Formation of flow coated high catalytic activity thin films from the low temperature sol-gel titanium butoxide precursor

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The low temperature sol-gel approach is used in which the titanium butoxide (IV) precursor is hydrolyzed in the presence of acetic and nitric acids to form a bidentate acetate complex (1538, 1429 cm^{-1} IR doublet). It is known that the role of the acetic acid as a chemical modifier controls the condensation and oligomerization reactions, but other effect of the complex acetate ligand comprises the preferential crystallization of the titania into the anatase phase. In addition, it is found here, that the presence of such a ligand at acidic pH values considerably impacts the nanostructure i.e. the formation of smooth hydrophobic anatase films containing fine non-aggregated nano-crystallites with auto-assembled micro pores. The resulting anatase-acetate nano-crystalline material is used to form thin films by the flow coating process. 4.2 nm size crystalline anatase and fully dispersed nanoparticles form a pattern of ultra-small crystallites as shown by TEM that are presumably responsible for the remarkable smooth and macro porous thin films with applications in photo-catalysis.

Key words: A. Peptization, B. Ultra-small anatase particles, A, Flow coating, A. Sol-gel stable anatase sol.

Introduction

The maximum suspension stability achieved with experimental specimens is based on the maximum zeta potential values and the degree of dispersion of the particles depends strongly on the concentration and strength of the peptizer as reported by Al-Awady [1]. Bischof and Anderson [2] produced non-aggregated TiO$_2$ sol by peptization; They found that the hydrolysis of titanium isopropoxide or titanium ethoxide in excess water followed by peptization with acids (nitric, chlorhidric and sulfuric) yields a sol comprised of Titania particles. Anatase has been found to have an isoelectric point ranging from 4.7 to 6.7 [1]. At a 1-2 pH well below the isoelectric point, the surface of Ti02 would have a net positive charge yielding a non-aggregated sol. Non-aggregated sols can produce gels with high particle packing, on the other hand, aggregated sols results on an open structure, and higher porosity [3].Peptization affect photo catalytic activity of TiO$_2$ thin films. Vinogradov [4] obtained TiO$_2$ films by the low-temperature sol–gel method by means of different peptizers concluding its strong effect on the catalytic activity of the prepared samples.

Chemical additives such as organic acids (acetic acid), gSlycols, β-dicarbonyl ligands (ethyl acetoacetate (EACAC)) have often been used as chelating ligands that not only may influence the structure-property behavior [5-9], but may also exert an important effect on the stability of suspensions. In ceramics, It has been shown for example, that ascorbic acid forms complexes with nano-alumina surface through ligand exchange mechanisms and that steric stabilization is suggested for such nano-powder suspensions [10]. In the field of clays, significant enhancement of the zeta-potential (ζ) in heavy loam type soil samples treated with solutions of 1-hydroxypropane-1,1-bisphosphonic acid (HEDPA), 1,2-diaminoethane-$N,N,N\_,N\_$-tetraethanoic acid (EDTA), citric acid, and succinic acid was observed for a relatively broad range of concentrations and pH. [11].

The sol-gel process is one of the most used technologies to prepare thin oxide coating from solution or colloidal suspension. Since, this process produce films with good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost and good optical properties [12, 13]. In fact, deposition of nanoparticles from solution is a rapid simple and scalable method for creating nano- and micro-porous materials with high surface-to-volume ratio [14-16]. Haimi et al. and Phadke [17] obtained nano-porosity low roughness anatase (TiO$_2$) thin films by non-aqueous sol-gel dip-coating process, using titanium (IV) n-butoxide solution. The sol gel-flow coating method is an adequate technique to produce nansostructured thin films from colloidal suspension, allowing for self-assembly and the generation of functional nano-objects [18]. A dynamic self-assembly enabled by solvent evaporation represents a rapid and inexpensive route towards obtaining ordered

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structures over large areas. Mittal et al. [19] nanostructured thin films by directing the assembly of ellipsoidal TiO_2 nanoparticles by flow coating. Kim et al. [18] produced stripes, grids and ribbons by flow coating, using a non-aqueous dispersed sol of CdSe nanoparticles functionalized with ligands.

In the present work, anatase titania thin films were prepared from well dispersed sols prepared out of titanium butoxide (IV) precursor that was hydrolyzed in the presence of acetic and nitric acids to form a bidentate acetate complex $Ti(BuO)_4$. This ligand played a fundamental role on controlling thin film microstructure in particular, limiting particle size, sol stability and micro-porosity auto assembly. Films were formed by flow coating the sols on glass substrates that enabled processing into well-organized texturized homogeneous structures during the instantaneous solvent evaporation stage.

