CHEMICAL ENGINEERING TRANSACTIONS

VOL. 43, 2015

A publication of AIDIC

The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543125

Transparent Nanostructured Titania Coatings with Self-cleaning and Antireflective Properties for Photovoltaic Glass Surfaces

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Transparent titania (TiO_2) coatings having self-cleaning and antireflection (AR) properties, for application as surface functional layer in cover glasses of photovoltaic (PV) devices, were prepared, characterized and tested. The coating preparation is made by forming first a nanosol through controlled hydrolysis of a tetraisopropyl orthotitanate (TIPT) precursor. The nanosol is then deposited on the glass substrates by dip-coating with a subsequent step of calcination. This work reports the effect of the preparation parameters on both optical and morphological properties of the obtained coatings. The nanostructure and texture of the samples were characterized by X-ray diffraction, UV-vis spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM), while transmittance measurements were carried out to assess the AR properties. Self-cleaning properties were investigated by water contact angle measurements and photocatalytic activity tests. Films with good optical characteristics and high transmittance (T losses < 1 % compared to bare glass) have been obtained at low dip-coating speed (6 mm/s) and high nitric acid concentration (HNO_3 0.5 N). The best transmittance values were obtained by calcination of the sample at 500 °C, but a higher amount of acid catalyst in the nanosol synthesis allows to reduce the calcination temperature to 400 °C, while maintaining good optical properties and crystallinity of the thin film.

1. Introduction

With the fast expansion of the use of PV devices for a decentralized energy production, often on the roof of buildings where periodic maintenance is difficult to made, the problem of fouling of these devices by dust and organic contaminants present in the air is becoming a serious issue. In addition, there is the need to reduce the reflection of light in order to improve cell adsorption capability, and at the same time decrease reflectivity to avoid glare that might interfere with activities in nearby areas.

In conventional PV silicon solar cells front glass layers are used as optical-coupling element and protective material against debris and aggressive air agents (Deubener et al., 2009). Although current front glasses for PV panels already contain surface coatings to improve AR properties, it is interesting to analyze the possibility to have a single layer having both AR and self-cleaning properties, photocatalytic properties to eliminate air contaminants deposited on the surface and good transparency at the same time (Dobrzański et al., 2012). Among the materials employed as cover layer for PV cells, thin films of TiO_2 are often used (Gronet and Truman, 2007). In fact, titania exhibits high photo-reactivity (Centi and Perathoner, 2009) and -stability, and good mechanical, chemical and thermal resistance together with low toxicity and costs. The functional characteristics of TiO_2 are related to its crystal structure and morphology and they are affected by many factors such as manufacturing method, process and heat treatments. Self-cleaning properties should be combined to an efficient photocatalytic activity, in order to reduce the accumulation of contaminants on PV surface and contribute to improve device efficiency. Self-cleaning and AR properties depend on the surface

Please cite this article as: Salvaggio M.G., Passalacqua R., Abate S., Perathoner S., Centi G., 2015, Transparent nanostructured titania coatings with self-cleaning and antireflective properties for photovoltaic glass surfaces, Chemical Engineering Transactions, 43, 745-750 DOI: 10.3303/CET1543125

nano-texture and roughness. The latter influences the optical properties of the thin film and depends on the preparation procedure (Harada et al., 2013). Being industrial scalability of the procedure, and cost as well, a critical aspect, in this work we have focused attention on a simple, cost-effective and easily scale-up method: sol-gel preparation of a nanosol followed by dip-coating and thermal annealing of the film. It offers several advantages: i) good homogeneity, ii) easy composition control, iii) low processing temperature, iv) large area coatings availability, v) scalability and low equipment costs.

Aim of this work, is to study the characteristics of nanosol solutions and the preparation conditions used to realize TiO_2 thin films suitable to be applied as transparent self-cleaning and AR coatings for PV cells. In particular, we discuss here some of the critical parameters in the preparation which determine the final functional properties:

- during the preparation of the nanosol solution: nitric acid concentration and extent of hydrolysis
- during dip-coating process*:* number of coating layers, rate of glass extraction during dip-coating process
- during thermal annealing: time and temperature of the heat treatment.

