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DEVELOPMENT OF NANOPARTICLE SHAPE MEASUREMENT AND ANALYSIS FOR PROCESS CHARACTERIZATION OF TiO_2 NANOPARTICLE SYNTHESIS

Liang-Chia Chen and Chie-Chan Ho

Graduate Institute of Automation Technology, National Taipei University of Technology, 1, Sec. 3, Chun-Hsiao E. Rd., Taipei 106, Taiwan

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Abstract. This article presents the development of nanoparticle form measurement for process characterization of the nanoparticle fabrication process known as the submerged arc nanoparticle synthesis system (SANSS) to prepare nanoparticles with desired particle roundness. An in-process sample preparation and particle sizing system using dynamic light scattering principle was developed to analyze the particle shape properties and characterize the nanoparticle synthesis process. The particle shape contours were measured by a transmission electron microscope with optical magnification of x100k to quantify the nanoparticle sphericity. Significant amount of the particle measurement for each experiment was performed to ensure data accuracy. The experimental results revealed that the discharge pulsed peak current plays the most significant effect on the sphericity of the TiO_2 particles and the best sphericity of prepared nanoparticles can be achieved approximately 1%.

1. INTRODUCTION

Nanoparticles with potentially useful size- and shape- dependent properties have the advantages of ultra-fine size, high surface area, useful interfacial defects and interface-dominated characteristics, and so are extensively utilized as key components in electronics and optical devices, pharmaceuticals, paints, coatings, superconductors, semiconductors and catalysis, among other things [1]. However, to be applicable to the development of innovative products or processes, nanoparticle shape characteristics are the important properties for successful application. In fact, the reproducible preparation of shape-controlled particles using the popular colloid-chemical approach is difficult. Using in-process measurement technique and particle's image analysis, the research characterizes the synthesis of TiO_2 nanoparticles by a process known as the Submerged Arc Nanoparticle Synthesis System (SANSS) [2,3] for preparation of TiO_2 nanoparticles with improved sphericity. The SANSS being integrated with an in-process particle measurement system, shown in Fig. 1, was developed to prepare nanofluids containing nanoparticles using submerged electrode arcing with a working temperature up to 6000 °C to generate a suspension of nanoparticles [2]. TiO_2 nanoparticles can be automatically sampled and analyzed by a fiber-based nanoparticle size analyzer using dynamic light scattering principle for detection of particle size and distribution. The particles are further measured by a transmission electron microscope (JEOL JSM-1200EX II TEM) and the developed image analysis techniques, to de-

