



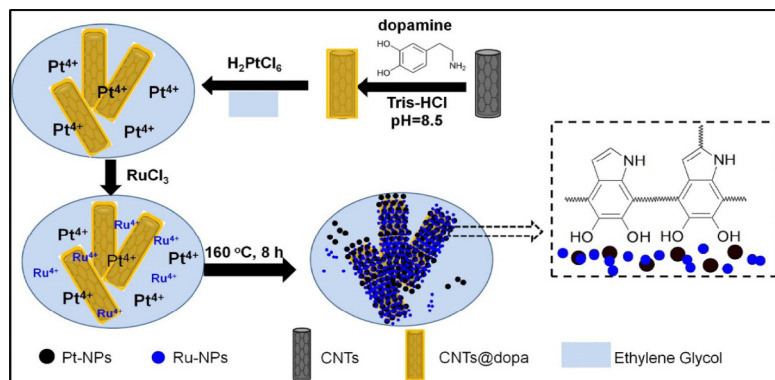
Regular Article

Facile and one-pot synthesis of uniform PtRu nanoparticles on polydopamine-modified multiwalled carbon nanotubes for direct methanol fuel cell application

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GRAPHICAL ABSTRACT

PtRu NPs immobilized on the P Dop coating-modified MWCNTs – bimetallic alloy catalysis used as the direct methanol fuel cell application.



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ABSTRACT

A facile, environment-friendly and one-pot synthesis method for the preparation of high performance PtRu electrocatalysts on the multiwalled carbon nanotubes (MWCNTs) is reported. Herein, bimetallic PtRu electrocatalysts are deposited onto polydopamine (P Dop) – functionalized MWCNTs by mildly stirring at room temperature. Without the use of expensive chemicals or corrosive acids, this noncovalent functionalization of MWCNTs by P Dop is simple, facile and eco-friendly, and thus preserving the integrity and electronic structure of MWCNTs. Due to the well improved dispersion and the decreased size of alloy nanoparticles, the PtRu electrocatalysts on P Dop-functionalized MWCNTs show much better dispersion, higher electrochemically active surface area, and higher electrocatalytic activity for the electrooxidation of methanol in direct methanol fuel cells, compared with the conventional acid-treated MWCNTs.

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1. Introduction

The direct methanol fuel cells (DMFCs) have received considerable attentions for applications in transportation, portable electronics, and residential power sources, due to their high energy density, relatively low operating temperatures, zero or low emission of pollutants and minimal corrosion problems. However, the commercial viability of DMFCs is still hindered by several factors, including the low catalytic activity of electrodes both for the oxygen reduction reaction (ORR) and for the methanol oxidation reaction (MOR), the high costs of the Pt-based electrocatalysts, and the susceptibility of the catalysts to be poisoned by the CO-like intermediates formed in the methanol oxidation reaction [1,2]. In spite of all these problems, Pt-based electrocatalysts has been a consecutive hot topic in the electrocatalyst field [3–6].

The most common solutions to these problems are to combine platinum with other metals such as Ru, Ni, and Co [7–9], and meanwhile develop the morphology and distribution of the metals on proper supports [10–12]. Over the last two decades, various Pt-based bimetallic catalysts have been studied [13–15]. Among them, PtRu alloy catalyst is a leading candidate as a DMFCs anode since it shows high catalytic activity for methanol oxidation reaction as well as strong tolerance against carbon monoxide poisoning [16–18], and in particular, the Ru in the PtRu alloy can easily oxidize the CO intermediate to CO₂ by the bifunctional mechanism [19]. Furthermore, these fabrication methods generally involve the reduction of metal ions using reducing agents such as hydrazine hydrate [20], sodium borohydride [21], formaldehyde [22], ascorbic acid (AA) [23,24] and dimethyl formamide [25] and most of these reductants are highly toxic and pose potential environmental and biological risks. Therefore, there is an urgent need to exploit eco-friendly, cost effective and highly active catalysts for methanol oxidation [26].

On the other hand, as well realized that the proper selection of the carbon supporting materials for PtRu nanocatalyst would be helpful to overcome the problems such as slow kinetics of the oxidation reaction and poor tolerance to CO poisoning. Compared with smooth Pt and PtRu bulks, carbon-supported Pt and PtRu nanoparticles (NPs) show higher current efficiency for methanol oxidation due to their larger surface areas whereby the soluble intermediates formed are more readily adsorbed and oxidized to CO₂ before they are transported away from the electrode surface by the continuous flow of electrolyte [27]. In this regard, nanocarbons such as carbon nanoparticles, carbon nanotubes (CNTs), and graphene are thus used as the supporting materials for PtRu nanocatalyst in the anode of DMFC or DEFC [28].