Experimental

The experimental route to film formation is framed in Fig.1. The nano-crystalline anatase colloid was obtained by the aqueous acidic sol gel low temperature process. $Ti(OBu)_4$ was added into distilled water to form a precipitate, that was centrifuged, washed, and redispersed in acid as detailed elsewhere [20]. It was then heated at 90 °C and vigorously stirred under reflux conditions for 12h, becoming a translucent blue-white dispersion. The flow coating technique that is ideal for self-assembly and the generation of controlled nanostructures consists of an angled knife blade rigidly attached to a vertical and horizontal motorized translation stage (Fig. 2). The nanoparticles solution is loaded and trapped between two plates by capillary forces that leads to migration and deposition of nano-particles towards the contact line, caused by an outward flow driven by solvent evaporation [19, 21]. 20 µL of nano-crystalline anatase colloidal suspension containing 12 wt. % solid particles was placed between the substrate and the blade. Subsequently, the substrate is moved at a constant velocity and a fixed blade angle to form the film. Finally, the nano-crystalline thin films were dried at 100 °C for 5 min. The film backing up the substrate was soda lime glass (corning 2947). These glasses were thoroughly washed and rinsed with deionized water and ethanol, previously to the film formation.

The resulting thin film nanostructures were characterized to determine crystallinity, particle size, ligands and roughness in the film obtained by flow coating. Thin films nanostructures were examined by a TEM Philips TECNAI 20 super Twin, at 200 kV. TEM samples were directly observed from titania thin films. Film thickness was measured by scanning electron microscopy (SEM, JSM-7600F) field emission scanning electron microscope,
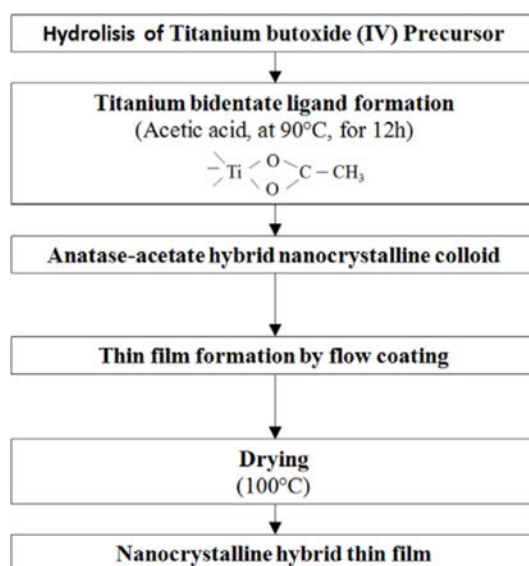

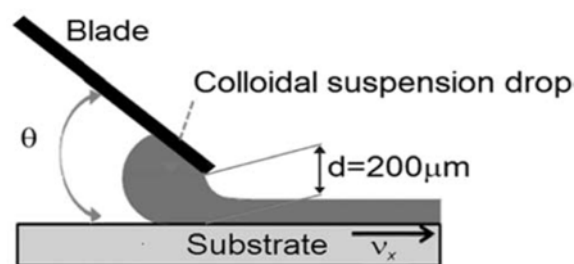**Fig. 1.** Experimental route for the low temperature thin film formation.

Fig. 2. Scheme of the flow coating process.

JEOL. IR spectra measurements were carried out by means of a Bruker Tensor 27 spectrometer in the 2400-1000 cm^{-1} wave number range. Roughness was assessed by AFM JEOL JSPM-5200 in the tapping mode.

Degradation of methylene blue dye was used to determine the photo catalytic activity of the anatase thin film. Thin films and the methylene blue solutions were irradiated with a 4-W UV lamp (UVP Inc.). 200 µL of methylene blue solution were put on anatase nano-crystalline hybrid thin film under UV light during 0, 5, 20, and 40 min, to evaluate the photo catalytic activity of the anatase film.

Results

Anatase nanoparticles were obtained through a sol-gel route in which the titanium butoxide (IV) precursor is hydrolyzed in the presence of acetic acid to form a bidentate acetate complex as seen by FTIR in Fig. 3, that displays the 1538, 1429 cm^{-1} doublet which stands for the asymmetric and symmetric stretching vibrations of the carboxylic group coordinated to Ti as a bidentate ligand. The gap of 109 cm^{-1} between these signals
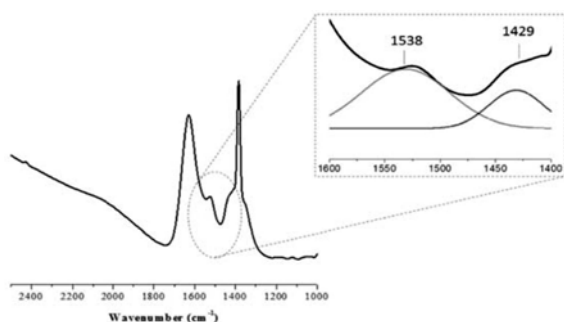
Fig. 3. Infrared spectra of the 1538, 1429 cm^{-1} doublet of the acetate bidentate ligand.