Corresponding author: Liang-Chia Chen, e-mail: lcchen@ntut.edu.tw

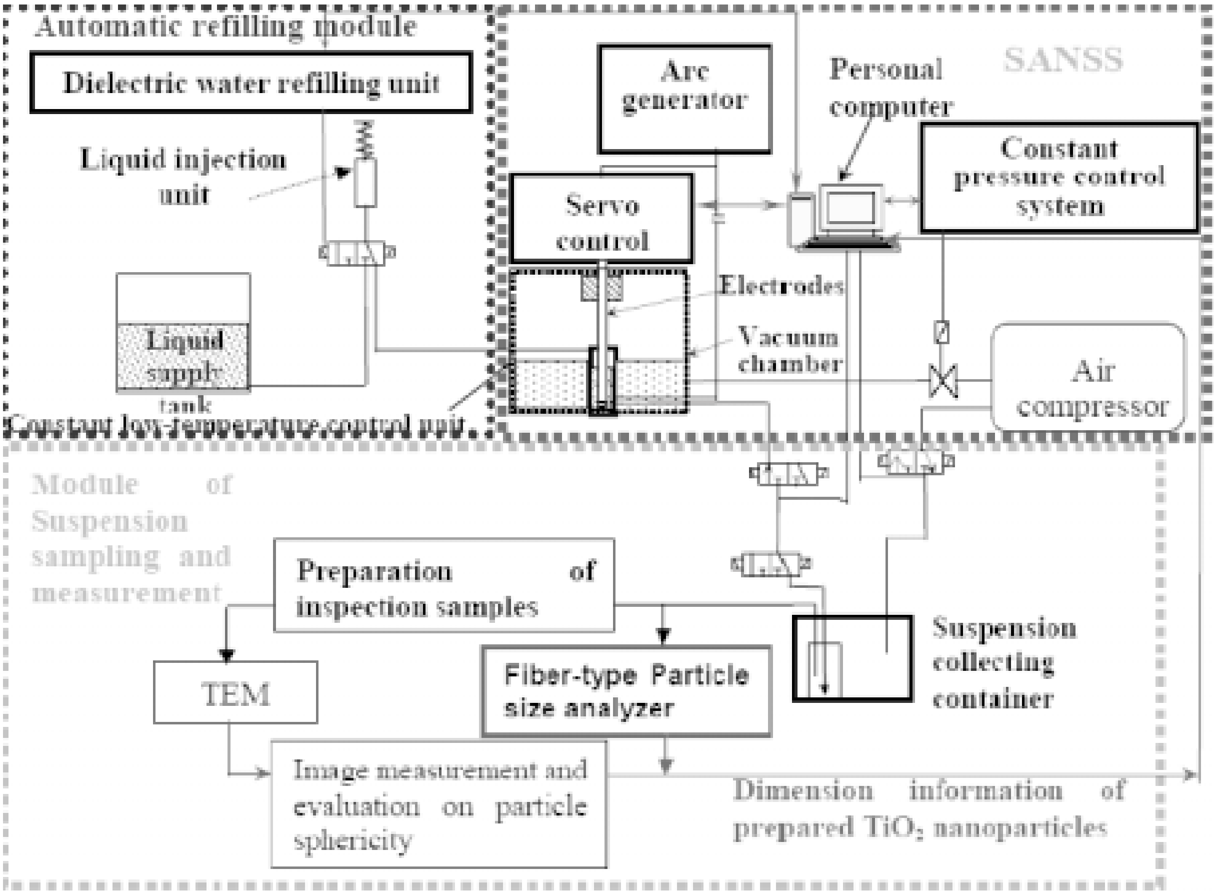


Fig. 1. Schematic diagram of SANSS being integrated with an automatic in-situ particle sampling and laser-scattering sizing device.

tect the sphericity and form uniformity. Using the Taguchi method, the process parameters of SANSS were carefully characterized optimized on the particle sphericity. The following section first presents the methods for preparation of the TiO_2 particles for the size and form measurement.

2. EXPERIMENT AND MEASUREMENT OF PARTICLE SPHERICITY

2.1. In-process particle sampling and sample dispersion method

An in-process particle suspension sampling and dimension measurement, shown in Fig. 1, was developed to sample TiO_2 nanofluids automatically from the vacuum chamber of the SANSS for particle size and shape analysis [4,5]. Most importantly, to characterize the relationship between the process parameters and the particle form roughness, an in-process measurement module was established to characterize the particle size, distribution and form sphericity. The particle size and distribution can be measured using a nanoparticle size analyzer equipped with an optical fiber probe for on-line particle sizing [6]. The nanoparticle size analyzer was successfully developed using the optical probe as an in-situ measuring device for particle characterization. It has a diameter measurement range up to 6000 nm and repeatability of ±3 nm within a standard deviation. Prior to the shape measurement, it is vital to disperse the prepared TiO_2 particles suspended in nanofluids into separate measurable particles, which sphericity can be accurately evaluated using TEM and the developed image analysis method. Our experiment results reveals that the secondary particle size was identified significantly related to the PH value of the TiO_2 nanofluids, where the particles can be uniformly dispersed for a nanofluid solution at a

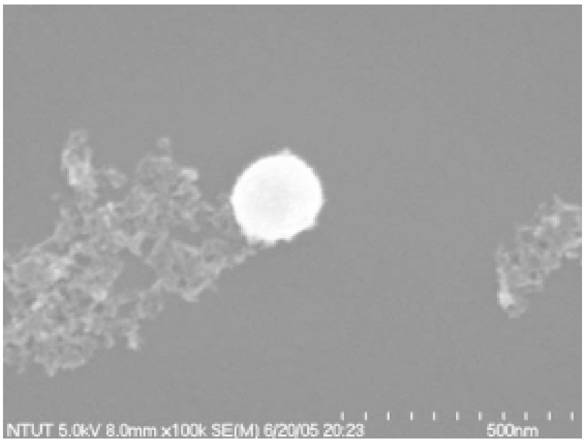


Fig. 2. The surface of TiO_2 particles was covered by a irregular oxidized layer.

