Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 1177–1183
www.elsevier.com/locate/jeurceramsoc

Applying the experimental statistical method to deal the preparatory conditions of nanometric-sized TiO_2 powders from a two-emulsion process

Ching-Shieh Hsieh [a], Hong Zhu [b], Tsong-Yang Wei [c], Zen-Ja Chung [c], Wein-Duo Yang [d,*], Yin-Hsia Ling [d]

[a] *Department of Applied Chemistry, Fooyin University, Ta-Liao 831, Taiwan, ROC*
[b] *Department of Chemistry, Beijing Jiaotong University, Beijing 100044, PR China*
[c] *Chemical Engineering Division, Institute of Nuclear Energy Research, Lungtan, Taoyuan 325, Taiwan, ROC*
[d] *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan, ROC*

Received 24 March 2007; received in revised form 27 September 2007; accepted 7 October 2007
Available online 11 January 2008

Abstract

Nanometric-sized titanium oxide powders have been synthesized successfully through the two-emulsion method. It was found that the anatase phase is formed at 400 °C and converted to rutile phase as heat-treated at 700 °C. The synthesized TiO_2 powders exhibit particle sizes at 10–30 nm, in a specific surface area of about 30–88 m^2/g. Furthermore, the surface response method (including Box-Behnken design) was applied to deal with the preparatory conditions of the two-emulsion process. It reveals that the optimal preparatory conditions were obtained at the volume ratio of surfactant/*n*-hexane = 0.03, volume ratio of water/oil = 0.04, molar ratio of acetylacetone/titanium isopropoxide = 4, molar ratio of isopropanol/titanium isopropoxide = 23.1. By combining the optimal settings of those variables, a nanometric-sized TiO_2 powder has been obtained with specific surface area of 96 m^2/g. It demonstrates the photocatalytic degradation of methylene blue solution effectively by exposing the as-synthesized TiO_2 powders in aqueous solution under ultraviolet light.

Keywords: Nanometric powders; Emulsions; TiO_2; Powder preparation

1. Introduction

Titania has been examined showing three crystalline forms: anatase, brookite and rutile. Rutile phase is the most thermodynamically stable among these crystalline forms, anatase and brookite are metastable and can be transformed to rutile by a heating process. However, the rutile form titania has been widely used as pigments, cosmetic ingredients as well as catalyst support.[1] The nanoscale anatase form TiO_2 has been focused on fields of nature and life such as, purification and treatment of water and air, the photoelectrochemical solar cell, etc.[2–4] Recently, scholars have become interested in studies to treat the suspension system of nanometric-sized TiO_2 powders or the reaction system containing materials in which TiO_2 fine powders were anchored due to its relatively wider band gap property and high activity.[5]

There are a variety of techniques available for producing ceramic particles or thin films, including conventional aqueous precipitation,[6] hydrothermal processing,[7] sol–gel method[8] and gas-phase reaction.[9] However, the preparation of nanoparticles is much more difficult than that of microparticles. Among the various techniques, powders obtained by the precipitation of precursor from solution are the most realizable technique because of their simplicity, safety, and low cost. However, the conventional aqueous precipitation method often produces irregular-shaped powders with a wide size distribution. In recent years, the microemulsion method[10,11] has been studied and utilized widely as a key technique to synthesize oxide nanoscale powders owing to the products which have characteristics of being well dispersed, of controlled size and with narrow-size distribution. Tai et al. have successfully synthesized the nanoparticle size ZrO_2 by using two-emulsion precipitation techniques, where the mean

* Corresponding author.
E-mail address: ywd@cc.kuas.edu.tw (W.-D. Yang).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.10.002

size of spherical ZrO_2 particles of a few tens of nanometers can be prepared.[10,12]

In particular, acetylacetone[13–15] is a known chelating agent with titanium alkoxides since it significantly changes the hydrolysis behaviors as a nucleophilic reactant and replaces the alkoxy group, thus giving rise to a new molecular precursor. In the hydrolysis reaction of ligand acetylacetone, less electronegativity of alkoxy groups is rather quickly reduced, while the more electronegative ligand of acetylacetone groups persists as a complex within the metallic group. It has been reported that the use of a modified organometallic precursor leads to better ions homogeneity, enhances the powder's properties, and reduces the powder synthesis temperature.[16,17]

Experimental statistical methods are often used in the design of experiments and the significant factors of the preparatory conditions can be tested by analysis of variance. This is also a reliable method to simplify the process of identifying the most influential preparation variables, and the optimal preparatory conditions are singled out.[18,19] However, there have been few studies to investigate the optimization of experimental conditions in the preparation of nanometric-sized TiO_2 powders by two-emulsion method.

