

TiO₂ THIN FILMS PREPARED BY USING SUPERCRITICAL AND PRESSURIZED FLUIDS; THE EFFECT OF VARIOUS EXTRACTION CONDITIONS ON MICRO/STRUCTURAL PROPERTIES OF THIN FILMS

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ABSTRACT

In this study the extraction approach opening up the possibility to prepare directly (without any subsequent thermal processing) crystalline and pure nanostructured TiO₂ thin films has been investigated. Namely, processing by supercritical carbon dioxide with parallel injection of modifiers (water and/or methanol) in a flow regime was explored in order to remove organic precursors used during sol-gel synthesis and to crystallize TiO₂ thin films. Titania films were deposited on soda-lime glass substrate by dip-coating method, using the sol prepared by sol-gel process controlled within reverse micelles of non-ionic surfactant Triton X-114. The effect of various extraction conditions (*i.e.* temperature, pressure, volume and flow rate of solvents) on micro/structure and purity of thin films was thoroughly studied by means of X-ray diffraction and Raman spectroscopy.

INTRODUCTION

TiO₂ (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 (for anatase), 3.0 eV (for rutile) and 3.1 eV (for brookite). 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. 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 [1-3]. Since micro/structural 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 [4], *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.

A thermal treatment at elevated temperature (calcination), which is commonly used within most of preparation procedures of nanostructured semiconductor thin films, serves as a simple tool of possible tuning of semiconductor micro/structural properties. On the other hand, it mostly lead to uncontrollable undesirable effects in thin films such as an excessive sintering, crystallite growth or recrystallization, which cannot be predicted. In last years this standard thermal processing was overcome by supercritical carbon dioxide drying combined with thermal processing. Nanostructured titania thin films as well as powders with significantly enlarged surface area and improved electronic properties showing enhanced photocatalytic performance were synthesized [5-7]. Besides that, several works reported on utilization of extraction by 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 [8, 9]. It was shown that utilization of this combined extraction technique leads to direct crystallization of titania, namely by the effect of pressurized water. Besides that, the carbon content originating from used organic precursors (surfactant, solvent, metal precursor) was totally removed from nanostructured titania by subcritical/supercritical methanol drying [9]. The advantage of utilization of this unique combination of solvents – water and methanol – consists not only in their low price and availability, but mainly in their chemical universality to dissolve broad range of compounds showing different polarity. Besides the water capability to dissolve polar compounds, methanol can dissolve both polar as well as lipophilic compounds. Thus, this extraction technique may be applied for removal of various types of surfactants (nonionic, amphiphilic, ionic) which are likely used *e.g.* as pore structure-directing agents in sol-gel syntheses.

Based on this knowledge, the motivation of this work is to explore the extraction approach which could lead to purification and direct crystallization of TiO₂ thin films without any subsequent thermal processing. The extraction by supercritical carbon dioxide with parallel injection of modifiers (water and/or methanol) in flow regime has been tested. The effect of various extraction conditions (*i.e.* temperature, pressure, volume and flow rate of solvents) on micro/structure and purity of thin films prepared by sol-gel process controlled within reverse micelles of non-ionic surfactant Triton X-114 has been thoroughly studied by means of X-ray diffraction and Raman spectroscopy.

MATERIALS AND METHODS

Gel titania thin films were deposited on soda-lime glass substrates 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.

Sol preparation. The molar composition of titania sol was following; cyclohexane : Triton X-114 : water : Ti(OCH₂(CH₃)₂)₄ = 11 : 1 : 1 : 1. 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 period. A prepared sol was left standing in a closed glass bottle for 4 hours to stabilize. More details about sol preparation were reported in our previous work [8].

