Electrochimica Acta 97 (2013) 253–258

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Electrochemical performance and electroreduction of maleic acid on Ce-doped nano-TiO_2 film electrode

Fengwu Wang[a,*], Xiaoyun Yan[b], Mai Xu[a], Shudong Li[b], Wenyan Fang[a]

[a] School of Chemistry and Chemical Engineering, Huainan Normal University, Huainan, Anhui 232001, PR China
[b] School of Chemical Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, PR China

ARTICLE INFO

Article history:
Received 4 December 2012
Received in revised form 24 February 2013
Accepted 2 March 2013
Available online 13 March 2013

Keywords:
Sol–gel
TiO_2 film electrode
Electrocatalysis
Maleic acid
Cerium

ABSTRACT

A Ce-doped nano-TiO_2 film electrode was synthesized by the sol–gel method. The structural, morphological and electrocatalytic activity of as-prepared TiO_2 films on titanium substrate surface were studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Electrocatalytic properties were evaluated by studying the electroreduction of maleic acid (MA) on the Ce nano-TiO_2 film electrodes in sulfuric acid solutions. The results demonstrated that the optimum molar ratio of Ce:Ti was 0.003:1. The Ce nano-TiO_2 electrode showed a higher electrocatalytic activity (4.5 times higher peak current) than the undoped nano-TiO_2 electrode, which resulted in a high yield of succinic acid (SA) (98%) and a high current efficiency (91%) in the galvanostatic preparative reduction.

1. Introduction

Titanium dioxide (TiO_2) is a well known metal oxide semiconductor providing extensive applications from photocatalyst to electrode material [1–4]. In the field of electrochemistry, TiO_2 has been demonstrated as the most important semiconductor electrode material. Beck et al. developed a TiO_2 cathode whose surface behaves as a stable redox electron carrier [5,6]. Meanwhile, some interesting electrochemical and electrocatalytic properties of various TiO_2 electrodes have been demonstrated. Recently, TiO_2 electrodes have been used as electrocatalyst in the reduction of organic compounds such as maleic acid [7,8], nitroanilines [9], 1-nitroso-2-naphthol [10], nitrobenzene [11] and *p*-nitrobenzoic acid [12] and so on.

It is technologically important to control the doping as it affects the performance of the materials. Many researchers have begun to explore the dopants influence on semiconductor nanocrystals and the unusual and size-specific optical and electronic behaviors [13].

Compared to many metal ions, rare earth (RE) ions are considered as the ideal dopants to modify the crystal structure, electronic structure and optical properties of TiO_2 [14–17], because RE elements have the 4f electron configuration, which reduce electron–hole pair recombination, leading to enhanced activity [18]. In recently years, numerous studies of RE ions have been focused on the photocatalytic activities [19–22]. However, to the best of our knowledge, the electrochemical properties of RE metal doped TiO_2 have seldom been presented so far.

In this paper, Ce-doped nano-TiO_2 film electrodes were prepared by the sol–gel method. Their electrochemical properties were studied by CV and EIS. Their structure and composition were investigated by XRD, SEM and XPS. Their electrocatalytic properties were evaluated by studying the electroreduction of MA in aqueous sulfuric acid solutions.

2. Experimental

2.1. Materials and apparatus

Titanium (TA_1, purity 99.7%) was purchased from the Far East Ti Equipment Co., Shanghai, China. Tetra-butyltitanate [Ti $(OBu)_4$] (TBOT; ≥97%), MA, $Ce(NO_3)_3{\cdot}6H_2O$, acetyl acetone (AcAc; 99%), Sodium dodecyl benzenesulfonate [$C_{18}H_{29}NaO_3S$], absolute ethanol, ethanediol, hydrogen fluoride (HF; ≥40%), HNO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and all solutions in the experiments were prepared using doubly distilled water.

