

Fabrication and catalytic properties of Pt and Ru decorated TiO₂/CNTs catalyst for methanol electrooxidation

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Abstract

Highly ordered anodic titania nanotube arrays provide a large surface area for electrodepositing nickel nanoparticles which are used as the catalyst for carbon nanotube growth. Pt and Ru nanoparticles, approximately 3 nm in diameter, are uniformly electrodeposited on the as synthesized titania-supported carbon nanotubes (CNTs), constructing a novel catalyst for electrocatalytic oxidation of methanol. An enhanced and stable catalytic activity is obtained due to the uniformly dispersed Pt and Ru nanoparticles, and the large CNT network facilitating the electron transfer between the adsorbed methanol molecules and the catalyst substrate. An oxidation peak current density of 55 mA/cm² is achieved at a low Pt load of 0.126 mg/cm² with a Pt/Ru mole ratio of 1:1.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention for their low weight, high power density, low operating temperature and low pollutant emission [1–4]. It is known that platinum is the only single component catalyst showing a significant activity for methanol oxidation reaction (MOR). Pure platinum, however, is readily poisoned by the strongly adsorbed CO-like intermediates, by-products in methanol electrooxidation. In order to improve methanol electrooxidation activity, many efforts have been devoted to the synthesis of Pt-based alloy catalysts such as PtMn [5], PtSn [6], PtOs [7], PtIr [8], and PtRu [9,10], the benchmark anode catalyst. The addition of Ru to Pt greatly inhibits the CO poisoning via an effective oxygen-transfer step from electrogenerated Ru–OH at a lower onset potential as compared with that at pure Pt catalyst [11]. The enhanced anode activities are explained by a bifunctional mechanism and ligand (electronic) effect

[12,13]. The efficiency of MOR can be improved by impregnating/depositing the binary Pt/Ru system on conductive supports such as carbon powder, carbon blacks, carbon nanofibers and carbon nanotubes [14,15]. It is interesting to mention that a multi-wall CNT-decorated Pt/Ru catalyst yields ~35–39% higher power densities than the carbon-supported Pt/Ru catalysts with the same Pt/Ru loadings, particle sizes, and surface area [16].

Titanium dioxide, a large-band-gap semiconductor, is an excellent candidate as photocatalysts in the oxidation of a wide variety of organic and inorganic substances [17,18]. Titanium dioxide shows high adsorption ability to methanol, corresponding with a high photocatalytic activity [19,20]. Nanoscale TiO₂ film has attracted considerable interests due to large specific surface area and unique chemical and physical properties as compared with powdered and colloidal TiO₂. Nanotubular TiO₂ with length of hundreds micrometers was fabricated [21–23] and would be a promising support for methanol electrooxidation. To our knowledge, however, no work has been reported on using nanotubular TiO₂/CNTs composite as support to disperse Pt and Ru nanoparticles for methanol electrooxidation.

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In this work, the CNTs modified nanotubular TiO₂ was prepared as a new support for the Pt and Ru nanoparticles loading. The catalytic activity of the resultant architecture was investigated with respect to the Pt/Ru nanoparticles loading and the nanotube pore size. The catalytic role of the titania nanotubes was also investigated by comparing the catalytic activity of using graphite instead of TiO₂ as substrate.

2. Experimental section

Titanium foil (99.8%, 0.127 mm thick) was purchased from Aldrich (Milwaukee, WI). Sodium fluoride, citric acid, nickel nitrate, methanol, sulfuric acid, hexachloroplatinic (IV) acid and ruthenium chloride of analytical reagent grade were purchased from commercial sources and used as supplied. A 10 mM H₂PtCl₆ solution was prepared in water, while a 10 mM RuCl₃ was prepared in 2 M HCl to prevent the hydrolyzation. Doubled-distilled water was used throughout the experiment.

