Electrochimica Acta 55 (2009) 305–310

Contents lists available at ScienceDirect

Electrochimica Acta

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

The photoelectrochemical properties of N3 sensitized $CaTiO_3$ modified TiO_2 nanocrystalline electrodes

Shuming Yang[a,*], Huizhi Kou[a], Hongjun Wang[a], Ke Cheng[b], Jichao Wang[a]

[a] *College of Chemistry and Chemical Engineering, Institute of Applied Chemistry, Xinyang Normal University, Henan 464000, China*
[b] *Key Laboratory of Special Functional Materials, Henan University, Kaifeng, Henan 475001, China*

ARTICLE INFO

Article history:
Received 18 June 2009
Received in revised form 2 August 2009
Accepted 27 August 2009
Available online 3 September 2009

Keywords:
DSSC
$CaTiO_3$
Surface modification
Spectro-electrochemistry
Energy barrier
Photoelectric conversion efficiency

ABSTRACT

The preparation of nanoporous TiO_2 electrodes modified with $CaTiO_3$ layers and their application in dye-sensitized solar cells (DSSCs) were reported. The as-prepared $TiO_2/CaTiO_3$ electrodes were characterized by XPS and XRD, indicating that a thin $CaTiO_3$ layer was formed on the surface of nanoporous TiO_2 electrodes. Compared with bare TiO_2 electrodes, $CaTiO_3$ modified TiO_2 electrodes presented more dye adsorption. Moreover spectroelectrochemical studies showed that the concentration of free electrons in the conduction band of TiO_2 was remarkably increased after surface modification. As a result, the photocurrent and photoelectric conversion efficiency of the modified electrodes were increased. The influence of the thickness of $CaTiO_3$ layer on the photoelectrochemical properties of the modified electrodes was investigated. Experiment results showed that proper thickness of the modification layer is crucial to the photoelectrochemical properties of modified electrodes. The highest conversion efficiency reaches 9.23% under irradiation of 100 mW cm^{-2} white light, obtained with the electrode $TiO_2/CaTiO_3$(45 min), a 34% increase than that of bare TiO_2 electrodes.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been attracting much attention due to their high energy conversion efficiency and as a low-cost alternative to commercial solar cells based on silicon [1–7]. After decades' development, the photoelectric conversion efficiency of a DSSC as high as 11% has been achieved under AM 1.5 simulated solar light [8]. The high conversion efficiency achieved with DSSCs may be attributed to the nanoporous TiO_2 electrodes which possess large surface to volume ratio, and as a result, the dye molecules adsorbed on nanoporous TiO_2 film are tremendously increased, leading to improved efficiency of solar cells [9]. However, due to the small size of the semiconductor particles in the photoelectrode, the space charge layer, which separates the photo-generated electron and hole, may not form at the electrode/electrolyte interface [10–13]. So the photo-induced electrons in the conduction band of semiconductor, which are injected from the excited state of the dye, have two important recombination processes: back-reacting with the oxidized dye and reducing I_3^- to I^-.

In order to suppress the recombination processes and improve the conversion efficiency, one effective approach is the interfacial modification of nanoporous TiO_2 films with oxide coating layer such as SrO [14], $BaCO_3$ [15], MgO [16] and so on. This thin layer could separate the injected electrons with the redox couple, and thereby suppressing the charge recombination.

It has been observed in our previous work that the light to current conversion efficiency of nanoporous TiO_2 electrodes was enhanced when the electrodes were capped with SrO [14], $MgTiO_3$ [17] and different sulfides on surface [18,19]. We report here on the fabrication of N3 sensitized $CaTiO_3$ modified TiO_2 electrodes and the influence of the thickness of the $CaTiO_3$ layer on the photoelectrochemical properties of electrodes.

