



Photocatalytic and photoelectrochemical properties of sol–gel TiO₂ films of controlled thickness and porosity



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ABSTRACT

Nonporous and mesoporous TiO₂ films of well-defined thicknesses were synthesized by the sol–gel technique with dip-coating as the deposition method. Due to the potential applications as self-cleaning surfaces and photoanodes in water splitting activities of the prepared TiO₂ films were evaluated for the photodegradation of model ink 2,6-dichloroindophenol and water photooxidation in aqueous media containing an inorganic salt. Thickness and mass parameters of the TiO₂ films depend linearly on the number of deposition cycles (dip-coating, drying and calcinations). Due to different viscosities of the precursor, thicknesses of a single layer of nonporous and mesoporous titania film were 65 nm and 300 nm, respectively. The crucial effect of film mass on the decolourization of solid organic films was confirmed. Photocurrent in aqueous electrolyte depends strongly on the type of conductive substrate. It is about five times lower for indium doped tin oxide (ITO) which was confirmed to be due to the increase of resistivity of ITO conductive layer during calcinations. Mesoporous films reveal significantly lower photocurrents than nonporous films which can be explained by insufficient charge transfer in mesoporous films consisting of very small mesopores.

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1. Introduction

Thin films of titanium dioxide deposited on various supports are very useful photocatalysts in a number of applications, primarily in environmental protection and in alternative energy generation. In the first field TiO₂ coatings can oxidatively decompose organic deposits to inorganic products, such as CO₂, H₂O and mineral acids [1,2]. Consequently, the dust particles no longer stick to the irradiated surface and can easily be washed off by rain water. Second application of TiO₂ photocatalyst films is the photoelectrochemical water splitting [3]. Photogenerated electrons can be transferred via an external circuit to the auxiliary electrode. Holes formed may act as an oxidant, in this particular case to evolve molecular oxygen. On the auxiliary electrode, electrons are used to evolve hydrogen.

Great advantages of TiO₂ are its low price, high stability and nontoxicity [4]. However, for practical applications, there are two important film parameters which should be addressed. The first is the amount of photocatalytically-active material (film thickness), which often determines the amount of light absorbed. The second

is the film porosity. Porous films of TiO₂ are more effective when the photodecomposition mechanism includes reactants or intermediates adsorbed on the surface. Furthermore, mesoporosity may ensure the fast transport of O₂ and H₂O, which are crucial for the photocatalytic degradation of organic deposits [5,6]. On the other hand, particulate porous films can lack the electronic conductivity essential for the efficient photocurrent generation [7,8].

The sol–gel technique enables TiO₂ photocatalyst films to be prepared in a way that controls surface properties such as composition, thickness and morphology [9,10]. This technique consists of several steps: (i) precursor synthesis, (ii) precursor deposition (usually by dip-coating), (iii) drying, and (iv) calcination at elevated temperatures. Layer thickness can be controlled by viscosity of the sol–gel precursor and by the withdrawal rate during dip-coating. Thicker (or multilayer) films can be obtained by repeating steps (ii), (iii) and (iv) [11]. A combination of the sol–gel technique with the addition of a suitable surfactant can be used to synthesize TiO₂ films of well-defined porosity [12].

The aim of this work was to investigate the photocatalytically active sol–gel TiO₂ coatings with particular focus on the effect of the layer thickness and porosity. Due to the potential applications (self-cleaning surfaces, photoelectrochemical water splitting, etc.) we focused on (i) photocatalytic degradation of thin solid films (degradation of the model ink 2,6-dichloroindophenol), and on the study

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of (ii) photocurrent and open circuit potential in aqueous media containing an inorganic salt.

2. Experimental

2.1. Glass substrates

As conductive substrate two types of transparent conductive glass (TCO) were used. Indium tin oxide (ITO) conducting glass slides (5–15 Ω /square, size 50 × 12.2 × 1.1 mm) supplied by Delta-Technologies Ltd. and fluorine tin oxide (FTO) conducting glass slides (8 Ω /square, size 75 × 15 × 2 mm) supplied by Hartford Glass Company, Inc.

2.2. Preparation of nonporous TiO₂ films

Nonporous films were prepared using titanium(IV) isopropoxide (97%, Sigma-Aldrich) as TiO₂ precursor, absolute ethanol and ethyl acetylacetate (99% p.a. Fluka) as solvent and nitric acid (p.a. 65% Penta) as catalyst based on the method reported previously [11,13]. 11.6 ml of absolute ethanol (p.a. Penta) was added drop wise under stirring to 8 ml of Titanium isopropoxide. 11.6 ml of absolute ethanol was mixed with 2.75 ml of ethyl acetylacetate and 0.2 ml of nitric acid was added to the isopropoxide mixture. Thus prepared sol was stirred under vigorous stirring for 24 h. TCO substrates were dip-coated with prepared TiO₂ sol (withdrawal speed 60 mm min⁻¹). By repeating the above procedure TiO₂ layers with various thicknesses (from 1 layer to 5 layers) were prepared. Deposited films were calcined at 500 °C for 1 h.

