静電噴霧法によるコロイダル粒子の構造化と形態的特性の調整：シリカとススの事例研究

Electrospray-Assisted Structuring and Morphological Property Tuning of Colloidal Particles: Case Studies of Silica and Soot Colloids

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Abstract

This study employs the electrospray method to tune the physical and optical properties of colloidal nanoparticles. Colloidal silica nanoparticles with negative and positive zeta potentials are deposited on a silicon wafer by electrospraying them in both negative and positive modes. The morphology and size of the deposited particles are analyzed by microscopy and a strong correlation between the colloid surface charge and the electrospray charging mode is found. The electrospray method is also applied to prepare and investigate soot particulate layers derived from candle combustion. Raman spectral analysis is performed on the particle layers and a difference in the relative intensity of G-band and D-band between hydrophobic and hydrophilic particles is observed. The absorbance spectra (190–2500 nm) of the particle layers are measured and the electrospray-deposited particles are found to show higher absorbance in the near-infrared region than the candle-direct-deposited particles. This difference is attributed to the change in morphology of nanoparticle layers formed by each route.

Introduction

Electrospray method is one of the most popular ionization techniques, especially in the field of mass spectrometry of large and complex molecule. In general, it is believed that the induction-charging process of complex biomolecules inside the aerosol droplet does not cause fragmentation of the molecules. It was reported that that charge distribution inside a droplet is not a kind of surface distribution charge (Storozhev, 2004). 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. The aggregation state of particles produced by electrospray may relate to the intrinsic properties of starting material and electrospray process (Li, *et al.*, 2011). In the present study, the relationship between the charges (i.e. zeta potential) of colloidal nanoparticles in both negative (N)- and positive(P)-values and the electrospray charge mode (P or N) was investigated. The role of zeta potential in electrospray-derived particle morphology and their optical properties was mainly investigated.

Soot nanoparticles derived from burning candle have been applied as the anode of batteries with high surface area and porosity (Kakunuri and Sharma, 2015). Hdrophobic properties of candle-soot-derived particle layers have also been investigated, and they exhibit a super-hydrophobic effect, which may correlate to the organic content, aggregate size, and the bond structure (Liang et al., 2014). It is critical to investigate optical characteristics of soot nanoparticle (layers) derived from combustion (e.g., candle burning) because the structural bond is fairly sensitive to the formation process during combustion. In the present study, two routes for collecting and depositing candle soot particles on substrates were compared: (i) direct deposition from a candle-flame and (ii) electrospray deposition from soot suspensions. The effects of these deposition methods on the properties of soot nanoparticle layers were investigated and insights for their potential applications were provided.

Experimental

Silica: The opportunity to study further the interaction of the charges contained in colloidal nanoparticles with induced external potential of the electrospray method is possible due to the newly developed silica colloidal particles having positive zeta potential (Nippon Aerosil Co. Ltd., Evonik Group). Therefore, the combination of the polarity of the spray mode with the polarity of the zeta potential can be performed. Colloidal silica nanoparticle samples with P- or N-zeta potentials were electrosprayed in P- or N-voltage mode and deposited on a flat silicon wafer (n-type).

Soot: An experimental system has been developed to directly deposit the soot particles from candle flame. The set up simply utilizes semi-open glass tube equipped with candle position control by utilizing smooth mechanical shifting by a syringe pump. The system was intended to maintain a constant position of collecting substrate relative to the position of the wick. This could be critical since the properties of the soot deposited from the interior of the flame exhibit super-hydrophobic properties and the soot from tips of the flame show a hydrophilic nature. Glass plates were used as collecting substrates. Deposited soot particles (flame interior soot particle) were dispersed in ethanol or water with an ultrasonic homogenization until well-dispersed “ink like” suspension was formed. Ethanol was chosen instead of water to ensure an "easier" spraying condition.

Results and Discussion

Silica: For the “same-polarity” (P-P or N-N) the particles tend to repel each other, resulting in sharp

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edges on aggregated particles due to the repulsive forces. In the case of “opposite-polarities” mode (P-N or N-P), smoother edges of non-porous large particles are observed due to weakening of fission charges (Fig.1). In the "same-polarity" mode, as the droplet undergoes subsequent solvent evaporation, the mass of the droplet reduces and the repulsive forces between the "like (similar) charge" on the droplet surface increases. Simultaneously, the charge between the droplet surface and the particle may increase the repulsive forces, which may make the “unstable” particle structure. In the mode with “reverse polarity”, there are competitions between two forces: (i) repulsive force among charges on the droplet surface and (ii) attractive force between the opposite charges on the droplet and particle. The opposite charge between droplet and particle surface may weaken the repulsive forces on the droplet surface. This condition makes a more “stable” particle structure.

