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Microwave-assisted synthesis of double-shell PtRu/TiO₂ catalyst towards methanol electro-oxidation

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ABSTRACT

A facile synthetic route was employed to prepare double-shell PtRu/TiO₂ catalyst successfully without any stabilizer, in which Ru precursor was reduced by microwave and Pt precursor was in-situ reduced on Ru/TiO₂ using L-ascorbic acid as the soft reductant. The morphology, structure and composition of as-prepared catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis of X-ray (EDX), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry and chronoamperometry demonstrate the enhancement of electrocatalytic activity and stability towards the methanol electrooxidation of PtRu/TiO₂ in comparison with Pt/TiO₂, Pt/C (JM) and PtRu/C (JM). Furthermore, the activity for methanol oxidation reaction (MOR) is much higher in alkaline media than that in acidic media. The improved activity and stability could be attributed to the synergetic effects of Pt–Ru and the electrochemically stable TiO₂.

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Introduction

Direct methanol fuel cells (DMFCs), as promising alternatively power sources for a variety of transportation and portable applications, have attracted many interests due to their high energy density (6100 Wh kg⁻¹), environmental sustainability, low toxicity, high energy-conversion efficiency and compact system [1–4]. However, their insufficient durability and high cost issues are main challenges that hinder and delay the further and large-scale commercially application of DMFCs. The reason for DMFCs anodic catalysts with poor reaction

activity is mainly the poisoning effect of CO on the commonly used Pt catalyst, which limits the utilization of noble metal. CO adsorbs on Pt surface strongly, resulting in blocking the active surface and prohibiting further methanol oxidation reaction (MOR) [5].

The ways to improve the electrocatalytic activity are various by changing the composition, preparation methods, morphology and supports [6,7]. In view of this, the Pt-based catalysts combining Pt with a second metal, such as Sn [8], Ni [9], Pd [10,11], Au [4,12–14], Ru [15] or metal oxides, such as MoO_x [16], NiO_x [9], TiO_x [17], WO₃ [18], CeO₂ [19] have been researched. Among all these systems, the PtRu bimetallic

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catalysts have been regarded as one of the most promising catalyst for MOR. The addition of Ru will improve the CO tolerance of Pt and reduce the Pt loading compared with Pt alone catalysts [20]. Two mechanisms could explain the effect of Ru called the bifunctional mechanism [21] and the ligand effect [22]. Various methods have been developed to prepare nanocatalysts, such as physical vapor deposition, colloidal synthesis, and impregnation [23–25]. Microwave-assisted polyol method has been reported to be an easy and fast technique allowing time and energy saving for preparing nanoparticles in narrower particle size distribution and with smaller particle size compared with conventional oil-bath heating method [26,27]. Notably, the catalysts are prepared without any stabilizing agents during the whole synthesis process. In order to improve the catalytic performance of catalysts, bimetallic catalysts have been fabricated in the form of porous, alloys and core–shell structures [28–31]. The porous catalysts show high active surface area leading to enhanced catalytic activity. Different groups have reported the excellent performance of this specific structure [32–35]. The PtRu catalysts in alloyed form have been considered as high active ones. However, the inner interfaces of Pt–Ru in the alloyed nanoparticles are not accessible to the reactant molecules, leading to low Pt utilization. In order to utilize the unused Pt lying beneath the surface layer, the core–shell catalysts, where a monolayer or several layers of Pt are dispersed on another metal layer or core, have attracted increasing attention [36]. And the catalysts with core–shell structure exhibit excellent catalytic properties [31,37–39]. It is well known that metal catalysts with supports exhibit better durability and improved activity compared to bulk metal catalysts without supports. Highly conductive carbon blacks with high surface areas have been commonly used as the support of the commercial fuel cells electrocatalysts. However, all carbon supports suffer the issue of carbon corrosion in varying degree, leading to loss of catalyst and finally affecting the overall performance of the fuel cells. Therefore, searching for non-carbonaceous based supports is vitally important to solve this issue. Titanium oxide or titania materials show excellent corrosion resistance and electrochemical stability even in acidic medium, promoting researches of these as catalyst supports in fuel cells [40,41]. In addition, other advantages including non-toxic, easily available and low cost make them a promising support for Pt electrocatalysts [42]. Wang et al. showed that the performance of the catalyst toward methanol oxidation was improved by adding TiO₂ [17]. The presence of an additive such as SiO₂, TiO_x and WO_x could also stabilize the PtRu catalysts and improve the interaction between noble metal particles and the support, which will inhibit the dissolution of Ru from the PtRu system [43].

