

# Ultrasonic-assisted pH Swing Method for the Synthesis of Highly Efficient TiO<sub>2</sub> Nano-size Photocatalysts

Bernaurdshaw Neppolian · Evrim Celik ·  
Masakazu Anpo · Heechul Choi

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**Abstract** A new route for the preparation of nanocrystalline TiO<sub>2</sub> particles based on the pH swing method assisted by ultrasonic irradiation in the presence of a surfactant (Pluronic P-123) has been successfully achieved. The prepared TiO<sub>2</sub> catalysts were calcined from 400 to 800 °C and characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Fourier transformed infra-red spectroscopy (FTIR), gas adsorption measurements (BET) and thermogravimetric measurements (TAG/DTA) analyses. Characterization results revealed that the enhancement in the particle size of TiO<sub>2</sub> by the pH swing method could be controlled by combining the pH swing with ultrasonic irradiation. Increasing the calcination temperatures led to an increase in both the particle and pore size, whereas the surface area and pore volume gradually decreased. A synergistic effect was

observed in the combined process of pH swing with ultrasonication, yielding small TiO<sub>2</sub> particles as well as high surface area, pore volume, pore diameter, and crystalline anatase phase. The activity of the catalysts was investigated for the oxidation of 4-chlorophenol (4-CP). TiO<sub>2</sub> prepared with 15 times pH swing and calcined at 700 °C was found to show the highest rate for the oxidative degradation of 4-CP when compared to the TiO<sub>2</sub> sample prepared with just 1 time pH swing and to the commercial P-25 TiO<sub>2</sub> Degussa photocatalyst. Thus, a novel approach in controlling the various physico-chemical parameters of TiO<sub>2</sub> nanoparticles was developed.

**Keywords** pH swing method · Ultrasonic irradiation · Surfactant · TiO<sub>2</sub> photocatalysts · 4-Chlorophenol

## 1 Introduction

The synthesis of mesoporous TiO<sub>2</sub> nanoparticles has attracted a great deal of attention due to the unique characteristics of the mesoporous nanoparticles which are different from macro-size particles. Especially, in studies of environmental and electronic applications, TiO<sub>2</sub> nanoparticles show tremendous changes in activity. They are widely used in environmental cleaning processes as photocatalysts, in the fabrication of solar-fuel cells, light emitting diodes, and other useful applications [1–10]. In addition to environmental remediation processes, much attention has been focused on mesoporous TiO<sub>2</sub> for solar cells and fuel cells since TiO<sub>2</sub> nanoparticles are highly efficient materials [2–5]. In fact, Haque et al. [2] have reported the importance of mesoporous TiO<sub>2</sub> nanoparticles for the preparation of highly efficient light emitting diodes.

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B. Neppolian · E. Celik · H. Choi (✉)  
Environmental Nano-particle Laboratory, Department  
of Environmental Science and Engineering, Brain Korea 21  
for Future Environmental Fusion Technology, Gwangju Institute  
of Science and Technology (GIST), 1-Oryong-dong, Buk-Gu,  
Gwangju 500-712, South Korea  
e-mail: hcchoi@gist.ac.kr

B. Neppolian  
e-mail: b\_neppolian@yahoo.com

E. Celik  
e-mail: evrim@gist.ac.kr

M. Anpo  
Department of Applied Chemistry, Graduate School  
of Engineering, Osaka Prefecture University,  
Gakuen-Cho 1-1, Sakai, Osaka 599-8531, Japan  
e-mail: anpo@ok.chem.osakafu-u.ac.jp

In recent years, the application of ultrasound, as a new technology for the preparation of nanoparticles, especially  $\text{TiO}_2$ , has been explored [11–20]. During this method, ultrasonic waves consisting of compression and rarefaction cycles produce cavitation bubbles in a liquid. After several compression cycles, the cavitation bubbles collapse violently and adiabatically at extremely high temperatures of up to 5,000 °C and pressures of about 500 atm. [11, 20]. Such extreme temperatures and pressures within a small reactor can induce many changes in the morphology of  $\text{TiO}_2$  nanoparticles during the preparation process. Generally, ultrasonic irradiation is favorable for the fragmentation of  $\text{TiO}_2$  particles and also increased high-velocity interparticle collisions among the particles which can prevent the formation of larger particles. These two effects are, thus, important advantages in the use of ultrasonic irradiation for the preparation of nanomaterials [12, 20].

Yang et al. [21] firstly synthesized large-pore mesoporous and high surface area semiconductor metal oxides such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{WO}_3$  and  $\text{SnO}_2$ , using amphiphilic poly (alkyl oxide) block co-polymers as a structure-directing agent. Since the application of surfactant for the synthesis of mesoporous  $\text{TiO}_2$  was implemented, many researchers have prepared  $\text{TiO}_2$  with surfactants [15, 21–26] along with ultrasonic irradiation to synthesize nanoparticles.

