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## SYNTHESIS OF NANOSIZED TiO<sub>2</sub> PARTICLES VIA ULTRASONIC IRRADIATION AND THEIR PHOTOCATALYTIC ACTIVITY

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### Abstract

The photocatalytic degradation of *p*-nitrophenol has been studied on TiO<sub>2</sub> nanoparticles prepared by hydrolysis of titanium tetraisopropoxide using ultrasonication technique coupled with sol-gel method. The titania particles prepared with ultrasonic irradiation shows the higher activity on the photocatalytic decomposition of *p*-nitrophenol compared to those prepared without ultrasonic irradiation.

*Keywords:* Nanosized titania, ultrasonication, sol-gel method, photocatalytic degradation of *p*-nitrophenol

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## INTRODUCTION

Nanocrystalline powders of titania are widely used as catalysts in photocatalytic reactions, gas sensors, white pigment materials [1]. The synthesis of nanocrystalline particles with controlled size and composition is of technological importance because they have more active sites for achieving enhanced performance. Up to now, many methods have been established for the synthesis of titania [2,3], the sol-gel technique being the most often used.

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Unfortunately, the sol-gel derived precipitates are amorphous in nature, which requires further treatment to induce crystallization [4]. The sonochemical synthesis has been described elsewhere, which has been employed to prepare amorphous metals and oxides [5, 6]. The use of ultrasound to enhance the rate of reaction become a routine synthetic technique for many homogeneous and heterogeneous chemical reaction [7].

In this paper, we prepared nanosized TiO<sub>2</sub> particles by hydrolysis of TTIP (titanium tetraisopropoxide) with and without ultrasonic irradiation coupled with sol-gel method. The physical properties of prepared nanosized TiO<sub>2</sub> particles were investigated. We also investigated the effect of R ratio (H<sub>2</sub>O/TTIP) and calcination temperature on the physical properties of nanosized TiO<sub>2</sub> particles, and examined the activity of TiO<sub>2</sub> particles as a photocatalyst for the decomposition of *p*-nitrophenol .

## EXPERIMENTAL

To prepare nanosized titania particles, titanium isopropoxide (97%, Aldrich) was used as a precursor of titania. For the preparation of pure titania particle, precursor was slowly added dropwise to pure water under vigorous stirring at room temperature. This solution was mixed for 6 h with rapid agitation (3500 rpm) and then was washed and filtered.

Sol samples formed by the hydrolysis process were treated with and without ultrasonic irradiation in an ultrasonic cleaning bath (Branson, USA, 115V, 2kW, 38kHz) for 1 h. The produced TiO<sub>2</sub> particles were separated in a centrifuge at 10,000 rpm for 10 min and were then washed by distilled water. The particles were dried at 100°C for 24 h and were then calcined at 300 ~ 700°C for 3 h.

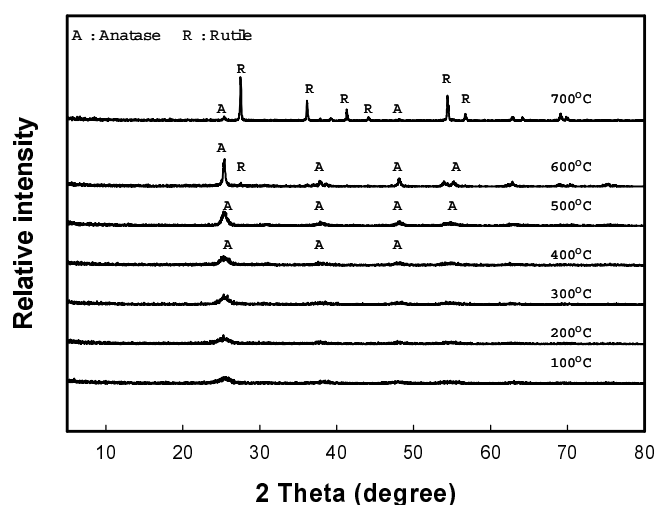
The major phase of the obtained particles was analyzed by X-ray diffraction (Rigaku D/MAXIIC) using Cu-K $\alpha$  radiation. The crystallite size of the prepared particles was determined from the broadening of the anatase main peak at  $2\theta = 25.3^\circ$  by the Scherrer equation [8]. The particle size and external morphology of the prepared particles were observed on a Transmission Electron Microscope (TEM, JEOL, JEM-2020) of 200kV accelerating voltage. The BET surface area of the prepared particles was determined by nitrogen adsorption isotherms at liquid N<sub>2</sub> temperature (77K). The particles were evacuated at 573 K prior to N<sub>2</sub> adsorption.

