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Synthesis and Size-Control of TiO_2 Photocatalyst Nanoparticles Preparation Using Sol-Gel Method

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Abstract: Nanocrystalline titania powders were synthesized at room temperature (~ 22°C) by a sol-gel method and using $TiCl_4$ as a precursor with ethanol solution and argon gas environment, without any other materials. After mixing for different times, the gel solution was formed. The gel solution was aged and prepared using ultrasound irradiation. Then the sol-gel dried and calcined in different tempertures. Our results showed that anatase was only phase in titanium oxide powders up to 500°C. When the calcination increased in the region after 500°C, the phase transformation from anatase to rutile occurred in TiO_2 nanopowders but anatase phase was still dominant. The size of anatase nanocrystallines was controlled and obtained by changing the synthetic parameters. The average grain size of anatase nanoparticles was obtained in the range from 4 nm to 32 nm.

Key words: TiO_2 nanoparticles · $TiCl_4$ · Sol-gel method · Anatase phase · Ultrasound waves

INTRODUCTION

Today scientists and people are interested in producing and using clean improved energy and clean living. For this purpose it is necessary to prepare materials with new properties. One of these materials which have recently been considered is titanium dioxide. TiO_2 exists in three different crystalline habits: rutile (tetragonal), anatase (tetragonal) and brookite (orthorombic) and each have their own applications [1-4]. TiO_2 is a versatile functional material due to its many unusual properties such as high refraction index, hydrophilicity [4], biocompatibility [5], semiconductivity, corrosion resistance, low-cost, widely available, nontoxic and physicochemically stable substance [1-6]. TiO_2 is now widely used as white pigment in paint and cosmetic products, photonic crystal for photonic band-gap materials, nonlinear optics [1, 2, 6], gas sensors [7, 8], coating for bone implants, component in electroceramics [9, 10], electrodes in lithium batteries and as a photocatalysis [11-15]. Using photocatalysis is proposed to improve the efficiency of some devices such as solar cells [15].

In comparison to other phases, using anatase phase of TiO_2 nanoparticles with controlled diameters, the high homogeneity, good morphology, high surface area and porosity is very suitable to photocatalystic applications because of higher electron mobility, lower fixed dielectric and density [3, 12-20]. However, thermodynamic stability is particle-size dependent and at particle diameters below 15 nm, anatase is more stable that rutile [4].

With studying synthetic methods developed for the preparation of nanostructured TiO_2, a wide variety of approaches including flame synthesis, ultrasonic irradiation, chemical vapor deposition, as well as sol-gel route have been reported. The sol-gel has been a method for the preparation of nano-sized TiO_2 with anatase phase [19-22]. This method based on the mixing, polymerizing, hydrolysis, aging and calcination of various titanium molecular precursors in aqueous solutions or an organic solvent [1-5, 23, 24]. All these factors with new condition can be used for making and controlling the diameter of nanoparticles [25, 26]. In view of the synthetic methods there is no letter, known to us, which is used amount of solvent and precursor, mixing method, gelatinizing time,

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pH control, aging, using ultrasound waves [26] and calcination temperature for synthesis and controlling of the diameter of TiO_2 nanoparticles.

In the present work, anatase TiO_2 nanoparticles have synthesized by the sol-gel route and just combine $TiCl_4$ as a precursor with ethanol solution. We have investigated how to control the size and morphology of TiO_2 nanoparticle with changing the synthesis parameters.

MATERIALS AND METHODS

Synthesis Method: 3.5 ml $TiCl_4$ (99.5% Merck) was slowly added dropwise into 35.0 ml ethanol (99.8% Merck) under stirring at a temperature of about 22°C and argon gas environment. A large amount of HCl gas was exhausted during the mixing process. At first, light yellow solution was obtained and it was then gelatinized for several times under air atmosphere with 88% humidity and the sol-gel formed. The pH of the solution was 1.0-1.5. After the formation of the sol-gel, each prepared solution was put in the aging process for 3 hours. We then prepared each gel-solution under ultrasound irradiation from 25 to 35 minutes (exposed with the ultrasound waves at 40 kHz and 60 Watt power). The final sol-gel was dried at 80°C therefore; a dry-gel was obtained. Eventually, dry-gel calcinated in the ranging from 120 to 600°C for one hour and TiO_2 nanopowders were obtained.

