Available online at www.sciencedirect.com

ScienceDirect

Electrochemistry Communications 8 (2006) 1713–1718

electrochemistry communications

www.elsevier.com/locate/elecom

Charge transfer reductive doping of nanostructured TiO_2 thin films as a way to improve their photoelectrocatalytic performance

Thomas Berger [a,b], Teresa Lana-Villarreal [a], Damián Monllor-Satoca [a], Roberto Gómez [a,*]

[a] *Departament de Química Física i Institut Universitari d'Electroquímica, Universitat d'Alacant, Apartat 99, E-03080 Alacant, Spain*
[b] *Institute of Materials Chemistry, Vienna University of Technology, Veterinärplatz 1/GA, A-1210 Vienna, Austria*

Received 17 July 2006; accepted 3 August 2006
Available online 1 September 2006

Abstract

Nanostructured TiO_2 films can be reversibly doped by applying a potential of $-0.6\ V_{Ag/AgCl}$ in aqueous 0.1 M $HClO_4$ for several minutes. This charge transfer reductive doping causes significant changes of the cyclic voltammograms in the dark. Furthermore, an up to 6-fold increase of the efficiency for water photooxidation is observed upon electrochemical reductive doping. Both observations are explained by the build-up of a space charge layer through agglomerates of appropriately sized and shaped nanoparticles.

Keywords: Titanium dioxide; Nanoporous electrode; Charge transfer reductive doping; Photoelectrochemical water oxidation; Electron accumulation

---

1. Introduction

The high potential of nanostructured semiconductor electrodes (thin films) for the utilization of solar energy in photoelectrochemical cells and for the decontamination of air and wastewaters has recently sparked a great interest in the systematic manipulation and optimization of their photoelectronic properties. However, these efforts are complicated by the fact that nanostructured electrodes are highly complex systems, which makes the investigation of the underlying structure-reactivity relationship a challenging task.

Due to the fact that electrolyte solutions can permeate the porous matrix characteristic of nanostructured electrodes, no significant macroscopic electrical field exists in the semiconductor film [1,2]. Electron transport, therefore, occurs by diffusion rather than by migration and as a consequence, charge carrier recombination critically depends on the nature of the film as well as on the interfacial reaction rate. In this case, recombination processes cannot be suppressed by an external voltage bias. However, decreasing the recombination rate of charge carriers is an important task in order to improve the performance of nanostructured electrodes.

Reductive doping has been previously shown to be a way of improving the photoelectrochemical response of compact polycrystalline [3,4] and single crystal TiO_2 electrodes [5–7]. In both cases a cathodic pretreatment led to a photocurrent enhancement for the water photooxidation reaction, which was attributed to an increased conductivity of the respective electrode.

On the other hand, electron accumulation in nanostructured electrodes is intimately related to charge compensation by counter ions [8,9]. Lyon and Hupp [8] showed by combined spectroscopic, electrochemical and microgravimetric measurements that electron accumulation in nanostructured TiO_2 electrodes in contact with aqueous electrolytes is quantitatively accompanied by charge compensating proton adsorption or intercalation:

$$Ti^{IV}O_2 + e^- + H^+ \leftrightarrow Ti^{III}(O)(OH^+)$$

Furthermore, an increase of the hydrophilicity of polycrystalline and amorphous TiO_2 electrodes was observed after cathodic polarization and attributed to an enhanced density of surface hydroxyl groups [10]. Accumulated elec-

---

[*] Corresponding author. Tel.: +34 96 5903400; fax: +34 96 5903537.
E-mail address: Roberto.Gomez@ua.es (R. Gómez).

1388-2481/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2006.08.006

trons were detected spectroscopically due to their optical absorption in the Vis/NIR and due to their paramagnetic properties by electron paramagnetic resonance (EPR) [11].

In the present study we report on the electrochemical reductive doping of nanostructured TiO_2 films: electrons are injected into the TiO_2 film by the application of a negative potential whereas charge compensation is accomplished by the adsorption/intercalation of protons from the electrolyte. It was found that, by means of such an electrochemical doping, the (photo)electrochemical behavior of the nanoporous electrodes can be systematically tuned in a mild way, without the need of performing intrusive thermal pretreatments, which change the stoichiometry or the intrinsic defect concentration of the semiconductor.