Fig. 3. TEM picture of uniformly dispersed TiO_2 particles after the particle dispersion treatment.

PH value ranging between 5.6 and 6.7. With such a PH value control, the particles can be effectively separated into single ones and ready for shape measurement. Meanwhile, the prepared Ti particles may be oxidized after suspending within the dielectric water for a period of time and the surface of particles may form irregular shape of an oxidized layer, shown in Fig. 2. Because the layer is harmful to accurate measurement of the particle roundness, the TiO_2 nanoparticles are strategically separated from the dielectric fluid straight after being sampled and are prepared to become a thin layer using a speed-controlled spinning machine under a vacuum environment. The thin layer of inspected particles is prepared in a way that single particles are separated uniformly as shown in Fig. 3, where the overlapping condition of particles can be minimized.

2.2. Image analysis for particle sphericity evaluation

Fig. 4 illustrates that the sphericity of TiO_2 particles can be accurately evaluated using a detected particle image obtained by a JEOL JSM-1200EX II TEM, the developed image processing techniques and the min-max sphericity estimation algorithm [7]. The quality of FE-SEM pictures of TiO_2 nanoparticles could suffer due to poor conductibility of the particles. Our experiment results indicate that the image contrast quality of particle TEM images is in general superior to the one from FE-SEM. Thus, the TEM is applied to detect accurate particle contours for roundness evaluation. Following this, accurate particle contours are reliably detected by Laplacian edge detection with a subpixeling resolution up to 1/50 pixel. The sphericity of each particle contour is subsequently calculated using a developed min-max fitting algorithm, where the degree of particle roundness is defined as the dissimilarity between the maximum and minimum radii of the circles enclosed in the detected contour. Meanwhile, the calculated value is normalized due to the fact that it is proportional to the diameter of the particle. In each experiment, more than 1000 measurements of particle sphericity for each experiment are made to ensure the data accuracy of the measurement based on a 95% confidence level.

3. RESULTS AND DISCUSSION

The research applied the Taguchi experiment methodology to perform process characterization on particle sphericity. In the experiment, TiO_2 nanoparticles were obtained by varying the four selected parameters listed in Table 1. For the process setup of the SANSS, the breakdown voltage

Table 1. Process control factors and the associated factor levels employed in Taguchi experiments.

	A(*T*) Processing temperature (°C)	*B*(*I*) Electric voltage (Ampere)	$C(t_{on})$ On-time period (μs)	$D(t_{off})$ Off-time period (μs)
Level 1	0	2	2	2
Level 2	10	4	3	3
Level 3	20	6	4	4

Table 2. Results of Taguchi experiment. The left segment of the table is the design of L orthogonal array used. The value of average sphericity is the average measured sphericity of 1000 TiO_2 particles obtained from each experiment.

Exp.	A	B	C	D	Averaged Sphericity (%)	Standard deviation
1	1	1	1	1	1.02	0.1264
2	1	2	2	2	2.26	0.2541
3	1	3	3	3	4.52	0.2856
4	2	1	2	3	1.4	0.1597
5	2	2	3	1	2.85	0.3021
6	2	3	1	2	3.88	0.5210
7	3	1	3	2	1.43	0.1765
8	3	2	1	3	2.76	0.2784
9	3	3	2	1	4.09	0.6321

Table 3. ANOVA analysis of the Taguchi experimental data.

	Analysis of Variance:	Mean = -7.5903	Sigma = 4.61571		
	SS	df	MS	F	p
Factor1 (Temperature)	2.9354	2	1.46768	1.34423	0.426579
Factor2 (Current)	161.7432	2	80.87159	74.06968	0.013321
Factor3 (On-time duration)	3.5759	2	1.78796	1.63758	0.379136
Factor4 (Off-time duration)	2.1837	2			
Residual	2.1837	2	1.09183		

is set at 220 volts and the pressure of the operating chamber at 30 Torr level for the general operation of the SANSS. The particle sphericity data were analyzed in terms of signal-to-noise ratio (*S*/*N*) representing an index of data quality and the particle sphericity standing for an index of particle roundness. An experimental setup of $L_9(3^4)$ orthogonal array was designed for process characterization. The results of the Taguchi experiment are reported in Table 2 and Fig. 5 shows the *S*/*N* ratios calculated on the basis of the defined normalized sphericity of TiO_2 nanoparticles. It shows that Factor B (discharge current) has the strongest influence on the quality index *S*/*N*, whereas the rest of parameters have similar effects and much less impact on the quality index than Factor B. To further evaluate the effects of process parameters on the particle sphericity, Fig. 6 was obtained to quantify the relationship between the particle form property and the process variables. Similarly, it reveals that Factor B has the most significant effects on determining the quality of particle sphericity of the TiO_2 nanoparticles prepared by the SANSS while the other parameters play a weak effect. These results

