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DEVELOPMENT OF NANO-ORDER POWDER VIA ELECTROSPRAY

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ABSTRACT

Nano-order particleshave recently beingutilized for uniform surface coating and thin film production in food, biomedical and pharmaceutical applications due to their high specific surface area. In this study, production of nano-orderparticles from Zinc Oxide (ZnO) powder using electrospray method was developed.ZnO suspensions of different pH were prepared by dispersing ZnO powder in distilled water followed by sonication. The zeta potential value and particle size distribution of the prepared ZnO suspensions were in the range of-17 to -53 mV and 104-197 nmrespectively.ElectrosprayedZnO suspensions were maintained under Taylor cone mode by manipulating the voltage supply in order to obtain stable and monodisperse droplets. Scaling law models were used to determine the theoretical mean droplet size based on conductivity value of the suspensions.The collected droplets wereanalyzed visually with scanning electron microscope (SEM). The results showed that mean droplet size obtained from this experiment was smaller than the theoretical ones and strongly dependent on suspension conductivity. Findings of the present study also confirmed that electrospray is a promising approach for producingnano-order particles.

***Keywords**: Electrospray, nanoparticle, Zinc oxide, Scaling laws*

INTRODUCTION

Recently, enormous advances have been achieved in particle and powder technologyand the focus have been switched from macro to micro and micro to nano scales as a result of significant differences in the physical, chemical and mechanical properties realized in the nano scale [1].

Nanoparticles can be synthesized either through gas phase by using furnace generators, glowing-wire aerosol generator, spark-discharge generator, flame synthesis, plasma synthesis and laser ablation [2] or from liquid phasevia atomization method [3]. A well-defined particles morphology and characteristics can be generate from a liquid solutions with specified composition. Therefore, generating particles using liquid atomization techniques is favorable. Among atomization methods employed, the best candidate is a method that able to produce narrow size distribution of droplets with small enough start up sizes. These goal can be achieved through a method called Electro-Hydrodynamic Atomization (EHDA) or Electrospray [1].

Electrospray is a method of liquid atomisation by electrical forces[4]. In brief, a liquid is forced through a capillary nozzle and electric field is applied to the nozzle. As the liquid which hold a surface tension passes through the nozzle, the electric field induces a surface charge on a surface of liquid drop, which forms at the tip of the nozzle. When the electric field applied reaches a critical value, repulsive electrical forces will overcome the surface tension of a droplet and the liquid meniscus transformed into a conical shape followed by emanation of jet with high charge density. This mode is commonly known as Taylor-cone jet mode[5]. The charged droplets will breaks into an aerosol and undergo solvent evaporation, producing a dried, fine droplets which then converted into particles because of phenomena called droplet fission and finally deposited on various type of substrate.

Electrospray has been used widely on producing thin-film coating as mostly reported by previous authors[5], [6][7]. However, for this project, the objective is more onto developing the system and verifying the required parameters into producing nano-order particles. This means that the project involves catching the electrosprayed particles and analyzing if the particles are in nano-orders, disregarding the coating process.

In this study, Zinc Oxide was used as a model to investigate potential of Electrospray to produce nano-order particles. Zinc Oxide (ZnO) is an insoluble ceramic material that mainly used for anti-microbial activity due to their photocatalytic activity under UV light. The effectiveness or efficiency of anti-microbial activity posed by these powders is affected by particle size. The particle size of these materials can be controlled by processing parameters. The nano-structured ZnO powder possess significant effect on selective adsorption / separation processes [8].

MATERIALS AND METHODS

Material preparation

The Zinc Oxide powder is provided by Approfit Zinc Oxide Manufacturing Sdn. Bhd. Puchong, Malaysia.Mean particle size of the supplied powder was 7 µm or 7,000 nm.An aqueous ZnO suspensions (5% w/v) in deionized water with pH in the range of 5.22 to 9.57 were prepared. To provide intense and uniform dispersion of the ZnO powder in deionised water, the samples were ultrasonicatedat 100% amplitude for 4 minutes using 20 kHz probe system; power 400 W with vibrating titanium tip of 1 inch (Digital Sonifier Model 450, Branson Ultrasonics Co. Danbury, Connecticut, USA).

Zeta potential and particle size of the samples in liquid phase were measured usingZetasizer Nano ZS.The rationale of acquiring the zeta potential values for the suspensions is to make sure that the particles will be able to maintain suspended within the liquid during electrospray instead of depositing as sediment onto the walls of the syringe or nozzle.

