Journal of Organometallic Chemistry 769 (2014) 1–6

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Organometallic precursor route for the fabrication of PtSn bimetallic nanotubes and Pt_3Sn/reduced-graphene oxide nanohybrid thin films at oil–water interface and study of their electrocatalytic activity in methanol oxidation

S. Jafar Hoseini [a, *], Zahra Barzegar [a], Mehrangiz Bahrami [a], Mahmoud Roushani [b], Mehdi Rashidi [c]

[a] Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj 7591874831, Iran
[b] Department of Chemistry, Faculty of Sciences, Ilam University, Ilam 69315516, Iran
[c] Department of Chemistry, Faculty of Sciences, Shiraz University, Shiraz 71454, Iran

ARTICLE INFO

Article history:
Received 30 April 2014
Received in revised form
3 July 2014
Accepted 8 July 2014
Available online 17 July 2014

Keywords:
Organometallic
Bimetallic nanotube
Thin film
Oil–water interface
Methanol oxidation

ABSTRACT

This report discusses synthesis of PtSn nanotubes and Pt_3Sn reduced-graphene oxide (RGO) nanohybrid thin films *via* a simple reduction of organometallic precursors including [$PtCl_2$(cod)], (cod = *cis*, *cis*-1,5-cyclooctadiene), in the presence of [$Sn(CH_3)_4$] at toluene–water interface. The structure and morphology of the thin films were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive analysis of X-ray (EDAX) techniques. TEM measurements revealed that the PtSn bimetallic thin films contain nanotubes with diameters in the 8–10 nm range and 200–800 nm in length. However, TEM image of Pt_3Sn/RGO bimetallic nanohybrid thin films showed a good distribution of bimetallic nanoparticles (NPs) on the RGO support with average diameter of 8 nm. The electrocatalytical activities of tin alloys thin films were evaluated using methanol as model molecule. The PtSn nanotubes and Pt_3Sn/RGO nanohybrid thin films show a higher catalytic activity in methanol oxidation reaction than that for the Pt NPs films with the lower Pt loading.

Introduction

Low-temperature fuel cells offer a promising energy source for near future energy demands [1,2]. Within the low-temperature fuel cell category, direct methanol fuel cells (DMFCs) stand out due to their high energy density, efficiency, low weight, compact cell assembly, easy handling and distribution [3–5]. However, the commercialization of DMFCs was hindered by the high cost and reliability issues of effective anode and cathode catalysts [6]. Platinum is most widely used as catalysts in fuel cell, but it has relatively low methanol oxidation reaction (MOR) kinetics at the anode, is easily poisoned by carbon monoxide (CO), and is not stable in the acidic conditions, in addition to its high cost. These factors reduce its active surface area, performance and lifetime, and limit its application [3–5]. In recent years, the tailored design of Pt-based bimetallic alloys has attracted considerable interest because they are preferable electrocatalyst candidates for fuel cells [7,8]. In comparison with monometallic Pt nanostructures, alloying with inexpensive non-noble metal can reduce the usage of Pt and lower the cost of the catalyst, and the catalytic activity is often maintained or even becomes higher depending on the chemical nature of metal [9,10]. Among various Pt-metal alloys studied thus far, PtSn alloys represent an interesting group of catalysts not only for hydrogenation and dehydrogenation reactions, but also for electro-oxidation of CO, methanol, ethanol, and ethylene glycol [11–15]. Previous evaluations on single crystals and thin films of Pt_3Sn for catalytic CO oxidation suggest that Sn as an alloy component can enhance CO oxidation on Pt by promoting H_2O dissociation on Sn to form SnOH and by altering electronic properties of Pt through its bonding with Pt, weakening the CO adsorption on Pt [16–18]. All these studies have indicated that the PtSn alloys should be a more promising catalyst in methanol electro-oxidation, in which CO is an intermediate product that could poison the noble metal catalysts

Abbreviations: DMFCs, direct methanol fuel cells; NPs, nanoparticles; MOR, methanol oxidation reaction; cod, *cis*,*cis*-1,5-cyclooctadiene; XRD, X-ray diffraction; TEM, transmission electron microscopy; CV, cyclic voltammetry; NHE, normal hydrogen electrode; RGO, reduced graphene oxide; fcc, face-centered-cubic.

* Corresponding author. Tel.: +98 741 2223048; fax: +98 741 3342172.
E-mail addresses: jhosseini@yu.ac.ir, sjhoseini54@yahoo.com (S.J. Hoseini).

http://dx.doi.org/10.1016/j.jorganchem.2014.07.004
0022-328X/

[19]. Recently, considerable attention has been paid to produce PtSn catalysts with a high surface area for high catalytic performance and utilization efficiency [20,21].

Carbon-based catalyst supports, such as carbon black, carbon nanotubes and graphene, are used to provide good dispersity and thus large effective surface area of the supported catalyst particles. Graphene-Pt composites have been attempted in the fuel cells, such as the methanol oxidation cells [22–24] and the oxygen reduction cells [25,26]. Therefore, a simple method for fabrication of high quality thin films of Pt-based nanocomposites is demanded.