2. Experimental

Nanoporous electrodes were prepared by spreading aqueous slurries of commercial TiO_2 nanoparticles (Table 1) over 1.5 cm^2 of a F:SnO_2-coated transparent conducting glass plate (U-type Asahi Glass Co) or, alternatively, over Ti metal substrates. Afterwards the films were annealed and sintered for 1 h at 450 °C in air.

Photoelectrochemical measurements were performed at room temperature in a three-electrode cell equipped with a fused silica window. All potentials were measured against and are referred to a Ag/AgCl/KCl(sat) reference electrode, whereas a Pt wire was used as a counter electrode. Measurements were performed with a computer-controlled Autolab PGSTAT30 potentiostat. In all experiments a N_2 purged 0.1 M solution of $HClO_4$ (Merck p.a.) in ultrapure water (Millipore Elix 3) was used as working electrolyte. Cyclic voltammograms (CV) were recorded between −0.6 V and +0.8 V at a scan rate of 20 mV/s. A 300 W Xe lamp (Oriel) equipped with a water filter was used for UV–Vis irradiation. The applied light irradiance was measured with an optical power meter (Oriel model 70310) equipped with a bolometer (Ophir Optronics 71964) to be 500 mW cm^{-2} in the case of polychromatic irradiation ($3.2\ eV < E < 6.2\ eV$) and 1 mW cm^{-2} when using a 355 nm interference filter (Newport 10LF10-355).

3. Results and discussion

A microstructural analysis of the samples was performed by BET isotherm determination, Raman spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM) after removing the nanoporous film from the as-prepared electrodes. Fig. 1 shows representative TEM images together with the corresponding particle size distributions. PI-KEM (Fig. 1a) and P25 samples (Fig. 1b) are characterized by crystallites with well-defined surface planes. The Sachtleben and Alfa Aesar samples on the other hand consist of crystallites of elliptical and spherical shape, respectively (Fig. 1c and 1 d), whereas no pronounced surface planes are observed. XRD and Raman spectroscopy (results not shown) reveal that the PI-KEM and Degussa P25 samples consist of mixtures of anatase and rutile (with estimated ratios of 1:1 and 4:1, respectively), whereas pure rutile and anatase phase were found for the Sachtleben and Alfa Aesar samples, respectively. Nitrogen physisorption experiments at 77 K were carried out to determine the specific surface area and the pore volume of the samples (Table 1).

Fig. 2 shows CVs for PI-KEM (Fig. 2a), P25 (Fig. 2b), Sachtleben (Fig. 2c) and Alfa Aesar electrodes (Fig. 2d) in 0.1 M $HClO_4$ in the dark before and after charge transfer reductive doping. Before doping the voltammograms of all the electrodes are characterized by the presence of a well-defined pair of peaks located between −0.2 V and 0 V. These peaks are characteristic for nanostructured films and have not been observed on polycrystalline electrodes [12]. Grätzel et al. [13] attributed them to the reversible filling of surface states below the conduction band edge. A similar interpretation has been given by Boschloo and coworkers [14,15]. Only recently Fabregat-Santiago et al. [16] developed a phenomenological model which allows to analyze the basic features of experimental CVs. Taking into account exclusively capacitive currents, peak widths of $\sim 2 \cdot k_B \cdot T$ are predicted for monoenergetic band gap states. The widths of the peaks reported above (50–100 mV) are in line with this estimate ($2 \cdot k_B \cdot T =$ 52 meV at 298 K). A location of the corresponding band gap states at the TiO_2 surface, where interactions with the electrolyte are expected to cause a broadening of the respective peak width, is, therefore, unlikely. The sharp energy distribution of the band gap states and their virtual absence in polycrystalline electrodes point rather to the involvement of the particle–particle interface. Therefore, we tentatively attribute the couple of peaks between −0.2 V and 0 V to trap states located at grain boundaries (GB).

On the other hand, at potentials more negative than −0.2 V, a large reversible capacitive current is observed in all cases, which is connected to electron accumulation within the nanoporous film coupled to H^+ uptake from the electrolyte (H insertion). Such an intrinsic film capacitance can be calculated according to [16]:

Table 1
Structural characterization of nanostructured electrodes prepared from different commercially available TiO_2 samples

Sample	Crystal structure	Surface area ($m^2\ g^{-1}$)	Film thickness (μm)	Pore volume ($cm^3\ g^{-1}$)
PI-KEM	A(50%) + R(50%)	27	8	0.10
P25	A(80%) + R(20%)	51	6	0.18
Sachtleben	R	62	8	0.20
Alfa Aesar	A	30	8	0.14