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Preparation of a porous nanocrystalline TiO_2 layer by deposition of hydrothermally synthesized nanoparticles

J. Beusen[a], M.K. Van Bael[a,c], H. Van den Rul[a,c], J. D'Haen[b,c], J. Mullens[a,*]

[a] *Hasselt University, Institute for Materials Research, Inorganic and Physical Chemistry,*
Agoralaan Building D, B-3590 Diepenbeek, Belgium
[b] *Hasselt University, Institute for Materials Research, Materials Physics,*
Wetenschapspark 1, B-3590 Diepenbeek, Belgium
[c] *IMEC vzw, Division IMOMEC, Agoralaan Building D, B-3590 Diepenbeek, Belgium*

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Abstract

In this work, a porous nanocrystalline anatase TiO_2 layer is prepared by tape casting a viscous dispersion of nanoparticles. Phase pure anatase titanium dioxide nanoparticles with a particle size of 10–20 nm are prepared by a very simple low temperature (100 °C) hydrothermal synthesis route in a pressure vessel, using only water as the medium and Ti(IV)-isopropoxide as starting material without additives. The size, shape and phase composition of the particles are studied by means of X-ray diffraction and transmission electron microscopy. A dispersion of the as-prepared nanoparticles with a narrow particle size distribution, confirmed by photon correlation spectroscopy, is prepared. After increasing the viscosity of this dispersion by addition of hydroxypropyl cellulose, anatase titanium dioxide layers are tape cast on a transparent conducting metal oxide substrate. Pores are induced by burning out the organic additive at 450 °C. The morphology and the final phase composition of the deposited TiO_2 layers are examined by X-ray diffraction and scanning electron microscopy.

Keywords: Anatase; TiO_2; Suspensions; Films; Tape casting

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1. Introduction

Nanocrystalline titanium dioxide (TiO_2) layers have attracted great scientific and technological attention because of their potential application in photovoltaic cells,[1–4] as photocatalysts,[5,6] as dielectric ceramics[7] or in gas sensors[8]. Because TiO_2 is a low cost, non-toxic, chemically inert, wide band-gap semiconductor showing a high photoactivity, it has several advantageous properties for implementation in the above-mentioned applications. Crystalline titania films are frequently prepared by means of sputtering,[9] chemical vapour deposition[10] or wet-chemical synthesis routes such as sol–gel.[11–13]

In this study nanocrystalline titanium dioxide layers are prepared by deposition of a dispersion of hydrothermally synthesized TiO_2 nanoparticles. For the preparation of nanocrystalline particles, wet chemical synthesis routes including sol–gel,[14–17] hydrothermal[18–23] and precipitation[24] methods are widely used. Most solution-based synthesis routes yield a precursor that needs a further heat treatment to induce oxide formation and crystallization. However, the required high temperature treatment frequently causes particles to form strong agglomerates and may induce particle growth or undesired phase transformation.[25] The hydrothermal synthesis route represents an alternative to calcination for promoting crystallization at milder temperatures. Chemical reactions occur in an aqueous medium under heating and high pressure. Generally in hydrothermal synthesis, a reduced agglomeration of particles is achieved and crystallization can occur without extensive particle growth.

Many papers have been published on the synthesis of crystalline TiO_2 nanoparticles using the hydrothermal route. In the water-based routes, additives are used to induce peptization[2,19–21] before hydrothermal treatment in order to control the particle size or hydrothermal treatment is carried out at temperatures above 150 °C.[1,2] Earlier reported, low temperature

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[*] Corresponding author. Tel.: +32 11 26 83 08; fax: +32 11 26 83 01.
E-mail addresses: jorge.beusen@uhasselt.be (J. Beusen), marlies.vanbael@uhasselt.be (M.K. Van Bael), heidi.vandenrul@uhasselt.be (H. Van den Rul), jan.dhaen@uhasselt.be (J. D'Haen), jules.mullens@uhasselt.be (J. Mullens).

