Journal of Molecular Catalysis A: Chemical 335 (2011) 199–204

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Electro-oxidation of hydrazine on gold nanoparticles supported on TiO_2 nanotube matrix as a new high active electrode

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ARTICLE INFO

Article history:
Received 14 July 2010
Received in revised form
10 November 2010
Accepted 27 November 2010
Available online 17 December 2010

Keywords:
Hydrazine electro-oxidation
Titanium dioxide nanotubes
Gold nanoparticle

ABSTRACT

Au/titanium dioxide nanotubes (Au/TiO_2-NTs) catalysts are prepared by a simple method using galvanic deposition of gold nanoparticles on TiO_2-NTs as support. TiO_2-NTs are fabricated by anodizing titanium foil in a dimethyl sulfoxide (DMSO) fluoride-containing electrolyte. Scanning electron microscope and energy-dispersive X-ray spectroscopy results indicate that nanotubular TiO_2 layers consist of individual tubes of about 50–80 nm diameters and gold nanoparticles with a size range of 30–40 nm are well-dispersed on the surface of TiO_2-NTs support. The electro-catalytic properties of Au/TiO_2-NTs catalysts toward electro-catalytic oxidation of hydrazine are investigated by cyclic voltammetry. Compared to flat gold electrodes, Au/TiO_2-NTs catalyst shows much higher electrochemical activity. This may be attributed to the uniform dispersion of gold nanoparticles on TiO_2-NTs, smaller particle size and unique properties of TiO_2-NTs support. In addition, the mechanism of hydrazine electrochemical oxidation catalyzed by Au/TiO_2-NTs is investigated.

1. Introduction

Direct methanol fuel cell is expected as a hopeful candidate for direct fuel cell application systems. However, the efficiency and power output of direct methanol fuel cells are low because of severe poisoning of the anode catalyst by reaction intermediates such as CO and methanol crossover through the electrolyte membrane [1]. Hydrazine is an important high-performance fuel in aerospace propulsion applications, which also impresses promising potential applications in fuel cells. Hydrazine is an ideal fuel for a direct fuel cell system because it does not exhaust environmentally loading materials such as CO_2. Hydrazine is a compound with high hydrogen content (12.5 wt.%). Its hydrogen storage capability is higher than that of sodium borohydride (10.6 wt.%) and equivalent to that of methanol. The direct hydrazine fuel cell demonstrates a higher electromotive force of 1.61 V which is close to that of the direct borohydride fuel cell (1.64 V) and higher than that of the direct methanol fuel cell (1.21 V). When hydrazine is used as a fuel to power the direct hydrazine fuel cell, only nitrogen and water will be formed. However, specific precautions should be observed when using hydrazine solution as a fuel for the direct hydrazine fuel cell because hydrazine is toxic and carcinogenic compound [2]. The direct hydrazine fuel cell concept was first suggested in the 1960s [3]. Very few researches on the direct hydrazine fuel cell development have been done [4–7]. It is considered that more attentions should be paid to develop the direct hydrazine fuel cell technology due to the merits mentioned above. Noble metals such as platinum [3], palladium [8,9], silver [10] and gold [11,12] are very active in the anodic oxidation of hydrazine. However, they tend to lose reactivity as they precipitate, aggregate or form a surface film. Immobilization of the noble metal nanoparticles in an active matrix may enhance the overall reactivity of the catalytic metal centers. The performance of electrodes mainly depends on the morphology properties and surface area of the electrodes. In order to retain its high electroactivity, different matrices have been used for the immobilization of noble metal particles. Among these, inorganic nanostructure materials are more promising because of their regular structure, high active surface area for immobilization of metal particles, and good chemical as well as thermal stability [13]. Since the discovery of carbon nanotubes, increasing attention has been paid to the study of nanostructures such as nanotubes, nanorods and nanowires. Titanium dioxide can be formed with different morphologies such as nanoparticles, nanofibres, nanotubes and nanosheets. Titanium dioxide nanotubes are very biocompatible, inexpensive, environmentally benign, and chemically as well as thermally stable inorganic material [14]. Titanium dioxide nanotube arrays have demonstrated a number of important applications including gas sensors, solar cells, photo-catalysts, tissue engineering, biosensors and electro-catalyst [15–18]. Our recent studies have shown that the immobilization of the metal nanoparticles in an active matrix improves the electro-catalytic activity to a great extent [19–24]. In the present work, we prepared a promising hydrazine electro-

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doi:10.1016/j.molcata.2010.11.034

catalyst based on the co-immobilization of gold nanoparticle on titanium dioxide nanotubes arrays and compared it with flat gold electrode in terms of the electrochemical activity for hydrazine oxidation using cyclic voltammetry (CV). Additionally, the temperature dependence and the mechanism of hydrazine oxidation reaction on Au/TiO_2-NTs have been discussed. The surface morphology and element analysis of gold coating on titanium dioxide nanotubes were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively.

2. Experimental

2.1. Chemicals, solutions and electrochemical equipment

Hydrazine (Merck) and dimethyl sulfoxide (DMSO) (Merck) were used as received. 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 assembly. A platinum sheet of the geometric area of about 20 cm^2 was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel electrode (SCE). Electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical System run by Powersuite Software.

