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Pore-arrayed hydrogen molybdenum bronze: Preparation and performance as support of platinum nanoparticles for methanol oxidation

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HIGHLIGHTS

- Pore-arrayed H_xMoO_3 was prepared by using polystyrene spheres as templates.
- Electrocatalyst with platinum nanoparticles dispersed on pore-arrayed H_xMoO_3 was developed.
- Pore-arrayed H_xMoO_3 reduces particle size and increases specific surface area of platinum.
- Pore-arrayed H_xMoO_3 improves electrocatalytic activity of platinum toward methanol oxidation.

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ABSTRACT

A novel electrocatalyst for methanol oxidation is fabricated by decorating platinum nanoparticles on pore-arrayed hydrogen molybdenum bronze (H_xMoO_3). In this fabrication, pore-arrayed H_xMoO_3 is prepared with polystyrene monolayer as a template, and platinum nanoparticles are decorated on the resulting pore-arrayed H_xMoO_3 by using a current pulse technique. The fabricated electrocatalyst is investigated with a combination of physical characterizations from X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy, and electrochemical measurements including cyclic voltammetry, chronopotentiometry, chronoamperometry, and cell discharge test. It is found that the platinum decorated on pore-arrayed H_xMoO_3 (Pt/p-H_xMoO_3) is more uniform, has smaller particle size and exhibits improved electrocatalytic activity and stability for methanol oxidation, compared to that on non-pore-arrayed H_xMoO_3 (Pt/H_xMoO_3). The peak current for methanol oxidation in cyclic voltammetry is improved from 4.89 mA cm^{-2} for Pt/H_xMoO_3 to 6.41 mA cm^{-2} for Pt/p-H_xMoO_3, and the time for abrupt potential change in chronopotentiometry is enhanced from 498 min for Pt/H_xMoO_3 to 576 min for Pt/p-H_xMoO_3. The improved performance is attributed to the larger specific surface area of the pore-arrayed H_xMoO_3, which favors the formation of smaller Pt nanoparticles.

1. Introduction

Direct methanol fuel cell (DMFC) is considered to be one of the most possible commercialized fuel cells because of its high energy density, cheap resources, low emissions and mild operating temperature [1,2]. However, there are still some drawbacks that hinder the commercialization of DMFC [3]. One of the major challenges is the use of noble metal platinum as anodic catalyst. Platinum is very expensive and tends to be poisoned by the adsorption intermediates CH_zO_{ads} ($0 \le z \le 4$) generated from the incomplete oxidation of methanol [4,5]. Therefore, it is necessary to develop effective electrocatalysts with low amount of platinum and high activity toward methanol oxidation [6,7]. To date, there has been considerable interest in developing Pt-based alloys such as PtRu [8], PtMo [9], PtAu [10], PtW [11], PtSn [12], PtRh [13], PtNi [14] and PtPd [15], which can reduce the use of platinum as well as improve its electrocatalytic activity. Similarly, Pt nanoparticles incorporated in metal oxides such as MoO_x [16], TiO_2 [17], MnO_2 [18], CeO_2 [19],

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and WO_x [20] have been found to be effective to increase the activity of the electrocatalysts toward methanol oxidation.

Among the metal oxides, different forms of molybdenum in acidic media have received much attention. In acidic media, MoO_x can form a nonstoichiometric and electroconductive hydrogen molybdenum bronze (H_xMoO_3, $0 < x \leq 2$) compound [21–23]. It has been known that the activity of platinum toward methanol oxidation can be improved by using H_xMoO_3 as support [24–27]. This improvement is ascribed to the proton spillover between Pt and H_xMoO_3. The redox couple H_xMoO_3/H_yMoO_3 ($0 \leq y < x \leq 2$) is reversible. The hydrogen molybdenum bronze with higher amount of hydrogen (H_xMoO_3) is easily oxidized on the platinum to form the hydrogen molybdenum bronzes with less hydrogen (H_yMoO_3). The latter plays a role as proton acceptors, which help the further oxidation of the adsorption intermediates CH_zO_{ads} ($0 \leq z \leq 4$) on platinum.

The morphology of the support is obviously important for the activity of the electrocatalyst. Two-dimensional (2D) ordered pore arrays (films) have exhibited their distinctive structural features in catalysts because of their high specific surface area and an orderly arrangement of pores [28,29]. The ordered pore arrays can be synthesized by electron-beam lithography [30], micro-contact printing [31], electrochemical etching [32] and self-assembly techniques [33], etc. Among these techniques, self-assembly technique is facile and favors the universal morphology-controlled growth of large-scale ordered pore arrays.

In this work, self-assembly technique was adopted to fabricate pore-arrayed H_xMoO_3 and a new composite as the electrocatalyst for methanol oxidation was developed by decorating platinum nanoparticles on pore-arrayed H_xMoO_3 using current pulse technique. The morphology, structure, composition, and electrocatalytic activity of the resulting electrocatalyst were investigated with X-ray diffraction, scanning electron microscopy, cyclic voltammetry, chronopotentiometry, chronoamperometry, and cell discharge test, with a comparison of the electrocatalyst, platinum supported by non-pore-arrayed H_xMoO_3.

