

Titanium dioxide nanoparticles obtained by Sol Gel Method: Effect of the catalyst acids

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Resumen

Nanoanopartículas de óxido de Titanio han sido obtenidas por el proceso de sol-gel. El isopropóxido de Titanio fue hidrolizado en medio ácido con pHs entre 0.5 y 1. La hidrólisis fue catalizada con HCl, HNO₃ o HClO₄, y se estudió su influencia en la formación de las fases cristalinas del dióxido de Titanio, como el rutilo, anatasa y brookita. El proceso de peptización fue estudiado con Espectroscopias Visible e Infrarroja. El tratamiento hidrotérmico a 220 °C por 12 h produjo nanopartículas bien definidas, que fueron observadas por Microscopía Electrónica de Transmisión. La estructura cristalina fue estudiada por difracción de rayos X. Solamente la fase anatasa se obtuvo cuando se usó HClO₄, sin embargo usando HCl y HNO₃ la razón entre anatasa/rutilo está relacionado con el pH de la solución inicial y la cantidad de la fase de anatasa se incrementa cuando el pH de la solución se incrementa. Algunas muestras presentan trazas de la fase brookita.

Abstract

Titanium dioxide nanoparticles have been obtained by sol-gel process. Titanium isopropoxide was hydrolyzed in acidic medium at pH values between 0.5 and 1. The hydrolysis was catalyzed with HCl, HNO₃ or HClO₄, and studied their influence in the formation of titanium dioxide crystalline phases, i.e. rutile, anatase and brookite phases. The peptization process was studied with Visible and Fourier Transform Infrared (FTIR) spectroscopic techniques. Hydrothermal treatment at 220 °C for 12 hours permits the fabrication of well defined nanoparticles as it was observed by Transmission Electron Microscopy (TEM). The crystal structure was obtained by X-ray diffraction (XRD). Only the anatase phase was obtained using HClO₄, however using HCl and HNO₃ the anatase/rutile ratio is related to the pH of the initial acidic solution and the amount of anatase phase has increased when the pH of this solution increased. Some samples have traces of brookite phase.

1. Introduction

Nowadays, titanium dioxide is one of the most studied and researched material. Its nanoparticles have multiple applications in several fields such as optical devices, gas sensors, catalysts, solar cells, etc. being a crucial factor how is synthesized. The TiO₂ crystalline phases are rutile, anatase and brookite. Both phases, anatase and rutile, have been used in the sensitized solar cells and as photocatalyzer [1]; mixing of both phases enhanced the photocatalyzer performance [2, 3]. The rutile phase has shown to have a high refractive index and good chemical stability, being appropriate for high temperature applications [4,5].

Several methods and techniques have been implemented to produce TiO₂ nanoparticles,

especially anatase phase. The anatase crystalline phase of TiO₂ has been obtained from aqueous solutions of TiO₂ [6], TiCl₄[7-9] or TiOCl₂ [10], or by hydrothermal treatment using titanium alcoxides [11-13], including peptization process [14,15]. Complementary process is the hydrothermal treatment that assures not organic molecules remain in the product and a complete crystallization is ensured [16-18].

Among these several methods, the sol-gel allows us the synthesis of TiO₂ nanoparticles from titanium alkoxide precursors but there is not an established procedure for defining the key conditions to control the fabrication of their different phases. It was reported that anatase and rutile crystalline phases were

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obtained by neutralization of TiCl_4 or acidic hydrolysis of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ with HCl [6], however, hydrolysis of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ at high acidic conditions with HNO_3 has been reported to generate either rutile [19] or anatase [20] crystalline phases.

Other authors have researched about the pH effect on the TiO_2 nanoparticles, at wide range [21,22,23] using either nitric acid or ammonium in order to adjust the pH. In consequence some properties of titania appears strongly, showing different aggregation, morphology, surface charge and particle size, dependent on acidic or basic medium.

In this work we focus on the effect of using HCl , HNO_3 or HClO_4 in the hydrolysis of titanium isopropoxide for synthesizing anatase and rutile, the two most common crystalline phases of titanium oxide. Our results are referred to a small range of pH in the initial solution, between 0.5 and 1 in which both crystalline structures of TiO_2 were obtained.