The electrochemical measurements were carried out by an Autolab PGSTAT302N electrochemical workstation system (Metrohm). The surface morphology of the electrodes was analyzed by using FE-SEM (JSM-6700F, JEOL, Japan) with an operating

---

* Corresponding author at: School of Chemistry and Chemical Engineering, Huainan Normal University, Dongshan Road (West) 232001, Huainan, Anhui Province, PR China. Tel.: +86 0554 6863586; fax: +86 0554 6863586.
E-mail addresses: fengwuwang@163.com, xuma2215@sina.com (F. Wang).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.03.009

voltage of 0.5∼30 kV. The crystalline structure of the coated film analyzed by XRD (X'Pert PRO) with Cu Ka radiation ($\lambda = 1.541841$ Å) over the range of $2\theta = 20–70°$ at room temperature. XPS spectra were recorded by Thermo ESCALAB 250 Instrument with Al Kα X-ray source (1486.60 eV, 150 W).

2.2. Preparation of Ti/nanoTiO$_2$ and Ti/Ce-nanoTiO$_2$ electrodes

The Ce nano-TiO_2 film electrode was manufactured as follows [23,24]: 10 mL of TBOT (0.0294 mol) and 0.1 g of a surfactant ($C_{18}H_{29}NaO_3S$) were dissolved in 25 mL of absolute ethanol with stirring for several minutes, then 0.88 mL of AcAc was added as suppressant to given solution A. The solution A was stirred (magnetic stirrer) for 1 h. Solution B consisting of a mixture of deionized water (1.8 mL), absolute ethanol (12 mL), an appropriate amount of $Ce(NO_3)_3\cdot 6H_2O$ (the molar ratio of Ce/Ti corresponding to 0.000, 0.001, 0.002, 0.003, 0.004, and 0.005) and a few drops of a concentrated HNO_3 solution was obtained as solution B (pH = 2∼3) was added dopwise to the stirred solution A. The obtained mixture was stirred for 15 h at room temperature and a yellow and transparent doped TiO_2 sol was obtained. Titanium strips were used as the substrates, which were mechanically polished to a mirror-like smoothness with number 2000 emery papers and anodized in a ethanediol solution containing 20 wt.% HF for 0.5 h. Then the titanium strips sonicated in acetone, ethanol and distilled water for 15 min and were allowed to dry in air at room temperature. The doped TiO_2 sols coated on pure titanium substrates were calcined at 450 °C for 30 min in air. Then they were cooled to room temperature. This process was repeated four or five times to afford the Ce-doped nano-TiO_2 film electrodes were obtained. Pure TiO_2 sols were prepared following the same procedure as described above, except for the addition of $Ce(NO_3)_3\cdot 6H_2O$ into the solution B. Pure TiO_2 sol was used to get undoped nano-TiO_2 film electrodes.

The sample with the optimum ratio of Ce (Ce/Ti molar ratio = 0.003) was denoted as Ti/Ce nano-TiO_2 electrode and the pure TiO_2 film electrode was denoted as Ti/nanoTiO_2 electrode.

2.3. Electrochemical measurements

The CV curves and EIS measurements were measured in a three-electrode cell undivided glass cell. Either a 1 M H_2SO_4 solution or solutions of MA at different concentrations in 1 M H_2SO_4 were used as the electrolyte. A Ti/Ce nano-TiO_2 electrode or Ti/nano-TiO_2 electrode (surface area of 0.01 cm^2), a platinum foil and a saturated calomel electrode (SCE) served as working, counter and reference electrodes, respectively. The potential was between 0.0 and −1.2 V at different sweep rates. The deaerated solution was acquired by purging the solution with pure argon gas for 10 min to remove oxygen prior to the experimental runs. All measurements were performed at room temperature (25 °C).

