FABRICATION OF ORGANIC AND INORGANIC NANOPARTICLES USING ELECTROSPRAY

A Thesis

by

PARAG B. DEOTARE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2007

Major Subject: Electrical Engineering

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Approved by:

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ABSTRACT

Fabrication of Organic and Inorganic Nanoparticles Using Electrospray.

(May 2007)

Parag B. Deotare, B.E., University of Pune, India

Chair of Advisory Committee: Dr. Jun Kameoka

A new fabrication process of organic and inorganic nanoparticles and cups by electrospraying blended polymer-sol-gel solutions followed by calcination has been investigated. Because of low viscosity and high surface tension of blended polymer-sol-gel solutions, an electrostatically extruded continuous liquid jet from the spray source became tiny droplets with diameter of less than 1μm in transit. They were collected as dried formats at the counter electrode. These are then calcinated to eliminate polymers as well as cross-link sol-gel material. Silica nanocups have been fabricated using the above technique and the probable methods to control their morphology by varying the ionic concentration have been investigated. Experiments with biodegradable polymers, like Poly Lactic Acid (PLA) and polyvinylpyrrolidine (PVP) to fabricate nanoparticles using the above technique, have also been carried out. The potential use of such biodegradable particles in drug delivery has been demonstrated. This method can encapsulate drug in the particles without the need of any stabilizer which can cause unwanted effect on the drug. The effect of solvents, polymer concentration and deposition distance on morphology and diameter of particles was also investigated on PLA particles. This process is a simple and efficient approach for producing nanocomposite cups that cannot be made by an aggregation method and also nano/micro particles which may find their use in drug delivery and filtration media. Finally, a new technique to sort the particles based on their dimensions is demonstrated. Because of interactions between charged droplets and a non-linear

electrostatic field, nanoparticles with different dimensions are deposited at different locations. By using this principle, silica nanocups have been sorted into three groups with mean diameters of 0.31 μm, 0.7 μm and 1.1μm and a standard deviation of 20%.

To My Parents and Dr. Kameoka

ACKNOWLEDGMENTS

Behind every endeavor, there are people who make it happen. The making of this thesis is the result of many invisible hands helping in every way and I express my deepest gratitude to all of them.

First and foremost, I would like to express my profound sense of gratitude and indebtness to my advisor, Dr. Jun Kameoka, Asst. Professor, Department of Electrical and Computer Engineering, Texas A&M University, College Station, USA for his supervision, noble guidance and constant encouragement in carrying out my research.

I wish to express my sincere thanks to Nick Jing and Tom for their invaluable help with the SEM.

I also wish to express my gratitude to Miao Wang, Hyungduk Ko and Pei-Tsiang Tsou for their valuable discussion and help.

Last but not the least I would like to thank all the staff members of my department for their constant support.

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CHAPTER I

INTRODUCTION AND ORGANIZATION OF REPORT

A. Introduction

In this thesis, a new fabrication process for making organic and inorganic nanoparticles is demonstrated. This process includes electrospraying blended polymer sol- gel solutions. Because of low viscosity and high surface tension of these solutions, electrostatically extruded continuous liquid jet from the spray source breakdown into tiny droplets with diameter of less than 1μm in transit. These particles are collected in dried formats at the counter electrode. Due to interactions between charged droplets and nonlinear electrostatic field, nanoparticles with different dimensions are deposited at different locations. By using this principle we are able to sort nanoparticles based on their dimensions. The application of this fabrication technique for incorporating drug in the particles is also studied.

B. Organization of Report

We start with an introduction which gives the complete gist of the research, basically about electrospraying which is the new fabrication techinque introduced in this thesis work.

Chapter II comprises of the literature survey. Traditional particle fabrication techniques along with their advantages and disadvantages have been discussed. The use of micro/nano particles in drug delivery and the feasibility of electrospray in their fabrication has been briefed.

The journal model is *IEEE Transactions on Automatic Control*.

Chapter III discusses the materials used for the experiments and the method used for sample preparation. The experimental setup used for the experiments is also explained.

Chapter IV deals with the modified experimental setup used for sorting the fabricated particles during electrospraying.

Chapter V presents the results for silica nanocups, PLA particles and the sorting method. The discussion about the result data is also carried out in this chapter.

Finally, chapter VI sums up the thesis with the conclusions and ideas for future work.

CHAPTER II

LITERATURE SURVEY

The research about nanoparticles has obtained substantial attention over the past few years due to their unique and tremendous potential applications. For instance, sensors [1], drug delivery [2], biological labelling [3], consumer products like cosmetics and sun screens [4], and composite materials are currently investigated as potential applications.

A. Traditional Fabrication Techniques

Nanoparticles are fabricated by two methods. One is the top-down approach that breaks down a bulk material into smaller pieces by applying mechanical or electromagnetic energy. This method is simple, however, it is difficult to make particles with smaller diameter, especially less than 1μm particles. The other one is the bottom-up approach that aggregates an atom or molecule to form nano scale structures. This approach includes sol-gel processing [5], chemical vapour deposition (CVD) [6], plasma or flame spraying synthesis, atomic or molecular condensation. In addition to inorganic nanoparticles, organic nanoparticles can be manufactured by using self-assembly [7] technique. This assembling technique relies on the natural tendency of molecules to aggregate and form larger structures. Because of uniform crystal growth, the shape of these particles is always spherical.

Most of the fabrication processes produce a broad distribution profile of their diameters. Currently, to sharpen this broad profile, there are some sorting techniques utilized. However, normally sorting process is not efficient since it is limited to low productivity [8]. For instance, centrifugal separation has been used only for large diameter particles [9]. High-pressure liquid chromatography [10], fractional crystal-

lization [11] and gel electrophoresis [12] are some other sorting techniques. Thin film composite nanofabrication membrane [13] was also utilized to achieve sorting. These fabrication as well as sorting techniques produce nanoparticles either with standard deviation as large as 30% or have very low productivity. Most importantly all the processes produce only one particle distribution at a time. So, to produce different diameter particles the complete process has to be repeated.

B. Electrospray

To overcome the above drawbacks, we investigated a new fabrication technique that can create spherical and non-spherical nanocomposite particles/cups by using an electrospray. Previously, the fabrication of non-spherical particles has been reported. Poly-methyl methacrylate (PMMA) porous cups were made using the electrospray technique. However, the average diameter of these cup structures was micron scale and the difficulty to make nano scale cups was also described. The setup for the experiments is similar to the one in [14]. The electrospray technique is discussed under the experimentation section. Briefly, electrostatic field extrudes the polymer jet from the electrospray source and the continuous polymer jet is split into individual small droplets due to the surface tension of solution and electrostatic force. Then, the individual cups are formed in transit to the counter electrode.

C. Drug Delivery

The enhanced chemical and physical properties of micro and nanoparticles make them ideal for sensors, drug delivery, cosmetics and dyes. Biodegradable polymer nanoparticle has become an important research area due to their potential applications in drug delivery systems [15] [16] [17]. These particles help in delivering various drugs

over a long period of time. PLA being biocompatible has been studied for such applications. The control of the drug release can be achieved by controlling the polymer composition in the nanoparticles [18]. Studies [16] [19] related to the size of nanoparticles suggested their influence on the ease of transportation of these particles and the cellular uptake. [20] investigated the use of PLA nanoparticles for drug targeting. In most of the polymer nanoparticles fabrication processes mentioned earlier, the size of the nanoparticles is controlled by the addition of a stabilizer, which prevents further aggregation of the particles. This stabilizer is added to the solution containing the polymer and the drug to be encapsulated. Addition of the stabilizer may have an adverse effect on the encapsulated drug. Hence, the choice of the stabilizer gets restricted and its concentration has to be precisely controlled to avoid degradation of the drug. Electrospraying does not forecome these problems. In this thesis, the fabrication of PLA micro/nano particles as small as 30nm and the investigation of their diameter and morphology with different PLA concentration in two solvents, chloroform and dichloromethane (DCM) has been reported.

