



Electrodeposition fabrication of pore-arrayed hydrogen tungsten bronze as support of platinum nanoparticles for electrocatalytic oxidation of methanol oxidation



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ABSTRACT

Pore-arrayed hydrogen tungsten bronze ($p\text{-H}_x\text{WO}_3$) is fabricated with polystyrene as template by electrodeposition and used as the support of platinum nanoparticles as electrocatalyst ($\text{Pt}/p\text{-H}_x\text{WO}_3$) for methanol oxidation. The surface morphology, structure, and compositions of $p\text{-H}_x\text{WO}_3$ and $\text{Pt}/p\text{-H}_x\text{WO}_3$ are characterized with scanning electron microscope (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The activity and stability of $\text{Pt}/p\text{-H}_x\text{WO}_3$ toward methanol oxidation are evaluated in 0.5 M H_2SO_4 + 1.0 M CH_3OH solution by cyclic voltammetry (CV), chronoamperometry (CA), and chronopotentiometry (CP), and cell discharge test. The characterizations from SEM, XRD, TEM, and FTIR demonstrate that $p\text{-H}_x\text{WO}_3$ contains uniform pores of about 200 nm and the platinum particles can be uniformly distributed with an average size of 3.01 nm on it. The electrochemical evaluations indicate that $\text{Pt}/p\text{-H}_x\text{WO}_3$ exhibits better activity and stability toward methanol oxidation than the platinum supported by non-pore arrayed H_xWO_3 .

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1. Introduction

Direct methanol fuel cell (DMFC) is attractive due to its advantages, including high-energy density, convenient handling of liquid fuel and mild operating temperature [1,2]. Some issues need to be solved before DMFC is put into commercialization [3], one of which is the slow kinetics for methanol oxidation. Platinum as electrocatalyst for methanol oxidation is easy to poison by the adsorbed intermediates $\text{CH}_2\text{O}_{\text{ads}}$ ($0 \leq z \leq 4$) generated from the incomplete oxidation of methanol [4]. It has been demonstrated that the electrocatalytic activity of platinum can be improved by its modification with other metals, such as Ru [5], Mo [6], W [7], Sn [8], Ni [9], Os [10], etc., or metal oxides, such as MoO_x [11–13], TiO_2 [14], MnO_2 [15] and WO_x [16]. Among these composites, tungsten oxide-based electrocatalyst is most promising because of the better chemical stability of tungsten oxide than other metals or oxides [17,18].

Tungsten trioxide (WO_3) is known to be able to form hydrogen tungsten bronze (H_xWO_3 , $0 < x \leq 2$) in acid solution, which is nonstoichiometric and electroconductive [19]. H_xWO_3 functions as proton donor or acceptor through the change of tungsten valence and yields a proton spillover effect between platinum and H_xWO_3 , facilitating the further oxidation of the adsorbed intermediates $\text{CH}_2\text{O}_{\text{ads}}$ ($0 \leq z \leq 4$) on platinum and thus improving the activity of the electrocatalyst [20,21].

Two-dimensional (2D) ordered pore arrays (films) have a high specific surface area and an orderly arrangement of pores, exhibiting unique properties and potential applications in catalysis [22,23]. Colloidal crystals are good template in the fabrication for 2D ordered pore arrays (films), which is facile and favors the universal morphology-controlled growth of large-scale ordered pore arrays [24]. There are lots of methods to grow ordered porous materials based on colloidal crystal templates. Compared with the complicated and expensive methods, such as molecular beam epitaxy [25], metalorganic chemical vapor deposition [26] and pulsed laser ablation method [27], electrodeposition from precursor solutions is low-cost, high efficiency and environmental friendliness.

In our previous reports, we have demonstrated that pore-arrayed tungsten or molybdenum oxide, prepared by sol-gel

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method, can improve the electrocatalytic activity and stability of platinum nanoparticles toward methanol oxidation [28,29]. In this work, we reported the fabrication of pore-arrayed hydrogen tungsten bronze ($p\text{-H}_x\text{WO}_3$) by electrodeposition with 2D colloidal monolayer template and developed an electrocatalyst ($\text{Pt}/p\text{-H}_x\text{WO}_3$) for methanol oxidation by decorating platinum nanoparticles on $p\text{-H}_x\text{WO}_3$ via magnetron sputtering.

Although there are lots of publications on the preparations of ordered nanostructured porous films and their applications in catalysis, optical devices, surface-enhanced Raman scattering (SERS), sensors, etc, the electrodeposition fabrication of pore-arrayed hydrogen tungsten bronze and its application as the support of platinum particles have never been reported before. It is the first time to introduce the electrodeposition for the fabrication of pore-arrayed hydrogen tungsten bronze.

2. Experimental

2.1. Fabrication of $p\text{-H}_x\text{WO}_3$

The strategy and manipulation for the fabrication of $p\text{-H}_x\text{WO}_3$ are illustrated in Scheme 1. Firstly, polystyrene (PS) spheres were synthesized by using an emulsifier-free emulsion polymerization technique [30], and coated on a glass substrate by spin-coating method [31]. PS monolayer on the glass substrate was integrally floated off on the distilled water surface, and then picked up with an ITO substrate, followed by heating at 80°C for 4 h. The area of PS on ITO substrate (PS/ITO) was $1.0\text{ cm} \times 1.0\text{ cm}$.

