



Roughened TiO₂ film electrodes for electrocatalytic reduction of oxalic acid to glyoxylic acid



Fengming Zhao, Fei Yan, Yang Qian, Yinghua Xu, Chun'an Ma*

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou City 310032, Zhejiang, PR China

ARTICLE INFO

Article history:

Received 16 January 2013
Received in revised form 14 March 2013
Accepted 16 March 2013
Available online 6 April 2013

Keywords:

Roughened TiO₂ film electrode
Anodic oxidation
Porous structure
Electrocatalytic reduction
Oxalic acid
Glyoxylic acid

ABSTRACT

Roughened TiO₂ film electrodes were prepared by anodic oxidation method in 1.0 M sulfuric acid solution. The prepared electrode and the electrode after electrolysis were characterized by XPS and SEM. It was observed that the roughened surface disappeared and 0.5–1 μm holes formed after electrolysis. While TiO₂ film always existed on the surface of the anodized electrode. The adsorption and reduction of oxalic acid at the prepared electrode likely benefited from this porous structure. The electrocatalytic properties of the roughened TiO₂ film electrode towards the electrocatalytic reduction of oxalic acid to glyoxylic acid were evaluated by CV, in situ FTIR and preparative electrolysis experiments. Experimental evidence was presented that the roughened TiO₂ film electrode exhibited higher electrocatalytic activity for the reduction of oxalic acid. In addition, a new mechanism of the electrocatalytic reduction of oxalic acid was proposed, in which TiO₂/Ti(OH)₃ redox couple plays an important role in the reduction of oxalic acid.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous catalytic hydrogenation is a most useful technique for the addition of hydrogen to carbon–carbon, carbon–nitrogen, carbon–oxygen double bonds and nitro groups. Compared with traditional catalytic hydrogenation, electrocatalytic hydrogenation can be carried out at more moderate conditions (room temperature and normal pressure) [1–5]. Most frequently, industrial hydrogenation mainly relies on heterogeneous catalysts. TiO₂ as a stable redox electron carrier has been used as heterogeneous catalyst in electrocatalytic reduction of organic compounds containing carbon–carbon, carbon–nitrogen, carbon–oxygen double bonds and nitro groups [6–9]. Owing to its distinct properties such as redox selectivity, high stability, easy preparation, manufacturable at atmospheric conditions and environmentally friendly [10–15], enormous efforts have been devoted to the research of TiO₂ material applied in organic electrochemistry.

Numerous applications of electrocatalytic hydrogenation are found in pharmaceutical, food and other industries [16,17]. Some early studies employing TiO₂ film electrode in organic electrosynthesis showed that TiO₂ film electrode as a heterogeneous catalyst has good electrocatalytic activity. Illustrative examples of electrocatalytic hydrogenation reactions are the addition of hydrogen to unsaturated organic compounds, such as alkenes, aldehydes [18]

and nitro compounds. For instance, electrocatalytic reduction of maleic acid to form succinic acid on the TiO₂ film electrode prepared by different methods has been studied [19–21]. The results indicated that the TiO₂ film electrode has an excellent electrocatalytic activity for the reduction of maleic acid. Electrocatalytic reduction of diethyl oximinomalonate (DEOM) at a Ti/nanoporous TiO₂ electrode prepared by sol–gel method was investigated. The results suggested that Ti/nanoporous film electrode can be successfully used for the reduction of DEOM to diethyl aminomalonate [8]. The application of the TiO₂ film electrode for the reduction of aromatic nitro compounds such as nitro salicylic acid [22], nitro aniline [6] and nitro benzene [7,23–25] has been studied extensively. The TiO₂ film electrode also has electrocatalytic activities for organic compounds containing carbon–oxygen double bonds. Chu et al. [26] studied the electrocatalytic reduction of furfural on the nano-TiO₂ film electrode synthesized by sol–gel method. It was found that the Ti/nanoporous TiO₂ film electrode had electrocatalytic activities for the reduction of furfural to furfuryl alcohol. Consequently, this material is potentially important for organic electrosynthesis and may be important for a better understanding of nanostructure materials.

Electrocatalytic reduction of oxalic acid to produce glyoxylic acid is one of the electroorganic processes that have been commercialized. However, there still remain some problems which are not incompletely resolved. The main problem is that the cathode material (lead) can be easily deactivated [27–29]. So, it is very necessary to find replaceable cathode materials for the reduction of oxalic

* Corresponding author. Tel.: +86 571 88320830; fax: +86 571 88320413.

E-mail addresses: zhaofm@zjut.edu.cn (F.M. Zhao), science@zjut.edu.cn (C.A. Ma).

acid. Our previous work using TiO₂ film electrode prepared by anodic oxidation method to electrocatalytic reduction of maleic acid has been reported [20]. This anodic oxidation method has obvious advantages over the other preparation methods. Its rapidity, simplicity and lower cost make it the promising preparation method in large production of TiO₂ film electrodes. Considering the wide applications of TiO₂ film electrodes in organic electrosynthesis, we want to use the roughened TiO₂ film electrode prepared by anodic oxidation to replace lead electrode in oxalic acid.

In this paper, we first use this type of electrode to replace lead electrode to the electrocatalytic reduction of oxalic acid. Using this heterogeneous catalyst that presents a better activity/selectivity than traditional catalysts would be a surprising new tactic for the electrocatalytic reduction of oxalic acid to glyoxylic acid. Roughened TiO₂ film electrodes with enhanced surface area were prepared by anodic oxidation method. The prepared electrodes were used for the electrocatalytic reduction of oxalic acid to glyoxylic acid in saturated oxalic acid solution. Furthermore, the mechanism of the electrocatalytic reduction of oxalic acid to glyoxylic acid at the roughened TiO₂ film electrode was also discussed. The application of the roughened TiO₂ film electrode prepared by anodic oxidation in the electrocatalytic reduction of oxalic acid to glyoxylic acid would contribute to remarkable advances in industrial production. The main significance of this paper is using the stable hypo-d-oxide type selective electrocatalyst for specific hydrogenation processes in organic electrosynthesis and contributes to predicting a process window for the application of the roughened TiO₂ film electrode in other organic electrosynthesis.