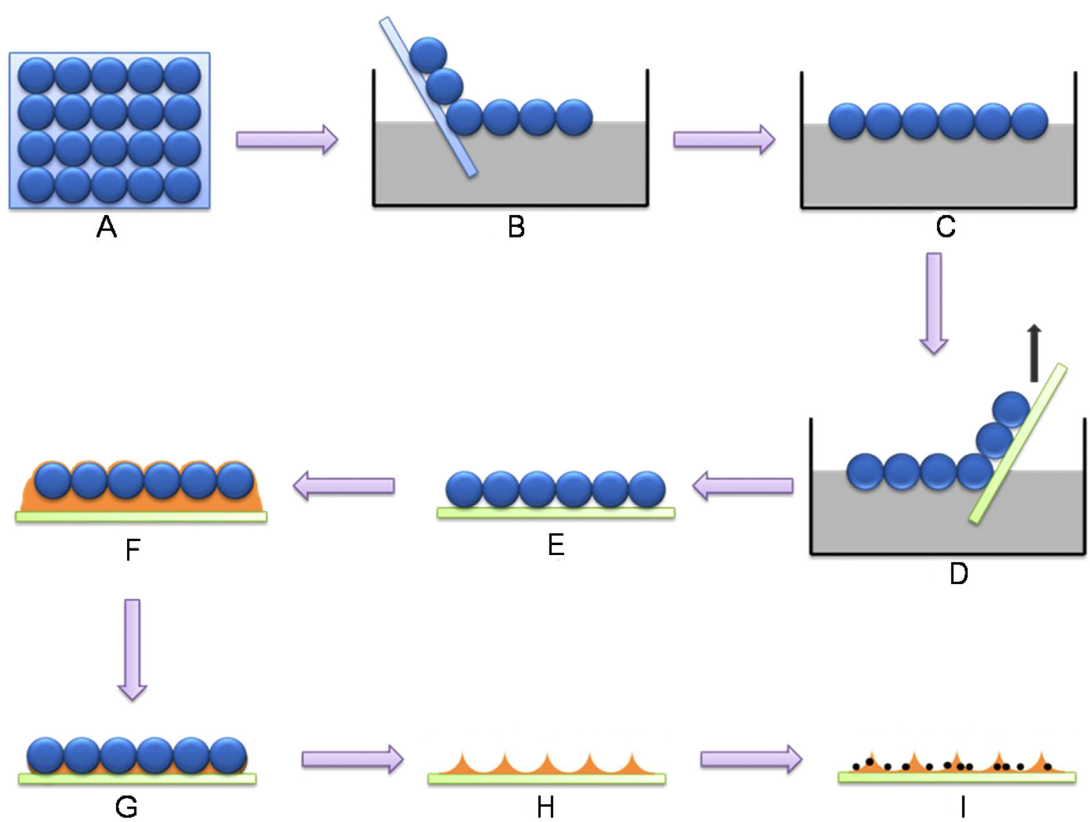
2. Experimental

2.1. Preparation of pore-arrayed H_xMoO_3

Firstly, polystyrene (PS) spheres were synthesized by using an emulsifier-free emulsion polymerization technique [34], and coated on a glass substrate (GS) by spin-coating method [35]. Then PS monolayer was obtained by immersing PS/GS into distilled water and floating PS on ITO (effective area was 1.0 cm × 1.0 cm) surface, as described in Scheme 1. On the other hand, H_xMoO_3 sol was freshly prepared by reducing H_2MoO_4 with formaldehyde as reductant. H_2MoO_4 was obtained by dropping H_2SO_4 solution into ammonium molybdate solution under magnetic stirring. Then H_xMoO_3 sol was dropped onto PS/ITO substrate and dispersed among PS spheres to form PS-H_xMoO_3/ITO. After being dried for 2 h at 80 °C, PS-H_xMoO_3/ITO was immersed into toluene to remove PS spheres for forming pore-arrayed H_xMoO_3.

2.2. Platinum nanoparticles decorated on pore-arrayed H_xMoO_3

Platinum nanoparticles were decorated on pore-arrayed H_xMoO_3 by using a current pulse technique with a cathodic pulse (−0.01 A, 0.3 s) and an anodic pulse (+0.1 A, 0.3 s) for 20 cycles. The decoration was performed in 5 mM H_2PtCl_6 + 0.1 M H_2SO_4 solution, with platinum sheet as the counter electrode, Ag/AgCl/saturated KCl electrode as the reference electrode and pore-arrayed H_xMoO_3/



Scheme 1. Strategy and manipulation for synthesizing Pt/p-H_xMoO_3 on ITO substrate. (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): H_xMoO_3 sol was dropped onto PS sphere monolayer; (G) Integrity of H_xMoO_3 and PS sphere monolayer; (H): pore-arrayed H_xMoO_3; (I) platinum particles supported by pore-arrayed H_xMoO_3.