Electrochimica Acta 266 (2018) 305–311

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Facile synthesis of composition-tunable PtRh nanosponges for methanol oxidation reaction

Qingqing Lu [a, b], Jianshe Huang [a], Ce Han [a], Litai Sun [a, b], Xiurong Yang [a, *]

[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, Jilin, China*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, China*

ARTICLE INFO

Article history:
Received 18 December 2017
Received in revised form
29 January 2018
Accepted 3 February 2018
Available online 6 February 2018

Keywords:
Platinum
Rhodium
Nanosponges
Electrocatalyst
Methanol oxidation reaction

ABSTRACT

Currently, the synthesis of desired Pt-based electrocatalysts for methanol oxidation reaction (MOR) remains a challenge in terms of controlling the particle morphology, composition, and electrochemical property. In this study, we present a rapid and facile method for the formation of bimetallic PtRh nanosponges (NSs) by the co-reduction of two metallic precursors using sodium borohydride at room temperature in the absence of any surfactant. Their compositions can be directly tuned by changing the ratio between Pt and Rh precursors. PtRh NSs were obtained in a high yield of three-dimensional (3D) foam-like nanostructure with interconnected pores. Interestingly, the electrocatalytic performance of as-synthesized PtRh NSs was composition-dependent, and they exhibited remarkably improved methanol oxidation activity as compared to Pt NSs and commercial Pt/C catalyst. PtRh NSs were also found to be much more stable as evidenced by the chronoamperometric measurement. Their superior electrochemical properties are ascribed to the 3D porous nanostructure, alloy effect, and clean particle surface. This work provides a simple and effective method to prepare highly active electrocatalysts toward MOR in acid medium.

1. Introduction

Porous materials have received extensive attention over the past several decades owing to their high surface area, low density, fast mass transfer, and superior thermal conductivity [1–5]. They have been used in broad fields such as gas adsorption [6], catalysis [7], energy storage [8], drug delivery [9], and sensor [10]. A great number of synthesis strategies have been developed to prepare porous materials including template-directed method [11,12], selective leaching [13,14], freeze drying [15], self-assembly approach [16], and so on [17]. For example, Li et al. fabricated mesoporous gold films with tunable pores by utilizing diblock copolymers as soft-templates [18]. Ordered macroporous titania was achieved by spontaneous assembly in alkoxide-water solutions without using any surfactant [19]. Although considerable efforts have been made in synthesizing porous materials, a simple and rapid method for scalable production is still highly desirable.

In recent years, proton exchange membrane fuel cells (PEMFCs), which directly convert chemical energy into electrical energy, have been recognized a promising power source for electric vehicles and portable electronics [20]. Among various types of PEMFCs, direct methanol fuel cells (DMFCs), using methanol as liquid fuel, offer advantages of high energy density, near-zero environmental pollution, low operation temperature as well as convenient fuel storage and transportation. Further development of DMFCs greatly relies on the rational design of highly efficient electrocatalysts for methanol oxidation reaction (MOR). Because of the poisoning effect and sluggish kinetics associated with pure metal platinum, it is necessary to develop alternative Pt-based bi/multimetallic nanomaterials to improve the electrocatalytic activity and durability [21]. Previous studies have demonstrated that alloying Pt with a second metal such as Au, Ru, Pd, or Rh can exhibit superior electrochemical performance relative to their single metal counterparts due to the so-called bifunctional and ligand effect [22–27]. Among various Pt-based catalysts, bimetallic PtRh nanoparticles are of particular interest for electrocatalysis [28]. First, Rh can activate water decomposition to produce surface oxygen species at a potential of 250 mV lower than Pt, which facilitates the removal of

---

[*] Corresponding author.
E-mail address: xryang@ciac.ac.cn (X. Yang).

https://doi.org/10.1016/j.electacta.2018.02.021
0013-4686/

intermediates and the further methanol adsorption on Pt surface [29]. Second, Rh has excellent corrosion resistance in the strongly acidic medium, thus making PtRh alloys more stable in acid environment [30]. Besides, the surface Rh sites may also adsorb underpotentially deposited hydrogen and participate in the dehydrogenation reaction during the MOR, thereby accelerating the electrochemical process when alloying with Pt [31]. Therefore, bimetallic PtRh nanomaterials are potential catalyst system for MOR in acid medium.

The morphology control over PtRh nanocrystals have been used to further improve their electrocatalytic performance. For instance, Zhang et al. proposed a modified high-temperature self-assembly strategy to synthesize PtRh alloy porous nanostructure in the presence of oleylamine [32]. The as-prepared 3D porous nanostructure with different compositions showed higher catalytic activity and better stability for MOR as compared to bulk PtRh nanoparticles and commercial Pt/C catalyst. Wang's group reported that the Rh/Pt ultrathin nanowires prepared by a two-step, seed-mediated approach displayed superior electrocatalytic activity and selectivity toward ethanol oxidation reaction (EOR) [33]. However, the developed method usually required harsh reaction conditions such as multi-step synthesis, organic solvent, and high-temperature. Also the composition of PtRh nanocrystals cannot be precisely controlled, and the structure-directing agent is detrimental to their electrochemical performance. To the best of our knowledge, the facile synthesis of clean PtRh nanomaterials with controllable composition and porous structure remains a great challenge.

