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Synthesis of TiO_2 particles by reverse microemulsion method using nonionic surfactants with different hydrophilic and hydrophobic group and their photocatalytic activity

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Abstract

TiO_2 nanoparticles were prepared using hydrolysis of titanium tetraisopropoxide in W/O microemulsions consisting of water, nonionic Brij series surfactants with different hydrophilic and Tween series surfactants with different hydrophobic group, and cyclohexane. The properties of these particles were characterized by TEM, XRD, FT-IR, TGA and DTA. The photocatalytic degradation of *p*-nitrophenol has been studied in order to compare the photocatalytic activity of prepared nanosized titania. TiO_2 particles calcined at 500 °C have a stable anatase phase which has no organic surfactants and the product completely transforms into the anatase phase above 300 °C and the rutile phase begins to appear at 600 °C regardless of surfactants. The particles are shown to have a spherical shape and have an uniform size distribution but the shape becomes distorted with a decrease of hydrophilic group chain length according to rapid hydrolysis of water and titanium alkoxide. In addition, the crystallite size and crystallinity increase with a decrease of hydrophilic and hydrophobic group chain length and an increase of calcination temperature. The photocatalytic activity increases with an increase of hydrophilic and hydrophobic group length and the titania calcined at 500 °C shows the highest activity on the photocatalytic degradation of *p*-nitrophenol regardless of surfactants.

Keywords: Nanosized titania; Brij surfactant; Tween surfactant; Reverse micelle; Photocatalytic degradation of *p*-nitrophenol

1. Introduction

Up to the present time the most widely used methods for the elimination of organic pollutants from water have been adsorbed over activated carbon, chemical oxidation, and an aerobic biological treatment. All these processes suffer from several disadvantages. Adsorption is not a destructive process so that a further step is needed for the elimination of the organic compounds, while the chemical oxidation does not generally result in the complete mineralization of the organic compound and it is economically favorable only for significant concentrations of pollutant. Biological treatment has several drawbacks, such as the low reaction rate, the difficulty of disposal of the activated sludge and the very narrow range of pH [1,2]. None of this disadvantage is shared by methods based on the utilization of light, i.e. photocatalysis using semiconductors irradiated by near UV-light. The complete mineralization of the organic compound with the absence of dangerous residual intermediate compounds and the possibility of working over wide ranges of operational conditions make the photocatalytic method preferable or, at least, competitive with the others.

Phenol and its derivatives are some of the most refractory pollutants present in industrial waste water. Their high stability and solubility in water are the main reasons why the degradation of these compounds to non-dangerous levels is a very difficult process [3]. In particular, 4-nitrophenol and its derivatives result from the production processes of pesticides, herbicides and synthetic dyes. These pollutants have high toxicity and carcinogenic character.

Recently, there has been a lot of interest in nanosized particles [4]. Many methods have been developed to control the size of nanoparticles such as Langmuir–Blodgett films [5], vesicles [6], reverse microemulsions [7] and surface-active supports [8]. Microemulsions provide a microheterogeneous medium for the generation of nanoparticles. The formation of particles in such systems is controlled by the

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reactant distribution in the droplets and by the dynamics of interdroplet exchange. The surfactant stabilized by microcavities provide a cage-like effect that limits particle nucleation, growth and agglomeration [9,10].

TIO_2 is most extensively studied for its wide applications in sensors, pigments, catalysis or photocatalysis as well as in many high performance ceramics. The preparation method of nanosized TiO_2 is mainly comprised of sol–gel [11], whose main disadvantages are that costly organic solvents are required. The direct hydrolysis of titanium salt [12] and chemical vapor deposition procedure in which $TiCl_4$ vapor is oxidized at very high temperatures can be used to prepare nanosized TiO_2. Water-in oil (W/O) microemulsions have been successfully employed to obtain ultrafine particles of controlled size of a variety of materials [13,14]. In addition, they are clear, thermodynamically stable fluids of mixtures of water, oil, and surfactants, and have been established as excellent microreactors for producing either organic or inorganic nanometer size, which are fairly monodispersed. Our previous work also reported that the nanosized titania particles were able to be prepared by the microemulsion method using different surfactants and they showed the high photocatalytic activity [15–17].