Deposition of thin films. Ultrasonically cleaned and dried soda-lime glasses were dipped into the sol by using a dip-coater 4 idLab. The deposition conditions were following: the immersion velocity 15 cm/min, the delay in the sol 30 s, the emergence velocity 6 cm/min. After 4 h standing on air the deposited gel thin films (Figure 1) were fixed in a Teflon holder and were extracted in a commercial SFE unit (Applied Separations, USA) by using supercritical carbon dioxide with parallel injection of modifiers (water and/or methanol) in a flow regime at various experimental conditions (see Table 1). After this processing titania thin films were obtained.



Figure 1: As-prepared gel titania thin film (1 layer) deposited on a soda-lime glass.

Sample code	T (°C)	p (MPa)	CO ₂		Modifier/s
			Flow (L/min)	Volume (L)	wt.% or flow (mL/min)
1	50	30	0.5	50	-
2	150	10	-	-	H ₂ O (4 mL/min, ~300 mL)
5	50	30	0.5	50	H ₂ O (30 wt.%)
6	50	30	0.5	50	CO ₂ saturated with H ₂ O via globules
7	150	30	0.5	50	H ₂ O (30 wt.%)
8	150	10	0.5	50	H ₂ O (30 wt.%)
10	50	30	0.2	50	H ₂ O (18 wt.%)
12	50	30	0.5	150	H ₂ O (18 wt.%) + CH ₃ OH (18 wt.%)

Table 1: Investigated extraction conditions.

Characterization of thin films. The micro/structural properties of thin films were investigated by X-ray diffraction and Raman spectroscopy.

X-ray diffraction measurements over titania thin films were performed on a Panalitical-MPD laboratory diffractometer in the parallel beam geometry with a Cu anode, with a Goebel mirror in the incident beam and a parallel plate collimator in the diffracted beam. The X-ray

patterns were obtained as simple detector 2θ scans with a constant incidence angle of the X-ray beam 1.5 deg.

Raman spectra were collected using a dispersive Nicolet Almega XR spectrometer equipped with Olympus BX 51 microscope. Excitation laser source (473 nm) with an incident power of 5 mW with 256 expositions with 0.5 s duration was used for collecting the spectra. The laser beam was focused to a spot of 0.6 mm in diameter. The incident energy was minimized to avoid thermal effects as a consequence of the laser irradiation. Spectral resolution of the instrument was 1.93 cm^{-1} and the spectrometer was calibrated using crystalline silicon standard with line at 520 cm^{-1} .

RESULTS

Determined micro/structural properties such as the crystallinity/amorphousness, phase composition and purity of TiO_2 thin films prepared at different extraction conditions are summarized in Table 2. XRD patterns and Raman spectra recorded over selected TiO_2 thin films are shown in Figure 2a and b, respectively.

Sample code	XRD		Raman spectroscopy
	character	crystalline polymorph	Surfactant bands
1	amorphous	-	$\sim 3072, 2919, 1617, 1458$ and 1272 cm^{-1}
2	crystalline	anatase	-
5	amorphous	-	$\sim 3070, 2900, 1609$ and 1459 cm^{-1}
6	amorphous	-	$\sim 3068, 2900, 1600, 1480$ and 1270 cm^{-1}
7	evidence of crystallization	-	-
8	crystalline	anatase + brookite	-
10	amorphous	-	$3072, 2926, 1617$ and 1266 cm^{-1}
12	evidence of crystallization	-	2933 cm^{-1}

Table 2: Micro/structural characteristic and purity of TiO_2 thin films prepared under investigated extraction conditions.

