed with appropriate anhydrous ethanol and adaptive Nafion (Nafion® 117, Sigma-Aldrich) to form a uniform solution of 3 mg·mL^{-1} catalysts, while the concentration of Nafion was 0.25%. Then, all the catalysts containing 6 μg of Pt were respectively loaded onto the surface of GCE, and dried naturally. Several activation scans were performed in 0.5 M H_2SO_4 until repeatable cyclic voltammetry curves (CVs) were achieved, and only the last CVs were used to compare the activity of the catalysts.

3. Results and discussion

3.1. The physical properties of catalysts

As shown in Fig. 1, the TEM images and percentage particle size histograms clearly exhibit that the $Pt_1Ru_{0.5}Sn_{0.5}$ (A), Pt_1Ru_1 (C) and