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(below 150 °C), hydrothermal synthesis routes for titanium dioxide nanoparticles start from $TiCl_4$ as the titanium source[22,23] or use alcoholic solvents in the process which can then be termed solvothermal.[16] Chlorine in the resulting material can be disadvantageous and alcoholic solvents imply a higher cost and ecological risk than water.

To prepare porous layers from a sol or a paste of nanoparticles, organic compounds have been added as pore formers and thickeners such as polyethyleneglycol,[1,3,26] vinyl-type polymers[26] and cellulose polymers.[2,26]

In the present paper crystalline anatase TiO_2 nanoparticles are synthesized, to the best of our knowledge, for the first time at a low temperature (100 °C) using a water-based additive-free hydrothermal synthesis route starting from Ti(IV)-isopropoxide solely. In order to deposit homogeneous anatase layers by tape casting, a dispersion of these nanoparticles with hydroxypropyl cellulose (HPC) as the thickener and pore forming agent is prepared.

2. Experimental

2.1. Synthesis of nanoparticles

Nanoparticles of titanium dioxide are synthesized by a hydrothermal synthesis route. Therefore a Ti(IV)-hydroxide is precipitated by hydrolysis of Ti(IV)-isopropoxide ($Ti(iOPr)_4$, 98+%, Acros) in 100 ml of distilled water. The hydrolyzed precipitate is filtered and thoroughly washed with distilled water. Distilled water is added to the white precipitate until a suspension results that contains about $0.5\,mol\,l^{-1}$ Ti(IV). This suspension is hydrothermally treated in a stirred, stainless steel pressure vessel (Parr 5521 High Pressure Compact Laboratory Reactor, autogeneous pressure, 40% filled). In this way three samples have been synthesized under the following conditions: 2 h at 100 °C (sample 2 h100), 2 h at 200 °C (sample 2 h200) and 24 h at 200 °C (sample 24 h200). The resulting white suspensions are poured in a Petri dish and the water is evaporated in an oven under flowing air at 60 °C to produce a white powder.

2.2. Synthesis of coating paste

In order to prepare a coating paste, 1 g of the as-obtained white titania powder is dispersed by stirring in a diluted aqueous nitric acid (HNO_3, p.a., Acros) solution (about 0.2 M HNO_3) under heating (80 °C for 8 h)[27] resulting in a HNO_3-treated dispersion of 5 wt% titania.

The viscosity of the dispersion is increased by the addition of an aqueous solution of hydroxypropyl cellulose (HPC) (average MW 100,000, Acros). In a separate container a HPC solution (20 wt% in water) is prepared by dissolving 10 g HPC in 40 g distilled water, followed by continuous stirring for 20 h. The resulting clear polymer solution is added to the titania dispersion in a 1:1 weight ratio. In this way, a highly viscous white coating paste is obtained.

2.3. Preparation of TiO_2 layers

Titanium dioxide layers are deposited on indium tin oxide (ITO) coated glass substrates (soda lime glass/SiO_2/ITO, 12 Ω/sq ITO, 2.5 cm × 4.0 cm, Visiontek Systems Ltd.). Before deposition of the layers, the substrates are cleaned by means of a three-step procedure: a treatment in an ultrasonic bath for successively 30 and 10 min in a beaker filled with detergent (Ultramet 2 Sonic Cleaning Solution, 5 vol.% in distilled water, Buehler) and acetone (p.a., Acros), respectively, followed by a final cleaning step of 10 min in boiling isopropanol (p.a., Acros). Layers are deposited by tape casting (Film Applicator Coatmaster 509, Erichsen Testing Equipment) the highly viscous white coating paste at room temperature. The blade moves forward at a fixed speed of 80 mm/s and the distance between the blade and substrate (blade thickness) is varied between 60 and 120 μm. After deposition each layer is subjected to a drying step of 10 min at 60 °C in an oven under flowing air. For multiple layer deposition the dried layer is cooled down to room temperature before depositing the next layer. Finally, to burn out the organic substances the samples are placed in a horizontal tube oven and heated in dry air at a heating rate of 10 °C/min from room temperature up to 450 °C, followed by a 30 min soak at this temperature. In this way a macroscopically homogeneous TiO_2 layer is obtained.

