Novel and facile synthesis of transparent-monolithic TiO₂ gels by sol-gel method based on an esterification reaction

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Transparent TiO₂ monoliths were obtained through a modified sol-gel route from titanium isopropoxide as a precursor. By controlling the hydrolysis of this precursor through the intermediate of esterification reaction between acetic acid and isopropanol at 40 °C, transparent TiO₂ xerogel monoliths were obtained. The monoliths prepared by this method were transparent in the wavelengths between 400 nm and 700 nm. Fourier transform infrared (FT-IR) spectroscopy suggested that the acetic acid played also an active role as a chelating agent, forming Ti[(OH)_y(OOCCH₃)_x] less reactive species. Powder X-ray diffraction confirmed the amorphous-to-anatase phase transformation with the formation of unknown Ti-containing complex at 90 °C. Only anatase TiO₂ could be observed in the samples calcined at 250 °C and 450 °C. Optical aspects of the gel (transparent-transluscent transformation of monolithic gel) and gelation time were controlled by changing the amount of external water.

Keywords: sol-gel; esterification; TiO₂; monoliths; transparent

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1. Introduction

Titanium dioxide, TiO₂, due to its unique physical and chemical properties such as high refractive index and high dielectric constant, has been used as a material for numerous applications in the field of photoluminescent materials [1], photocatalysis [2, 3], optics [4] and electrode materials [5]. For higher performance of these applications, it is necessary to control the shape of TiO₂ nanoparticles in desired structures, such as powders, films and monolithic gels. To achieve the flexible control of the shapes, sol-gel route based on titanium alkoxides precursors has been investigated and the synthesis of TiO₂ powders and films has been reported [6–8].

The preparation of pure TiO_2 monolith by the sol-gel method is not so common because two major problems arrive. One is a control of reaction rates which are typically too fast, resulting in precipitates or amorphous particles after addition of water. Another problem is the destructuration of the alcogel during the aging and drying processes [9].

Those two problems are not met so drastically in case of SiO_2 [10].

Thus, the control of reactivity of metal alkoxides is necessary in order to obtain sols and monolithic gels with desirable properties. The best known approach to control the hydrolysis and condensation during the sol-gel processing is the addition of chelating agents or modifiers such as acetyl acetone [11], diols [12], carboxylic acids (e.g. acetic acid) [13–16].

Conventionally, acetic acid has been adopted to control the hydrolysis of titanium sources based on slow release of water through the esterification reaction between acetic acid and alcohols. Recently, we have reported the preparation of transparent titania xerogel-monolith by controlling the hydrolysis of this precursor through the intermediate of the esterification reaction between acetic acid and methanol [17]. This method takes substantial time (90 days) to obtain a transparent monolithic gel.

The number of papers on the chemical modification of titanium alkoxide with acetic acid is undergoing an exponential increase. As often occurs in the case of an explosively growing subject,

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a certain degree of confusion is present in the literature. This is mainly due to the variety of synthetic methods and the selected ratios of Ac/Ti to prepare the new catalyst.

In all the experiments reported in the literature, the gel can be only obtained when water or acidified water (nitric acid) is added to the solution containing precursor alkoxide and acetic acid. The optical aspet of gel (transparent, transluscent and opaque) depends on the amount of water heterogeneously added to the solution.

However, to the best of our knowledge, there has been no report on the synthesis of transparentmonolithic TiO₂ gels obtained by a modified solgel method via the chemical modification of titanium isopropoxide with esterification mixture. This is an efficient method for introducing water homogeneously (*in situ*) into a solution and therefore avoiding the problems associated with mixing irregularities. This method takes only substantial time (3 days) to obtain a transparent monolithic gel. The precipitate formation never occurs. FT-IR spectra of the samples suggest that the acetic acid is chemically bound to the titanium by bridging acetates leading to Ti[(OH)_v(OOCCH₃)_x] oligomers.