Nanoparticles generation

The production of Zinc oxide nanoparticles were performed using electrospray system. The electrospray setup (Fig.1) consisted of 5ml Terumo disposable plastic syringe equipped with flat-end needle which act as a nozzle. Flow rate of the zinc oxide suspensions were controlled using syringe pump (Atom). Electrostatic forces generated by Electrostatic Controller 3A – 615 N (Singapore Quality)with negative polarity was connected to the nozzle. For particles collection, acrylic pipe with inner diameter of 26 mm, connected to a self-fabricated diffuser was used as a transferring medium and particles generated were collected using a carbon tape, stacked at the desired position inside the acryclic tube. The position of the collecting media was determined by The electrospray was conducted for 25 minutes, with a fixed flow rate of 6.25ml/hr under cone-jet mode. Formation of cone-jet mode was observed using a digital camera with high magnificent. Parameters to produce cone-jet mode were recorded and used to estimate initial droplet size using equation proposed by previous author.

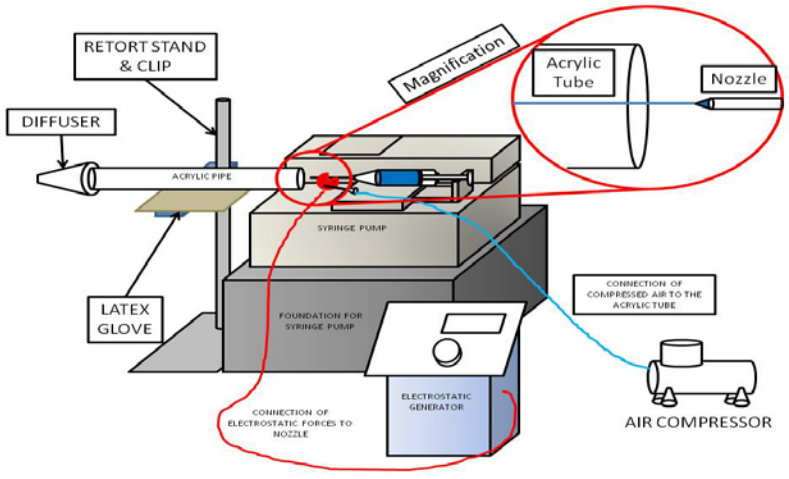

Fig. 1: Electrospray setup

Initial droplet size estimation using Scaling laws

The production of nanoparticles through electrospraying was studied by a few authors. These authors had modelled the scaling laws to predict the mean droplet sizes which supposed to reflect the particles size. In this study, scaling laws proposed by Hartman [9], Fernandez de la Mora and Loscertales [10], and Ganan-Calvo[11] in equations (1), (2) and (3), respectively were used to estimate initial droplet size and the result is compared with the experimental data.

$$d_d = \left(\frac{16\rho\epsilon_0 Q^3}{\gamma K}\right)^{1/6} \quad (1)$$

$$d_d = 1.66\epsilon_r^{-\frac{1}{6}}\left(\frac{Q\epsilon_r\epsilon_0}{K}\right)^{\frac{1}{3}} \quad (2)$$

$$d_d = 1.2164\left(\frac{Q\epsilon_r\epsilon_0}{K}\right)^{\frac{1}{3}} \quad (3)$$

where d_d, ρ, ϵ_0, Q, γ, K and ϵ_r represent the liquid density (kgm^{-3}), electrical permittivity of vacuum ($C^2N^{-1}m^{-2}$), liquid flow rate (m^3s^{-1}), surface tension of the liquid (Nm^{-1}), conductivity of the liquid (Sm^{-1}) and relative permittivity, respectively.

Characterization

The morphology and size of the electrosprayed particles collected on the carbon tape were analyzed by Scanning Electron Microscope (SEM). The purpose of analyzing the samples collected with scanning electron microscope (SEM) is to further validate the theoretical calculations using the modelled scaling laws by previous authors. Measurement of the Energy-dispersive X-ray spectroscopy (EDX) is carried out to identify the presence of ZnO from the analyzed samples.