In this paper, we prepared nanosized TiO_2 particles via hydrolysis of titanium tetraisopropoxide (TTIP) in water-in-oil reverse micelles using nonionic surfactants with different hydrophilic and hydrophobic group. The physical properties, such as a crystallite size and crystallinity, were investigated by TEM, XRD, FT-IR, TGA and DTA. We also investigated the effect of calcination temperature as well as the hydrocarbon chain length of surfactant and hydrophilic group on the physical properties of nanosized TiO_2 particles, and examined the activity of TiO_2 particles as a photocatalyst for the decomposition of *p*-nitrophenol.

2. Experimental

2.1. Preparation of catalysts

A polyoxyethylene (20) sorbitan monolaurate, monopalmitate, monostearate, and trioleate (Tween 20, 60 and 85, respectively) with a different hydrophobic group and Brij 52 (polyoxyethylene glycol hexadecyl ether polyoxyethylene-2-cetyl ether), Brij 56 (polyoxyethylene glycol hexadecyl ether polyoxyethylene-10-cetyl ether), Brij 58 ((polyoxyethylene glycol hexadecyl ether polyoxyethylene-20-cetyl ether) with a different hydrophilic group, were employed in this work and their properties are listed in Table 1. TiO_2 nanoparticles were prepared by hydrolysis of titanium tetraisopropoxide (TTIP) in W/O microemulsions consisting of water, surfactant, and cyclohexane.

Reverse microemulsion solution was prepared by dissolving 0.045 mol of surfactants in cyclohexane and by adding a required amount of distilled water. The water-clear appearance of the solution indicated the formation of the microemulsion. The hydrolysis of TTIP was carried out at 30 °C in a sealed four-way flask (500 ml). The reaction was initiated by adding the TTIP solution into the reverse microemulsion with stirring for 1 h. The TiO_2 particles precipitated were separated in a centrifuge at 10,000 rpm for 2 min and were then washed with ethanol using Soxhelt extractor for 24 h to remove organics and surfactants from the particles. The particles were dried at 105 °C for 12 h and then calcined at 200–800 °C for 3 h.

Table 1
Properties of Brij and Tween surfactants used in this study

Surfacatnts	Average number of carbons in aliphatic tail (*n*)	Average number of oxyethylene group (*m*)	Average molecular weight	HLB[a]
Brij				
52	16	2	330	5.3
56	16	10	683	12.9
58	16	20	1124	15.7
Tween				
20	20	20	1228	16.7
60	26	20	1312	14.9
85	48	20	1839	11.0

[a] Hydrophile lipophile balance.

2.2. Characterization of catalysts

The dried fine powder of synthesized TiO_2 was subjected to thermo gravimetric-differential thermal analysis (TG-DTA, Perkin-Elmer) to determine the temperature of possible decomposition and phase changes. The samples were heated at the rate of 10 °C/min from 50 to 900 °C.

The major phase of the obtained particles was analyzed by X-ray diffraction (Rigaku D/MAXIIC) using Cu Kα radiation. The average crystallite sizes of anatase and rutile were determined according to the Scherrer equation using the full width at half maximum (FWHM) date of each phase after correction the instrumental broading [18].

The chemical structure of the prepared particles was examined using the Fourier transform infrared spectrophotometer (FT-IR, Bruker, IFS-88) in the 400–4000 cm^{-1} frequency range.

The particle size and external morphology of the prepared particles were observed on a Transmission electron microscope (TEM, JEOL, JEM-2020) of 200 kV accelerating voltage.

2.3. Activity test

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 0.1 g/L and 20 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 (Shimazu UV-240).

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the typical DTA and TGA thermodiagrams for the TiO_2 particles prepared using different surfactants. From the TGA analysis, the weight of particles sharply decreases up to 350 °C and slowly decreases from 350 to 600 °C, and no more decrease is observed up to 900 °C regardless of surfactants. The weight losses of the particles prepared using Brij 58 and Tween 85 surfactant were 85% and 45%, respectively. It is thought that the difference on the weight loss is due to the molecular weight of surfactants.

