



Nano Structural Properties of TiO_2 - SiO_2

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ABSTRACT

We report on the synthesis, morphology, chemically and structurally of SiO_2 - TiO_2 nanostructure. The SiO_2 - TiO_2 nanostructure was synthesized by a method based on the sol-gel method. In the present work, binary reactive powders in the SiO_2 - TiO_2 systems have been obtained using the sol-gel method, by the simultaneous gelation of all cations. Composite powders and coating on glass have been characterized by XRD, XRF, SEM and FTIR. X-ray diffraction showed the formation of nano crystalline anatase and rutile phases. Scanning electron microscopy revealed that aggregation structure formed by increasing the calcinations temperatures. The weight percent of ingredient in production was obtained by using XRF. The average crystallite size was calculated by using X-ray diffraction analysis. FTIR spectra showed that Ti-O-Si, O-Si-O and Si-O-Si bonds are formed and indicated that titanium is in four-fold coordination with oxygen in the SiO_4^{4-} . The effects of chemical compositions and the strong process on the surface topography and the crystallization of anatase were studied.

Key words: Nano structure, TiO_2 , sol-gel method.

INTRODUCTION

Titania is known to have three natural polymorphs, i.e. rutile, anatase, and brookite. Only anatase (figure 1) is generally accepted to have significant photocatalytic activity. Titanium dioxide (TiO_2) is well known as a photocatalyst and widely applied for air and waste water purification. One of the possible ways to modify the property of TiO_2 crystallites is by adding a second semiconductor into the TiO_2 matrix. SiO_2 has been incorporated into the TiO_2 matrix to enhance the photocatalytic process¹⁻³. SiO_2 has high thermal stability, excellent

mechanical strength and help to create new catalytic sites due to interaction between TiO_2 and SiO_2 ⁴ also, SiO_2 acts as a carrier of TiO_2 and helps to obtain a large surface area as well as a suitable porous structure⁵. Due to their good resistance against alkaline solutions SiO_2 - TiO_2 coatings are attracting the attention of many scientists. Their alkaline resistance is strongly controlled by their surface state.

The sol-gel process is one of the versatile methods to prepare ceramic materials. Currently, the sol-gel process is employed quite often for

synthesis of nanosize catalytic materials. The incorporation of an active metal in the sol during the gelation stage allows the metal to have a direct interaction with support, therefore the material possess special catalytic properties. The design of advanced ceramics depends on the availability of powders with outstanding properties in terms of composition, purity, size, and size distribution. Sol-gel processes allow synthesis powders to have a more elaborate structure. The synthesis of inorganic materials such as metal oxides with different morphologies for specific applications has attracted a considerable amount on interest in recent years, and has been a challenging issue for chemists and material researchers. It is well recognized that the properties of materials highly depend on size, morphology, and dimensionality⁶, three crucial geometric parameters. Many chemical and physical routes are explored by chemists and material researchers to control those parameters and to obtain various shapes of materials such as tubes, rods, plates, and so on [7], including the template method, laser ablation, chemical vapor deposition, hydrothermal method, etc. Among the many chemical techniques for the fabrication of materials, sol-gel processing as a moderate and adjustable method has emerged as an alternative route to control the size, morphology, structure, and physical and chemical properties of inorganic oxides⁸. The sol-gel process is commonly applied to synthesis such TiO₂ materials owing to its several advantages such as low temperature processing and the ability to prepare materials in various shapes, compared with the conventional preparation procedures of glass and ceramics^{9,10}.

EXPERIMENTAL

Proceeding and Details

In this work we prepare TiO₂ by using hydrolysis procedure of TiCl₄ which is transformed to anatase by heating it at 300, 500, 700 and 900 °C. It obviously depends on the preparation procedures and TiO₂ content in combination. Anatase is generally transformed to rutile if calcinations temperature and TiO₂ content increase. By adding more SiO₂ to TiO₂, the obtained powder trend to crystalline structure.