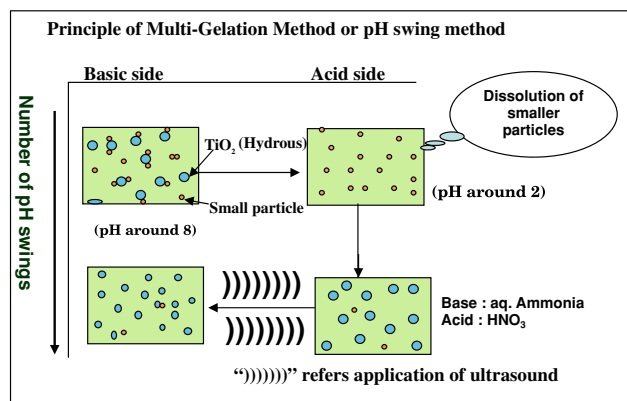
The pH swing method is another method for the preparation of mesoporous  $\text{TiO}_2$  without any structure-directing agent. Our previous findings using the pH swing method also yielded  $\text{TiO}_2$  samples with high surface area, pore size and pore volume [6]. In the earlier method, we alternated the addition of  $\text{TiCl}_4$  (as an acid solution) and aqueous ammonia (as a basic solution) to water at regular intervals without adjusting the pH of the reaction mixture [6]. Although the  $\text{TiO}_2$  prepared by pH swing led to mesoporous  $\text{TiO}_2$  with nano-size particles, the increase in particle size by increasing the pH swing numbers could not be controlled and the activity for the oxidative degradation of organic compounds was not as high as that of commercial catalysts.

However, based on the principles of this pH swing method, a new approach was investigated combining the use of ultrasonic irradiation and a surfactant with the pH swing method. The morphology of the  $\text{TiO}_2$  particles prepared with this newly adapted method was investigated and compared with the photocatalytic properties of other  $\text{TiO}_2$  catalysts. In order to compare the photocatalytic degradation performance, 4-chlorophenol was used as a pollutant [27, 28]. In this combined approach,  $\text{TiO}_2$  was synthesized by the pH swing method in the presence of the P-123 surfactant under ultrasonication and the results are discussed here.

## 2 Experimental

### 2.1 Catalyst Preparation

The principles behind the multi-gelation method of synthesizing the  $\text{TiO}_2$  particles are illustrated in Fig. 1. The  $\text{TiCl}_4$  solution was prepared by mixing equal weights of  $\text{TiCl}_4$  with crushed ice made from distilled water. The  $\text{TiO}_2$  photocatalysts were prepared by the alternate addition of a  $\text{TiCl}_4$  solution (7 mL) and aqueous ammonia solution (9 mL) into hot water (1,000 mL) with 10 g of a triblock co-polymer, Pluronic P-123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , BASF Company, USA), as the surfactant (premixed under vigorous stirring), heated and maintained at 80 °C under vigorous stirring. The pH swings were carried out with an ultrasonic bath type instrument under ultrasonic irradiation (Branson 8510, USA). After the reaction was completed, the catalysts were kept in an ultrasonication bath for 1 h for further irradiation. In the controlled pH swing method, 1 M  $\text{HNO}_3$  acid was used to bring down the pH to around 2 at each swing time and aqueous ammonia was used to adjust the pH at around 8. A white precipitate of hydrous  $\text{TiO}_2$  particles was formed. The complete process was then referred to as “one pH swing”. After 5 min, the alternate addition of the same quantity of both  $\text{TiCl}_4$  (7 mL) and aqueous ammonia (9 mL) was carried out to the same hydrous  $\text{TiO}_2$  particle system. This is referred to as “two pH swings”. In this way, photocatalysts with two different pH swing numbers, 1 and 15 times, were prepared under the same experimental conditions. Finally, a white precipitate of the hydrous  $\text{TiO}_2$  was first washed with excess ethanol to remove the P-123 and then with water, filtered, and dried at 120 °C for 15 h. The dried  $\text{TiO}_2$  was then calcined at various temperatures (400–800 °C) with an electric furnace under a flow of air and then ground to fine powder using a pestle and mortar.



**Fig. 1** Schematic representation of pH swing method with ultrasonication

## 2.2 Characterizations

The crystalline structure and morphology of the TiO<sub>2</sub> particles (anatase, rutile and brookite) were investigated by X-ray powder diffraction (XRD, Rigaku RDA-1A X-ray diffractometer, D/MAX Ultima III, Japan) analysis using Cu K $\alpha$  radiation with a Ni filter. The morphology and size distribution of the photocatalysts were recorded by transmission electron microscopy (TEM, JEOL, JEM 2100, Japan). Before analyses, the samples were placed on the surface of copper grids and dried under ambient conditions. The N<sub>2</sub> BET surface area, pore volume, pore-size distribution, porosity, and pore diameter of the photocatalysts were determined by a BET analyzer (Micromeritics, ASAP 2020, USA). The surface-OH groups of the photocatalysts were determined by Fourier transformed infra-red spectroscopy (FTIR) using KBr in pellet form (FTIR, JASCO FT/IR-460 Plus, Japan). Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a TGA-50A/DSC-60A analyzer (Shimadzu, Japan).

