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Preparation of TiO_2 nanoparticles by submerged arc nanoparticle synthesis system

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ABSTRACT

This study investigated the effects of process parameters on geometrical features of titanium dioxide (TiO_2) nanoparticles synthesized by the submerged arc nanoparticle synthesis system (SANSS). The synthesis process involves vaporizing a pure titanium rod by a submerged arc in deionized liquid under a controlled vacuum environment, followed by rapid quenching of the vaporized titanium gas by a cooling system, thus forming nanocrystalline powders. Our experimental results revealed that the electric current for preparing the nanoparticle suspension had significant impact on the size, distribution and surface sphericity of the nanoparticles synthesized, while other process parameters including pulse duration and temperature of deionized water also had moderate influence on the geometrical properties. With the set of parameters selected through process analysis, TiO_2 nanoparticles having an average particle diameter of 65 nm with a size disparity of 60 nm and particle sphericity of 3.8% can be synthesized.

1. Introduction

Geometrical characteristics of nanoparticles have been considered extremely crucial for developing novel materials and products [1,2]. Traditional methods for fabricating nanoparticles, such as gas phase synthesis and sol–gel processing, sometimes result in undesirable variations in particle size of up to 50%. Moreover, the relationship between process parameters and morphology of synthesized particles remains largely unknown, making it difficult to control the size and shape of the prepared nanoparticles within a desired range.

The synthesis of titanium dioxide (TiO_2) nanoparticles by a process known as the submerged arc nanoparticle synthesis system (SANSS) [3–5] is characterized by an in-cycle particle measurement system [6]. The SANSS was developed to prepare a suspension of TiO_2 nanoparticles using a submerged electrode with a working temperature of up to 6000 °C. The nanofluids were sampled and analyzed by a fiber-based secondary size analyzer for the detection of particle size and distribution. Nevertheless, the size distribution of TiO_2 nanoparticles dispersed in the prepared suspension still ranged from 30 to 250 nm [5]. Furthermore, their sphericity was found to be more than 10% of the particle diameter. It is obvious that the geometrical features obtained were far from the desired objective of achieving a well-controlled particle size of less than 100 nm with a narrower diversity and a good surface sphericity of less than 5%. Hence, this study investigated the impact of important SANSS process parameters including applied electric current, voltage, pulse duration and temperature of deionized liquid on the geometrical properties of nanoparticles synthesized.

2. Experimental design and analysis

The schematic diagram of SANSS is depicted in Fig. 1. The generation of nanoparticle suspension is briefly detailed here [3,5,6]. A pure titanium rod is first submerged in deionized water in the vacuum chamber. After setting the related system parameters, the heating source produces an arc of high temperature between 5000 and 20,000 K to melt the metal rod [3]. The rod is melted and vaporized in the region where the arc is generated. In addition, the neighboring deionized water is simultaneously vaporized by the high-temperature arc. The vaporized metal within the vacuum chamber then undergoes nucleation, condensation and growth. With process parameters including pressure of chamber and temperature of deionized water controlled within a desired level, the submerged arc can be generated steadily. Consequently, nanoparticles of diameter ranging from 30 to 250 nm can be fabricated and dispersed in deionized water.

As mentioned above, the vaporized metal undergoes three stages, namely nucleation, condensation and growth, thus becoming nanoparticles suspended in deionized water. According to the nucleation theory, the nucleating rate of unit volume (I) can be modeled by the number of atoms in the raw material, the change in free energy (ΔG) when the new phase is formed, the required activation energy when atoms pass through interfaces, the absolute temperature, and other parameters such as the Planck and Boltzmann constants [7,8]. As can be expected from the above relationship, the change in free energy is a critical parameter affecting the nucleating rate when the process temperature is maintained constant. The saturation during material transformation from solid to gaseous state can be significantly influenced by ΔG.

