*Refereed Proceedings*

*The 13th International Conference on Fluidization - New Paradigm in Fluidization Engineering*

Engineering Conferences International *Year* 2010

# DEVELOPMENT OF A CONTINUOUS NANOPARTICLE COATING WITH ELECTROSPRAYING

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# DEVELOPMENT OF A CONTINUOUS NANOPARTICLE COATING WITH ELECTROSPRAYING

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## ABSTRACT

Coating of micron-sized particles (host particles) with nanoparticles can result in modifying the surface properties of host particles leading to various applications. This work presents a novel concept of combining the electrospraying of nanoparticles onto the charged particles entrained out of the fluidized bed for developing a continuous coating process. By controlling the processes to effectively charge and contact particles using electric forces, we are able to fine-tune the properties of the obtained nano-coated particles.

## INTRODUCTION

The emerging nanotechnology has allowed various applications of nanomaterials to develop. Deposition of nanoparticles on surfaces of other materials can result in the modification of material properties for various applications such as changing the hydrophobic or hydrophilic behaviour, anti-reflex performance or the catalytic activity (1). Furthermore, deposited nanoparticles on surfaces can set up functional chemical contact points (2). In the pharmaceutical industry there is interest in active nanomaterials that interact with biological systems (3).

Several coating techniques are well known such as dry coating and solvent based coating. The difficulty in the first method lies in dispersing dry nano-size particles for coating. On the other hand, in the solvent based coating, the coating is produced in a liquid medium, thus requiring evaporation of solvent and extra drying step (4). Electrohydrodynamic atomization (EHDA), also called electrospraying, offers a solution for dispersing and depositing nanoparticles on a substrate such as micron sized particles. In order to enhance the efficiency of deposition, the charged nature of the nanoparticles can be exploited to coat host particles. EHDA leads to unipolar charging of nanoparticles, while host particles can be charged with opposite polarity by means of tribocharging. When these particles are mixed in an appropriate way, the mutual electrostatic attraction force between the negative and positive charge will result in the deposition of a coating. Once coated, the van der Waals forces keep the nanoparticles from detaching from the host particles. Thus, electrospraying offers a solution for dispersing and depositing nanoparticles on a substrate.

Electric charges generated in gas-solid fluidized beds have mostly been a problem leading to particle agglomeration, particle-wall deposition, and electrical discharges. Continual particle-particle and particle-wall collisions generate the triboelectric charges which are normally alleviated by controlling the humidity of the fluidizing gas, grounding the fluidized bed, or adding anti-electrostatic agents. Recently, developments have been made to utilize this very phenomenon in the fields of electrostatic powder coating (5) and plastic separation (6). Having two different bed materials such as PVC and PET, Lee and Shin (7) have charged the material in a fluidized bed tribocharger, and dry separated the polymers in an electrostatic separator.

## APPROACH & RESULTS

The ultimate goal of this study is to build a system which can coat nanoparticles onto host particles in a continuous manner. The following components have been separately investigated before combining them as a complete process: 1 Electrospraying of nanosuspension (Table 1); 2 Stationary tribocharging of host particles; 3 Continuous tribocharging of host particles.

Table 1. Host and guest particles for electrospraying.

| Type | Host | Guest |
|---|---|---|
| Material | Alumina/Glass | Polystyrene |
| Size | 165μm/50-200 μm | 65nm/100nm |
| Charging | Tribocharging | Electrospraying |
| Applied Polarity | Positive | Negative |