In this study, an experimental statistical method was used to find the influential factors for the synthesis of TiO_2 from the two-emulsion method. Here, titanium isopropoxide was used as the raw material, and acetylacetone as a chelating agent. The selected influential factors were assembled as the preparatory conditions and the number of required experiments was then decreased. The effects of the most influential factors on the powder were investigated and finally the optimal conditions were determined.

2. Experimental

2.1. Synthesis of TiO_2 powders

Titanium isopropoxide [$Ti(O\text{-}i\text{-}C_3H_7)_4$, density $0.995\,g\,cm^{-1}$, purity 98%] was reacted with acetylacetone to obtain a Ti-acetylacetonate precursor. In an exothermic reaction, degassed water was added and the mixture was then stirred vigorously to produce a yellowish clear solution.

n-Hexane was used for oil phase; Span 40 and isopropyl alcohol (IPA) were applied for surfactant and co-surfactant, respectively. The aqueous phase in one of the microemulsion was an aqueous solution (0.3 M) of titanium acetylacetonate, whereas the aqueous phase in the other microemulsion was the precipitating agent ammonium hydroxide (1.2 M), with the same volume ratio of water/oil (w/o). These two microemulsions were mixed by vigorous stirring at room temperature.

Due to the continuous collisions and coalescence of the droplets of water-in-oil microemulsion, the reacting species in the two microemulsions, Ti^{4+} and ammonium hydroxide, respectively, come in contact with each other and react. This leads to the formation of titanium hydroxide precipitation within the microemulsion.

The resultant slurry was distilled at 120–130 °C for about 3 h to remove the unreacted water and most of the oil. The precipitates of TiO_2 precursor were filtered and washed with ethyl alcohol and repeated with deionized water to remove the residual surfactants and ions, then dried at room temperature for 24 h. Finally, white TiO_2 powder was obtained by calcining the amorphous precursors to form an anatase TiO_2 structure. A schematic diagram for the preparation of TiO_2 particles in microemulsion is shown in Fig. 1.

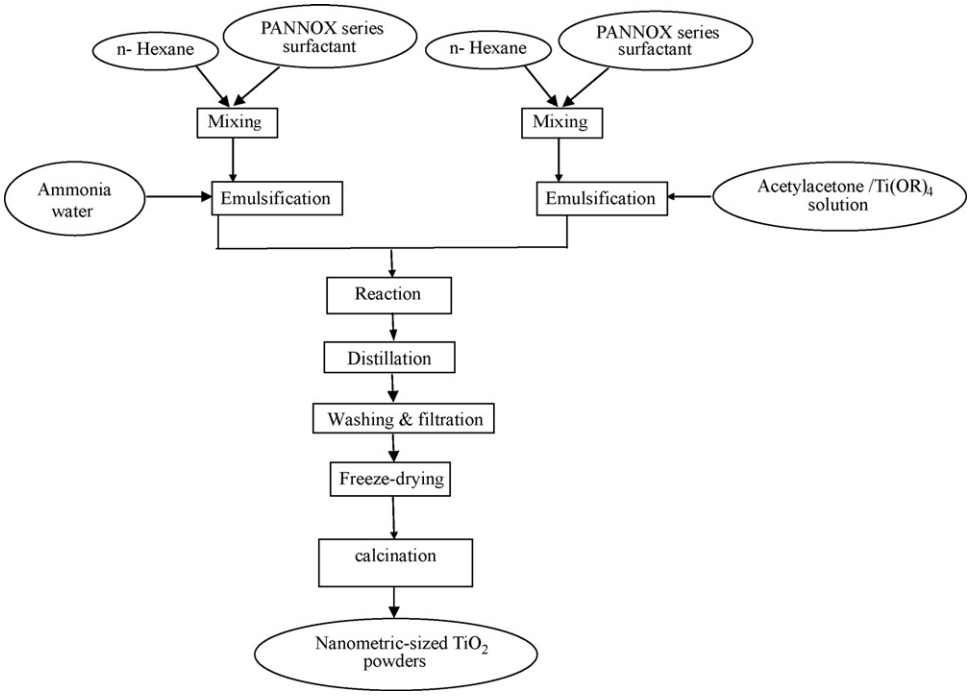

Fig. 1. Schematic illustration of the preparation of nanometric-sized TiO_2 from two-emulsion method.

The particles thus prepared in the constrained microreactors of microemulsion droplets are expected to be fairly uniform and homogeneous and have a higher surface area with very small particle size.

