



Influence of solution chemistry on the properties of hydrothermally grown TiO₂ for advanced applications

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ABSTRACT

It is demonstrated that the properties of hydrothermally deposited titanium (IV) oxide (TiO₂) films are greatly affected by the solution chemistry. Anatase TiO₂ films grown using i-PrOH presented the best reversible photoinduced hydrophilic response, reaching a contact angle (CA) of 15° and 83% photocatalytic activity as well as measurable photoconductivity. Inclusion of as low as 0.02 M NaOH in the solution resulted in films probably consisted of sodium titanate exhibiting good photoinduced properties, which makes it a promising candidate for various applications. In contrast, rutile TiO₂ films prepared using EtOH as a solvent showed weak photoinduced activity. The correlation of solution chemistry with the morphology and the photoinduced properties of the materials are discussed.

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1. Introduction

Titanium (IV) oxide (TiO₂) or titania is one of the most promising semiconductors for applications in various technologies such as solar cells [1] photocatalysis [2], anti-fogging and self-cleaning or anti-bacterial coatings [3] having the added advantage of being a non-toxic and low-cost material [4]. The photoinduced properties involved in these applications can be regulated by controlling the TiO₂ crystallographic structure and morphology [5]. In addition, transparent conducting applications can already be realised for TiO₂ by doping with Nb [6].

Anatase and rutile TiO₂ have been widely studied as photocatalysts [7], anatase exhibiting a higher activity than rutile due to its particular band structure [8]. Furthermore, surface roughness is an important parameter for the photocatalytic activity of this material [5]. Photocatalysis takes place on the surface of the film under the presence of adsorbed water molecules. The wider is the exposed surface of the films the higher is expected to be the number of photocatalytic events. The efficiency of the effect per unit of film area will thus be enhanced by a corresponding increase of the ratio of the actual surface of the films to the

deposited area. Such an increase is the natural consequence of surface roughness.

TiO₂ with such properties can be developed using several techniques such as sputtering [9], chemical vapour deposition (CVD) [10], hydrolysis [11], sol-gel methods [12] and hydrothermal synthesis [13–15], most of them requiring costly equipment and/or vacuum and/or high temperatures and/or hazardous chemicals. Hydrothermal synthesis is a “one pot” process, requiring non-hazardous chemicals, low temperatures and atmospheric pressure. Moreover, it can be expanded to large substrates with the only shortcoming being the long preparation times needed for full coverage. Finally, with this method, the structural and morphological characteristics of the samples can be tailored by simply controlling the solution chemistry (precipitation/dispersion conditions affecting the thermodynamic stabilization of the system) [16]. Therefore, hydrothermal synthesis seems to be a rather attractive technique for the deposition of TiO₂.

The aim of the present work is to provide insight on the correlation of solution chemistry with morphology and photoinduced properties of hydrothermally grown titanium oxide, at 95 °C on Corning 7059 substrates. It is noteworthy that under appropriate conditions, it is possible to grow sodium titanate with good reversible photoinduced hydrophilic and photocatalytic activity.

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2. Experimental

The growth of titanium oxide on Corning 7059 was performed by the hydrothermal method using as precursors three different solutions: (series 1) TTIP ($\text{Ti}[(\text{OCH}(\text{CH}_3)_2)_4]$), propanol (*i*-PrOH, $(\text{CH}_3)_2\text{CHOH}$) and MilliQ water, (series 2) TTIP, ethanol (EtOH, $\text{CH}_3\text{CH}_2\text{OH}$) and MilliQ water and (series 3) TTIP, *i*-PrOH, MilliQ water and 0.02 M NaOH/*i*-PrOH solution. For growth using *i*-PrOH as solvent, the solution preparation involved initially the stirring of 12 M *i*-PrOH with 0.1 M MilliQ H_2O , followed by the addition of 0.03 M TTIP. For growth using EtOH, the solution preparation involved the same procedure as for series 1 but instead of *i*-PrOH, EtOH was used. Finally, for growth using 0.02 M NaOH/*i*-PrOH, the procedure is the same as in series 1 with the further addition of 10 ml, 0.02 M NaOH/*i*-PrOH under continuous stirring. In each case, the solution was placed in a Pyrex glass bottle with polypropylene autoclavable screw cap, with the substrate positioned on the bottom, and was heated at 95 °C for deposition periods of 20 h, 30 h, 40 h and 50 h in a regular laboratory oven. After deposition, the samples were thoroughly washed with the respective solvent (*i*-PrOH or EtOH), in order to eliminate residual salts, and dried in air at 95 °C.