2. Experimental Procedure

Colloidal solutions were obtained adding slowly drops of titanium isopropoxide (Aldrich 99%) to a vigorous stirred concentrated acidic solution (HCl , HNO_3 or HClO_4) at room temperature. The pH of this acidic initial solution was fixed in the range between 0.5 and 1. The resulting solution was heated at 70°C for 2 h to obtain particle peptization, and finally, in order to get the nanoparticles, it was auto-cleaved in a stainless steel chamber at 220°C for 12 h. After the hydrothermal treatment a transparent solution and a white precipitate was obtained. The white precipitated was washed and dried at 100°C overnight in a dry oven.

3. Results

3.1 Peptization characterization

After the hydrolysis, 1 cm^3 of each homogeneous peptized solution was filled in a quartz cell and its optical transmittance at 550 nm was monitored by using an Optometrics RS 350 single beam spectrophotometer. Figure 1 shows the optical transmittance measured at 550 nm of the hydrolyzed colloidal solutions prepared

from acidic medium of HCl , HNO_3 , or HClO_4 with different pHs as a function of the peptization time. The optical transmittance of the colloidal solutions prepared from HCl and HClO_4 has similar behavior (Figs. 1 a and c), when pH decreases accelerated the transparency of the solution.

For colloidal solutions hydrolyzed with HNO_3 , there is not correlation (Fig. 1b) between the pH and transmittance, although the sample with the lowest pH is the most transparent.

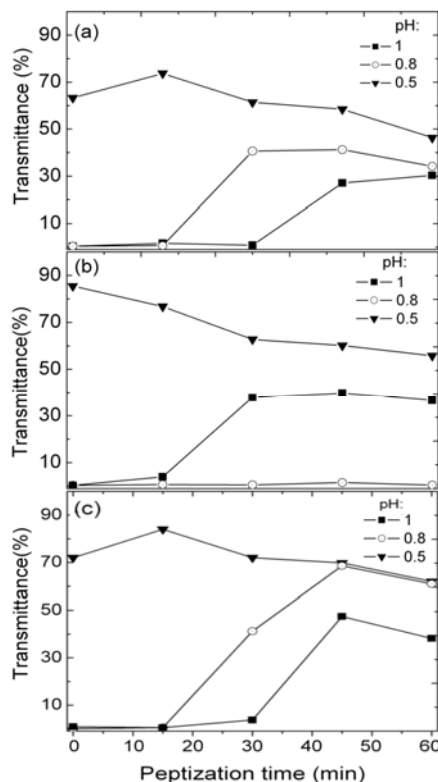


Figure 1. Transmittance at 550 nm of the hydrolyzed colloidal solutions prepared from acidic medium of (a) HCl , (b) HNO_3 , or (c) HClO_4 with different pHs as a function of the peptization time.

3.2 Characterization of particles before and after hydrothermal process

Fig. 2 shows the Fourier Transform Infrared Reflectance (FTIR) spectra for titanium dioxide particles obtained from two different catalyst acids (HCl , HNO_3), during the peptization (fine line) and after (bold line) the hydrothermal process. The samples were dried onto a glass substrate and an aluminum mirror was used as the reflectance reference. It is observed that the absorption peak around

1000 cm^{-1} (which can be ascribed to Ti-O group) is shifted with time to lower wavenumbers, and after the hydrothermal process this absorption peak takes place at 960 cm^{-1} . The intensity peaks associated to CO_2 (2340 cm^{-1}) and OH (around 1700 cm^{-1}) decreased.