## 2.3 Photocatalytic Activity Measurements

The photocatalytic activity was compared by the reaction rates for the oxidative degradation of 4-chlorophenol (4-CP). The photocatalyst (300 mg) was suspended in a quartz cell with an aqueous solution of 4-CP ( $2.5 \times 10^{-4}$  M, 200 mL). Prior to UV light irradiation, the suspension was stirred for 30 min under oxygen atmosphere under dark conditions. The sample was then irradiated at 24 °C using UV light (transmitting range,  $\lambda$  200–800 nm) from a 300 W Xe Arc lamp (Oriel Lamp, Model 66984, USA) with continuous stirring under oxygen atmosphere. At periodic intervals, up to 5 mL aliquots were taken from the system and filtered through a Millipore filter to remove the TiO<sub>2</sub> particles. The percentage of degradation was then analyzed by a UV-Vis spectrophotometer at 225 nm (UV-mini 1240, Shimadzu) and the mineralization of 4-CP (TOC) was measured by a TOC analyzer (Pollution & Process Monitoring, England).

## 3 Results and Discussion

### 3.1 Principle of pH Swing Method with Ultrasonication

In this study, we have introduced the surfactant-mediated (Pluronic P-123) synthesis of TiO<sub>2</sub> by a combination of pH swing with ultrasonication, as depicted in Fig. 1. With the pH swing method, the addition of acid can dissolve the smaller particles of hydrous TiO<sub>2</sub> (Fig. 1) leaving only the

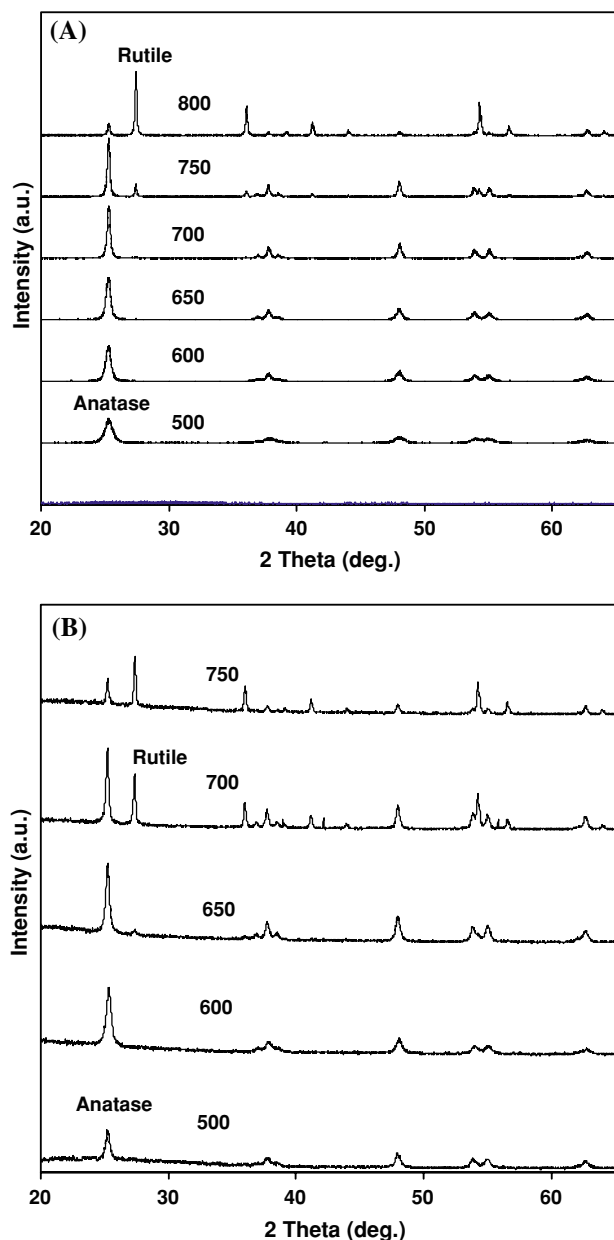
larger particles. When the number of swings increases, the size of the particles also increases and this is the main drawback of the pH swing method [6]. However, by applying ultrasonication during the pH swing method, it is more easy to control the growth of the particles with respect to an increase in the number of pH swing times, as is detailed in our recent report on the influence of ultrasonication in controlling the particle size [20]. During pH swing, the particle size steadily increases along with the number of pH swings, however, this combined approach was successful in controlling the size of the particles, as depicted in Fig. 1.