The preparation of TiO₂-SiO₂ gel is below,

such that Tetraethyl-Orthosilicate (TEOS) (Merk, ≥ 99) was hydrolyzed with di-ionized water in that ethanol. Ethanol acts as a mutual solvent. TEOS, in ethanol was hydrolyzed with water containing acetic acid at room temperature for 30 min. The solution was then mixed with titanium chloride TiCl₄ (Merk, ≥ 99) at 0 °C in specific molar ratio to obtain various content of TiO₂. After 30 min stirring at room temperature, the sol was vibrated for 20 min in ultrasonic bath to deconglomerate particles and then relaxed at room temperature for 30 min. The sol was stirred at 60 °C until it become gel and remove ethanol (about 24 hours). After gelation, samples were dried at 60 °C to remove water and acetic acid and leave a white to light yellow lump depends on TiO₂ content. After that the lump samples were milled with mortar and calcinated in 300, 700 and 900 °C. The thermal gradient during experiments procedure was 55 (deg/min) and the samples were put in oven during 2 hours at calcination temperature stated above. The procedure was shown in Fig. 2. The corresponding molar ratios of TEOS-TiCl₄-Ethanol-H₂O-CH₃COOH are shown in Table 1 that A and B are molar ratio of TEOS and TiCl₄ composition.

The composition, structure and surface morphology of the TiO₂- SiO₂ powder were investigated by XRF (model: ARL 8680 S Switsland), XRD (GBC-MMA007 Australia), FT.IR (Fourier Transform Infrared absorption) and FE-SEM (Field Emission Scanning Electron Microscopy) (S-4160, Hitachi 2000).

RESULTS AND DISCUSSION

The weight percent of ingredient in production was obtained by using XRF technique and given in in Table 2. The XRD patterns were measured on X-ray powder diffractometer by using, 1.54 in table 2. The XRD patterns were measured on X-ray powder diffractometer by using radiation, 0.05 step size in where the speed was 10-using K α (Cu):1.54 Å radiation, 0.05 step size in where the speed was 10 deg/min. The XRD patterns of SiO₂-TiO₂ show an amorphous phase at room temperature and crystallizes directly from amorphous to anatase phase at temperature as low as 300 °C. As one can see in Fig.3 some sharper peaks are revealed that indicate (110) and (101)

Table 1: Materials and corresponding molar ratio

Materials	TEOS	TiCl ₄	Ethanol	H ₂ O	CH ₃ COOH
Symbol	A	B	C	D	E
Molar ratio	A	B	7(A+B)	10(A+B)	2(A+B)

Table 2: The result of XRF analysis

Sample	Weight Percent
100	70.75%TiO ₂ -29.25%SiO ₂
200	59.43%TiO ₂ -40.57%SiO ₂
300	54.94%TiO ₂ -45.06%SiO ₂
400	44.1%TiO ₂ -55.90%SiO ₂
500	33.88%TiO ₂ -66.12%SiO ₂
600	31.76%TiO ₂ -68.24%SiO ₂

orientations (anatase phase) for low content of TiO₂ at >300 °C. By increasing the content of TiO₂ in powder mixture, the rutile phase has transited from anatase phase. The size of nano TiO₂ grains were calculated by Scherer's formula and these results shown in (Table 3). Some researchers [11,12] found that formation of anatase crystallites attributed to the lower surface energy, which is important in the nucleation of crystals, of anatase nanocrystallites than that of rutile. Fig. 3 show the XRD patterns of the TiO₂-SiO₂ powder correspond to content in Table. 2. at different calcination temperatures. In addition, Fig. 4 show the XRD patterns at fixed calcination temperature but different content as well. It is clear that by increasing the temperature, the intensity of peaks in XRD patterns increase and crystallization are observable. The Samples with TiO₂ content above 44% have rutile and anatase phases together whereas samples with lower content have only anatase phase. Figs. 3 and 4 and Tab.3 show that, by increasing the TiO₂ content, rutile percent in mixture is explicit more than anatase and the particle size grows by increasing the calcination temperature. Since the atomic radius of Si atom is smaller than Ti, the TiO₂ particle experience a contraction and its crystal growth is retarded due to the Si atom. This agrees with the small value of average grain size which has been calculated by using Scherer's equation.