Prior to anodization, the titanium foil (3 mm × 15 mm) was decreased by sonication in acetone and then ethanol. The titanium samples were anodized in an electrolyte containing 0.2 M citric acid and 0.1 M NaF at room temperature for 5 h in a conventional two-electrode system with a platinum cathode, producing nanotube arrays with pore diameters of 50 nm, 90 nm, 110 nm and 140 nm at anodization voltages of 10 V, 15 V, 20 V and 25 V, respectively. Ni nanoparticles were electrodeposited inside the as-prepared titania nanotubes as catalysts for the growth of carbon nanotubes via chemical vapor deposition (CVD) by decomposing acetylene in a vacuum furnace for 30 min at 700 °C [24]. After removing the Ni catalysts by immersing the TiO₂/CNT electrode in 10 M HNO₃ for 30 min, Ru and Pt nanoparticles were electrodeposited on it in sequence using chronopotentiometry at a current density of 1.5 mA/s in a standard three-electrode configuration with the TiO₂/CNT working electrode, a platinum auxiliary electrode, and a Ag/AgCl (saturated by KCl) reference electrode by an electrochemical working station (CHI 660B; CH Instruments, Inc., Austin, TX). Topology of the TiO₂/CNTs was characterized by scanning electron microscopy (SEM) (JSM6700F, JEOL, Japan, operating at 5 KV) and transmission electron microscopy (TEM) (JEM3010, JEOL, Japan operating at 300 KV). An energy dispersive X-ray (EDX) spectrometer fitted to the scanning electron microscope was used for the elemental analysis. The efficient electrode area (both sides) is 0.6 cm².

Catalytic activities of MOR on the catalysts were performed by cyclic voltammetry (CV). To obtain reproducible and reliable results, the CV experiments were performed in a fresh solution containing 1.0 M CH₃OH and 0.5 M H₂SO₄ in the potential ranging from 0.2 to 1.0 V at 100 mV s⁻¹ for 20 cycles for every measurement. Before recording CV, the electrode was immersed in the test solution for 10 min to allow the system reaching a sta-

ble state. All the electrochemical experiments were carried out at room temperature in nitrogen saturated solution.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the topography and configuration of nanotubes and TiO₂/CNT/Pt architecture. Fig. 1a shows that uniform TiO₂ nanotubes were formed with a pore size of about 90 nm in diameter and a length of about 320 nm (shown in the inset of Fig. 1a). Fig. 1b shows long CNTs in diameter of 90 nm formed on TiO₂ substrate. Fig. 1c shows the TiO₂ substrate after removing the surface CNTs of the TiO₂/CNTs electrode by sonication, showing a CNTs-embedded porous annealed TiO₂ substrate, which is because that CNTs began to form inside the TiO₂ nanotubes at 650 °C [25] before the distortion of the titania nanotubes at 680 °C [26]. Such a CNTs-embedded TiO₂ substrate facilitates the electron transfer due to its enhanced conductivity. The TiO₂ nanotubes were disintegrated during the CNT growing process at 700 °C, existing in the mixture of rutile and anatase phase based on previous results [26,27].

The disorderly distributed CNTs provide a large surface area for the dispersion of Pt/Ru nanoparticles and a conductive network for electron transfers. The TEM image given in the inset of Fig. 1b shows uniformly distributed Pt nanoparticles at an average size of ~3 nm on the CNT network. After removing the surface CNTs of the TiO₂/CNT electrode, residual Pt nanoparticles are observed on the substrate as shown in Fig. 1c, indicating that the Pt nanoparticles disperse within the whole CNT network. The corresponding EDS spectrum given in Fig. 1d shows the presence of Ti, Pt, C, and O, with a Ti:O atomic ratio of 1:2. The uniformly dispersed ~3 nm Pt nanoparticles are essential to a high catalytic activity.

3.2. Effect of Pt loading on catalytic activity

Platinum shows high activity for methanol oxidation and was used as anode electrocatalysts for many years [27–29]. Fig. 2 shows the effect of different Pt loading on electrocatalytic activity for MOR. Two distinct anodic peaks are observed between 0.4 and 0.7 V corresponding to the methanol oxidation [30,31]. The forward anodic peak current density (*I*_{pa}) increased obviously with increasing the Pt loading, while the forward anodic peak potential (*E*_{pa}) is almost constant up to 0.126 mg/cm² Pt loading, after which the *E*_{pa} significantly shifts to positive direction, possibly due to the decrease in electrocatalytic activity caused by the aggregation of Pt particles [32]. The optimum Pt loading of 0.126 mg/cm² was therefore used in this work.

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