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Particulate structures produced by electrosprays of colloidal silica suspensions in both negative and positive zeta potentials

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Interaction between surface charge (zeta potential) of colloidal silica nanoparticles and the charge-induced droplets suspended in the gas phase by electrospray is investigated for the first time based on the particle physical (morphology, size, and size distribution) and optical properties. Colloidal silica nanoparticles having negative and positive zeta potential were subjected to electrospray in both negative and positive mode, and deposited on a substrate (silicon wafer). Visual observation of the substrate with particle deposition shows various white shades, corresponding to the changes in optical properties, as supported by the ultraviolet-visible–near-infrared spectroscopy. Microscopic analysis revealed the strong correlation between the colloid surface charge and charging mode (positive or negative) of the sprayed droplets to the particle morphology and size. The findings of the present study demonstrate the capability of the electrospray method to tune the physical and optical properties of colloidal silica nanoparticles with different surface charges.

1. Introduction

The nature of the "soft charging" process has made the electrospray method one of the most popular ionization techniques, especially in the field of mass spectrometry of large and complex molecule [1]. The charging process has the advantage of decreasing mass-to-charges ratio (m/z) of the molecule to the range of common mass analysis instrumentation. It is also referred to as "soft ionization" due to less residual energy being retained in the analyte molecules [2]. In general, it is believed that the induction-charging process of complex biomolecules inside the aerosol droplet does not cause fragmentation of the molecules. An example is the usage of electrospray with aerosol sizing technique (differential mobility analysis) to investigate the interaction of colloidal nanoparticles with ligands [3]. However, the conformational changes of the protein molecules due to droplet-charge induction were also reported [2,4]. During electrospraying, Banerjee [4] assumed that the analyte of protein inside the droplet lies on the neutral core of the droplet. By changing the solvent from water to acetic acid at different pH and polarities, it can be shown that the mass spectrum exhibits multimodal charge distribution. In electrospray, the charging state of the aerosol droplet also mainly depends on droplet size. In the recurring droplet fission, droplet size decreases and the number of charges carried by a droplet decreases following the Rayleigh limit [5]. In well dispersed colloid, the single particle (e.g. 20–30 nm range) in one droplet has been verified via a deposition-based experiment [6]. It also flexibly covers a wide range of particle sizes with good particle dispersibility [7,8].

Several efforts have been made to study the interaction and structure of charge distribution inside a droplet, but only a few studies have discussed the charge interaction with analyte or particles confined inside the droplet. Storozhev [9] theoretically discussed the charge distribution in a dielectric droplet using continuum medium approximation. The approximation step calculated free energy of the ions in dielectric droplet as a function of presence of other ions. The result showed that charge distribution inside a droplet is not a kind of surface distribution charge. Considering this fact, non-closed surface charge distribution of the droplet may lead to a "non neutral" region existing in the "core." If this condition were satisfied, there would be a possibility that the induced electric field might interact with native-charged distribution of colloidal particles [10,11].

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Other studies discussed the role of zeta potential during spray drying (including electrospray-based), using negatively-charged silica and positively-charged polystyrene nanoparticles to obtain hollow silica [12,13]. The correlation between effective charge of polymer nanoparticle in suspension and charge states of the same particle in gas phase due to electrospray ionization has been investigated [14]. The aggregation state of particles produced by electrospray may relate to the intrinsic properties of starting material and electrospray process [15,16]. In the present study, we investigated the relationship between the charges (i.e. zeta potential) of colloidal nanoparticles in both negative- and positive-values and the electrospray charge mode (positive or negative). The role of zeta potential in electrospray-derived particle morphology and their optical properties was mainly investigated.

2. Experimental

The opportunity to study further the effect and interaction of the native charges contained in colloidal nanoparticles with induced external potential of the electrospray method is now possible due to the newly developed silica (SiO_2) colloidal particles having positive zeta potential (Nihon Aerosil Co. Ltd., Japan). Therefore, the combination of the polarity of the spray mode (positive or negative voltage) with the polarity of the zeta potential (positive or negative) can be performed. Colloidal silica nanoparticle samples with positive (P-) or negative (N-) zeta potentials were electrosprayed in positive (P-P, N-P) and negative (P-N, N-N) voltage mode and deposited on a flat surface (silicon wafer, n-type, thickness: 350 ± 20 μm).

General set up of electrospray apparatus is schemed in Fig. 1. It consists of a metal capillary tube (with inner diameter below 0.42 mm and outer diameter 0.65 mm) as fluid channel connected to a high voltage DC power supply (Matsusada Precision Inc., Japan). To maintain the continuity of liquid supply, the tube can be coupled with a syringe-pump (KD Scientific, Japan). The experimental conditions are summarized in Table 1.