During the reaction, the droplets serve as microreactors where nucleation, crystal growth and nuclei agglomeration occur. Thus, the size, size distribution, and shape of produced particles from emulsion precipitation are related to the emulsion droplets and can be controlled better than the conventional precipitation, in which two solutions of reactant are mixed directly.

2.2. Experimental statistical method

The aim of optimization was to find the optimized conditions of the experimental variables. Based on the results obtained in preliminary experiments, we chose the following four variables as the experimental variables: (1) volume ratio of surfactant/*n*-hexane (*A*), (2) volume ratio of w/o (*B*), (3) ammonia concentration (*C*), (4) molar ratio of isopropanol/titanium isopropoxide (*D*). Hence, these variables were selected to find the optimized conditions for a higher Brunauer, Emmett and Teller (BET) specific surface area of nanoscale TiO_2 powder using Box-Behnken design and response surface methodology (RSM).

The range and levels of the experimental variables investigated in this study are given in Table 1. The central values (zero level) chosen for experimental design were a volume ratio of surfactant/*n*-hexane 0.02, volume ratio of w/o 0.03, ammonia concentration 4 M, molar ratio of isopropanol/titanium isopropoxide 15.4.

2.3. Characterization analysis

Characteristics of the calcined titania powders were analyzed: the crystalline phase identified by an X-ray diffractometer (XRD) (RIGAKU, Rint-2000) and the surface structure and particle morphology examined by a transmission electron microscope (TEM) (Philips, M-200).

However, the great emphasis placed on surface area measurements in this paper was examined. A certain amount of as-prepared TiO_2 powders were grounded in an agate mill for 5 min to reduce the aggregation of powders. The specific surface areas of the nanometric-sized TiO_2 powders were measured using a MICROMERTICS ASAP 2010 surface area analyzer. Previously adsorbed gases were removed prior to the measurement by degassing the samples in N_2 at 150 °C, 10^{-3} torr for 4 h. Then, a mixture gas of N_2 (adsorbent) and He (carrier) was passed through the sample tube. When the sample tube is immersed in liquid nitrogen, the sample adsorbs nitrogen. The amount of nitrogen adsorbed was measured and the surface area was calculated by the BET equation.

Table 1
The actual and code levels of the experimental variables

Variable	Code level		
	−1	0	+1
A: volume ratio of surfactant/*n*-hexane	0.01	0.02	0.03
B: volume ratio of w/o	0.01	0.03	0.05
C: ammonia concentration (M)	2	4	6
D: molar ratio isopropanol/titanium isopropoxide	7.7	15.4	23.1

2.4. Photocatalytic measurements

A reactor, irradiated by the light source placed above the methylene blue solution at a certain position, was utilized to perform the photocatalytic experiments. The volume of the reactor was 250 ml, and continuous stirring was used to maintain the uniformity of both concentration and temperature. A 369 nm UV lamp was used as the light source and 0.5 g of TiO_2 catalyst powder was added into 150 ml of 10 ppm methylene blue solution to measure the photodegradation activity of as-prepared photocatalyst. The photodegradation runs lasted several hours and samples were taken for examination during the interval of degradation. The concentration of methylene blue was measured at the maximum absorption wavelength of 664 nm by a HITACHI U-2800 UV–vis spectrophotometer.

3. Results and discussion

3.1. Characteristics of emulsion

3.1.1. Microemulsion stability

There are many factors, including volume ratio of surfactant/*n*-hexane, volume ratio of w/o, ammonia concentration, molar ratio of isopropanol/titanium isopropoxide, that influence the stability of emulsion and further change the particle morphology and size distribution of synthesized powders. For the stability of microemulsion, isopropyl alcohol (IPA) is found to be suitable with the surfactant of Span surfactant. The addition of co-surfactant to the formation yields the low interfacial tension required to produce the small droplets. Alcohols with short-chain amphiphilic molecules are frequently used as a co-surfactant to reduce interfacial tension.

Table 2 shows the effect of w/o volume ratio on the microemulsion stability at room temperature. When the volume ratio of w/o is lower than 3/100, the microemulsion exhibits a stable condition for 10 h without adding any co-surfactant. Particularly, the volume ratio of w/o at 1/100 showed a clear stable solution over 12 h. However, as the volume ratio w/o increases, the stability of emulsion decreases. For example, when the volume ratio w/o is at 4/100, the amount of IPA required for 250 g

Table 2
The effect of w/o volume ratio on the microemulsion stability at room temperature

Volume ratio of w/o	Concentration of NH_4OH (M)	Molar ratio of acetylacetone/Ti	Stability of emulsion (stable over, h)
1/100	12	4	12
2/100	12	4	12
3/100	12	4	10
4/100	12	4	8*
5/100	12	4	3*

* In which case co-surfactant, IPA, was applied.