2. Experimental

2.1. Materials and solutions

Optically transparent electrodes (OTE) were fabricated on an F-doped SnO_2-coated glass substrate. Water ($R = 18\,M\Omega$) from an easy pure RF system was used in the preparation of all solutions. $Ti(OCH(CH_3)_2)_4$, propylene carbonate, *tert*-butylpyridine, ethyl cellulose and LiI were purchased from Acros. 1-Propyl chloride, terpineol, *N*-methyl-imidazole, $CaCl_2$, $TiCl_4$ and acetonitrile purchased from the Beijing Reagent Co., were reagent grade, while acetonitrile was distilled over P_2O_5. The dye N3 ($Ru[L_2(NCS)_2]$, L = 2,2′-bipyridine-4,4′-dicarboxylic acid) was synthesized according to the literature [2]. The synthesis of 1-methyl-3-propylimidazolium iodide (PMII) followed the procedure described in literature

---

[*] Corresponding author. Tel.: +86 0376 6393736; fax: +86 0376 6393736.
E-mail address: smyang2006@163.com (S. Yang).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.08.055

[17]. For dark current and photoelectrochemical measurements, the electrolyte is 0.5 mol L^{-1} LiI, 0.05 mol L^{-1} I_2, 0.5 mol L^{-1} 4-*tert*-butylpyridine and 0.3 mol L^{-1} 1-methyl-3-propylimidazolium iodide in 1:1 acetonitrile–propylene carbonate.

2.2. Preparation of the dye-sensitized nanoporous electrodes

Nanoporous TiO_2 electrodes: nanoporous TiO_2 films were prepared from colloids with particles of about 20 nm diameter. The preparation of the colloids and film fabrication were similar to that reported [20]. Typically 48 mL of titanium iso-propoxide was poured into 250 mL water under vigorously stirring. After addition of 2 mL of 70% nitric acid, the mixture was heated to 80 °C and kept for 2 h. 100 ml of the sol solution was put in an autoclave and heated at 230 °C for 12 h. Resulting precipitate was washed with ethanol which was then removed by rotary-evaporator. 16.9 g of terpineol and 20.85 g of 10% ethyl cellulose ethanol solution were added to the TiO_2 paste. This mixture was then dispersed under sonication, and ethanol was removed by rotary-evaporator. The final pastes were grounded with a mill.

TiO_2 sol was spread on the substrates by a glass rod with adhesive tapes as spacers. The films were dried at 125 °C and sintered at 450 °C for 30 min in air and finally cooled to room temperature. The TiO_2 thin film was dipped in 50 mmol L^{-1} $TiCl_4$ aqueous solution at 70 °C for 30 min and again sintered at 450 °C for 30 min.

$TiO_2/CaTiO_3$ electrode: surface modified $TiO_2/CaTiO_3$ electrodes were fabricated by dipping as-prepared TiO_2 thin films in a 50 mmol L^{-1} $CaCl_2$ and 50 mmol L^{-1} $TiCl_4$ mixture aqueous solution at 70 °C for different time, and then washed consecutively with water and ethanol, and finally sintered in air at 450 °C for 30 min. The dipping time is 15, 45 and 75 min respectively. For convenience, the modified electrodes are denoted as $TiO_2/CaTiO_3(t)$, where t is dipping time.

For dye sensitization, the $TiO_2/CaTiO_3$ or TiO_2 electrodes were immersed in 5×10^{-4} mol L^{-1} N3 absolute ethanol solution for 12 h at room temperature. To minimize adsorption of impurities from moisture in the ambient air, the electrodes were dipped in the dye solution while they were still warm (80 °C). The dye-sensitized electrodes were then rinsed with ethanol thoroughly and dried.

2.3. Instrumentation

X-ray photoelectron spectroscopy (XPS) was collected on an ESCALab 220i-XL (Thermo Co.) with Al K_α as X-ray source and operated at voltage of 15 kV and current of 20 mA. X-ray diffraction (XRD) measurements were performed on a D8 diffractometer (Bruker Co.) with Cu Kα (λ = 1.5405 Å) radiation over the 2θ ranges of 20–60° to identify the phase structure of samples. The absorption spectra were recorded on an UV-1240 spectrophotometer (Shimadzu, Japan). Electrochemical and photoelectrochemical experiments were performed on a CH800 electrochemical analyzer (CH Instrument). A sandwich-type solar cell was assembled in the photovoltage–photocurrent measurements. The N3 sensitized $TiO_2/CaTiO_3$ or TiO_2 electrode was used as the photoanode and a Pt coated F-doped SnO_2 electrode as the photocathode. Both electrodes were sealed with Surlyn 25. A 500 W xenon lamp was used as the source of excitation. A KG4 filter (Schott) was set in the light beam to protect the electrodes from heating, and a GG420 cutoff filter (Schott) was used to prevent the TiO_2 film from being excited by light with wavelength less than 400 nm. To get a given band-pass of light, the light beam was passed through a group of filters (Ealing Co.). The effective illumination area of a flat window is 0.196 cm^2. Spectro-electrochemistry measurements were undertaken according to published literature [21,22]. Measurements were carried out in a typical three-electrode system, in which TiO_2 or $TiO_2/CaTiO_3$ electrode, a platinum wire and a saturated calomel electrode (SCE) acted as working, counter and reference electrodes respectively, and the electrolyte solution was 0.1 mol L^{-1} $LiClO_4$ in dry acetonitrile. A quartz cell with three electrodes and electrolyte was put in the compartment of a Shimadzu UV–vis spectrophotometer, and the absorption spectra were recorded as LSV was scanned.

