Applied Catalysis A: General 427–428 (2012) 35–42

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Platinum nanoparticle-decorated TiO_2 nanotube arrays as new highly active and non-poisoning catalyst for photo-electrochemical oxidation of galactose

Mir Ghasem Hosseini*, Mohamad Mohsen Momeni

Electrochemistry Research Laboratory, Department of Physical Chemistry, Chemistry Faculty, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:
Received 26 December 2011
Received in revised form 29 February 2012
Accepted 19 March 2012
Available online 26 March 2012

Keywords:
TiO_2 nanotubes
Platinum nanoparticle
Photo-catalytic
UV-cleaning
Galactose
Microemulsion

ABSTRACT

Platinum nanoparticles were doped on the TiO_2 nanotube using a microemulsion method. The TiO_2 nanotube arrays were successfully fabricated by the anodizing of titanium sheets. The morphology and surface analysis of the Pt-TiO_2 nanotubes were investigated using SEM, EDX and XRD respectively. The electro-oxidation of galactose on this catalyst in alkaline medium was studied using cyclic voltammetry and chronoamperometry methods. The results showed that the oxidation peak currents on the Pt-TiO_2 nanotubes for galactose oxidation are larger than those on a smooth platinum electrode and confirmed the better electro-catalytic activity and stability of these new catalysts. The photo-catalytic properties of the TiO_2 make the Pt-TiO_2 nanotubes electrode reusable after a short UV treatment, and the electro-oxidation current density of the Pt-TiO_2 nanotubes after UV-cleaning can be re-established.

1. Introduction

Direct electrochemical oxidation of carbohydrates is of a very high interest from several points of from biomedical applications involving blood sugar analysis, fuel cells applications to ecological approaches like waste water treatment in food industrials. Carbohydrates that comprise more than 80% of available biomass are the most abundant compounds. The ideal fuel for fuel cells in power generation systems is the direct use of a fuel like carbohydrates in the form of a liquid phase [1–4]. This allows easier use with negligible energy input for the enrichment of the fuel. Fuels such as glucose, galactose or other carbohydrates can easily be utilized by mixing them directly in the electrolyte without the use of any auxiliary reforming equipment, membrane barriers, or additional microbial cultures. Great efforts have been made to develop catalytically active electrode materials for this reaction in the past two decades. Various authors have shown that various carbohydrates can be oxidized directly at a variety of electrode materials, including metals such as platinum [5], gold [5,6], copper [5,7–9], indium [5], rhodium [5], nickel oxide [10], tungsten oxide [11] and ruthenium oxide [12]. However, systematical study showed that these electrodes were subject to serious poisoning due to adsorbed intermediates from the oxidation of carbohydrates [13]. To mitigate the poisoning effect, significant attention has been focused on preparing new electrodes with high electro-catalytic activity. Immobilization of the noble metal nanoparticles in an active matrix may enhance the overall reactivity of the catalytic metal centers. For a good electro-catalyst, both the high catalytic activity and the low cost must be considered to meet the final purpose of wide commercialization of fuel cells. High surface area electro-catalytic electrodes are of interest for fuel cell technology. The high surface area electro-catalysts can be made by sintering, electro-deposition or dispersion of active electro-catalytic materials on a proper support with a relatively high surface area. During search for novel and stable support for the noble metal catalysts, TiO_2 nanotubes come into sight because of their good physical and chemical properties and high stability in acidic and alkaline solutions. Titanium dioxide nanotubes are very biocompatible, inexpensive and environmentally benign [14,15]. Titanium dioxide nanotube arrays have demonstrated a number of important applications including gas sensors, solar cells, photo-catalysts, tissue engineering, biosensors and electro-catalyst [16–19]. TiO_2 nanotubes can be synthesized by different methods including sol–gel, hydrothermal, template and anodic oxidation [20–25]. Obviously, if TiO_2 nanotubes can be directly produced on a metallic titanium substrate by the anodic oxidation method, it would be advantageous and convenient for fuel cell applications where an electric current collector is required. Moreover, the morphology and the structure of the TiO_2 nanotubes layer can also be easily modulated by changing the anodic oxidation conditions [26]. Our recent studies have shown that the immobilization of the metal nanoparticles in a porous matrix improves the electro-catalytic activity to a

---

* Corresponding author. Tel.: +98 4113393138; fax: +98 4113340191.
E-mail address: mg-hosseini@tabrizu.ac.ir (M.G. Hosseini).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.03.027

great extent [27–36]. In this context, we used from microemulsion method to coverage of TiO_2 nanotubes with platinum nanoparticles and tested it as a new electro-catalyst for galactose oxidation in alkaline medium. In recent years, electro-oxidation of different carbohydrates has been studied thoroughly [37–40]. To the best of our knowledge, carbohydrates electro-oxidation with assistance of UV illumination is not reported in the literatures. The surface morphology and element analysis of platinum coating on TiO_2 nanotubes were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively. Due to the large surface area, good electrical conductivity, and unique photo-catalytic properties of TiO_2 nanotube, the resultant Pt-TiO_2 nanotube electrodes not only have high catalytic activity, but also have self-cleaning ability which gives them a reusable feature. The same technique can be employed to prepare electro-catalysts with excellent electro-catalytic activity and re-usable property for galactose electro-oxidation.

