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Article

N-doped carbon modified Pt/CNTs synthesized by atomic layer deposition with enhanced activity and stability for methanol electrooxidation

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ABSTRACT

A Pt/CNTs catalyst coated with N-doped carbon (*x*NC-Pt/CNTs) is synthesized by atomic layer deposition (ALD) and applied in methanol electrooxidation reaction. Pt nanoparticles and polyimide (PI) are sequentially deposited on carbon nanotubes (CNTs) by ALD. After annealing at 600 °C in H_2 atmosphere, the PI is carbonized to produce porous N-doped carbon. Upon coating with a moderately thick layer of N-doped carbon, the optimized 50NC-Pt/CNTs show higher activity, better long-term stability, and improved CO resistance towards methanol electrooxidation compared with Pt/CNTs and commercial Pt/C (20 wt%). X-ray photoelectron spectroscopy characterization result indicates that the Pt–CO bond is weakened after N-doped carbon coating and CO adsorption on the Pt surface is weakened, leading to superior electrocatalytic performance.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted great attention as a reliable power source for electric vehicles and portable devices due to its high energy conversion, high power density, and environmental friendliness [1,2]. However, the widespread commercial application of DMFCs is not yet achieved because of the limiting electrocatalytic materials. Conventional Pt-based materials are the most effective catalysts for the methanol oxidation reaction (MOR) compared to other noble metals such as Ru, Pd, Au, Ag, etc. [3,4]. However, Pt-based catalysts suffer from several issues including (1) poor abundance and high cost, (2) low catalytic efficiency, and (3) catalyst poisoning originating from the strong interaction between intermediate CO species and Pt active sites [5–7].

Tremendous efforts have been devoted to developing catalytic materials with excellent activity, good stability, and high CO tolerance. Ultrafine Pt particles can effectively enhance the catalytic efficiency due to their high surface area and large number of edges and corners [8,9]. Alloying Pt with a second metal such as Pd, Ru, Fe, Co, Ni, etc. also remarkably improves the catalytic activity and CO tolerance with an accompanying reduction in cost [10–13]. Exploiting supports with advanced structures and surface properties can also increase the electrocatalytic performance of DMFCs [14]. For example, doping nitrogen into carbon materials accelerates the nucleation and growth of Pt NPs into small particles with uniform dispersion [15,16]. Doping also improves the intrinsic properties of carbon materials, which increases the catalyst efficiency [17,18]. However, N-doped carbon materials are usually prepared at

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extremely high temperatures, high pressures, and in an ammonia atmosphere; such harsh conditions increase the preparation difficulty and cost [19].

The interface between the metal nanoparticles and the support plays an important role in catalysis. The rational design and engineering of metal-support interfaces is crucial in developing highly efficient catalysts [20,21]. Atomic layer deposition (ALD) is a thin-film deposition technique based on sequential surface reactions by alternately injecting gaseous precursors and reactants. The self-limiting character of the procedure allows the synthesis of ultrafine nanoparticles and ultrathin films on the atomic scale [22]. ALD can be used to modify the surface of metal nanoparticles by coating the surface with nanofilms. The film thickness can be precisely controlled, allowing for the optimization of the interface between the metal particles and the coating [22]. In our previous work, Pt nanoparticles were easily deposited on an inert CNT surface using O_3 as the reactant gas and $MeCpPtMe_3$ as the Pt precursor [23,24], and porous N-doped carbon nanofilms were obtained by pyrolyzing PI films deposited by molecular layer deposition (MLD)[25].

Herein, ALD is used to synthesize porous N-doped carbon coated Pt/CNTs catalysts. The size of the Pt particles and the thickness of the N-doped carbon film are highly controlled by adjusting the number of ALD cycles. The activity of the optimized sample is 2.7-times higher than that of commercial Pt/C (20 wt% Pt). Moreover, the long-term stability and CO resistance of the catalyst are also considerably improved.