High saturation of the nucleating condition also depends greatly on the temperature difference between the submerged arc and deionized water. In other words, high nucleation rate can be achieved when the raw material is vaporized at high temperature and rapidly condensed at low temperature. However, uniform nanoparticles cannot be synthesized by the SANSS under insufficient saturation rate.

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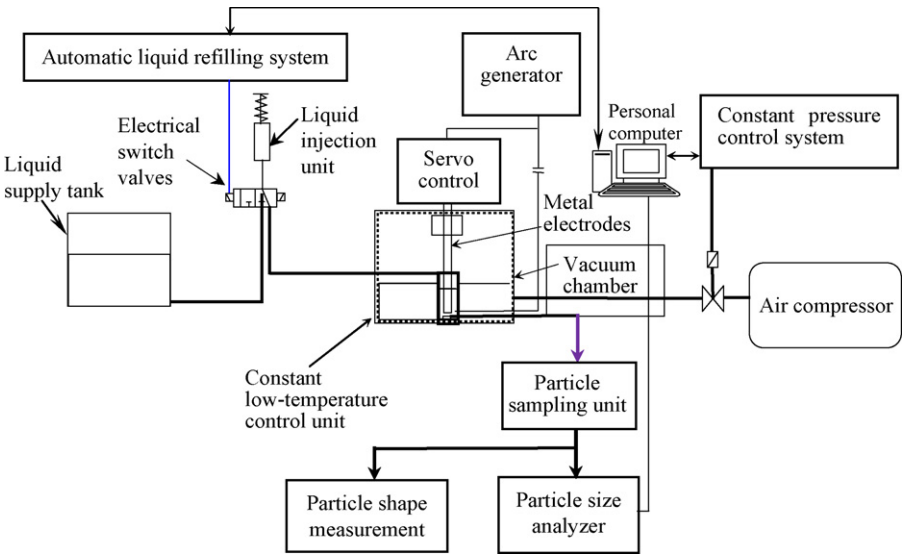

Fig. 1. SANSS developed for fabrication and measurement of nanoparticles.

Radius of nuclei during condensation is a main determinant of nanoparticle property. To obtain nanoparticles with desired geometrical size and shape, it is important to reduce the critical radius of condensation nuclei. The radius (r) of cluster formed from gaseous state is influenced by the free energy [9]. Following condensation and nucleation, the next process is particle growth, which is another factor affecting the final nanoparticle size. The diameter of nanoparticles is governed by the amount of particles produced in one unit volume of reaction gas, concentration of the vaporized metal, molecular weight and density [10]. The growth rate of nucleus is controlled primarily by concentration of the vaporized metal and temperature of deionized water. The arcing temperature has a more critical influence on nanoparticle size since the growth rate of nucleus is significantly affected by the frequency of metal transfer from gaseous state (β) to solid state (α) on the interface [10].

3. TiO_2 nanoparticle preparation and shape characterization

Fig. 2 shows the in-cycle nanofluid measurement system developed for extracting TiO_2 nanofluids from the vacuum chamber for size and shape analysis of TiO_2 nanoparticles [6]. The system comprises a heating source, a parameter control unit, a collection unit, a deionized water supply unit, an ambiance control module and a section for automatic nanofluid extraction [11]. After the metal electrode is vaporized and the nanoparticles synthesized are suspended in dielectric water for a pre-set duration, a pre-set quantity of nanoparticles are extracted and transferred into the nanofluid collector for sampling. Two sets of particle analyzers are employed to determine the characteristics of nanoparticles, such as particle size, shape and distribution. The secondary particle size and distribution of TiO_2 nanoparticles are first measured using a fiber-based nanoparticle size analyzer equipped with an optical fiber probe for on-line particle sizing [6]. The secondary particle diameter is determined by dynamic light scattering principle. The nanofluid is further collected and processed to further characterize the geometrical properties of TiO_2 nanoparticles using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