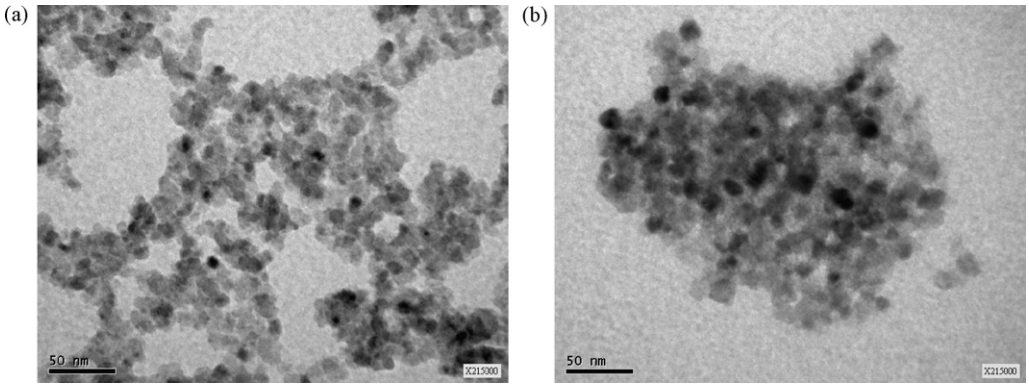

Fig. 2. The TEM morphologies of the TiO_2 powders prepared at various volume ratios of w/o by the emulsion method. (a) 1/100 and (b) 4/100.

n-hexane is 10 g, and the microemulsion is more stable with more IPA added to the system. Furthermore, the emulsion prepared at volume ratio of w/o at 5/100 is highly unstable, and can only demonstrate a clear condition for 3 h by adding IPA co-surfactant. The observation is in agreement with the report of Lee et al.[20] who have demonstrated the effects of IPA surfactant amount, Zr^{4+} concentration, and volume ratio of w/o on the stability of emulsion using heptane as the oil phase. It is concluded that low volume ratio of w/o and low Zr^{4+} concentration favor the formation of emulsion.

Fig. 2 shows the TEM morphologies of the titania powder prepared at various volume ratios of w/o by the emulsion method. It reveals that the shape of the synthesized particles was almost spherical and the size of the powders ranged from 10 to 30 nm. The powders prepared from volume ratio of w/o at 1/100 had a relatively uniform and spherical with less aggregation as shown in Fig. 2(a). As the volume ratio of w/o was increased, the particle size had more aggregation and was bigger. The particle sizes of powders obtained from volume ratio of 4/100 were estimated to be 20–30 nm (Fig. 2(b)). The particle size was further checked by an X-ray diffractometer by using Sherrer's equation.

It was evident from these figures that the particle size was very small and that the size of the synthesized particle increased the particle and aggregation with the increased volume ratio of w/o. This suggests that less ratio of w/o promoted the formation of powders with a uniform size distribution due to the fast reaction in small size of emulsion and homogeneous precipitation.[10] This result indicated that volume ratio of w/o could enhance the control of the size, size distribution and the morphology of the titania powders.

Table 3
The powder properties of nanometric-sized TiO_2 prepared at various volume ratios of w/o and calcined at 400 °C

Volume ratio of w/o	D_{TEM} (nm)	S_{BET} (m^2/g)	D_{LPD} (nm)	D_{LPD}/D_{TEM}
1/100	10–15	88	40	3.21
2/100	15–25	80	71	3.54
3/100	18–28	73	127	5.50
4/100	20–30	30	160	6.42

3.1.2. Powder properties

The powder properties of the nanometric-sized TiO_2 powders prepared from various volume ratios of w/o calcined at 400 °C through two-emulsion process are shown in Table 3. It is indicated that the TiO_2 powders have BET surface area between 30 and 88 m^2/g and particle sizes at 10–30 nm. The surface areas of powders prepared from this method (two-emulsion process) are much more than those prepared by convectional aqueous precipitation method, and also more than those by sol–gel process (<80 m^2/g). A higher surface area anatase that forms titania powder with higher catalytic activity could be applied as a photoelectrochemical solar cell.