Fig.5 shows FE-SEM pictures of the TiO₂-SiO₂ powder. This figure shows spherical and agglomerated TiO₂-SiO₂ nano-particle which was obtained using different molar ratios of reagents; the molar ratio of the solvent is also important. With a lower molar ratio of solvent (ethanol), agglomerated silica particles were obtained. Park and Kim¹³ have shown when a narrow size distortion is required, a small molar ratio of ethanol should be employed.

Nano-size of TiO₂-SiO₂ particles with spherical shape observed in specific condition. Spherical shape is obvious when calcination temperature and TiO₂ content in mixture increase compare to low content TiO₂ that cause random or dendrite shape in mixed oxides.

The particle size grows relatively by increasing calcination temperature and TiO₂ content. This is due to the suppressive effect of SiO₂ on the crystal growth of TiO₂. This is accordance with the result of XRD analysis, which shows that the restriction of crystal growth of TiO₂ particles.

The FT-IR spectrum of TiO₂-SiO₂ are shown in the Figs. 6 and 7. It consists of several bands at 1740, 1630, 1060-1220, 950, 798 and 650-740 cm⁻¹. The peaks in the spectra have been assigned according to the literatures¹⁴. The band at 1630 and 3300 cm⁻¹ are assigned to OH bending and stretching vibrations respectively. It can be ascribed to the stretching of silanol groups interacting through hydrogen bonds with water molecules. The vibration in the range 1060-1220 cm⁻¹ is assignable to Si-O-Si vibration mode of isolated Si-OH groups. The absorption band about 1070 cm⁻¹ represents the characteristic bonds of Si-O-Si asymmetric stretching. The band near 950 cm⁻¹ refers to Ti-O-Si asymmetric stretching. The peak near 798 cm⁻¹ may be assigned to the O-Si-O

Table 3: The analysis of XRD patterns correspond to Table 2. The size of grain is derived by using Scherer's equation .The phase is also extracted from database of XRD patterns (A= Anatase, R= Rutile). The angle (2θ) correspond to more insensitive peak relevant to anatase or rutile phase

Temperature: As-Prepared				Temperature: 300 °C			
Sample	Size (nm)	Phase Anatase or Rotile	Angle (2θ)	Sample	Size (nm)	Phase Anatase or Rotile	Angle (2θ)
100	6	R	27.40	100	8	A	25.40
					12	R	27.60
200	4	A	25.35	200	11	A	25.15
	7	R	27.35		24	R	27.45
300	6	R	27.35	300	8	R	27.50
400	3	A	25.20	400	8	A	25.50
					12	R	27.60
500	6	A	25.60	500	6	A	25.30
600	4	A	25.10	600	6	A	25.40
	Temperature: 700 °C				Temperature: 500 °C		
100	16	A	25.50	100	10	A	25.40
	14	R	27.60		16	R	27.50
200	13	A	25.35	200	28	A	25.30
	10	R	27.30		16	R	27.45
300	9	A	25.25	300	10	A	25.45
	18	R	27.50		25	R	27.50
400	10	A	25.40	400	6	A	25.40
	8	R	27.35		7	R	27.40
500	10	A	25.30	500	13	A	25.35
600	7	A	25.35	600	4	A	25.30

Temperature: 900 °C

sample	Size (nm)	Phase Anatase or Rotile	Angle (2θ)
100	13	A	25.15
	33	R	27.45
200	23	A	25.30
	37	R	27.40
300	47	A	25.30
	30	R	27.45
400	13	A	25.25
	12	R	27.35
500	15	A	25.30
600	7	A	25.30

vibration mode of SiO_2 . The absorption band observed at about 950 cm^{-1} is associated with titanium in four-fold coordination with oxygen in the Si associated with titanium in four fold coordination with oxygen in the SiO_4^{-4} structure. Other titanium-associated absorptions occur in broad bands at $240\text{--}400\text{ cm}^{-1}$ and $650\text{--}730\text{ cm}^{-1}$. These lie just below the host-silica absorptions at 450 and 798 cm^{-1} . In spite of the result of Y. Zhao *et al.*¹⁵, this

band does not still in the spectrum after heating treatment at 600°C . We found that the intensity of the IR absorption peak is function of temperature

