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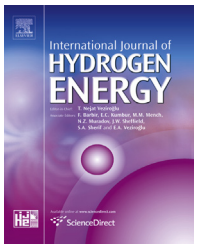

Silver/titania nanocomposite-modified photoelectrodes for photoelectrocatalytic methanol oxidation

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ARTICLE INFO

Article history:
Received 19 May 2014
Received in revised form
10 July 2014
Accepted 13 July 2014
Available online 4 August 2014

Keywords:
Ag/TiO_2
Thin film
Photoelectrochemistry
AACVD
Methanol oxidation

ABSTRACT

Silver deposited titania (Ag/TiO_2) nanocomposite thin films were fabricated by the simple sonochemical deposition of Ag on preformed aerosol-assisted chemical vapor deposited TiO_2 thin films. The photelectrocatalytic performance of a newly fabricated Ag/TiO_2-modified photoelectrode was studied for methanol oxidation under simulated solar AM 1.5G irradiation (100 mW/cm^2). The Ag/TiO_2-modified photoelectrode showed a photocurrent density of 1 mA/cm^2, which is four times that of an unmodified TiO_2 photoelectrode. The modification of Ag on the TiO_2 surface significantly enhanced the photoelectrocatalytic performance by improving the interfacial charge transfer processes, which minimized the charge recombination. Density functional theory (DFT) calculation studies revealed that methanol could be easily adsorbed onto the Ag surfaces of Ag/TiO_2 via a partial electron transfer from Ag to methanol. The newly fabricated Ag/TiO_2-modified photoelectrode could be a promising candidate for photoelectrochemical applications.

Introduction

A direct methanol fuel cell (DMFC) has attracted vast academic and industrial interest in past decades because of its ease of handling, high energy density, and low operating temperature [1,2]. The basics concept of a DMFC involves methanol oxidation and oxygen reduction on a precious metal catalyst. Thus, the high performance of a DMFC requires a catalyst with high electrocatalytic activity [3,4]. However, the

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http://dx.doi.org/10.1016/j.ijhydene.2014.07.066

existing DMFC suffers from several factors, including the use of precious metals such as Pt in both its anode and cathode. A Pt catalyst tends to get poisoned by strong CO adsorption [5–7].

As one efficient strategy to improve the device performance and reduce the amount of precious metals in the catalyst, researchers have been developing alternative anode materials using photocatalysts such as TiO_2 [8], TiO_2/Pt–Ru [9], TiO_2–Au [10], nanoporous TiO_2–Au [11], TO_2–poly oxometalate (POM) [12], TiO_2/POM–Au [13], and Degussa-TiO_2/POM–Au [14]. So far, Au-modified TiO_2-based nanocomposites have been the most commonly used materials to explore photoelectrocatalytic methanol oxidation. Considering the cost of Au, it is essential to search for alternative metals for photoelectrocatalytic methanol oxidation in DMFC applications. Recently, many studies have focused on loading silver (Ag onto TiO_2 for several multifunctional applications because of its low cost, good photoresponse, and non-toxicity relative to other metals such as Pt, Au, Ru, and Pd [15–18]. Several methods for loading Ag nanoparticles onto TiO_2 have been reported, such as the pulse current deposition of Ag onto an electrodeposited TiO_2 nanotube [15], ultrasound-aided photochemical deposition of Ag onto TiO_2 nanotube arrays [18], photoreduction of Ag on anatase TiO_2 [17], one-step solution method [19], chemical reduction method [20] and dip-coating of Ag onto sol–gel TiO_2 [16]. It has been found that the presence of Ag on a TiO_2 thin film results in greater excitation due to surface plasmon resonance. Moreover, Ag can tune the band-gap energy and retard the charge recombination [21,22]. However, most of the reported synthesis method generally requires a relatively long synthesis time [16,19], addition of reaction agent or reducing agent [20] or specific substrates to assist the reduction of Ag nanoparticle, some post-treatments including high temperature induce sintering process is needed. In some of these methods, the distribution of nanoparticles is difficult to control because of the spontaneous aggregation of clusters. One of the main challenges in fabrication of noble metal/TiO_2 is the time concern during the preparation with the elimination of additive and yet well dispersed nanoparticle on TiO_2 surface is obtained. Based on the above discussion, the present work is aimed to achieve rapid and simple way for the fabrication of well dispersed of Ag deposited TiO_2 thin film using sonochemical method without the using any surfactant and reducing agent.

