Catalysis Today 189 (2012) 93–100

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

Effect of deposition of Ag nanoparticles on photoelectrocatalytic activity of vertically aligned TiO_2 nanotubes

P.A. Gross, S.N. Pronkin*, T. Cottineau, N. Keller, V. Keller, E.R. Savinova

Laboratory of Materials, Surface and Processes for Catalysis, LMSPC (UMR-7515), ECPM-UdS-CNRS, 25 Rue Becquerel, 67087 Strasbourg, France

ARTICLE INFO

Article history:
Received 19 December 2011
Received in revised form 8 March 2012
Accepted 19 March 2012
Available online 24 April 2012

Keywords:
Titania nanotubes
Ag photodeposition
Photoelectrochemical cell

ABSTRACT

Deposits of Ag nanoparticles on TiO_2 nanotubes have been prepared by ex situ photochemical deposition after substrate impregnation in $AgNO_3$ solution. SEM demonstrated that nanoparticles with average size 40 ± 12 nm are uniformly distributed over the substrate without agglomeration. XPS analysis indicated that concentration of precursor electrolyte allows to control the amount of deposited Ag.

For the first time the effect of Ag nanoparticles deposition on photoelectrochemical properties, namely on the photocurrent of water decomposition of TiO_2 nanotubes was studied. Depending on the illumination (visible vs. UV–visible), the applied bias, and the amount of deposited Ag, the latter may lead either to an increase or a decrease of photocurrent. Possible origins of the positive and the negative effect of Ag deposition on the photoelectrochemical activity of TiO_2 are discussed.

1. Introduction

Wider utilization of solar energy is hardly feasible without development of methods for the energy storage, for example, by energy-to-fuel transformation. Photoelectrochemical water splitting is a promising "on spot" method of hydrogen generation by solar light, which does not require large installations or expensive materials [1–3]. In comparison with the conventional photocatalytic reactor, photoelectrochemical cell (PEC) has an advantage of spatial separation of anodic and cathodic processes, *i.e.* oxidation and reduction reactions. This lifts off the necessity of product separation and may result in higher energy transformation efficiency by suppression of the reverse reaction. Since the pioneer work of Fujishima and Honda [4], TiO_2 remains the most studied and the most conventional catalyst for photoanodes in the water splitting process due to several reasons [5]. The position of conduction and valence bands of TiO_2 satisfies thermodynamic requirements for water dissociation. Moreover, TiO_2 is the most resistant against (photo)-corrosion, the least expensive and the most abundant semiconductor material satisfying thermodynamic requirements for water dissociation. However, despite large number of studies devoted to the improvement of the photocatalytic activity of TiO_2, summarized in recent reviews [5,6], the energy transformation efficiency is still too low for the practical utilization of TiO_2-based photoanodes for the hydrogen production. Two main problems of the application of TiO_2 in photocatalysis are (i) relatively large band gap, 3.2 eV for anatase, which requires UV photons ($\lambda < 390$ nm) for electron–hole pair formation and (ii) low mobility of charge carriers resulting in recombination of most of photogenerated electron–hole pairs. Thus, the main activities towards the improvement of the photocatalytic properties of TiO_2 were focused on: (i) the extension of the absorption band of TiO_2 into the visible light region, and (ii) the improvement of the charge separation efficiency.

One of the approaches for the improvement of the visible light absorption of TiO_2 is to change its composition by doping. In particular, doping of TiO_2 by metal cations was found to be an effective approach to shift the absorption edge to the visible range [5,7,8]. However, the metal doping approach is limited by the stability of the resulting materials: loss of the activity due to leaching of the dopant is a common case. Asahi et al. have predicted [9] theoretically and proved experimentally that doping by non-metals, especially by substitutional nitrogen results in an enhanced absorption of visible light photons and higher rate of photocatalytic decomposition of acetaldehyde in the gas phase. Since then positive influence of non-metal doping on the activity of TiO_2 in photocatalytic processes under visible light illumination has been reported in numerous publications ([6] and refs. within). However, in photoelectrochemical processes, like water decomposition, both positive [10] and negative [11] effects of N-doping have been reported. The negative effect was attributed to the charge trapping at the dopant sites leading to an enhanced charge recombination. Distribution of the dopant concentration in TiO_2 strongly influences the activity of doped TiO_2.

Morphology also strongly affects photocatalytic activity of TiO_2 due to its influence on the charge separation efficiency.

* Corresponding author. Tel.: +33 3 68 85 26 34.
E-mail address: sergey.pronkin@unistra.fr (S.N. Pronkin).

0920-5861/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2012.03.054

Nanostructured TiO_2 materials, most commonly films of TiO_2 nanoparticles, are usually utilized for higher surface-to-volume ratio. However, charge transfer in these materials is often limited by the charge recombination at grain boundaries due to the contact resistance and charge trapping [12]. Hartmann et al. [13] have recently demonstrated significantly higher photocurrent and quantum efficiency in a photoelectrochemical cell for a mesoporous TiO_2 layer with continuous structure prepared by sol–gel method in comparison with a nanoparticulate layer. Thereupon supported ordered layers of TiO_2 nanotubes (TiO_2-NTs) offer promising morphology for photoelectrochemical applications. These layers can be synthesized electrochemically by anodization of Ti substrate in fluoride-containing solution. The morphology of the nanotubes, namely, their internal diameter, wall thickness, length are controlled by anodization parameters, such as electrolyte composition, temperature, anodization voltage, and time [14,15]. Significant improvement of the efficiency of photoelectrocatalytic water decomposition by utilization of TiO_2-NTs based photoanodes has been demonstrated.

