

STRUCTURAL STUDY OF TAILORED TITANIA THIN LAYERS

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Received May 7, 2008

Accepted August 1, 2008

Published online October 3, 2008

Thin nanolayers of titania prepared by repeated dip-coating of silica glass into a transparent homogeneous sol made from nonionic surfactants with various numbers of oxyethylene units were studied. Calcination in air stream was used to convert transparent gel layers into anatase layers. The surface morphology, roughness, structure and texture properties were estimated by nitrogen physical adsorption, X-ray diffraction characterization, atomic force microscopy, transmission and scanning electron microscopy. Additionally, the contact angle determination was tested as a rapid method for evaluation of the titania layer surface quality. The influence of the number of oxyethylene units in surfactants on texture and structure properties of the prepared titania layers was found and discussed.

Keywords: Sol-gel processes; Thin films; Texture; Nanostructures; AFM; XRD; Nitrogen adsorption.

Lately, a huge research interest in nanoporous titania with special attention to its photocatalytic properties, which significantly widens its promising application potential, has been noticed¹⁻⁵. Nowadays titania is prepared in various forms like nanotubes, powder particles and also transparent thin layers deposited on carriers⁶⁻⁹. Thin titania layers deposited on suitable carriers seem to be the optimal arrangement for industrial application of photocatalytic reactions. To achieve high photocatalytic activity it is necessary to prepare crystalline anatase with a suitable grain size, purity and texture morphology. For optimization of the photocatalytic activity the knowledge

of structural and textural properties of titania layers is indispensable. Also the guaranty of the reproducible preparation of titania with precisely defined properties is necessary for potential industrial applications. Usually, the authors use various surfactants with different chain lengths¹⁰⁻¹³ for synthesis of the fine crystalline TiO₂. Studies concerning relations between photocatalytic activity of the prepared titania, structure and texture properties and the surfactant chain length have appeared only rarely¹⁴⁻¹⁶. Therefore, our study is focused on the relationship between the number of oxyethylene units in nonionic surfactants used for preparation of a set of various titania layers by dip-coating via the sol-gel method and morphology, roughness, type of titania phase and textural properties of the prepared titania layers. Additionally, the contact angle determination as a rapid and easy method suitable for evaluation of the surface quality of prepared titania layers has been tested, too.

EXPERIMENTAL

Sol Preparation and Layer Deposition

Nano-TiO₂ was synthesized by a sol-gel process. Titanium(IV) isopropoxide (Ti(OCH(CH₃)₂)₄, Aldrich, 99.999%) was added drop by drop into formed inverse micellar solution made from cyclohexane (Aldrich, 99.9+%, HPLC grade), nonionic surfactant Triton X (Aldrich) and water. Detailed characteristics of five tested Tritons X with various lengths of polar (hydrophilic) part are summarized in Table I. The molar ratio of cyclohexane/Triton X/water/Ti(OC₃H₇)₄ was kept⁷ at 11:1:1:1.

First, cyclohexane, Triton X and water was gradually mixed and vigorously stirred for 15 min for homogenization and formation of inverse micelles. Then, the titanium(IV) isopropoxide was regularly dropped to the micellar solution under continuous stirring. After

TABLE I
Physical and chemical properties of tested Tritons X

Type of Triton	Molecular formula	No. of oxyethylene units	Molecular weight g/mol	Density g/cm ³
Triton X102	C ₃₉ H ₇₂ O _{13.5}	12.5	756.0	1.100
Triton X100	C ₃₃ H ₆₀ O _{10.5}	9.5	624.8	1.070
Triton X114	C ₂₉ H ₅₂ O _{8.5}	7.5	558.8	1.058
Triton X45	C ₂₃ H ₄₀ O _{5.5}	4.5	404.6	1.037
Triton X15	C ₁₇ H ₂₈ O _{2.5}	1.5	272.4	1.050

the isopropoxide addition the sol was stirred for additional 10 min for homogenization and then left standing for two hours to stabilize. In this way the sol for dip-coating was prepared.

Ultrasonically cleaned glasses were dipped into the sol (40 ml) with velocity 6 cm/min and kept in the sol for 10 s. After 4 h stabilization the rigid gel layer was formed. The content of organics was reduced by calcination (400 °C, 4 h, 1 °C/min) in air stream. After this treatment a thin layer of transparent nanoporous titania was obtained. To guarantee the homogeneity of the titania layer this procedure was repeated at least four times.