Herein, we report for the first time a simple method to investigate the performance of an Ag/TiO_2-modified photoelectrode for the photoelectrocatalytic oxidation of methanol. Ag/TiO_2 thin films were fabricated by the sonochemical deposition of various quantities of Ag on TiO_2 thin films and characterized by suitable techniques. The Ag/TiO_2-modified photoelectrode was used to explore methanol oxidation under simulated solar AM 1.5G irradiation (100 mW/cm^2). The modification of the TiO_2 thin film with Ag significantly boosted the performance of the photoelectrochemical cell. The influence of the Ag content on the TiO_2 was also studied in relation to methanol oxidation. The good photoresponse against photoelectrocatalytic methanol oxidation revealed that the fabricated Ag/TiO_2 thin film is a potential candidate for photoelectrochemical cells.

Experimental methods

Materials

Titanium isopropoxide (TTIP, 98%) was purchased from Acros Organics and used as such for thin film deposition. Silver nitrate ($AgNO_3$) was purchased from Merck. Methanol and HCl were purchased from Systerm. Indium tin oxide (ITO)-coated conducting glass plates with a surface resistance of 7 Ω/sq were commercially obtained from Xin Yan technology limited, China.

Preparation of Ag-loaded TiO_2 thin film

The Ag/TiO_2 thin films were prepared using the previously reported aerosol-assisted chemical vapor deposition (AACVD) method [22]. Initially, TiO_2 thin films were prepared on ITO substrates using a homemade AACVD assembly. For the TiO_2 deposition, TTIP was added to methanol, and this solution was used to generate an aerosol at room temperature using an ultrasonic air humidifier operating at 60 Hz. Argon gas was passed through the aerosol mist at a flow rate of 200 mL/min to carry the aerosol droplets into the reactor chamber, and the deposition was conducted at 450 °C for 90 min. The film was then cooled and stored in air. Post-treatment of the TiO_2 thin films was carried out by immersing the films into 0.1 M HCl for 30 min. Then, the thin films were removed and rinsed with de-ionized water and dried in an oven at 60 °C. Finally, the TiO_2 thin films were immersed into $AgNO_3$ solutions (1, 5, and 10 mM) and stimulated using an ultrasonic generator (Kudos) at a frequency of 50 kHz for 30 min to obtain the Ag-loaded TiO_2 thin films. The films were washed with de-ionized water and dried in air. The obtained films were stored in the dark.

Characterization techniques

The surface morphologies of the Ag/TiO_2 thin films were examined using FEI Nova NanoSEM 400-field emission scanning electron microscopy (FESEM). The surface topography and

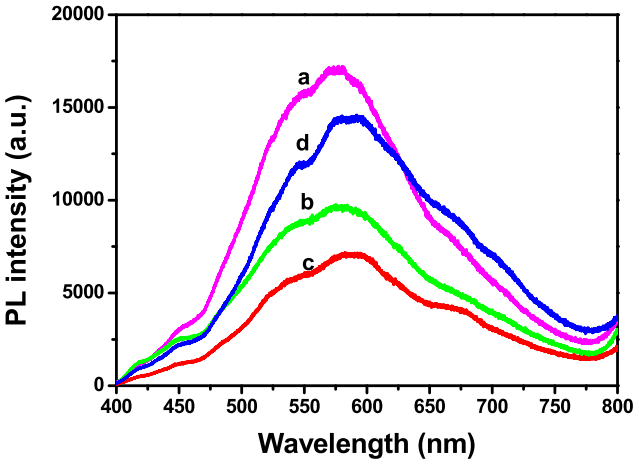

Fig. 1 – Photoluminescence spectra of (a) TiO_2 and Ag/TiO_2 nanocomposite thin films with (b) 1, (c) 5, and (d) 10 mM of Ag content.