### 1 Electrospraying of nanosuspension

Electrospraying refers to a process where a liquid jet breaks up under influence of electrical forces (8,9). A liquid is pumped through a nozzle with a low flow rate. An electric field is applied over the liquid by applying a potential difference between the nozzle and a counter electrode. When the electric stress overcomes the surface tension, the emerging droplet from the tip of the nozzle is transformed into a conical shape. From the cone apex a jet emerges which breaks up into charged monodisperse like droplets. This spraying mode is one of the electrospraying modes and called the cone-jet mode. The cone-jet mode is desired, because it is possible to control the droplet size. Unipolar charge of the droplets prevents their coagulation and dispersion is enhanced. The size of the droplets can be in the order from nanometers to several microns. The application of electrospraying of suspensions of nanoparticles has been demonstrated recently (10). When nanoparticles are added to the base fluid in the electrospraying process, charged liquid droplets seeded with nanoparticles are generated. The utilization of a volatile liquid leads to its fast evaporation. Thus the droplets shrink in size but charge density in the droplet increases and at a critical limit, corresponding to the Rayleigh charge limit, they will break up into smaller droplets. As a result of progressive evaporation and break up, the characteristic diameter may be reduced to the scale of the nanoparticles. A schematic representation of the proposed mechanism is given in Figure 1. Electrospraying such a suspension generates a spray of charged nanoparticles with a density depending on their initial concentration in the suspension.

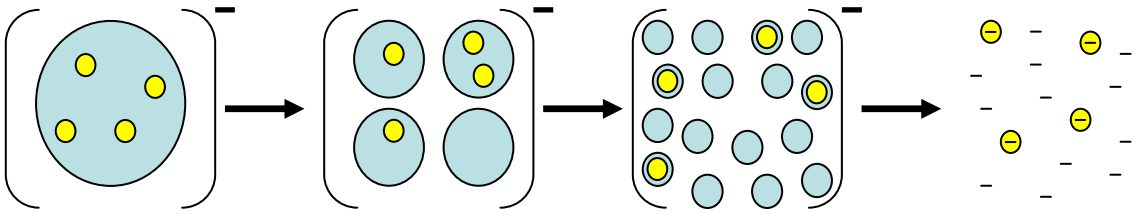

Figure 1. Scheme of scattering mechanism in nanosuspension EHDA. Left: a charged liquid droplet seeded with nanoparticles. Middle: the droplet shrinks due to liquid evaporation and Rayleigh break up. The nanoparticles are distributed over the new generated droplets after each Rayleigh break up. Right: upon total drying a spray of charged nanoparticles is obtained.

For application in this work, a suspension of polystyrene nanoparticles (65 nm) in water was diluted with ethanol. Stable suspensions of 0.03 vol.% polystyrene nanoparticles in mixtures of ethanol/water at various ratios were prepared and characterized as shown in Table 2. The spray properties are affected by the particle concentration and the ethanol fraction. Furthermore, the particle size distribution, PSD, of the nanosuspensions is measured using a NanoTrack analyzer, which utilizes dynamic light scattering with laser diffraction.

Table 2. properties of nanosuspensions.

| Fluid | Density | Electrical Conductivity | Surface Tension | Viscosity | Ethanol | Water | Particle fraction |
|---|---|---|---|---|---|---|---|
| - | $Kg/m^3$ | S/m | N/m | Pa*s | ml | ml | - |
| Suspension 1 | 788.48 | 4.00E-4 | - | 9.72E-4 | 9.50 | 0.5 | 4.43E-3 |
| Suspension 3 | 869.75 | 3.9-E-3 | 1.83E-2 | 1.60E-3 | 3.00 | 0.00 | 9.09E-2 |
| Suspension 4 | 837.46 | 5.80E-3 | 1.79E-2 | 1.09E-3 | 6.00 | 0.00 | 6.05E-2 |
| Suspension 9 | 1094 | 2.15E-3 | 2.78E-2 | 2.60E-3 | 24.00 | 3.00 | 3.83E-3 |

## 2 Stationary tribocharging of host particles

Tribocharging is based on charging a body by surface contacts, such as rubbing, with a second body of a different kind of material. The charging mechanism is believed to be based on the transfer of electrons according to the work function model. The work function is defined as the minimum energy required to transfer the weakest bound electron from a body to infinity. The effectiveness of this transfer depends on the difference in work function between the two chosen materials. For that reason it was of importance to select an appropriate contacting material for alumina and glass bead particles. With simple charging experiments different materials were investigated as a potential contacting material. From the obtained triboseries (Figure 2), Teflon (PTFE) was chosen as the most effective material for charging. This material charges alumina and glass beads with a net positive polarity.