When Brij series are used as surfactants, DTA analysis also shows the endothermic peak at 100 °C and two exothermic peaks at 250 and 370 °C. It is thought that the peak at 100 °C is due to free adsorbed water, and the peak at 250 °C is due to the decomposition of the surfactant and residual OH group. In addition, the peak at 370 °C is due to the combustion of residual alkoxy group and surfactants. When Tween series are used as surfactants, DTA analysis also shows the endothermic peak at 100 °C and three exothermic peaks at 410, 520 and 580 °C. It is thought that the peak at 100 °C is due to free adsorbed water, and the peak at 410 °C is due to the decomposition of the surfactant and residual OH group. In addition, the peak at 520 °C corresponds to the crystallization of the amorphous phase into the anatase phase. Above 580 °C, it can be assumed that the product begins to transform the anatase phase into the rutile phase.

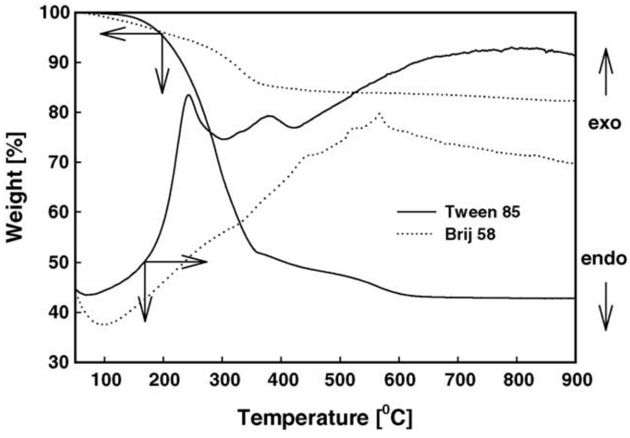

Fig. 1. TGA-DTA curves of nanosized TiO_2 powders prepared using Brij 58 surfactant and Tween 85 surfactant.

It is reported that the transition of the anatase phase into the rutile phase occurs between 450 and 800 °C and the difference in the transition temperature depends on the kind of precursors, the preparation conditions of particles, and the property of particles [19]. In the titania particles prepared using reverse microemulsion, it is confirmed that the anatase phase begins to transform into the rutile phase at 600 °C from the XRD results.

3.2. X-ray diffraction analysis

Fig. 2 shows the XRD patterns of the TiO_2 particles prepared using Brij 58 and Tween 60 as surfactants calcined at different temperature. The major phase of all the prepared particles is an anatase structure and a rutile peak is observed above 600 °C regardless of surfactant.

It is well known that the calcination improves the crystallinity of the particle, and the amorphous TiO_2 changes into the anatase phase and the anatase phase changes into the rutile phase with an increase of calcination temperature. The XRD data of the particles dried at 105 °C indicate that it is amorphous. The particles calcined at 500 °C are identified as a nanocrystalline anatase. This result indicates that the transition from the amorphous to the anatase phase has taken place at this temperature range. 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 Scherrers equation [18] and is listed in Table 2. One can see that the crystallite size of the anatase phase is increased from 7 to 21 nm as the calcination temperature increased from 300 to 600 °C in the case of Brij 58. However, the size

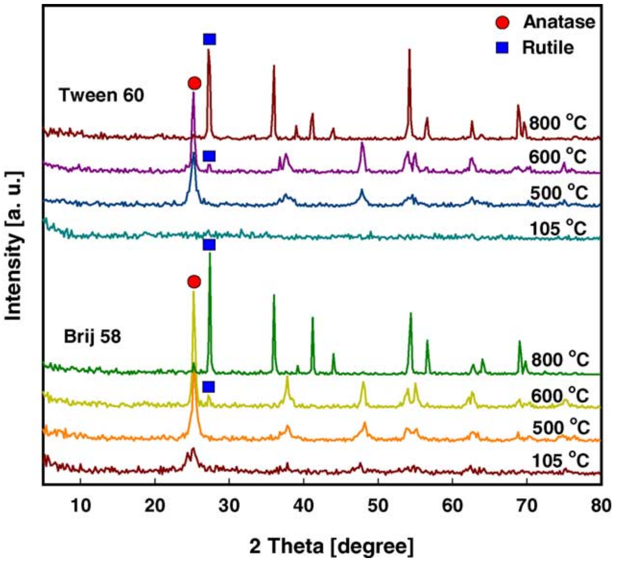

Fig. 2. XRD patterns of nanosized TiO_2 powders calcined at different temperature using Brij 58 surfactant and Tween 60 surfactant.