Characterization of TiO_2 Nanoparticles: X-ray diffraction (XRD) at 30 kV was used to identify the crystalline phases and to estimate the crystallite size. The XRD patterns were recorded with 2θ in the range of 10-80° by step scanning, using 2θ increments of 0.02° and a fixed counting time of 5 sec/step, with a GBC-MMR, employing Cu_K_α radiation. Scanning electron microscopy (SEM) with type Philips-XL30 at 16 kV and transmission electron microscopy (TEM) with type Phillips CM-120 at 100 kV were used to further examine the crystallite (particle) size, the crystallinity and morphology of the as-synthesized TiO_2 samples.

RESULTS AND DISCUSSION

We have synthesized titania powders with combined $TiCl_4$ as a precursor and ethanol under special circumstances. At first $TiCl_4$ reacted with ethanol and a large amount of HCl gas exhausted and $TiCl_x(OH)_{4-x}$ species was produced in the solution. Then, in process of mixing and acid environment, $TiCl_x(OH)_{4-x}$ absorbs a little amount of water from atmosphere to form Ti-OH bound. In polymerization and hydrolysis process, Ti-OH bounds formed …-Ti-O-…-Ti-OH strings. In hydrolysis process and while mixing solution, these long strings formed smaller Ti-O-Ti strings. With closing and development of Ti-O-Ti strings, three dimensional

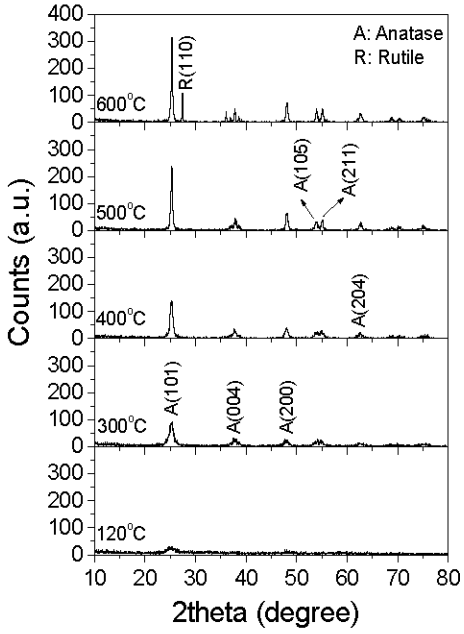

Fig. 1: The XRD patterns of TiO_2 powder samples and gelatinized for 24 hours

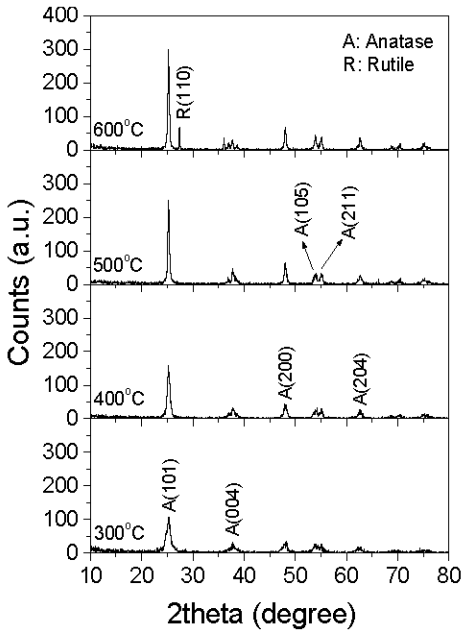

Fig. 2: The XRD patterns of TiO_2 powder samples and gelatinized for 72 hours

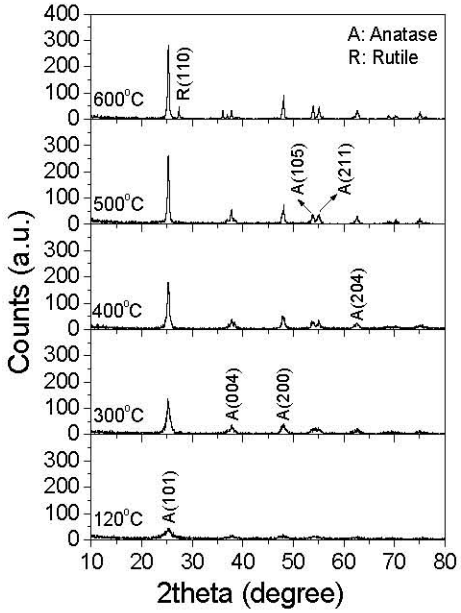

Fig. 3: The XRD patterns of TiO_2 powder samples and gelatinized for 120 hours

Table 1: Nanocrystallites diameter (nm) and weighing percentage of anatase phase in different gelatinization times and calcination temperatures