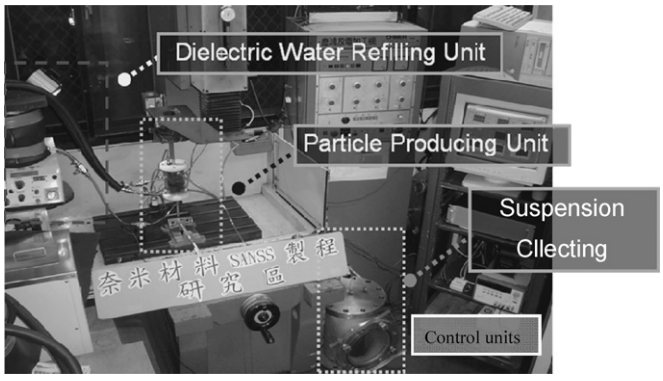

Fig. 2. Hardware system for fabrication and sampling of nanoparticles.

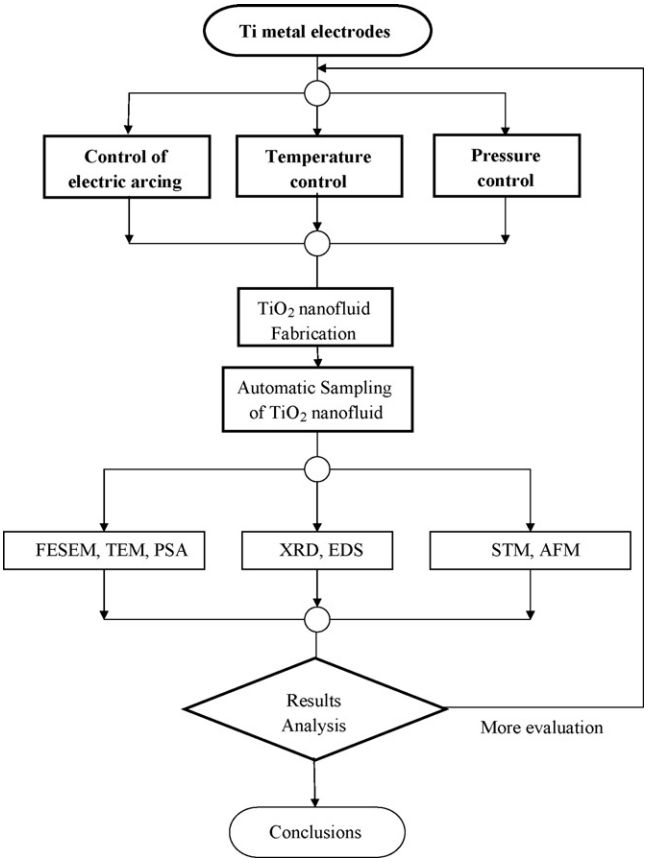

Fig. 3. Flowchart of procedures for TiO_2 nanoparticle fabrication and process characterization.

Table 1
Modulated range of process parameters for nanoparticle synthesis.

Electric current I (A)	On-time pulse duration t_{on} (μs)	Off-time pulse duration t_{off} (μs)	Working breakdown voltage V (V)	Electrode gap b (μs)
25–0.5	2–2400	2–2400	50–110	$10.268 + 8.984I$

Table 2
Modulated range of temperature and pressure for nanoparticle synthesis.

Volume of chamber (mm^3)	Pressure of chamber (Torr)	Temperature of dielectric liquid (°C)	Volume of dielectric liquid (cm^3)
1.52×10^7	20–760	5–45	250

To ensure production of high-quality nanoparticles for process characterization, the following three precautions must be taken.

1. Particle synthesis time for each batch should be controlled, so that the particle properties are consistent and reproducible by the same set of synthesis parameters.
2. pH value of the nanofluid should be controlled within a range of 5.6 and 6.7. Uniform distribution of the suspended TiO_2 particles prepared can ensure effective surface measurement of individual particles.
3. Nanofluid and particles synthesized should be kept free from any possible oxidation and maintained clean for accurate contour measurement.