Sample Characterization

Textural properties. Textural properties of samples were evaluated from nitrogen physical adsorption-desorption isotherms at 77 K obtained with the ASAP2020M instrument (Micromeritics, U.S.A.) on titania powders prepared from the same sol as titania layers. Before analysis, samples were dried at 105 °C for 24 h in vacuo (10^{-6} Pa).

Mesopore surface area (S_{meso}) and micropore volume (V_{μ}) were evaluated from measured nitrogen physical adsorption-desorption isotherms at 77 K by two independent methods: modified BET equation¹⁷ and t-plot constructed by nonporous TiO_2 standard isotherm¹⁸. Results from both methods were identical. Pore-size (r_p) was determined by BJH method by using nonporous TiO_2 standard.

Organic elemental analysis. The purity (carbon content in %) of powders was specified on the Elementar vario EL III (Elementar Comp.). The detection limit of the analysis was 0.1%.

Atomic force microscopy (AFM). Surface topography and roughness were measured by the atomic force microscope (AFM – Metris – 2001A – NC, Burleigh Instruments Inc.). A commercially available silicon probe was used. All AFM measurements were carried out in the contactless mode at ambient atmosphere and room temperature. The scan area varied from $1.2 \mu\text{m} \times 1.2 \mu\text{m}$ to $25 \mu\text{m} \times 25 \mu\text{m}$. Scans were made with resolution 256×256 pixels.

X-ray diffraction (XRD). X-ray diffraction measurements for the layer characterization were performed on the Panalytical-MRD 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° .

Contact angle. Contact angles for the titania layers were measured with a device developed at the Masaryk University, Brno. The device is equipped with an efficient Carl Zeiss lens and See System A40 software for data evaluation. For the contact angle measurement the water drops with volume about $2 \mu\text{l}$ were used. To estimate the reproducibility, the contact angle measurement was repeated at least five times for every sample.

Scanning electron microscopy (SEM). Dry sample particles were deposited directly onto 3 mm disks made of SPI carbon double sided adhesive tape. Samples were then sputter-coated with gold and examined in the Aquasem scanning electron microscope in the secondary electron mode at 15 kV. The digitally recorded images were processed by AnalySis 3.2 software.

Transmission electron microscopy (TEM). Sample particles, ca. 1 mm in diameter, were incubated in anhydrous acetone (3×2 h). After that, the particles were transferred into a 25% (v/v) Vestopal (Fluka) solution in acetone and placed on a rotator at room temperature for 24 h. Then, acetone was allowed to evaporate for 24 h. Subsequently, the samples were immersed into a fresh 100% Vestopal resin and after 48 h transferred into gelatin capsules

filled with fresh 100% Vestopal. The resin was polymerized at 60 °C for 48 h. Ultrathin sections were cut on the LKB ultramicrotome (type 4801 A) with a glass knife. Unstained ultrathin sections were examined with the Philips CM100 electron microscope at 80 kV and appropriate magnification. Digital images were recorded with the MegaViewII slow scan camera and processed with AnalySis 3.2 software.

RESULTS AND DISCUSSIONS

Five various Tritons X (with 1.5–12.5 oxyethylene unit) were used for testing the influence of the hydrophilic part length on the quality of the resulting titania layers. In Table II, textural properties of calcined TiO₂ prepared with all tested Tritons X are summarized. As can be seen, there is no relation between textural properties of the prepared titania and the length of the surfactant hydrophilic part. All prepared samples possess the similar pore structure; all samples have the same pore radius – 1.7 nm (from adsorption branches of isotherms) and about 25% of pores are micropores. The only difference can be found in the specific surface areas of mesopores. For titanias prepared from surfactants with 4.5–12.5 oxyethylene units, the surface area varied between 61–102 m²/g with no obvious dependence. The mesopore surface area of the sample prepared with the shortest hydrophilic part (1.5 oxyethylene units) was approximately five times lower (15 m²/g). The residual carbon content was in all cases lower than 0.1%, i.e. below the detection limit.