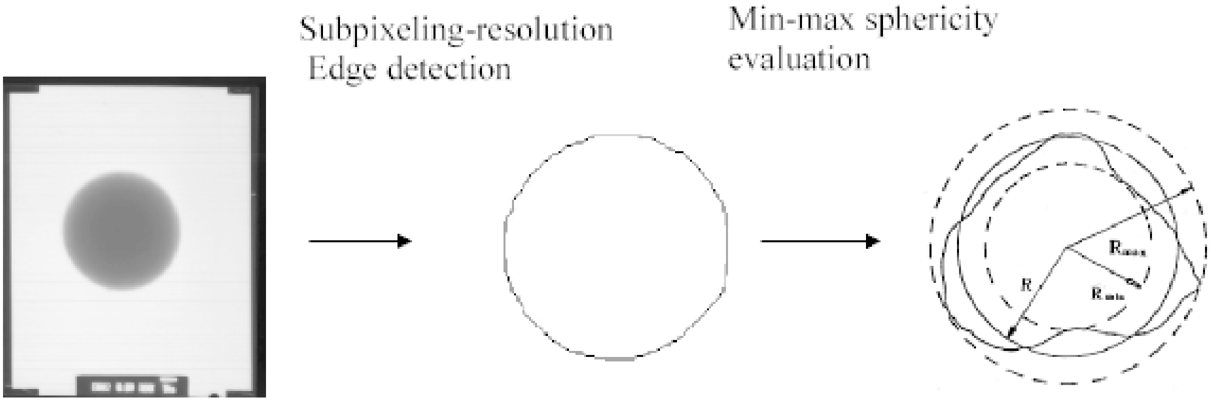


Fig. 4. Particle sphericity evaluation using the developed image processing techniques and the min-max sphericity estimation.