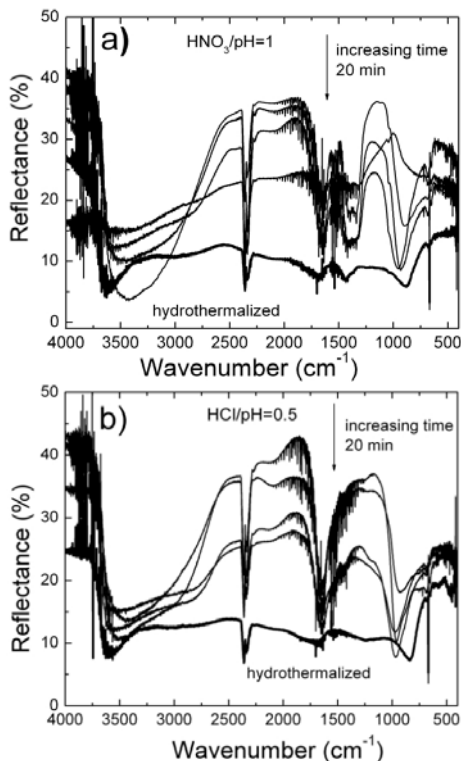


Figure 2. FTIR spectra of different colloidal solutions hydrolyzed with (a) HCl (pH=0.5) and (b) HNO_3 (pH=1) at different peptization times compare with hydrothermalized samples.

Fig. 3 shows the TiO_2 FTIR spectra prepared from acidic medium of HCl, HNO_3 , or HClO_4 with different pHs. The absorption peak around 3600 cm^{-1} (see Figs. 3a,b,c) can be assigned to the stretching vibrations of different O-H hydroxyl groups. Typical Ti-O vibrations group are identified at 960 cm^{-1} [24]. It is observed that when HCl and HNO_3 are used the absorption peak is shifted from 960 cm^{-1} towards higher wavenumbers concomitant to the pH from 0.5 to 1.0. When HClO_4 was used, this behavior was not observed. It was also identified peaks at 667, 580 and 465 cm^{-1} corresponding to Ti-O and Ti-O-Ti groups [24, 25].

3.3 Structural characterization of particles

In order to identify the different crystalline

phases of TiO_2 , X-ray diffraction (XRD) measurements were performed in a Philips X'pert diffractometer. The influence of the acidic medium in the XRD patterns of the TiO_2 is observed in Fig 4. The X-ray diffractograms of TiO_2 powder obtained from HCl and HNO_3 hydrolysis are shown in Figs 4a and 4b, respectively. From the diffractograms it can be deduced that both anatase and rutile phases are present; the anatase is promoted at pH~1, and when the pH decreased the rutile proportion increased. Whereas the TiO_2 powder obtained from HClO_4 hydrolysis is mainly anatase at the pH studied and small amount of brookite.

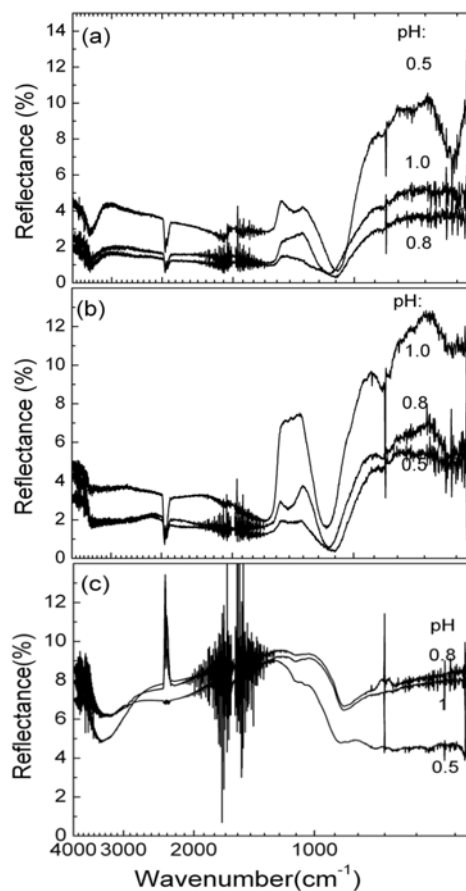


Figure 3. FTIR spectra from TiO_2 colloidal solutions hydrolyzed with (a) HCl, (b) HNO_3 , and (c) HClO_4 after hydrothermal treatment.

The grain size, D , was calculated by using the Scherrer's equation:

$$D = 0.94 \lambda / (\beta \cos \theta), \quad (1)$$

here θ is the Bragg's angle of diffraction for the peak, λ is the X-ray wavelength in the K_α band for Cu, equal to 1.54 Å, and β is the full width at half of the maximum diffraction

peak. Table 1 shows the grain size of the fabricated powders; the crystalline grain size of the anatase phase is between 8 nm and 12 nm, whereas the crystalline grain size of rutile is in the range of 17 nm and 33 nm. The anatase proportion, A_p , was estimated using the intensity of the rutile peak at the (100) plane, $I_{rutile}(100)$, and the anatase peak at the (101) plane, $I_{anatase}(101)$, by the relation [26].