2.4. Characterization techniques

Analysis of size and shape of the primary particles of the as-synthesized titania powder by transmission electron microscopy (TEM) is performed on a Philips CM12-STEM. For this purpose a small amount of the dried powder is suspended in distilled water; a drop of this suspension is applied on a coated grid (Formvar/Carbon 200 Mesh Cu) and dried under an IR-lamp. The particle size distribution of the particles in dispersion is determined by means of photon correlation spectroscopy (PCS) with a ZetaPALS 90Plus/BI-MAS Particle Sizing Option (Brookhaven Instruments Corporation). The sample used for these measurements is a dispersion obtained by diluting the HNO_3-treated dispersion of titania powder 100 times with distilled water. The crystallographic phase of the nanoparticles and the resulting layers is studied at room temperature by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with Cu Kα1 radiation. Scanning electron micrographs (SEM) of the layers are obtained on a FEI Quanta 200FEG-SEM, equipped with secondary electron (SE) and back scattered electron (BSE) detectors. The layer thicknesses are determined by means of profilometry (Sloan Dektak[3] Surface Profiler). The thickness of each sample is measured at 10 different locations from which a mean value is calculated.

3. Results and discussion

3.1. Influence of hydrothermal conditions on properties of nanoparticles

For the preparation of TiO_2 nanoparticles Ti(IV)-isopropoxide is used as the starting product. Hydrolysis