Aggregation was increased if the ratio of w/o increased hence the specific surfaces in the cases were decreased. The specific surface area measured for the powder obtained from higher ratio of w/o was small, and agglomeration and particle size large. The specific surface area of TiO_2 was largest for the molar ratio of w/o at 1/100 applied. It was 88 m^2/g. The specific surface area investigation supports the results of the TEM micrographs. After calcination of the equivalent BET particle diameter, it can be inferred that most of particles of Fig. 2 are composed of smaller primary crystallites. Table 3 shows that the mean particle size obtained by TEM (D_{TEM}) is smaller than that obtained by the laser particle size distribution analyzer (D_{LPD}) for the calcined powders. The means that the higher w/o ratio leads to the formation of larger crystals and the agglomeration process is also promoted. This can be seen by calculating the ratio D_{LPD}/D_{TEM}.

3.1.3. XRD analyses

The XRD patterns of TiO_2 powders prepared at volume ratio at 1/100 and calcined at various temperatures are shown in Fig. 3. At 400 °C, (1 0 1) plane of anatase was examined revealing that the crystallization of TiO_2 converting to anatase form takes place. This is lower than the crystallization temperature found for the powders synthesized from $Ti(OEt)_4$-HCl-H_2O-EtOH system by other works.[21] At 500 °C, the crystallinity of anatase phase is enhanced remarkably. Above 700 °C, the powder begins to transform to the crystalline phase of rutile form, and at 800 °C anatase modification disappeared dramatically. Indeed, rutile form of TiO_2 dominated the crystal phase at

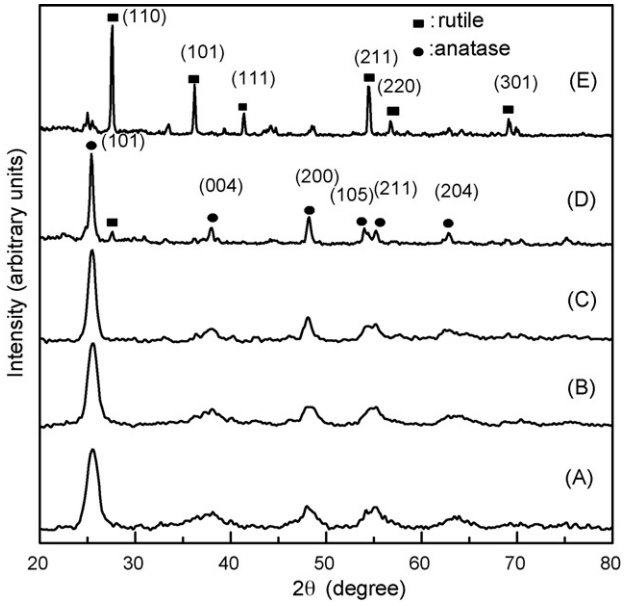

Fig. 3. The XRD patterns of the Ti precursors calcined at various temperatures. (A) 400 °C, (B) 500 °C, (C) 600 °C, (D) 700 °C, and (E) 800 °C.

the molar ratio of about 93%. This transformation temperature seems to be lower than that of the observation of the usual TiO_2 crystals (900–1000 °C).[22]

3.2. Optimal preparatory conditions

3.2.1. Optimization by response surface methodology

The range and the levels of the experimental variables investigated in this study are given in Table 1. The central values (zero level) chosen for experimental design were volume ratio of surfactant/*n*-hexane 0.02, volume ratio of water 0.03, ammonia concentration 4 M, and molar ratio isopropanol/titanium isopropoxide 15.4. In developing the regression model, the experimental variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (1)$$

where x_i is the coded value of the *i*th experimental variable; X_i, actual value of the *i*th experimental variable; X_0, actual value of the *i*th experimental variable at the central point; ΔX is the step change value.

Several experimental designs have been considered to study such regression. For this study, we selected Box-Behnken design for 4 variables. Based on Box-Behnken design, a set of 29 experiments was carried out. The surface area of as-prepared nanometric-sized TiO_2 powder from every run of the experimental designs, according to the factors assigned to the columns, was measured at least twice within the deviation of 5% as shown in Table 4. Statistical software package Design-Expert 6.0 was used to analyze the experimental results. According to the RSM methodology, a full second-order polynomial model was used to fit the independent variables using the following equation:

$$Y = b_0 + b_1A + b_2B + b_3C + b_4D + b_5A^2 + b_6B^2 + b_7C^2 + b_8D^2 + b_9AB + b_{10}AC + b_{11}AD + b_{12}BC + b_{13}BD + b_{14}CD \quad (2)$$

where Y is the predicted response; $b_0, \ldots, b_{14}$, coefficients of the model; A, B, C, D are the coded process variables.