As described in Scheme 1, H_xWO_3 was prepared by cycling PS/ITO for 1 cycle between -0.2 V and 0.5 V at a scan rate of 20 mV s^{-1} in $4\text{ mM Na}_2\text{WO}_4 + 2\text{ M H}_2\text{SO}_4$ solution, forming PS- H_xWO_3 composite. A platinum sheet and $\text{Ag}/\text{AgCl}/\text{saturated KCl}$ electrode were used as the counter electrode and reference electrode, respectively. PS- H_xWO_3 was dried for 2 h at 80°C and PS spheres were removed by heating at 450°C for 2 h to form $p\text{-H}_x\text{WO}_3$.

2.2. Platinum nanoparticles decorated on $p\text{-H}_x\text{WO}_3$

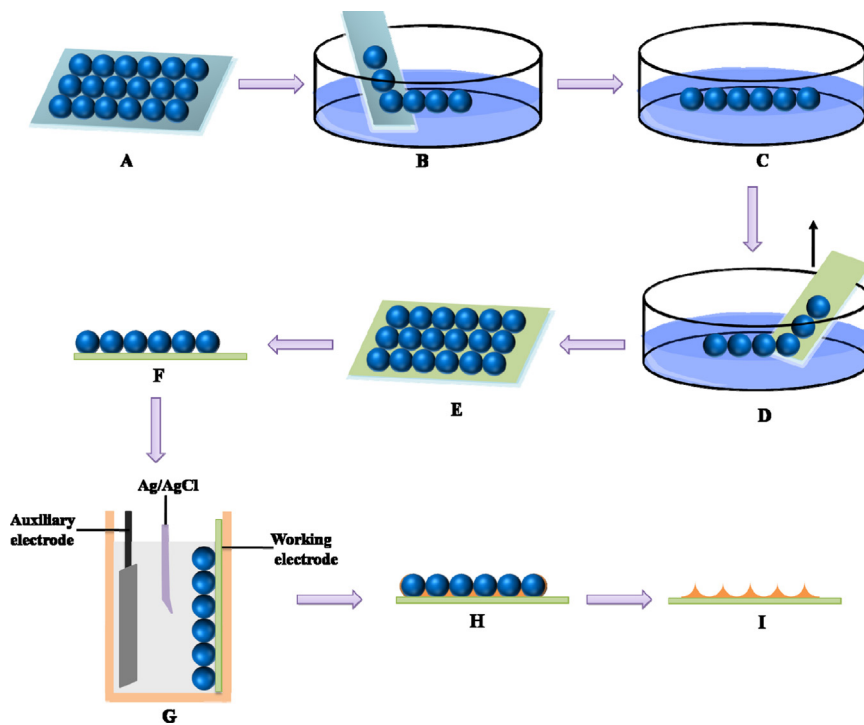
Platinum decorated on pore-arrayed H_xWO_3 ($\text{Pt}/p\text{-H}_x\text{WO}_3$) was prepared by magnetron sputtering using a machine of JEOL (JFC-1600) AUTO FINE COATER. The amount of Pt was controlled by sputtering current and time. For comparison, the electrocatalysts, platinum nanoparticles decorated on ITO and non-pore-arrayed H_xWO_3 , were also prepared under the same sputtering conditions, denoted as Pt/ITO and $\text{Pt}/\text{H}_x\text{WO}_3$, respectively. The sputtering current and time were 20 mA and 15 s , respectively.

2.3. Characterization and measurements

X-ray diffraction analyses were carried out with a D8 Advance X-ray diffractometer operated at 30 kV and 20 mA with $\text{Cu K}\alpha$ radiation. The morphology was observed by using scanning electron microscopy (JEM-6510, BRUKER TENSOR 27). TEM observation was performed on a transmission electron microscopy (TEM, JEM-2100HR). FTIR was performed on Fourier transform infrared spectrophotometer (Spectrum One).

Cyclic voltammetry, chronopotentiometry and chronoamperometry were conducted in a three-electrode cell at room temperature on AUTOLAB (PGSTAT302 N). The electrolyte used was $0.5\text{ M H}_2\text{SO}_4$ solution with or without $1.0\text{ M CH}_3\text{OH}$. ITO with electrocatalyst was used as the working electrode, a platinum sheet as the counter electrode, and an $\text{Ag}/\text{AgCl}/\text{saturated KCl}$ electrode as the reference electrode.

The single cell was set up for the determination of discharge performance. The membrane-electrode-assembly (MEA) was fabricated according to the method in the literature [32]. $0.5\text{ g Pt}/\text{H}_x\text{MoO}_3$ or $\text{Pt}/p\text{-H}_x\text{MoO}_3$ was used in the anode, which was stripped directly from ITO electrode. Cathode was prepared with Pt/C ($20\text{ wt.}\%$ Pt, Johnson Matthey Company) as electrocatalyst in a platinum loading of 1 mg cm^{-2} . Nafion 117 (DuPont Company) was used as the membrane. The cell performance was measured on a



Scheme 1. Strategy and manipulation for the fabrication of $p\text{-H}_x\text{WO}_3$. (A) PS spheres on a flat glass substrate fabricated by spin coating; (B) PS spheres transferred into deionized water; (C) PS sphere monolayer floating on the deionized water; (D) PS sphere monolayer transferred onto an ITO substrate; (E) PS sphere monolayer on ITO substrate; (F) PS sphere monolayer was bonded to the ITO substrate by heating; (G) Electrodeposition; (H) Integrity of H_xWO_3 and PS sphere monolayer; (I) $p\text{-H}_x\text{WO}_3$ after removing PS spheres.

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