Using the same set up, charged current of the spray droplet was monitored and measured. The distances between nozzle and substrate were adjusted from 20 mm to 120 mm, while the other parameters were fixed. This experiment may provide a "brief" description of the aerosol droplet charging state. The electrospray setup was equipped with connection from the conductive substrate to the ground via a high resolution electrometer/ammeter (Advantest R8240, Japan). Main parameters which may be related to dry condition or size of aerosols are type of starting colloids and distance between nozzle and substrate. The electrospray deposition was performed at open atmosphere (1 atm); spraying time was 45 min. and the distance between nozzle and substrate was 160 mm.

Before deposition, several preliminary analyses of the negative and positive zeta potential nanoparticles were conducted. The zeta potential and particle size distribution by dynamic light scattering (DLS) of the both types of silica colloidal nanoparticles were measured (Zetasizer, Malvern Instruments, UK); meanwhile, the surface tension, which has direct effect to the electrospray process due to force balance, was also measured (Kyowa, DY-700, Japan). The role of surface tension is to ensure the "cone jet" mode stability in the term of equilibrium between induced high voltage and fluid mechanical properties of the liquid droplet and also affecting maximum number of charges contained in a droplet [5,17]. The particle layers deposited on the surface of silicon wafer by electrospray deposition were also characterized by UV–Vis-NIR spectrometer (MSV-370, JASCO, Japan)

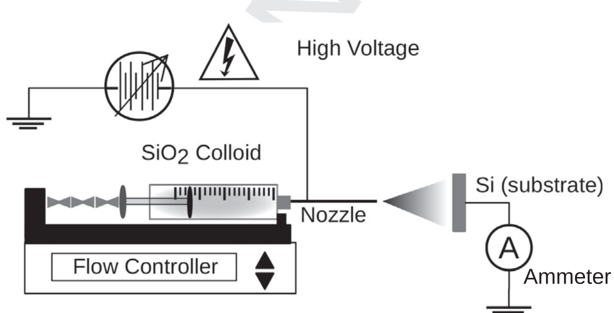

Fig. 1. Experimental set up of the electrospray deposition system.

Table 1
Experimental conditions.

Zeta potential & concentration	Spray Voltage (−) 4.2 kV	Voltage (+) 4.2 kV
Negative, 0.05 wt%	T = 14.7 °C **1**[a] Humidity 38.8%	T = 15 °C **2**[a] Humidity 38.2%
Positive, 0.05 wt%	T = 17.0 °C **4**[a] Humidity 35.3%	T = 17.5 °C **3**[a] Humidity 34.9%

[a] The numerical label to distinguish every experimental run.

3. Results and discusion

3.1. Spray current

The scale of sprayed currents can provide supporting data describing how strong the cloud droplets were charged. Our electrospray system is also able to provide the information indirectly by measuring the charged current in the closed-loop electric circuit [5]. At constant temperature and humidity conditions, the longer distance may form smaller (or more dried) droplets due to the solvent evaporation. Fig. 2 shows charged current of positive and negative sample with positive or negative zeta potential and also pure solvent (ethanol) as comparison. From the chart, it is clear that the positive spray is almost a reflection of the negative one. "Fluctua-

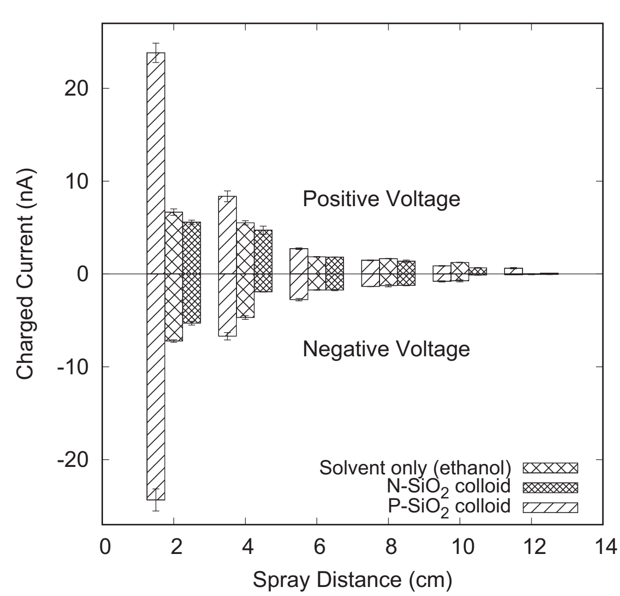

Fig. 2. Spray current of ethanol and colloidal samples with both positive (P-) and negative (N-) zeta potential, sprayed with positive or negative mode.

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