By using the regression analysis method, the regression model in the coded form was established as follows:

$$Y = 81.84 - 1.87A + 7.91B - 0.56C + 3.94D - 3.88A^2 - 18.72B^2 + 0.87C^2 - 1.98D^2 + 14.43AB + 1.37AC + 0.16AD - 2.36BC + 3.36BD - 5.37CD \quad (3)$$

where Y is the specific surface area of nanoscale TiO_2 powder; A, volume ratio of surfactant/*n*-hexane; B, volume ratio of w/o; C, ammonia concentration; D is the molar ratio isopropanol/titanium isopropoxide. The R^2 (multiple correlation coefficient) of the regression model obtained from analysis of variance (shown in Table 5) is 0.8707, which means that the model can explain 87.07% variation in the response.

Table 4
Box-Behnken design and experimental results

Trial no.	*A*	*B*	*C*	*D*	BET (m^2/g)
1	−1	−1	0	0	71.96
2	1	−1	0	0	33.78
3	−1	1	0	0	51.47
4	1	1	0	0	70.99
5	0	0	−1	−1	70.53
6	0	0	1	−1	79.06
7	0	0	−1	1	88.77
8	0	0	1	1	75.83
9	−1	0	0	−1	70.72
10	1	0	0	−1	75.46
11	−1	0	0	1	76.23
12	1	0	0	1	81.60
13	0	−1	−1	0	48.56
14	0	1	−1	0	72.94
15	0	−1	1	0	59.82
16	0	1	1	0	74.76
17	−1	0	−1	0	89.71
18	1	0	−1	0	80.01
19	−1	0	1	0	79.26
20	1	0	1	0	75.04
21	0	−1	0	−1	51.81
22	0	1	0	−1	64.53
23	0	−1	0	1	55.41
24	0	1	0	1	81.55
25	0	0	0	0	83.65
26	0	0	0	0	88.31
27	0	0	0	0	77.58
28	0	0	0	0	70.00
29	0	0	0	0	89.67

Table 5
ANOVA of RSM regression analysis

Mode	Sum of squares	d.f.	Mean of squares	*F*-value	*P*-value
Model	4422.83	14	315.92	6.73	0.0005
Residual	656.99	14	46.93		
Total	5079.82	28			

Table 6
Comparison of actual value and predicted value

Trial no.	Actual value	Predicted value
1	71.96	67.63
2	33.78	35.04
3	51.47	54.60
4	70.99	79.70
5	70.53	72.00
6	79.06	81.61
7	88.77	90.06
8	75.83	78.75
9	70.72	74.07
10	75.46	70.01
11	76.23	81.64
12	81.60	78.21
13	48.56	54.29
14	72.94	74.83
15	59.82	57.89
16	74.76	68.99
17	89.71	82.64
18	80.01	76.15
19	79.26	78.77
20	75.04	77.77
21	51.81	52.66
22	64.53	61.77
23	55.41	53.83
24	81.55	76.36
25	83.65	81.84
26	88.31	81.84
27	77.58	81.84
28	70.00	81.84
29	89.67	81.84

3.2.2. *Optimization of the preparatory conditions*

The regression model can be used for prediction, process optimization, and process control. Comparisons of experimental values and predicted values from the regression model are shown in Table 6. From Table 6, it is observed that agreement is satisfactory. According to the regression model, the optimized conditions of experimental variables could be searched. The optimized conditions of experimental variables were 0.03 for volume ratio of surfactant/*n*-hexane, 0.04 for volume ratio of water, 2 M for ammonia concentration, 23.1 for molar ratio isopropanol/titanium isopropoxide. The predicted maximum specific surface area was calculated to be 94 m^2/g. In order to confirm the predicted results, experiments using the optimized conditions were performed, and a value of 96 m^2/g was obtained.

3.2.3. *Photocatalytic activity of TiO_2 powders*

The concentration of methylene blue, which was decolorized, was determined by a UV–vis spectrophotometer. The photocatalytic decolorization of methylene blue is pseudo-first-order reaction and its kinetics may be expressed as follows[23]:

$$\ln(C/C_o) = -kt \quad (4)$$

where k is the apparent reaction rate constant, C_o and C are the initial concentration and the reaction concentration of methylene blue, respectively.