2. Experimental

The esterification reaction between isopropanol (Riedel de Haein, 99.8 %) (27 mL) and glacial acetic acid (Panreac, Spain, 99.9 %) (20 mL), (molar ratio AcOH/isopropanol = 1) was carried out in a 250-mL round-bottom flask with a heating mantle on the top of a ring on the stand. The reaction was carried out without acid catalysis. The round bottom flask was carefully clamped in the bottom of a vertical reflux condenser. The cooling water entered the lower side arm of the condenser and collected at the upper side arm. The reaction mixture was brought to boiling using the Variac rheostat. The mixture was allowed to reflux for 60 minutes and then cooled slightly. 30 mL of the esterification mixture was added dropwise to 10 mL of Ti(IV)-isopropoxide (from Sigma-Aldrich, 97 %) under a continuous stirring at 40 °C during 30 min and 120 min. From the solution mixed for 30 min,

5 mL of transparent solution was poured on a glass Petri dish and then covered with a plastic film. 15 mL of the same solution was left in two glass tubes and then covered with a plastic film until the formation of transparent gel within one week. Holes were made in the film with a needle to control the speed of evaporation at room temperature. After gelification, the transparent gel was maintained by cooling at T < 0 °C. The solution mixed for 120 min was left in a glass tube at room temperature until gelification after three days. The flow chart of the synthesis of transparent and transluscent gels are shown in Fig. 1.



Fig. 1. Flow chart of the synthesis of transparent and translucent gels.

For comparison, a new sample with high acetic acid content (AcOH/Ti = 10) was also prepared by the same procedure. A white precipitate was formed after 30 min. The precipitate so obtained was aged overnight at room temperature to ensure conclusion of the hydrolysis.

Fourier transform infrared (FT-IR) spectroscopy study was carried out with a Nicolet Impact 400 spectrometer in the 4000 cm⁻¹ to 400 cm⁻¹ wavenumber range using a spectral resolution of 4 cm⁻¹ and a scan number of 40. In case of samples in a powder form, the pellets were made by adding 300 mg of KBr to 1 mg sample (0.3 %). This technique can, however, generate a phenomenon of diffusion greater for

high values of the wave number if the pellets are not perfectly transparent. For liquid samples or samples containing solvents (esterification reagents, titanuim isopropoxide), three drops of a sample were deposited on KBr pellets. The sampling was performed in a glove box to avoid hydrolysis due to ambient humidity. Before analysis, titanium isopropoxide was pre-distilled. Traces of water were removed from the glacial acetic acid by adding some acetic anhydride in the presence of a small quantity of CrO₃.

The unreacted acetic acid was determined volumetrically by titration of the solution with NaOH (1 M). The detailed results are listed in Table 1.

The crystallographic structure of the samples was determined by X-ray powder diffraction on an advanced D8, Bruker, Germany under monochromatic CuK α radiation. The data were collected in the 2 θ range of 10° to 60° with a step size of 0.028 and a counting time of 5 s/step. The anatase peaks measured by XRD analysis were assigned by comparing with those of PCD database. The spectra were recorded on samples dried at 90 °C. The UV-Vis absorption spectra were determined with a Perkin Elmer Lamda 950 spectrophotometer using PTFE (polytetrafluoroethylene) as a reference. The spectra were recorded in 200 nm to 800 nm wavelength range.

3. Results and discussion

3.1. Esterification reaction

The esterification reaction leads to progressive formation of water and isopropyl acetate *in situ*. The infrared spectrometer was used to get a visual evidence that a chemical change has occurred in an isopropyl acetate condensation reaction between isopropanol and acetic acid:

 $C_3H_7OH + CH_3COOH \rightarrow CH_3COOC_3H_7 + H_2O (1)$

The water produced *in situ* by the esterification reaction is difficult to identify because its vibration bands are masked by the presence of hydroxyl groups (–OH) of isopropanol and acetic acid. Thus, to highlight the esterification reaction, we followed

the formation of isopropyl acetate, which is produced in the same proportions as the water. FT-IR spectra of acetic acid, isopropanol, isopropyl acetate and water are shown in Fig. 2.



Fig. 2. FT-IR spectra of (a) acetic acid, (b) isopropanol, (c) isopropyl acetate, (d) water. The dashed lines correspond to the bands of isopropyl acetate.

The main bands of the isopropyl acetate (spectrum c) obtained after subtraction of the bands of the two reactants are given in Table 1 and correspond to those indicated in the literature [18]. It is well known that esterification is a reversible reaction limited by the low equilibrium conversion and slow reaction rate between reagents. Therefore, it was not surprising to find some unreacted acetic acid and isopropanol in the esterification mixture. The unreacted acetic acid was determined by titration of the solution with NaOH (1 M) (Table 2).