X-ray diffraction (XRD) measurements were performed using the $\text{Cu K}\alpha$ line of a Rigaku (RINT 2000) Diffractometer. Raman measurements were carried out in the 100–700 cm^{-1} wavenumber range using the 473 nm excitation of a Nicolet Almega XR micro-Raman Spectrometer. UV–vis transmittance measurements were performed with a PerkinElmer Lambda 950 spectrometer over the wavelength range of 250–1000 nm. Surface imaging was carried out on an atomic force microscope (AFM) in tapping mode (Digital Instruments–Nanoscope IIIa) using Si cantilevers. Contact angle (CA) measurements were performed by positioning a 10 μL distilled, deionised Millipore water droplet on the surface of the samples. Images of the droplet were captured by a CCD camera and the CA was subsequently determined by applying an image-processing algorithm. Photoinduced hydrophilicity was evaluated by irradiating the samples with 4 mW cm^{-2} UV light of a Hg lamp, centred at 365 nm, for predetermined periods of time, at ambient conditions. The same lamp was used to acquire photoconductivity measurements from the ohmic part of corresponding current–voltage (*I*–*V*) curves of samples having sputter-deposited gold

contacts separated by 2.5 mm. Finally, the photocatalytic activity of the samples was assessed utilising a stearic acid test. At first the samples were coated with stearic acid by spin coating a 30 μL droplet of stearic acid diluted in chloroform (0.1 M solution) and subsequent drying at 80 °C in air for 10 min. The test was performed by recording the reduction of the IR absorbance of the C–H stretching band of stearic acid (2800–3000 cm^{-1}), under UV illumination, after certain time intervals. IR absorbance was recorded with a Fourier transform infrared spectrometer (FTIR) (IRPRESTIGE-21, Shimadzu), in transmission mode and UV illumination was provided by a black light blue lamp centred at 365 nm and having a power density of 2 mW cm^{-2} . Each characterization method was conducted on at least three samples prepared under the same conditions for consistency and reproducibility.

3. Results and discussion

Since growth times shorter than 20 h resulted in TiO_2 films with no photoinduced response, a range of deposition periods 20–50 h was chosen for our studies. Propanol was selected based on considerations of similar procedures reported in the literature [17,18], while ethanol was used for the control of the morphological characteristics of the films via the alteration of precipitation rate of the solution [19]. Regarding the choice of using sodium hydroxide in these experiments, this was based on experiments reported in the literature, indicating that in such a way, the size and the shape of the nanoparticles can be controlled [20,21] (resulting in an increase surface to volume ratio) and the photocatalytic activity of the films can be enhanced [22]. The sodium hydroxide solutions were prepared in *i*-PrOH since water accelerates precipitation, which in turn inhibits deposition of enough material. Furthermore, NaOH concentrations higher than 0.02 M resulted in powdery films, since no coherent hydrothermal growth occurred. Thus, the NaOH concentration had a significant influence on the solution and the consequent growth chemistry, occurring at the substrate surface. Our results indicated that control of the precipitation rate of the solution and the deposition of coherent films can be achieved for NaOH concentration around 0.02 M. All grown samples passed the Scotch tape test (removal of an X shaped piece of sticking tape) [23] and were stable in air for

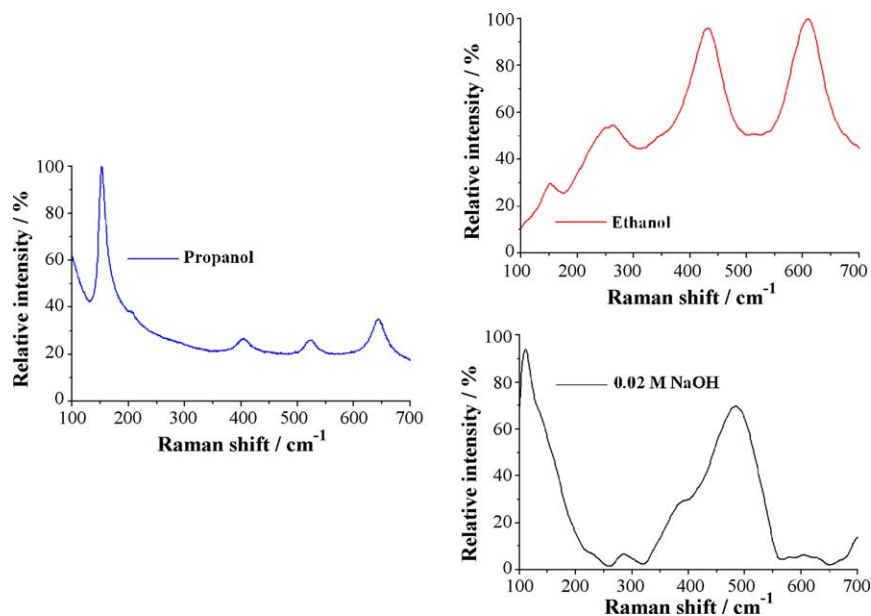


Fig. 1. Raman spectra of the grown films on Corning 7059 for a deposition time of 50 h using *i*-PrOH, EtOH and 0.02 M NaOH/*i*-PrOH.

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