

SUSPENSION STABILITY OF TITANIA NANOPARTICLES STUDIED BY UV-VIS SPECTROSCOPY METHOD

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Received: March 2011

Accepted: January 2012

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Abstract: Ultraviolet-Visible (UV-Vis) spectroscopy was used, in the current investigation, to explore the dispersion and stability of titania nanoparticles in an aqueous media with different types of dispersants. Hydrochloric and nitric acids as well as ammonia were used to determine the stability of the suspension in the acidic region (pH=2.5) and basic area (pH=9.5), respectively. In addition, for measuring sustainability of suspension and creating steric, and electrosteric repulsive forces, ethylene glycol and ethylene glycol plus ammonia were employed, respectively. UV-V is spectrometry was applied to realize the effect of nano titania concentrations and different types of dispersants of samples containing different amounts of nano titania and different types of dispersants on stability of TiO₂-containing suspensions. In addition, the stability of dispersion could be evaluated in colloidal mixtures containing ethylene glycol plus ammonia. It was demonstrated that the mixtures containing ethylene glycol plus ammonia were stable over a period of 4 days. To support the UV-Vis results, other techniques such as atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed to study the degree of agglomeration of titania nanoparticles in terms of morphology and size.

Keywords: Titania; UV-Vis spectroscopy; Nanoparticles; Suspension stability.

1. INTRODUCTION

The study of nanomaterials has attracted a great interest in the recent years, due to their remarkable applications concerning several realms of science. Nanotechnology has the potential to create several fresh materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production [1]. On the other hand, dealing with nanopowders is a complicated issue and a very difficult one, mainly because of their toxicity and propensity to agglomeration as a result of their high surface area. However, particle dispersion in a liquid media has been found to be a promising approach to result in suspensions with a higher uniformity [2-3]. Investigation on dispersion of nanoparticles using different techniques has become an important and difficult issue [4-5]. In this regard, the propensity to coagulate can be defeated using numerical routes such as follows: 1) Electrostatic repulsions between similarly charged particles, resulted from the formation of

an electric double layer, 2) Repulsive steric forces improving dispersion of solid particles by addition of organic mixtures, based on the interaction between the adsorption layers of admixture and 3) Electrosteric mechanism generated by polyelectrolytes [6].

Many investigations have been performed on the dispersion stability of materials, using different methods such as electron microscopy (TEM and SEM) [7-8], atomic force microscopy (AFM) [9], Raman spectroscopy [10] and ultraviolet-Visible (UV-Vis) spectroscopy [11]. Salzmänn et al. [12] have studied the effect of several dispersants on single-walled carbon nanotube (SWCNT) dispersions by applying UV-Vis techniques. Fazio et al. [13] also reported the effect of dispersants' type and concentration on dispersion of two commercial and one synthesized titania nanopowders. They took the advantage of zeta-potential measurements and particle size distribution to characterize the nano titania suspensions.

Nanosized titania is produced worldwide in

large quantities and has received much research attention because of its unique properties for applications such as pigments, cosmetics, paper, fine ceramics, as well as photocatalysts for environmental purification, catalyst supports, and dielectric materials [14-16]. Owing to the very strong Van-der-Waals interactions, TiO_2 nanoparticles almost incline to form aggregates or hard agglomerates. On the other hand, stable dispersion of TiO_2 nanoparticles in water is such a significant challenge that only few reports are available in the literature considering the stability of TiO_2 nanoparticles in aqueous solution. pH and surface charges of the solution mainly determine the stability of TiO_2 nanoparticles in aqueous solution [17]. The charge properties of titanium dioxide particles in aqueous media have been studied by several authors. Zhou et al [18] adopted surfactant to prepare the nano- TiO_2 powder using hydrolysis method, with the result of obtaining TiO_2 particles of the homogeneous dispersion, narrow particle distribution and homogeneous size. Hu et al [19] utilized $\text{Ti}(\text{SO}_4)_2$ and $\text{CO}(\text{NH}_2)_2$ to synthesize nano- TiO_2 by harmonious precipitation and it was found to improve the particle size distribution of TiO_2 in case of adding complex surfactants.

