PREPARATION AND CHARACTERIZATION OF THIN NANOCRYSTALLINE TIO_2 LAYERS

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Abstract. Thin nanolayers of titania prepared by repeated dip-coating of silica glass into transparent homogeneous sol from nonionic surfactants with various number of oxyethylene units were studied. Calcination in the air flow and/or extraction by supercritical CO_2, subcritical H_2O and subcritical CH_3OH were used to convert transparent gel layers into anatase layers. The influence of individual surfactants on the surface morphology, roughness, structural and textural properties was evaluated.

Keywords: Sol-gel method, thin films, texture, nanostructure, AFM, XRD, nitrogen adsorption.

1. Introduction

Recently, a huge research interest to nanoporous titania with special attention to its photocatalytic properties, significantly widening their promising application

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potential, was noticed.[1–5] Nowadays, titania is prepared in various forms such as nanotubes, powder particles and transparent thin layers deposited on carriers[6–9] to optimize its photochemical efficiency. To achieve high photo-catalytic activity it is necessary to prepare crystalline anatase with suitable grain size, purity and textural morphology. Thin titania layers deposited on suitable carriers seem to be an optimal solution for industrial applications of the photo-catalytic reactions. For optimization of the photocatalytic activity the knowledge of structural and textural properties of titania layers is indispensable. Unfortunately, such studies appear only rarely.[10] Therefore our study was focused on preparation of a set of various titania layers by dip-coating via sol-gel method controlled in inverse micellar environment with tailoring textural and structural properties for photoactivity.

2. Experimental

2.1. SOL PREPARATION AND LAYER DEPOSITION

Nano-TiO_2 was synthesized by sol-gel process. Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, Aldrich, 99.999%) was added into formed inverse micellar solution of cyclohexane (Aldrich, 99.9+%, HPLC grade), nonionic surfactant Triton X-(Aldrich) and water. The molar ratio of cyclohexane/Triton X-/water/ $Ti(OC_3H_7)_4$ was kept at 11/1/1/1.[7]

Firstly, the solution of cyclohexane, Triton X and water was intensively stirred for 15 min for homogenization and formation of inverse micelles. Then, the titanium isopropoxide was regularly dropped into the micellar solution under continued stirring. After the addition of the isopropoxide the sol was stirred for additional 10 min and then left for 2 h for stabilization. In this way the sol for dip-coating was prepared.

Ultrasonicly cleaned glasses were dipped into the sol with velocity 6 cm/min and kept in the sol for 10 s. After 4 h of stabilization the rigid gel layer was formed. The organic content was then reduced by calcination in air stream and/or extraction by supercritic CO_2, subcritical H_2O and subcritical CH_3OH. After this treatment the transparent nanoporous titania thin layer was obtained. To guarantee the homogeneity of the titania layer surface this procedure was repeated at least three times.

To explain the influence of the number of oxyethylene units in Triton X on the textural and structural layer characteristics, five different Triton X (102, 100, 114, 45 and 15) were used for layer preparation. Their characteristics are summarized in Table 1 and for better imagination the structural formula of Triton X is shown in Figure 1.

TABLE 1. Characteristics of used Triton X.

Type of Triton	Triton X-102	Triton X-100	Triton X-114	Triton X-45	Triton X-15
Molecular formula	$C_{39}H_{72}O_{13.5}$	$C_{33}H_{60}O_{10.5}$	$C_{29}H_{52}O_{8.5}$	$C_{23}H_{40}O_{5.5}$	$C_{17}H_{28}O_{2.5}$
Number of oxyethylene units	12.5	9.5	7.5	4.5	1.5

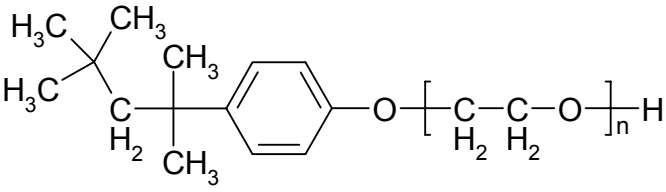

Figure 1. Structural formula of the surfactant Triton X molecule.

2.2. TREATMENT OF PREPARED GEL LAYERS

The samples were purified by calcination and three different extraction techniques and/or their combination: (a) supercritical fluid extraction (SFE), (b) subcritical water extraction (SWE) and (c) pressured solvent extraction (PFE).

Samples were calcined at 400°C for 4 h with temperature ramp 1°C/min in an air flow.

SFE was performed with a PrepMaster extractor (Suprex, USA) equipped with VaryFlow restrictor operating at 40°C. Carbon dioxide of SFE/SFC purity was used as extraction medium. The samples were placed in a 10 ml stainless steel extraction vessel and purified at 400 bar and 100°C with a CO_2 flow rate 1.5 ml/min for 500 min.

SWE and PFE were performed with the same system: a common HPLC pump (Varian, Series 200) equipped with a GC oven and Valco needle valve as a back pressure restrictor. Ultra pure water or methanol (gradient grade, Merck) was used for extraction at 5 ml/min flow rate; samples were purified in a 100 ml extraction vessel for 200 min.

2.3. SAMPLE CHARACTERIZATION

Textural properties of the samples were evaluated from nitrogen physical adsorption-desorption isotherms at 77 K obtained with the ASAP2020M (Micromeritics, USA).