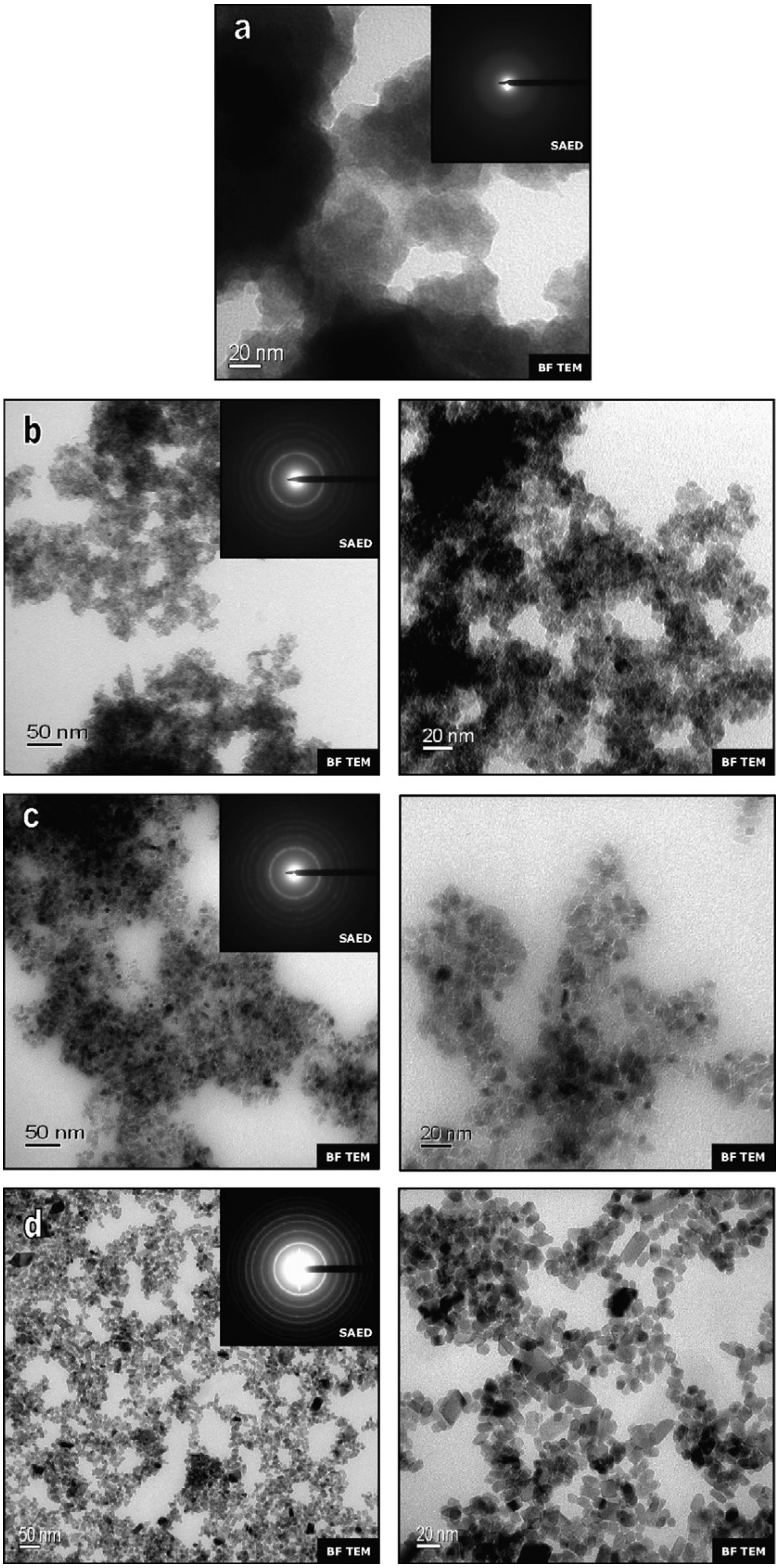

Fig. 1. Bright-field TEM images and electron diffraction patterns of Ti(IV)-hydroxide precipitate (a) and of TiO_2 nanoparticles synthesized by hydrothermal treatment at: (b) 100 °C during 2 h; (c) 200 °C during 2 h; (d) 200 °C during 24 h.

of Ti-isopropoxide results in a Ti(IV)-hydroxide precipitate. Analyzing the washed precipitate with TEM (Fig. 1a) reveals that no crystalline TiO_2 particles have formed yet, as shown by the absence of diffraction rings in the electron diffraction pattern. X-ray diffraction analysis (Fig. 2a) also confirms the non-crystallinity of the Ti(IV)-hydroxide precipitate. To crystallize the precipitate, it is subjected to a hydrothermal treatment under different conditions in order to determine how these influence the size and the crystallographic phase of the formed TiO_2 particles. According to TEM micrographs (Fig. 1b–d) particles with a particle size of 10–20 nm are formed in all samples (2 h100, 2 h200 and 24 h200). The crystallinity of the nanoparticles is confirmed by the electron diffraction pattern. XRD analysis (Fig. 2b–d) makes it possible to indicate that all three samples consist of phase pure anatase titanium dioxide. Comparing these particles with commercial P25 TiO_2 demonstrates that the as-obtained anatase TiO_2 nanoparticles with a size of 10–20 nm are significantly smaller than the 30 nm commercial P25 titania powder containing both anatase and rutile phase. Grätzel[2] reported also smaller 15 nm anatase titanium dioxide nanoparticles synthesized by a water-based hydrothermal route. However in his work, Ti-isopropoxide is modified with acetic acid, peptization with HNO_3 is applied before the hydrothermal treatment and hydrothermal conditions are 12 h at 230 °C. In Fig. 1 it is obvious that a higher reaction temperature or a longer reaction duration do not significantly change the particle size or crystallographic TiO_2 phase. However, of all the conditions that have been tested, the nanoparticles of the sample 24 h200 show the most pronounced grain boundaries.