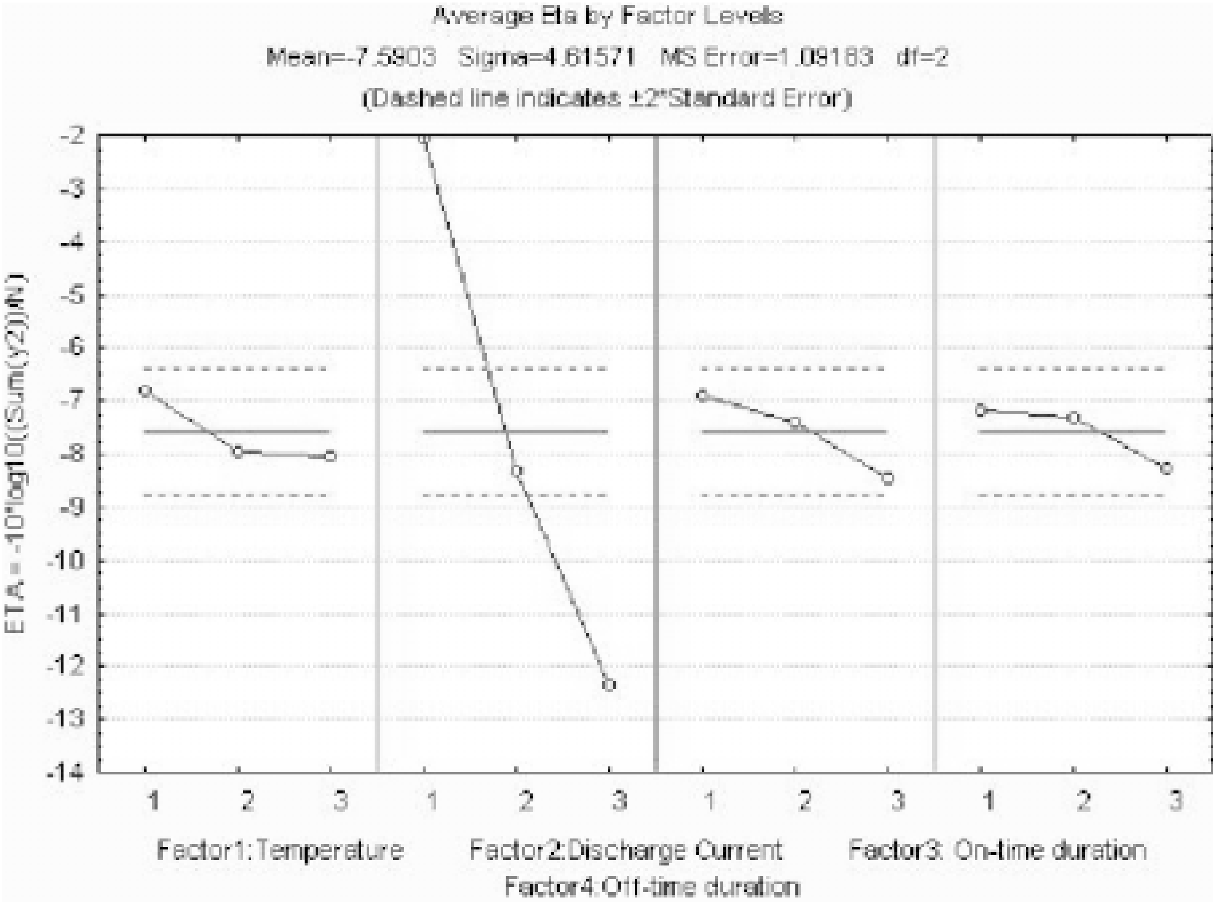


Fig. 5. Relationship between *S*/*N* values and each control parameter.

conclude that the sphericity of the prepared particles is considerably affected by the arcing discharge current) in the SANSS. The less the current employed in the SANSS, the better the particle roundness can be achieved.

The analysis of variance (ANOVA) shown in Table 3 also confirmed that the electric current was the most important process parameter affecting the process response in comparison with the other parameters. To check the shape sphericity of the