One useful technique to evaluate the stability of ceramic suspensions is zeta potential measurement which is widely used as an important criterion [20]. A high absolute value of zeta potential is attributed to a well-dispersed suspension. According to the zeta potential values [13], the isoelectric point (IEP) of titania nanopowder is about 4.5 - 6.0. However, to access a stable suspension of ceramic particles, the slurry needs a zeta potential variation of about ± 40 eV from IEP. Therefore, [13], the optimized conditions to produce a stable suspension of nano titania with electrostatic mechanism is either in pH range of 2.5-3.5 and 9.5-10.5; i.e. in acidic pHs and basic ones, respectively. Hence, in the present article, for investigating the effect of different dispersion media on stability of nano titania suspension, hydrochloric and nitric acid were introduced to determine the stability of the suspension in the acidic region (pH about 2.5) and ammonia in the basic area (pH about 9.5). In addition, for measuring sustainability and

creating steric and electrosteric repulsive forces ethylene glycol and ethylene glycol plus ammonia were used, respectively. Likewise, the dispersion of nano titania particles in water suspension has been studied using UV-Vis spectroscopy and the desirable amount of dispersant and titania has been discussed. Besides, UV-Vis spectroscopy measurements have been employed as a novel method to quantitatively characterize colloidal stability of the dispersions.

2. EXPERIMENTAL PROCEDURE

Nano TiO_2 powder, used in this study, was Degussa P25 obtained from Beijing Entrepreneur Science & Trading Company Ltd. of China. The average diameter of the nano powder has been reported by the supplier to be 21 nm and the specific surface area (BET) of the powder was reported 50 m^2/g . Five different additives, including hydrochloric acid (Merck, Germany), nitric acid (Merck, Germany), ammonia (extra pure (99.99%), Dr. Mojallali chemical lab. Iran) and ethylene glycol (Merck, Germany) were used as dispersant materials. Samples preparation process was the same for all the specimens. The proper amounts of mentioned dispersant was added to 100 ml distilled water followed by the addition of 0.25, 0.5, 0.75 and 1g of nano titania. pH of suspension was adjusted to a desired value, then; the suspension was stirred for 30 min using a magnetic stirrer and subjected to a subsequent treatment in an ultrasonic bath for 60 min and ultrasonic probe for 5 min. The specimens were stirred again for 30 min using a magnetic stirrer. The stability of the nano titania suspension is determined by measuring the sediment volume versus the sediment time. Measurements of the sedimentation rate were made in 100 mL cylinders, by observing the height of the interface between the settling suspension and its supernatant. While, in most cases, the supernatant was clear, it was observed to display a cloudy appearance in more dilute slips.

Moreover, the dispersion stability of nano- TiO_2 aqueous suspension was evaluated by the absorbance of suspension using a model mini1240 Shimadzu UV-Visible spectrometer.

The degree of absorbance is proportional to the amount of the particles per unit volume so that it can denote the dispersion stability of the particles in the aqueous solution. The absorbance of the well-stabilized suspension is ascribed to the decrease of aggregation sedimentation [11]. An atomic force microscope (operated in contact mode) of model DME-02, as well as a scanning electron microscope (vega Tescan) were also employed. The AFM and SEM sample preparation was carried out by setting a drop of liquid on a glass substrate, followed by drying via a desiccator.

3. RESULTS AND DISCUSSION

Fig. 1 depicts sediment time of nano titania suspensions with different dispersants as a function of titania concentration, extracted from

Table 1. Table 1 displays the sedimentation time during which a white layer of titania particles is formed at the bottom of the container. Formation of the above mentioned layer, as shown in Fig. 2, does not exhibit an identical process in all the specimens and may be developed incompletely for some samples. For instance, while formation of this layer on the last specimen has been difficult (as long as one complete day) and the whole suspension has remained milky and pale, formation of the white layer has been complete at the bottom of the container for the additive free sample and the retained suspension is clear.