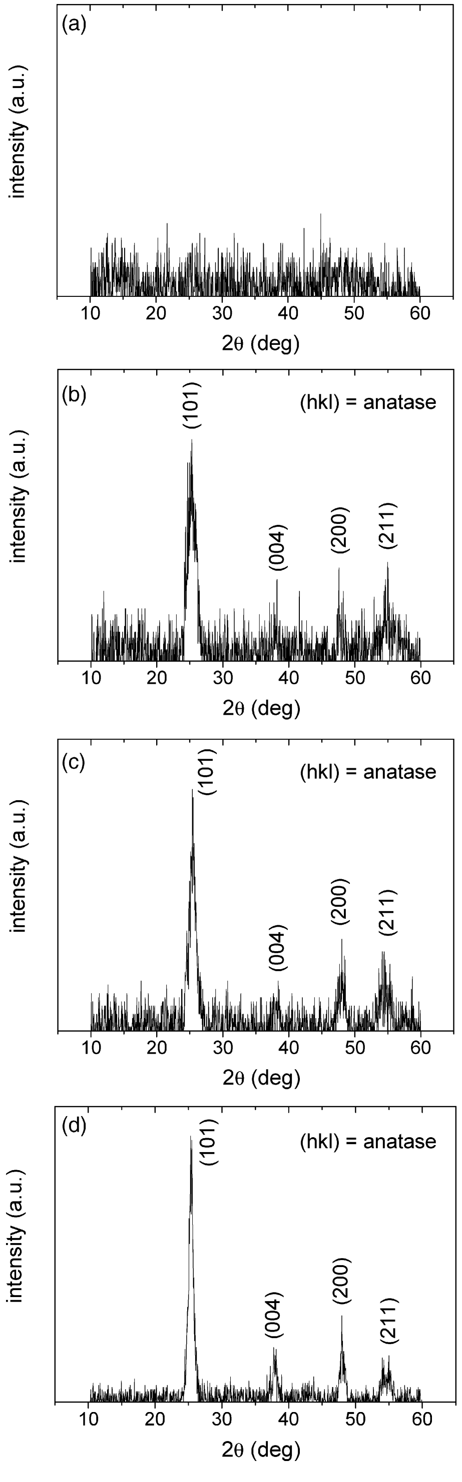

Fig. 2. Powder X-ray diffraction spectra (XRD) of Ti(IV)-hydroxide precipitate (a) and of TiO_2 nanoparticles synthesized by hydrothermal treatment at: (b) 100 °C during 2 h; (c) 200 °C during 2 h; (d) 200 °C during 24 h.

In summary, this study shows that it is possible to synthesize uniform anatase titanium dioxide nanoparticles with a particle size of 10–20 nm at a temperature of only 100 °C in a pressure vessel, by a hydrothermal route starting from Ti-isopropoxide without additives and using only water as a medium. The 2 h100 nanoparticles will be used for the subsequent experiments.

3.2. Particle size distribution of a dispersion of nanoparticles

Ito et al.[27] have reported that by stirring the TiO_2 nanoparticles in a diluted aqueous nitric acid solution under heating (80 °C for 8 h) HNO_3 is adsorbed on the TiO_2 surface (TiO_2/NO_3^-) which leads to an enhanced dispersion due to the electrostatic forces between the particles. The particle size distribution of a diluted dispersion of the 2 h100 anatase TiO_2 nanoparticles is analyzed with dynamic light scattering also known as photon correlation spectroscopy. In Fig. 3 the number of particles (percentage) as a function of particle diameter is displayed on the basis of intensity (Fig. 3a) and number (Fig. 3b). In the intensity graph (Fig. 3a), beside particles and/or aggregates of particles with a size smaller than 100 nm also aggregates of particles with a size larger than 400 nm can be observed. Because the intensity of scattering of a particle is proportional to its diameter, the number graph (Fig. 3b) gives a better idea of the particle size distribution in the dispersion since there the influence of large aggregates is less important. According to the graph on the basis of number more than 90% of the particles in the sample have a particle size between 15 and 30 nm. Since TEM analysis indicates that the particles have a size of 10–20 nm, it can be stated that a large percentage of the nanoparticles appear in the dispersion as single particles or in clusters of a few particles. Using this dispersion is therefore very interesting for the subsequent deposition of homogeneous layers.