CHAPTER III

EXPERIMENTATION

A. Sample Preparation

The experiments were carried out with spin-on-glass (SOG) (purchased from Futurrex, Inc.) and poly lactic acid (PLA) sol-gel solutions. The solutions for the first part of the experiments consisted primarily of SOG with 1, 0.5 and 0.3 percentage of polyvinylpyrrolidine (PVP) (Aldrich, MW 1 300 000) concentration by weight respectively. These solutions were blended for more than 5 hours using a magnetic stirrer to obtain a uniform solution. Chloroform and dichloromethane (DCM) were the two solvents used for preparing PLA sol-gel solutions. Solutions with PLA weight percentage of 0.5, 2, 3 and 5 were prepared in either chloroform or DCM. Then, the polymer solutions were electrosprayed onto the silicon counter electrodes. The silicon counter electrodes with nanocups or nanoparticles were then baked to eliminate polymers as well as cross-link sol-gel material. The baking temperature for SOG was $850°C$ for about 3 hours and $50°C$ for 2 hours for PLA.

B. Experimental Setup

The experimental set up of electrospray system is shown in Fig. 1. It consists of an electrospray source which consists of a syringe needle and a counter electrode. The deposition distance between the counter electrode and the source can be varied. A syringe pump (Harvard Apparatus) provided a constant flow rate and a variable power source provided the required negative potential to be applied between the needle and counter electrode.

While spraying SOG solution the distance between the needle and electrode

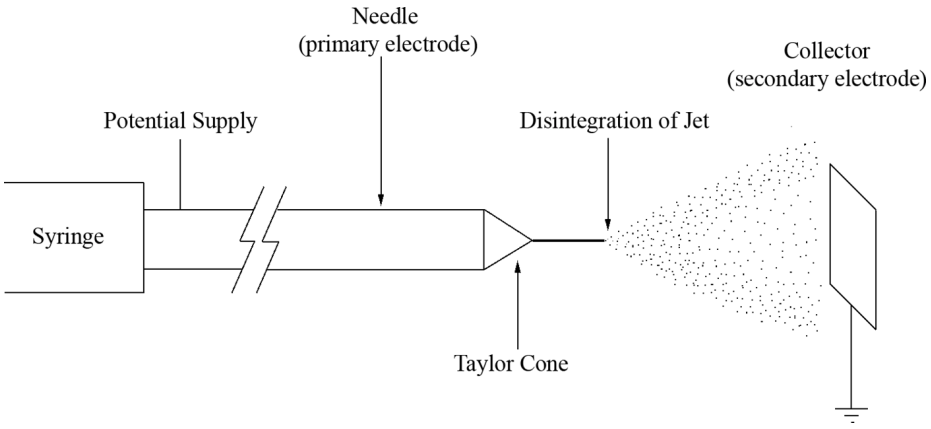


Fig. 1.: The experimental setup showing the electrospray mechanism.

was kept constant at $12cm$ with a negative potential of $4.4kV$ between them and a flow rate of $10\mu l\ min^{-1}$. For Electrospraying PLA the distance between the needle and counter electrode was varied between 7 - $17cm$ with a constant flow rate of $5\mu l\ min^{-1}$. A negative potential of $4kV$ in case of chloroform and $5kV$ in case of DCM was applied.

C. Electrospraying

Electrospraying is explained as follows [21]. An electric field was developed by applying a potential between the needle and the counter electrode. Surface charges, which are proportional to the resulting electric field, were formed on the surface of the sol-gel solution droplet at the tip of syringe. These charges exert an outward electrostatic pressure which is in opposition to the pressure developed by surface tension resulting in the formation of the Taylor cone at the tip of the needle. Above a critical value of the field, the electrostatic forces overcome the surface tension of the solution resulting in the extraction of a liquid jet from the Taylor cone. Then, the extruded polymer jet was separated into small droplets with diameter less than $1\mu m$ because of low viscosity and high surface tension of blended polymer-sol-gel solutions. These

droplets were dried in transit and collected on a silicon wafer substrate placed on the counter electrode.

CHAPTER IV

SORTING OF NANOPARTICLES

Most of the nanoparticle fabrication processes produce a broad distribution profile of their diameters. The current sorting techniques utilized to sharpen this broad profile are not efficient due to their limitation on productivity. Some fabrication techniques do produce sharp distribution profiles but all the techniques have an important drawback of producing only one particle distribution at a time. So, to produce different diameter particles the complete process has to be repeated. Electrospraying technique discussed earlier has been modified to overcome these drawbacks [22].

A. Modified Experimental Setup

The modified experimental set up is shown in Fig. 2. The only modification was the introduction of floating electrodes. Electric potential was applied between the needle and the counter electrodes and the particles were collected at various floating electrodes. The orientation of the floating electrode was also different from that of the counter electrode. The distance between the needle and the collection floating electrodes was varied to investigate the effect of deposition distance on particle diameter distribution.

SOG solution mixed with 0.3% by weight of PVP was used for this experiment. Then, the solution was extruded to create nanocups by the electrostatic force between the counter electrode and the source. Under this experiment, the influence of nanocup collection was studied with the counter electrode placed at a distance of $16cm$ from the needle. A negative potential of $7.4kV$ was applied to create the electrostatic field. Silicon substrate was placed on the counter electrode, $11cm$ below the needle axis. The reason for offsetting the substrate was that the spray does not take place along

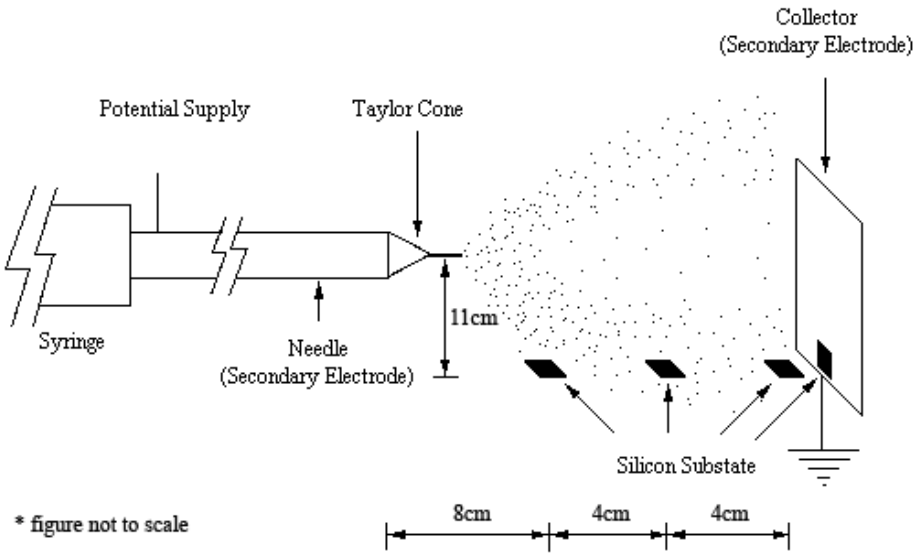


Fig. 2.: The Modified Experimental Setup. Three floating electrodes, one counter electrode and electrospraying source that is connected to the pumping system.

the axis of the needle but along a conical surface with its apex at the tip of the needle. Silicon substrates were also placed as the floating electrodes which were located $8cm$, $12cm$ and $16cm$ from the needle. These floating electrodes were also placed $11cm$ below the needle axis but were orthogonal to counter electrode plane as shown in Fig. 2.