Fig. 3 is the flowchart illustrating the procedures for TiO_2 nanoparticle synthesis and process characterization. The parameter control system is employed to control and select various process parameters for the preparation of TiO_2 nanofluids. In this process, the critical governing parameters including applied electric current, pulse duration, off-time duration, breakdown voltage, electrode gap, pressure of vacuum chamber and temperature of deionized water are selected to investigate their relationship with the geometrical properties of the particles synthesized. To conduct an effective process analysis, the modulated range of process parameters was designed to include their full variation range, as shown in Tables 1 and 2.

In addition, three-dimensional morphology of the prepared particles is also examined using by an AFM (NT-MDT SPM Solver P47). Mounted to the silicon surface with a muscovite mica sheet ($H_2KAI_3(SiO_4)_3$) for inspection, the TiO_2 nanoparticles can be individually measured by a microcantilever (fabricated by NANOSENSORS Corp.) having a tip radius of 5 nm under tapping mode. To eliminate potential image distortion caused by excessive probe tip effects, image deconvolution is employed to ensure measurement accuracy [12].

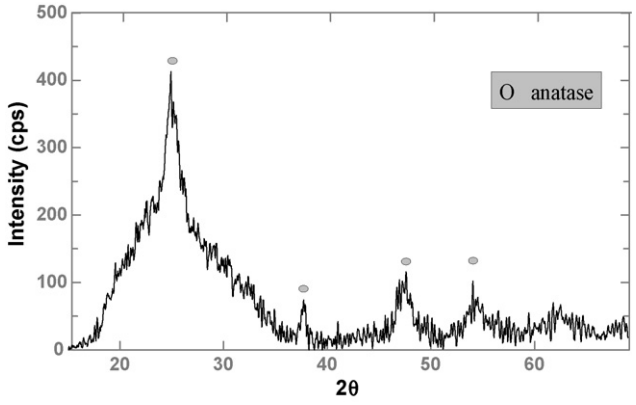

Fig. 4. XRD pattern of nanoparticles prepared.

4. Results and discussion

4.1. Composition analysis of prepared TiO_2 nanoparticles

It is vital to understand the composition and structure of the synthesized nanoparticles. The nanoparticle suspension prepared by the SANSS under high temperature and vacuum pressure contains only three elements, namely Ti, O and H. Fig. 4 illustrates the XRD pattern of nanoparticles prepared. As can be seen, the nanoparticles are TiO_2 with the form of anatase. Instead of pure Ti nanoparticles, TiO_2 nanoparticles were generated due to the reaction of titanium with oxygen dissolved in the deionized water or air. Hence, the suspension appears gray in the beginning of the sampling process and gradually turns white after being exposed to air for a period of time.

4.2. Effect of discharge current on geometrical properties of nanoparticles

Figs. 5–7 show respectively TEM images of TiO_2 nanoparticles prepared under discharge currents of 1.63, 3.5 and 7.0 A, with other process parameters including breakdown voltage, pulse duration, temperature of deionized water and pressure maintained constant. As can be seen, the larger the discharge current, the larger the nanoparticles are produced. In opposite, when the current was increased from 1.63 A to a higher value, the average particle size was also increased from 110 nm to a larger value.

Fig. 8 shows the AFM contour image and Fig. 9 displays the cross-sectional surface profile of the prepared TiO_2 nanoparticles, which reveals the particle surface morphology such as surface sphericity

