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Preparation of nanocrystalline titania thin films by using pure and water-modified supercritical carbon dioxide

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ABSTRACT

Processing by pure and water-modified (30 wt.%) supercritical carbon dioxide and by subcritical water were utilized for the direct preparation of highly pure TiO_2 anatase thin films without any subsequent thermal treatment. One step processing was compared with the two or three step processing combining pure and modified CO_2. The effect of temperature (40–150 °C) and the amount of CO_2 (100–200 g) passed through the high-pressure column on the (micro)structure and the purity of TiO_2 thin films were examined at pressure of 30 MPa. Prepared thin films were characterized with respect to the structural properties and purity by Raman spectroscopy. The most promising thin films were analysed with respect to microstructural properties by means of X-ray diffraction to determine the phase composition, the crystallite-size and the crystallite-size distribution. 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 desired crystalline structure of anatase was obtained. The anatase crystallites growth was mainly influenced by the presence of water. Anatase crystallites sizes of 2–12 nm were obtained depending on the processing method on both investigated substrates (soda-lime glass and monocrystalline Si) on which the TiO_2 thin films were deposited. Using one step or multi-step processing by water-modified supercritical CO_2 any undesirable effects such as Na^+ ions diffusion from the soda-lime glass substrate to the one-layer TiO_2 film, having negative effect on crystallization of anatase, did not take place. The universality of developed processing by pure and water-modified supercritical CO_2 for preparation of TiO_2 anatase thin films was successfully confirmed for two different substrates.

1. Introduction

TiO_2 (Titanium dioxide, titania) belongs thanks to its excellent photochemical performance and other photo-induced phenomena under UV light (with wavelength < 365 nm) among materials under keen scientific interest. It has been explored in a form of thin films in many application areas; as sensing films of gas sensors, coatings for self-cleaning surfaces or with antimicrobial activity, an electrode material or photocatalyst promising in waste water and air treatment technologies. Titania is a semiconductor with the band gap energy of 3.2 eV, 3.0 eV and 3.1 eV that belong to its crystal structure of anatase, rutile a brookite, respectively. Despite the fact that anatase shows higher band gap energy than rutile or brookite, anatase exhibits higher photoactivity. The reason of this performance is a different structure of energy bands; the energy of anatase conductive band is higher than that of rutile or brookite [1,2]. Practically it means the enhanced reduction capability of excited electrons which are needed for the formation of free radicals which finally participate in the degradation e.g. of organic pollutants [3–5]. Since microstructural properties such as the crystallite size on nanosize level and shape, crystallite size distribution, phase composition, oxygen vacancy, microstrain etc. crucially affect photo-electrochemical response and photocatalytic performance of titania thin films [6], e.g. via the effect on their electronic and optical properties, it is very important to know and control all preparation and processing steps to avoid undesirable effects within microstructure of thin films.

Commonly used method for the preparation of pure and crystalline TiO_2 thin films is calcination [7,8]. However, this approach

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has some disadvantages such as excessive sintration, crystallite growth or recrystallization. Moreover, during calcination the microstructural properties such as crystallite-size and phase composition, having the influence on the photocatalytic activity, cannot be controlled.

In last years this standard thermal processing was overcome by supercritical carbon dioxide drying combined with thermal processing. It was found that the pre-treatment using supercritical carbon dioxide proposed for lowering the process temperature of sol-gel derived metal oxide thin films as well as powders helps to enlarge surface area significantly and improve electronic properties showing enhanced photocatalytic performance [9–11].

Wei et al. [12] engaged in the effect of the post-treatment of mesoporous crystalline TiO_2 thin films by a supercritical CO_2 ($scCO_2$) on the photovoltaic performance. In their study, a serie of TiO_2 thin films composed of mesopores and nanoparticles were prepared by a spin-coating process and then statically treated by $scCO_2$ for 30 min at pressures of 34.5 MPa and 58.6 MPa and at temperatures ranging from 60 to 100 °C. The films were calcined at temperature of 400 °C for 3 h before the characterization and solar cell fabrication. The mesopores in the TiO_2 thin film without the $scCO_2$ treatment collapsed after calcination at temperatures above 400 °C, while the films treated by $scCO_2$ exhibited an enhanced thermal stability and well-preserved porosity.