RESULTS AND DISCUSSIONS

Properties of zinc oxide sample in liquid phase

To study the nanoparticles generation using electrospray method, three samples with pH value of 5.22, 7.23 and 9.57 and zeta potential of -17, -30 and -53 kV, respectively, were prepared. The pH is adjusted with regards to the zeta potential values to produce stable suspension [12, 13]. The stable suspension is supposed to be having small agglomerations which assures smaller particle agglomerate sizes during electrospraying. The zeta potential value of ZnO at different pH was measured using zeta-sizer equipment, equipped with auto-titration unit. The result obtained (Fig. 2) shows that point of zero charge (isoelectric point, IEP) of zinc oxide is at pH 3.1. However, IEP of ZnO reported by previous authors ranges from 8.7 to 10.3. This may be attributed to the presence of impurities in the ZnO samples due to bulk handling, the occurrence of charge reversal phenomena and formation of zinc hydroxo species as explained in previous journals [14].

Particle size of zinc oxide in liquid phase were measured to reflect the particle sizes occurring in the samples before the particle is converted into gas phase. These suspensions were ultrasonicated before undergo particle size measurement analysis to make sure that effective dispersion of particles is obtained. The result depicted in Fig.2 shows that the particle size of zinc oxide in liquid phase is inversely proportional to the absolute zeta potential value. The higher the zeta potential, the lower the particle size. This can be explained by charge repulsion between zinc oxide molecules at higher zeta potential thus preventing the molecules from agglomerated[15].

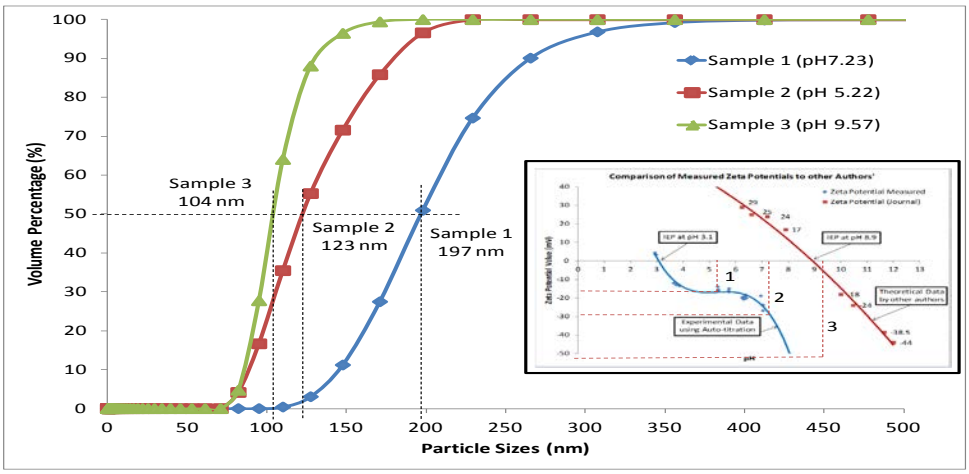

Fig. 2: Mean particle size of zinc oxide sample at different pH

Electrospray parameters to produce zinc oxide nanoparticles

The production of ZnO nanoparticles using electrospray method was performed under cone-jet mode condition. A stable cone-jet is favourable because it allows formation of monodispersed droplet, which is a great interest in industrial and academic applications[4]. To produce a stable cone-jet, a lot of parameters need to be taken into account which includes flow rate, supplied voltage and nozzle tip to collector distance. Therefore, for this study, the flow rate of the liquid suspension pumped through the capillary was fixed at 6.25ml/hr and other parameters involved in producing cone-jet mode were investigated and recorded in Table 1.

Table 1: Processing parameter for the electrospray under cone-jet mode

Sample	Voltage (manipulated to obtain stable Taylor cone and jet)	Current (observed)
1	1.14 kV	0.25 μA
2	1.00 kV	0.24 μA
3	0.77 kV	0.13 μA

Besides voltage and current, other determined parameters to produce cone-jet during electrosprayingwere the distance of tube-to-nozzle tip which was 5 mm and length of the tube which was 30 cm. The selection of tube length was with consideration of stable Taylor cone and jet, and particles collection at the end of the final wet droplet travel distance in the tube.

Result from SEM

Scanning Electron Microscope (SEM) imaging provides images of the captured droplet with the particles. The SEM images shown in Fig. 3 is used to verify the theoretical results from using the scaling laws modelled by previous authors while result obtained from EDX confirmed the presence of ZnO components in the collecting media for all three samples studied.