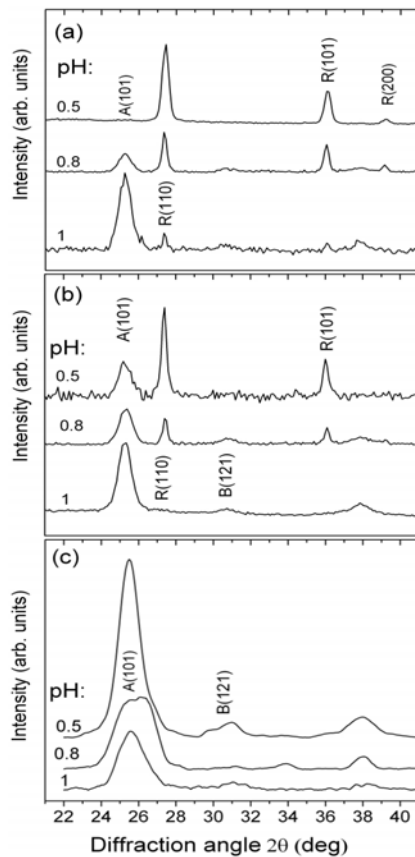


Figure 4. X ray diffraction patterns of TiO_2 powders obtained with different pH using (a) HCl, (b) HNO_3 and (c) HClO_4 in titanium isopropoxide hydrolysis.

$$A_p = (1 + 1.265 I_{rutile}(110)/I_{anatase}(101))^{-1} \quad (2)$$

Table 1 shows the results of the calculated A_p values; it can be deduced from those results that the pH has an influence of modulation of the crystalline phase proportion; for example, at pH ~ 1, the use of HNO_3 in the hydrolysis shows to be more efficient to promote the anatase phase than the HCl, whereas the use of HClO_4 did not promote the rutile phase at all.

Table 1. The grain size of anatase, $D_{anatase}$, of rutile D_{rutile} and the anatase proportion, A_p , and corresponding pH of the acidic solution and hydrolysed with HCl, HNO_3 and HClO_4 .

	pH	$D_{Anatase}$ (nm)	D_{Rutile} (nm)	A_p
HCl	0.5	-	17	0
	0.8	10	33	0.26
	1.0	10	28	0.78
HNO_3	0.5	10	22	0.25
	0.8	13	25	0.52
	1.0	12	-	1
HClO_4	0.5	16	-	1
	0.8	6	-	1
	1.0	8	-	1

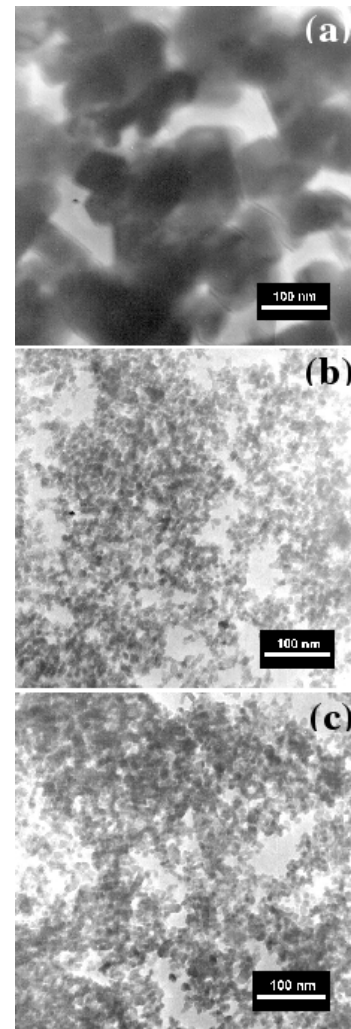


Figure 5. TEM micrographs of TiO_2 powders hydrolyzed with HCl at a) pH=0.5, b) pH=0.8 and c) pH=1.0 .