	Gelatinizing time (hours)		
Calcination temperature (°C)	24	72	120
120	4.10	---	5.50
300	7.23	9.50	11.00
400	12.15	14.01	15.80
500	20.10	23.00	24.30
600	28.06	30.14	32.55
X_A (%)	82.70	87.60	90.50

polymers were made and fromed $Ti(OH)_4$. TiO_2 nanoparticles were formed with $Ti(OH)_4$ molecules at special thermal conditions and according to equation the following [2, 24]:

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (1)$$

XRD spectra can check degree of nanomaterials' crystalline. Figs. 1, 2 and 3 show the XRD patterns of the as-prepared samples calcined at 120- 600°C and gelatinized for 24, 72 and 120 hours.

The average crystallite sizes of the samples were estimated for sharp peak considering Debye-Scherrer's equation ($D= 0.9\lambda/\beta_{hkl}.\ Cos\ \theta_{hkl}$) and XRD patterns [1, 27] (as shown in Table 1). where, D is the crystallite diameter, λ is the X-ray wavelength of $Cu\_K_{\acute{a}}$, θ_{hkl} is the Bragg's angle in degrees and β_{hkl} is the broadening of the *hkl* diffraction peak measured at half of its maximum intensity (in radians).

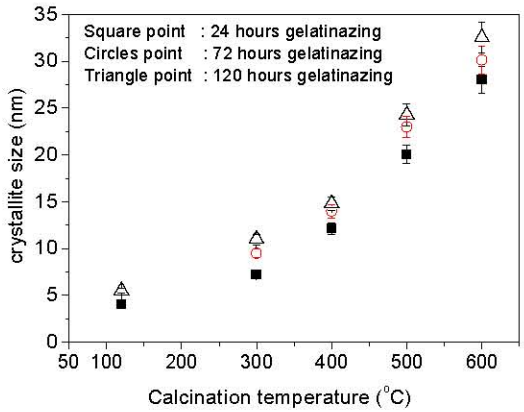

Fig. 4: crystallite size vs. calcination temperature

Fig. 4 shows the average size of crystallites vs. the calcination temperature. According to Fig. 4, when calcination temperature was increased from 120 to 600°C, the average crystallite sizes of anatase phase changed from 4.1 nm to 28.06 nm and from 5.5 nm to 32.55 nm in the gelatinizing time for 24 and 120 hours. In a calcination step at temperatures ranging from 300 to 600°C, the average crystallite sizes of anatase phase changed from 9.5 nm to 30.14 nm in the gelatinizing time for 72 hours.

All XRD patterns exhibited anatase peak up to calcination temperature 500°C. The rutile (1 1 0) diffraction peaks were appeared in the XRD patterns of the samples calcined from 500 to 600°C. The mass fraction of anatase phase in powders is counted in terms of the relative intensity of maximum anatase phase peak (101) and maximum rutile phase peak (110), the formula is as follows: $X_A = [1+1.265\ I_R/I_A]^{-1} \times 100$. In this equation, X_A is the contents of anatase phase in powders, I_A is the intensity of maximum anatase phase peak (101), I_R is the intensity of maximum rutile phase peak (110) and 1.265 is the scattering coefficient [28, 29].

The mass fraction of anatase phase in powders was calculated and the results are shown in the Table 1. According to Table 1, the mass fraction of anatase phase in powder samples is very high as calcination temperature increases from 500 to 600°C. Therefore dominant and further phase is anatase.

Fig. 5 shows scanning electron microscopy (SEM) images of the TiO_2 nanoparticles calcinated at 300°C and gelatinized for 24 and 120 hours. These figures show that high homogeneity emerged in the samples surface by increasing the gelatinizing time. Whatever the gelatinizing time was less, samples surface were severely agglomerated. With increasing the gelatinizing time, boundaries between nanoparticles were better and the morphology of particles changed to the spherical shape and nanopowders were less agglomerated.