Comparison of Fig. 1 (a) and (b) showed that increasing titania concentration gave rise to the reduction of stability time in all samples. For instance, the time required for nano powders to be settled down to the bottom of vials and create a solid layer from the suspension, stabilized with

Table 1. Stability time of TiO_2 suspensions with variable concentrations of TiO_2 .

TiO_2 Concentration	Stability time (min)					
	Without additive (pH=6.5)	HCl (pH=2.5)	HNO_3 (pH=2.5)	5%wt EG	NH_3 (pH=9.5)	NH_3 +EG (pH=9.5, 5% EG)
0.25	27	91	112	240	360	720
0.5	24	76	91	192	315	660
0.75	21	65	73	141	282	630
1	18	56	64	105	210	612

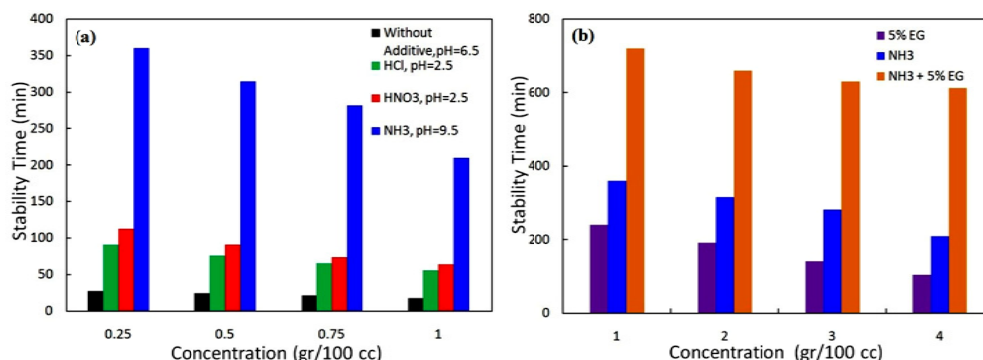


Fig. 1. Stability time versus TiO_2 concentration with different type of additives (a) electrostatic mechanism (b) steric and electrosteric mechanisms.

HNO_3 , declined from 112 to 64 minutes, while the titania concentration rose from 0.25 to 1 g/100 ml. This behavior may be explained based on the attraction and repulsion forces between particles. The increment in the concentration of titania nanoparticles results in the shortening of distance between particles and, hence, the gradual establishment and increase of repulsive forces.

According to Table 1 and Figure 1(a), the acidic and basic media have a vital rule on the stability time of titania suspensions. For instance, the sample stabilized with NH_3 at basic region ($\text{pH}=9.5$) with 0.25 concentration of titania nanoparticles has a stability time about 360 minutes while the stability time for the same suspension stabilized with HNO_3 ($\text{pH}=2.5$) and HCl ($\text{pH}=2.5$) at acidic region are 112.5 and 91.35 min, respectively. The reason lies in this fact that OH^- groups in basic media have larger space size than the H^+ groups in the acidic region. Therefore, in spite of existence of repulsive forces which cause an electrostatic stability, the above fact generates an extra steric repulsion which accompanies higher stability times in the basic media. Tkachenko et. al [17] recently reported the influence of ionic and nonionic surfactants on aggregative stability and electrical surface properties of aqueous suspensions of titanium dioxide. They showed that pH conversions had important role on stabilization of nonionic surfactants.

As shown in Fig. 1(b), the sample prepared by

NH_3+EG displayed the highest stability time compared to other suspensions. In other words, electrostatic repulsive mechanism in the sample stabilized with NH_3+EG has the highest efficiency to stabilize the nano titania suspension in comparison with steric and electrostatic mechanisms.