TiO_2 thin films processed by scCO_2 (Sample 1) were amorphous as expected (Figure 2a). Concerning their purity, in Raman spectra the surfactant bands attributed to valence and deformation vibrations $\nu(\text{C-H}, 3072\text{ cm}^{-1})$, $\nu(-\text{C-H}, 2919\text{ cm}^{-1})$, $\nu(\text{C=C}, 1617\text{ cm}^{-1})$, $\nu(\text{C-C aliphatic}, 1272\text{ cm}^{-1})$ and $\delta(\text{H-C-H}, 1458\text{ cm}^{-1})$ were observed (Figure 2b), indicating that the solubility of surfactant in scCO_2 is not sufficient and it needs to be enhanced to totally remove the surfactant from films. Using pressurized water extraction at 150°C and 10 MPa (Sample 2) the crystallization of anatase occurred (Figure 2a), however, the films were not homogeneous with respect to their appearance. The purity of the films was not determined. Based on both previous observations, the extraction by supercritical carbon dioxide with parallel injection of water in two different arrangements was tested (Sample 5 and 6). In both cases, when scCO_2 at 50°C and 30 MPa was saturated by 30 wt.% of H_2O (Sample 5) or via

wetted globules (Sample 6), titania thin films were amorphous with some carbon content. However, increased temperature 150°C at 30 MPa with 30 wt.% of H₂O in scCO₂ (Sample 7) initiated the crystallization of films. At lower pressure of 10 MPa at 150°C with 30 wt.% of H₂O in scCO₂ (Sample 8) even the anatase–brookite mixture crystallized. The improved crystallization of titania thin films at lower pressure at temperature 150°C will be probably associated with enhanced solubility of surfactant in such mixture of supercritical and pressurized fluids. The lowered flow of scCO₂ (0.2 mL/min) at lower H₂O concentration of 18 wt.% (Sample 10) did not result in crystallization of titania films. Using extraction by scCO₂ modified with 18 wt.% of H₂O and 18 wt.% of CH₃OH (Sample 12) the initial crystallization of anatase thin film was detected. Besides that, the purity of titania thin films (the degree of surfactant removal from thin film) was significantly improved in comparison *e.g.* with Sample 7.

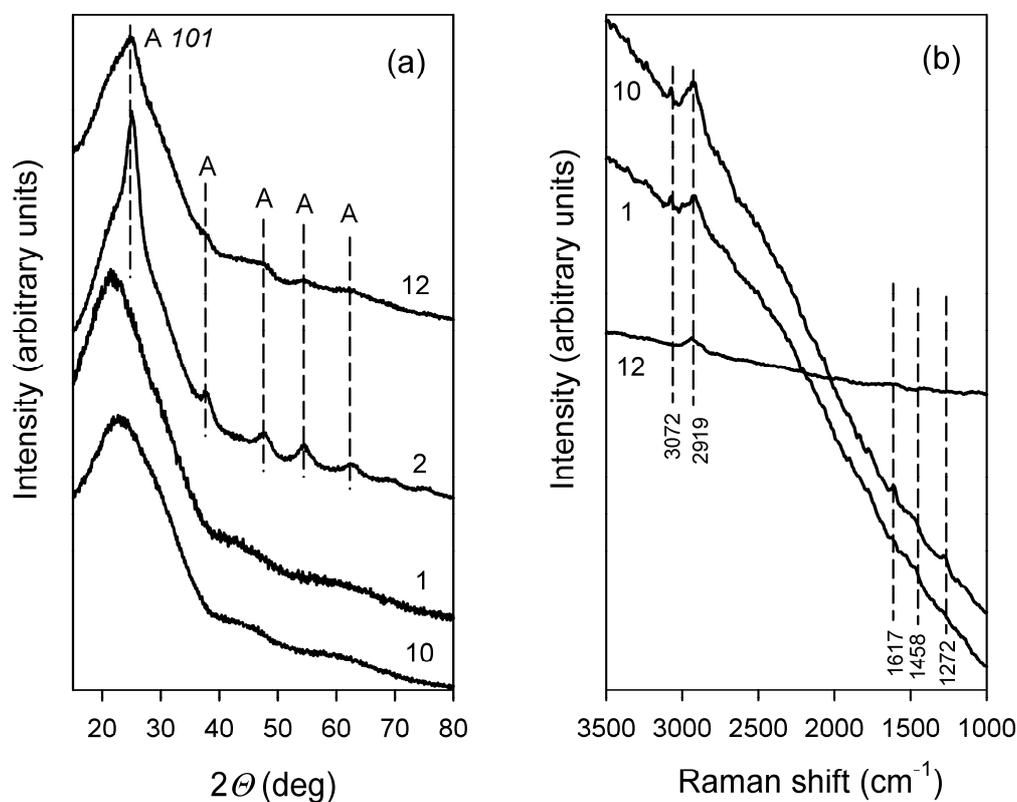


Figure 2: (a) XRD patterns and (b) Raman spectra showing surfactant bands recorded over selected TiO₂ thin films.