### 3.2 X-ray Powder Diffraction (XRD)

Figure 2 shows the XRD patterns of all the TiO<sub>2</sub> catalysts prepared by pH swing coupled with ultrasonication in the presence of the P-123 surfactant and calcined at different temperatures from 400 to 800 °C. The peaks that appear at around  $2\theta = 25^\circ, 38^\circ, 48^\circ, 55^\circ,$  and  $63^\circ$  correspond to the diffraction patterns of (101), (112), (200), (211), and (264) planes, respectively, of pure anatase. Similarly, the peaks at around  $2\theta = 27^\circ, 35^\circ, 41^\circ,$  and  $57^\circ$  correspond to the diffraction patterns of (110), (101), (111) and (220) planes, respectively, of the pure rutile phase of TiO<sub>2</sub>. The crystallinity of the TiO<sub>2</sub> particles was quantitatively estimated with the relative intensity of the (101) diffraction peak of the pure anatase [29]. It was clearly seen that the anatase peak intensity (101) gradually increased, becoming stronger and narrower with an increase in the calcination temperatures, indicating the enhancement of TiO<sub>2</sub> crystallization. Maximum crystallinity with a higher anatase phase (95%) was attained at a calcination temperature of 700 °C for the 15 pH swings prepared catalysts, as shown in Fig. 2a, whereas at the same calcination temperature, around a 43% rutile phase was exhibited for the 1 pH swing prepared catalysts, as shown in Fig. 2b. The pH swing method could prevent the phase transition from anatase to rutile until 600 °C at higher pH swing numbers, as has been observed earlier studies. However, in this study, mostly an anatase phase was retained in the 15 times pH swing prepared TiO<sub>2</sub> nanoparticles up to 700 °C. These results clearly indicate the effect of pH swing in preventing phase transition from anatase to rutile that was not subject to effects of ultrasonic irradiation.

### 3.3 BET Analysis

Sheng et al. [26] have reported on TiO<sub>2</sub> synthesized with a surfactant under the influence of ultrasonication and possessing a surface area of 152 m<sup>2</sup>/g, pore volume of 0.3 cm<sup>3</sup>/g, and an average particle size of 5.6 nm. Also, Yu et al. [15] have synthesized TiO<sub>2</sub> catalysts with a surfactant



**Fig. 2** XRD patterns of TiO<sub>2</sub> photocatalysts prepared by pH swing method with ultrasonication and calcined at different temperatures for 3 h: (a). 15 time pH swings; (b). 1 time pH swing

assisted by ultrasonication and calcined at 400 °C, possessing a surface area of 128 m<sup>2</sup>/g, pore size of 9.2 nm, and pore volume of 0.3 cm<sup>3</sup>/g. The surface area, pore size and pore diameter values of the TiO<sub>2</sub> prepared with 1 time pH swing (see Table 1) were almost similar to the results reported by Yu et al. [15] and Sheng et al. [26]. However, in this study, it is interesting to note that the TiO<sub>2</sub> prepared with 15 times pH swing and assisted by ultrasonication in the presence of the P-123 surfactant and calcined at 400 °C exhibited two times higher surface area (315 m<sup>2</sup>/g), high pore size (13 nm) and high pore volume (0.927 cm<sup>3</sup>/g), as shown in Table 2, when compared with previous reports by Sheng et al. [26] and Yu et al. [15]. This study emphasizes the importance of increasing the pH swing numbers in combination with ultrasonication in the presence of a surfactant. An increase in the pH swing numbers was shown to have a significant effect on the surface area and all of the important parameters of the TiO<sub>2</sub> particles. Thus, for the formation of smaller particles with high surface area, not only the combination of pH swing with ultrasonication but also the assistance of ultrasonication with a surfactant was found to be essential. Such a coupled approach is, thus, shown to be an efficient technique for the synthesis of TiO<sub>2</sub> nanoparticles.

The TiO<sub>2</sub> photocatalysts prepared without using P-123 surfactant exhibited less surface area and less pore volume when compared with those prepared using P-123. For example, the catalysts calcined at 700 °C without P-123 possessed 19 m<sup>2</sup>/g BET surface area, while a surface area measuring 45 m<sup>2</sup>/g was observed for P-123. Similar results have been reported by Yu et al [15]. The physico-chemical characteristics such as, surface area, crystallinity, particle size, etc., of TiO<sub>2</sub> catalysts prepared by 15 times pH swing were less than those prepared using P-123 surfactant irrespective of the different calcination temperatures from 400 to 750 °C. Thus, this work was mainly focused on the preparation of TiO<sub>2</sub> using P-123 under the influence of ultrasonication, adopting pH swing method.

With the pH swing method, parameters such as particle size, surface area, pore size, pore diameter, and percentage of anatase phase, show enhancement with an increase

**Table 1** TEM average particle size, XRD anatase/rutile ratio, BET specific surface area, pore size and pore volume of TiO<sub>2</sub> prepared by 1 time pH swing with ultrasonication

Catalysts <sup>a</sup>	Particle size TEM (nm)	Anatase: rutile (%)	BET surface area (m <sup>2</sup> /g)	Pore-size (nm)	Pore-volume (cm <sup>3</sup> /g)
400	15	Anatase	123	14	0.423
500	18	Anatase	70	18	0.303
600	23	Anatase	56	18	0.237
650	28	86:14	44	19	0.191
700	35	57:43	25	20	0.109
750	60	36:64	12	16	0.046

<sup>a</sup> Calcination temperatures (°C/3 h)

**Table 2** TEM average particle size, XRD anatase/rutile ratio, BET specific surface area, pore size and pore volume of TiO<sub>2</sub> prepared by 15 times pH swing with ultrasonication