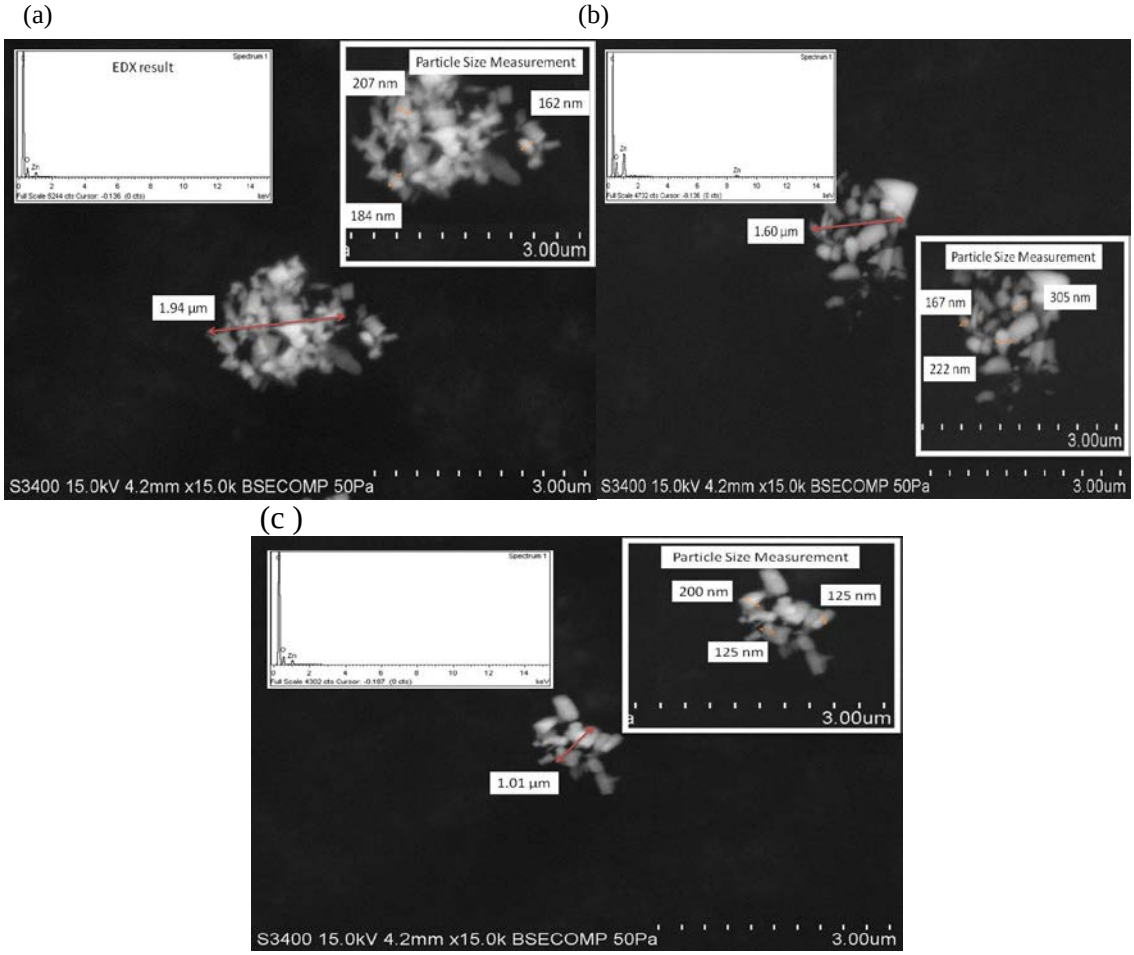

Fig. 3: SEM images and EDX result for zinc oxide sample with different pH; (a) pH 7.23, (b) pH 5.22, (c) pH 9.57.

The result of the mean droplet and particle sizes from different samples identified through the SEM imaging is summarized in Table 2 with ZnO in pH 9.57 have the smallest droplet and particle size.

Table 2: Average of mean droplet and particle size from SEM

Sample	Average droplet size (μm)	Averageparticle size (μm)
Sample 1 (pH 7.23)	2.987	0.184
Sample 2 (pH 5.21)	1.980	0.231
Sample 3 (pH 9.57)	1.353	0.150

The readings taken from the SEM images cannot represent the whole distribution of the mean droplet sizes for every sample because the sites taken for SEM imaging are completely random. The inconsistent droplet sizes could be due to multi-jet formation in between the cone-jet mode. Multi-jet formation may cause non-monodisperse droplets to be electrosprayed.

Predicted droplet size from Scaling laws

The mean droplet sizes obtained from SEM imaging as obtained from the results above will be compared to the theoretical scaling laws modelled by various authors. This step further validates the effectiveness of the electrospraying system developed.The parameters to predict the mean droplet size formulae proposed by Fernandez de la Mora and Loscertales[10], Gañán-Calvo [11], and Hartman et al. [9]were obtained from literature.