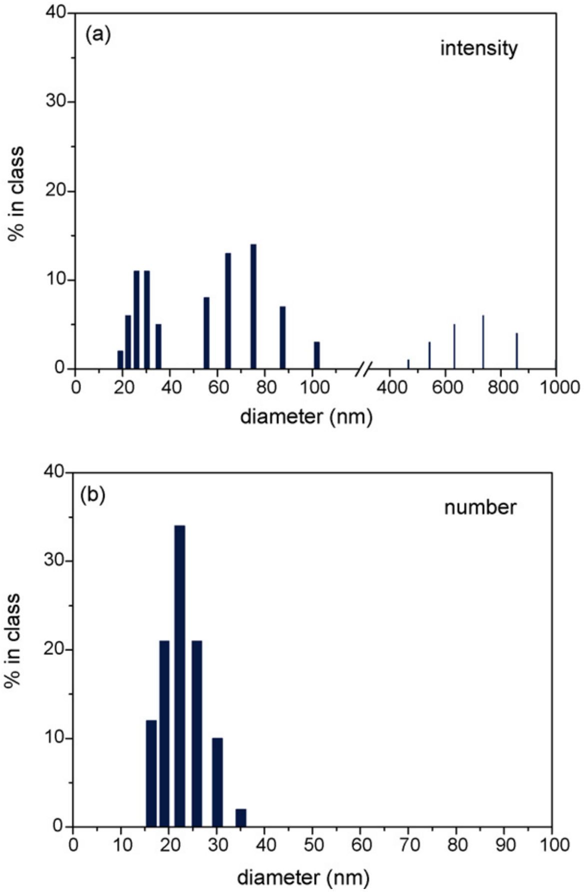

Fig. 3. Particle size distribution of dispersion of 2 h100 anatase TiO_2 nanoparticles by photon correlation spectroscopy on the basis of (a) intensity and (b) number.

3.3. Influence of organic compound on homogeneity of the layer

Several organic compounds have been tested as pore former and thickener to prepare thick porous layers from the dispersion of the TiO_2 nanoparticles: polyethylene glycol (PEG), polyvinyl alcohol and hydroxypropyl cellulose (HPC). Based on various deposition experiments from viscous dispersions with different concentrations of the tested organic compounds, a viscous dispersion with 10 wt% HPC was seen to give the best result with respect to the macroscopical homogeneity of the resulting titania layer.

3.4. Morphology and phase formation of TiO_2 layer

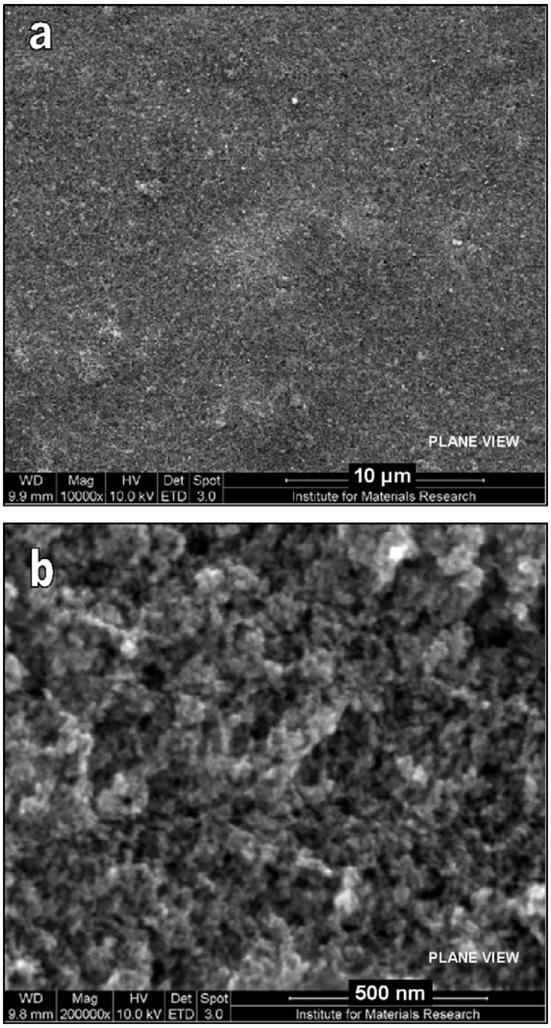

Fig. 4. Plane view SE SEM images of TiO_2 layer deposited on ITO coated glass and crystallized at 450 °C during 30 min (a and b).