CHAPTER V

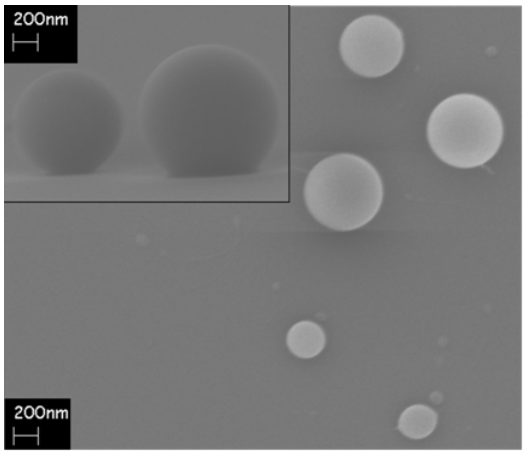
RESULTS AND DISCUSSION

Initial experiments with solution containing PVP showed the formation of spherical beads. Electrospraying SOG resulted in the formation of hemispherical nanocups. This triggered the research following the foreseen potential application of these cups. Results with PLA showed beads with varying morphology for change in PLA concentration. Detailed discussion of the above results follows:

A. Silica Nanocups

Fig. 3a shows the scanning electron microscope (SEM) image of PVP beads formed after electrospraying a solution containing 6% PVP in a 50-50% mixture of ethanol and water. The spherical morphology of the beads is easily seen from the inset image in Fig. 3a. Fig. 3b and 3c show the images of silica nanocomposite-cups formed after electrospraying of SOG with 0.3% PVP solution. These observations prove that the nano cups are indeed formed during transit of the extruded droplets to the counter electrode and not due to the impact of the droplets with the substrate surface. Experimenting with varying deposition distances showed the same result. A negative potential of $4.4kV$ was applied between the needle tip and the counter electrode with a distance of $12cm$. The syringe pump was set at a flow rate of $10\mu l\ min^{-1}$. The average wall thickness of the cups was about 20% of the outer diameter. Almost all the cups were hemispherical with the average height of about 50% of the outer diameter. These hemispherical structures may be created by the surface charge of the droplets which were extruded in the electrospraying process.

The calcination process was investigated by comparing the dimensions of nanocups before and after the calcination. Nanocups collected on the counter electrode were



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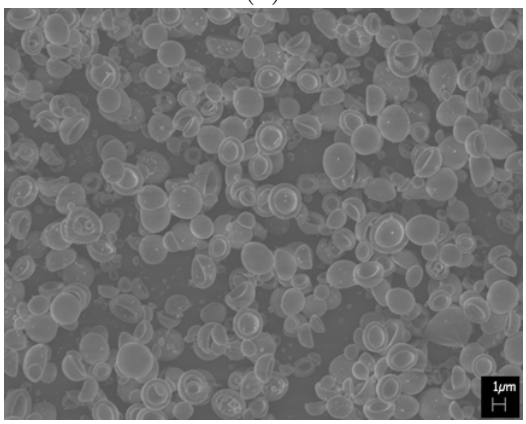

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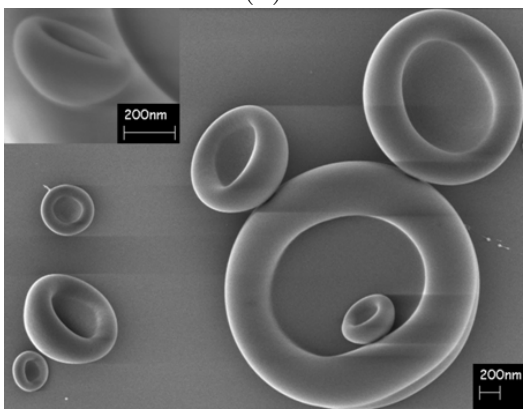
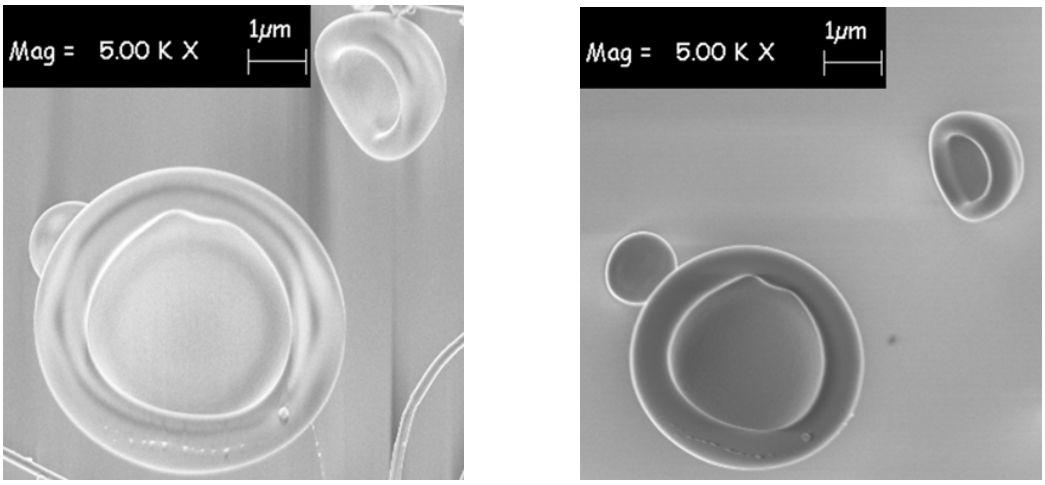


(c)

Fig. 3.: SEM images of PVP spherical beads and SiO_2 nanocups. (a) PVP spherical beads formed with 6% PVP concentration and (b) and (c) SiO_2 cups with 0.3% PVP concentration.

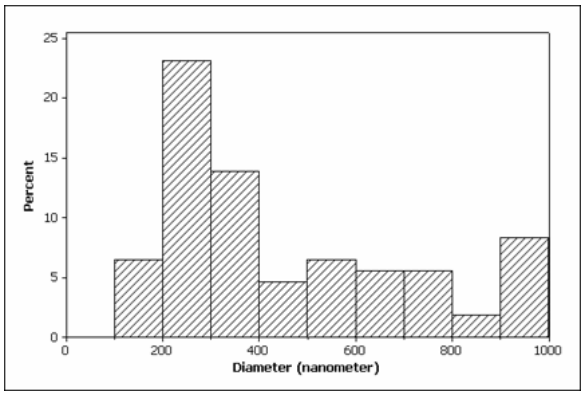


(a) (b)

Fig. 4.: SEM images showing shrinkage in the SiO_2 cup size after baking in air for 3 hours at $850°C$ (a) Before and (b) After baking.

calcined in air at $850°C$ for about 3 hours to remove the polymer and also to cross link the sol-gel material. Fig. 4 shows the SEM images of before and after the calcination. From these images, it was found that the outer diameter of the larger cup before and after baking is $3.36\mu m$ and $2.4\mu m$ respectively. A 28% shrinkage in diameter was observed due to the elimination of polymers. The same ratio of change was observed in the height, thus it was concluded that the shrinkage of nanocups due to the calcination process was isotropic. This result was normally true for most nanocups.