Surface morphology and homogeneity of selected TiO₂ thin films prepared by using supercritical carbon dioxide drying with parallel injection of modifiers - water and methanol – can be seen in Figure 3a and b. It is visible in a case of Sample 10 that the TiO₂ thin films were highly homogeneous without any evident surface defects. In a case of Sample 12 the TiO₂ films were also homogeneous, but possessing different color indicating different crystallinity and/or purity.

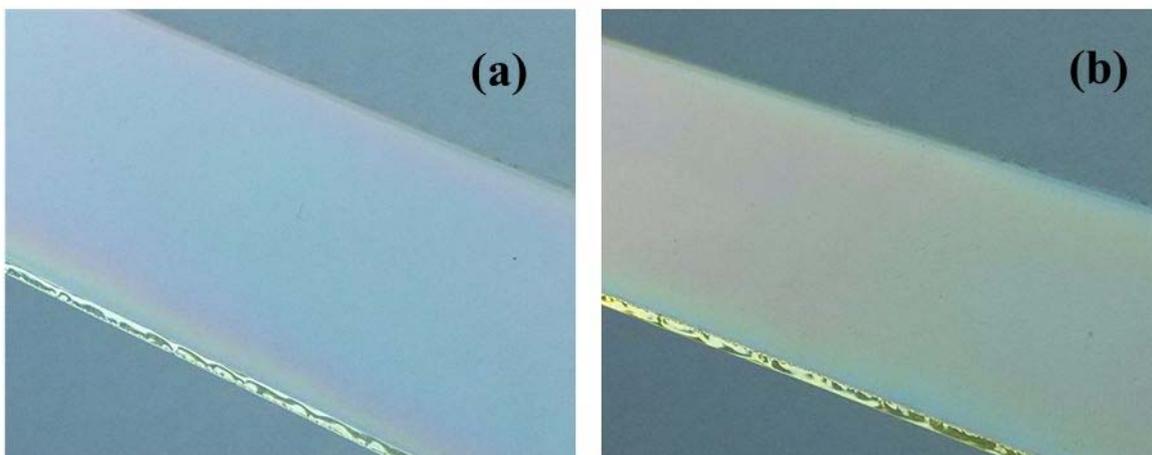


Figure 3: Pictures of TiO₂ thin films prepared by using supercritical carbon dioxide drying with parallel injection of modifiers, 1 layer; (a) Sample 10 (scCO₂ + H₂O (18 wt.%), 50°C, 30MPa, flow 0.2 mL/min) and (b) Sample 12 (scCO₂ + H₂O (18 wt.%) + CH₃OH (18 wt.%), 50°C, 30MPa, flow 0.5 mL/min).

CONCLUSION

Preparation of TiO₂ thin films by using (i) supercritical carbon dioxide combined with modifiers such as water and/or methanol and (ii) pressurized water in a flow regime was investigated. Using pressurized water extraction the crystallization of anatase thin films took place, but films were not homogeneous concerning their appearance. Extraction by scCO₂ with 30 wt.% of H₂O at 30 MPa and elevated temperature 150 °C led to initiation of TiO₂ anatase crystallization. Crystallization of TiO₂ films occurred also at lower pressure of 10 MPa. Addition of CH₃OH caused significant enhancement of solubility of used surfactant in scCO₂ and thus it resulted to TiO₂ thin films of higher purity.

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