The liquid flow rate, Q was set at 6.25 ml/hr, which is within the range of 0.1 to 10 ml/hr suggested by Jaworek[16] . ϵ_0 is the electric permittivity of a vacuum which is found to be 8.85 x 10^{-12} $C^2N^{-1}m^{-2}$ [17]. As only 5 weight % of ZnO is dispersed in deionised water, the properties of water will be used as a basis for other parameters. γ is assumed to be the surface tension of water, 0.072 Nm^{-1}. μ, the absolute viscosity of the liquid (water) is 0.000862 $kgm^{-1}s^{-1}$ at 25°C. The density of the liquid (water), is 1000 kgm^{-3}. The relative permittivity of the liquid (water), $\epsilon_r$is a dimensionless number with magnitude of 78.55. Relative (static) permittivity, $\epsilon_r$was previously acknowledged as dielectric constant [18].

The aqueous sample conductivity, K of each sample were measured using conductivity probe and tabulated in Table 3.

Table 3: Measured sample pH and conductivity

Samples	pH	Conductivity (μScm^{-1})
Sample 1	7.23	85
Sample 2	5.217	18.92
Sample 3	9.572	53.6

Liquid conductivity means the measurement of all ions present in the liquid at certain pH.It was found out that conductivity cannot be correlated to pH because pH is just an indication of the H^+ ions concentration while conductivity illustrates the concentration of ions in the solution, the ability for the ions to dissociates and their speed of diffusions [19]. Certain substance of fairly neutral pH, such as seawater, may have a lot of ions that conduct.However, it can be found that theoretical conductivity is a function to pH can be shown in Figure 4.8 below which conductivity was measured with pH for pure water and assuming no presence of foreign ions. The relationship is further illustrated with a second curve line added when nitric acid (HNO_3) is employed as pH control agent.

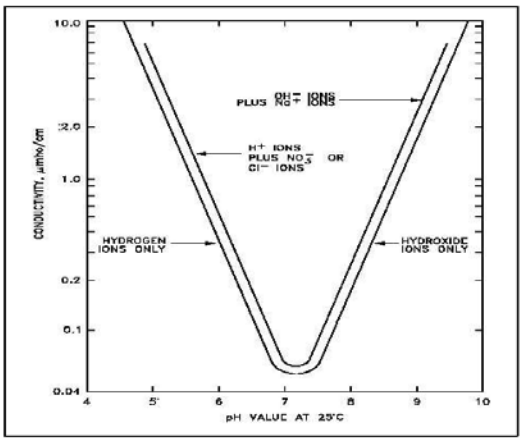

Fig.4: Theoretical conductivity as a function of pH

Therefore, with regards to the theoretical conductivity in Fig. 4, the result draws to a possibility that the ZnO sample at pH 7.23 prepared in deionised water consists of other impurities or ions that affects the conductivity of the solution.As mentioned earlier in previous section, the presence of impurities is proposed and formation of Zinc hydroxo species affects the surface charges of each particle suspended in the solution. These impurities and zinc hydroxo species will alter the amount of available ions for conductivity which therefore, could be the reason why certain sample has low conductivities.

In accordance to Fig.4which illustrates the theoretical conductivity to pH, the experimental result as shown in Table 3 require the adjustment of conductivity for the sample at pH 7.23. The conductivity is adjusted to 10 μScm^{-1} in oppose to the measured 85 μScm^{-1} (Fig.)