Table 2
Physical properties and photocatalytic activity of nanosized TiO_2 powders calcined at different temperature

Calcination temperature (°C)	Brij 58[a]			Tween 60[a]		
	XRD		Activity	XRD		Activity
	Structure[b]	Crystallite size[c] (nm)	k'[d] ($\times 10^{-3}$ min^{-1})	Structure[b]	Crystallite size[c] (nm)	k'[d] ($\times 10^{-3}$ min^{-1})
300	A	7	0.5	A	4	1.0
400	A	8	1.4	A	6	1.4
500	A	10	2.1	A	10	1.6
600	A/R	21/–	2.0	A/R	25/–	0.5
700	A/R	38/54	0.8	A/R	35/43	0.3
800	R	59	0.4	R	51	0.3

[a] W_0 ratio (H_2O/surfactant molar) = 0.5, R ratio (H_2O/TTIP molar) = 2.

[b] A = anatase, R = rutile.

[c] Obtained by Scherrer equation.

[d] Apparent first-order constant(k') of photocatalytic degradation of *p*-nitrophenol.

of rutile crystallites calcined at 600 °C cannot be measured because of small intensity of the peak. When Tween 60 is used as a surfactant, the similar tendency is shown. The crystallite size of the anatase phase is increased from 4 to 25 nm as the calcination temperature increased from 300 to 600 °C.

Table 3 shows the crystallite size of titania particles prepared using different surfactants. When Brij series are used surfactants, the crystallite size decreases from 17 to 10 nm with an increase of hydrophilic group chain length. It is known that the formation of water pool in a reverse microemulsion is occurred from the dispersion of water by the hydrophilic group of surfactant. With a decrease of hydrophilic group chain length, the formation of water pool in the reverse microemulsion becomes loose and then the crystallite size increases by the rapid hydrolysis of water and titanium alkoxide.

When Tween series are used surfactants, the crystallite size decreases from 12 to 9 nm with an increase of hydrocarbon (hydrophobic group) chain length. Since the Tweens possess identical hydrophilic groups, the difference in their property may be ascribed to the hydrocarbon chain length. With an increase of hydrocarbon chain length, the size of reverse micelles decreases because the hydrocarbon chain prohibits the access of the water near the micelles.

3.3. FT-IR analysis

Fig. 3 shows the IR spectra for the TiO_2 particles calcined at a different temperature using Brij 58 and Tween 60 as surfactants in the range of 400–4000 cm^{-1}. The IR spectra show very similar tendency regardless of surfactant.

When the prepared particles are dried at 105 °C without a calcination, the strong bands at 1450 and 1530 cm^{-1} due to residual organic surfactants are observed. However, the intensity of these bands decreases with an increase of the calcination temperature. No band due to residual organic surfactants is observed with a calcination at 500 °C. This result suggests that the TiO_2 particles calcined at 500 °C have a stable anatase phase which has no organic surfactant. The broad absorption peak appearing near 3400 cm^{-1} relates to a stretching vibration of Ti–OH group. At 1620 cm^{-1}, a band assigned to water also appears. The OH band intensities show a significant decrease in the case of calcination at high temperature. It is reported that the physisorbed water is easily removed from the surface but the decrease in the OH band intensities bonded to TiO_2 may be attributed to the OH population produced by a dehydroxylation of the surface titania [20]. The OH band intensities also decrease with an increase of the calcination temperature. This result suggests

Table 3
Physical properties and photocatalytic activity of nanosized TiO_2 prepared using different surfactants

Preparation conditions[a]	XRD		TEM	Activity k'[b] ($\times 10^{-3}$ min^{-1})
	Structure	Crystallite size[c] (nm)	Crystallite size (nm)	
Brij[d]				
52	Anatase	17	16	1.4
56	Anatase	13	14	1.7
58	Anatase	10	10	2.1
Tween[e]				
20	Anatase	12	14	1.5
60	Anatase	10	12	1.6
85	Anatase	9	10	2.7

[a] Calcination temperature = 500 °C.

[b] Apparent first-order constant(k') of photocatalytic degradation of *p*-nitrophenol.

[c] Obtained by Scherrer equation.

[d] W_0 ratio (H_2O/surfactant molar) = 2, R ratio (H_2O/TTIP molar) = 2.

[e] W_0 ratio (H_2O/surfactant molar) = 0.5, R ratio (H_2O/TTIP molar) = 2.