The changes in surface morphology, optical properties and roughness of TiO_2 films were analyzed by using different characterizing methods: SEM, AFM and UV/Vis spectroscopy, measurements of water droplet contact angle and photocatalytic activity as dependent on the thin film preparation conditions.

2. Experimental

2.1. Nanosol preparation and thin film deposition

A nanosol/dip-coating method was used for TiO_2 thin film preparation. The nanosol solution was obtained through controlled hydrolysis of tetraisopropyl orthotitanate (TIPT, $Ti(C_3H_7O)_4$ 97 % from Aldrich) mixed with acetylacetone (AcAc), nitric acid (0.1, or 0.5 N) and absolute ethanol (EtOH) as solvent (Vaiano et al., 2014). The molar ratio of the nanosol was the following: TIPT:AcAc:EtOH:HNO_3=1:1:40:1. HNO_3 is used as catalyst, the water content associated to the nitric acid solution itself acts as hydrolysis agent. AcAc is used as chelating ligand. It occupies some of the coordination sites of the alkoxide, lowering the extent and rate of hydrolysis, meanwhile helping in forming a stable nanosol (Dunuwila et al., 1994). The pH of the nanosol solution is a key factor for controlling the final morphology and thickness of the film (Ghamsari and Bahramian, 2008). The 1:1 ratio between water and alkoxide ensures a controlled hydrolysis-condensation reaction with mainly linear reticulation.

The nanosol preparation was carried out in glove box under N_2 atmosphere at r.t. by dropwise addition of absolute ethanol and nitric acid to a solution of TIPT, AcAc and ethanol under vigorous stirring. The obtained nanosol having a viscosity of 2.15 mm^2/s is transparent, yellow and ready for dip-coating (also in glove box). Its viscosity was measured by a kinematic Cannon Manning Sem-Micro Viscometer.

The nanosol can be easily prepared using the above indicated molar ratios and conditions. Its reproducibility is good, and also the properties of the deposited films, as shown by the characterization data reported in the following sections.

Films were deposited on microscope glass slides (75x25x1 mm) using a home-made dip-coating apparatus. Before deposition, each substrate was ultrasonic cleaned in acetone/ethanol (1:1) followed by 37 % HCl, rinsed with distilled water and finally kept in oven at 110 °C overnight. The glass substrates were immersed into the nanosol solution and then withdrawn at different controlled speeds of 6, 10, 24 and 60 mm/s, respectively. Several samples, characterized by single or multiple (5 times) coating, were prepared using different acid concentrations and dip-coating speeds. For both types, after each dip-coating procedure, the sample was dried in N_2 atmosphere for 2h at r.t., kept in a vacuum oven at 200 °C for 1h, and finally calcined at 400, 450 or 500 °C for 1h. In all cases, transparent TiO_2 thin films were obtained.

2.2. Characterization techniques

G-XRD were recorded to analyse the phase composition and crystallite size of the TiO_2 thin films. To acquire the x-ray diffraction patterns a Philips X-pert 3710 X-ray diffractometer with monochromatic CuK_α radiation at 40 kV and 30 mA was used. Spectra were collected at 0.5 ° incident angle with scan rate of 0.02 °/s. The samples were studied in the 20-80° 2Θ range. The crystallite size of the TiO_2 thin films was estimated from XRD line broadening using the Scherrer equation.

Surface morphology and cross-section of the films were examined with a Jeol-JSM 5600LV scanning electron microscope (SEM) operating at 20 kV on specimens previously covered with a gold thin layer.

Surface roughness and morphology of the TiO_2 films were evaluated by a Perception atomic force microscope (AFM), operating in contact mode using a pyramidal silicon tip with a nominal radius of 2 nm. The necessary image correction, i.e. tilting in the x- and y-direction, and root mean square roughness (RMS) calculation were carried out using AFM Gwyddion software.

Transmittance spectra were recorded in the 200-1500 nm range using a Jasco V-570 UV/VIS/NIR spectrophotometer equipped with an integrating sphere mod. ISN-470 to determine the optical properties (T %), the refractive index (n) and the film thickness (d). (Sreemany and Sen, 2004)

Photo-catalytic tests were performed on TiO_2 samples soiled with Methyl Orange (MO), a model compound simulating organic pollutant contamination, under light irradiation (AM 1.5G, 100 mW/cm^2), in order to evaluate their photo-catalytic activity. After depositing a 10^{-5} M aqueous solution of MO on the TiO_2 film surface, the film was irradiated and transmittance spectra, at regulated time intervals, were recorded and compared with that obtained for a bare glass surface contaminated in the same way.