Typical properties of the charged glass beads are shown in Table 3. These results are obtained by rolling glass beads in a Teflon cup on a roller bank. We observed that the smaller is the particles, the lower is the charging per particle. It is important to remember that in a tribocharging process, the particles obtain charge by contacting or rubbing against the surface of the charging material. Larger glass beads will slide and hit the walls of the Teflon cup with a larger power and create

greater friction than smaller size glass bead, when cup is rolled. Hence, larger powder particles will charge better.

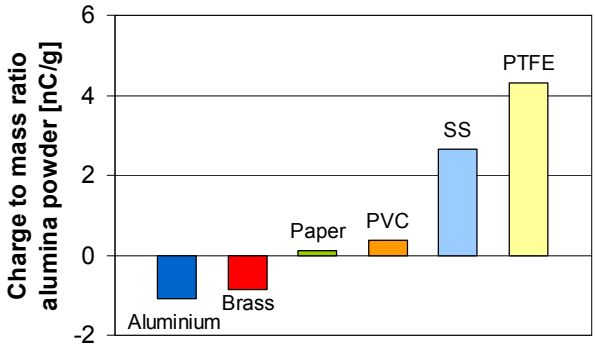


Figure 2. Determined triboseries of alumina powder by simple experiments. Charge to mass ratio based on accumulated charge of alumina samples with given mass. (PVC = polyvinylchloride, SS = stainless steel, PTFE = polytetrafluorethylene.)

The level of charge on a spherical solid particle is limited by its surface charge density. At a certain level of surface charge density, the self-generated electric field at the surface of the particle will exceed its limit and a fraction of electrons or ions will be ejected from the surface by the repulsive forces among the electrons or ions.

Table 3: Properties of charged glass beads from rolling glass beads in a Teflon cup on a roller bank.

| **Parameter** | **542 µm** | **197 µm** | **510 µm** | **242 µm** | **Units** |
|---|---|---|---|---|---|
| Charging | 8.65E-8 | 1.30E-7 | 1.14E-7 | 1.90E-8 | C $gr^{-1}$ |
| Charge per particle | 1.94E-11 | 1.36E-12 | 1.98E-11 | 3.43E-13 | C |
| Charge limit of particle | 2.45E-11 | 3.33E-12 | 2.17E-11 | 4.80E-12 | C |
| Elementary charges per particle | 1.21E8 | 8.50E6 | 1.23E8 | 2.14E6 | # $bead^{-1}$ |
| Surface charge density | 1.97E-5 | 1.08E-5 | 2.421E-5 | 1.89E-6 | C $m^{-2}$ |
| Relative humidity | 22 | 32 | 51 | 58 | % |
| Rolling time | 20 | 20 | 20 | 20 | min |
| Rolling velocity | 0.18 | 0.18 | 0.18 | 0.18 | m $s^{-1}$ |

The tribocharging of the particles will not only be effected by the particle size, but also by particle's composition and humidity. Nieh and Nguyen (11) have conducted charging experiments with 550 µm glass beads in dry air of 1% and 42% relative humidity, RH, in a copper pipe system and obtained an average charge of 6.60E-12 C and 2.0E-12 C per particle, respectively. Our results with 542 µm glass beads charged in a PFA Teflon cup for 20 minutes at 41 rpm and at 45% RH indicate 1.31E-11 C per particle, which is higher than those reported. Similar trend is observed for smaller beads of 196 µm charged by Nieh and Nguyen (11) at 4.08E-13 C per bead at 25% RH, while we have charged 200 µm glass beads to an average charge of 1.36E-12 C per bead at 32% RH. In this work, 540 µm glass beads obtained a surface charge density of 1.97E-5 C $m^{-2}$ when charged at 22% RH and 200 µm glass beads obtained a 1.08E-5 C $m^{-2}$ surface charge density when charged at 32% RH. The obtained glass bead charging is in all cases larger when compared with results reported in literature. This difference can be attributed to possible composition variations in materials used.