suggests that the acetate acts preferentially as a bidentate rather than as a bridging ligand between two titanium atoms [22]. The formation of the nano-size anatase nuclei is seen by Fig. 4 giving rise to the anatase carboxylate complex that conceptually describes the surface chemisorption process of anatase nanoparticles towards a bidentate ligand providing high stability to the resulting hybrid nano-structure. Anatase fully
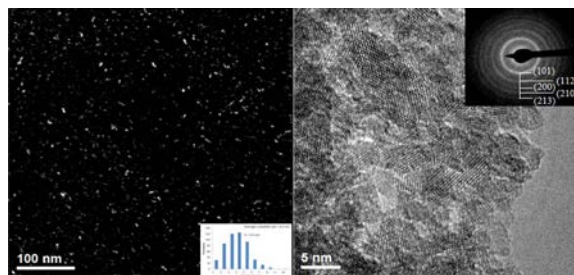

Fig. 5. Dark Field TEM, HRTEM and electron diffraction (inset) of nano anatase powders showing highly dispersed and fully crystalline powders.

dispersed nanoparticles are clearly shown in Fig. 5 (left picture) by means of dark field TEM; The average ultra-small particle size statistically determined is 4.2 ± 1.5 nm (inset). Fig 5 (right picture) is a HRTEM micrograph of the ultra-small anatase particles and its
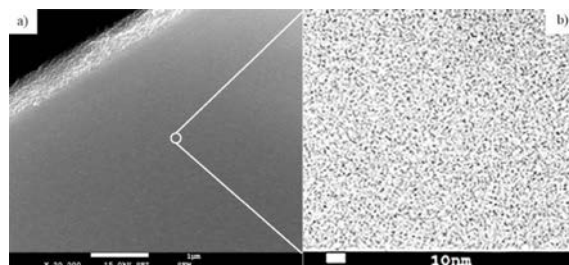

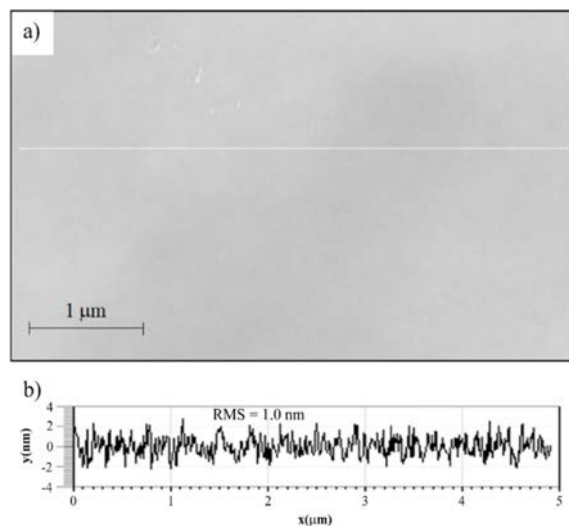**Fig. 6.** FESEM of flow coated thin film. Zoom high resolution image Shows micro porosity within particlesl.

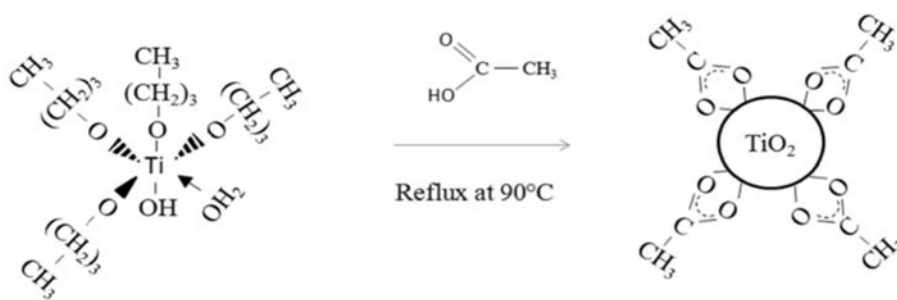**Fig. 7.** AFM showing thin film roughness (1.0 nm RMS).