3.2. Effect of acetic acid and *in situ* water on acetate coordination mode

The esterification mixture obtained at 75 °C during 60 min (described above) was mixed with a desired amount of Ti(OC₃H₇)₄ precursors under stirring for 30 min. The experiments were performed with Ti = 0.034 mol, molar ratio AcOH/Ti = 5.5 and H₂O/Ti = 4.5 (Table 1). After intimate mixing, a drop of the solution was placed on KBr pellet for FT-IR measurement (Fig. 3). As shown in the spectrum (Fig. 3c), the bands at

	AcOH	+ iPrOH «	\rightarrow iPrOAc	$+ H_2O$
$T = 0 \min n_i \pmod{2}$	0.34	0.34	0	0
$T=60 \min n_f (mol)$	0.19	_	0.15	0.15

Table 1. Quantity of reagents and products in the esterification mixture after reaction time 60 min at 75 °C.

Table 2. Vibration frequencies of isopropyl acetate identified by infrared spectrometry after esterification reaction time 60 min at 75 °C.

Frequency	Attribution	Frequency	Attribution
vibration [cm ⁻¹]		vibration $[cm^{-1}]$	
617	_	1184	vC–C
870	-	1250	vC–O
935	-	1378	$\nu_{sym}C-H$
1016	_	1448	$\nu_{anti-sym} \text{ CH}$
1120	-	1754	ν C=O

 1006 cm^{-1} , 1127 cm^{-1} and 1168 cm^{-1} , 2965 cm^{-1} and 2870 cm^{-1} , characteristic of Ti(O–C) stretching vibration of isopropoxy groups OC₃H₇ bonded to titanium ions have disappeared [19].



Fig. 3. FT-IR spectra of: (a) $Ti(OC_3H_7)_4$, (b) mixture of esterification components, (c) transparent solution obtained after the addition of $Ti(OC_3H_7)_4$ to the mixture of esterification after 30 min, (d) after 120 min.

This excludes partially the presence of acetate ligands or hydrolyzed species, such as $Ti(OC_3H_7)_x(OOCCH_3)_yOH$ and $Ti(OC_3H_7)_xOH_y$ in the mixture [20]. The formation of -OH

groups (bands at 3400 cm^{-1} and 1633 cm^{-1}) in $Ti[(OH)_v(OOCCH_3)_x]$ species is then favored with high hydrolysis rates for a medium amount of water. The band at 1633 cm^{-1} is strongly screened by the dominant bands at 1553 cm⁻¹ and 1453 cm^{-1} . This result is similar to that published by Ivanda et al. [21] for the modification of Ti(IV)-isopropoxide through an esterification reaction between acetic acid and alcohol. The authors proposed that the hydroxylation of titanium alkoxide with water molecules generated in situ by esterification provided excellent control of the hydrolysis and condensation rate. The bridging acetates in $Ti[(OH)_{y}(OOCCH_{3})_{x}]$ species have appeared in FT-IR spectrum. The peaks at 1029 cm⁻¹, 1049 cm⁻¹, 1351 cm⁻¹, 1453 cm^{-1} , 1553 cm^{-1} , 1607 cm^{-1} (inset) and 1614 cm⁻¹ are assigned to adsorbed acetic acid on Ti sites [22-25]. In particular, the bands at 1614 cm^{-1} , 1553 cm^{-1} and 1453 cm^{-1} reveal that the acetate species (asymmetric $v_{asym}(COO)$ and symmetric $v_{svm}(COO)$ stretching vibrations) resulting from the acetic acid dissociation may bind to the Ti as a bidentate acetate ligands. The frequency separation ($\Delta v = 100 \text{ cm}^{-1}$) between the doublets at 1553 cm^{-1} and 1453 cm^{-1} indicates a coordination in bidentate geometry and suggests a bridging configuration. The peaks at 1795 cm^{-1} , 1296 cm^{-1} and 1410 cm^{-1} are due to the free AcOH molecules with monomeric and dimeric

(1720 cm⁻¹) forms [26]. Based on the above results, we suggest that we now have a polymeric titanuim acetate, such as $Ti[(OH)_y(OOCCH_3)_x]$ much less reactive species, with x and y between 0 and 2, from which all OC₃H₇ groups have completely disappeared (942 cm⁻¹) [27]. After gelification of the transparent solution under controlled conditions, the gels obtained are transparent.