A biannular quartz glass reactor with the lamp immersed in the inner part was used for all the photocatalytic experiments. The batch reactor was filled with 500 mL of an aqueous dispersion in which the concentration of titania and of *p*-nitrophenol were 0.067 g/L and 100 mg/L, respectively and magnetically stirred to maintain uniformly both concentration and temperature. A 500 W

high-pressure mercury lamp (Kumkang Co.) was used. The circulation of water in the quartz glass tube between the reactor and the lamp allowed to cool the lamp and to warm the reactor at the desired temperature. Nitrogen was used as a carrier gas and pure oxygen was used as an oxidant. The samples were immediately centrifuged and the quantitative determination of *p*-nitrophenol was performed by a UV-vis spectrophotometer (Shimadzu UV-240).

## RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the TiO<sub>2</sub> particles prepared using ultrasonic irradiation and calcined at different temperatures. The major phases of all the prepared particles are anatase structure and a rutile peak is observed above 600°C.



**Fig. 1.** XRD patterns of nanosized TiO<sub>2</sub> powders prepared with ultrasonic irradiation at different calcination temperatures

Anatase crystallinity increases with an increase in calcination temperature up to 500°C. Upon increasing the temperature to 600°C, the rutile peak appears. In addition, the crystallinity increases with an increase of the calcination temperature because higher ordering in the structure of titania particles makes X-ray peak to be sharper and more narrow.

The crystallite size of the particles can be determined by the Scherrer's equation [8] and the particle size of titania particles is shown in Table 1. One can see that the crystallite size of the anatase phase is increased from 5.1 to 21.6 nm as the calcination temperature increases from 300 to 600°C. In addition, the crystallite size of titania particles prepared by with and without ultrasonic irradiation is marginally different.

**Table 1**

Physical properties of nanosized TiO<sub>2</sub> powders prepared with and without ultrasonic irradiation at different calcination temperature and their photocatalytic activity

Calcination temperature(°C)	BET	XRD	TEM	Activity	
	Surface area (m <sup>2</sup> /g)	Crystallite size(nm) <sup>c</sup>	Crystallite size(nm)	<sup>d</sup> k'(min <sup>-1</sup> )x10 <sup>-3</sup>	
TiO <sub>2</sub> <sup>a</sup>	200	189	5.9	-	-
	300	111	6.5	-	10.2
	400	103	7.1	-	-
	500	63	11	22	14.1
	600	30	25.2	-	-
TiO <sub>2</sub> <sup>b</sup>	200	198	5.1	-	-
	300	125	6.5	-	10.8
	400	108	7.4	-	15.1
	500	69	9.0	14	17.0
	600	25	21.6	-	11.7
	700	-	48.4 <sup>e</sup>	-	5.0