Surface topography and roughness were measured by the Atomic Force Microscopy (AFM – Metris – 2001A – NC, Burleigh Instruments Inc.). A commercially available silicon probe was used. All AFM measurements were carried

out in the non-contact mode under ambient atmosphere and at room temperature. The scan area varied from 1.2 × 1.2 μm to 25 × 25 μm. Scans were made with 256 × 256 pixels resolution.

The sample crystallinity was characterized by X-ray diffraction (XRD). For all samples the Seifert-FMP or the Panalytical-MPD laboratory diffractometer with a Cu anode in the conventional focusing Bragg-Brentano experimental arrangement was used.

3. Results and Discussions

By dissolving the initial metal alkoxide in reverse micelles (of Triton X) the hydrolysis with a controlled amount of water, contained inside the micelle, takes place. At low water/surfactant molar ratio the generation of uniform spherical nanoparticles is expected. Micelles become entrapped in the forming inorganic matrix as an ordered liquid-crystalline phase that after treatment should be transformed into rigid nanocrystals essential for photocatalytic activity.

The surface topography and roughness of calcined layers for all used Triton X are shown in Figure 2. It is clearly seen that the surface layer prepared from Triton X15 and X45 surfactants are nearly smooth without presence of crystallites. Surfaces layers from Triton X114, X100 and X102 are somewhat rough with the size of crystallites in the range 6–10 nm. This is confirmed by XRD analysis (see Figure 3), where the shapes of curves for Triton X15 and 45 are similar to pure glass and do not indicate any crystalline phase; the curves for layers from Triton X114, 110 and 102 demonstrate clearly the presence of a crystalline phase. The phase analysis confirmed the presence of nearly pure anatase with a small amount of brookite.

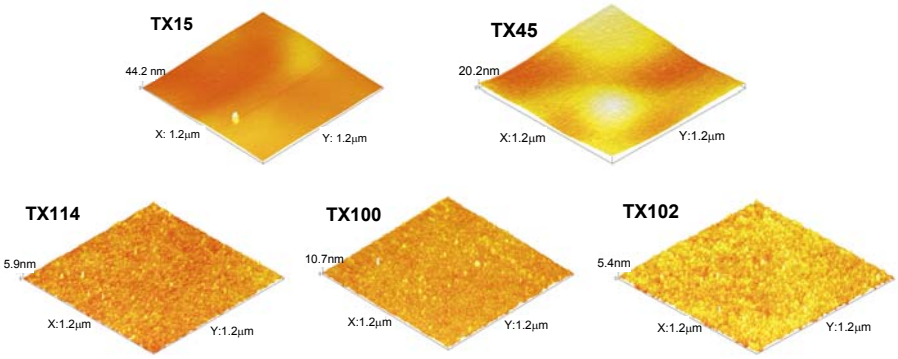

Figure 2. Photographs of calcined layers from AFM analysis.

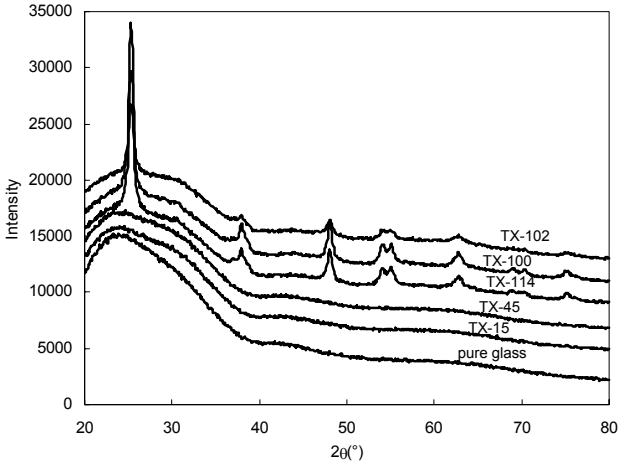

Figure 3. XRD patterns of pure glass and calcined films deposited on glass.

The influence of the treatment for removal of organic matter is shown in Table 2. Obviously, an ideal removal of the organic matter should preserve the order of the template structure. The common thermal treatment may result in the collapse of the forming structure and cause a significant decrease of surface area. This is noticed in Table 2, where the BET surface areas for all surfactants and calcination and extraction are summarized. The specific surface area of extracted samples is three to four times higher than for samples treated by calcination.

TABLE 2. Specific surface areas of calcined and extracted layers.

	Calcination	SFE $S_{BET}[m^2/g]$	SWE+PFE
TX-15	28.3	–	–
TX-45	70.2	292.6	250.4
TX-114	80.1	281.3	233.6
TX-100	77.5	278.7	246.3
TX-102	74.3	310.4	248.2

4. Conclusions

The influence of various surfactants used for preparation of titania thin layers on the surface morphology, roughness, structural and textural properties was studied. It was confirmed that thermal treatment causes an important decrease of specific surface area as compared to the organic matter removal by extraction, which results in approximately three times higher surface areas. It was

determined that the number of oxyethylene units in surfactant influences the morphology of the layer surface; more than 7 units leads to a crystalline phase and less than 4.5 units leads to an amorphous phase.

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