Fig. 2 displays the dispersion state of nano titania after one day. In the dispersant free samples, aggregates of nano powders can be seen in Fig. 2a to be initially settled to the bottom of vials. After one day remaining, both NH_3 and $\text{NH}_3+5\text{wt.}\% \text{ EG}$ solutions demonstrate a homogeneous appearance. By contrast, nano powders in both HCl and HNO_3 solutions become unstable and sediment on the bottom of vial after one day, as shown in Fig. 2b and c. Such an observation reveals the higher contribution of NH_3 and $\text{NH}_3+5\text{wt.}\% \text{ EG}$ solutions to the separation of nano powders and conversion of aggregates into the smaller particles compared to HCl and HNO_3 .

Fig. 3 shows UV-Vis spectra of electrostatic stabilized samples after soaking time of 1 day. As can be seen in the figure, the absorption is dependent on not only the wavelength but also the type of dispersant. The diversities of UV-Vis absorption between the samples containing additives and one with no additive demonstrate the dispersion efficiency in different samples. In other words, the additives have caused the nano titania particles to segregate from each other and has prevented them from forming agglomerates,

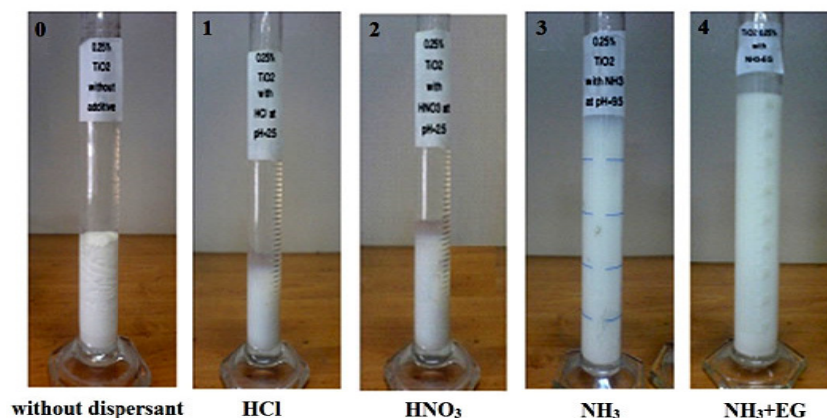


Fig. 2. Appearance of TiO_2 suspensions after one day.

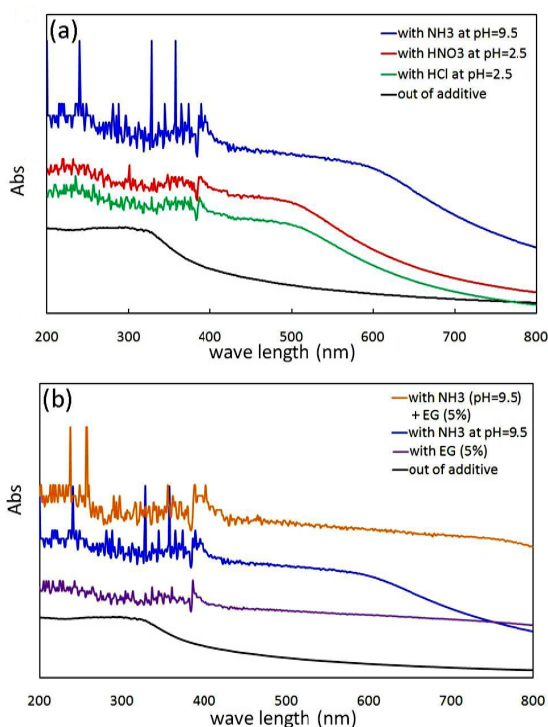


Fig. 3. UV-Vis absorption spectra of different stabilized (a) electrostatic (b) steric and electrosteric samples after soaking time of 14 days.