Catalysts <sup>a</sup>	Particle size TEM (nm)	Anatase : rutile (%)	BET surface area (m <sup>2</sup> /g)	Pore-size (nm)	Pore-volume (cm <sup>3</sup> /g)
400	Amorphous	Anatase	315	13	0.927
500	15	Anatase	115	18	0.508
600	18	Anatase	75	22	0.385
650	21	Anatase	64	24	0.337
700	28	97:03	45	24	0.229
750	34	86:14	22	26	0.136

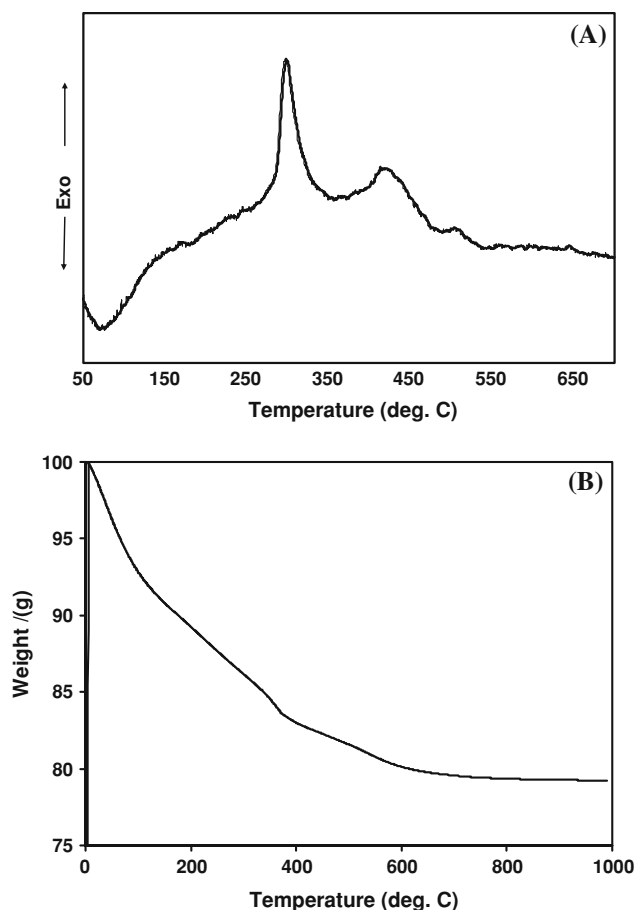
<sup>a</sup> Calcination temperatures (°C/3 h)

in the number of pH swings. However, in the combined preparation method, the particle size decreased with an increase in the number of pH swings upon ultrasonication (Tables 1 and 2), although all other parameters showed an increase similar to the uncombined method. For example, the average particle size of the TiO<sub>2</sub> at 1 time pH swing was 28 nm, whereas the average particle size with 15 times pH swing was 21 nm under the same experimental conditions (at 650 °C calcined). This is in contrast to the case of the pH swing method without ultrasonication in which the particle size of the TiO<sub>2</sub> catalysts prepared under similar conditions without ultrasonication and P-123 increased from 8 to 12 nm by increasing pH swings numbers from 5 to 15. In general, pH swings will dissolve the smaller particles and leave only the larger particles. However, when the particles were subjected to ultrasonication, the growth of the particles was affected due to fragmentation and also an increase in high-velocity interparticle collisions, preventing the formation of large particles [20]. Furthermore, the average particle sizes of TiO<sub>2</sub> without ultrasonication, in the absence of P-123 surfactant, and with pH swing numbers increasing from 5 to 15 were 8–12 nm. However, the particle size was increased to 28 nm for 1 time pH swing and to 21 for 15 times pH swings. The increase in particle sizes even after the influence of ultrasonication is mainly due to the presence of surfactant. The surfactant generally increases the particle size along with pores, which in turn enhances the surface area more efficiently [15, 26]. This is an additional advantage of P-123 with ultrasonication using pH swing method.

This combined approach of using ultrasonication coupled with pH swing and a surfactant is, thus, an important advantage enabling the synthesis of TiO<sub>2</sub> nanoparticles with high pore volume and pore diameter as well as well-controlled particle sizes.

### 3.4 TGA/DTA Studies

The TGA/DTA curves of the TiO<sub>2</sub> catalysts prepared by 15 times pH swing are shown in Fig. 3. The DTA curves of the as-prepared TiO<sub>2</sub> catalyst, i.e., without calcinations, is



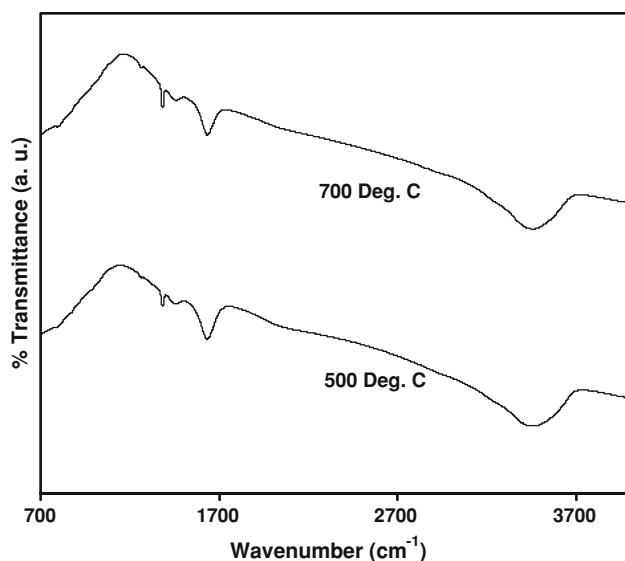
**Fig. 3** TGA/DTA curves of as prepared TiO<sub>2</sub> photocatalysts by 15 times pH swing: (a) DTA curve; (b) TGA curve