The initial proof of concept of the stationary coating has been carried out combining the electrospraying and tribocharging of particles using alumina and glass beads. First, the particles are charged in a Teflon cup by rolling. Then the charged particles
are brought in the vicinity of an electrospray of the nanosuspension by positioning it on a metal plate, which functioned as the counter electrode, as shown in Figure 5. The nanosuspension was pumped through a needle (ID 0.61 mm) by a syringe pump (NE-500), and sprayed on the target with exposure time varying between 30 to 600 sec at flow rates ranging between 0.4 and 1.0 ml/hr. An electric field between the needle and a metal base plate was created by applying a high voltage (-8.5 kV) to the needle. The distance between the needle and the base plate was 4.5 cm. A typical scanning electron microscope (SEM) image of the coated glass bead is shown in Figure 3. Inspection of the surface with the SEM for longer spraying time indicated that a multilayer of nanoparticles was deposited on the surface (not shown here).

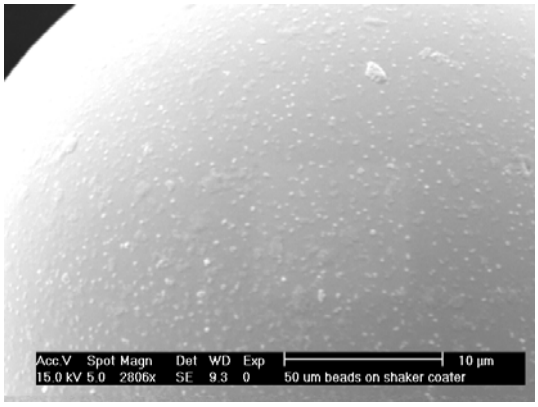


Figure 3. SEM image of 50 micron glass beads coated with 100 nm nanoparticles.

**3 Continuous tribocharging of host particles**

The next aim was to continuously charge the host particles and feed to the falling curtain set-up for electrospraying. The idea of using a fluidized bed to charge particles originated from the presence of electrostatic charges in fluidized beds which is normally known to pose problems of agglomeration and charge build-up resulting potentially in explosions. In fact, fluidized bed has been used to study tribocharging of particles (12,13), and to generate charges (14).
Entrainment of particles from fluidized bed is a well known and investigated phenomenon albeit poorly predicted. Briens et al. (15) studying the size distribution of particles entrained from fluidized bed using solids ranging from 69 µm cracking catalyst to 850 µm polyethylene report the smallest particles not being the most easily entrained out of the bed. On the other hand, the entrainment of the fines has not been affected by the fluidized bed containing a mixture of large and fine particles (16). Investigating the bipolar charging of particles, Ali et al. (17) conclude the smaller particles tribocharge oppositely to the larger size particles in a fluidized bed. This was further confirmed by Mehrani et al. (18) with varying material of host and fine particles between glass beads, polyethylene, silica and Larostat 519 (anti-electrostatic agent). Significant amount of charges is carried out from a fluidized bed by entrained fines. Thus, this phenomena of entraining charged particles out of a fluidized bed is investigated as the continuous charging of particles for electrospraying.

A unique Faraday cup fluidized bed was build where the inner surface of the bed was interchangeable. Shown schematically in Figure 4, the outer and inner shells of the fluidized bed were made of copper, with distributor and insulator between the shells made of Teflon material. Insertion of the tube made it possible to change the fluidized bed wall material from copper, Plexiglas, Teflon, PMMA, PVC to glass.