The photodegradation reaction rate of methylene blue by the as-prepared TiO_2 powders obtained from run 2, run 15, and the optimal experiment were measured as shown in Fig. 4. The apparent reactant rate constant is 1.01×10^{-3} min^{-1}, 1.48×10^{-3} min^{-1}, and 1.86×10^{-3} min^{-1}, for run 2, run 15, and the optimal experiment, respectively. Clearly, the apparent rate constants depend on the surface area of powder. The rate constant increases with increasing surface area in expectation.

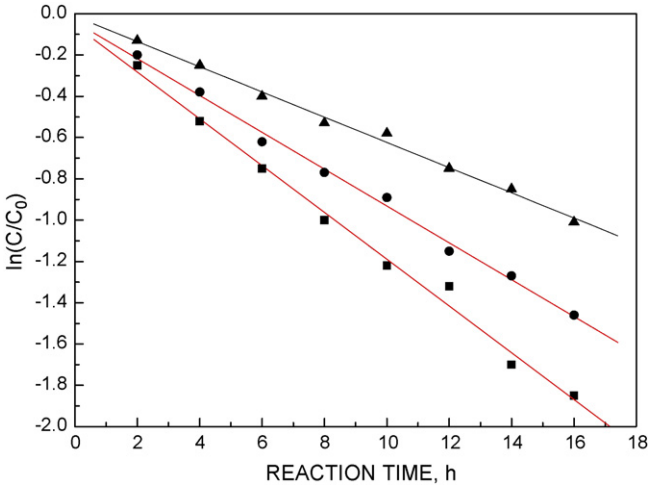

Fig. 4. The photodegradation reaction rate of methylene blue by the as-prepared TiO_2 powders obtained from run 2, run 15, and the optimal experiment. (▲) Run 2, (●) run 15, and (■) optimal experiment.

4. Conclusions

The nanometric-sized titanium oxide powders with spherical morphology have been synthesized successfully through two-emulsion method, which is caused by the reaction between two solutions of reverse emulsion, one containing Ti^{4+} chelated with acetylacetone aqueous droplets and the other aqueous ammonia droplets, with the same water/oil (w/o) ratio and mixed together to form a slurry of titania precursor. The adopted experimental variables were volume ratio of surfactant/*n*-hexane, volume ratio of water, ammonia concentration, and molar ratio isopropanol/titanium isopropoxide.

It is obviously found that as the volume ratio of w/o increases, the stability of microemulsion is decreased; it can be concluded that low volume ratio of w/o, such as volume ratio of w/o at 1/100, favor the formation of emulsion and resulting in a finer particle size obtained at 15 nm. From the results of XRD analysis and TEM observation in this study of the TiO_2 powders, it was found that the anatase phase is formed at 400 °C and converted to rutile phase as heat-treated at 700 °C. The synthesized TiO_2 powders exhibit particle sizes at 10–30 nm, specific surface area about 30–88 m^2/g.

Furthermore, the surface response method (including Box-Behnken design) was applied to deal with the preparatory conditions of the two-emulsion process. It reveals that the optimal preparatory conditions were obtained at the volume ratio of surfactant/*n*-hexane = 0.03, volume ratio of w/o = 0.04, molar ratio of acetylacetone/titanium isopropoxide = 4, molar ratio of isopropanol/titanium isopropoxide = 23.1. By combining the optimal settings of those variables, it has obtained a nanometric-

sized TiO_2 powder with specific surface area at 96 m^2/g. Finally, photocatalytic degradation experiments were examined and they demonstrated that methylene blue remarkably enhanced the degradation in the presence of TiO_2 powders prepared from the optimal conditions under ultraviolet light.

Acknowledgement

The authors wish to thank the Institute of Nuclear Energy Research for financial support of this work.