The surface wettability was evaluated by measuring the contact angle of water droplets deposited on the film surface under ambient conditions. The acquired images have been elaborated with a Matlab software to obtain the average contact angles.

3. Results and discussion

3.1 Crystalline structure and morphology

The dip-coating deposition from nanosol solutions allows obtaining smooth, transparent, compact and crack-free TiO_2 films after calcination in relatively mild conditions. G-XRD results show that the initial film (dried, but not calcinated) is amorphous, but already by calcining in air at 400 °C the crystalline TiO_2 anatase phase is only present. Further increase of the calcination temperature up to 500 °C leads to a slightly sharpening of the XRD reflections, but no other crystalline phase becomes evident. Only for calcinations temperatures above 600 °C, small reflections of TiO_2 rutile phase could be detected.

For a good transparency, but also to realize a good and compact film as well as to control the functional properties of the film, as discussed later, it is important to have specific size of the TiO_2 nanoparticles (grain size). Figure 1A shows the effect of the calcination temperature, in the 400 – 500 °C range, on the grain size (determined from G-XRD data) of TiO_2 nanoparticles, for two samples prepared with different concentration of nitric acid during the preparation of the nanosol (0.1 and 0.5 N).

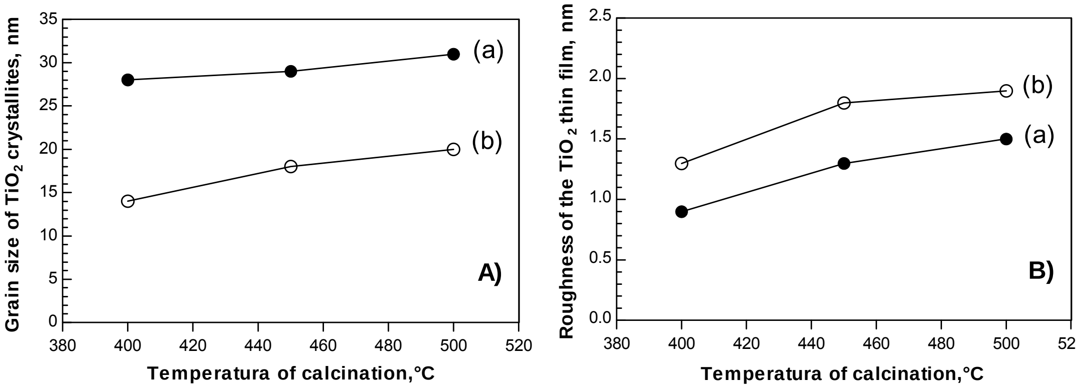

Figure 1: Effect of the calcination temperature on A) grain size of TiO_2 nanoparticles and B) roughness of the TiO_2 thin film, for two samples prepared with different concentration of nitric acid during the preparation of the nanosol: 0.1 (a) and 0.5 N (b). Other parameters of preparation: sample prepared by repeating 5 times the dip-coating procedure, 6 mm/s as rate used for extracting the sample from nanosol during dip-coating process.

The grain size determines also the surface roughness (RMS) of the thin film which was acquired by AFM (Figure 1B). At a fixed calcination temperature, the crystallite size decreases when the HNO_3 concentration of the nanosol increases, as also found by Jin et al. (2010). The effect of calcination temperature is more marked in the samples prepared with the higher HNO_3 concentration. The increase of HNO_3 concentration enhances the nucleation rate and thus smaller grains are present in the final film. The smaller crystallite size leads to an increase in surface roughness (Figure 1B).

AFM measurements (Figure 2) evidence the presence of nano-roughness in the film, although the appearance (for example, by microscopy) is of a smooth surface, crack- and porous-free. Nanocones with typical heights in the 1-3 nm range with few of them high up to 10-12 nm are also present. It should be noted that although the glass substrate shows some surface roughness, the presence of the titania films changes significantly the properties.

The morphology and thickness of the TiO_2 films were examined also by SEM. The surface of the film is smooth, uniform and dense. However, the underlying structure is composed of an agglomerate of particles with average size of 30 nm, in agreement with XRD data (Figure 1A).