2.2. Preparation of titanium dioxide nanotubes (TiO_2-NTs) catalyst support

TiO_2-NTs arrays were prepared by anodizing of pure titanium sheet in a non-aqueous fluoride-containing electrolyte. Titanium discs were cut from a titanium sheet (purity %99.99, 1 mm thickness) and mounted using polyester resin. Titanium samples were degreased by sonicating in acetone and ethanol followed by rinsing with distilled water. Anodic films were grown from titanium by potentiostatic anodizing in a DMSO electrolyte containing 2 vol.% HF at a constant voltage of 40 V for 8 h at room temperature using a platinum sheet as counter electrode.

2.3. Preparation of Au/TiO_2-NTs/Ti catalysts

Au/TiO_2-NTs/Ti catalysts were prepared by the electrodeposition of gold on as-prepared TiO_2-NTs/Ti support. Electrodeposition experiments were carried out at a water-bath thermostat. After anodizing of titanium, the samples were ultrasonically cleaned in distilled water for 10–20 min to remove surface contaminants. Then the TiO_2-NTs/Ti electrodes were immerged into the bath for electrolytic deposition. Deposition of gold on TiO_2-NTs/Ti electrodes was performed under galvanostatic conditions. The deposition conditions were a current density of 5 mA/cm^2 for 10 min, in an acid bath containing $KAu(CN)_2$ in presence of a pH 4 citrate buffer. The temperature is maintained at 45 °C.

2.4. Physical characterization

Morphology, alignment, and composition of the TiO_2 nanotubes array and gold coating on TiO_2-NTs/Ti substrates were characterized with a Philips scanning electron microscope (SEM) and EDX.

3. Results and discussion

3.1. Characterization of the electrodes morphology

Fig. 1 shows SEM micrographs of the titanium dioxide nanotubes prepared by anodic oxidation. The average tube diameter was about 50–80 nm, which can be used as good carrier of particle catalyst. Also the thickness of TiO_2-NTs layer was in the range of 100–140 nm. Fig. 2 illustrates the SEM micrographs of gold nanoparticles electrodeposited on titanium dioxide nanotubes. It can be seen that the gold nanoparticles with diameters around 30–40 nm are distributed in an almost homogeneous manner on top of TiO_2 nanotubes. Fig. 3 shows the EDX spectrum of Au/TiO_2-NTs/Ti after 10 min electroplating of gold on anodized titanium.

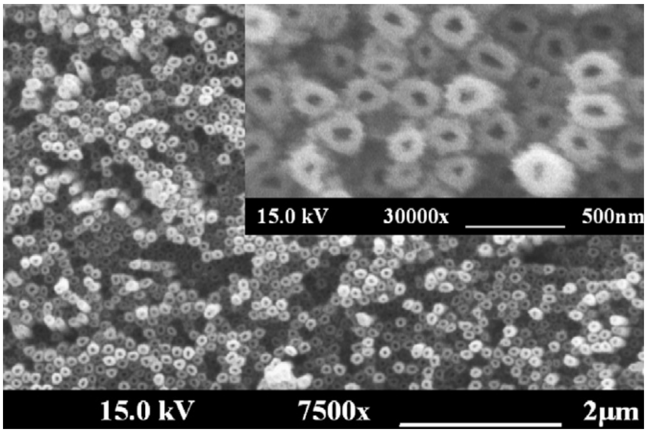

Fig. 1. The surface morphology of the TiO_2-NTs/Ti as support prepared by anodizing of titanium.

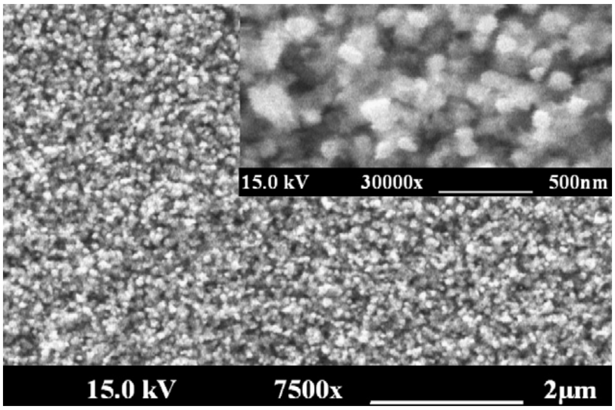

Fig. 2. The surface morphology of gold coating on the Au/TiO_2-NTs/Ti electrode.

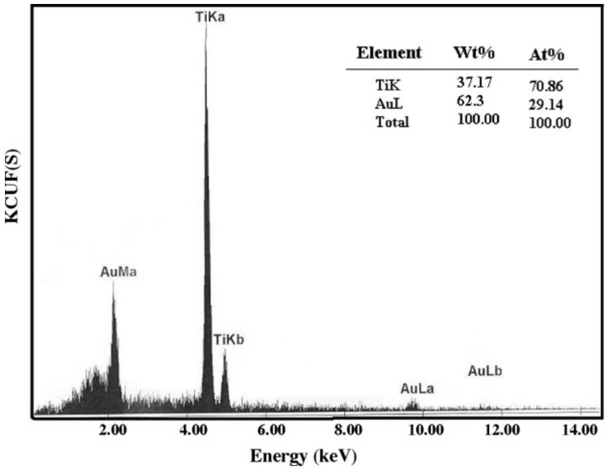

Fig. 3. EDX of Au/TiO_2-NTs/Ti electrode after 10 min electroplating of gold on anodized titanium.