so that a higher surface area of TiO_2 particles after dispersion could be achieved. It seems that the combination of NH_3 and EG has led to the better consequences. Through this, the total area of titania particles which exposed to UV radiation were increased, resulting in more excitations. Hence, by improving the quality of the dispersion, a higher absorption in the UV-Vis spectra is expected. Likewise, the highest absorption of ultraviolet radiations in suspension stabilized by NH_3 +EG, confirmed the higher efficiency of electrosteric repulsive forces in comparison with electrostatic and steric mechanisms. This behavior is attributed to this fact that the absorbed ions in electrostatic mechanism form a charged layer around the particles preventing the aggregation, while in steric mechanism, on the other hand, a volume restriction component as well as a mixing or osmotic component are the two influential factors on stabilization of suspension [6]. Therefore, the electrosteric stabilization, due to possessing both

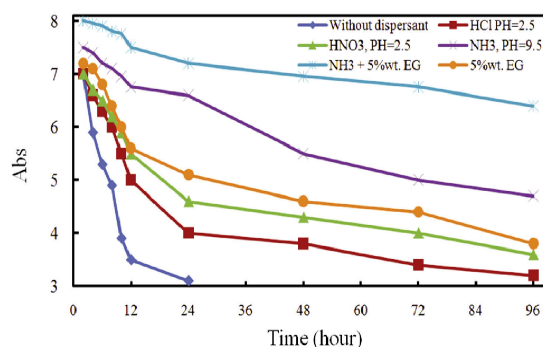


Fig. 4. UV-Vis absorption of samples with electrostatic steric and electrosteric stabilized mechanisms in comparison with no stabilized sample in $\lambda = 300$ nm.

advantages of electrostatic and steric stabilizations, exhibits a more efficient role in stabilization of suspensions compared to the other stabilization mechanisms.

The dispersion state and the long-term stability of each sample can be examined more quantitatively by UV-Vis spectroscopy, as shown in Fig. 4, where the absorbance at the wavelength of 300 nm is plotted against time of still- standing for dispersion samples. According to this figure, the suspension with NH_3 +EG dispersant displays the highest value of the absorption against time. This means that the dispersion remains stable for at least 4 days. On the contrary, in the samples containing no or other dispersants, the faster decline in absorption over the same period of time demonstrates that the samples have been unsteady and have undergone a quicker sedimentation. In addition, variable types of dispersants in the acidic region (HCl and HNO_3 ones) have shown an identical absorption tendency and sedimentation time (Fig. 1) which can be related to the effect of pH on suspension stability. The absorption curves clearly indicate an order of dispersability NH_3 +5wt.% EG > NH_3 > HNO_3 > HCl, since the dispersed amount of nano powder is linearly proportional to the UV absorbance. Furthermore, the absorbance of NH_3 +5wt.% EG has experienced no specific variation over a period of 4 days, suggesting that the dispersion by NH_3 +5wt.% EG is not temporal. Besides, the absorbance in NH_3 drops down to 70% of its initial value after 2 days, with

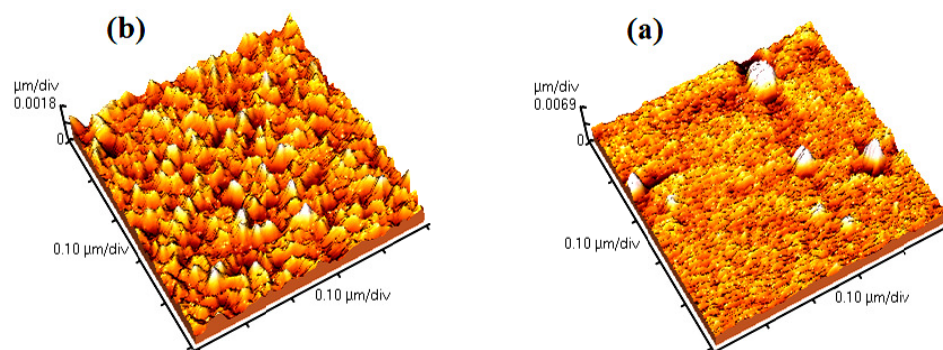


Fig. 5. AFM images from samples containing nano titania dispersed with (a) no additive, (b) NH_3 +EG dispersant.