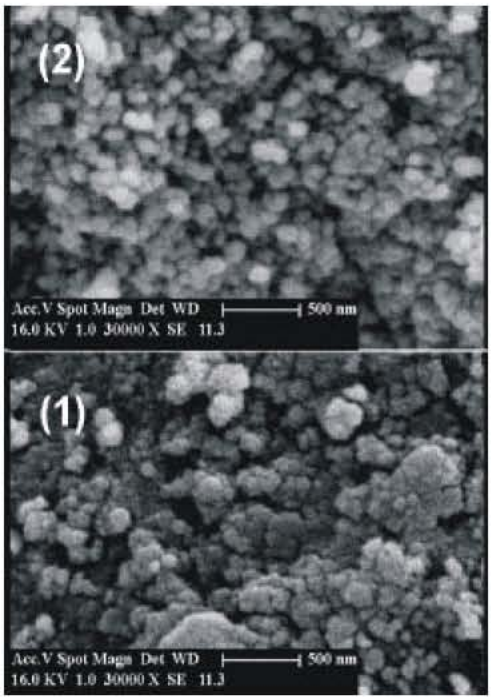

Fig. 5: SEM micrographs showing morphologies of TiO_2 powder samples made in calcination temperature 300°C and gelatinization time (1) 24 and (2) 120 hours

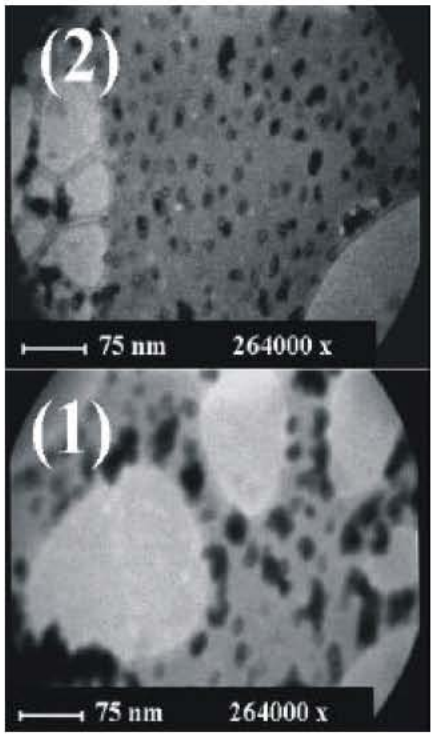

Fig. 6: TEM pictures of TiO_2 powders which gelatinized for the 120 hours and calcined for 1 hour at (1) 400 and (2) 500°C

These micrographs express clearly that using high gelatinizing times causes more homogeneity and increases the average size in the powder sample surface. Fig. 5 shows that TiO_2 nanoparticles were agglomerated when the sol was stringed in short time. In these figurs all dispersed particles were observed with size less than 100 nm.

Transmission electron microscopy (TEM) was used to further examine the crystallinity, morphology and size of particles. Fig. 6 shows TEM images taken from powder samples made in the gelatinization time for 120 hours and calcinated at various temperatures. Fig. 6 shows that the shape, crystallinity and spherical morphology of TiO_2 nanoparticles were strongly depended on the calcination temperatures. TEM micrograph (Fig. 6-1) indicated that the nanoparticles were small, in about 15 nm and the dispersivity and homogeneity of particles was not good when the calcination temperature was 400°C.

As shown in Fig. 6, the as-prepared powder in the lower calcination consisted of particles with poor agglomeration. The size of particle increased and the dispersivity and homogeneity was improved with the increase of the calcination. When calcination temperature increased to 500°C, the average grain size of anatase nanoparticles were obtained in the range 18- 22 nm (Fig. 6-2) and the size of the nanoparticles were quite uniform. The results of the TEM images are in good accordance with the results of the XRD patterns (Fig. 4 and Table 1).

CONCLUSION

Anatase TiO_2 nanoparticles was successfully synthesized by the sol-gel method using $TiCl_4$ as a precursor and just ethanol solution. The size of anatase TiO_2 nanoparticles anatase phase could be promoted by decreasing the gelatinizing time and using ultrasound waves. The diameter of anatase TiO_2 nanoparticles increased with increasing calcination temperature and/or gelatinization time; moreover the crystallinity, homogeneity and morphology of TiO_2 nanoparticles became better. Independent changes of calcination temperature and/or gelatinization time accompanied by ultrasonic waves and specific pH value could alter diameter of the TiO_2 nanoparticles.

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