Fig. 4. Surface chemisorption of anatase nanoparticles toward bidentate ligand binding.
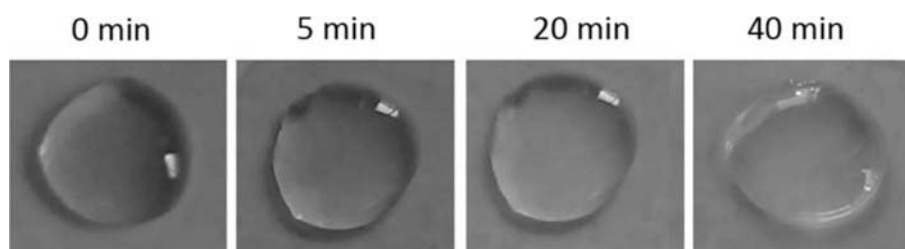

Fig. 8. Photo catalytic degradation of methylene blue drop on the 560 nm thick anatase hydrophobic film under UV light 0, 5, 20, and 40 min.

corresponding (101), (112), (211), diffracting planes shown by electron diffraction (inset). Fig. 6 is a FESEM characterization of flow coated thin films mounted onto soda lime silica glass. The film depicted is a 660 nm thick smooth finish anatase; The picture at the right hand side is a high resolution image that shows the dark, well rounded micro-pores located within the fine, well dispersed nano-particles. Fig. 7 is an AFM micrograph displaying the thin film specular finish free of micron size defects and a surface roughness average value (RMS) of 1.0 nm. Fig. 8 shows drops of 200 µL of methylene blue solution on anatase thin film under UV light irradiation being degraded by the anatase 4.2 nm particles for up to 40 min. Despite the very low amount of anatase is involved in the reaction and the fact that the drops do not wet the surface, it suggests a high photo catalytic activity of the film. The hydrophobicity and the high contact angle of the films is self-evident by the same Fig.

Discussion

A key finding of this research has been the synthesis of unusually ultrafine non-aggregated anatase powders of 4.2 nm average particle size which has led to readily flow coating transparent 660 nm thick films that are free of defects, so smooth as to present specular reflection, and exhibit high photo catalytic activity. The effect of the acetic acid to form a titanium alkoxo carboxylate complex during the Sol-Gel synthesis has been dealt with elsewhere [7] and may have multiple effects. It can control the hydrolysis and condensation reactions up to a point in which the nano-crystalline nuclei do not grow any further because of the limiting action of the bidentate ligand [20] thus, rendering ultrafine anatase particles. Also, the chelate carboxylate ligand may act as a peptizer increasing the stability of the sol by the steric hindrance mechanism [15]. Further dispersion of particles was achieved through the use of acidic conditions, since the zeta potential within the 1-2 pH range is well below the isoelectric point, thus rendering a stable sol. The combined effect of the above conditions may be responsible for the very high sol stability experimentally accomplished and that was reflected on the unique compact nanostructure, disclosing about 1 nm rounded micro pores that may be related to the anatase linking carboxylate ligand as suggested in the literature [17]

The resulting thin films low RMS values of surface roughness may be the effect of gels with an efficient packing of fully dispersed ultra-fine anatase nanoparticles relevant as photo-catalytic material. The absence of large porosity brings about the hydrophobicity of the films as the water drops do not wet the anatase thin films. The 4.2 nm size anatase nanoparticles may be expected to significantly exceed the photo catalytic efficiency of larger grained 11-100 nm anatase particle size, since the very high surface area of the 4.2 nm particles may be nearly one order of magnitude higher than that of the larger particles [23, 24]. One of the reasons that we observed high film photo-catalytic efficiency may be the strongly non-aggregated nature of the ultra-fine anatase particles; Since, some authors [18] offset the surface area advantage of ultra-fine particles on the grounds of particle segregation. The films present the phenomenon of hydrophobicity as might be anticipated considering the absence of defects and large pores within the films. Such phenomenon may occur, considering the experimental films only have micro pores, as it is known by the literature that materials with pores larger than 50 nm, progressively present less hydrophobicity [25].

Conclusions

Peptization of Ultra-small anatase particles achieved through the use of acidic media i.e. acetic and nitric acids results on the formation of a bidentate acetate complex that presumably influences particle size and dispersion. The sol is stable at the acidic range, 1-2 pH well below the isoelectric point of the anatase. Such stable and fully dispersed anatase primary particles allows the formation of flow coated transparent, homogeneous, specular thin films free of large defects. The non-aggregated nature of the particles presumably leads to the well compacted nanostructure and the outstanding micro-porosity that is presumably responsible for the self-evident hydrophobicity of the films. The extremely small particle size and the high photo-catalytic activity of the thin films may also be the result of the highly dispersed nano-particles.

Acknowledgments

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