Fig. 3d gives the FT-IR spectrum recorded for the same solution (described above) after reaction time 120 min. Due to complexity of the experiment, the titration of unreacted AcOH was very difficult at this stage. However, we can observe that the acetic acid interacted more strongly with the Ti atoms. This strong interaction has been further confirmed by the increase of the bands at 1029 cm⁻¹, 1049 cm⁻¹, 1553 cm⁻¹ and 1453 cm⁻¹, assigned to acetate groups bonded to Ti atoms. The weak band at 1345 cm⁻¹ is attributed to (CH₃) bending of acetate adsorbed onto the surface of titania.

The frequency shift of the band centered in the range of 1725 cm^{-1} to 1714 cm^{-1} together with the increase of the band at 1290 cm^{-1} suggest that some monodentate acetate ligands that exhibit these bands in the same region should be linked to Ti atoms. They can also be attributed to free AcOH but their intensity seems to be too high to be due to AcOH only. Furthermore, the band at 1248 cm⁻¹, characterstic of isopropyl acetate molecule rapidly increases with increasing reaction time with respect to isopropyl acetate before modification (spectrum b). This result reveals that the isopropanol C₃H₇OH (945 cm⁻¹) originated from $Ti(OC_3H_7)_4$ can participate in the esterification reaction 1. Based on the law of chemical equilibrium (law of mass action), the equilibrium of Fischer esterification can be driven to the left (formation of isopropyl acetate and water) by using an excess of isopropanol. Therefore, it is not surprising to detect a large amount of isopropyl acetate in the medium.

Fig. 4 shows the FT-IR spectra recorded for the xerogels obtained after drying the previous gels at T = 90 °C (where T > T_{boiling} isopropyl-acetate). Compared with Fig. 3, clear bands around 846 and 640 cm⁻¹ can be observed in Fig. 4, which can be assigned to the vibration of the Ti–O–Ti moiety in titanium oxide network, suggesting the formation of TiO₂. Simultaneously, the absorption bands of the acetate ligands at 1714 cm⁻¹ and 1290 cm⁻¹ disappear indicating that the monodenetate has transformed into the structure of Ti–O–Ti by a ploycondensation reaction [28]. It must be pointed out that the intensities of the peaks at 1553 cm⁻¹ and 1453 cm⁻¹ noticeably decreased and have shifted toward smaller wavenumbers, ultimately reaching 1534 cm⁻¹ and 1435 cm⁻¹. It can be assumed that the decrease in intensity results from breaking of the acetate bridges.



Fig. 4. FT-IR spectra of xerogels obtained after drying the gels at T = 90 °C: (a) xerogels obtained from the solution (30 min); (b) (120 min); (c) pure TiO₂ xerogel.

3.3. X-ray diffraction studies

The powder X-ray diffraction (XRD) patterns of the samples are shown in Fig. 5. No obvious diffraction peaks are observed in the XRD pattern of the sample synthesized for 120 min, suggesting that the xerogels adopt an amorphous phase. Another possible reason is that the content of crystalline phase in the sample is below the detection limit of this technique. To confirm this supposition, we evaluated the XRD of a new sample prepared with high acetic acid content (AcOH/Ti = 10) and dried at 90 °C. From the spectra in Fig. 5 (b to d) it can be seen that this sample is composed of amorphous phase, unknown Ti-containing complex and a small, but not negligible fraction of anatase (Pearson's Crystal Data PCD# 1003622). The XRD pattern is similar to that observed by Liao et al. [29]. They prepared anatase TiO₂ catalysts of different morphologies by solvothermal reactions of titanium n-butoxide and acetic acid (AcOH/Ti = 180) at different reaction temperatures of 120 °C to 180 °C. They showed that the sample prepared at 170 °C was composed of anatase TiO₂ and an unknown Ti-complex $Ti_6O_6(AcO)_6(OBu)_6$. Further study should be carried out to identify this complex. The synthesis route followed in this work confirms the formation of Ti-complex even at AcOH/Ti = 10, which has not been reported elsewhere. However, only anatase TiO₂ can be observed for the sample calcined at 250 °C and 450 °C.



Fig. 5. XRD patterns of as-prepared samples obtained:
(a) during 120 min, after drying at T = 90 °C;
(b) sample with AcOH/Ti = 10, heated at 90 °C;
(c) calcined at 250 °C; (d) at 450 °C.