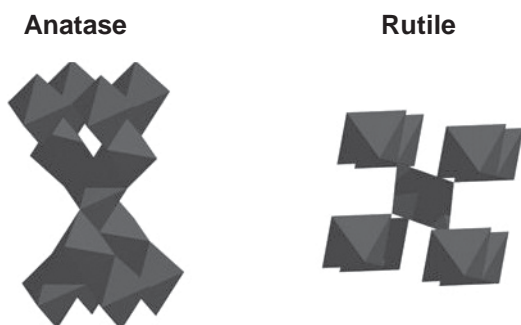


Fig. 1: Schematic model of anatase

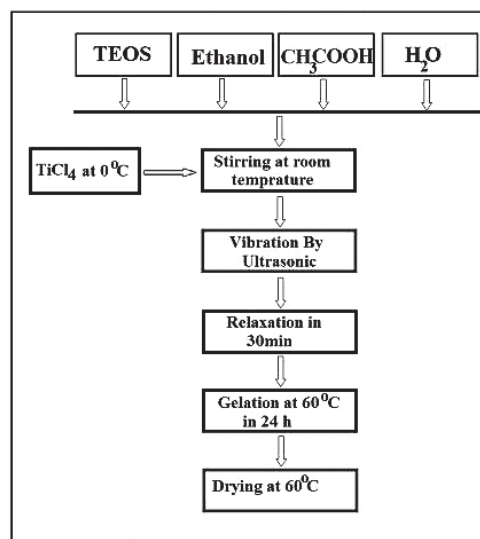


Fig. 2: The procedure for preparing $\text{TiO}_2\text{--SiO}_2$ in mixture

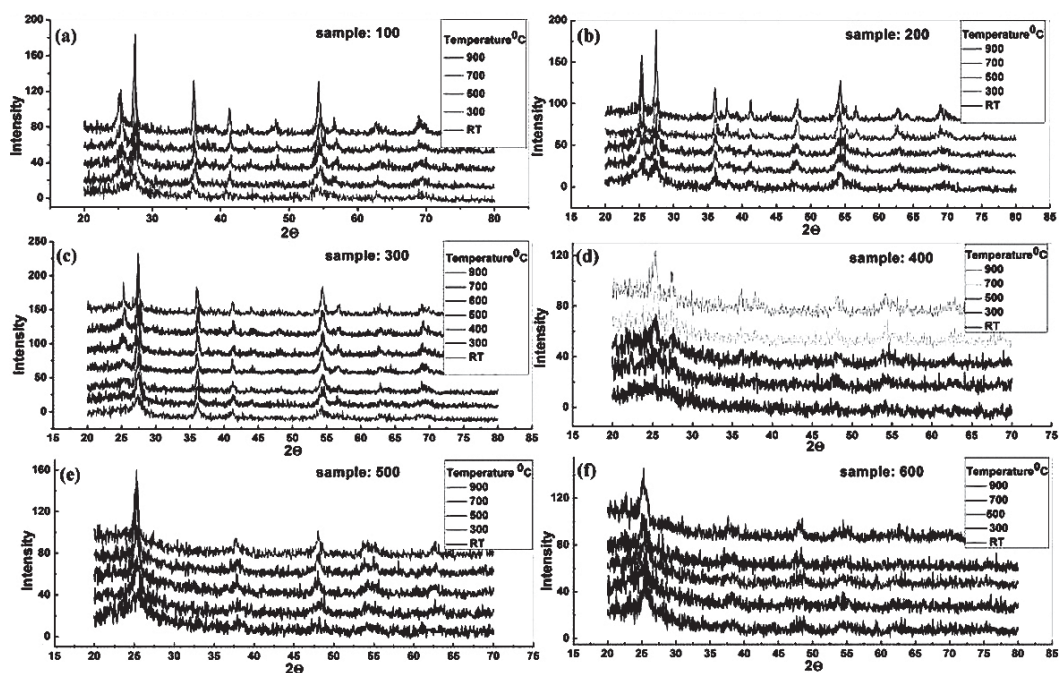


Fig. 3: XRD patterns of the $\text{SiO}_2\text{--TiO}_2$ powder correspond to content in table 2. at different calcination temperature. The inset table shows calcinations temperature