Recently the self-assembly of various nanostructures including nanoparticles (NPs), one-dimensional (1D) nanostructures, and two-dimensional (2D) nanostructures, at a liquid–liquid interface have been developed to produce high-quality nanofilms [27,28]. The interfacial self-assembly offers an easy and inexpensive route for film fabrication. Most important advantages of this assembly strategy are the significant simplicity and universality found in almost all of the related low dimensional nanostructures. Therefore, it is believed that this novel method can be adopted for the construction of nanofilm-based devices [29–31]. The quality of the film is generally better than that of the films fabricated by other methods such as the layer-by-layer assembly or spin coating methods [27]. The method used to prepare thin film at the oil–water interface involves dissolving relevant precursor in organic layer and injecting appropriate reducing reagent in the aqueous layer. The product formed by the reaction at the interface contains ultra-thin nanocrystalline particles. This method, developed by Rao and coworkers, has extensively been used in synthesizing of different nanostructures thin films [32–41]. Previously, we have investigated the effect of different stabilizers on the structure and catalytic activity of platinum NPs thin films at oil–water interface [34]. Also, we have reported the effect of different organoplatinum(II) and organopalladium(II) complexes on the morphology and size of Pt NPs and PtPd NPs at oil–water interface in the absence of stabilizer [42,43]. Recently, we fabricated Pd NPs/reduced graphene oxide (RGO) thin film as effective catalysts for Suzuki–Miyaura reaction in water [44].

In recent years, organometallic strategies have appeared as a valuable alternative for the synthesis of nanostructure materials. Two main advantages can be predicted when using organometallic precursors:

- the metal is pre-reduced, either in a low oxidation state or in a formal oxidation state which nevertheless corresponds to a net reduction of the metal (e.g. linked to olefin or alkyl ligands);
- the substitution of suitable organic ligands in mild conditions should give a surface not containing unfavorable impurities for the chemical or physical properties of the resulting nanostructures. [45,46]

To the best of our knowledge, there is no report concerning fabrication of PtSn or Pt_3Sn/RGO thin film at liquid–liquid interface. In this paper, we first present an effective strategy for the synthesis of PtSn bimetallic nanotubes and Pt_3Sn/RGO nanohybrids at toluene–water interface in the absence of stabilizer by reduction of organometallic complexes including $[PtCl_2(cod)]$, (cod = *cis*,*cis*-1,5-cyclooctadiene), in the presence of $[Sn(CH_3)_4]$ at toluene–water interface. Then, a glassy-carbon electrode was modified with the PtSn or Pt_3Sn/RGO thin film for application in the MOR.

Experimental

All of the chemical compounds were purchased from Merck Company. The $[PtCl_2(cod)]$ complex was synthesized using reported procedure [47]. X-ray diffraction (XRD) patterns of the as-prepared electrocatalysts were recorded using a Bruker AXS (D8, Avance) instrument equipped with Cu-Kα radiation ($\lambda = 1.54184$ Å). Transmission electron microscopy (TEM) images of the electrocatalysts were recorded using a Philips CM-10 TEM microscope operated at 100 kV.

Preparation of PtSn bimetallic thin film at the toluene–water interface

An equimolar solution of $[PtCl_2(cod)]$ (0.5 mM) and $[Sn(CH_3)_4]$ (0.5 mM) in toluene (25 ml) was sonicated for 5 min to prepare a colorless solution. This solution was stand in contact with double distilled water (25 ml) in a beaker (100 ml). Once the two layers were stabilized, an appropriate volume of aqueous $NaBH_4$ (5 ml, 0.1 M) was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a coloration of the liquid–liquid interface. With the passage of time, the color became more vivid, finally resulting in a film at the liquid–liquid interface.

Preparation of Pt_3Sn/RGO stabilized-bimetallic thin film at the toluene–water interface

Graphene oxide (GO) was prepared from graphite powder in accordance with the modified Hummers–Offeman method [44,48–50] and was exfoliated by dispersing 10 mg of GO powder in 25 ml of double distilled water followed by sonication for 10 min. These bimetallic alloy nanohybrids were prepared following the above mentioned procedure, using $[PtCl_2(cod)]$ (0.75 mM) and $[Sn(CH_3)_4]$ (0.25 mM) complexes as organometallic precursors in toluene (25 ml) and $NaBH_4$ as a reducing agent in water.

Electrode preparation

To transfer thin films from liquid–liquid interface to the surface of glassy carbon electrode, the toluene phase (top phase) was removed slowly by a syringe and then the surface of glassy carbon electrode was inserted into the liquid phase and pulled out.

Electrochemical measurements

The catalysts were characterized using an Autolab Potentiostat/Galvanostat PGSTAT12 (Eco Chemie, Switzerland). All characterizations were conducted at room temperature in a standard three-electrode system using an Ag/AgCl (sat. KCl) reference electrode, a platinum wire counter electrode and glassy carbon coated with prepared electrocatalysts as a working electrode. However, all potentials in the manuscript are converted to values with reference to a normal hydrogen electrode (NHE). The glassy carbon electrode area diameter was 2 mm. All cyclic voltammograms (CVs) were recorded under the same conditions.

Results and discussion

In this study, PtSn bimetallic nanotube thin film and Pt_3Sn/RGO nanohybrid thin film were synthesized by the reduction of $[PtCl_2(cod)]$ in the presence of $[Sn(CH_3)_4]$ complex as tin precursor, at the toluene–water interface as shown in Scheme 1. These complexes were dissolved in toluene at room temperature and then contacted with water. The aqua solution of $NaBH_4$ was injected into the interface with minimal disturbance to initiate the reduction and thin film formation was indicated by the interface color change from colorless to black.

The crystal structures of the bimetallic thin films were investigated by XRD. Fig. 1(a) shows the XRD pattern recorded for the PtSn