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Surface-modified anodic TiO_2 films for visible light photocurrent response

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Dedicated to Professor Ullrich Zenneck on the occasion of his 60th birthday.

Abstract

N-doped titania thin films were prepared by anodic oxidation of titanium sheets and subsequent heat treatment in the presence of urea pyrolysis products at 400 °C. The resulting films are modified predominantly at the surface. They exhibited a significant photocurrent response upon visible light irradiation inducing an incident photon-to-current efficiency of 1.5% at 400 nm. The flatband potential was anodically shifted by 0.2 V as compared to the unmodified film. Photocurrent transients revealed that nitrogen-centered intra-band-gap states, responsible for visible light response, induce also enhanced recombination as indicated by a cathodic "overshoot" after turning off the light. This recombination can be inhibited by the presence of iodide.

Keywords: Photocurrent; Visible light; Anodic TiO_2; Nitrogen modification; Flatband potential

1. Introduction

Titanium dioxide is due to its non-toxicity and excellent stability one of the most promising semiconductors for solar energy conversion [1,2]. Under irradiation with UV light electron-hole pairs are generated which can be utilized for redox reactions or photocurrent generation. However, because of the wide band gap of ~3.2 eV TiO_2 can utilize only the UV part of solar radiation (2–3%). Therefore strong efforts are made presently to shift its photoresponse to the much larger visible fraction. One promising approach is the modification or doping with nitrogen species. Such materials have been prepared by calcining titanium hydroxide with aqueous ammonia [3] or with an ammonium salt [4], calcining TiO_2 at 550–600 °C under an atmosphere of ammonia and argon [5], treating TiO_2 nanoparticles with triethylamine at room temperature [6], mechanochemical methods [7], DC magnetron or radio-frequency sputtering [8,9], ion implantation [10,11], or by calcining solid mixtures of titania or titanium hydroxide and urea [12,13]. Typically, N1s binding energies of ca. 396 eV and ca. 400 eV were reported for these materials – the first value suggests the presence of nitridic nitrogen [5,9,12], the latter points to molecularly chemisorbed γ-N_2 [5], interstitial NH species [14], hyponitrite [4,13,15] or to an NO site within the TiO_2 lattice [16–19]. Based on theoretical calculations [5,18,20] and experimental evidence [4,8,21,22] the enhanced light absorption and photocatalytic activity in the visible range has been ascribed to occupied surface states located up to ca. 0.75 eV above the valence band edge of TiO_2, consisting of a rather narrow and isolated band of N 2p states partially mixed with O 2p valence band states of TiO_2 [8,20–22].

Drawing on our work on the modification of TiO_2 powders for visible light photocatalytic activity [4,13,15,23,24], we investigated also N-modified electrodes as potential systems for visible light photovoltaics. Herein we report on a simple method for surface modification of thin compact TiO_2 films prepared by anodic oxidation of titanium which

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offers a relatively cheap and well controllable fabrication of TiO_2 films [25–27]. Flatband potential and photocurrent action spectra measurements were performed to obtain basic information on the mechanism of the visible light photocurrent response of these electrodes. Moreover, it has recently been shown that anodization of titanium can be used for fabrication of highly porous and nanotubular TiO_2 structures, which promises a variety of novel applications [28–31].

2. Experimental

Titanium (99.6% purity, Advent Research Materials, England) samples were foils (1.5 × 1.5 cm) of 0.1 mm thickness. Prior to the electrochemical treatment, they were degreased by sonicating in acetone and isopropanol successively, followed by rinsing with deionized water and finally dried with nitrogen gas.

For anodization experiments the titanium foil was placed onto a copper plate and then pressed against an O-ring in an electrochemical cell, leaving an area of 1 cm^2 exposed to the electrolyte. The anodization set-up consisted of a DC voltage source (Gossen, Germany) and a conventional three-electrode configuration with a platinum flag (1 × 2 cm) as a counter electrode and a Haber–Luggin capillary with a Ag/AgCl (3 M KCl) electrode as a reference electrode. The potential between working and reference electrode was measured using a Keithley digital multimeter. The growth of anodic TiO_2 layers was performed in H_2SO_4 (1 M) and consisted of a potential ramp from the open-circuit potential to 30 V with a sweep rate of 1 V/s followed by holding the samples at 30 V for 20 min. Assuming the reported growth rate of 2.5 nm/V for TiO_2 films formed below the breakdown voltage [26,32], such layers are approximately 75 nm thick. After anodization the samples were rinsed with deionized water and blown dry in a nitrogen stream.