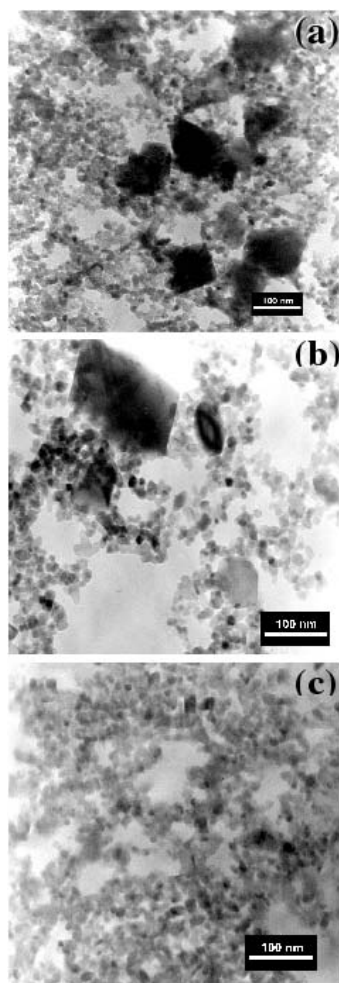


Figure 6. TEM micrographs of TiO_2 powders hydrolyzed with HNO_3 at a) $\text{pH}=0.5$, b) $\text{pH}=0.8$ and c) $\text{pH}=1.0$.

3.3 Morphological characterization of particles

Particles morphology was studied with STEM Philips EM-400 instrument operated at 80 kV. Figs. 5, 6 and 7 show the micrographs of particles obtained at different pH of the hydrolysis using HCl, HNO_3 and HClO_4 , respectively. When HCl was used in the hydrolysis (Fig. 5), it is observed that particles size are of the order of 100 nm in which nanopowders prepared at $\text{pH}=0.5$ were slightly larger than those prepared with either $\text{pH}=0.8$ or $\text{pH}=1$. In the case of HNO_3 a mix of large particles (~ 100 nm size) and particles of the order of 20 nm are observed (Fig. 6). This can be conciliated with the presence of two crystalline phases in the nanopowders fabricated using HNO_3 at $\text{pH}=0.5$ as observed by X-ray diffraction, in which larger particles

should correspond to rutile crystallites and the smaller ones to anatase. This fact is also observed in Fig. 6b, in which a mix of phases were identified by X-ray diffraction, but not in Fig. 6c, in which only anatase is present. Finally, when HClO_4 was used (Fig. 7) a mix of large particle (100 nm size) and particles of the order of 20 nm is observed.

4. Discussion

Titanium dioxide nanoparticles preparation by sol-gel involves two principal steps: Precipitation of Ti(IV) ions from alcoxides and then acidic peptization. It was reported that unpeptized precipitated is amorphous and after peptization process it is obtained a crystalline phase [27]. Transmittance of the hydrolyzed solutions depict some tendency: after one hour titania nanoparticles have a defined structure, hence samples transmittance are in a well defined range (30 – 50%).

Peptization process involves redispersion in acidic solution of titanium(IV) precipitates from hydrolysis. This acidic solution causes proton adsorption onto the surface of the precipitates making them positively charged. Particles of the amorphous aggregate once formed with a loose bonding broke down into smaller particles and an equilibrium was reached at last. At that time, the particles were so small that the suspension became optically transparent, that we can see in transmittance spectras. We can accentuate that at lower pH corresponds higher transmittance in all the samples that means H^+ ions in the acidic solution rearranged the particles.

According to the ligand field theory, in solution titanium(IV) ions exist as six-fold coordinated structural units, where the fundamental structural units in all the three TiO_2 crystals (namely anatase, rutile and brookite) are $[\text{TiO}_6]$ octahedron, having different modes of arrangement and links [27]. In the rutile form, TiO_6 octahedra link by sharing an edge along the c-axis to form chains. These chains are then interlinked by sharing corner oxygen atoms to form a three-dimensional framework, whereas in anatase, the three-dimensional framework is formed only by edgeshared bonding among $[\text{TiO}_6]$ octahedrons. Then rutile or anatase phase could be formed, depending on whether $-\text{OH}$

or oxo-bridges are formed between the two metal centers during condensation.