shown in Fig. 3a and exhibits two exothermic peaks. A deep valley at around 80 °C represents a small endothermic effect corresponding to the ethanol and adsorbed water on the mesoporous TiO<sub>2</sub> [15, 26]. The exothermic peaks appearing at around 300 and 420 °C can be attributed to the removal of the surfactant P-123 and crystallization of amorphous TiO<sub>2</sub>, respectively. A small exothermic peak observed at 510 °C is attributed to the combustion of carbonized P-123 which is left over due to the quickly rising temperature during DTA analysis. A small peak at 646 °C is attributed to the transformation of a

small portion of TiO<sub>2</sub> from anatase to rutile phase. The TGA curve shows two weight losses (Fig. 3b), the first at around 100 °C corresponding to the removal of ethanol and adsorbed water on TiO<sub>2</sub>. The second weight loss of 18% at around 250–450 °C and corresponding peaks in DTA indicate the removal of the P-123 surfactant. Weight loss in the TGA curve stabilizes after 600 °C, corresponding to the DTA patterns.

### 3.5 FTIR Spectra

Figure 4 shows the FTIR spectra of the TiO<sub>2</sub> photocatalysts prepared by 15 pH swings with ultrasonication and calcinations at 500 and 700 °C. The FTIR spectra of all the other TiO<sub>2</sub> catalysts showed almost similar patterns as these 15 pH swing samples. In Fig. 4, two peaks appear at around 1,650 and 3,400 cm<sup>-1</sup>, corresponding to the physically adsorbed water molecules and surface hydroxyl groups [15, 16]. Apart from these two peaks, no other peaks related to the surfactant or other C–C bonds were obtained. This clearly indicates that all the surfactant molecules are completely combusted during calcination at 500 °C. There is no surfactant or any other organic molecules present in the TiO<sub>2</sub>. The peak intensity at 1,650 cm<sup>-1</sup> for the catalysts calcined at 500 °C was found to be higher than those calcined at 700 °C. It is known that at higher calcination temperatures, the surface hydroxyl groups (~3,400 cm<sup>-1</sup>) diminishes and mostly disappear after 600 °C. However, the TiO<sub>2</sub> samples calcined at 700 °C had more surface hydroxyl groups, leading to the higher activity of the TiO<sub>2</sub> catalysts.



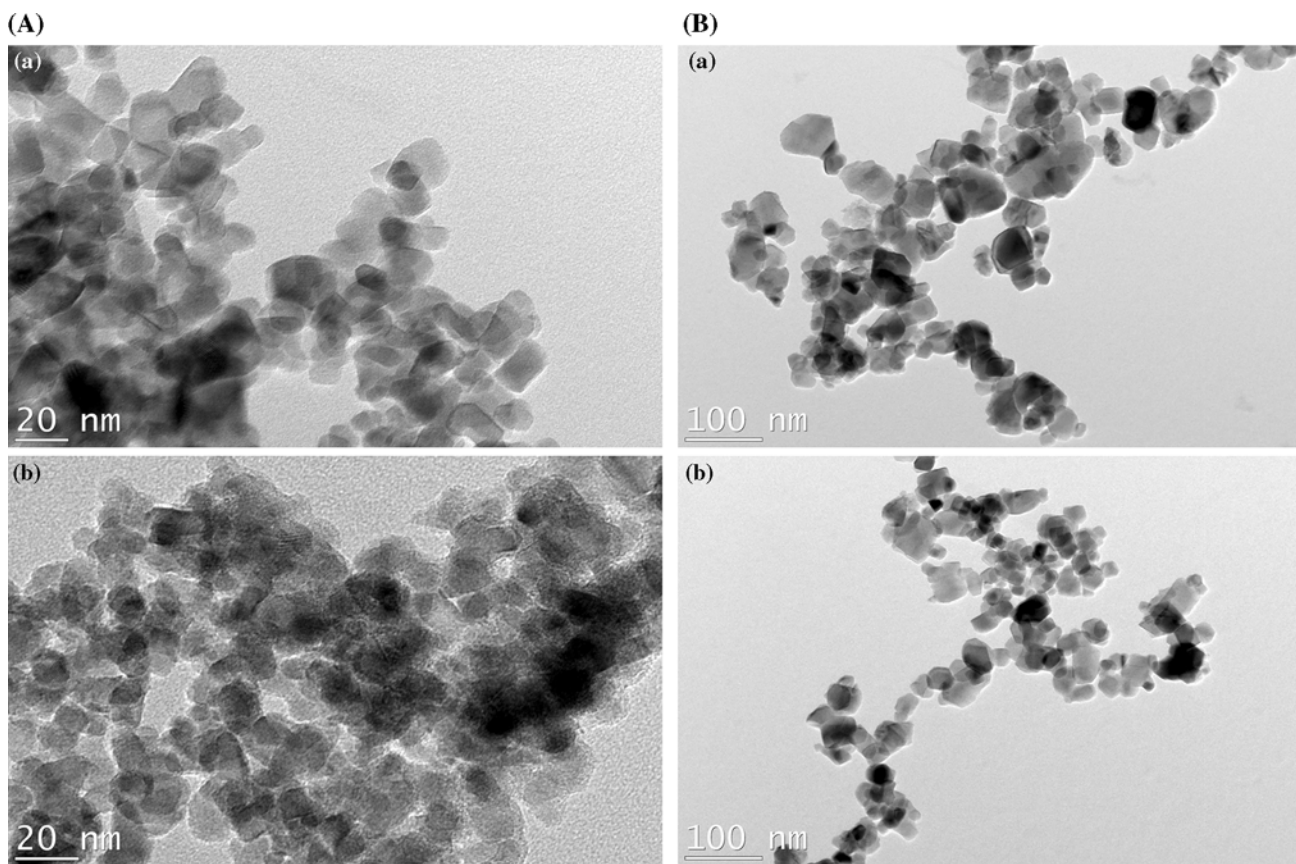
**Fig. 4** FTIR spectra of TiO<sub>2</sub> photocatalysts prepared by 15 times pH swing and calcined at 500 and 700 °C for 3 h