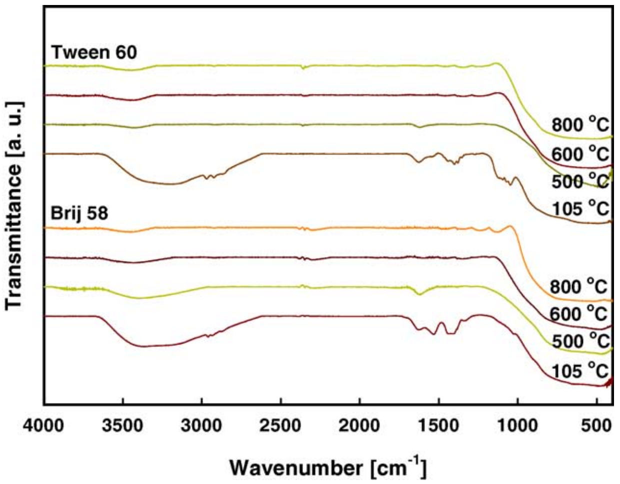

Fig. 3. FT-IR spectra of nanosized TiO_2 powders calcined at different temperature using Brij 58 surfactant and Tween 60 surfactant.

that this process is also responsible for the sintering of the catalysts, by collapsing the smaller pores of TiO_2, as it is shown in the crystallite size summarized in Table 2.

3.4. TEM analysis

In this study, the microemulsions were formed by mixing the surfactant, water and cyclohexane within the reactor and then, the addition of TTIP into the reactor gave a rise to the formation of TiO_2 particles by the hydrolysis. After a rapid agitation for 1 h, transparent and white particles were stably dispersed within the reactor. These particles were dried and calcined at desired temperature, and then used to examine the size and morphology of prepared particles by TEM. The TEM images of the TiO_2 nanoparticles prepared using Brij series surfactants are shown in Fig. 4.

As shown in Fig. 4, the particles are shown to have a spherical shape but the shape becomes distorted with a