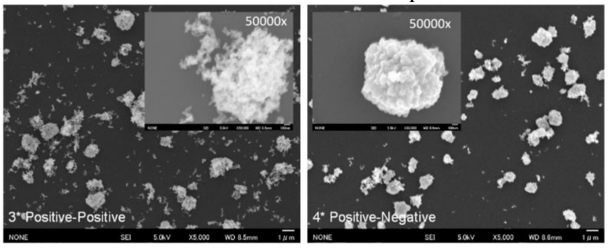

Fig. 1 SEM images of particles deposited on substrates at different combinations of zeta potential of silica colloids with polarity of electrospray (P-P, P-N).

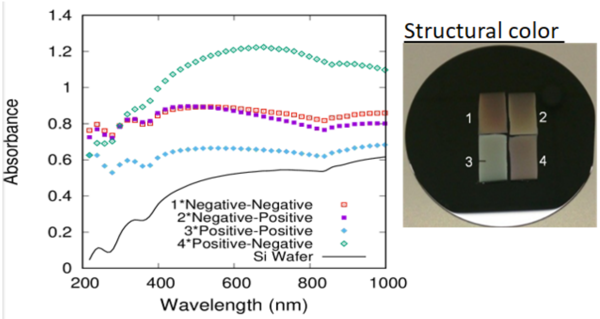

Fig.2 Absorption spectra of silica particle layers (N-N, N-P, P-P, P-N) (Left). Changes in the structural colors of four samples (Right)

Silica: For the N-sample, the change in voltage polarity has a slight effect on the spectrum shape in the UV region, becoming gradually stronger in optical and near IR regions (Fig.2). For the P-sample, the voltage polarity adjustment from P to N significantly shifts the absorbance peak to the red region. Various white shades of the particle layers are obtained and can be seen by bare eyes (Fig.2, photographs). The optical inter-particle nearest distance (ND) may correlate with these apparent colors. The effect of the spraying mode (P or N) changes the average of the ND. The particle layer obtained from the N-spray has longer ND and wider distribution compared to those of P-spray.

Soot: After 5-min spray (Fig.3), the hydrophobicity (CA) increased then decreased with operation-time. The results may correlate to increasing thickness and change in surface roughness. Spray-route shown heavily aggregated by necking and overlapping structure. The size of particles in spray-route is larger than those of direct-route. Larger (primary) particles may indicate the "active" properties of soot due to the adsorption of matters in the liquids. Layers derived from spray-route are invariant to the shape of the Raman spectrum, which is indicated by the preservation of the intensity ratio of G and D-bands. Deposition in shorter time indicates the stronger intensity of Raman spectra, compared with those of longer time deposition. This may be because the lower density particles enhanced the scattering process by interference.

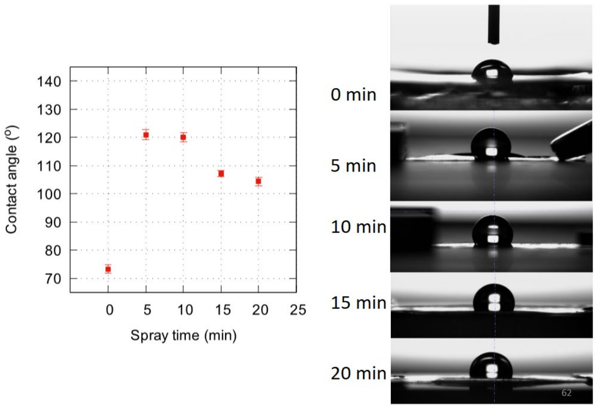

Fig.3 Hydrophobicity vs. spraying times (Left); Static contact angle (CA): Water drop in soot layers (Right)

Conclusion

Electrospraying of colloidal silica nanoparticles in both N- and P- zeta potential was conducted and the effects of the spraying voltage polarity on the morphology, size distribution and optical properties of the product structures were investigated. The combination of experimental parameters changes the optical properties of the silica particle layers. Soot particles from the candle flame are deposited by direct- and spray routes. The Raman spectra between direct-route and spray-Route show no significant change in the structure of soot particles. This means that the electrospraying is invariant to the bond structure of soot particles suspended in the aerosol droplet. Comparing to the direct-route, spray-route can obtain more controllable soot particle layers.

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