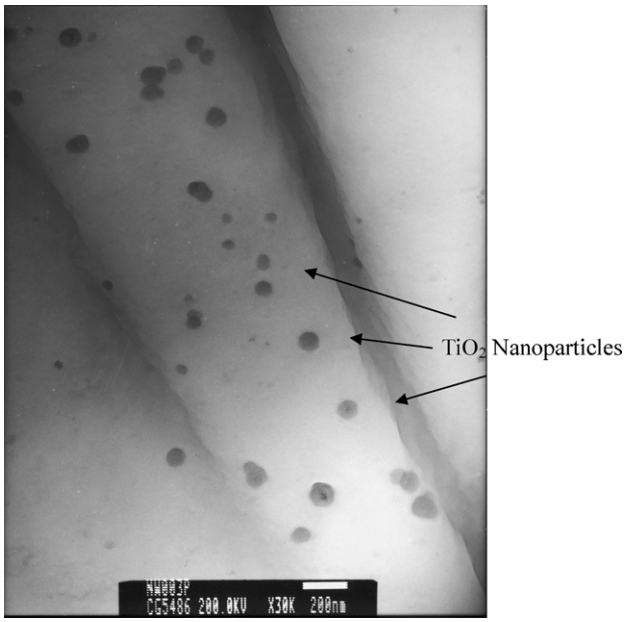

Fig. 5. TiO_2 nanoparticles prepared by discharge current of 1.63 A.

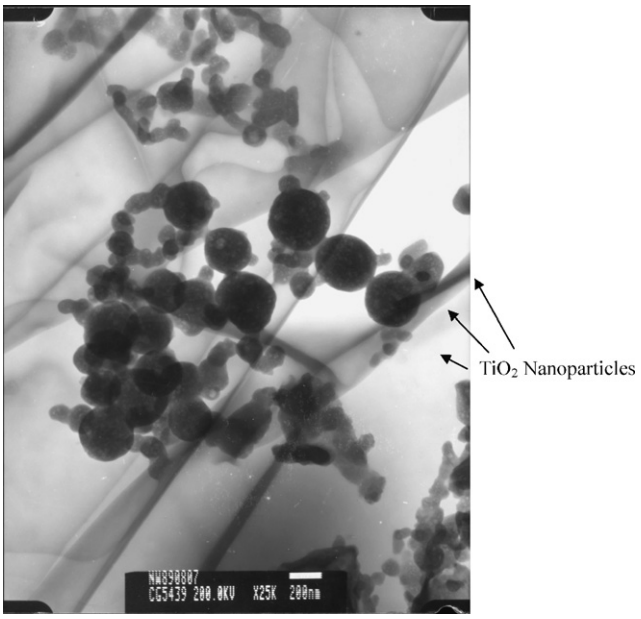

Fig. 6. TiO_2 nanoparticles prepared by discharge current of 3.5 A.

and morphology. According to the AFM measurements shown in Fig. 10, the sphericity of prepared nanoparticles deteriorated from 3.0% to 6.1% when the discharge current was increased from 1 to 10 A. In general, there is a decline in sphericity of nanoparticles with decreasing discharge current. Moreover, it was observed in Fig. 11 that particle sphericity also deteriorated for TiO_2 particles with smaller diameter. This phenomenon can be easily accounted for since the definition of particle sphericity involves using particle diameter as the denominator. The above findings confirm that discharge current is an important factor determining geometrical properties of nanoparticles prepared.

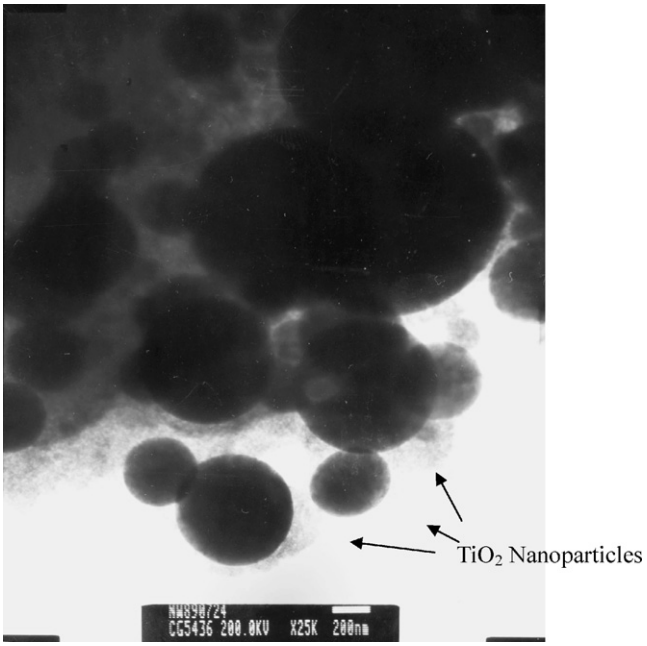

Fig. 7. TiO_2 nanoparticles prepared by discharge current of 7.0 A.

