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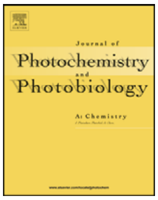

Effect of thickness of ALD grown TiO_2 films on photoelectrocatalysis

Mikko Heikkilä*, Esa Puukilainen, Mikko Ritala, Markku Leskelä

Laboratory of Inorganic Chemistry, Department of Chemistry, P.O. Box 55, FI-00014 University of Helsinki, Finland

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ABSTRACT

Atomic layer deposited TiO_2 films were used for photoelectrocatalysis for the first time. Films with different thicknesses were grown and comprehensively characterized by structural and photoelectrochemical techniques. Methylene blue was used as a model substance in photocatalytic and photoelectrocatalytic degradation studies. In both cases, degradation rate was observed to saturate above certain film thickness. The reason for saturation could not be explained by the electrical parameters alone, and it was suggested that film morphology and crystalline structure are of major importance in this case.

1. Introduction

Photocatalysis by titanium dioxide is an advanced oxidation process widely studied in recent decades in, for example, water and wastewater purification [1]. Basics of photocatalytic process have been covered in several review articles [2–8]. In short, when semiconductor material is irradiated with photons of energy greater than or equal to the bandgap energy of semiconductor, valence band holes and conduction band electrons are formed. These electron–hole pairs then either migrate to the surface and participate in redox reactions or recombine on their way. The oxidative power of the holes and the hydroxyl radicals that are formed is the key to the photocatalytic degradation of harmful substances. Usually photocatalysis is done with particle slurries which makes the catalyst removal very difficult. By immobilizing the particles to surfaces, this drawback can be circumvented but at the same time the reactive surface area is significantly diminished. Another drawback in photocatalysis is the recombination of the generated electron–hole pairs. This can be reduced, e.g. by adding electron scavengers in the electrolyte [9], precipitating noble metals on photocatalyst surface [3] or by making composite structures [10]. The most efficient way to reduce the recombination and enhance the photocatalytic process is to separate the charges by applying an electric field across the immobilized TiO_2 layer. This process is usually referred as photoelectrocatalysis.

Photoelectrochemical splitting of water by TiO_2 was demonstrated already in early 1970s by Fujishima and Honda [11]. Photoelectrocatalytic destruction of organics was first reported by Vinogdopal et al. [12] followed shortly by Kim and Anderson [13]. Photoelectrochemical disinfection of water was first reported by Butterfield et al. [14]. Reviews concentrating on photoelectrocatalysis alone are rare but Egerton and Christensen have written a couple [15,16]. Rajeshwar et al. discuss the subject to some extent in their recent review on heterogeneous photocatalysis of organic dyes [8].

The effect of layer thickness on photocatalysis has not been studied much. In addition, the reported optimum thicknesses vary a lot and most of the studies have been done with sintered particles instead of dense layers. Photoelectrocatalytic studies of this kind are even more scarce with only few publications during the last decade [17,18]. The aim of this study was to investigate the effect of TiO_2 film thickness on photoelectrocatalytic degradation of commonly used model substance methylene blue. ALD was used to deposit the films since it provides excellent thickness control and produces very dense and uniform layers necessary for this kind of study [19]. In addition to photocatalytic degradation studies, the films were characterized in detail to further understand the effect of thickness on degradation rate.

2. Experimental

TiO_2 films were grown from $Ti(OMe)_4$ (Aldrich, 95%) and water in a flow type F120 ALD reactor (ASM Microchemistry Oy, Helsinki, Finland) using a process described earlier by Pore et al. [20]. 5 cm × 5 cm borosilicate glass and indium tin oxide (ITO) covered glass were used as substrates. Prior to the deposition the substrates were cleaned ultrasonically first in ethanol and then in deionised

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* Corresponding author. Tel.: +358 9 191 50216; fax: +358 9 191 50198.
E-mail address: mikko.j.heikkila@helsinki.fi (M. Heikkilä).

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water, after which they were rinsed with water and 50% ethanol and dried with N_2.

The ALD reactor was operated at about 10 mbar pressure. Nitrogen (made on site by Schmidlin NG3000 generator, rated purity of 99.9995%) was used as a carrier gas and for purging between precursor pulses. The titanium precursor was evaporated from an open boat at 130 °C inside the reactor. Water was held at room temperature in an external reservoir and was led into the reactor through needle and solenoid valves. Precursor pulse lengths were 0.5 and 0.6 s N_2 purges were applied in between. Films with six different thicknesses were deposited at 325 °C.

Transmittance spectra of the films grown on borosilicate were measured with a Hitachi U-2000 spectrophotometer in a wavelength range of 190–1100 nm. Film thicknesses and refractive indices were determined by fitting the measured transmission spectra [21].

Film crystallinity and phase was determined with a PANalytical X'Pert PRO MPD X-ray diffractometer using Cu Kα-radiation. Grazing incidence X-ray diffraction (GIXRD) measurements were performed using a Göbel mirror and 0.18° parallel plate collimator, and the incident angle was 1°. XRD measurements were also performed in the Bragg–Brentano configuration using automatic divergence and antiscattering slits set to 10 mm irradiated length. PIXcel detector was used for both geometries. Film morphology was studied with a Hitachi S-4800 field emission scanning electron microscope (FESEM). For AFM studies a Veeco Instruments Multimode V with Nanoscope V controller was used. Samples were measured in tapping mode in air using phosphorus-doped silicon probe (RTESP) delivered by Veeco Instruments. Several scans were performed from different parts of the samples to check the uniformity of the surface. Final images were measured from a scanning area of 2 μm × 2 μm with a scanning frequency of 0.5 Hz and no image processing except flattening was made. Roughness values were calculated as root-mean-square values (R_q).