SEM analysis (Fig. 4a and b) shows in plane view that the titanium dioxide (multiple) layer, obtained by tape casting the viscous dispersion of nanoparticles and after thermal treatment, is porous and the pores are homogeneously distributed along the surface. A similar morphology is reported by Grätzel.[2] He describes the preparation of a porous TiO_2 layer deposited by screen printing of a viscous paste containing ethylcellulose. Ito et al.[27] also published a report on the preparation of porous titanium dioxide layers with a comparable film morphology, obtained by tape casting a viscous dispersion using PEG and a cellulose polymer. However, they employed commercial P25 TiO_2 nanoparticles which are larger in size. The nanoparticles of 10–20 nm that were obtained in our study can be distinguished in the SEM picture (Fig. 4b).

In order to get an idea of the morphology inside the layer a cross-section of the layer is examined by SEM (Fig. 5). In this way pores throughout the whole layer are identified. The layer shows a uniform film thickness of about 2 μm after burning out the organic substances. The layer thickness, determined with profilometry, matches the value obtained by SEM.

X-ray diffraction data (Fig. 6) of the layer show only peaks of anatase TiO_2. This means that after dispersing the anatase titanium dioxide nanoparticles, by treating with a diluted aqueous nitric acid solution under heating, and thermal treatment of the deposited layer at 450 °C no change in TiO_2 phase occurred. A thermogravimetric analysis (not shown) of the viscous dispersion containing HPC revealed that all organic substances are burned out at the temperature of 450 °C. The fact that only the anatase phase is present in the layers is very interesting with respect to their application in dye-sensitized solar cells. In these

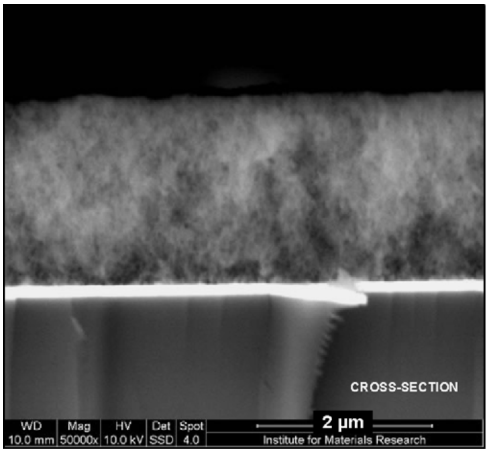

Fig. 5. Cross-section BSE SEM images of TiO_2 layer deposited on ITO coated glass and crystallized at 450 °C during 30 min.

devices as high as possible a fraction of anatase is desired, since this crystalline phase of titanium dioxide has the advantage of transporting electrons with higher efficiency.[28,29] Also the fact that the layers are porous is interesting for implementation in dye-sensitized solar cells.

3.5. Influence of blade thickness and number of layers on the layer thickness

When aiming at the implementation of the TiO_2 layer in a dye-sensitized solar cell, a thick layer of a few micrometers (1–25 μm) is required.[29] Therefore, the thickness of the porous nanocrystalline titanium dioxide layers, obtained by tape casting the viscous dispersion of nanoparticles and thermal treatment at 450 °C for 30 min, is studied as a function of the distance between the blade and the glass substrate (blade thickness) (60–120 μm) (Fig. 7a) and as a function of the number of layers deposited with a blade thickness of 120 μm (Fig. 7b). The thickness of the titanium dioxide layers increases linearly with increasing blade thickness (60–120 μm) (Fig. 7a). The maximum thickness of the multiple layer is limited by the distance between the blade and the blank substrate. When a number of layers are deposited with the same blade thickness of 120 μm, the thickness of the resulting layer will approach the value of 120 μm in the limit. Therefore the curve of layer thickness as function of the number of layers deposited with blade thickness 120 μm (Fig. 7b) cannot be linear. However the first part of the curve, for the deposition of one to four layers with blade thickness 120 μm, can be observed as almost linear.