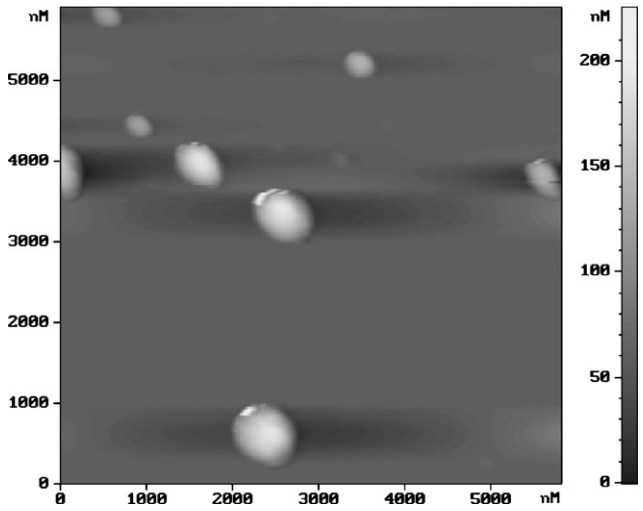

Fig. 8. Contour image of prepared TiO_2 nanoparticles scanned by AFM.

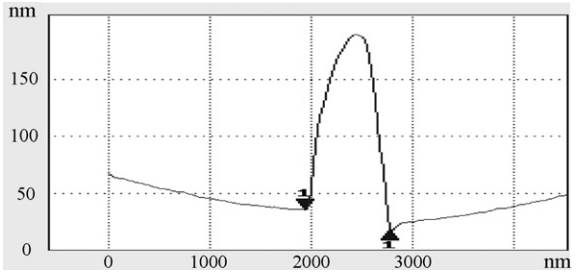

Fig. 9. Cross-sectional surface profile of prepared TiO_2 nanoparticles scanned by AFM (Note: The display scale for X-axis and Y-axis are different, so the circle profile shown in this figure is not round but distorted).

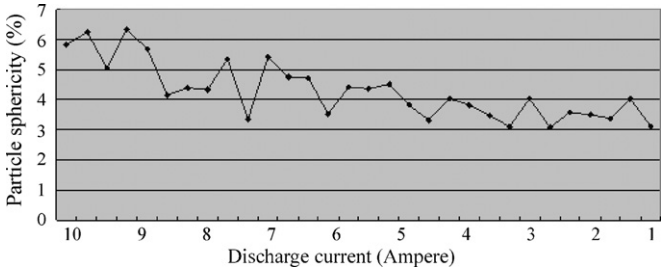

Fig. 10. Relationship between sphericity of prepared TiO_2 particles and discharge current employed in SANSS.

4.3. Process conformation trial

Table 3 lists the parameter levels selected through process analysis after considering their impact on geometrical proper-

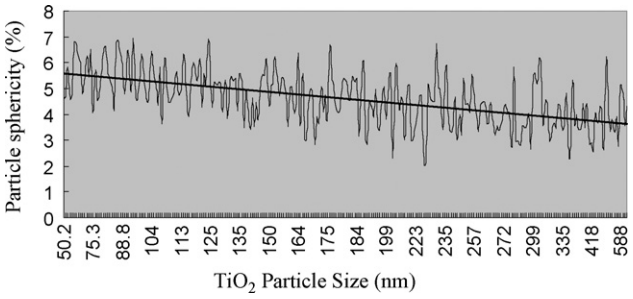

Fig. 11. Relationship between the size and sphericity of prepared TiO_2 particles.