3.4. UV-Vis absorption spectra

UV-Vis absorption spectra of transparent TiO_2 xerogel and TiO_2 anatase (commercial) are shown in Fig. 6. As expected, TiO_2 anatase characteristic absorption occurs in UV region in a wavelength of around 300 nm to 400 nm (3.2 eV). For transparent TiO_2 xerogel, the absorption spectrum changes dramatically in relation to neat anatase TiO_2 and spawns over the visible region (400 nm

to 700 nm), suggesting transparency of the material in the visible range. The results are similar to those reported in the literature for synthesized polymer TiO₂ [30, 31], ZnO [32] and ZrO₂ [33] films in an organic phase made of polycarbonate or polyesters, methyl methacrylate, such as polycaprolactone, poly(D,L-lactic acid), oleic acid and carboxylic acid. Mono- and bidentate complexes can be formed between titanium oxo groups and organic acid after condensation and oligomerization, providing a good homogeneity in the final material and maintaining transparency in the visible range.



Fig. 6. UV-Vis absorption spectra of: (a) transparent TiO_2 xerogel (obtained during 120 min after drying at T = 90 °C) and (b) TiO_2 anatase (commercial).

3.5. Optical aspect of gel

As reported in the preceding sections, all FT-IR features typical of $Ti(OC_3H_7)_4$ bonds have completely disappeared. This suggests that we now have a polymeric titanuim acetate $Ti[(OH)_y(OOCCH_3)_x]$. This species is less hydrolyzed than $Ti(OC_3H_7)_xOH_y$, increasing therefore the time of gelation. Upon aging for a week in glass tubes (Fig. 7a), the viscosity of the transparent solution gradually increased and stabilized to form transparent and yellowish gels. The gel appearance has not changed with changing of volume. There are two reasons responsible for this result. One possible reason is that the low temperature causes a decrease in reaction rate

of esterification and low generation of water *in situ*. Another reason is that the presence of small water content cannot hydrolyze and condense easily the new Ti[(OH)_y(OOCCH₃)_x] complex. The later species is slightly soluble and can be dissolved *in situ* in H₂O from esterification for a week without any further hydrolysis reaction. Hence, the formation of precipitate is suppressed. For practical use, the same transparent solution was coated on a glass Petri dish using the same experimental conditions described above (Fig. 7b). After drying at 90 °C over night, the sample was crashed in the form of shiny granules under the effect of heat flow (Fig. 7c).



Fig. 7. (a) transparent monolithic gel obtained after one week (two different volumes); (b) transparent gel coated on a glass Petri dish; (c) transparent xerogel obtained after heating at 90 °C; (d) optical gel transformation from transparent to transluscent (1: transparent solution prepared for 120 min, obtained after three days), (3: transluscent gel with 3 mL of water), (4: transluscent gel with 6 mL of water).

Doeuff et al. [34] showed that the transparent monolithic gel can be obtained only when external water is intentionally added to the transparent solution containing the titanium alkoxide and acetic acid. The reported experimental conditions were: AcOH/Ti = 1.5, H₂O/Ti = 4 and Ti = 0.8 mol·L⁻¹. This is not the case of this study. We focused only on the esterification reaction as an elegant resource to generate water homogeneously *in situ*.

When esterification reaction still advances at room temperature, the viscosity gradually increases up to a certain limit, indicating the presence of higher amount of water produced *in situ* from the condensation between excess of C_3H_7OH and unreacted acetic acid. In such case, there is an optical gel transformation from transparent to monolithic transluscent gel within three days (Fig. $7d_1$). Note that the viscosity of the transluscent gel can be maintained by adding 3 or 6 mL of external water (Fig. 7d, sample 3 and sample 4). Because the esterification reaction is reversible, the equilibrium (reaction 1) is driven to the left by adding water [35]. The gel remains transluscent without any precipitate.

4. Conclusions

A reliable protocol has been established that allows to prepare transparent and tansluscent, monolithic gels without any precipitate formation. That protocol implies the chemical modification of titanium (IV) isopropoxide by esterification products without external addition of water. The chemical modification changes the hydrolysis and condensation behavior of the $Ti(OC_3H_7)_4$ by the formation of a new molecular precursor $Ti[(OH)_v(OOCCH_3)_x]$ with the release of all isopropoxy OC₃H₇ groups. The bridging acetates are then less hydrolyzed than the isopropoxy groups, which allows avoiding the formation of precipitates in the presence of excess water. This increases the gelation time, favors polycondensation, and leads to monolithic gels where high polymers rather than small colloidal particles are present. The sample prepared with high acetic acid content (AcOH/Ti =10) is composed of amorphous phase: an unknown Ti-complex and an anatase phase.

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