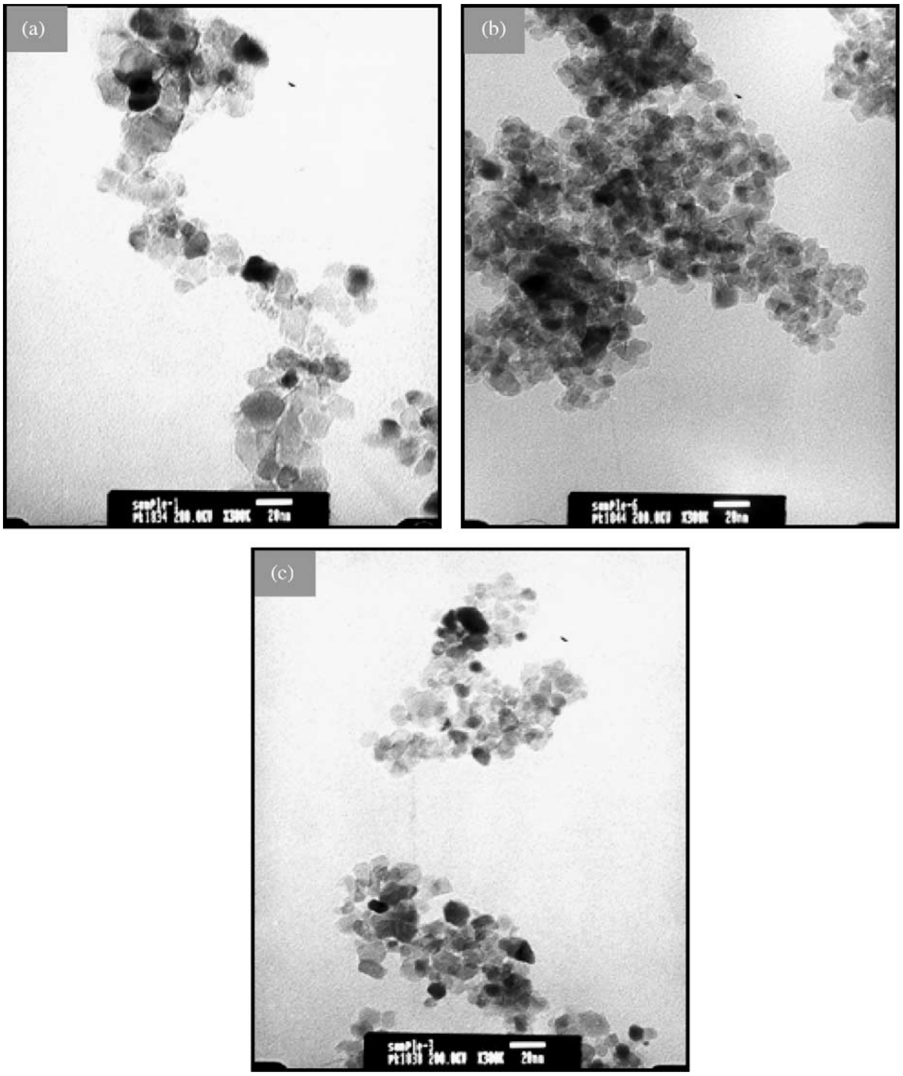

Fig. 4. TEM images of nanosized TiO_2 powders prepared using Brij series surfactants: $W_0 = 0.5$, $R = 2$ and calcined at 500 °C, (a) Brij 52, (b) Brij 56, (c) Brij 58.

decrease of hydrophilic group chain length according to rapid hydrolysis of the water and the titanium alkoxide. In addition, the size of particles increases from 10 to 16 nm with an increase of hydrophilic group chain length and shows similar values with XRD results.

Fig. 5 shows the TEM images of the TiO_2 nanoparticles prepared using Tween series surfactants. The particles are also shown to have a spherical shape and have an uniform size distribution but the agglomeration increased compared to anionic surfactants [21]. In addition, the crystallite size decreased from 14 to 10 nm with an increase of hydrocarbon chain length. It is thought that the size of reverse micelles decreases because the hydrocarbon chain prohibits the access of the water near the micelles with an increase in hydrocarbon chain length.

3.5. Photocatalytic activity test

It is well known that photocatalytic oxidation of organic pollutants follows Langmuir Hinshelwood kinetics [22].