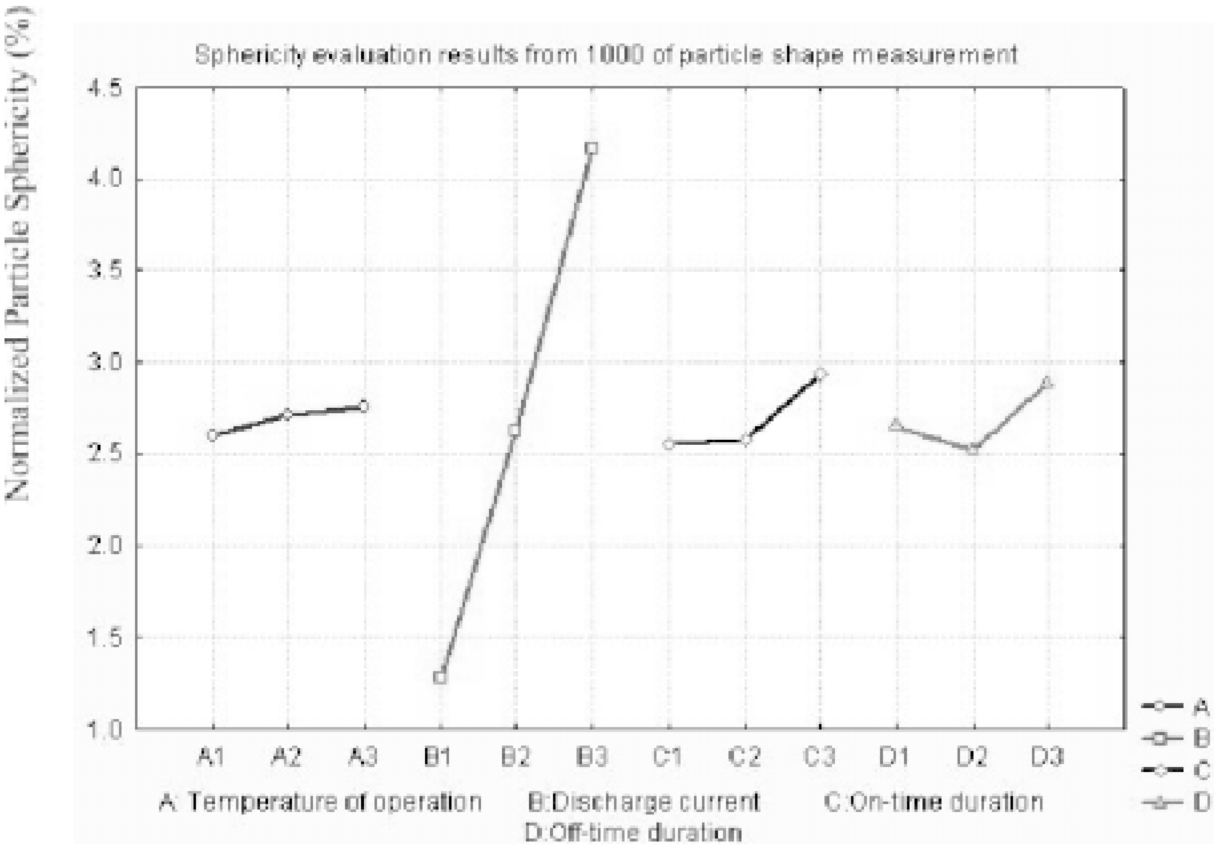
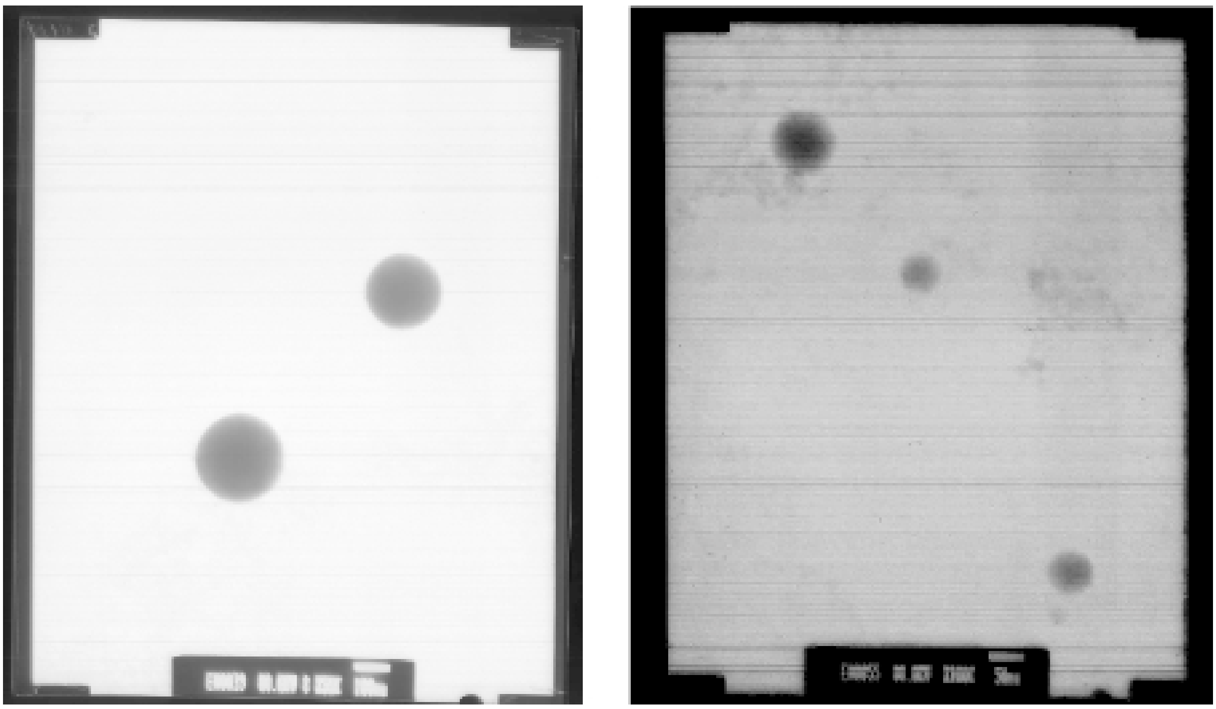


Fig. 6. Relationship between the particle sphericity and each control parameter.



(a) (b)

Fig. 7. TEM pictures of TiO_2 nanoparticles prepared from the optimized run: (a) the particle size larger than 100 nm (b) the particle size less than 100 nm.