The influence of PVP concentration to the diameter of nanocups was investigated. Fig. 5 shows the histogram of the diameter of nanocups made from three different concentrations of PVP. The average diameter with 1%, 0.5% and 0.3% PVP was found out to be $850nm$, $564nm$ and $545nm$ respectively. It was observed that as the concentration of PVP decreased, the cup diameter also decreased. It was seen that the percentage of sub micron size cups increases from nearly 70% to 84% as



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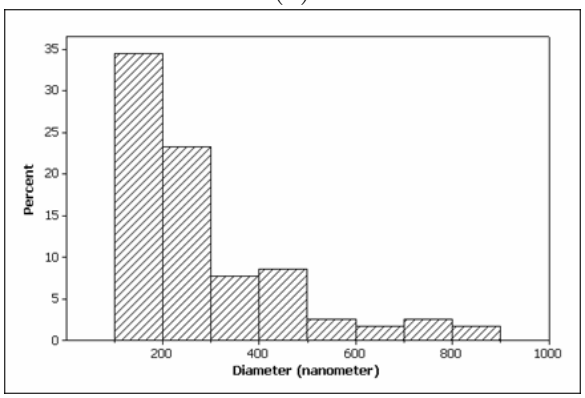

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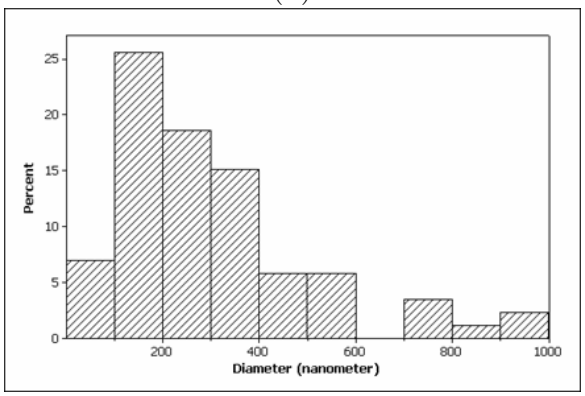


(c)

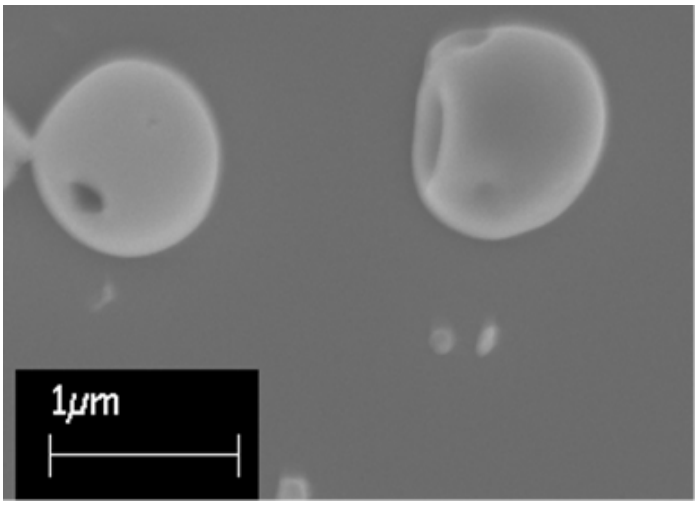
Fig. 5.: SiO_2 particle diameter distribution as a function of particle diameter. (a) 1% PVP (b) 0.5% PVP and (c) 0.3% PVP concentration.

the PVP concentration decreases from 1% to 0.3% respectively. Since small diameter cups get easily covered by the large ones, most of the cups seen earlier in Fig. 3b are larger than a micron. Concentrations above 1% PVP resulted in formation of continuous fibers. This was because of the increase in the viscosity of the polymer sol-gel solution with the increase in PVP concentration, which prevents the fiber jet to disintegrate into tiny droplets.

The influence of ion concentration of the polymer sol-gel solution on the morphology of the cups was also studied. Fig. 6 shows the SEM images of cups fabricated from SOG sol-gel solution with and without distilled water. The 0.3% PVP solution with an addition of 0.1% distilled water by weight is prepared and electrospun. The cups formed from this solution are almost spherical with a significant reduction in the pore size by comparing to the one made form PVP solution without distilled water. This may be due to the resulting change in ion concentration in the solution, though SOG and water are immiscible, suggesting the role of charged particles in the formation of the peculiar cup shape.

B. PLA Particles

Fig. 7a shows the SEM image of beads formed by electrospraying 0.5% PLA by weight in chloroform. The beads are droplet shaped and nearly 80% of them are less than a micron in size, ref Fig. 8a. Further increasing the PLA concentration to 2% resulted in formation of PLA rods as shown in Fig. 7b. The length of these rods varied from 10-35μm, while their thickness varied between 3-8μm. Fig. 7c shows the effect of increasing the PLA concentration to 3%. Oval shaped beads are formed but the major axis dimensions are now in micrometers. Nearly 75% of the oval beads had their major axis measured between 6-10μm. Finally, Fig. 7d shows the formation