Comparatively, CNTs have attracted special attention as catalyst supports in fuel cell applications owing to their unique properties, such as large surface areas, high chemical resistibility, and superior mechanical strength. In addition, the hairlike structure of CNTs allows for entanglements among nanotubes, enabling better electron conductivity than traditional carbon systems [29]. From this context, numerous studies have reported higher electrocatalytic activities of Pt-based NPs supported on CNTs as compared with those deposited on high-surface-area carbon [30,31]. However, most of the established protocols to prepare CNTs-based electrocatalysts involve covalent functionalization of CNTs [29,32,33] leading to the severe disruption of nanotubes' intrinsic electronic properties and thus increasing application expenditures. Other strategies consist of an adsorption of small organic coupling molecules [34], polyelectrolytes [14,15], polymers [17] or surfactants [35] to enable strong affinity of metal NPs on nanotubes. Nevertheless, such noncovalent modification introduces an issue of concern that the molecules adsorbed on the surfaces of NPs may adversely affect their catalytic efficiencies.

Polydopamine (Pdp), which with a molecular structure similar to that of DOPA (3,4-dihydroxy-L-phenylalanine), moved into the spotlight as a novel coating material since 2007 [36]. One of Pdp's valuable features lies in its chemical structure that incorporates many functional groups such as catechol, amine and imine. These functional groups can serve as both the starting points for covalent modification with desired molecules and the anchors for the loading of transition or noble metal ions, which can further realize the emergence of diverse hybrid materials by virtue of its powerful reducing capability toward these metal ions under basic conditions. Liu et al. [37] firstly reported that Pdp coatings contain abundant positively charged sites because of the nitrogen containing groups in the structure of Pdp, which enables Pdp to absorb on the surface of carbon materials through π - π interaction and electrostatic interaction, forming electrostatic repulsion between carbon materials and thus preventing them from aggregating in aqueous solution. To the best of our knowledge, however, this Pdp-involved, noncovalent modification strategy has not been reported in the case of PtRu bimetallic catalysts in DMFC application.

Inspired by Liu's work, herein, we developed an efficient PtRu electrocatalyst, showing highly electrocatalytic activity for methanol oxidation and with excellent carbon monoxide (CO) tolerance. As one part of significance in this work, we presented a facile and straightforward process to attach the PtRu nanoparticles (NPs) on the Pdp-modified MWCNTs (CNTs@Pdp). In this process no stabilizers (i.e., organic species, surfactants) for NPs and harsh pretreatments for MWCNTs are required. The as-prepared CNTs@Pdp can form a stable suspension for several weeks in the absence of any stabilizers and accordingly the re-stacking of the CNTs is effectively inhibited, which thus supply ideal anchorage points for the PtRu NPs attachment; meanwhile, the chemical and crystallographic features, morphology, as well as electrocatalytic activity of the obtained catalysts were studied in detail via X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), etc. As indicated, the Pdp coating with an approximate several nanometers in thickness was uniformly deposited on MWCNTs, which leads to a homogeneously distribution of PtRu NPs, and this consequently brings about significantly enhanced electrocatalytic activity for the methanol oxidation reaction (MOR).

2. Experimental section

2.1. Materials

The multiwalled carbon nanotubes (MWCNTs, purity = 95%, average diameter = 10–20 nm, length = 5–15 μ m), Shenzhen Nanotech Port Co., Ltd. Hexachloroplatinic (IV) acid hexahydrate (H₂PtCl₆·6H₂O), ruthenium trichloride (RuCl₃), Aladdin Reagent (Shanghai) Co., Ltd. 2-amino-2-hydroxymethylpropane-1,3-diol (tris), Sinopharm Chemical Reagent Co., Ltd. Dopamine hydrochloride, Alfa Aesar. All chemicals were of analytical grade and used as received.

2.2. Preparation of samples

2.2.1. The purification of MWCNTs

Proper quantities of crude MWCNTs were added into a three-necked flask containing sulfuric acid and nitric acid in the ratio of 3:1 by volume. The suspension was sonicated in an ultrasonic bath for 40 min and then heated to 120 °C and refluxed for 3 h. After centrifugation and later washing with hot distilled water until pH 7.0, the purified MWCNTs were dried in a vacuum oven at 35 °C for 24 h.

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