The film thickness was proportional to the number of the repeated dip-coating ($C_1 \rightarrow C_5$) and there is no evidence of separation in layers. No evidence of film delamination was observed, confirming the good mechanical properties of the samples. Moreover, it is possible to note that there is no evidence of cracks and pores even if surface nano-roughness was detected by AFM.

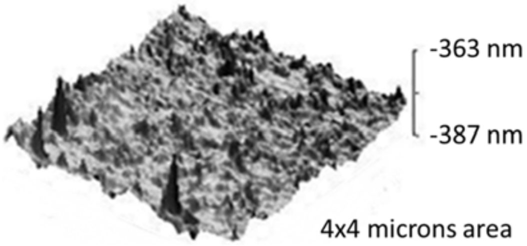

Figure 2: AFM image of a sample calcined at 500 °C and prepared using a 0.1 N concentration of HNO_3 during nanosol. Other parameters as in Figure 1. The RMS value of the film is 1.533 nm.

3.2 Optical properties

Optical transmittance spectra have been recorded in the wavelength range 200 – 1,500 nm. All acquired spectra measure the transmittance of thin film present on both sides of glass substrate, due to the characteristics of the dip-coating procedure. In the optical spectra we can distinguish two main regions: (i) at $\lambda < 350$ nm where light transmission is cut from the strong absorption of the glass substrate itself, and (ii) at $\lambda > 600$ nm, where d-d transitions of titanium ions are present (Yu et al., 2002).

In the 350 – 1,500 nm range, some weak interference fringes deriving from air/thin film and thin film/ substrate interfaces, are also detected. Increasing from one to five times the dip-coating procedure ($C_1 \rightarrow C_5$), there is no significant change in T % above 400 nm, but a more intense absorption between 350 and 400 nm is observed, related to a slight blue band-gap shift due to 2D quantum confinement. Increasing the coating numbers better mechanical and functional properties were obtained, while maintaining, at the same time, high optical transmittance.

The transmittance of the thin TiO_2 film decreases when the number of coating layers increases. In particular, passing from the cleaned glass substrate to the one-coated film, the transmittance value decreases at 550 nm from 97.3 % to 96.6 % and become 96.4 % for the five-coated film. By taking into consideration the absorbance of the glass substrate itself and that the titania film is present on both sides of the glass substrate, the transparency of these TiO_2 films is excellent, with less than about 1 % loss of transmittance even in the five-coated samples. These characteristics are related to the presence of small grains.

Various parameters influence the optical behavior of the TiO_2 thin films. Increasing the HNO_3 concentration during the nanosol preparation, lead to an increase in the transmittance of the samples. In these conditions, as shown in Figure 1, the TiO_2 crystallite particle size becomes smaller and it is possible to have a better densification during calcination. The obtained films are thus thinner and characterized by a consequent higher transmittance. Instead, at lower calcinations temperatures (450 and 400 °C), the influence of the acid is minor. This is reasonably due to the not well-organized crystalline structure.

As concern the dip-coating speed, the variation of the extracting rate of the sample from the nanosol solution during the dip-coating process (from 6 to 24 mm/s) influences the film thickness (Figure 3). The latter was calculated by the Swanepoel method (Sreemany and Sen, 2004), according to Landau-Levich equation. It also shows that the AR behavior, related to the refractive index (n), is favored in case of thinner film. The refractive index n increases with the dip-coating speed. This is attributed to a decrease in film porosity (denser nanoparticle packing) and a parallel increase in film thickness.

No significant variations in transmittance spectra of TiO_2 films due to different calcination temperatures are observed. This means that can be also used heat treatments at low temperature to induce high optical properties of the TiO_2 thin films. In doing so, is obtained a significant energy saving and a lower environmental impact of the film production process, and also the possibility of using other types of supports different from glass (such as some flexible polymers) which can hold out up to 400 °C.

3.3 Photocatalytic activity

Self-cleaning properties of titania coatings also depend on the ability to photo-catalytically oxidize organic pollutants adsorbed on their surface, thus preventing the surface fouling. In order to evaluate this capability, experimental assessments were carried out. In particular, the photocatalytic behaviour of a TiO_2 sample calcined at 400 °C was compared with that of the bare glass substrate and evaluated in terms of MO conversion after 30 min of irradiation. In these conditions no MO degradation from bare glass substrate was observed, whereas the sample with titania coating showed a MO conversion of ~16.5 %, thus evidencing a good photocatalytic activity if considering the lower calcination temperature (400 °C) of the TiO_2 sample.

