



# Fabrication of hollow platinum–ruthenium core–shell catalysts with nanochannels and enhanced performance for methanol oxidation



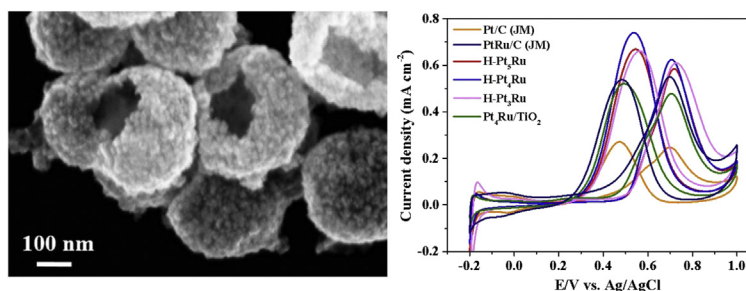
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## HIGHLIGHTS

- Hollow Pt/Ru core–shell catalysts with nanochannels were synthesized.
- Integrity of the Pt shell could be easily controlled by varying the  $\text{H}_2\text{PtCl}_6$  content.
- The H–PtRu catalysts showed high catalytic activity for MOR.
- The H–PtRu catalyst with high Ru content showed the highest stability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This work reports the preparation of hollow PtRu core–shell catalysts with  $\text{TiO}_2$  as template, in which the Pt nanoparticles (NPs) grow on the exterior surface of Ru layer. The quantity of Pt NPs is easily tailored to control the integrity of Pt shell through varying the concentration of  $\text{H}_2\text{PtCl}_6$  solution. Scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and selected-area electron diffraction (SAED) are used to characterize the structure and morphology of H–PtRu. The core–shell structure is confirmed by the high-angle annular dark-field scanning TEM (HAADF-STEM) with energy-disperse X-ray spectroscopy (EDX). The electrochemical performance of H–PtRu is investigated by cyclic voltammetry and chronoamperometry. Results show that the catalytic activity of H–PtRu toward methanol oxidation reaction (MOR) is ~2.5 times higher than that of Pt/C (JM), and the electrocatalytic stability improves with the increase of Ru content. Furthermore, H–PtRu exhibits better stability for methanol oxidation compared to Pt/C (JM) and PtRu/C (JM).

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are considered to be a commercially attractive electrochemical energy converter for

portable applications due to its low operating temperature, simple system design, high energy-conversion efficiency [1–3]. Up to now, the platinum (Pt) and Pt-based catalysts are still the most efficient and indispensable nanomaterials for anodic electrocatalytic reactions in DMFCs [4,5]. However, as a precious metal, Pt counts for a major part of the overall cost of a fuel cell, which is one of the most challenging issues for its commercial application. Furthermore, CO and intermediate species resulting from incomplete methanol

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oxidation adsorb strongly on Pt active sites increasing the anodic overpotential at a given current density [6]. Thus, developing new anodic catalysts to improve the catalytic performance and reduce the amount of Pt used is an urgent need for the development of DMFCs.

The catalytic activity for MOR could be improved according to the bi-functional mechanism and the ligand effect [7,8]. In the ligand effect, the addition of another metal can reduce the Pt loading and modify the electronic structure by changing the d-band of Pt. In the bi-functional mechanism, the introduction of a second metal could also produce oxygen-containing species at a lower potential, which can benefit the reaction with the CO-like intermediate species and improve the poisoning tolerance and durability of the catalysts. The ruthenium (Ru) with low price has been universally acknowledged as one of the most effective metals added to Pt, and the Pt–Ru bimetallic catalysts show high activity for methanol oxidation reaction (MOR) at relevant operating fuel cell voltages.

Hollow metallic or bimetallic spheres have several beneficial properties, such as high specific surface, material saving, low density, and cost reduction, having attracted considerable attention [9,10]. Besides, it is well recognized that the electrocatalytic properties are strongly dependent on the size, structure, morphology of the nanocatalysts [11,12]. Among various nanostructures, the nanoporous catalysts with large specific area, nanochannels, nanometer-scale pores and highly ordered networks, have attracted much attention for years [13]. The porous frameworks can not only increase the active area accessible to the reactant molecules but also provide efficient mass transfer compared with solid counterparts [14–16]. And the porous structure with nanoconfined space could make the molecule stay longer in the vicinity of the catalyst surface, indicating highly frequent interaction between the molecule and electrode surface. Therefore, it is an efficient approach of engineering porosity or hollow structure into Pt-based nanocatalysts to improve the catalytic activity and stability. The methods of preparing porous or hollow Pt-based structures are various, such as template synthesis [17,18], dealloying method [19,20], surfactant-assisted synthesis [21,22] and so on. In this current work, the hollow or nanoporous structure was synthesized via template removal with the titanium dioxide (TiO<sub>2</sub>) as the hard template. TiO<sub>2</sub> owns the advantages of stability in acidic and oxidative environments, nontoxicity and low cost [23], which has been used as a potential material for many applications in photocatalysis, photovoltaics and gas sensors [24]. And there are also many reports studying their role as the catalyst support or additive for the Pt-based catalysts [25–27]. However, it has been reported that the TiO<sub>2</sub> was only used as the template to prepare AuPt NPs assembling hollow spheres for MOR [28,29]. And the reported hollow PtAu catalyst just showed slightly improved activity for MOR compared to Pt/C (JM). It is crucial to find and prepare other hollow Pt-based catalysts meeting the requirement of excellent catalytic activity for the electrooxidation of methanol.