2.3. Preparation of mesoporous TiO₂ films

Mesoporous films were prepared by supramolecular templating with amphiphilic triblock copolymer Pluronic P123 [14,15]. The stock solution for the film deposition was prepared as follows: 10.2 ml HCl (37%, Aldrich) was added drop wise to 14.4 ml of titanium ethoxide (Aldrich) under vigorous stirring. Separately, 5.0 g of a triblock copolymer Pluronic-P123, HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H (Aldrich), was dissolved in 56 ml of butan-1-ol (Aldrich) and added to the HCl + Ti(EtO)₄ solution. The precursor solutions were aged under stirring at ambient temperature for at least 3 h. The layers were deposited by dip-coating, withdrawal rate was 60 mm min⁻¹. Withdrawal rates higher than 90 mm min⁻¹ result in the partial fall off the film. Subsequently, the layers were calcined in air at 350 °C for 2 h, heating rate: 1 °C min⁻¹. For preparation of thicker films consisting of more layers, the described procedure was repeated. To form well-developed anatase crystals in the framework these multilayer films were thermally post-treated at 510 °C in air for 2 h, heating rate: 1 °C min⁻¹ [16].

2.4. Film characterisation

Mass of TiO₂ layers was obtained using mass balance with precision 0.01 mg. Film thickness was measured by profilometry (DEKTAK). Nonporous films exhibited the typical interference spectra associated with thin films; a feature which allowed the thicknesses of the titania films to be calculated from the reflectance spectra using the NanoCalc software (Ocean Optics) [11]. The location and presence of characteristic diffraction lines were observed by X-ray diffractometer (Seifert-XRD 3000; Panalytical HighScore Plus). These data were also used to estimate the crystalline size.

2.5. Photocatalytic activity measurement

The disadvantage of photo-oxidative degradation of dyes is usually a long time which is needed to complete decolourization of the solution [17]. Another possibility to fast testing of self cleaning glass is to use model ink based on redox indicator. Such ink consists of dye which can be irreversible reduced to another colour or to colourless form. Typical dye complying these requirements is resazurin (7-Hydroxy-3H-phenoxazin-3-one 10-oxide) [18]. The only disadvantage is that the change of colour of such ink is from blue to pink. There is another suitable ink containing the dye 2,6-dichloroindophenol (DCIP) where the colour change is from blue to colourless [19–21]. This is very convenient from the point of self-cleaning ability demonstration. The redox indicator ink contains besides DCIP also hydroxyethylcellulose which serves as binder and glycerol which acts as hole trap. Photogenerated holes can oxidize glycerol to glyceraldehyde or to glyceric acid while separated electrons reduce DCIP to its colourless leuco form [19,22]. The model ink was prepared by mixing 18 g of 0.5% (m/m) solution of hydroxyethyl cellulose (Fluka) with 1.8 g of glycerol (Sigma-Aldrich) and 30 mg of 2,6-dichloroindophenol. This well mixed solution was applied on the TiO₂ film by the dip-coating method, afterward the ink layer was dried in an oven (70 °C, 10 min). The amount of photoreduced dye in the model ink was determined using visible spectroscopy at the wavelength 630 nm.

2.6. Photoelectrochemical activity measurement

Polarization curves and the open circuit potential (OCP) measurements seem to be suitable for the assessment of the photo-electrochemical efficiency of the TiO₂ thin films. Photoelectrochemical properties of TiO₂ films illuminated from the front side (from film/electrolyte interface) were tested in a three electrode arrangement [23,24]. The TiO₂ thin film on TCO served as the working electrode, the saturated calomel electrode (SCE) as the reference and a platinum sheet as the counter electrode. 0.1 M solution of Na₂SO₄ was used as the electrolytic medium. The exposed TiO₂ film area (1 cm²) was defined by teflon tape. The electric contact was made by pressing stainless steel to upper part of FTO layer, not covered by TiO₂. The cell was connected to the optical bench (Melles Griot) which included optical filters and a shutter. As the source of radiation the DC Arc polychromatic high pressure mercury lamp (LOT LSH201/2 Hg, Xe) was employed with a characteristic broadband line source. Optical filters were utilized in order to ensure the layers exposure to the radiation of precise wave length (365 ± 10 nm). The incident intensity of the light when passing the filter was measured using a Hamamatsu S1337-1010BQ photodiode. The light intensity was influenced by the lamp age and thus decreased slightly during a few months period but were always in the range 1–2 mW cm⁻². The light intensities were always recorded before and after each experiment. The incident light intensity I [W cm⁻²] was recalculated to the incident photon flux intensity P [Einstein s⁻¹ cm⁻²]. The photocurrents were measured using Voltalab10 PGZ-100 potentiostat (software VoltMaster 4). The starting potential was around the value of OCP (–0.3 V to –0.5 V (SCE)), sweeping was positive towards the end potential 1.5 V (SCE). Incident photon to current conversion efficiency (IPCE) was calculated using the relation (1):

$$\text{IPCE} = \frac{j}{FP} \quad (1)$$

where j denotes for the photocurrent density [A cm⁻²], F is the Faraday constant (96,485 C mol⁻¹) and P is the incident light intensity [Einstein cm⁻² s⁻¹].

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