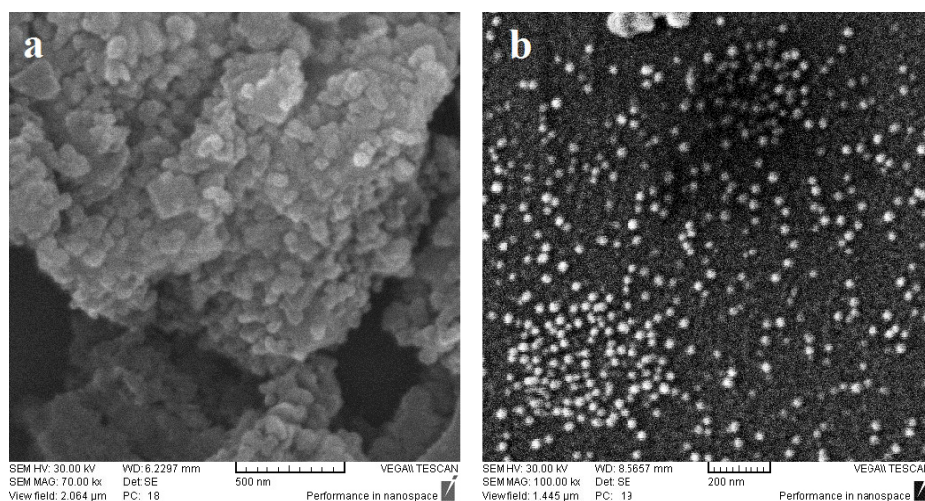


Fig. 6. SEM images of samples containing nano titania dispersed with (a) no additive, (b) NH_3 +EG dispersant.

no further significant change up to 100 h. On the other hand, the absorbance of 5%wt. EG, HNO_3 and HCl declines rapidly to 70, 65 and 55% of its initial value within one day, respectively, and further decreases to about 40% of its initial value after 4 days. The dispersion stability of sample without additive was found to be even worse than that of 5%wt. EG, HNO_3 and HCl. This result suggests that the homogeneous dispersions of nano titania achieved by 5%wt. EG, HNO_3 and HCl are only temporal and thus rely strongly on the time.

The quality of dispersion was further certified by atomic force microscopy (AFM) and scanning electron microscopy, as shown in Fig. 5 and 6

respectively. The sample without dispersant has clearly a continuous structure of agglomerates (Fig. 5(a)) while the sample containing NH_3 plus EG (Fig. 5(b)) exhibits the fragmentation of agglomerates and the separation of particles. As shown in Fig. 6(a), the agglomerates in the sample without dispersant can be obviously observed and Fig. 6(b) presents the sample containing NH_3 plus 5%wt. EG which illustrates the interruption of agglomerates and the segregation of particles.

4. CONCLUSIONS

Dispersion of nano titania was investigated by

UV-Vis spectroscopy. It was shown that increasing the concentration of nanopowders could decline the stability of suspension. The degree of agglomeration was determined to be the electrosteric stabilization and it was confirmed by AFM and SEM observations. The stability of TiO_2 nano particles could be maintained up to 100 h in case of optimized.