2.4. Preparative scale experiments

Preparative scale experiments were performed in a laboratory-made, divided H-type glass cell. An Aldrich Nafion117-type ion exchange membrane was used as the diaphragm. A 1 M H_2SO_4 containing the required amount of MA was used as catholyte and a 1 M H_2SO_4 solution was used as anolyte. An 8 cm^2 area of Ti mesh/Ce nano-TiO_2 electrode or Ti mesh/nano-TiO_2 electrode was prepared by the method described above and used as cathode. A 10 cm^2 dimensionally stable anode (DSA) was used. The glass cell was placed in a temperature-controlled water bath and the catholyte was stirred magnetically. The reactions were carried out at a current density of 58 mA cm^{-2}, the cell voltage being in the 3.80–4.10 V range. The solution after electrolysis was concentrated to half the volume and kept overnight, when the product SA separated out. The SA so obtained was purified by recrystallization and identified by its melting point.

3. Results and discussion

3.1. XRD characterization of the electrodes

The XRD patterns of Ce-doped (Ce/Ti molar ratio = 0.003) and undoped nano-TiO_2 films are presented in Fig. 1. From XRD analysis, the characteristic peaks of the TiO_2 at 2θ of 25.47°, 37.95°, 48.15°, 55.30° and 63.10° were observed and the Ce-doped film has a certain extent of peak broadening and passivation relative to the undoped, indicating lattice distortion in the TiO_2 crystal structure. The absence of peaks of dopant phase points out that the dopant is well dispersed in the TiO_2 phase [25–28]. The average crystallite size was determined from the Scherrer's equation using the diffraction peaks at 25.47° and the average nanocrystallite sizes were found to be 8 nm and 15 nm for Ce-doped and undoped nano-TiO_2.

3.2. Microstructure analysis

The SEM micrographs of Ti/Ce nano-TiO_2 (Ce/Ti molar ratio = 0.003) and Ti/nano-TiO_2 electrodes are shown in Fig. 2. This figure shows that the morphology of the undoped nano-TiO_2 films coated on titanium was rough (Fig. 2a). However, the surface uniformity was considerably increased and the particle size became smaller after Ce doping, as seen in Fig. 2b. This means that Ce ion doping can efficiently restrain the growth of particle size.

3.3. XPS analysis of the electrodes

XPS analyses of Ce doped nano-TiO_2 film (Ce/Ti molar ratio = 0.003) are represented in Fig. 3. The Ce $3d_{3/2}$ and Ce $3d_{5/2}$ band (0.14 at. % doping Ce in the peak table) were found to have two binding energy of 885.3 eV and 904.3 eV (Fig. 3a), the peaks have some migration compared with the binding energy of 882.4 eV and 889.9 eV of pure CeO_2 in Ce $3d_{3/2}$ and Ce $3d_{5/2}$ rotation orbit. The result indicated that the doped Ce ion and TiO_2 combined to form the Ce—Ti—O bond during the coating process. The results in Fig. 3b show an asymmetrical broadening toward the higher binding energy side of the major peak, indicating the presence of other species on the surface. The major peak at 529.8 eV was attributed to bulk oxygen of TiO_2 and the sub peaks at 531.4 eV was attributed to physisorption of OH [29]. A high resolution spectrum of the Ti 2p peak (Fig. 3c) shows that the surface oxide consists mainly of

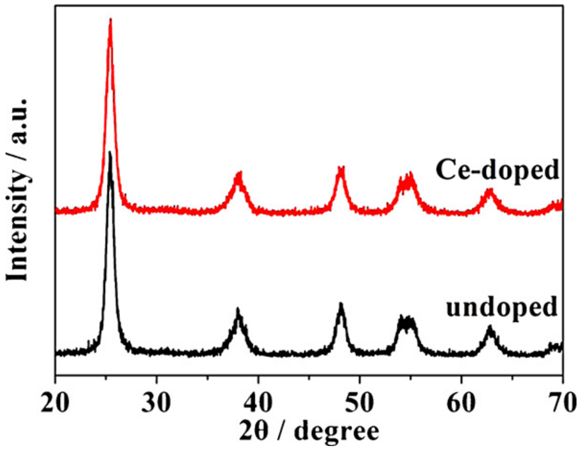

Fig. 1. XRD patterns of Ce-doped (Ce/Ti molar ratio = 0.003) and undoped nano-TiO_2 films.