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ScienceDirect
Electrochemistry Communications 10 (2008) 367–371
electrochemistry communications
www.elsevier.com/locate/elecom

Nitrogen-doped TiO_2 from TiN and its visible light photoelectrochemical properties

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Received 5 December 2007; received in revised form 19 December 2007; accepted 21 December 2007
Available online 2 January 2008

Abstract

Homogeneous titanium nitride (TiN) thin film was produced by simple electrophoreic deposition process on Ti substrate in an aqueous suspension of nanosized TiN powder. Nitrogen-doped titanium dioxide ($TiO_{2-x}N_x$) was synthesized by oxidative annealing the resulted TiN thin film in air. Photoelectrochemical measurements demonstrated visible light photoresponse for the electrode of annealed electrophoreic deposited TiN samples. It is found that the synthesized $TiO_{2-x}N_x$ electrode showed higher photo potential under white and visible light illumination than the pure TiO_2 electrode. The photocurrent under visible light illumination was also observed, which increased with the increase of deposition time of TiN thin films.

Keywords: Nitrogen-doped titanium dioxide; Titanium nitride; Electrophoreic deposition; Visible light; Water splitting

1. Introduction

TiO_2 has recently attracted a great deal of interest for a variety of applications such as using TiO_2 nanoparticles/films as photocatalysts in environment protection [1], photoelectron mediators for sensors, photosensitizers in light-emitting devices [2], and solar cells [3]. Since the pioneer work of Fujishima and Honda [4] for the discovery of photoelectrochemical splitting of water on titanium dioxide electrodes, water splitting based on semiconductors using solar energy has attracted extensive attention [5–9]. However, the inactivity in the visible light region limits the practically technological applications of TiO_2. The development of visible light-driven photocatalysts is one of the most important aspects to utilize the solar light. Many research groups have demonstrated that TiO_2 doped with non-metal elements such as nitrogen [3,10–19], boron [20], fluorine [21,22], sulphur [23,24] or carbon [5,25–29] showed photoresponse in the visible light region and higher photocatalytic activity [5]. Nitrogen-doped TiO_2 ($TiO_{2-x}N_x$) is considered as one of the best candidates in terms of its band-gap width. It has been found that substitutional N-doping is one of the most promising paths towards photocatalytical applications [10]. Reports on the beneficial effect of N-doping of TiO_2 have been published recently by Asahi et al. [10]. The cited authors found that the optical absorption edge of the nitrogen-doped $TiO_{2-x}N_x$ films was shifted to the proximity of 500 nm.

There were several approaches for the preparation of nitrogen-doped TiO_2 such as heat treatment of TiO_2 in ammonia atmosphere [14,15], sputtering in a gas mixture of N_2 with Ar [10] or, alternatively, by DC magnetron sputtering of titanium in $Ar/O_2/N_2$ mixture [30], and annealing TiN powder in air [31] or oxidation of TiN in thermal plasma [32]. Joung et al. prepared nitrogen-doped visible light-driven TiO_2 photocatalyst powders at different temperatures and with different calcination times in a cylindrical tubular furnace under a stream of ammonia gas [14]. Schmuki et al. [15] reported a simple approach to achieve N-doping of TiO_2 nanotubular layers through heat treatment in NH_3 atmosphere. Nitrogen doping of

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doi:10.1016/j.elecom.2007.12.037

TiO_2 after ammonia treatment at 600 °C, resulted in a photo-current density of 0.1 mA cm^{-2} at a bias potential of 0.5 V vs. Ag/AgCl in 0.1 M Na_2SO_4 electrolyte by irradiating with 450 nm light. Annealing the TiO_2 nanotubes in a nitrogen atmosphere at 350 °C resulted in increased photo-activity [8].

Titanium nitride films have become universally accepted coatings due to their high melting points, extreme hardness, high chemical stability, low electrical resistivity and golden color. The major applications of the films are protective coatings on steels, diffusion barriers in integrated circuit industry, and decorative coatings. Recently, it has been reported that TiN oxidation is one way to synthesize nitrogen-doped TiO_2 [31,32]. Oh et al. synthesized TiO_2 nanopowders by TiN oxidation using Ar–O_2 thermal plasma [32]. Morikawa et al. also reported the synthesis of N-doped rutile TiO_2 [31], but they did not study its photoelectrochemical properties.