Film processing using supercritical CO_2 accomplished with a batch-type reaction system was compared with conventional calcination by Asai et al. [13]. The TiO_2 precursor films on soda-glass substrates prepared by sol-gel coating using Ti-alkoxide solution were converted to crystalline TiO_2 (anatase with 12 nm crystal size) successfully by treatment in $scCO_2$ at a fluid pressure of 15 MPa and a substrate temperature of 300 °C whereas no crystallization occurred by conventional heat treatment at 400 °C.

Besides that, several works reported on utilization of pressurized water and supercritical/subcritical methanol in a flow regime which resulted in nanocrystalline titania powders with significantly enlarged surface area and purity comparable to usually thermally treated titania powders [14,15]. It was shown that utilization of this solvent combination leads to direct crystallization of titania, namely by the effect of pressurized water [14–17].

The motivation of this work was to design the improved supercritical fluid process which can lead to purification and direct crystallization of TiO_2 thin films without any subsequent thermal treatment. The processing by pure or water-modified supercritical CO_2 in a flow regime was investigated and compared with subcritical water processing. 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-domains. The effect of various processing conditions (i.e. temperature, pressure, volume and flow rate of solvents) as well as the type of substrate on microstructure and purity of TiO_2 thin films was thoroughly studied by means of Raman spectroscopy, X-ray diffraction, and contact angle measurements.

2. Materials and methods

2.1. Materials

Cyclohexane (p.a., Lachner, Neratovice, CR), Triton X-114 ((1,1,3,3,-Tetramethylbutyl)phenyl-polyethylene glycol, Sigma-Aldrich, USA), $Ti(OCH_2(CH_3)_2)_4$ (Titanium(IV) isopropoxide, Sigma-Aldrich, USA) and distilled water were used for the preparation of precursor solution of TiO_2 gel films. Carbon dioxide (>99.9%) for supercritical fluid processing was purchased from Linde Technoplyn (Prague, CR). Distilled water for subcritical water processing was treated ultrasonically for 30 min before utilization to remove bubbles.

For deposition of the films two types of substrate were used: soda-lime glass and monocrystalline Si (non-diffracting substrate).

2.2. Sol preparation and deposition of thin films

Gel titania thin films were deposited on substrates (soda-lime glass and monocrystalline Si) by dip-coating method, using the sol prepared by sol-gel process controlled within reverse micelles of non-ionic surfactant Triton X-114 in cyclohexane.

The molar composition of titania sol was following; cyclohexane: Triton X-114:water:$Ti(OCH_2(CH_3)_2)_4$ = 11:1:1:1 [14]. 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 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 pure and/or water-modified $scCO_2$ or subcritical water.

2.3. Supercritical fluid crystallization (SFC)

Air dried glasses with deposited gel thin films were fixed in a steel holder and immersed in the high pressure column (volume 150 ml; inner diameter 30 mm) filled in the bottom part with glass beads serving as solvent flow distributors. The column was connected with stainless steel capillaries and placed into the air-conditioned box. The SFC experiments were carried out in Spe-ed SFE apparatus (Applied Separations, USA) whose schema is shown in Fig. 1.

Carbon dioxide was sucked from a pressure container using a high-pressure pump cooled by water to 5 °C. $ScCO_2$ entered the lower end of the column at pressure of 30 MPa. The temperature of $scCO_2$ was maintained using a hot air ventilator in an oven. In experiments with modified CO_2, water was supplied at a constant flow rate by a high-pressure LCP 4020.3 (ECOM s.r.o.) and mixed with CO_2 before entering the column to reach concentration in $scCO_2$ 30 wt.%. The solution flowing from its upper end was expanded to the ambient pressure in a heated micrometer valve and the extract was collected in empty glass vial at the ambient temperature. The quantity of the gaseous CO_2 leaving the trap and its flow rate was measured using a gas meter. The CO_2 flow rate was adjusted to 0.8 g min^{-1} using the micrometer valve. Experimental conditions and design were changed as shown in Table 1.

2.3.1. One step processing

Experiment with pure CO_2 was carried out at constant pressure of 30 MPa, temperature of 150 °C and solvent amount of 100 g. When modified CO_2 was used, different temperature (40–150 °C) and pressure (10–30 MPa) were applied.

2.3.2. Multi-step processing

Combination of several steps with pure and water-modified $scCO_2$ was tested. Order of individual steps and temperature varied as shown in Table 1. In the first step, the pure or water-modified CO_2 at the temperature of 40 or 150 °C was used. After 100 g of CO_2 flowed through the column the conditions were changed and experiment continued. Second step was finished when 100 g of CO_2