Another approach to modify the photocatalytic properties of TiO_2 is the deposition of metal nanoparticles on its surface [5,16]. Presence of metal nanoparticles can be beneficial due to several factors. Catalytically active nanoparticles provide active surface sites for photocatalytic processes. In the case of the difference in Fermi levels of TiO_2 and metal, nanoparticles may act as an electron acceptor thus improving charge separation by formation of gradient of potential near semiconductor/metal interface. As a result, higher concentration of photogenerated charge carriers can be supported. Metal nanoparticles may induce electronic states in band gap (MIGS: metal-induced gap states) [17], which induces electron and hole formation by photons with energy below intrinsic band gap. Recently there is an increasing interest to utilize optical properties of nanoparticles, namely photon absorption by collective plasmon resonance, which may increase significantly photon absorption efficiency. In the latter aspect the most interesting metal for TiO_2 modification is, undoubtedly, silver, due to the plasmonic resonance of Ag nanoparticles in the optical range of UV and near-UV visible light [18]. Significant increase in the rate of colorant photocatalytic decomposition in liquid phase by TiO_2 particles after Ag deposition has been demonstrated in several studies [19–21]. To the best of our knowledge, the effect of Ag deposition on TiO_2 activity in phototelectrochemical cell was reported only recently by Sun et al. [22]. The authors demonstrated an increase in the incident photon to current conversion efficiency (IPCE) of TiO_2 photoanode, modified by Ag nanoparticles. Although the main interest of the cited paper was direct photocatalytic degradation of colorant on Ag/TiO_2 photocatalysts, their results motivated us to study in more details the nature of the effect of Ag deposition on TiO_2-NTs based photoanode and its photoelectrocatalytic activity in PEC water decomposition.

2. Experimental

2.1. TiO_2 nanotubes preparation by anodization

All electrochemical and photoelectrochemical measurements have been performed with BioLogic SP-300 potentiostat with 48 V voltage booster module. All experiments were done in potentiostatic mode in 3-electrode configuration. Mercury sulfate electrode (MSE) in saturated Na_2SO_4 have been used as the reference electrode (0.00 V MSE = 0.68 V NHE). The potentials in the paper are given in MSE scale. The currents presented in the paper as current densities are referred to geometric surface area of the electrode.

Ti foils with 99.6% purity were purchased from Mateck GmbH. Before anodization Ti substrate was cleaned for 15 min in ultrasonic bath, in a sequence of cleaning solvents first in *aqua regia* (1:3 HNO_3:HCl), then ethanol, acetone and finally ultrapure water. Anodization was performed in 100 ml of fresh electrolyte (0.1 M H_3PO_4 + 0.15 M NaOH + 0.25 M HF), which was prepared right before anodization. Ti foil was immersed into electrolyte between two larger Pt electrodes, parallel to the working electrode. The anodization cell consisted of the main Teflon compartment with working and counter electrodes, connected by glass bridge to the beaker with reference electrode in 0.1 M H_2SO_4 solution. The tip of the glass bridge in contact with anodization electrolyte was made of Teflon in order to minimize the contact of glass components with fluoride-containing electrolyte.

A 20 mV/s potential ramp was applied to the Ti foils from open circuit potential until potential reached 20 V. The 20 V potential was maintained for 2 h. The electrode was taken out of electrolyte while still keeping potential control until the contact was broken. The electrode was rinsed immediately with ultra pure water to avoid nanotube dissolution. Then the electrode was dried by N_2 stream. A thermal treatment was performed under air flow starting with a 5 °C/min ramp from room temperature to 550 °C. That temperature was maintained for 3 h, then the heating was stopped and the oven was allowed to cooled down.

2.2. Ag nanoparticles deposition on TiO_2 nanotubes by photodeposition

Solutions with various concentrations (100–0.1 mM) of $AgNO_3$ in ultra pure water were prepared by dissolution of solid $AgNO_3$. Anodized Ti electrodes were impregnated in $AgNO_3$ solution in ultrasonic bath for 5 min. Electrodes were then taken out, rinsed by ultrapure water and dried in a mild N_2 stream. Electrodes were finally placed in front of a Newport® QTH lamp (400 mW/cm^2; 2% UV) for 1 h. At the end of the illumination step electrodes are rinsed abundantly with ultra pure water.

2.3. Characterization of TiO_2-NTs and Ag/TiO_2-NTs electrodes

Samples were characterized by XPS and SEM methods. XPS analysis was performed by Multilab 2000 Thermoelectron spectrometer with Al Kα source (λ = 1486.6 eV). Morphology characterization was performed by SEM JEOL 6700F equipped with a field emission gun with extract potential 2.5 kV.

2.4. Analysis of Ag-TiO_2 electrodes

Electrochemical and photoelectrochemical (PEC) measurements were performed in an alkaline media composed of 0.01 M NaOH + 0.1 M Na_2SO_4 (pH 10) to minimize chemical dissolution of Ag. PEC measurements were performed in a 3-compartment cell with compartments for working, counter and reference electrodes separated by glass membranes. The compartment of working electrode was made of quartz. The same light source as for photodeposition was used in PEC measurements. The intensity of the light on the electrode was 90 ± 5 mW/cm^2 and regularly controlled by photometer ILT 900-C (International Light Technologies). Infrared and occasionally UV filter (Thorlab ACS, λ > 400 nm) were installed on the light pathway.

3. Results and discussion

3.1. Preparation of TiO_2-NTs

Anodization of Ti foil was performed in 0.1 M H_3PO_4 + 0.15 M NaOH + 0.25 M HF electrolyte. Upon immersion of Ti electrode into the electrolyte, the open circuit potential E_{OCP} decreased due to the dissolution of the native Ti oxide, but within several minutes