<sup>a</sup> prepared without ultrasonic irradiation,

<sup>b</sup> prepared with ultrasonic irradiation,

<sup>c</sup> obtained by Scherrer equation,

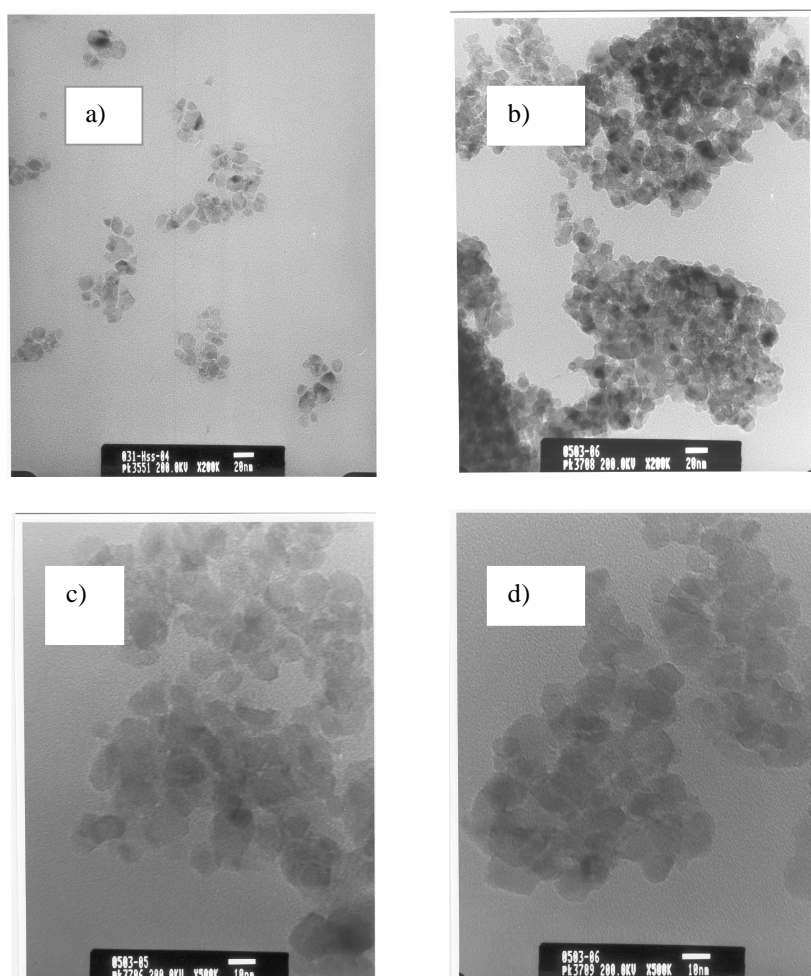
<sup>d</sup> apparent first-order constants(*k'*) of *p*-nitrophenol,

<sup>e</sup> rutile structure

The measured BET surface areas of titania particles prepared using ultrasonic irradiation and calcined at different temperatures from 200 to 600°C are in the range of 25-198 m<sup>2</sup>/g. These show slightly larger surface area compared to titania particles prepared without ultrasonic irradiation.

Figure 2 shows the TEM micrographs of the titania nanoparticles prepared with and without ultrasonic irradiation. The particles prepared with ultrasonic irradiation are shown to have a spherical shape and have a uniform size distribution (Fig. 2a) compared to those prepared without ultrasonic irradiation

(Fig. 2b). It clearly reveals the role of ultrasonication, which produces less agglomeration and more homogeneity in the particles. The crystallite size can be determined by counting the number of particle size in a given area and that is 14 nm prepared with ultrasonic irradiation but increases to 22 nm prepared without ultrasonic irradiation. The particle prepared without ultrasonic irradiation is shown to have larger value in particle size compared to that obtained from XRD analysis. This result indicates that the ultrasonication in the preparation of titania decreases the crystallite size by reducing the agglomeration of particles.



**Fig. 2.** TEM micrographs of nanosized TiO<sub>2</sub> powders prepared using different method: a) and c) with ultrasonic irradiation, b) and d) without ultrasonic irradiation

It is well known that photocatalytic oxidation of organic pollutants follows Langmuir-Hinshelwood kinetics [9,10]. Therefore, this kind of reaction can be represented as follows.

$$-dc/dt=kC \quad (1)$$

In addition, it can be integrated as follows:

$$C=C_0 \exp (-kt) \quad (2)$$

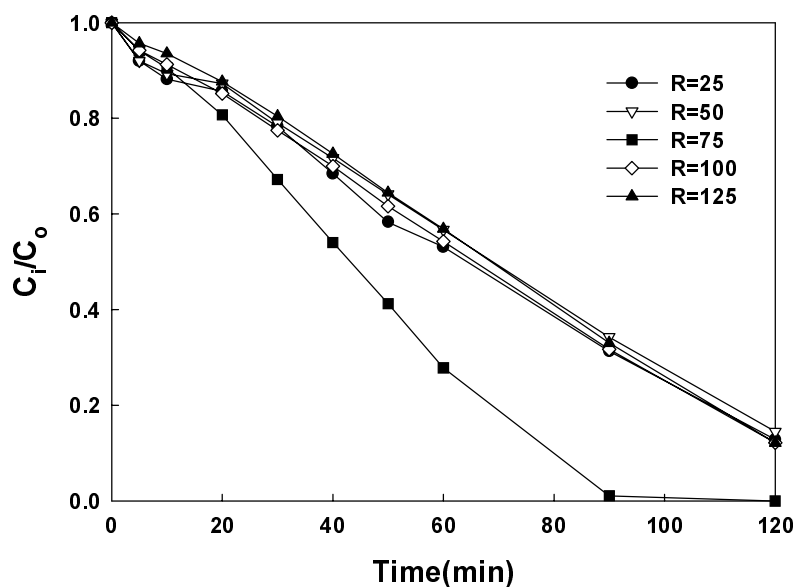
where  $C_0$  is initial concentration of the *p*-nitrophenol and  $k$  is a rate constant related to the reaction properties of the solute which depends on the reaction conditions, such as reaction temperature, pH of solution and the photocatalytic activity increases with increasing this value.

The photocatalytic activity for the decomposition of *p*-nitrophenol is examined and the result is shown in Table 1. The titania particles prepared with ultrasonic irradiation shows the higher activity on the photocatalytic decomposition of *p*-nitrophenol compared to those prepared without ultrasonic irradiation. This may be attributed to the fact that the former has a larger surface area and small crystallite size. It is consistent with the result that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases with a decrease of particle size [11]. It can be also confirmed that a small particle has a large illuminated surface area by the reason that the particles have a constant density at the same structure.

As shown in Table 1, the photocatalytic activity shows the highest value on the titania particle calcined at 500°C.

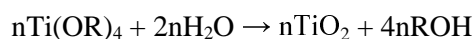
Titanium dioxide can take on any of the following three crystal structures: rutile, anatase, or brookite. Anatase-type titanium dioxide generally exhibits a higher photocatalytic activity than the other types of titanium dioxide as regards the decomposition of organic pollutants by suppressing the electron-hole recombination [12]. In the case of titania particle calcined at 600°C, the anatase and rutile phase are combined and amorphous phase are mixed with anatase phase at the titania particle calcined below 300°C. Therefore, the pure anatase titania calcined at 500°C shows the highest activity on the photocatalytic decomposition of *p*-nitrophenol.

Figure 3 shows photocatalytic degradation of *p*-nitrophenol over titania prepared by different R ratio. The photocatalytic activity shows a maximum value at the R ratio=75. In the preparation of titania by sol-gel process, the physical properties of titania depend on preparation conditions, such as R (water/alkoxide) ratio, calcination temperature and the addition of acid. It is well known that water plays an important role on the formation of nucleus and the growth of crystallites, and that the nucleus can be homogeneously formed in the  $R \geq 10$  [13].



**Fig. 3.** Photocatalytic decomposition of *p*-nitrophenol over TiO<sub>2</sub> prepared with various R ratios: C<sub>0</sub>=100 mg/L, W=0.067 g/L

Metal alkoxide needs 2 mol water in the preparation of titania, as in the following reaction:



It is well known that the formation of nucleus can readily occur rather than the growth of crystallite as the R ratio increases and crystallite size becomes small [13]. In the high R ratio, larger than 100, however, the aggregation of particles brings out the increase of particle size. Therefore, photocatalytic activity shows a maximum value at the R ratio=75 because of their small particle size effect.

In the present work, TiO<sub>2</sub> nanoparticles were prepared by hydrolysis of TTIP (titanium tetraisopropoxide) using ultrasonication technique coupled with sol-gel method. The photocatalytic degradation of *p*-nitrophenol has been studied by using batch reactor in the presence of UV light. The crystallite size of titania particles prepared by with and without ultrasonic irradiation is marginally different. The particles prepared with ultrasonic irradiation are shown to have a

spherical shape and have a uniform size distribution compared to those prepared without ultrasonic irradiation. The photocatalytic activity shows the highest value on the titania particle calcined at 500°C.

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