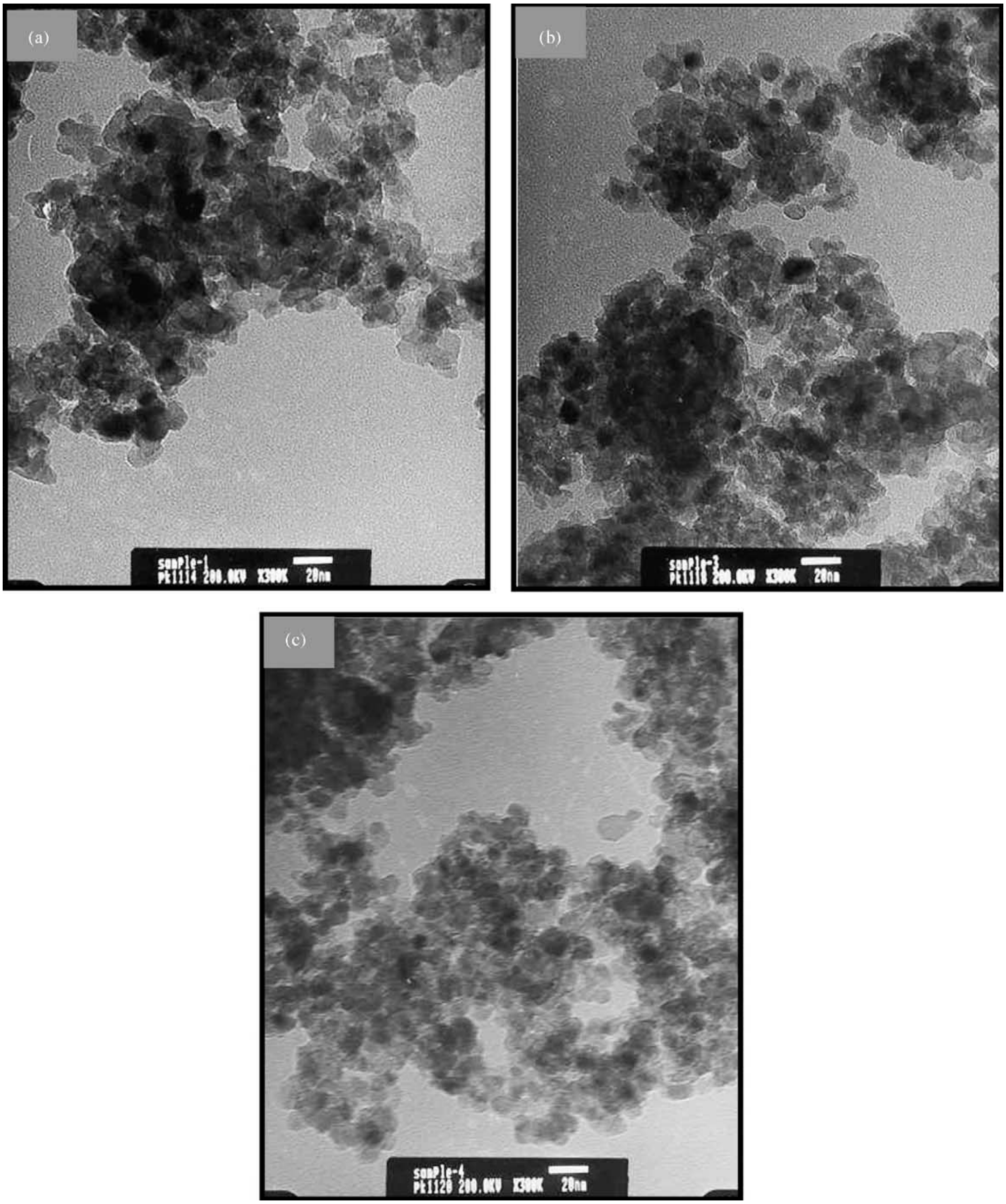

Fig. 5. TEM images of nanosized TiO_2 powders prepared using Tween series surfactants: $W_0 = 0.5$, $R = 2$ and calcined at 500 °C, (a) Tween 20, (b) Tween 60, (c) Tween 85.

Therefore, this kind of reaction can be represented as follows:

$$-\mathrm{d}c/\mathrm{d}t = kc \quad (1)$$

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 (k).

Table 3 shows the photocatalytic activity of *p*-nitrophenol over TiO_2 particles prepared by the microemulsion method using Brij and Tween series surfactants with a different hydrophilic and hydrophobic group chain length, respectively.

The photocatalytic activity increases with an increase of hydrophilic and hydrophobic group chain length. It is well known that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases with a decrease of particle size [23]. 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. Therefore, the crystallite size decreases with an increase of hydrophilic and hydrophobic group chain length and then enhances the rate of photodecomposition of *p*-nitrophenol.

As shown in Table 2, the photocatalytic activity shows the highest value on the TiO_2 particle calcined at 500 °C regardless of surfactants.

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 [24]. In the case of titania particle calcined at 700 °C, the anatase and rutile phase are combined and amorphous phase are mixed with anatase phase at the titania particle calcined at 300 °C. Therefore, the pure anatase titania calcined at 500 °C shows the highest activity on the photocatalytic decomposition of *p*-nitrophenol.

4. Conclusions

We synthesized TiO_2 nanoparticles by the hydrolysis of titanium tetraisopropoxide in W/O microemulsions consisting of water, nonionic Brij series surfactants with different hydrophilic and Tween series surfactants with different hydrophobic group, and cyclohexane. The physical properties, such as a crystallite size and crystallinity, were investigated by TEM, XRD, FT-IR, TGA and DTA. In addition, we investigated the photocatalytic degradation of *p*-nitrophenol over prepared nanosized titania.

From thermal analysis, TiO_2 particles calcined at 500 °C have a stable anatase phase which has no organic surfactants and the product completely transforms into the anatase phase above 300 °C and the rutile phase begins to appear at 600 °C regardless of surfactants. The TEM image shows that particles have a spherical shape and have a uniform size distribution but the shape becomes distorted with a decrease of hydrophilic group chain length according to rapid hydrolysis of water and titanium alkoxide. The average crystallite sizes of anatase and rutile were determined according to the Scherrer equation and the crystallite size and crystallinity increase with a decrease of hydrophilic group chain length and an increase of calcination temperature. When Tween series are used surfactants, the crystallite size increases with a decrease of hydrocarbon (hydrophobic group) chain length. The photocatalytic activity increases with an increase of hydrophilic and hydrophobic group length according to the small particle-size effect and the titania calcined at 500 °C shows the highest activity on the photocatalytic degradation of *p*-nitrophenol regardless of surfactants.

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