### 3.6 TEM Analysis

TEM analysis provides information on the particle size, morphology, and crystallinity of the TiO<sub>2</sub> catalysts. Figure 5 shows the TEM images of TiO<sub>2</sub> prepared by the pH swing method coupled with ultrasonication and calcined at 500 and 700 °C for 3 h as a representative catalyst. The average particle size of all the particles were obtained from the TEM images and are listed in Tables 1 and 2 while the TEM values are consistent with the XRD data. The morphology of the particles was mostly irregular in shape. The shape was not uniform with both 1 and 15 times pH swing catalysts, as shown in the Fig. 4b. It can be seen that the particle size of TiO<sub>2</sub> with 15 times pH swing are smaller than the catalysts with 1 time pH swing (Fig. 5B) due to the increase in pH numbers. Ultrasonication is, thus, seen to have a strong influence in the control of the particle size of TiO<sub>2</sub> during the pH swing method. The difference in particle size ranged from 20 to 40 nm in the case of TiO<sub>2</sub> prepared by 15 times pH swing, as shown in the TEM image (Fig. 5B).

### 3.7 Photocatalytic Activity of TiO<sub>2</sub> Nanoparticles

The photocatalytic activity of the catalysts was compared by the reaction rates for the oxidative degradation of 4-CP in aqueous phase. The TiO<sub>2</sub> catalysts prepared at 15 times pH swings and calcined at 700 °C exhibited higher photocatalytic activity for the degradation of 4-CP degradation than the other samples calcined at temperatures from 400 to 800 °C, as shown in Table 3. Similarly, for 1 time pH swing, the catalysts calcined at 650 °C showed the maximum efficiency for the degradation of 4-CP (Table 3). Moreover, Fig. 6 illustrates the percentage rate for the degradation of 4-CP by three different catalysts including the commercial P-25 Degussa TiO<sub>2</sub>. Figure 6 shows that 15 pH swing TiO<sub>2</sub> with 700 °C calcination showed the maximum percentage for the degradation of 4-CP, even higher than P-25. It is known that the photocatalytic degradation efficiency greatly depends on the particle size, surface area, and anatase/rutile phase ratio as well as the pore size and pore volume of the TiO<sub>2</sub> particles [6, 26]. In contrast, the catalysts calcined at 700 °C possessed a larger particle size (28 nm) with less surface area and pore volume (Table 2) but exhibited maximum degradation of 4-CP in 1 h irradiation time. A similar trend was observed with TiO<sub>2</sub> prepared with 1 time pH swing. The catalytic activity for the degradation of 4-CP was also enhanced by increasing the calcination temperature (Table 3). This can be ascribed to the increase in anatase crystallinity (Fig. 2). After 650 °C calcinations with 1 time pH swing and 700 °C with 15 times pH swings, a more rutile phase which is an undesired phase for photocatalytic degradation



**Fig. 5** TEM images of TiO<sub>2</sub> photocatalysts prepared by pH swing method with ultrasonication: **(A)** (a) 1 time pH swing and calcined at 500 °C, (b) 15 times pH swing and calcined at 500 °C; **(B)** (a) 1 time

pH swing and calcined at 700 °C, (b) 15 times pH swing and calcined at 700 °C for 3 h