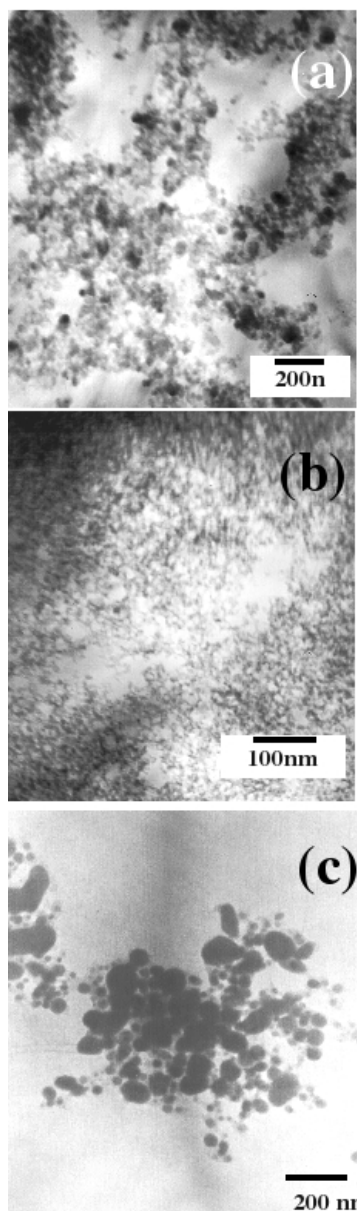


Figure 7. TEM micrographs of TiO_2 powders hydrolyzed with HClO_4 at a) $\text{pH}=0.5$, b) $\text{pH}=0.8$ and c) $\text{pH}=1.0$.

Results indicate the important role of the catalytic acids in the hydrolysis for determining the crystalline phases of the TiO_2 powders. TiO_2 -nanopowders subjected to hydrothermal processes, in which HCl , HNO_3 and HClO_4 acids were used in the hydrolysis with pH between 0.5 and 1, show that the grain size of neither anatase nor rutile phases have a concomitant dependence of the pH [28], but the kind of phase is highly depending on pH of HCl and HNO_3 .

Nanoparticles obtained from hydrolysis using HClO_4 give only anatase structure, whereas those obtained from HCl or HNO_3 with low pH (~ 0.5) promote structures with the predominance of rutile phase, and those with $\text{pH} \sim 1$ promotes the anatase phase. The anatase phase obtained from low concentration (higher pH) of HCl is in agreement with the HCl peptization of TiO_2 nanoparticles from metatitanic acid [29] and with the different acidic hydrolysis of titanium n-butoxide [30]. This can be understood considering that structural rearrangement of TiO_2 octahedral units into the amorphous TiO_2 is essential for the formation of anatase or rutile nuclei and it has been documented that NO_3^- and Cl^- anions present some degree of affinity to a titanium atom in an aqueous solution [31] which could go in favor of the rearrangement of TiO_2 . On the other hand the fact that ClO_4^- has stronger affinity than NO_3^- and this in turn stronger affinity than Cl^- to a titanium atom, the anatase phase is better promoted in HClO_4 than in HNO_3 , and this in turn better than in HCl medium, as it was deduced from X-ray diffraction measurements. This result is in agreement with that reported elsewhere [30]. Consequently, as mentioned above, acidity seems to play an important role in the phase transformation and crystal growth [13], but from these results the anionic “environment” is also an important factor to be consider for the promotion of the anatase phase, particularly it is strike the role of the anionic radius which in the following order $\text{HCl} < \text{HNO}_3 < \text{HClO}_4$ promote from less to more the anatase phase under the same acidity conditions.

5. Conclusions

We have obtained nanoparticles of TiO_2 by sol-gel method by using hydrolysis of titanium isopropoxide under large H^+ concentrations (pH between 0.5 and 1). Catalyst acids of the hydrolysis were HCl , HNO_3 and HClO_4 . In the range of work, for HCl and HNO_3 , the use of low pH values goes in favor of the formation of the rutile phase, whereas high pH values goes in favor of the formation of anatase, independent from the type of acid. The anatase particles and crystalline grain sizes were always smaller than those of rutile. The proportion of the anatase crystalline phase is promote better by

HClO₄ than HNO₃ and this better than HCl; an important factor seems to be that ClO₄⁻ anions have stronger coordination ability to a titanium atom than both NO₃⁻ and Cl⁻ anions.