In this work, a series of hollow PtRu core–shell spheres with nanochannels were prepared via in situ sacrificial template method without any surfactant. For the purpose of comparison, TiO<sub>2</sub>-supported PtRu (Pt<sub>4</sub>Ru/TiO<sub>2</sub>) was also prepared without removal of TiO<sub>2</sub>. Ru NPs with narrow size distribution were firstly prepared using the microwave-assisted method, which was supported on TiO<sub>2</sub> subsequently. The reduction of Pt precursor on Ru core was performed using L-ascorbic acid (AA) as the reducing agent. Notably, no surfactants were used in the whole preparing procedure, which can deleteriously affect the electrocatalytic performance by adsorbing on the active sites. The physical and electrochemical characterization of the as-prepared nanocomposites was investigated. Peak current densities from cyclic

voltammograms showed that the H–PtRu exhibited better catalytic activity toward MOR than Pt/C (JM) and Pt<sub>4</sub>Ru/TiO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

3-Aminopropyltrimethoxysilane (APTMS) was purchased from J&K. Ultrapure water used in the whole experiments was purified using the Millipore system. Nafion (perfluorinated ion-exchange resin, 0.5 wt% solution in a mixture of ethanol and water) was purchased from Aldrich. The other chemicals, such as ruthenium chloride (RuCl<sub>3</sub>), chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), L-ascorbic acid (AA), citrate acid and tetrabutyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), were of analytical grade quality and purchased from the Shanghai Chemical Factory (Shanghai, China).

### 2.2. Preparation of catalysts

H–PtRu nanocomposites were prepared using a crystalline growth method as shown in Fig. 1. Ru NPs prepared by microwave method were anchored on the surface of f-TiO<sub>2</sub> to obtain Ru/TiO<sub>2</sub> nanocomposites. At the moment when H<sub>2</sub>PtCl<sub>6</sub> and AA were added to Ru/TiO<sub>2</sub> solution, Pt NPs will grow on the Ru NPs through the reduction of H<sub>2</sub>PtCl<sub>6</sub> using AA due to large amounts of active sites on the surface of Ru NPs. The hollow sphere could form gradually with the addition of citrate acid at 100 °C. The details are displayed below. The NH<sub>2</sub>-functionalized TiO<sub>2</sub> precursor spheres (f-TiO<sub>2</sub>) were prepared according to the reported literature [28]. The preparation of Ru NPs was described as follows. A calculated RuCl<sub>3</sub> solution was added to a three-necked flask containing 20 mL of ethylene glycol to make the concentration of metals reach 0.15 g L<sup>-1</sup>. Subsequently, the solution was transferred to a microwave reactor after adjusting the pH to 10 and conducted at 130 °C for 10 min. The as-prepared Ru colloidal solution above was added to 60 mL water containing 10 mg f-TiO<sub>2</sub> spheres and stirred for 2 h to get Ru/TiO<sub>2</sub>. The products were finally separated by centrifuging and washed with Ultrapure water several times. Products were diluted with 10 mL Ultrapure water and divided into five aliquots. In a typical synthesis of H–Pt<sub>3</sub>Ru, 200 μL of H<sub>2</sub>PtCl<sub>6</sub> (0.0303 mol L<sup>-1</sup>) and 0.2 g AA were diluted with 30 mL Ultrapure water and added quickly into one aliquot of Ru/TiO<sub>2</sub> solution. When the above solution was heated to 100 °C, 0.2 g citrate acid was added into the mixed solution kept at 100 °C for 2 h to get the H–Pt<sub>3</sub>Ru. Finally, the as-prepared H–PtRu was centrifugated and collected in 2 mL of water. H–Pt<sub>4</sub>Ru and H–Pt<sub>5</sub>Ru were synthesized in the same way with 250 μL and 300 μL H<sub>2</sub>PtCl<sub>6</sub>, respectively. And the Ru loading is fixed in the as-prepared microspheres and the thickness of Pt shell can be effectively controlled by varying the amount of H<sub>2</sub>PtCl<sub>6</sub> solution. Pt<sub>4</sub>Ru/TiO<sub>2</sub> was prepared with similar method without addition of citrate acid.

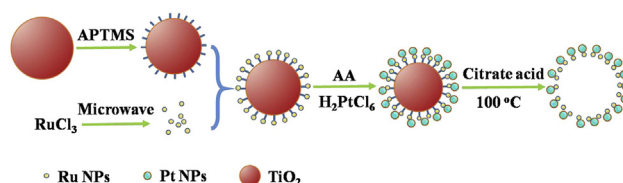


Fig. 1. Schematic diagram for the preparation of H–PtRu nanocomposites.

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