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Research Article

Sorting of Silica Nanocups by Diameter during Fabrication Process

Parag Deotare and Jun Kameoka

Department of Electrical and Computer Engineering, Texas A&M University, 3128 College Station, TX 77843, USA

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We demonstrated a new technique to sort nanoparticles based on their dimensions. Due to the interactions between charged droplets and a nonlinear electrostatic field, nanoparticles with different dimensions were deposited at different spatial locations on a given target substrate. By using this principle, we have been able to sort nanocups into three groups with mean diameters of $0.31\ \mu\text{m}$, $0.7\ \mu\text{m}$, and $1.1\ \mu\text{m}$ and a standard deviation of 20%. This technique improves the nanoparticle fabrication process not only by decreasing the standard deviation of its dimensions but also by increasing its yield since nanoparticles with different mean diameters can be generated at the same time.

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1. INTRODUCTION

Nanoparticles have become an important topic of research and have been developed for various applications like sensors [1], diagnostics, drug delivery [2], biological labeling [3], cosmetics [4], dyes, and so forth. The successful utilization of such applications depends on the uniformity as well as productivity of nanoparticles. Fabrication techniques such as sol-gel processing [5], chemical vapor deposition [6], self assembly [7], nanoprecipitation [8], and polymerization [9] are widely used. These fabrication processes produce particles with a broad distribution profile of their diameters. Currently, to sharpen this broad profile, several sorting techniques are utilized. However, the typical sorting process is not efficient since it is limited to low yield [10]. For instance, centrifugal separation has been used but only for large diameter particles [11]. High-pressure liquid chromatography [12], fractional crystallization [13], and gel electrophoresis [14] are some other sorting techniques. Thin film composite nanofabrication membranes [15] are also utilized to achieve sorting. These fabrication processes as well as sorting techniques produce nanoparticles either with standard deviation as large as 30% or having very low productivity. Most importantly all the processes produce only one particle distribution at a time. So, to produce different diameter particles the fabrication and sorting process has to be repeated.

To overcome these drawbacks, we present a new technique to sort nanoparticles depending on their diameter. The proper placement and orientation of the substrate used to collect nanoparticles played an important role in sorting. Since this sorting technique can be used without any extensive modification of the setup, it can be easily implemented. In addition, nanoparticles are easily removed from the substrate by ultrasonic treatment for about 15 minutes in distilled water. This process for sorting nanoparticles can yield particles for applications in drug delivery and life sciences.

2. EXPERIMENTAL SETUP

The experimental setup is shown in Figure 1. It consists of an electrospray source and a collection of floating electrodes as well as a counter electrode. A syringe needle is used as a source and is connected to a pump (Harvard Apparatus) to provide a constant flow of a sol-gel polymer solution. To establish a Taylor cone, a negative potential was applied between the needle and 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.

A spin on glass (SOG) (Futurrex, Inc.) solution mixed with 0.3% by weight of polyvinylpyrrolidone (PVP) (Aldrich, MW 1 300 000) was prepared for this experiment. Then, the

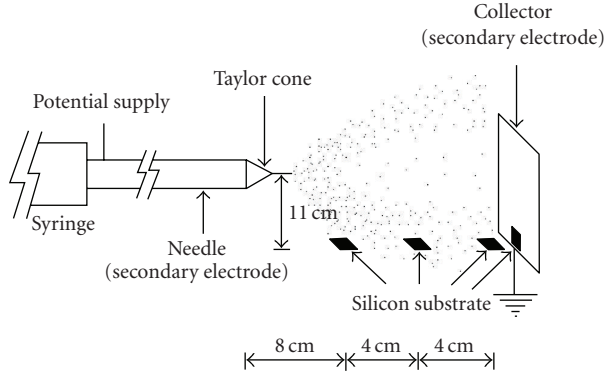


FIGURE 1: Experimental setup showing three floating electrodes, one counter electrode, and an electrospaying source that is connected to the pumping system.

solution was extruded to create nanocups [16] 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 16 cm from the needle. A negative potential of 7.4 kV was applied to create the electrostatic field. The silicon substrate was placed on the counter electrode, 11 cm below the needle axis. The reason for offsetting the substrate was that the spray does not take place along the axis of the needle but is along a conical surface with its apex at the tip of the needle. Silicon substrates were also placed as the floating electrodes, located at 8 cm, 12 cm, and 16 cm from the needle. These floating electrodes were placed 11 cm below the needle axis but were orthogonal to the counter electrode plane as shown in Figure 1.

