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The effect of type and concentration of modifier in supercritical carbon dioxide on crystallization of nanocrystalline titania thin films

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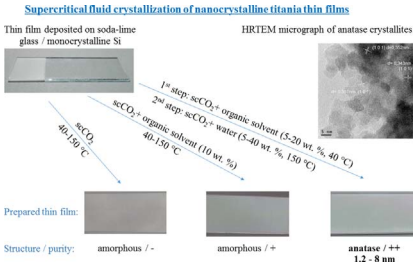
GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured TiO_2 anatase thin films were directly prepared using supercritical carbon dioxide ($scCO_2$) modified by organic solvent and water in two step processing. Organic solvent used as $scCO_2$ modifier at 30 MPa and 40 °C in the first step of processing was in the second step changed to water with simultaneous temperature increase to 150 °C which caused anatase thin films crystallization. The effect of the type of modifier (water, methanol, ethanol and acetone), concentration of modifier (5–40 wt.%) in $scCO_2$ and the amount of $scCO_2$ (50–200 g) passed through the high pressure column as well as the type of substrate (soda-lime glass and monocrystalline Si) on microstructure and purity of TiO_2 thin films were examined in both steps of processing. The prepared thin films were characterized with respect to their (micro)structural properties by Raman spectroscopy as well as X-ray diffraction, to their wettability by contact angle measurements and to their morphology by high resolution transmission electron microscopy.

Purity of the thin films was positively affected by modification of $scCO_2$ by organic solvents in the first step of processing. Ethanol was the most appropriate $scCO_2$ modifier in terms of TiO_2 thin film purity, anatase crystallite size and solvent toxicity. The crystalline structure of anatase, which size changed from 2 to 8 nm in dependence on experimental conditions, was obtained on both tested substrates without necessity of any thermal treatment of TiO_2 thin films. The largest crystallites of anatase were achieved when 10 wt.% of ethanol and 30 wt.% of water were added to $scCO_2$.

1. Introduction

Titanium dioxide (TiO_2, titania) belongs to the desired materials mainly for its ability to form a crystalline structure of anatase having a

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high photocatalytic activity, chemical stability, strong oxidation activity and non-toxicity. Anatase is used in environmental applications such as air and water purification [1–4] or the decomposition of organic substances [5], preferably in the form of thin films which are more acceptable from application point of view due to their fixation on the inert substrate surface. The photocatalytic activity of thin films depends on the phase composition as well as on hydrophilicity, specific surface area, crystallinity and crystallite size and shape [6–9]. These properties can be strongly influenced by chosen preparation method.

Calcination, the most commonly used method for titania transformation from amorphous to anatase structure, has many disadvantages. Recrystallization, excessive sintration and aggregation, crystallite growth and in a consequence of these processes a decrease in the specific surface area occurs [10,11]. Furthermore, the properties or photocatalytic performance cannot be easily controlled.

To avoid the negative prolonged exposure to high temperature, Wei et al. [12] combined the calcination of thin films with pre-drying by using supercritical carbon dioxide ($scCO_2$). This step helps to increase the titania specific surface area and improves the electronic properties leading to increased photocatalytic activity. Similar results found also other research groups that applied the post-treatment of sol-gel derived metal oxide thin films as well as powders after using supercritical carbon dioxide [13–15].

As discussed recently [16–20], water-modified $scCO_2$ and pure $scCO_2$ can be applied for the preparation of crystalline and highly pure nanostructured TiO_2 thin films directly, thus without the need of subsequent thermal treatment.

Asai et al. [16] used a batch-type reaction system for conversion of the TiO_2 precursor films on soda-glass substrates prepared by sol-gel coating using Ti-alkoxide solution to crystalline TiO_2. Anatase with 12 nm crystallite size was obtained at a pressure of 15 MPa and a temperature of 300 °C. When they exposed such thin films the conventional calcination at 400 °C no crystallization occurred.

The direct preparation of highly pure TiO_2 anatase thin films (without any subsequent thermal treatment) by pure and water-modified (30 wt.%) supercritical carbon dioxide and by subcritical water in a flow-type apparatus was realized by Sajfrtova et al. [17]. One step processing was compared with the multi-step processing combining pure and modified CO_2. High temperature had a positive effect on the crystallization as well as the purity of TiO_2 thin films during the one-step and multi-step processing. When TiO_2 thin films were exposed to water-modified supercritical CO_2 and temperature of 150 °C under pressure of 30 MPa, the anatase crystallites of sizes of 2–12 nm were obtained. The growth of anatase crystallites was mainly influenced by the presence of water.