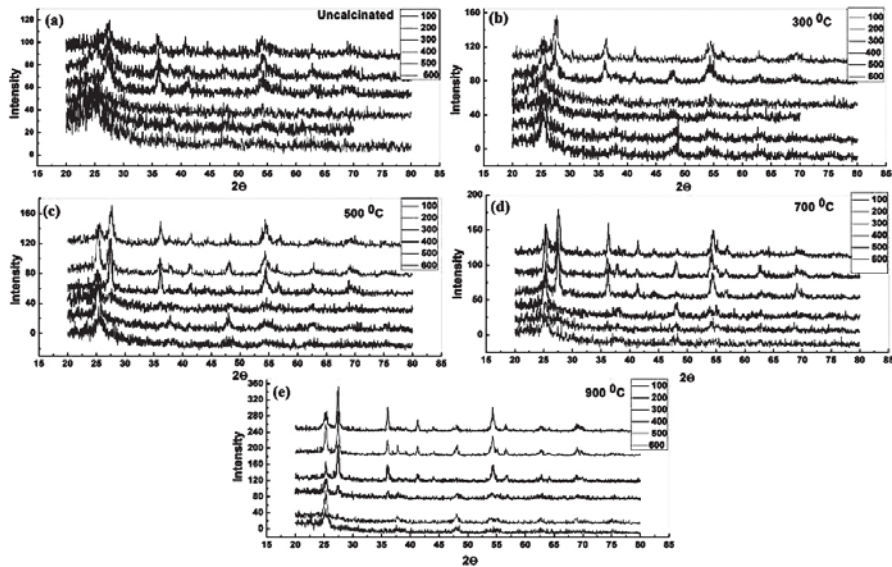


Fig.4. XRD patterns at fixed calcination temperature but different content. The inset table show sample number that has specific TiO₂ content

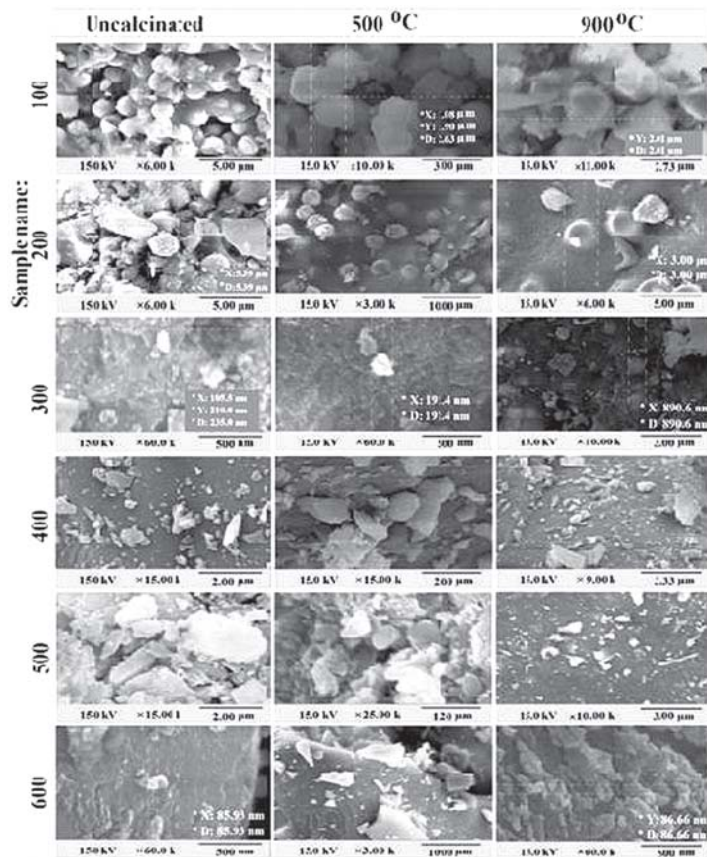


Fig. 5: FE-SEM images of the mixed oxide. Columns (rows) are found at calcination temperature (at the same content)