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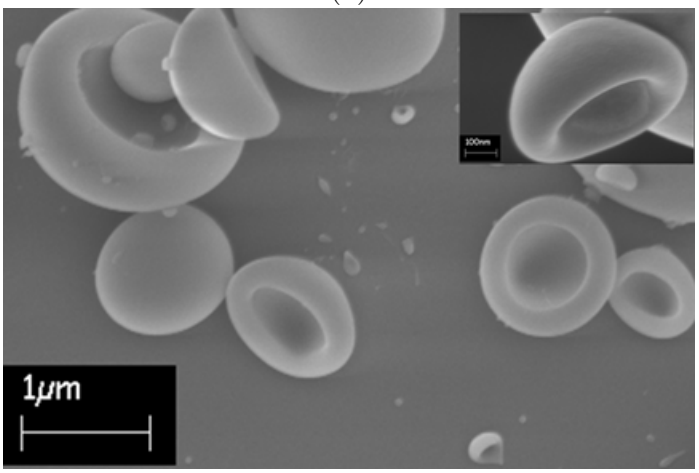
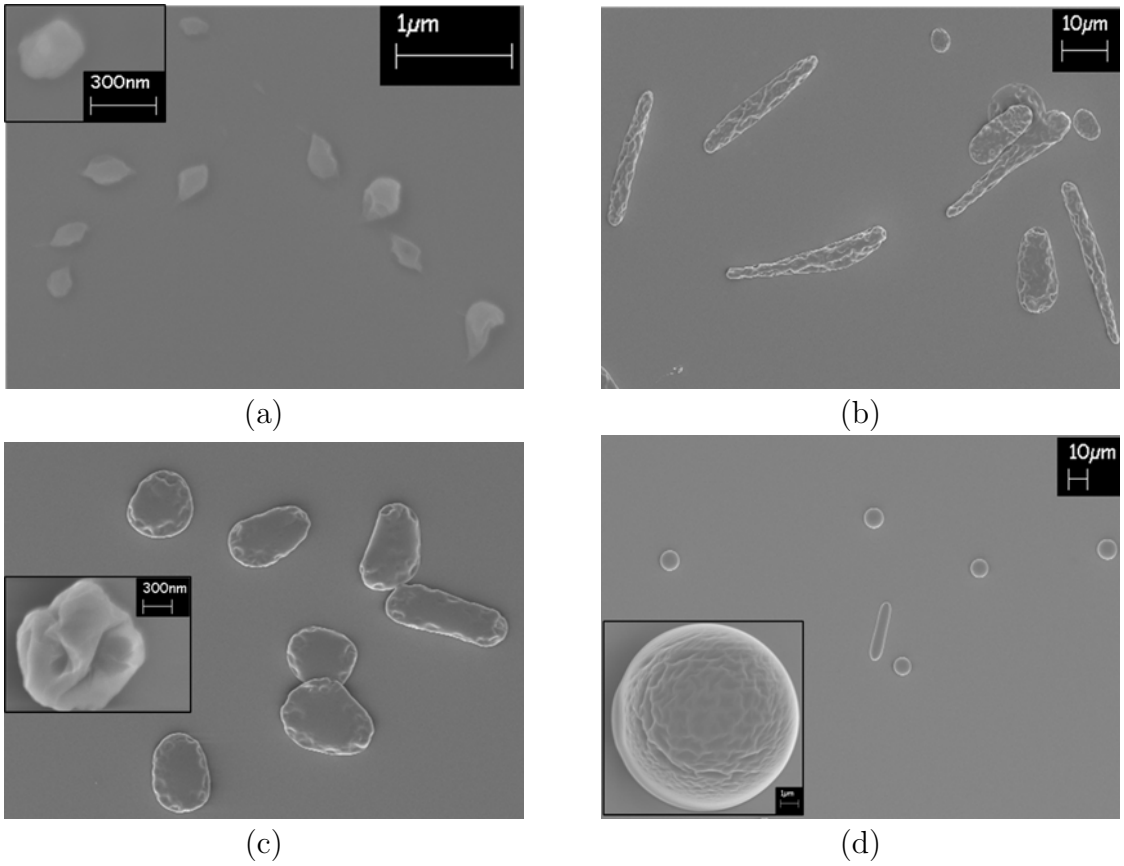


(b)

Fig. 6.: SEM image showing change in cup morphology and reduction in pore size due to change in ionic concentration by adding distilled water. (a) 0.3% PVP and 0.1% distilled water (b) 0.3% PVP.



(a) (b)

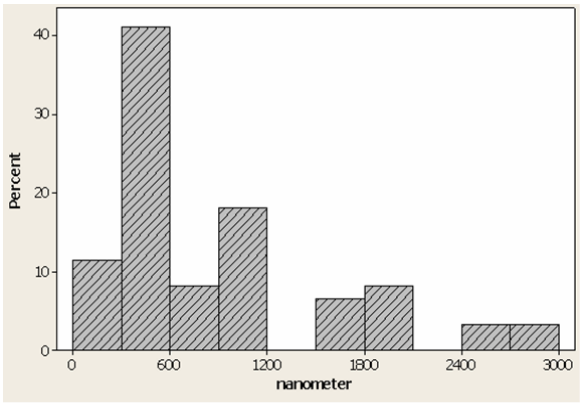
(c) (d)

Fig. 7.: PLA particles using chloroform. (a) 0.5% PLA (b) 2% PLA (c) 3% PLA (d) 8% PLA.

of spherical beads with diameters range of microns, after electrospraying polymer solution with 5% PLA concentration. More than 50% of the beads had diameter around $14\mu m$, Fig. 8b. The formation of rods at low concentrations of PLA may be explained in the following way. At low concentration levels, the effect of increase in the PLA concentration is more pronounced on the viscosity than the surface tension. But since this viscosity is not sufficient to form fibers, it results in rod shaped structures. As the concentration was further increased, the surface tension takes over and results in the formation of spherical microparticles.

The beads do not dry completely during their transit to the counter electrode. This is seen from the fact that the bead surface morphology changes when viewed under the SEM. To overcome this, they were baked at around $70°C$ in an oven. But it resulted in flattening of the beads due to low glass transition temperature. An alternative way was to dry the beads by passing hot air at about $50°C$. The surface of a dried bead was very rough as seen in Fig. 7c. This was due to the escaping solvent from the surface during drying. Fig. 8c shows the mean diameter and the standard deviation of PLA beads formed using chloroform. The mean diameter for 0.5%, 2%, 3% and 8% PLA concentration is $700nm$, $19000nm$, $8000nm$ and $10200nm$ respectively. The mean and standard deviation was very high in the second case since it results in rod formation and the numbers indicate the axial length of the rod and not the diameter.

The next set of experiments were carried out with DCM as the solvent. The particle size distribution was almost the same as in the earlier case. But the difference was seen in the morphology of the particles. Tendency to form hemispherical cup shaped structure as in case of SOG was seen from the SEM images ref. Fig. 9a . Fig. 9b shows the rods formed by electrospraying 2% PLA concentration solution. The rod formation in the case of DCM is seen even for 5% concentration though the



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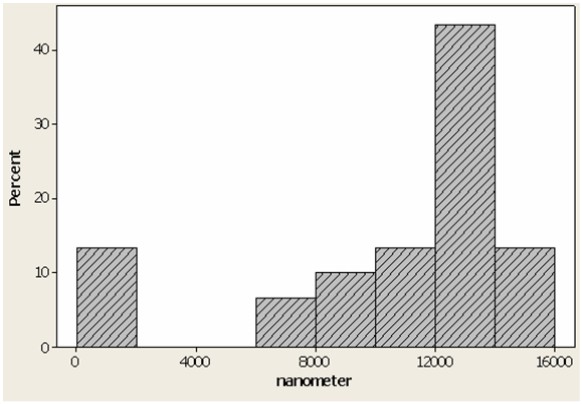

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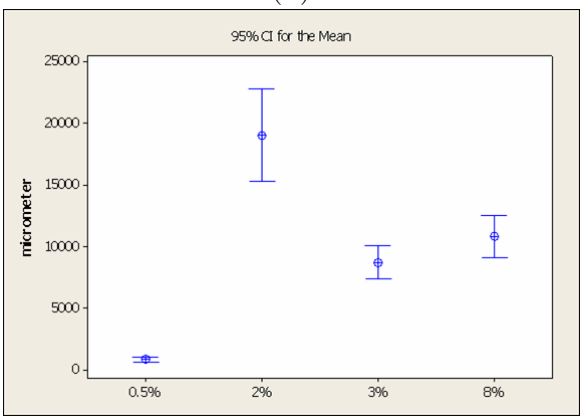
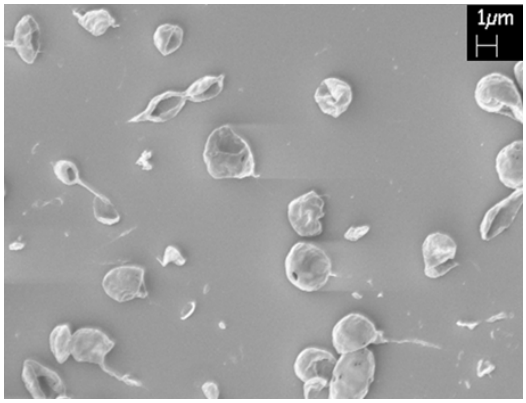


(c)

Fig. 8.: PLA particles with chloroform as solvent and collector distance of 7cm. (a) 0.5% PLA (b) 8% PLA (c) Standard deviation plot.