References

1. Spurr, R. A. and Myers, H. A., Quantitative analysis of anatase-rutile mixtures with an X-Ray diffractometer. *Analytical Chemistry*, 1957, **29**, 760–762.
2. Nguyen, T. V., Lee, H. C. and Yang, O. B., The effect of pre-thermal treatment of TiO_2 nano-particles on the performances of dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, 2006, **90**, 967–981.
3. Wang, Z. and Hu, X., Fabrication and electrochromic properties of spin-coated TiO_2 thin films from peroxo-polytitanic acid. *Thin Solid Films*, 1999, **352**, 62–65.
4. Takahashi, M., Tsukigi, K., Uchino, T. and Yoko, T., Enhanced photocurrent in thin film TiO_2 electrodes prepared by sol–gel method. *Thin Solid Films*, 2001, **388**, 231–236.
5. Kim, E. J. and Hahn, S. H., Microstructure and photoactivity of titania nanoparticles prepared in nonionic w/o microemulsions. *Microstructure and Processing*, 2001, **A 303**, 24–29.
6. Yuan, J., Chen, M., Shi, J. and Shangguan, W., Preparation and photocatalytic hydrogen evolution of N-doped TiO_2 from urea and titanium tetrachloride. *International Journal of Hydrogen Energy*, 2006, **31**, 1326–1331.
7. Yang, W. D. and Hung, K. M., Optimization of the experimental conditions for the preparation of a thin strontium titanate film by hydrothermal process. *Journal of Materials Science*, 2002, **37**, 1337–1342.
8. So, W. W., Park, S. B., Kim, K. J., Shin, C. H. and Moon, S. J., The crystalline phase stability of titania particles prepared at room temperature by the sol–gel method. *Journal of Materials Science*, 2001, **36**, 4299–4305.
9. Nakamura, I., Negishi, N., Kutsuna, S., Ihara, T., Sugihara, S. and Takeuchi, K., Role of oxygen vacancy in the plasma-treated TiO_2 photocatalyst with visible light activity for NO removal. *Journal of Molecular Catalysis A Chemical*, 2000, **161**, 205–212.
10. Zhang, R. B. and Gao, L., Preparation of nanosized titania by hydrolysis of alkoxide titanium in micelles. *Materials Research Bulletin*, 2002, **3**, 1659–1666.
11. Zhang, X., Zhang, F. and Chanb, K. Y., The synthesis of Pt-modified titanium dioxide thin films by microemulsion templating, their characterization and visible-light photocatalytic properties. *Materials Chemistry and Physics*, 2006, **97**, 384–389.
12. Tai, C. Y., Lee, M. H. and Wu, Y. C., Control of zirconia particle size by using two-emulsion precipitation technique. *Chemical Engineering Science*, 2001, **56**, 2389–2398.
13. AlguerÓ, M., Calzada, M. L., Quintana, C. and Pardo, L., Ferroelectricity of lanthanum-modified lead titanate thin films obtained by a diol-based sol–gel method. *Applied Physics*, 1999, **A68**, 583–592.
14. Selvaraj, U., Prasadarao, A. V. and Komarneni, S., sol–gel processing of oriented $PbTiO_3$ thin films with lead acetylacetonate as the lead precursor. *Materials Letters*, 1994, **20**, 71–74.
15. Moon, J., Suvaci, E., Li, T., Costantino, A. and Adair, J. H., Phase development of barium titanate from chemically modified-amorphous titanium (hydrous) oxide precursor. *Journal of the European Ceramic Society*, 2002, **22**, 809–815.
16. Zhang, L., Zhu, Y., He, Y., Li, W. and Sun, H., Preparation and performances of mesoporous TiO_2 film photocatalyst supported on stainless steel. *Applied Catalysis B: Environmental*, 2003, **40**, 287–292.
17. Kato, K., Tsuzuki, A., Torii, Y., Taoda, H., Kato, T. and Butsugan, Y., Morphology of thin anatase coatings prepared from alkoxide solutions containing organic polymer, affecting the photocatalytic decomposition of aqueous acetic acid. *Journal of Materials Science*, 1995, **30**, 837–841.
18. Hsieh, C. S. and Liou, T. S., Analysis of orthogonal array experiments using the multivariate orthogonal regression method. *Quality Engineering*, 2001, **13**(3), 449–455.
19. Morgenthaler, S. and Schumacher, M. M., Robust analysis of a response surface design. *Chemometrics and Intelligent Laboratory Systems*, 1999, **47**, 127–141.
20. Lee, M. H., Tai, C. Y. and Lu, C. H., Synthesis of spherical zirconia by precipitation between two water/oil emulsion. *Journal of the European Ceramic Society*, 1999, **190**, 2593–2603.
21. Takahashi, Y. and Matsuoka, Y., Dip-coating of TiO_2 films using a sol derived form $Ti(O\text{-}i\text{-}Pr)_4$-diethanolamine-$H_2O$-i-PrOH system. *Journal of Materials Science*, 1988, **23**, 2259–2266.
22. Hu, L., Yoko, T., Kozuka, H. and Sakka, S., Effect of solvent on properties of sol–gel-derived TiO_2 coating films. *Thin Solid Films*,0 1992, **219**, 18–23.
23. Syoufian, A. and Nakashima, K., Degradation of methylene blue in aqueous dispersion of hollow titania photocatalyst: optimization of reaction by peroxydisulfate electron scavenger. *Journal of Colloid and Interface Science*, 2007, **313**, 213–218.