3. RESULTS AND DISCUSSION

Figure 2(a) shows a SEM micrograph of nanocups fabricated with the substrate placed on the counter electrode, 16 cm away from the needle and 11 cm below the needle axis. Cups with diameters as small as tens of nanometer to a few micrometers are collected on the substrate. This generates a very broad particle diameter distribution.

Figures 2(b), 2(c), and 2(d) show SEM images of the electrospayed nanocups in which the distance between the counter electrode and the needle is kept constant at 16 cm and silicon collector substrates are placed at 8 cm, 12 cm, and 16 cm, respectively, as the floating electrodes. These substrates are again placed 11 cm below the axis of the needle and oriented orthogonal to the plane of the counter electrode. Sorting of the cups is immediately realized. Figure 2(b) shows nanocups collected on the floating electrode placed 8 cm away from the source. Only small cups with mean diameter around $0.31 \mu\text{m}$ are collected in this case. Figure 2(c) reveals that cups with slightly larger mean diameter of $0.7 \mu\text{m}$ are collected when the floating electrode is placed 12 cm away from the source. Finally, Figure 2(d) shows large cups with mean diameter of $1.1 \mu\text{m}$ collected on the floating electrode placed 16 cm 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 total surface charges in the droplet. Because the dimension of droplet is small, about $1 \mu\text{m}$ range, gravitational force [17], which is proportional to mass, is neglected. Thus, the deposition distance is determined strictly by the propelling coulombic force strength and an opposing air viscous drag acting on the droplet. The coulombic force (F_c) on the droplets in transit is given by

$$F_c = qE. \quad (1)$$

E is the electrostatic force and q is the total charges in the droplet and they are proportional to the radius cubed, that is, the volume of the particle

$$q \propto r^3. \quad (2)$$

The viscous drag force (F_d) is proportional to the area of the particles

$$F_d \propto r^2. \quad (3)$$

Hence, under the influence of an electrostatic field the larger droplets travel longer distances and are deposited further away from the electrospay source as compared to small particles which are deposited closer to the source. Also, larger drops show higher mobility (velocity per unit electrostatic field) which further aids in traveling longer distances [17]. This agrees with the results, which show that the mean diameter of the deposited particles increases as the collecting distance is increased. This holds true only up to a certain limit. With further increase in the drop diameter, the drop mass becomes dominant and adds a significant vertical component to the drop velocity. Figure 3 is a graph showing the mean diameter of nanocups as the function of substrate position and the standard deviation. The graph reflects that the sum of the three size distributions on the left results in the fourth distribution on the right. This indicates that the modified electrospaying method sorts the cups with different mean diameter along various collector distances. The mean diameter for the first three cases is $0.31 \mu\text{m}$, $0.7 \mu\text{m}$, and $1.1 \mu\text{m}$.

4. CONCLUSION

We have successfully modified the electrospaying technique to sort micro/nanocups based on their dimensions during the fabrication process. Particles can be sorted with different mean diameter with relatively small standard deviation and different particle distribution can be obtained at the same time. We demonstrated fabrication and sorting of nanoparticles with mean diameter of $0.31 \mu\text{m}$, $0.7 \mu\text{m}$, and $1.1 \mu\text{m}$ and a standard deviation of about 20%. The simple modification makes electrospaying a very efficient method to fabricate micro/nanoparticles for various applications.