Electrophoretic deposition (EPD) has been gaining increasing interest as an economical and versatile processing technique for the production of novel coatings or films on conductive substrates with the advantages of simple setup, low cost, time saving, and thickness uniformity. This method has the potential for industrial and low cost scale-up production. It represents a material processing technique in which charged particles in a suspension including an electrolyte, particles, additives and solvent are moved toward an oppositely charged electrode and are then deposited onto a substrate under an applied DC electric field. Many kinds of thin films such as TiO_2 [33,34] and CNT [35] have been successfully prepared by EPD process. In this work, for the first time, we prepared TiN thin films on titanium foil by an electrophoretic deposition process and directly annealed it in air for the preparation of nitrogen-doped TiO_2 thin film electrodes and demonstrated its visible photoelectrochemical response for water splitting.

2. Experimental details

2.1. Chemical and materials

TiN powder with a size of 40 nm was purchased from Kaier Company (99%, China). Other reagents were of analytical grade. Distilled water was used to prepare all the solutions.

2.2. Sample and electrode preparation

TiN film was produced by an electrophoretic deposition process on freshly polished Ti substrate in a suspension solution containing TiN powder. A home-made electrolysis cell was used to control the distance between the working electrodes and counter electrode. Before the deposition, the titanium substrate was mechanically polished with 600 and 1200 grade sand paper, and then chemically polished with an HF(40%)–HNO_3(65%)–H_2O (1:4:5 in volume) mixture for 30 s, and finally fully rinsed with purified water in an ultrasonic bath. After the electrophoretic deposition, both the TiN samples and the original Ti substrate were annealed at 350 °C for 1 h in air.

The photoelectrodes were fabricated by attaching a copper wire using silver paste. An epoxy was used to cover the electrode except for the used TiO_2 surface. The area of working electrode was estimated by its geometric dimension.

2.3. Apparatus

The current-potential curves in dark and photocurrent and photopotential measurement were performed with a CHI 660 electrochemical workstation (Shanghai Chenhua Instruments). For electrochemical experiments, the light intensity was measured by an Oriel radiant power energy meter (Oriel, USA) with a thermopile detector.

2.4. Photoelectrochemical measurements

The photoelectrochemical measurements were performed in 1.0 M KOH electrolyte in a cell with a quartz window. The working electrodes, Ti/TiO_2 and Ti/$TiO_{2-x}N_x$ were illuminated with 350 W Xe lamp from which infrared wavelengths were removed by a 6 cm water filter to obtain white light and the measured irradiance was 100 mW/cm^2. For visible light illumination, the light was passed through an optical filter, which cut off wavelengths below 390 nm. The irradiance measurement was 25 mW/cm^2. All of the measurements were performed at room temperature in a standard three-electrode configuration with a platinum plate as counter electrode and an Ag/AgCl as reference electrode.

3 Results and discussion

3.1. Preparation of TiN thin film and nitrogen-doped TiO_2 films

There are two distinct steps in the experimental preparation of nitrogen-doped TiO_2 films. Initially, TiN thin film was electrophoretically deposited on the surface of Ti substrate. Fig. 1 shows typical current-time transient curves of TiN thin film formation in a solution containing 10 g/L TiN powder under 10 V for 30 and 60 min. During the electrophoretic deposition, a magnetic stirrer and a teflon-coated stirring bar provided convective transport. As can be seen from Fig. 1, the current response during the electrophoretic deposition was very reproducible. In the beginning, the current decreased sharply within 40–60 s and then went to a relative steady state. A colored and uniform thin film of TiN could be obtained and the thickness of TiN can be controlled by the deposition time. The color of as–prepared TiN film is dependent upon the deposition time. The yellowish to vivid yellow uniform TiN thin films could be obtained when the deposition time