Matějová et al. [18] used $scCO_2$ in combination with subcritical water and methanol to obtain the nanocrystalline TiO_2 in thin film form. They demonstrated that addition of a small amount of water to $scCO_2$ causes the direct crystallization of titania thin films. Modification of carbon dioxide with organic solvent such as methanol contributes to the removal of organic precursors from titania used in the sol-gel synthesis and hence to the enhancement the purity of titania thin films. Concerning the preparation of TiO_2 in the powder form, combining $scCO_2$ and subcritical methanol or subcritical water and subcritical methanol, they achieved besides the crystallization an increase of specific surface area and purity of titania, exceeding the calcination [19,20].

Based on these findings [17–20], a supercritical CO_2 modified by organic solvents and water was used for a direct preparation of crystalline and pure nanostructured TiO_2 thin films. The combination of $scCO_2$ with water and organic solvent is advantageous in terms of their low price, easy availability and ability to dissolve a wide range of substances of different polarities. Modification of $scCO_2$ with an organic solvent was applied at pressure of 30 MPa and temperature of 40 °C (*i.e.* at high solvent power of $scCO_2$) in the first step of the processing in order to increase the solubility of organic precursors from the gel, and thus to reach the excellent purity of the final titania thin films compared to using pure $scCO_2$ [17]. TiO_2 crystallization was realized in the second step of processing by changing the modifier to water and by raising temperature to 150 °C. The effect of the type of modifier (water, methanol, ethanol and acetone) and concentration of modifier (5–40 wt.%) in $scCO_2$ as well as the amount of $scCO_2$ (50–200 g) passed through the high pressure column on microstructure and purity of TiO_2 thin films were examined in both steps at constant pressure of 30 MPa. All the experiments were performed over precursor titania gel thin films prepared by reverse micelles assisted sol-gel method, using hardly removable nonionic surfactant Triton X-114, however, forming uniform nano-crystallites. The prepared thin films were characterized by means of Raman spectroscopy, X-ray diffraction (XRD), high-resolution transmission electron microscopy analysis (HRTEM) and contact angle measurements.

2. Materials and methods

2.1. Materials

Carbon dioxide (> 99.9%, Linde Technoplyn Prague, CR) was used as a solvent in supercritical fluid processing. Ethanol (96%, p.a.), methanol (p.a.) and acetone (p.a.) applied as CO_2 modifiers were purchased from Lachner (Neratovice, CR). Distilled water was treated ultrasonically for 30 min before utilization to remove bubbles. Precursor solution of TiO_2 films was prepared from cyclohexane (p.a., Lachner, Neratovice, CR), Triton X-114 ((1,1,3,3,-Tetramethylbutyl)phenyl-polyethylene glycol, Sigma-Aldrich, USA), titanium(IV) isopropoxide ($Ti(OCH_2(CH_3)_2)_4$, Sigma-Aldrich, USA) and distilled water.

2.2. Sol preparation and deposition of thin films

Precursor titania gel thin films were deposited on two types of substrates (soda-lime glass and monocrystalline Si) by dip-coating method, using the sol prepared by sol-gel process controlled within reverse micelles environment of non-ionic surfactant Triton X-114 in cyclohexane, similarly as in our previous study [17].

The molar composition of titania sol was following; cyclohexane: Triton X-114: water: $Ti(OCH_2(CH_3)_2)_4$ = 11:1:1:1 [17,20]. In a shortcut, proper amounts of cyclohexane, Triton X-114 and water were mixed and vigorously stirred for 15 min for homogenization and formation of reverse micelles. Then, titanium (IV) isopropoxide was injected to micellar solution under vigorous stirring. After addition of titanium (IV) isopropoxide the sol was stirred for next 20 min. A prepared sol was left standing in a closed glass bottle for 4 h to stabilize. Ultrasonically cleaned and dried soda-lime glasses and monocrystalline Si were dipped into the sol by using a dip-coater 4 idLab. The deposition conditions were following: the immersion velocity 15 cm min^{-1}, the delay in the sol 30 s, the emergence velocity 6 cm min^{-1}. After deposition the substrates with gel thin films were left on air overnight and then were processed by proper investigated method using organic solvent- and/or water-modified $scCO_2$.

2.3. Supercritical fluid crystallization (SFC)

Glass slides with gel thin films were placed in a steel holder and placed

into the high pressure column (150 ml, inner diameter 30 mm) filled with glass beads serving as a solvent flow distributor. Crystallization was performed in the

Spe-ed SFE apparatus (Applied Separations, USA, for instrumentation details see Ref. [17]).

CO_2 chilled to 5 °C by cryostat was supplied from pressure bomb through a high pressure pump into the apparatus. Various types of liquid solvents (water, methanol, ethanol and acetone) were used as $scCO_2$ modifiers that were applied at a constant flow rate by the high