



COMMUNICATION

Ruthenium-platinum core-shell nanocatalysts with substantially enhanced activity and durability towards methanol oxidation



Jin Xie^a, Qinghua Zhang^b, Lin Gu^c, Sheng Xu^{a,d}, Peng Wang^{a,d}, Jianguo Liu^{a,*}, Yi Ding^e, Ying Fang Yao^a, Cewen Nan^b, Ming Zhao^a, Yong You^a, Zhigang Zou^a

^aNational Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

^bDepartment of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

^cBeijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

^dSub-Å Resolution Electron Microscopy Laboratory, Nanjing University, Nanjing 210046, China

^eInstitute for New Energy & Low-Carbon Technologies and School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

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Abstract

Platinum-based alloy nanocatalysts are highly attractive for both heterogeneous catalysis and electrocatalysis. However, their stability remains a major concern for their application under realistic operating conditions. We herein report a microwave-assisted synthesis of atomically ordered Ru-core Pt-shell (Ru@Pt) nanoparticles that show superior catalytic properties for methanol electrooxidation. The Ru@Pt catalysts are found to display higher methanol oxidation activity and CO-deactivation resistance than the commercial Pt-Ru catalysts. Shell-thickness variation induced properties is of great importance for core-shell catalysis. Above all, well-ordered Ru@Pt with sub-nm Pt shell exhibit superior durability in long-term and extreme operation condition in direct methanol

*Corresponding author. Tel.: +0086 25 83621219; fax: +086 25 83686632.

E-mail address: jianguoliu@nju.edu.cn (J. Liu).

fuel cell (DMFC). This type of core-shell catalysts thus hold great potential to be applied as high performance anode catalysts in DMFCs.

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Introduction

Among various kinds of fuel cells, DMFCs have been attracting significant interest and research efforts for its great potential to be commercialized as the major power source for portable electric devices, due to the facile storage and refilling characteristics of methanol fuel [1-3]. However, two critical issues have to be confronted when designing an effective methanol oxidation electrocatalysts: catalysts poisoning and metal dissolution. Firstly, methanol oxidation reaction (MOR) over Pt based electrocatalysts often produce strongly adsorbed intermediates such as CO and CH_x, which significantly poison the catalyst surfaces and retard the reaction kinetics, leading to rather low methanol oxidation activity [4]. Alloying Pt with other metals, such as Ru, Pd, Au and so forth, has been extensively investigated to improve CO tolerance and catalytic activity of the MOR catalysts [5-7]. Among them, Pt-Ru alloy was shown to have the best overall performance [8], which was traditionally attributed to a bi-functional mechanism or ligand effect [9,10]. However, ruthenium dissolution remains the major reason for the invalidation of fuel cells, especially at high potentials experienced during startup and shutdown [11-14]. Besides, Ru dissolving from anode may diffuse cross the membrane and cover active sites of the cathode catalyst, resulting in the severe degradation of ORR [11]. Therefore, it is of great urgency to fabricate catalysts with superior durability with improved corrosion resistance with methanol oxidation activity.

Compared to PtRu alloy nanocatalysts, Ru (core)-Pt (shell) catalysts (Ru@Pt) are highly promising for DMFCs. In this structure, the optimized controlled surface of Pt not only gives better protection against Ru-dissolution, but also increases the density of surface active site. Indeed, both theoretical calculations and temperature-programmed measurements have showed better performance in preferential CO oxidation in hydrogen stream for Ru@Pt nanoparticles (NPs), as compared with that of Pt-Ru nanoalloys or those of Pt shells with other metal cores [15]. Many types of Ru@Pt NPs synthesized by different methods were reported to have enhanced methanol oxidation activity [16,17]. However, in these studies, Ru NPs often existed in a disordered state as evidenced by very weak Ru signals in their XRD profiles [18,19]. And Pt atoms tend to diffuse into the disordered Ru cores through defects in order to reduce the cohesive energy of NPs. Therefore, partially alloying shell was often obtained instead of ordered Pt shell formation. The Ru@Pt catalysts reported in previous reports cannot fully solve the dilemma faced by DMFCs, because Ru-dissolution is inevitable under operation condition. Hsieh and co-workers reported well-ordered Ru@Pt NPs that showed excellent CO tolerance for hydrogen oxidation reaction when employing inexpensive reformat hydrogen [20]. We believe that Ru@Pt NPs with ordered Ru core with uniform Pt shells should amazingly suitable for employing in DMFCs. And the performance of this

type of Ru@Pt catalysts applied in DMFC should be further studied.

In this paper, we fabricate the Ru@Pt catalysts in the similar procedure introduced in previous reports [20-22]. And we innovatively employ microwave to heat the solvent, which conspicuously enhance efficiency and ensure the complete reaction of all precursors. The core-shell structure is confirmed by XRD and electron microscope technique. To clarify the activity and stability of Ru@Pt, a series of electrochemical measurements is conducted, including CO stripping, methanol oxidization and fuel cell tests. Surface electronic properties and strain effect of heterojunctions are clarified as the dominant factor in the catalytic performance. We further find that the thickness of Pt shell is another important factor in surface activity. The superior stability of Ru@Pt catalysts is illuminated after accelerated tests. To hit our target, JM-PtRu and JM-Pt are studied and the corresponding structure to electro-catalytic and stability correlation is presented as a reference.

Experimental section

Fabrication of Ru@Pt catalysts

In order to prepare optimized core-shell Ru@Pt catalysts, we performed a two-step ethanol reduction method. The first step is synthesizing carbon-supported Ru cores and the second step is coating Pt shells onto Ru cores. In a typical synthesis of Ru@Pt catalysts, 80 mL ethanol solution (99.99%) containing 150 μmol RuCl₃ was refluxed in the microwave oven at a power of 400 W for 20 min in a 250-mL flask, and the color of the solution turned to dark green from brown. Meanwhile, 170 mg carbon powder (Vulcan, XC-72) was dispersed in 50 mL ethanol by sonication for 20 min. The slurry was transferred into the reaction flask with 20 mL ethanol to assure a complete transfer and 5 mL 0.1 mol L⁻¹ NaOH aqueous solution was also injected. Then the reaction flask was heated in the microwave oven at a power of 400 W for 30 min. After the mixture cooled down to room temperature, the precipitates were filtered and collected. Dried in the vacuum oven for 10 h, the as-synthesized Ru/C sample was annealed in H₂/Ar at 450 °C for 1 h, then dispersed in 150 mL ethanol and refluxed at 80 °C for 20 min. After cooling, 3 mL ethanol solution containing 75 μmol H₂PtCl₆ was introduced and hyper-acoustic treatment for 20 min was used to ensure a uniform dispersion. At the same time, the pH of the mixture was adjusted to 10 with 0.1 mol L⁻¹ NaOH aqueous solution. Then the mixture was heated in the microwave oven at a power of 400 W for one hour. Typically the solution turned into colorless. The mixture was filtered and rinsed with copious amount of water to eliminate the Cl⁻ ions. And then the precipitate was dried in vacuum oven at 80 °C over night. The synthesized sample, named as

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