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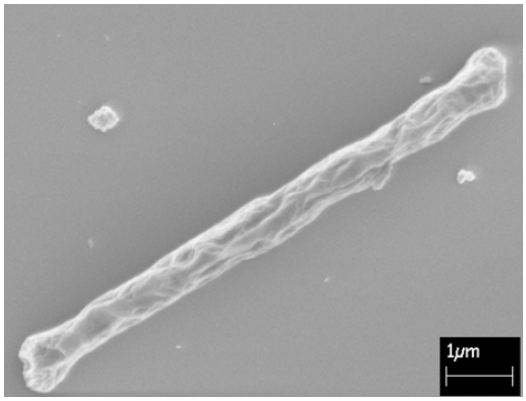

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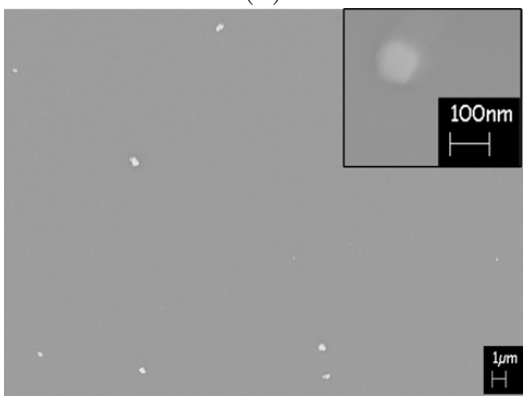


(c)

Fig. 9.: PLA particles with dichloromethane as solvent. (a) 0.5% PLA and collector distance of 7cm (b) 2% PLA and collector distance of 7cm (c) Collector distance of 17cm. Notice that the larger particles are all filtered.

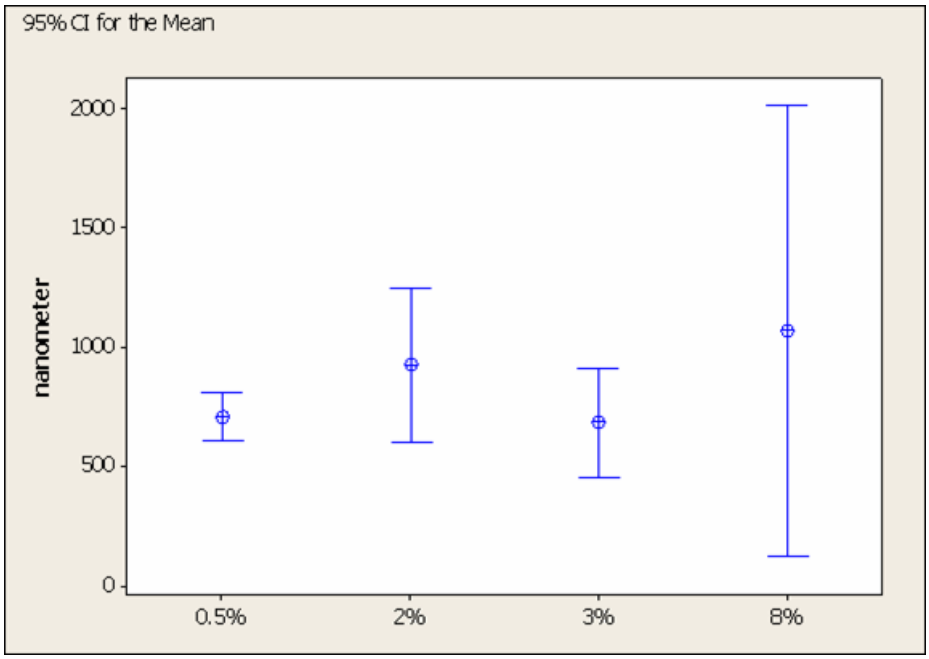


Fig. 10.: Standard deviation plot with dichloromethane as solvent and $7cm$ collector distance.

mean axial length decreases as the concentration is increased. The mean particle diameter for the four different PLA concentration is $700nm$, $900nm$, $650nm$ and $1050nm$ ref Fig. 10. As compared to the earlier case of using chloroform, a significant reduction in the mean diameter is observed by using DCM.

The effect of the deposition distance on the morphology of the beads was also studied. Too small distance resulted in flattened beads. This can be accounted for the fact that the solvent does not have enough time to evaporate during the transit from the electrospray source to the substrate and hence the bead remains in a semi fluid state at the time of impact with the substrate resulting in its flattening. The results show that in all the cases, more than 85% of the particles formed are under $100nm$ with the highest percentage of 96% occurring with 2% PLA. The particle size varied between $30nm$ to $150nm$. The mean diameter for the four cases is $80nm$, $75nm$,

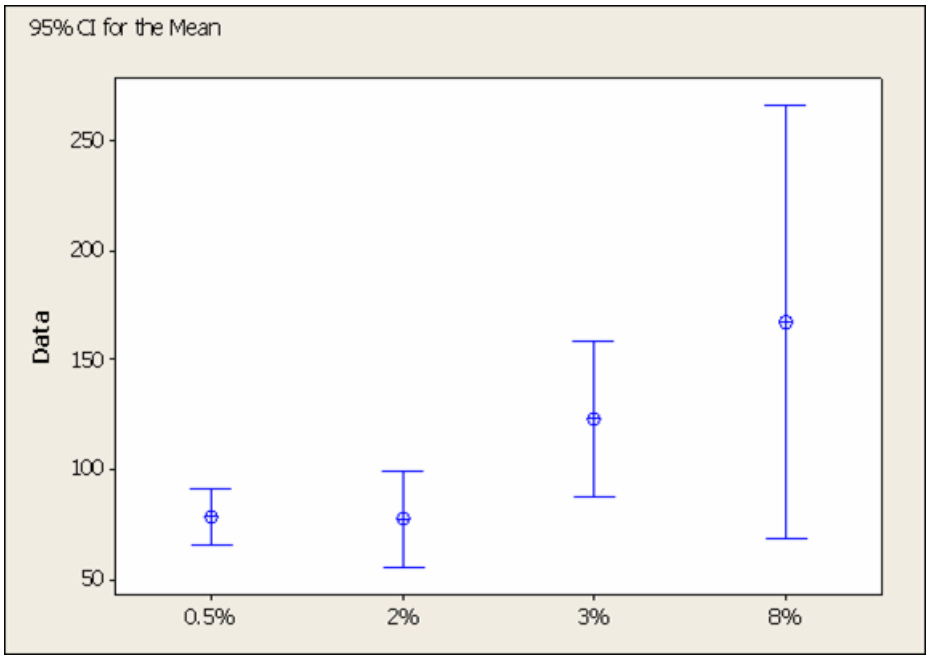


Fig. 11.: Standard deviation plot with dichloromethane as solvent and 17cm collector distance.

130nm and 170nm. Ref Fig. 9c and Fig. 11. The result is reduction in the standard deviation of the particle distribution. This is very important for applications like drug delivery which are particle diameter dependent.