6. Acknowledgments

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7. References

- [1] O'Regan B, Grätzel M. *Nature* 1991; 353:737-740.
- [2] Berry RJ, Mueller MR. *Microchem. J.* 1994; 59:28-32.
- [3] Tanaka K, MFV Capule, Hisanaga T. *Chem. Phys. Lett.* 1991; 187:73-76.
- [4] Rayne H, *Organic Coating Technology* Vol. II, New York (EE.UU.): Willey, 1961, pp. 751.
- [5] Kumar K-NP, Ketzer K, Burggraaf A. *J. Mater. Sci. Lett.* 1994; 13:59-61.
- [6] Yanagisawa K, Ovenstone JJ. *Phys. Chem. B.* 1999; 103:7781-7787.
- [7] Cheng H, Ma J, Zhao Z, Qi L. *Chem. Mater.* 1995; 7:663-671.
- [8] Park J-K, Kim H-K. *Bull Korean Chem. Soc.* 2002; 23:745-748.
- [9] Okuya M, Prokudina NA, Mushika K, Kaneko S. *J. of the European Ceram. Soc.* 1999; 19:903-906.
- [10] Kim S-J, Park S-D, Hwan Jeong Y. *J. Am. Ceram. Soc.* 1999; 82:927-932.
- [11] Wen T, Gao J, Shen J, Zhou Z. *J. Mater. Sci.* 2001; 36:5923-5926.
- [12] Falaras P., Xagas AP. *J. Mater. Sci.* 2002; 37:3855-3860.
- [13] Sugimoto T, Zhou X, Muramatsu A. *J. Colloid and Int. Sci.* 2002; 252 339-346.
- [14] Yoldas BE. *Am. Ceram. Soc. Bull.* 1975; 54:286-288.
- [15] Bischoff BL, Anderson M. *Chem. Mater.* 1995; 7:1772-1778.
- [16] Oguri Y, Riman RE, Bowen HK. *J. Mater. Sci.* 1988; 23:2897-2904.
- [17] Sugimoto T, Okada K, Itoh H. *J. Colloid Interface Sci.* 1997; 193:140-143.
- [18] Matijevic E. *J. Colloid Interface Sci.* 1977; 61:302-311.
- [19] Tang Z, Zhang J, Cheng Z, Zhang Z. *Mat. Chem. and Phy.* 2002; 77:314-317.
- [20] Barbé CJ, Arendse F, Comte P, Jirousek M, Lenzenmann F, Shklover V, Christophe, Grätzel M. *J. Am. Ceram. Soc.* 1996; 80:3157-3171.
- [21] Mahshid S., Askari M., Sasani Ghamsari M. *J. Mat. Proc. Tech* 2007; 189:296-300
- [22] Zhang W., Chen S., Yu S., Yin Y. *J. Crystal Growth* 2007; 308:122-129.
- [23] Yu J., Su Y., Cheng B., Zhou M. *J. Molec. Cat. A: Chemical* 2006; 258:104-112
- [24] Burgos M, Langlet M. *Thin Solid Films* 1999; 349:19-23.
- [25] Lopez T, Sanchez E, Bosch P, Meas Y, Gomez V. *Mat. Chem. and Phys.* 1992; 32: 141-152.
- [26] Spurr RA, Myers H. *Anal. Chem.*, 1957; 29:760-762.
- [27] Yang S, Liu Y, Guo Y, Zhao J, Xu H, Wang Z. *Mat. Chem. Phys.* 2002; 77:501-506.
- [28] Cot F, Larbot A, Nabias G, Cot L. *J. Eur. Cer. Soc.* 1998; 18:2175-2181.
- [29] Zhang R, Giau L. *Mat. Res. Bull.* 2001; 36:1957-1965.
- [30] Wu M, Lin G, Chen D, Wang G, He D, Feng S, Xu R. *Chem. Mater.* 2002; 14:1974-1980.
- [31] Sanchez C, Livage J, Henry M, Babonneau F. *J. Non-Cryst. Solids.* 1988; 100:65-76.