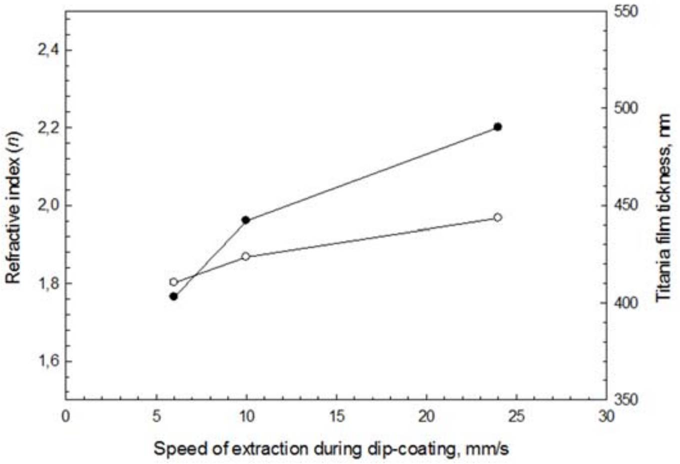

Figure 3: Titania film thickness and refractive index (n) for samples calcined at 500 °C, prepared using 0.1 N HNO_3 and 5 coating layers, but variable speed extraction during dip-coating procedure.

3.4 Contact angle

Measurements of contact angle of water drops on titania layers are useful to evaluate the self-cleaning properties of the coatings, because a higher contact angle favours the cleaning of the PV cells during raining from dust particles and other deposits.

We have observed that the contact angle of TiO_2 films depends on the characteristics of the nanosol used for film deposition. Increasing acid concentration during nanosol preparation leads to a decrease of grain size, from 31 to 20 nm for samples prepared using 0.1 and 0.5 N concentration of HNO_3 (other parameters as in Figure 1, calcination at 500 °C), and a corresponding increase in surface roughness (RMS) from 1.53 to 1.94 nm. This effect causes an increase of the contact angle of water droplets from 44 to 60 °. This increase determines an increase of rolling properties and, in turn, of the self-cleaning characteristics.

This behaviour is due to a different roughness profile of the two samples. The sample prepared with the higher concentration of nitric acid during nanosol stage, e.g. 0.5 N, shows a more regular micro-structure with respect to the sample with the lower concentration (0.1 N). This micro-texture favours the air trapping below the liquid and thus changes an hydrophilic surface (like titania) into an hydrophobic one.

4. Conclusions

The preparation method described in this work allows obtaining thin, dense, compact, nanostructured TiO_2 films with high optical transmittance. Various factors characterizing the preparation procedure (nanosol acid concentration, dip-coating speed, multistep dip-coating and calcination temperature) were investigated in order to evidence how they affect both optical and nanostructure properties. In particular, films with good optical characteristics and high transmittance (in the 94-96 % range) can be obtained at low speed of dip-coating (6 mm/s) and high HNO_3 concentration (0.5 N). Further aspects are discussed elsewhere (Salvaggio et al., 2015). In conclusion, the control of the preparation parameters in nanosol/dip-coating method allows preparing titania coatings having good adherence, stability and mechanical resistance, with high transparency and good AR properties, together with suitable surface nanostructure and photocatalytic activity for their use as self-cleaning materials. Research are on-going to improve their hydrophobic behaviour to facilitate the rolling of water droplets on the coating surface. The proposed nano-sol procedure requires simpler equipments and allows higher Ti-source utilization with respect to the generally applied physical deposition techniques (pulsed laser deposition, reactive evaporation and chemical vapor decomposition), resulting so a cost-effective method for the preparation of coating films in PV application.

Acknowledgements

Financial support by MIUR under the project “FOTOVOLTAICO - Nuove Tecnologie Fotovoltaiche per Sistemi Intelligenti Integrati in Edifici - PON01_01725” is gratefully acknowledged.
The authors also thank M. Lanza (CNR-IPCF, Messina) and A. Stassi (CNR-ITAE, Messina) for some measurements.

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