Herein, we extend the kinetically controlled sodium borohydride reduction method to synthesize bimetallic PtRh alloy nanosponges (NSs). Compared with the previously reported synthesis approaches for PtRh nanostructure, our proposed method is simply performed by mixing two metallic precursors with reducing agent at room temperature within 5 min, which effectively avoids the surface contamination and simplifies the experimental procedure. Their compositions can be readily tuned by varying the ratio of Pt and Rh precursors. Impressively, when used as the support-less catalyst for MOR, the as-prepared PtRh NSs show composition-dependent electrochemical activity and durability, and all cases are superior to pure Pt NSs and commercial Pt/C catalyst. Such an excellent catalytic performance can be ascribed to the 3D porous nanostructure, bimetallic alloys and clean particle surface.

2. Experimental

2.1. Chemicals and materials

Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was provided by Sinopharm Chemical Reagent Co, Ltd (Shanghai, China). Rhodium chloride ($RhCl_3 \cdot xH_2O$), sodium borohydride ($NaBH_4$), and Nafion (5 wt%) were purchased from Sigma Aldrich. Commercial Pt/C (20 wt%) was ordered from Alfa Aesar. All the materials were used as received without further purification.

2.2. Synthesis of bimetallic PtRh NSs

$Pt_{54}Rh_{46}$ NSs were synthesized as follows: An aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (0.1 M, 1.0 mL) and $RhCl_3 \cdot xH_2O$ (0.1 M, 1.0 mL) were quickly injected into 10 mL $NaBH_4$ aqueous solution (0.1 M) under vigorous stirring. The mixture was stirred for another 5 min at room temperature. Finally, the product was collected by centrifugation followed by washing three times with deionized water. Moreover, we varied the molar ratio of Pt and Rh precursors to 3/1, 1/3 and 1/0 to prepare $Pt_{73}Rh_{27}$, $Pt_{33}Rh_{67}$, and Pt NSs, respectively.

2.3. Characterization

Scanning electron microscope (SEM) images and energy-dispersed X-ray (EDX) spectra were taken on an FEI XL30 ESEM FEG filed emission scanning electron microscope operated at 25 kV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), high-angle annular dark-filed scanning TEM (HAADF-STEM), and the corresponding elemental mapping images were obtained using a JEM-2100F HRTEM operated at 200 kV. X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADANCE diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Nitrogen adsorption-desorption isotherms were measured using an automatic N_2 adsorption-desorption instrument (Quantachrome Autosorb Automated Gas Sorption System). The specific surface areas and the pore-size distributions were determined by using the Brunauer– Emmett–Teller (BET) and the Barrett–Joyner –Halenda (BJH) methods, respectively. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB-MKII spectrometer with Al Kα X-ray as the light source calibrated by C 1s level of 284.8 eV. The exact Pt concentration was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, X Series 2, Thermo Scientific USA). Electrochemical experiments were performed on a CHI 832 electrochemical workstation (Chenhua, China).

2.4. Electrochemical measurements

A standard three-electrode system was used, including a platinum wire as the counter electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode, and a glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode. Prior to the surface coating, the GCE was sequentially polished with 1.0, 0.3, and 0.05 μm alumina slurry, and then rinsed ultrasonically with deionized water. For each catalyst, 2 mg of powder was dispersed ultrasonically in 1 mL of water to get a homogeneous aqueous solution, and 3 μL of catalyst ink was coated on the electrode surface and dried at room temperature, followed by 3 μL of 0.05 wt% Nafion solution. The total loading amount for each sample is 6 μg, and the exact Pt concentration was determined by ICP-OES. Before the electrochemical measurement, the catalyst surface was cleaned in N_2-saturated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} between −0.2 and 1.2 V. The electrochemically active surface areas (ECSAs) were determined by integrating the charges (Q_H) for the hydrogen desorption region after double layer correction in the cyclic voltammograms (CVs) and assuming 210 μC cm^{-2} for the hydrogen monolayer adsorption (q_H) on the Pt surface [24]. Methanol electrooxidation measurements were conducted in a mixture of 0.5 M H_2SO_4 and 1.0 M CH_3OH solution in the potential window of 0.0 and 1.0 V with a scan rate of 50 mV s^{-1}. The durability tests were recorded at 0.6 V *vs.* Ag/AgCl in the 0.5 M H_2SO_4 and 1.0 M CH_3OH solution for 3600 s [26,27]. All the electrochemical measurements were carried out at room temperature.

3. Results and discussion

Herein, we demonstrate an aqueous solution synthesis of composition-tunable porous PtRh alloy NSs by simply mixing the two metallic precursors with reducing agent at room temperature. Although $NaBH_4$ reduction method was widely used to prepare PtRh nanoparticles [34–36], the ingenious control over the concentrations of two metal precursors and reducing agent to obtain porous nanostructure has not been achieved.

In the typical synthesis, the two metallic precursors were rapidly reduced to nuclei under the strong reducing condition, then they would spontaneously grow and fuse into network structure due to