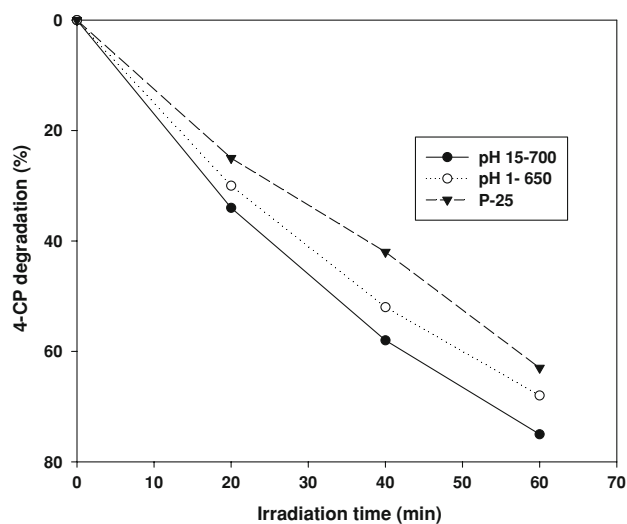
reactions was formed. Furthermore, Tryba et al. [32] have reported that the production rate of the OH radical is very high with standard TiO<sub>2</sub> photocatalysts (Japan) when calcined at 700 °C. They have estimated the production of OH radicals by a fluorescence method and found that the maximum production of OH radicals is achieved with TiO<sub>2</sub> catalysts calcined at 700 °C. They have reported a small content of the rutile phase <10 mass%, which is beneficial for OH radical production, suggesting that the photo-

formed electrons and holes were retarded, reflecting a high yield of OH radicals. Hence, the OH production rate is also proportional to the crystallinity of the anatase phase.

**Table 3** Comparison of % degradation of 4-chlorophenol using the TiO<sub>2</sub> photocatalysts prepared by 1 time pH swing, 15 times pH swings and P-25

Catalysts <sup>a</sup>	1 pH swing	15 pH swings
500	45	53
600	53	65
650	68	74
700	60	77
750	41	50
800	32	44
P-25	64	

<sup>a</sup> Calcination temperatures (°C/3 h)



**Fig. 6** Comparison of the rate of degradation of 4-chlorophenol using the TiO<sub>2</sub> photocatalysts prepared by 1 time pH swing and calcined at 650 °C, 15 times pH and calcined at 700 °C and P-25 TiO<sub>2</sub>

In addition, the crystallite size is also an important factor and showed significant influence in the production of OH radicals. It was found that TiO<sub>2</sub> particles of around 30 nm in size can produce more OH radicals [32]. They also emphasized that the lattice strain is minimum for TiO<sub>2</sub> at almost zero with the catalysts calcined at around 700 °C. When crystallite or rutile phase increases, the lattice strain also increases to a greater extent. The degradation rate of methylene blue in an aqueous phase showed maximum degradation with TiO<sub>2</sub> catalysts calcined at 700 °C, as reported by Tryba et al. [32].

All the important criteria, which Tryba et al. [32] mentioned for high catalytic activity, correspond well with the catalysts prepared by 15 times pH swing and calcined at 700 °C combined with ultrasonication in the presence of a surfactant (Table 2). The TiO<sub>2</sub> prepared with 1 time pH swing did not contribute to a high activity at 700 °C due to the formation of a more rutile phase (43%), which inhibits the production of OH radicals, as has been reported by Tryba et al. [32].

The supporting information by Tryba et al. [32] substantiates the higher activity of the catalysts prepared at 700 °C than all the other TiO<sub>2</sub> photocatalysts calcined at different temperatures. Furthermore, parameters such as the particle size, surface area, anatase/rutile ratio, and pore volume showed higher values when compared with our previous pH swing method [6]. It is evident that the ultrasonic-assisted pH swing method in the presence of a surfactant can produce TiO<sub>2</sub> nanoparticles with enhanced photocatalytic activity. This study clearly reveals that the catalytic activity depends not only on the particle size and surface area but also on the production of OH radicals while the generation of OH radicals depends on the crystallite size, lattice strain, anatase/rutile phase, and the calcination temperature.

Without using the surfactant P-123, the photocatalytic degradation of 4-CP was found to be 50% for the catalysts calcined at 700 °C using 15 times pH swings, which was less than P-25 catalysts. At the same time, 77% degradation of 4-CP was achieved with TiO<sub>2</sub> prepared with P-123 under similar experimental conditions. The catalytic activity of the TiO<sub>2</sub> catalysts without P-123 was insignificant across various calcination temperatures due to the low surface area and hence, this work was mainly focused on the preparation of TiO<sub>2</sub> using P-123 under the influence of ultrasonication, adopting pH swing method.

#### 4 Conclusions

A new route using an ultrasonic-assisted pH swing method for the preparation of TiO<sub>2</sub> with the surfactant P-123 enabled the synthesis of photocatalysts with

improved surface area, high crystalline, big size nanoparticles, and anatase/rutile phase content, when compared with TiO<sub>2</sub> prepared by ultrasonic-assisted sol-gel or other methods. The drawback of the pH swing method, i.e., the enhancement of particle size with respect to an increase in the number of pH swings could be surmounted by this coupled method. The catalysts developed by the combined process evidenced excellent activity, even higher than P-25. This method was, thus, found to be a versatile approach for the preparation of efficient nano-size TiO<sub>2</sub> photocatalysts suitable not only for environmental applications but also for electronic applications such as LED and solar cells.

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