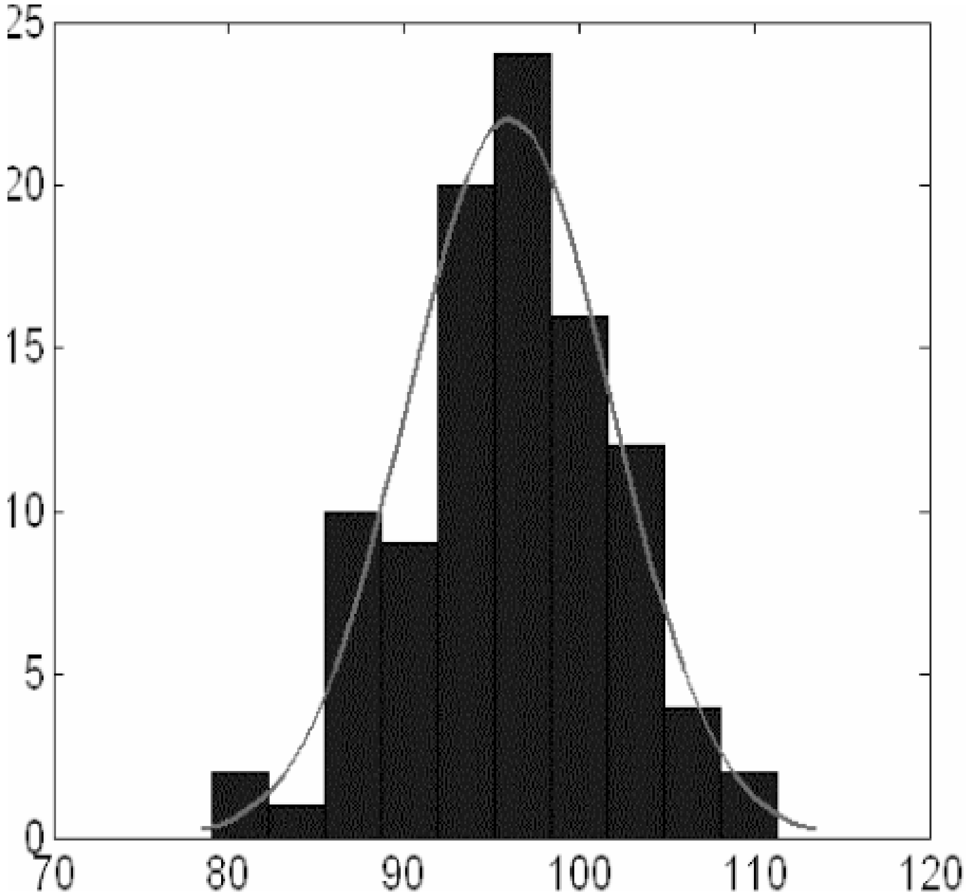


Fig. 8. Particle size distribution of TiO_2 nanoparticles prepared from the optimized run, in which the results were obtained by using the developed in-situ nanoparticle sizing analyzer.

prepared particles from the benchmark to the optimum, a confirmation trial under the selected optimal process parameters was performed. By analyzing Fig. 6, the optimised setup of A1–B1–C1–D2 can be easily determined for a confirmation trial. From measuring the defined sphericity of 1000 particles prepared from the confirmation run, the average particle sphericity was 1.03% of the particle diameter. It is noted that the particle sphericity was improved remarkably after the process parameters were optimized. The shape of the prepared nanoparticles was examined with TEM (shown in Fig. 7). Meanwhile, the secondary particle size and distribution of TiO_2 nanoparticles prepared from the optimized run was obtained using the developed in-situ nanoparticle sizing analyzer. The particle size was ranging between 80 and 110 nm, shown in Fig. 8.

4. CONCLUSIONS

The SANSS was investigated to characterize the relationship between the sphericity of prepared particles and the process parameters including the discharge electric energy, the discharge frequency and the operation temperature. More than 1000 particle measurement for each experimental setup were performed on their TEM images using the defined normalized roundness to ensure data accuracy. The experimental results have suggested that the electric discharge current has the most significant influence on the quality of the particle sphericity while the rest of factors play little impacts. With process optimization performed, the results indicate the particle sphericity can be greatly improved up to 1% of the particle size.

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