SEM analysis was used to determine the thickness of calcined titania films deposited on glass. As can be seen from Table III, the thickness of four repeatedly coated titania layers prepared with Tritons X with the longest hydrophilic parts (7.5–12.5 oxyethylene units) is nearly the same –

TABLE II
Textural properties of calcined TiO₂ layers for various Tritons X

Type of Triton	S_{BET} m ² /g	S_{meso} m ² /g	V_{μ} mm ³ _{liq} /g	r_{p} nm	Micropores %
Triton X102	113	82	23.3	1.7	27
Triton X100	85	61	18.3	1.7	28
Triton X114	139	102	29.3	1.7	27
Triton X45	112	87	20.5	1.7	22
Triton X15	21	15	4.1	1.7	29

ca. 1 μm . The sample prepared with Triton X45 (4.5 oxyethylene units) had a lower thickness – 842 nm; the lowest thickness was observed for the layers prepared with Triton X15. This result corresponds to the low surface area of titania layers prepared with Triton X15 and it is probably caused by steric reasons during hydrolysis and polycondensation for formation of the $-\text{Ti}-\text{O}-\text{Ti}-$ chain.

For a better illustration, Fig. 1A shows the SEM image of four titania layers prepared on glass and Fig. 1B the TEM image of titania crystals. In both cases the titania layers prepared from Triton X114 are shown.

The results obtained by XRD analysis offer a slightly different point of view. Figure 2 shows XRD patterns for calcined films prepared with five different Tritons X, deposited on glass together with the pattern of pure glass. It can be seen that diffraction patterns for titania prepared with Triton X15 and Triton X45 are similar to glass and do not indicate the presence of any crystalline phase. On the other hand, the results for titania layers with Triton X114, X100 and X102 clearly demonstrate the presence of crystalline phase and the phase analysis confirmed the presence of nearly pure anatase. The diameter of anatase crystallites evaluated by modified FOX

TABLE III

Thickness of calcined titania films deposited on glass (by SEM analysis)

Triton	X15	X45	X114	X100	X102
Thickness of four coated layers, nm	435	842	1000	909	1110

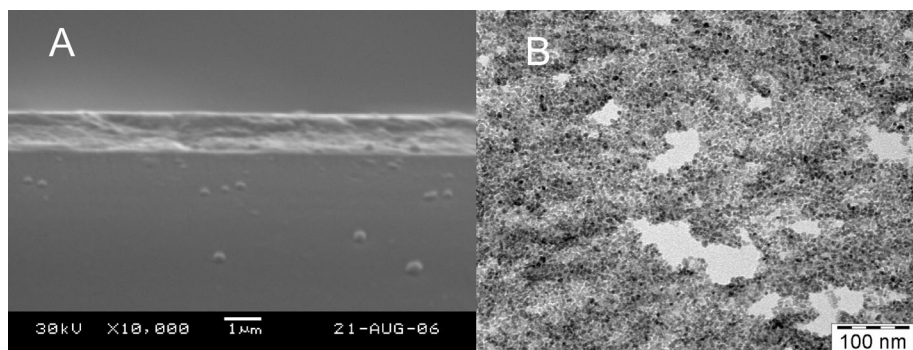


FIG. 1

SEM image of titania thin layer on glass prepared from Triton X114 (A), TEM image of titania crystals prepared from Triton X114 (B)

programme (developed at FMP CU) varied between 13–15 nm. It is twice larger than the crystal diameter determined for powder samples⁷. This may be caused by the required repeated calcination when the next layer is coated.

The findings obtained by XRD analysis were corroborated by AFM analysis (Fig. 3), where the surface topography and roughness of the calcined layers for all tested Tritons X are shown. It is seen that the surface layers

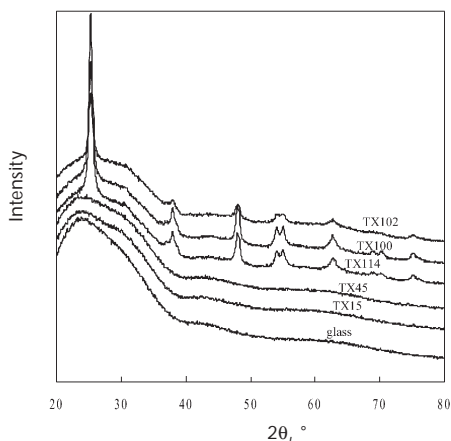


FIG. 2
XRD patterns of pure glass and calcined films (four deposited layers) synthesized with various Tritons X