Extra pure dry building air (Donaldson filter/dryer ultrapac 2000) at 1 bar controlled by a mass flow controller was used to fluidize the bed material. Temperature of the air remained between 24 – 28ºC with RH at 3.2-4.9 %. The bed was grounded to the electrometer (Keithley 6517A) which measured the accumulated change and its polarity. Data acquisition was controlled by a Labview based program. The system was enclosed in a wooden box to isolate from the surroundings, and preventing any particles to discharge to the atmosphere. Tribocharging of large and/or small particles was studied by changing the material of the fluidized bed column wall. Fluidizing bed medium (large particle) was glass beads of 400-520 μm of 0.20 kg. All this was done to charge the host particles (small glass beads) at 10 wt.% in a fluidized bed with bed material and wall that are selected to induce the most charges. The entrained particles once out of the fluidized bed were directed through a copper pipe and into an external faraday cup as shown in Figure 4. A voltage (-100 V) was applied to the copper pipe in order to avoid deposition of entrained particles. A 250 μm mesh was placed at the top of the fluidized bed to prevent any coarse bed material from being entrained. The charged and entrained host particles were collected in an external Faraday cup to measure the charges.

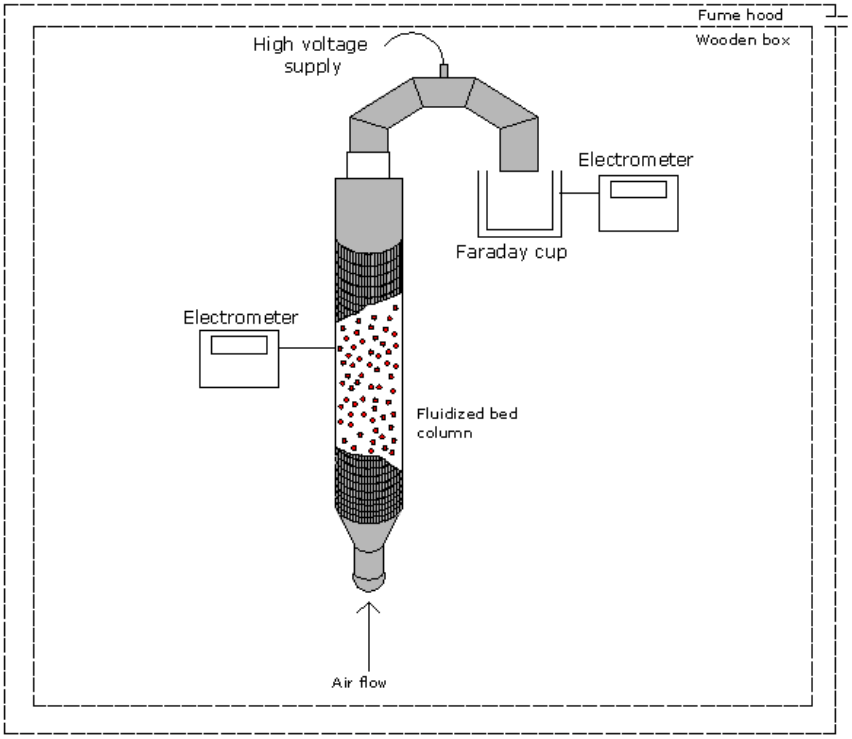


Figure 4 Experimental set-up for elutriation and capture of charged host particles.

Careful protocol of setting up each experiment was practiced to minimize the interference of dust layer on the column wall. A mixture of glass beads (90 wt.% of 400-520 μm and 10 wt.% 125-150 μm) was placed into the fluidized bed. The charge was recorded before fluidization, during bubbling fluidization, and during elutriation of fines by increased gas flowrate. As shown in Figure 5a, the net charge in the Faraday cup fluidized bed accumulated as a negative charge during the 5 min fluidization time, followed by an increase during the 10 min elutriation time owing to small particles carrying out the negative charges leaving behind the bed as positive.