REFERENCES

1. Buzea, C., Blandino, Robbie, K., "Nanomaterials and Nanoparticles: Sources and Toxicity." *J. Biointerphases*, 2007, 2, 17-172.
2. Kear, B., Colaizzi, J., Mayo, W., Liao, S., "On the processing of nanocrystalline and nanocomposite ceramics." *J. Scripta Mater.*, 2001, 44, 2065-2068.
3. Vasylykiv, O., Sakka, Y., "Synthesis and colloidal processing of zirconia nanopowder." *J. Am. Ceram. Soc.*, 2001, 84, 2489-2494.
4. Horn, R., "Surface forces and their action in ceramic materials." *J. Am. Ceram. Soc.*, 1990, 73, 1117-1135.
5. Lewis, J., "Colloidal processing of ceramics." *J. Am. Ceram. Soc.*, 2000, 83, 2341-2359.
6. Farrokhpour, S., "A review of polymeric dispersant stabilisation of titania pigment." *J. Advances in Colloid and Interface Sci.*, 2009, 151, 24-32.
7. Ridaoui, H., Jada, A., Vidal, L., Donnet, J., "Effect of Cationic Surfactant and Block Copolymer on Carbon Black Particle Surface Charge and Size." *J. Colloids and Surfaces*, 2006, 278, 149.
8. Kim, H., Kim, J., Kim, M., "Experimental study on CHF characteristics of water- TiO_2 nano-fluids." *J. Nuclear engineering and technology*, 2006, 38, 61-68.
9. Falvo, M., Helser, A., Chi, V., Brooks, F., Washburn, S., Superne, R., "Nanometer-Scale Rolling and Sliding of Carbon Nanotubes." *J. Nature*, 1999, 397, 236.
10. Wang, Z., Zhu, Q., H., Liu, H., Chen, Y., Yang, M., "Dispersing Multi-Walled Carbon Nanotubes with Water-Soluble Block Copolymers and Their Use as Supports for Metal Nanoparticles." *J. Carbon*, 2007, 45, 285.
11. Sharif, Sh., M., Golestani-Fard, F., Khatibi, E., Sarpoolaky, H., "Dispersion and stability of carbon black nanoparticles, studied by ultraviolet-Visible spectroscopy." *J. taiwan institute of chem. Eng.*, 2009, 40, 524-527.
12. Salzmänn, G., Chu, B., Chu, T., Tobias, G., Simon, A., Malcolm, L., "Quantitative Assessment of Carbon Nanotube Dispersions by Raman Spectroscopy." *J. Carbon*, 2007, 45, 907.
13. Fazio, S., Guzmán, J., Colomer, M., Salomoni, A., Moreno, R., "Colloidal stability of nanosized titania aqueous suspensions." *J. Eur. Ceram. Soc.*, 2008, 28, 2171-2176.
14. Vidal, A., "Developments in solar photocatalysis for water purification." *J. Chemosphere*, 1998, 37, 387.
15. Zhao, G., Kozuka, H., Lin, H., Yoko, T., "Sol-gel preparation of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ solid solution film electrodes with conspicuous photoresponse in the Visible region." *J. Thin Solid Films*, 1999, 339, 123-128.
16. Lia, H., Zhao, G., Chen, Z., Hana, G., Song, B., "Low temperature synthesis of Visible light-driven vanadium doped titania photocatalyst." *J. Colloid and Interface Sci.*, 2010, 344, 247-250.
17. Tkachenko, N., Yaremko, Z., Bellmann, C., Soltys, M., "The influence of ionic and nonionic surfactants on aggregative stability and electrical surface properties of aqueous suspensions of titanium dioxide." *J. colloid and interface sci.*, 2006, 299, 686-695.
18. Zhou, W., Tang, Sh., Q., Zhang, Sh., Y., Zhou, X., "Study on preparation of nano TiO_2 by hydrolyzation of titanium-salt coated with DBS." *J. Chinese Ceram. Soc.*, 2003, 31, 858-861.
19. Hu, X., Chen, D., Hu, X., Ying, H., "The effect of surfactants on the particle size and shape of TiO_2 ." *J. China Ceram. Indust.*, 2003, 10, 25-28.
20. Kosmulski, M., Durand-Vidal, S., Gustafsson, J., Rosenholm, J., "Charge interactions in semi-concentrated titania suspensions at very high ionic strengths." *J. Colloids and surface A*, 1999, 157, 245-259.