Table 3
Parameters selected for process confirmation trial.

Working breakdown voltage (V)	100 V
Electrical current (I)	1.63 A
On-time pulse duration (t_{on})	25 μs
Off-time pulse duration (t_{off})	100 μs
Temperature of dielectric liquid (T)	5–10 °C
Electrode diameter (D)	12 mm
Dielectric liquid	Deionized water

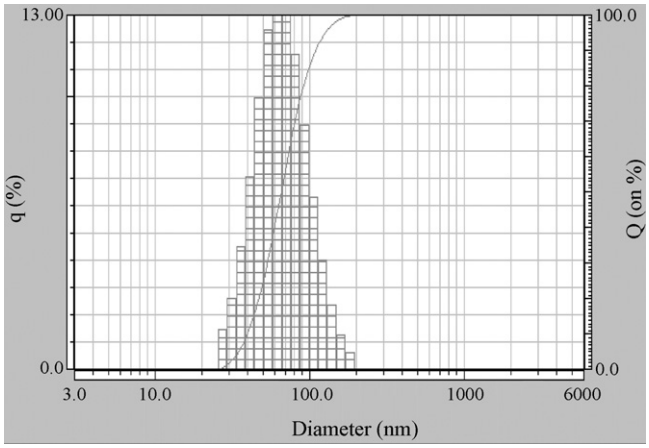

Fig. 12. Size distribution of TiO_2 nanoparticle suspension prepared using selected process parameters.

Fig. 13. TEM image of TiO_2 nanoparticles synthesized for process confirmation trial.

ties of nanoparticles. Conformation trials were then conducted on nanoparticles synthesized under the parameter levels listed. As seen in Fig. 12, the average diameter of nanoparticles in the generated suspension was 65 nm, as determined by the particle size analyzer. In this study, the particle size distribution ranged from 40 to 80 nm, which was much narrower than the previously reported range of 30–250 nm. Fig. 13 illustrates that the TEM image of the prepared particles, which were dispersed well in the suspension with a size disparity of 40 nm. The 3D contour image shown in Fig. 14 also confirms that the particles synthesized have an average spherical diameter of 65 nm. The above results demonstrate

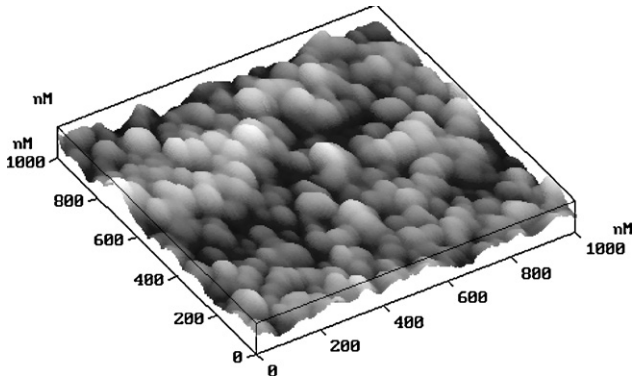

Fig. 14. 3D contour image TiO_2 nanoparticles synthesized for process confirmation trial.

that the size of TiO_2 particles synthesized by the SANSS can be effectively controlled within a nano-scale range when its average particle sphericity verified by AFM was 4.5%.

5. Conclusions

Through process characterization of SANSS parameters, this study selected a set of parameters including discharge current, breakdown voltage, pulse duration of applied electric arcing power, and temperature of deionized liquid for fabricating TiO_2 nanoparticles. These parameters all had impact on geometrical properties of the nanoparticles prepared. Discharge current showed significant impact on particle size and distribution, as well as sphericity of nanoparticles synthesized, while other parameters also showed moderate effects. With the set of parameters selected through process analysis, TiO_2 nanoparticles having an average particle diameter of 65 nm with a size disparity of 60 nm and particle sphericity of 3.8% can be synthesized.

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