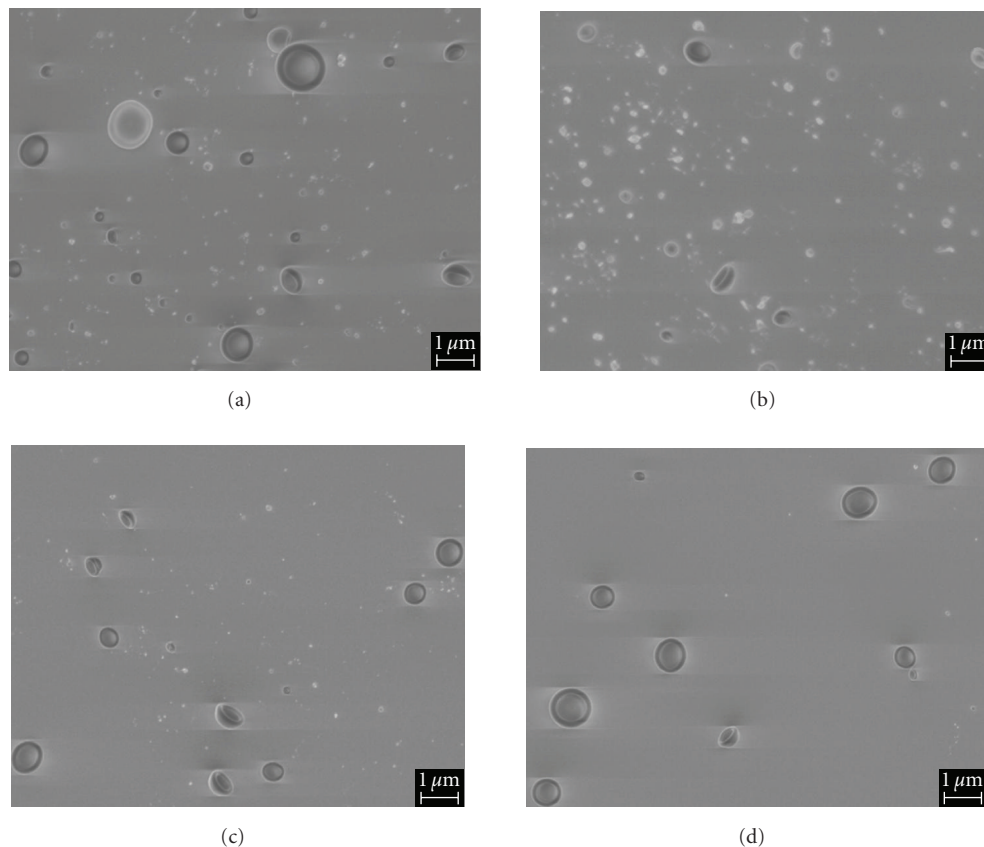


FIGURE 2: SEM images of nanocups collected at the electrodes. (a) Nanocups collected on the counter electrode that is located 16 cm away from the source. (b) Nanocups collected on the floating electrode 8 cm away from source. (c) Nanocups collected on floating electrode 12 cm away from the source. (d) Nanocups collected on floating electrode 16 cm away from the source.

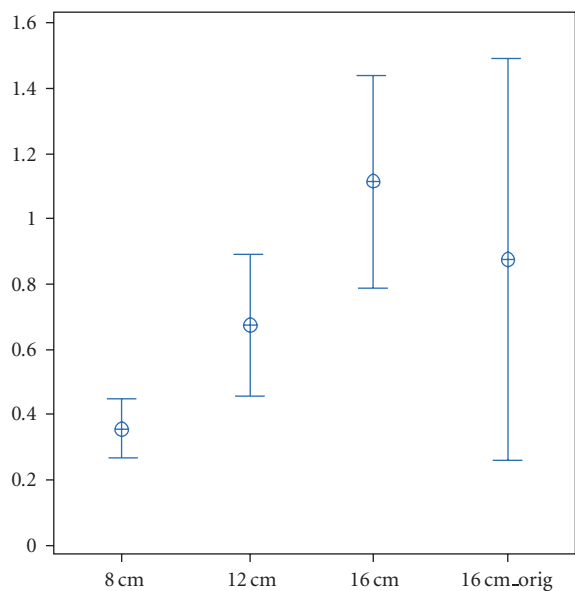


FIGURE 3: Graph showing diameter of nanocups as a function of the location of floating electrodes which are 8 cm, 12 cm, and 16 cm away from the source with the counter electrode placed at 16 cm, and 16 cm_orig is for the nanocups collected at the counter electrode placed 16 cm away from the source.

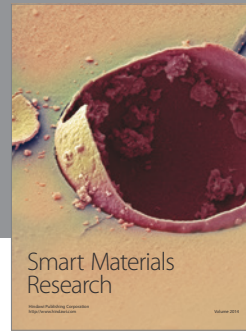
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