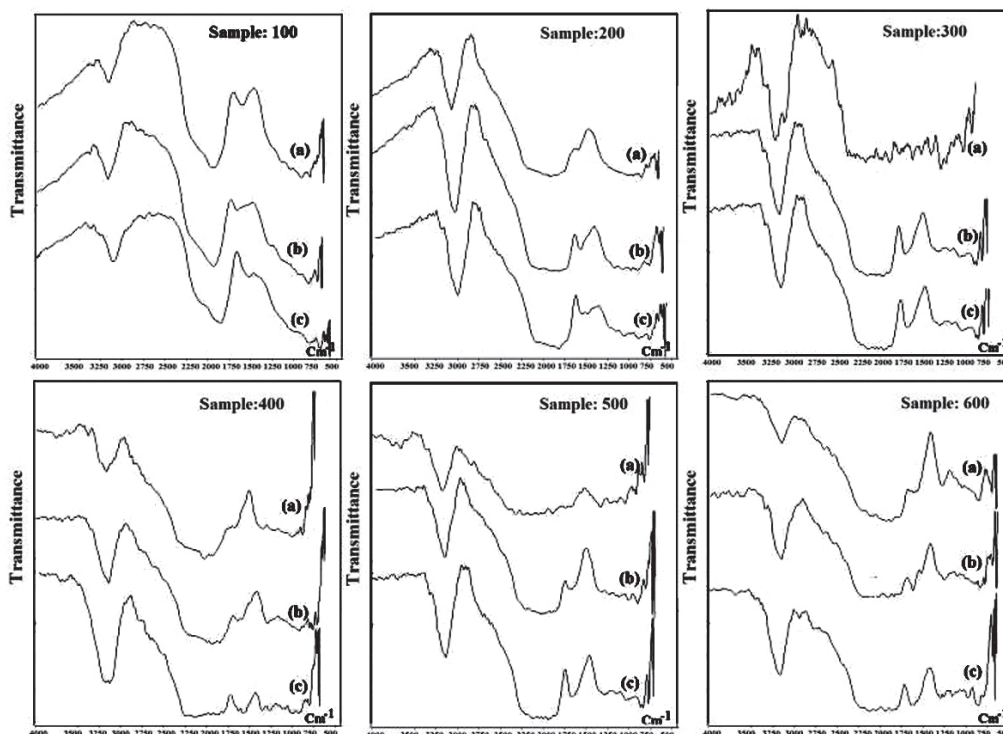


Fig. 6: FT-IR spectra of mixed oxides according to Table 2 that a, b and c refer to 900 °C, 500 °C and uncalcinated thermal treatment respectively