The reason for experimenting with PLA was due to its importance in drug delivery. Drug can be embedded in the particles and PLA being biodegradable, it would be released over a period of time. PLA particles were fabricated from a solution containing 8% PLA and 0.001% quantum dots in DCM. Quantum dots were used instead of a drug due to the ease in analysing them under the fluorescence microscope. Fig. 12a shows an optical image of the fabricated PLA particles. Comparing it with Fig. 12b, which is a fluorescence image shows the embedded quantum dots in it at the time of fabrication. These particles were immersed in water and allowed to degrade. Fig. 12c and Fig. 12d are the images of the same particles after 1 and

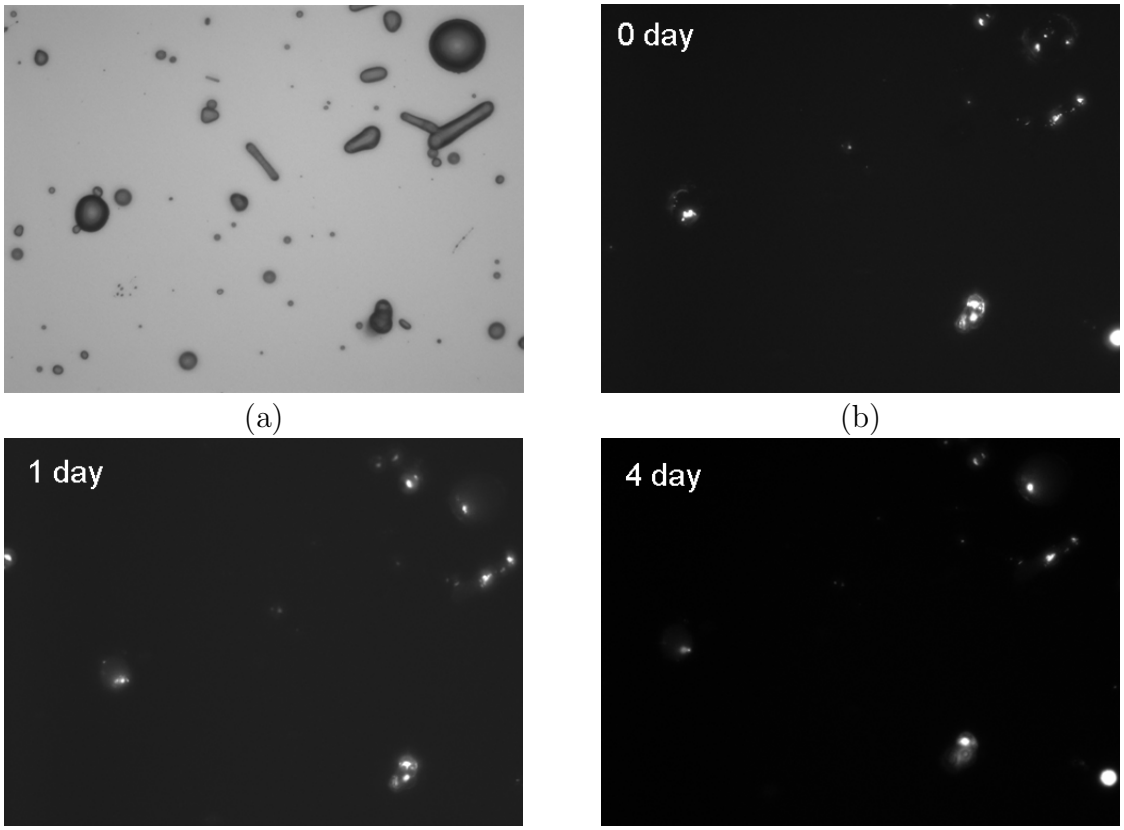
4 days respectively. These images prove the release of quantum dots from the PLA particles over a period of time. This is in analogy with drug being released from PLA particles.

C. Sorting

Fig. 13a shows the SEM micrograph of nanocups fabricated with the substrate placed on the counter electrode, $16cm$ away from the needle and $11cm$ below the needle axis. Cups with diameters as large as a few micrometer to tens of nanometers are collected on the substrate. This generates a very broad particle diameter distribution.

Fig. 13b, 13c and 13d show the SEM image of the electrosprayed nanocups in which the distance between the counter electrode and the needle is kept constant at $16cm$ and silicon collector substrates are placed at $8cm$, $12cm$ and $16cm$ respectively on the floating electrodes. These substrates are again placed $11cm$ below the axis of the needle and oriented orthogonal to the plane of the counter electrode. Sorting of the cups is immediately revealed. Fig. 13b shows nanocups collected on the floating electrode placed $8cm$ away from the source. Only small cups with mean diameter around $0.31\mu m$ are collected in this case. Fig. 13c reveals that cups with slightly larger mean diameter of $0.7\mu m$ are collected when the floating electrode is placed $12cm$ away from the source. Finally, Fig. 13d shows large cups with mean diameter of $1.1\mu m$ collected on the floating electrode placed $16cm$ away from the source. The sorting of cups is obvious and we see that as the floating electrodes are moved away from the source, the percentage of larger diameter cups is increased.

The sorting mechanism in this experiment can be attributed to the surface charges. The surface to volume ratio is inversely proportional to the radius of the particle. The charge density (charges per unit volume) is uniform throughout the



(a) (b) (c) (d)

Fig. 12.: PLA particles embedded with quantum dots showing the drug delivery concept. (a) Optical image of PLA particles (b) Fluorescence microscope image of PLA particles immediately after fabrication (c) Fluorescence microscope image of PLA particles 1 day after fabrication (d) Fluorescence microscope image of PLA particles 4 days after fabrication.