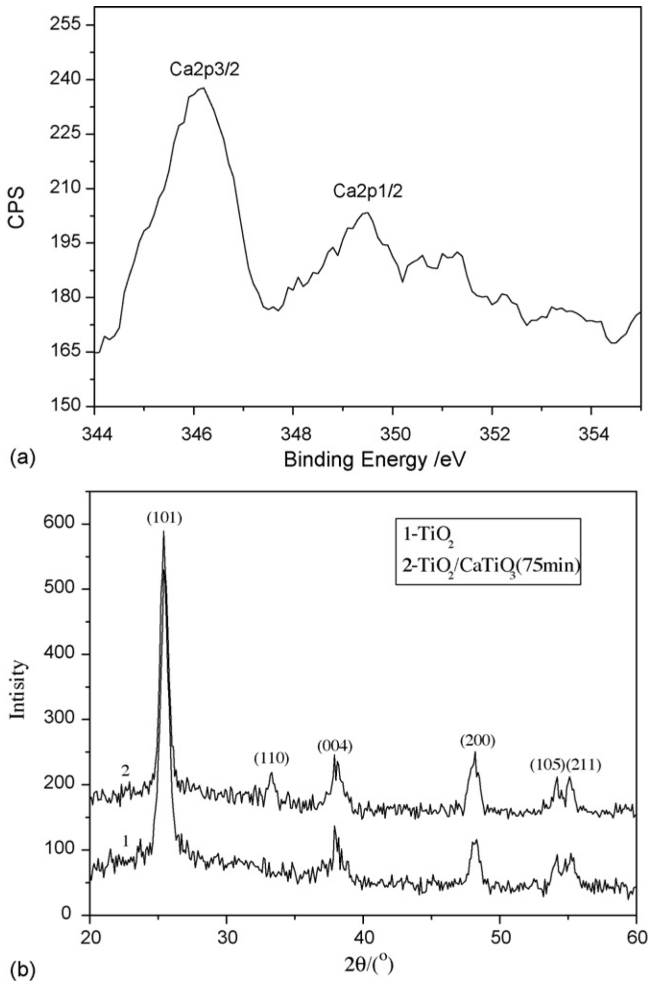

Fig. 1. (a) XPS spectra of Ca2p1/2 and Ca2p3/2 for $CaTiO_3$ modified TiO_2 film; (b) XRD patterns of TiO_2 and $TiO_2/CaTiO_3$(75 min) electrode.

3. Results and discussions

3.1. The formation of $CaTiO_3$ layer on the surface of nanoporous TiO_2 electrode

Formation of $CaTiO_3$ overlayer on the TiO_2 surface was detected by XPS and XRD measurements. Fig. 1a shows the XPS of the $CaTiO_3$ modified TiO_2 film.

Peaks at 346.1 and 349.5 eV can be assigned to Ca2p3/2 and Ca2p1/2, respectively, which agrees with the binding energies of Ca in $CaTiO_3$ reported in literature [23]. To further investigate the formation of calcium titanate, XRD spectra were measured for both $CaTiO_3$ modified and unmodified TiO_2 films (see Fig. 1b). There is a peak at 33.3° which corresponds to the strongest diffraction of the (1 1 0) lattice of cubic $CaTiO_3$ (JCPDS file 65-3287). Therefore, it was concluded that a thin $CaTiO_3$ layer was formed on the surface of nanoporous TiO_2 electrode.