Photoelectrochemical measurements, except for photocurrent spectra, were performed with an Autolab PGSTAT20 potentiostat using a three electrode setup with Pt as a counter electrode and 3 M Ag/AgCl as a reference electrode (Metrohm 6.0733.100). All potentials mentioned hereafter are related to this electrode. TiO_2 coated ITO was used as the working electrode. Active areas of the working and counter electrodes were about 20 cm^2. 120 ml of 0.1 M KCl aqueous solution was used as the electrolyte. Linear sweep voltammograms were measured towards anodic direction with a scanning speed of 10 mV/s. For photocurrent measurements, films were irradiated through the substrate with a 20 W black light (GE F20T12-BLB) that emits wavelengths 340–410 nm with a peak maximum at 365–370 nm. Intensity of the radiation was 1.5 mW/cm^2 at the substrate.

The photocurrent spectra were measured using a 300 W Xe lamp (Oriel 6259) as an irradiation source, and the wavelength was selected using a monochromator (Oriel 77700). The potential of the working electrode was set to +0.6 V using an Autolab PGSTAT100 potentiostat.

Electrochemical impedance spectroscopy was conducted using Solartron SI1286 electrochemical interface and Solartron SI1250 frequency response analyzer. The sample studied by EIS was a 160 nm TiO_2 layer grown on top of electron beam evaporated platinum. The platinum substrate was chosen instead of ITO in order to have only one oxide layer and therefore a simpler system to model. The impedance was recorded at constant polarization that was varied in 0.1 V steps between −0.4 and +0.8 V. The potential was let to stabilize for 15 min before each measurement. The impedance was measured as the current response to a superimposed sinusoidal voltage signal of 15 mV amplitude in a frequency range of 0.3–65,535 Hz. The equivalent circuit was fitted to the data using the ZPlot software supplied together with the Solartron equipment.

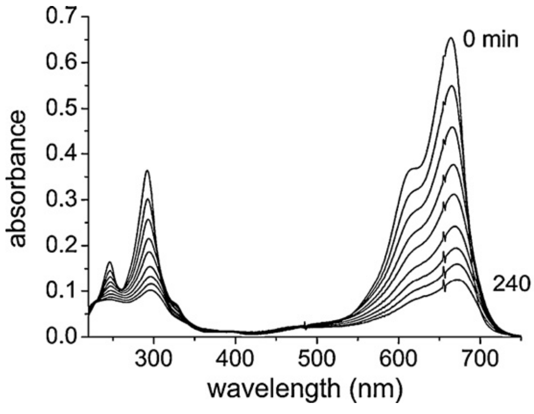

Fig. 1. Absorbance spectra of methylene blue in different stages of photoelectrocatalysis using 520 nm TiO_2 biased to +0.6 V vs. 3 M Ag/AgCl.

Aqueous solution of methylene blue (MB, $C_{16}H_{18}N_3Cl$, Oy Rohdoskeskus Ab) was used as a model substance for photocatalytic and photoelectrocatalytic degradations. MB was dissolved in 0.1 M KCl to give an initial MB concentration of 0.01 mM. The reactor was kept in dark for 1 h before starting the degradation study. During this time the solution was continuously bubbled with air in order to saturate the solution with oxygen that is necessary for photocatalytic degradations. The concentration change of MB during degradation was followed by measuring the value of absorbance maximum at 665 nm as a function of irradiation time with an HP 8453 spectrophotometer.

3. Results

3.1. Photocatalysis and photoelectrocatalysis of methylene blue

The absorbance spectra of MB in different stages of photoelectrocatalytic (PEC) degradation are shown in Fig. 1. The absorbances of all the four peaks decrease as a function of the degradation time which indicates that MB is being fully mineralized and no major by-products are formed.

The decrease of MB absorbance maximum at 665 nm as a function of degradation time is shown for photocatalysis (PC) and PEC in Fig. 2. The exponential decrease is observed especially for

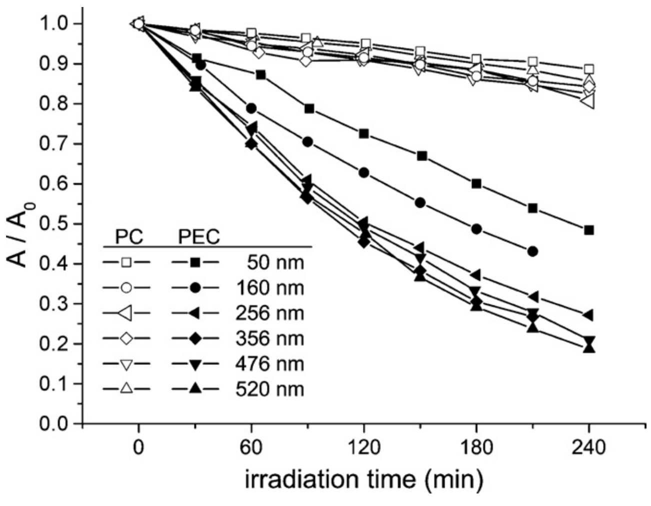

Fig. 2. The effect of film thickness on photocatalytic and photoelectrocatalytic degradation. Absorbance of methylene blue is related to initial value as a function of irradiation time. Films were biased to +0.6 V vs. 3 M Ag/AgCl during photoelectrocatalytic degradation.