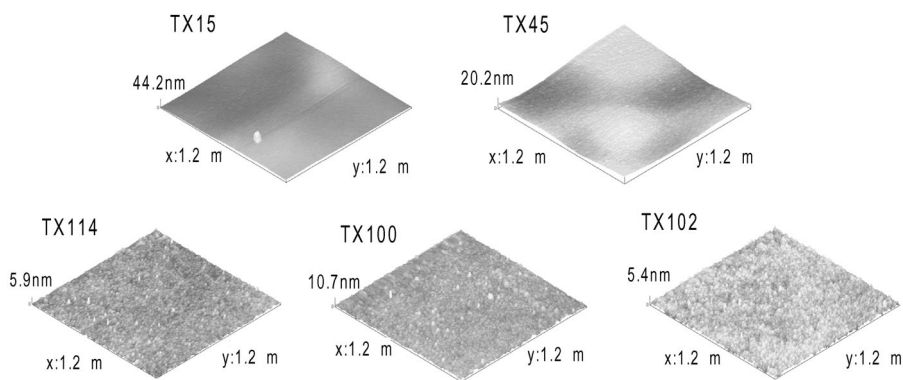


FIG. 3
Photographs of calcined layers from AFM analysis

prepared with surfactants Triton X15 and X45 are nearly smooth without the presence of crystallites. The surface layers prepared with Triton X114, X100 and X102 are somewhat rough with the size of crystallites in the range 10–14 nm.

Hence, for evaluation of surface quality of the prepared thin titania layers, it was necessary to apply sophisticated techniques (AFM, XRD) which require complex evaluation. Therefore the contact angle determination was judged as a rapid and easy method for evaluation of the surface quality of titania layers. The obtained results for all prepared samples are summarized in Table IV. As can be seen the determined mean contact angles increase in correspondence with the hydrophilic part length (the number of oxyethylene units) of Tritons X; the lowest contact angle (3.75°) was found for Triton X15 and the highest (27°) for Triton X102. The conspicuous change between amorphous and crystalline layers can be well seen, too. These results agree with those obtained by XRD and AFM analyses.

The reproducibility of the contact angle method was assessed for two titania layers with Triton X15 and three with X114. While the reproducibility for layers with Triton X15 is very good (deviation less than 1%), the results for Triton X114 layers are worse (ca. 10%). Clearly, the reproducibility of preparation of amorphous titania layers is very good, but the reproducibility of

TABLE IV
Measured and calculated contact angles for tested Tritons X

Type of Triton	Contact angle, °								Mean contact angle, °	Std. err. °
Triton X15	3.3 4.0	3.8 3.4	4.2 3.3	3.4 4.2	3.1	4.4	3.6	3.7 3.8	3.75	0.13
Triton X45	6.0	8.0	6.8	8.5	7.7			7.4	7.4	0.45
Triton X114	16.5 18.6 23.9	16.9 20 24.6	16 18.8 28.4	15.1 22.7 27.9	15.7 22.1 28.2		22.8	16.0 20.8 26.6	21.2	1.15
Triton X100	36.4	32.3	24.8	22	20	21.6	24.5	25.9	25.9	2.30
Triton X102	32.9	28.8	25.7	24.7	24.3	25.5	27	27.0	27	1.14

preparation of crystalline titania layers is worse for crystal size varying between 10–15 nm. Hence, the contact angle depends not only on the type of layer (amorphous, crystalline), but also on the size of titania crystals.

CONCLUSIONS

The influence of various surfactants used for the titania thin layer preparation on the surface morphology, roughness, structural and textural properties and contact angles was studied. It was shown that the number of oxyethylene units in the surfactant can significantly influence the morphology of the layer surface; more than 7 units lead to a crystalline phase and less than 4.5 units lead to an amorphous phase.

For rapid and easy determination of the surface quality of titania layers, the method based on the contact angle measurement was successfully tested. It was confirmed that the method can detect differences between crystalline anatase layers and amorphous layers of titania; this can be used for confirmation and authentication of the suitability of titania layers for utilization in photocatalysis.

The financial support of the Academy of Sciences of the Czech Republic, Program Nanotechnology for Society (KAN400720701) and of the Czech Science Foundation (Grant No. 203/08/H032) is gratefully acknowledged.

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