2. Experimental

2.1. Chemicals, solutions and equipment

Galactose (Merck, 99% purity) and ethylene glycol (Merck, 99% purity) were used as received. Hexachloroplatinic acid (98%) and sodium borohydride (98%) were purchased from Merck. *n*-heptane (HPLC grade, Scharlau) was used without any further purification. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT, 96%) was obtained from ACROS Organics. All other chemicals were of analytical grade and used without further purification. All electrochemical experiments were carried out at room temperature. Distilled water was used throughout. The electrochemical experiments were performed in a three-electrode cell arrangement. A platinum sheet with a geometric area of approximately 20 cm^2 was used as a counter electrode, while all potentials were measured with respect to a commercial saturated calomel reference electrode (SCE). The electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical system run by Powersuite software. All of the experiments were carried out at room temperature. To observe photo (UV)-enhanced catalysis, cyclic voltammograms of galactose oxidation were obtained with/without UV illumination. A 300 W Hg lamp was used as the UV light source.

2.2. Preparation of the TiO_2 nanotubes substrate

The self-organized TiO_2 nanotube arrays on pure titanium substrates were prepared by anodizing of a pure titanium sheet in a non-aqueous fluoride-containing electrolyte. Titanium discs were cut from the titanium sheet (purity 99.99%, 1 mm thickness) and mounted using a polyester resin. The titanium samples were degreased by sonicating in acetone and ethanol followed by rinsing with distilled water. The anodic films were grown from the titanium by potentiostatic anodizing in an ethylene glycol electrolyte containing 25×10^{-4}% W/V NH_4F at a constant voltage of 40 V using a platinum sheet as the counter electrode. The TiO_2 nanotube samples were then annealed at 450 °C in air for 3 h.

2.3. Preparation of the Pt-TiO_2 nanotubes electrode

The platinum nanoparticles were produced in a water-in-oil microemulsion consisting of n-heptane as the continuous oil phase, AOT as the surfactant and an aqueous solution of the metal precursor and reducing agent. The metal precursor and reducing agent-containing microemulsions were prepared by mixing the desired amounts of the proper chemicals to obtain microemulsions with 15 wt% of surfactant (AOT: sodium bis(2-ethylhexyl) sulphosuccinate) and following molar ratios of $[H_2O]/[AOT] = 8$, and aqueous phase concentrations of $[NaBH_4]/[Pt] = 7.5$, $[Pt] = 0.8$ M. The detailed process for preparation of the platinum nanoparticles can be found in Ref. [41]. For preparation of the Pt-TiO_2 nanotubes electrodes, the TiO_2 nanotube samples were first ultrasonically cleaned in distilled water for 5–10 min to remove any surface contaminants and then were immersed in a solution containing two mentioned mixture. Acetone was used to break the microemulsion and precipitate out the platinum nanoparticles on the TiO_2 nanotubes. Finally, the Pt-TiO_2 nanotubes electrodes were washed sequentially with n-heptane, acetone and hot distilled water to remove all of the remaining chemicals. All mentioned processing were performed in an ultrasonic bath. In order to determine how much Pt (mass) is present on the TiO_2 nanotube, the final platinum loading, as measured by dissolution of the deposit followed by atomic absorption spectroscopy (AAS) analysis was about 0.9 mg cm^{-2}.

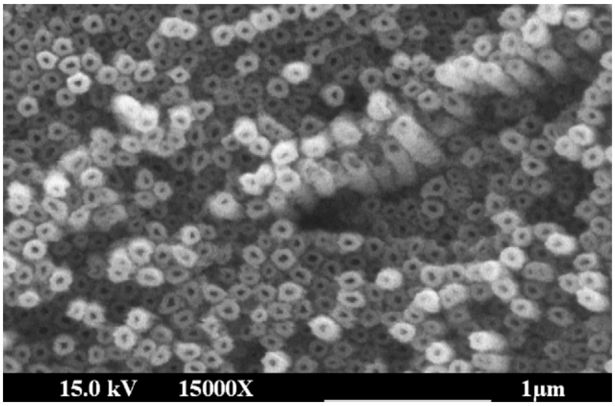

Fig. 1. Surface morphology of the TiO_2 nanotube arrays as a support prepared by the anodizing of titanium.

2.4. Surface morphology of electrodes

For characterizing Morphology, alignment and composition of the TiO_2 nanotubes array and platinum coating on the TiO_2 nanotubes substrates, a scanning electron microscope (Model XL30, Philips, The Netherlands) was employed with an accelerating voltage 15 kV. To identify the element composition, an energy dispersive X-ray (EDX Genesis fitted to the Philips SEM XL30) was employed with an accelerating voltage 16 kV. XRD analyses were performed with a XRD using Simens 5000 diffractometer with a Cu-K_α radiation source in scan mode.

3. Results and discussion

3.1. Characterization of the electrode morphology

Scanning electron microscopy (SEM) image of a typical TiO_2 nanotube array is shown in Fig. 1. The TiO_2 nanotubes are well-aligned and organized into a highly oriented array. The average diameters of these tubes are approximately 70–90 nm and thus can be used as good carriers for the catalyst particles. Fig. 2 shows images of the nanotubes after loading with the platinum nanoparticles using the microemulsion method at different magnifications. It can be seen that the platinum nanoparticles are distributed on the surface of the TiO_2 nanotubes. Fig. 3A shows the EDX plot of the platinum films on the TiO_2 nanotubes matrix. EDX results confirm the presence of the platinum nanoparticle on the surface film. Fig. 3B shows the XRD patterns of the TiO_2 nanotube array layers (a) before and (b) after being deposited with the