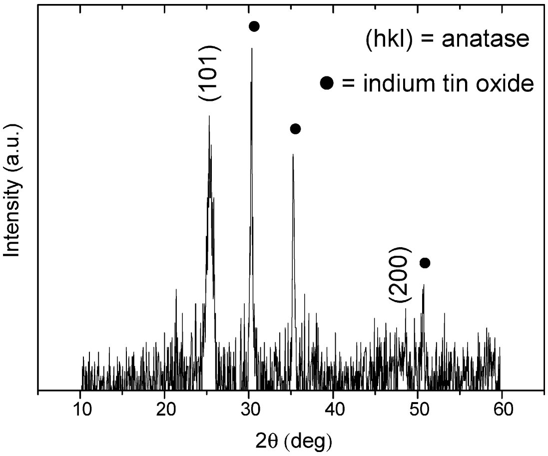

Fig. 6. X-ray diffraction spectrum (XRD) of TiO_2 layer deposited on ITO coated glass and crystallized at 450 °C during 30 min.

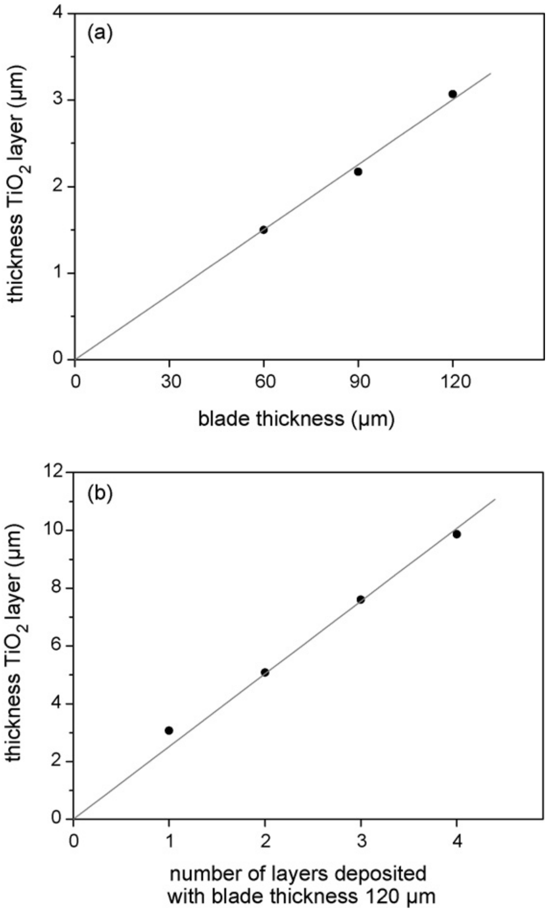

Fig. 7. Layer thicknesses of nanocrystalline TiO_2 layers obtained by profilometry as function of: (a) blade thickness; (b) number of layers deposited with blade thickness 120 μm.

4. Conclusion

In this study it is shown that a thick, porous, nanocrystalline, phase pure anatase TiO_2 layer can be deposited by tape casting a viscous dispersion of hydrothermally synthesized anatase titanium dioxide nanoparticles.

TEM micrographs and XRD spectra indicate that an additive-free hydrothermal synthesis route at a low temperature of 100 °C during 2 h, using only water as the solvent and starting from Ti-isopropoxide, enables the synthesis of uniform crystalline anatase TiO_2 particles with a particle size of 10–20 nm.

Combination of TEM and particle size distribution analysis, by photon correlation spectroscopy, proves that more than 90% of the TiO_2 nanoparticles appear in the dispersion as single particles or in clusters of a few particles.

SEM micrographs verify that the deposited nanocrystalline TiO_2 layer is porous after thermal treatment at 450 °C during 30 min. X-ray diffraction data show a phase pure anatase TiO_2 layer is obtained.

Further research regarding the use of these porous titanium dioxide layers in photovoltaic cells is now in progress.

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