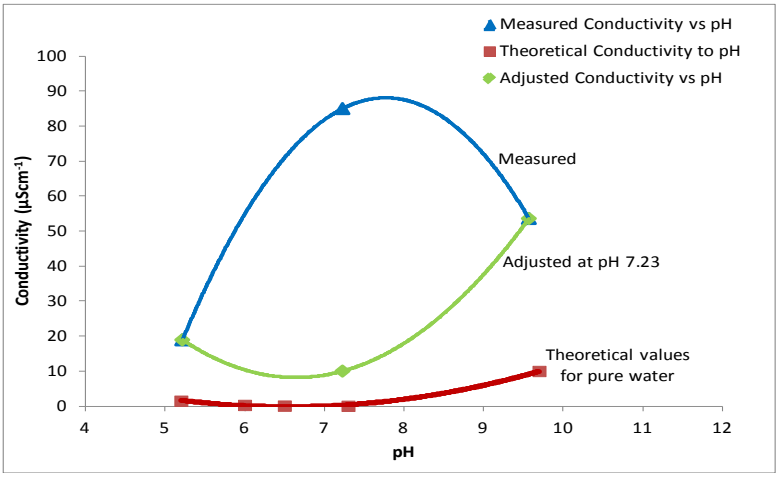

Fig.5: Adjustment of Conductivity at pH 7.23

The computed results of mean droplet size obtained from Scaling laws were compared to those obtained from SEM (Table 4). Graphical illustration is shown in Fig.6 where comparison can be made to the theoretical scaling laws result and the experimental result from SEM.

Table 4: Summarized theoretical formulae mean droplet size in comparison to SEM mean droplet size

Sample Properties			Theoretical Calculation (μm)			SEM imaging (μm)
	pH	Conductivity (μScm^{-1})	Hartman et al.	De La Mora	Gañán-Calvo	Average
1	7.23	10.00	14.12	7.83	11.87	2.98
2	5.22	18.92	13.26	6.91	10.47	1.98
3	9.57	53.60	11.15	4.88	7.40	1.35

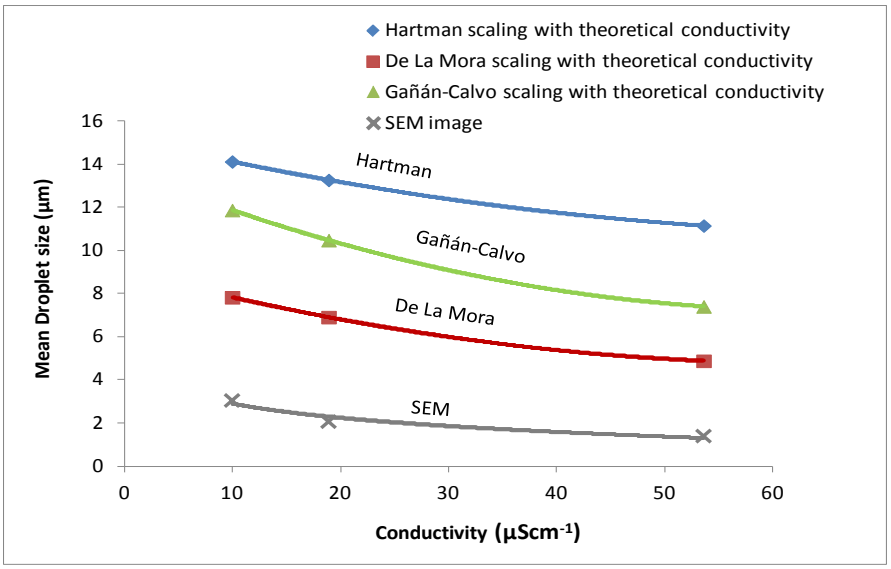

Fig. 6: Theoretical versus Experimental mean droplet size

With accordance to the theoretical conductivity, the results as illustrated in Fig.6 shows that mean droplet size reduce gradually with conductivity. For Hartman's [9] model for scaling laws, the mean droplet size reduces from 14.12µm to 11.15µm with the increment of conductivity from 10.0µScm^{-1} to 53.6µScm^{-1}. The similar trend can be seen with the model proposed by Gañán-Calvo[11] which records mean droplet size decrease from 11.87µm to 7.40µm with the increment of conductivity as mentioned earlier. De La Mora's [10] model measures from 7.83µm to 4.88µm with the respective conductivities.

The experimental SEM images result included in Fig.6 also indicate the agreement to the trend with the other models. However, the results from SEM images are lower than the theoretical ones which could be due to random selection during SEM analysis. The selection of droplet during SEM analysis depends on the technician's choice upon the clarity and resolution of each droplet analyzed. This selection cannot represent the whole distribution of droplet size as the images are randomly selected on certain sites only. Regardless of the slight inconsistencies occurring with the SEM images result, the theoretical model result given by De La Mora [10] is the nearest to the experimental data.

CONCLUSIONS

The electrospray system used in this study managed to produce a droplet size in the range of 1.353 to 2.987 µmand particle size ranging from 150 to 231 nm by using ZnO sample in different pH which is much lower than the initial ZnO powder size supplied by manufacturer. Further improvements and analyses can be carried out to further establish this system in producing nano-particle or in thin-film coating, as mentioned by the other authors relating to electrospray.

ACKNOWLEDGEMENT

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