For modification the anodized samples were placed into a 230 ml Schlenk tube connected via an adapter with a 100 ml round bottom flask containing 4 g of urea and heated in a muffle oven for 30 min at 400 °C. After the modification procedure the nitrogen-modified samples (TiO_2–N) were rinsed intensively with deionized water and blown dry in a nitrogen stream. For comparison, unmodified samples were prepared by heating the anodized samples in air at 400 °C for 30 min.

All photoelectrochemical measurements were performed with an electrochemical set-up consisting of a BAS Epsilon Electrochemistry potentiostat (BAS, West Lafayette, USA) and a three-electrode cell equipped with a flat quartz window. The electrodes were contacted and then pressed against an O-ring of a photoelectrochemical cell. Irradiated sample area was 0.78 cm^2. A platinum flag (1 × 2 cm) served as a counter electrode and a Ag/AgCl (3 M KCl) as a reference electrode. Nitrogen was passed through the electrolyte prior to the experiment whereas it was supplied only to the gas phase above the electrolyte during the experiment.

Photocurrent measurements were carried out in a $LiClO_4$ (0.1 M) electrolyte without or with addition of KI (0.1 M). The wavelength dependence of photocurrent was measured at a constant potential of 0.5 V vs. Ag/AgCl using a tunable monochromatic light source provided with a 1000 W Xenon lamp and a universal grating monochromator Multimode 4 (AMKO, Tornesch, Germany) with a bandwidth of 10 nm. Monochromatic light employed for excitation was chopped with light and dark phases of 5 s and a step of 10 nm. The value of photocurrent density was taken as a difference between current density under irradiation and in the dark. The incident photon-to-current efficiency (IPCE – the number of electrons generated in the external circuit divided by the number of incident photons) for each wavelength was calculated according to equation IPCE (%) $= (i_{ph}hc)/(\lambda Pe)100$, where i_{ph} is the photocurrent density, h is Planck's constant, c velocity of light, P the light power density, λ is the irradiation wavelength, and e is the elementary charge. The spectral dependence of lamp power density was measured by the optical power meter Oriel 70260 (Oriel, Stratford, USA) and is not corrected for losses in the electrolyte.

The flatband potential measurements were performed in HCl (0.1 M; pH 1.1), NaCl (0.1 M; pH 6.9) and NaOH (0.1 M; pH 12.3) electrolytes. Electrodes were illuminated by the full light of a 200 W Hg–Xe arc lamp (Spectral Energy, model LH-150) and the illumination intensity was varied by metal wire gauzes of different density. The potential data are plotted relative to the normal hydrogen electrode (NHE).

The chemical composition of the samples was characterized by X-ray photoelectron spectroscopy (PHI 5600 XPS) and all spectra were referenced to the C1s peak at 284.8 eV from the adventitious hydrocarbon contamination. Fitting of the XPS data was accomplished using XPSPEAK41 software.

X-ray diffractometry measurements were performed with X'Pert Philips glancing incidence diffractometer.

3. Results and discussion

According to the experimental set-up the electrode and urea were located in different reaction flasks connected by an adapter. Modification of the titania surface therefore has to occur by pyrolysis products of urea (ammonia, biuret, isocyanic acid, cyanamide, etc.) [33]. It seems likely that out of these ammonia is not responsible for modification since it was reported that this requires a temperature of 600 °C [5]. The best photocurrent response was obtained for electrodes modified at 400 °C, whereas by temperatures above or below the IPCE values were lower.

X-ray diffraction patterns (not shown) of both TiO_2 and TiO_2–N revealed anatase peaks apart from the signals of the underlying Ti substrate. For TiO_2–N no additional peaks were observed in comparison to TiO_2. Fig. 1 shows the XPS spectra of TiO_2 (a) and TiO_2–N (b). Interestingly, the N1s peak at 396 eV that is thought to evidence the pres-