On the other hand, the external Faraday cut collecting the entrained small particles recorded the accumulation of negative charges over time (Figure 5b). After 10 min of elutriation period, close to 100% of the fines were collected in the external Faraday cup. This section has successfully demonstrated the feasibility of charging and entraining host particles out of a fluidized bed for downstream electrospraying.

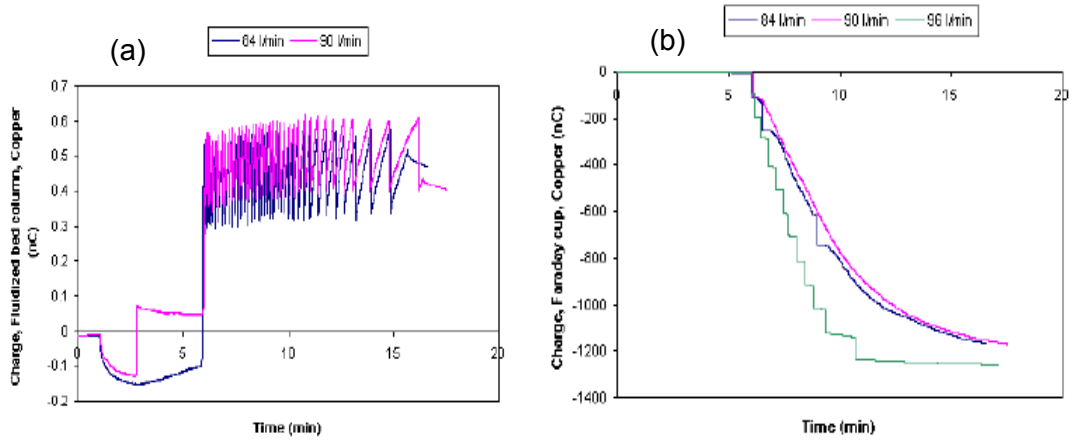


Figure 5. (a) Effect of gas velocity on the net charge in the fluidized bed column; (b) charge accumulation in the external Faraday cup from collecting the entrained particles (5 min fluidization and 10 min elutriation).

**Continuous coating**

In the current work, we did not yet couple the continuous tribocharging of the host materials and the continuous electrospray deposition. However, previously we have investigated the coating of continuously moving material on a vibrated conveyor (19) this has been shown to work well. More recently, we investigated the electrospray deposition of nanoparticles onto free-falling host particles. Figure 6 shows that also this technique yields good results. In near future, we will investigate the coupling of this continuous coating of free-flowing material with continuous tribocharging.

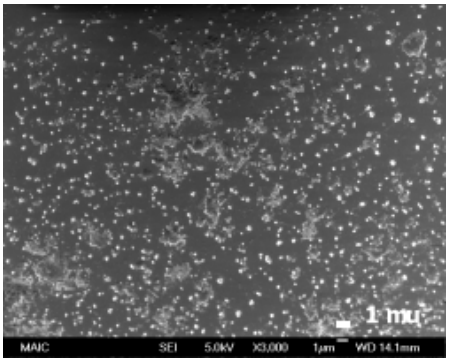


Figure 6. SEM image of 500 nm polystyrene particles deposited with electrospraying on a falling flow of 200 μm glass beads.

## CONCLUSIONS

A novel approach for coating microparticles with nanoparticles in a continuous process is presented. The approach is based on various processes; fluidization, tribocharging, elutriation, and electrospraying. These components to achieve continuous coating of nanoparticles on host particles have been investigated and proven successful. The proposed method eliminates several problems mostly associated with dispersion of nanoparticles and deposition efficiency of nanoparticles. Electrohydrodynamic atomization (EHDA) allows efficient dispersion of nanoparticles and coating the charged host particles with those nanoparticles more efficiently. Charged particles required in the EHDA are prepared through tribocharging of the host particles in a fluidized bed followed by entrainment. Higher fluidizing velocity has shown higher charges in the bed and of the entrained particles.

The continuous coating of falling material has shown good results, indicating that the two parts of the process can indeed be coupled.

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