2. Experimental

2.1. Materials

CNTs with a specific surface area of 40–70 m^2 g^{-1} and diameters in the 40–60 nm range were purchased from Shenzhen Nanotech Port Co. Ltd, China. $MeCpPtMe_3$, pyromellitic dianhydride (PMDA), and 4,4′-diaminodiphenyl ether (ODA) were obtained from J&K Scientific Ltd. All the materials were used as received.

2.2. Preparation of the catalyst

Typically, 8 mg of CNTs were dispersed in ethanol, dropped onto a quartz wafer (10 cm × 10 cm), and dried in air. Then, the quartz wafer was transferred to a homemade ALD chamber for Pt ALD. The CNTs were sequentially exposed to $MeCpPtMe_3$ and O_3. The pulse, exposure, and nitrogen purge times were 0.5, 8, and 20 s for $MeCpPtMe_3$ and 1, 8, and 20 s for O_3, respectively. The temperature of the chamber was maintained at 280 °C. $MeCpPtMe_3$ was maintained at 60 °C to provide enough vapor pressure. The number of cycles of Pt deposition was 20 for all samples. PI deposition was carried out after Pt deposition. The sample was sequentially exposed to PMDA and ODA. The pulse, exposure, and nitrogen purge times were 5, 10, and 30 s for PMDA and 3, 8, and 30 s for ODA, respectively. The temperature of the chamber, PMDA, and ODA was maintained at 160, 155, and 140 °C, respectively. The number of cycles of PI deposition was 40, 50, 60, and 70 to produce different samples. Finally, the as-prepared samples were transferred into a furnace and calcined in H_2/N_2 (5%) to pyrolyze the PI. During the pyrolysis process, the temperature was first raised from rt. to 600 °C at a rate of 3 °C min^{-1}, maintained at 600 °C for 2 h, and then lowered. The prepared samples were denoted as *x*NC-Pt/CNTs, where *x* is the number of cycles of PI deposition. For comparison, a catalyst with no PI coating (denoted as Pt/CNTs) was also prepared.

2.3. Electrochemical measurements

Electrochemical measurements were performed using a CHI 760D electrochemical workstation and a three-electrode cell at room temperature. The working electrode was prepared as follows. 1 mg of catalyst, 1 mL of ethanol, and 20 μL of Nafion solution (5 wt%, Aldrich) were mixed ultrasonically for at least 30 min. Then 10 mL of the ink was transferred onto a freshly polished glassy carbon (GC, 5 mm diameter) electrode and dried in air. A Pt foil served as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. Cyclic voltammetric (CV) and chronoamperometric measurements were carried out in an N_2-saturated aqueous solution of 1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} CH_3OH. A CO stripping test was conducted by immersing the as-prepared electrode in a CO-saturated 1 mol L^{-1} H_2SO_4 solution for 20 min and bubbling N_2 into the electrolyte for 30 min.

2.4. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a JEOL-2100F microscope operated at 200 kV. The Pt loading of the catalyst was determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES) on a Thermo Icap6300 apparatus. X-ray photoelectron spectra (XPS) were collected using an ESCALab-250 X-ray photoelectron spectrometer with an Al K_α source (1486.6 eV).

3. Results and discussion

The activity of the catalyst for methanol electrooxidation was measured by CV curves in a N_2-saturated aqueous solution of 1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} CH_3OH (Fig. 1). All CV curves present hydrogen adsorption and desorption peaks in the potential range of –0.2 to 0.1 V. The electrochemical activity can be described by the forward peak current density (I_f), which is generally regarded as the electrooxidation of methanol [26]. Zhang et al. [14] modified multiwalled carbon nanotubes with N-doped carbon quantum dots as Pt catalyst support, which achieved a current density of methanol electrooxidation of 0.42 A mg_{pt}^{-1}. Zhang et al. [27] synthesized TiN@nitrogen-doped carbon-supported Pt nanoparticles as high-performance anode catalysts for methanol electrooxidation and obtained a current density of 0.626 A mg_{pt}^{-1}. Zhao et al. [28] used a 3D porous N-doped graphene aerogel as support on which Pt nanoparticles were loaded, which achieved a current density of 0.544 A