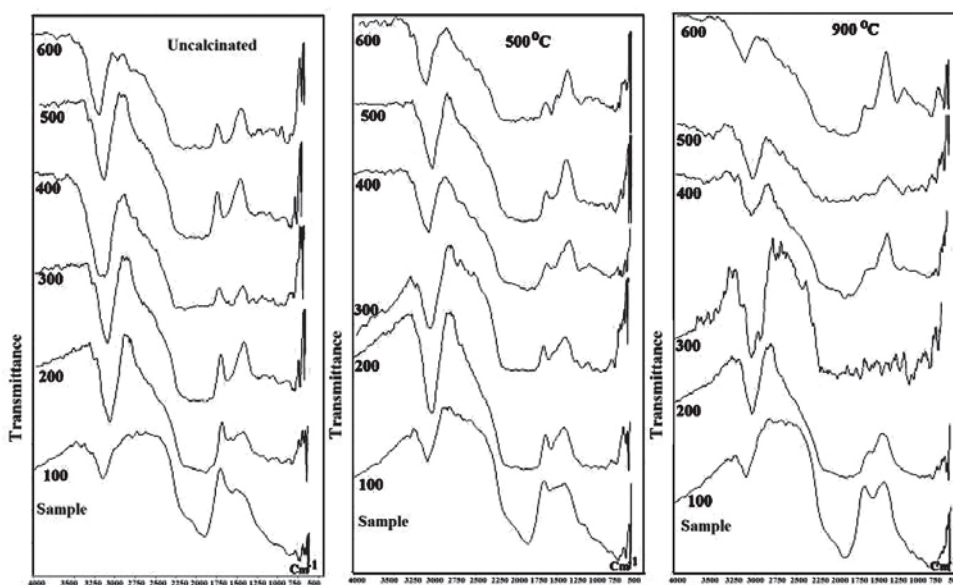


Fig. 7: FT-IR spectra of the mixed oxide at the same calcination temperatures and different TiO_2 contents. The sample number labeled in figs. Are introduced in Table. 3

and TiO₂ content. The prominent IR-active bands of pure silica are ascribed to TO modes of the SiO₄ network that have substantial motions of the light oxygen ions. These network modes involve vibrations of the bridging oxygen ions of corner-sharing SiO₄ tetrahedra. From this data, we could conclude that titanium is in four coordination with oxygen in the titanium is in four coordination with oxygen in the SiO₄⁻⁴ structure, and each component in the materials is mixed on an atomic scale¹⁶.

CONCLUSION

The sol-gel method can be effectively used for the synthesis of titania-silica particles with different SiO₂ content. The FT-IR analysis proves the successful synthesis of the desired materials.

The anatase phase of TiO₂ with nano-sized particles was also obtained for the calcination temperature <300 °C. By increasing the temperature and TiO₂ content in mixture, rutile phase is dominated than anatase phase. The effect of SiO₂ on crystalline growth procedure of TiO₂ is clearly observed at high concentration of SiO₂ which have not been reported before [17]. Furthermore, the SiO₂ particles in the TiO₂ matrix lead to the formation of smaller TiO₂ particles. The particle size grows relatively by increasing calcination temperature and TiO₂ content and this is in good agreement with XRD evaluation.

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REFERENCES

1. Yu J., Yu C. G. and Zhao X., *J. of Sol-Gel Sci. Technol.*, **24**: 95 (2002).
2. Meng X., Qian Z., Wang H., Gao X. and Yang M., *J. of Sol-Gel Sci. Technol.*, **46**: 195 (2008).
3. Zhou L., Yan S., Tian B. and Anpo M., *Mat. Lett.*, **60**: 396 (2006).
4. Ennaoui A., Sankapal B. R., Skryshevsky V. and Stiener M. C., *Sol Energy Mater. Sol cells*, **90**: 1533 (2006).
5. Chang P., Zheng M., Jin Y., Huang Q. and Gu M., *Mat. Lett.* **60**, 396(2003).
6. Scott R. W., Maclachlan M. J., Ozin G. A. and Curr O., *Solid State Mater Sci* 1999;**4**: 113-21 (2003).
7. Li M., Lebeau B. and Mann S., *Adv Mater* **15**: 2032-5 (2005).
8. Yin Y., Alivisatos A. P., *Nature*, **437**: 664-70 (2005).
9. Kato K., Tsuzuki A., Taoda H., Torii Y., Kato T., and Butsugan Y., *J. Mater. Sci.*, **29**: 5911-15 (1994).
10. Abe Y., Sugimoto N., Nagao Y., and Misono T., **104**: 164-69 (1988).
11. Gribb A. A. and Banfield J. F., *Am. Mineral.*, **82**: 717-28 (1997).
12. Zhang H. and Banfield J. F., *J. Mater. Chem.*, **8**: 2073-76 (1998).
13. Park and S. K. and Kim K. D., *Colloid and Surfaces Science*, **7**: 197-8 (2002).
14. Yu H.F., Wang Sh.M., *J. Non-Cryst. Solids*, 261 ,260 (2000).
15. Yongxiang Z., Linping X., Yongzhao W., Chunguang G. and Diansheng L., 93-95, 583-588 (2004).
16. Gribb A. A. and Banfield J. F., *Am. Mineral.*, **82**, 717-28 (1997).
17. Zhou L., Yan S., Tian B., Zhang J. and Anpo M., *J. Mat. Lett*, **60**: 396 (2006).