In this study, double-shell PtRu catalyst supported on TiO₂ (PtRu/TiO₂) was synthesized by microwave-assisted method without any surfactant. At first, the Ru/TiO₂ was prepared by assembling the Ru nanoparticles (NPs) and functionalized-TiO₂ (f-TiO₂) through electrostatic interaction, and Pt NPs were in-situ prepared on Ru/TiO₂ spheres to produce PtRu/TiO₂. The electrooxidation behaviors of methanol in acidic and alkaline medium were both investigated by cyclic voltammetry and chronoamperometric measurements. Results showed that the

as-prepared PtRu/TiO₂ was highlighted compared to Pt/TiO₂, commercial Pt/C (JM) and PtRu/C (JM) catalysts for excellent methanol oxidation activity and durability.

Experimental section

Chemicals

Water used in this work was purified using the Millipore system. 3-Aminopropyltrimethoxysilane (APTMS) was purchased from J&K. Nafion (perfluorinated ion-exchange resin, 0.5 wt% solution in a mixture of ethanol and water) was purchased from Aldrich. All other chemicals, such as ruthenium chloride (RuCl₃), chloroplatinic acid (H₂PtCl₆·6H₂O), L-ascorbic acid (AA) and tetrabutyl titanate (Ti(OC₄H₉)₄), were of analytical grade and purchased from the Shanghai Chemical Factory (Shanghai, China) without further purification.

Preparation of microsphere and modified electrodes

NH₂-functionalized TiO₂ precursor spheres (f-TiO₂) were synthesized according to the reported procedures [44]. The as-prepared f-TiO₂ had a good dispersibility and the average diameter was about 200 nm. The synthesis of TiO₂-supported double-shell PtRu catalyst is described as follow. At first, a certain amount of RuCl₃ dissolved in pure-water was added to 20 mL of ethylene glycol reaching the concentration of metals of 0.15 g L⁻¹. And the pH of the solution was adjusted to 10 by adding 1 mol L⁻¹ NaOH dropwise into ethylene glycol. The solution above was placed in a microwave reactor operated at 130 °C for 10 min, and cooled down to the room temperature. 80 mL water containing 10 mg f-TiO₂ spheres were added to the Ru colloidal solution above and stirred for 4 h. Ru/TiO₂ spheres were harvested via centrifuging and washing with pure water several times, and dispersed into 150 mL of the pure water. A specified volume of H₂PtCl₄ (0.0303 mol L⁻¹) and 0.2 g L-ascorbic acid dissolved in 4 mL of water were added quickly into 30 mL of Ru/TiO₂ solution or TiO₂ solution (containing 2 mg f-TiO₂ and 30 mL pure water) and kept at 80 °C for 2 h to get the PtRu/TiO₂ or Pt/TiO₂. At last, the as prepared double-shell PtRu/TiO₂ or Pt/TiO₂ spheres were centrifugated and collected in 1 mL of water.

The GC electrode was polished with 1, 0.3 and 0.02 μm alumina slurry sequentially to mirror and then ultrasonically washed in water and ethanol for 15 min. The cleaned GC electrode was dried at room temperature for further modification. Catalyst ink was prepared by diluting catalyst (PtRu/TiO₂, Pt/TiO₂, Ru/TiO₂, Pt/C (JM) (20 wt %), or PtRu/C (JM) (30 wt %)) with water to a calculated volume. A 5 μL of this slurry was pipetted out on the surface of the GC electrode and dried at room temperature to yield a metal loading of 64 ± 1 μg cm⁻². Then, 10 μL of Nafion (0.5 wt %) was dropped on the surface of the modified electrode.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku (miniflex) equipped with a Ni filter using Cu Kα radiation (λ = 1.54056 Å) at 35 kV and 15 mA to analyze the crystal

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