2. Experimental

2.1. Preparation of the roughened TiO₂ film electrode

Pure titanium sheets with purity more than 99% were chemically polished in a mixed solution of 12 ml nitric acid + 12 ml hydrogen peroxide + 5 g ammonium fluoride + 0.3 g urea for 30 s. The polished titanium sheets were ultrasonically cleaned in acetone and deionized water with resistance of 18 MΩ obtained from an ultrapure water purification system Milli-Q Plus (Millipore Inc.), respectively. Then they were followed by rinsing with deionized water, dried at 20 °C. The polished titanium sheet served as anode and two DSA electrodes as cathode. Roughened TiO₂ film electrodes were prepared by anodic oxidation method in 1.0 M sulfuric acid. The electrolyte temperature was maintained at 45 °C using a water thermostat. The operation voltage was 20.0 V and the processing time was 2 h. The prepared electrodes were cleaned in deionized water after anodic oxidation.

2.2. Characterization of the roughened TiO₂ film electrode

XPS measurements were carried out with a Kratos Axis Ultra DLD spectrometer (England) using a focused monochromatized Al Kα operated at 300 W. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. The surface structure of the roughened TiO₂ film electrode was observed by SEM using a Hitachi S-4700 II electron microscope (America). SEM measurements were operated at an accelerating voltage of 15.0 keV. The roughness of the roughened TiO₂ film electrode (10 mm × 10 mm) and the polished Ti electrode (10 mm × 10 mm) were determined by potential steps [30,31]. Potential steps experiments were carried out by PARC model 283, at 20 °C, in 1 M sulfuric acid aqueous solution. The working electrodes were a roughened TiO₂ film electrode and a polished Ti electrode, the counter electrode was a Pt electrode and the reference electrode was an aqueous saturated calomel electrode (SCE).

2.3. CV experiments

Cyclic voltammetric measurements were carried out using CHI660D electrochemical working station. A conventional three-electrode glass cell was used for the electrochemical measurement. A roughened TiO₂ film electrode (10 mm × 10 mm) was used as the working electrode. A platinum sheet and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. Other working electrode was a polished Ti electrode (10 mm × 10 mm). All potentials were recorded with respect to SCE. Cyclic voltammetric experiments were performed at 20 °C.

2.4. In situ FTIR experiments

In situ FTIR spectroscopic experiments were carried out on Nicolet 670 FTIR spectrometer equipped with a MCT-A detector cooled with liquid nitrogen. The spectroelectrochemical cell was provided with a CaF₂ disk window (diameter 32 mm and thickness 2 mm). The working electrode was a roughened TiO₂ film electrode (diameter 3.2 mm) with the surface pressed against the CaF₂ disk window to form a thin solution layer with a thickness of a few micrometers for IR measurements. Before the experiment the high purity nitrogen was used to remove the oxygen in the solution. To acquire in situ FTIR data, the spectral resolution was set at 8 cm⁻¹. The resulting spectrum recorded was defined as the potential-difference spectra and calculated by the following formula [32]:

$$\frac{\Delta R}{R} = \frac{R(E_s) - R(E_R)}{R(E_R)} \quad (1)$$

In this formula, $R(E_s)$ represents single-beam spectrum collected at the sample potential and $R(E_R)$ at the reference potential. As a result, positive-going bands denote the consumption of the reactant, while negative-going bands in the resulting spectra indicate the produce of intermediates and products in the thin layer solution.

2.5. Preparative electrolysis experiments

Preparative electrolysis experiments were carried out in an undivided cell with 100 ml volume. A roughened TiO₂ film electrode (30 mm × 30 mm), a polished Ti electrode (30 mm × 30 mm) and a Pb electrode (30 mm × 30 mm) for comparison served as cathode. Two dimensionally stable anode (DSA) electrodes (40 mm × 40 mm) were used as anode. Saturated oxalic acid solution (0.82 mol/l) was employed as the electrolyte and the volume of the solution was 97 ml. The electrolyte was stirred magnetically. The temperature of the cell was controlled at 20 °C using a water bath. The same current density (30 mA/cm²) was applied in all electrolysis experiments. The concentration of glyoxylic acid during the electrolysis processes was monitored and analyzed by ion chromatography system (Dionex ICS-1500).

3. Results and discussion

3.1. XPS and SEM characterization of the roughened TiO₂ film electrode

Fig. 1a shows the wide-scan spectrum for the prepared electrode. Characteristic peaks of Ti 2s, Ti 3s, Ti 2p, O 1s and C 1s appeared in Fig. 1a. Only Ti, O and C elements were detected on the surface of the electrode, while C is a calibration element. The wide-scan XPS spectra results revealed that the prepared electrode only contains Ti and O two elements. To investigate the chemical state of titanium, Ti 2p binding energies were studied by measuring the XPS spectra. High resolution XPS spectrum of Ti 2p of this electrode is shown in Fig. 1b. Two peaks for the Ti 2p in XPS spectrum were observed at 464.6 and 458.8 eV and assigned to Ti 2p_{1/2}

Download English Version:

<https://daneshyari.com/en/article/219097>

Download Persian Version:

<https://daneshyari.com/article/219097>

[Daneshyari.com](https://daneshyari.com)