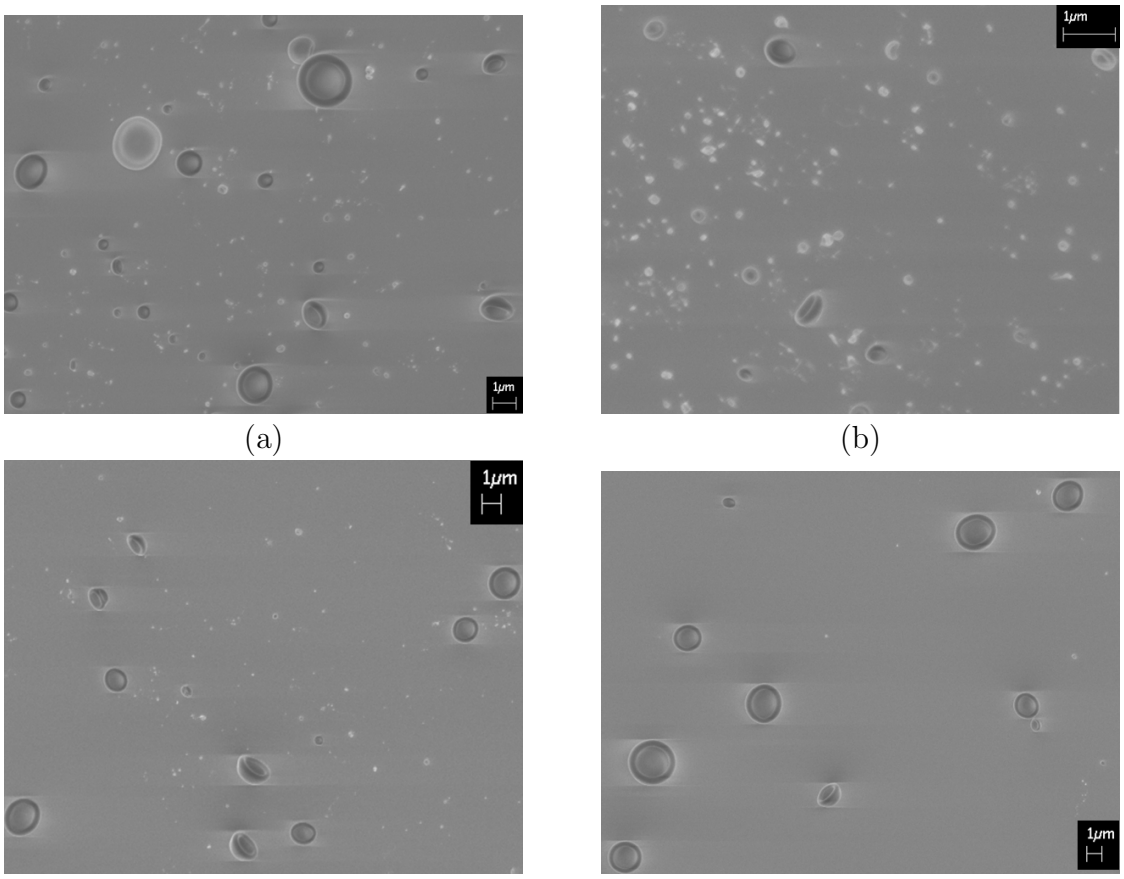


Fig. 13.: SEM images showing sorting of nanocups. (a) Nanocups collected on the counter electrode that is located 16cm away form the source. (b) Nanocups collected on the floating electrode 8cm away from source (c) Nanocups collected on floating electrode 12cm away from the source (d) Nanocups collected on floating electrode 16cm away from the source.

particle. Hence, the surface charge (charge per unit area) is proportional to the radius. The total surface charges are then proportional to the radius cubed, i.e. the volume of the particle. The drag force associated with these particles in transit is significantly less as compared to the force exerted by the electrostatic field. Hence, under the influence of an electrostatic field the larger particles travel greater distances and are deposited further away from the electrospray source as compared to small particles which are deposited closer to the source. This agrees with the results, which show that the mean diameter of the deposited particles increases as the collecting distance is increased. Fig. 14 is a graph showing the mean diameter of nanocups as the function of substrate position and the standard deviation. It immediately reflects out that the sum of the three graphs on the left results into the fourth graph. This indicates that the modified electrospraying method sort the cups with different mean diameter along various collector distances. The mean diameter for the first three cases is $0.31\mu m$, $0.7\mu m$ and $1.1\mu m$.

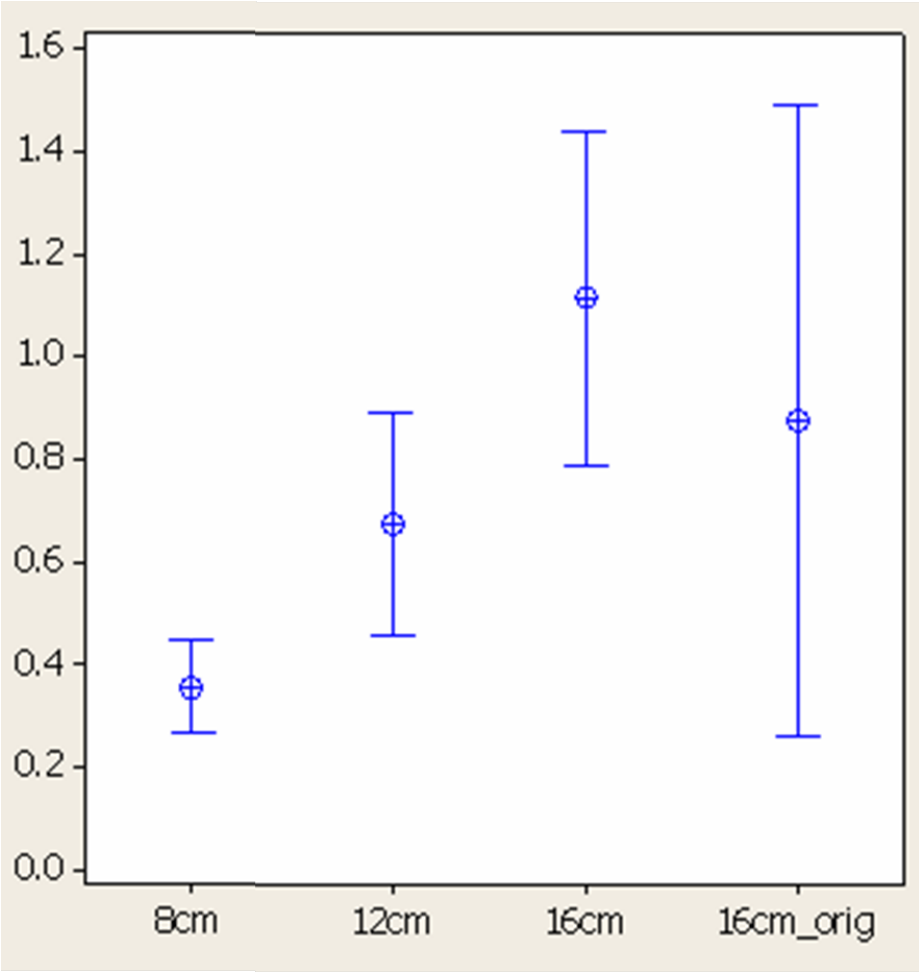


Fig. 14.: Graph showing diameter of nanocups as a function of the location of floating electrodes: Electrodes are placed at $8cm$, $12cm$ and $16cm$ away from the source with the counter electrode placed at $16cm$. And, $16cm\_orig$ is for the nanocups collected at the counter electrode placed at $16cm$ away from the source.

CHAPTER VI

CONCLUSION

A new technique of fabricating hemispherical silica nano cups by electrospraying polymer sol-gel solution has been demonstrated. After calcinations, nano cups with diameter as small as $50nm$ were fabricated. This technique is very simple and highly efficient compared to other known nanomaterial fabrication techniques such as self assemble nanoparticles. The diameter of silica nanocups could be controlled by the PVP concentration. This was also true with PLA particles. Lower the polymer solution concentration, it was found that smaller particles were fabricated. In addition, the morphology of silica nanocups changed by adding ions in polymer sol-gel solution. More ions in the PVP solution, the pore size became smaller and the shape would be more spherical. Varying the PLA concentration did the same for PLA particles. As the concentration was increased, the morphology changed from droplet shaped particles to rods and finally to spherical particles.

These nano structures may find their use in medical applications like drug delivery, cancer treatment and other products like cosmetics and dyes. These PLA beads find wide application in controlled drug delivery by functionalizing the surface. Small diameter particles are required for short time drug release, whereas for a sustained drug delivery over a long time, the size of the particles should be larger. The shape of the particle may also be an important parameter in the release of drug.

Finally, electrospraying technique was modified to sort the micro/nano silica cups based on their dimensions during the fabrication process. Particles can be sorted with different mean diameter with small standard deviation and different particle distribution can be obtained at the same time. Sorting of nanoparticles with mean diameter of $0.31\mu m$, $0.7\mu m$ and $1.1\mu m$ and a standard deviation of about 20% was

demonstrated.

Electrospraying is not only a simple and efficient technique of fabricating nanoparticles but it also provides an easy control on the drug release as well as its concentration. The simple modification makes electrospraying a very efficient method to fabricate micro/nano particles for various applications.

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