An open article by Wuled Lenggoro (2008)
http://empatlab.wordpress.com

TRANSPORT AND ASSEMBLY OF LIQUID-PHASE NANOPARTICLES VIA GAS-PHASE.

Current technological state of the art

Nanoparticle (i.e., having size below 100nm) properties, such as photocatalyst activity and quantum dot efficiency, are highly size-dependent, and accurate deposition/assembly technique, and size measurement with high-resolution for nanoparticles is critical. Particles with well-controlled size and chemical-composition are highly required for materials in the advanced/functional device. Among the synthesis methods (gas-, liquid-, and solid-state method), the liquid-phase/wet-chemical routes such as sol-gel and micro-emulsion methods are useful tools for fabricating small particles and these methods have been used for preparing metals, oxides, or non-oxide (e.g., sulfides).

Concerning the use of liquid-phase nanoparticles for further applications, we have developed a spray method (i.e. electrospray) for dispersing the liquid-phase nanoparticles in to the gas-phase without any agglomeration. The individual (non-agglomerate) or agglomerated particles derived from the liquid-phase nanoparticles could be used for (i) high-resolution size-measurement, (ii) novel thermal analysis of colloidal nanoparticles, (iii) assembling the nano-structure or particle layer, based on the highly-charged nanoparticles, and (iv) a tool for studying the health-effect of nanomaterials.

Technological benefits of the innovative characteristics of the work

For colloidal (liquid-phase) nanoparticles, particle size measurements are often performed using transmission electron microscopy (TEM), or laser-based dynamic light scattering (DLS). TEM measurements, however, are time consuming, as particle size typically has to be measured manually for a statistically significant number of particles and samples must be dried on appropriate media for viewing. While DLS allows for in situ particle size-distribution measurement, individual particles are not measured directly, rather, fluctuations in the intensity of measured light are correlated with the diffusion coefficient of the particles and fitting algorithms are necessary to determine the particle size distribution.

Here, for sizing the liquid-phase nanoparticles, we have used a gas-phase method (aerosol technique) such as the differential mobility analyzer (DMA). DMA in series with a particle counter has been used by the aerosol science community for several decades for rapid and accurate particle size-distribution measurement for particles in the 1–500 nm range. DMA act as particle size filters just as quadrupole mass spectrometers act as mass filters, only differing from quadrupoles in electrode configuration, and DMA are typically operated at atmospheric pressure and use a DC voltage difference only between electrodes. Because DMAs are run at atmospheric pressure, particle motion within the instrument is governed by a balance between the electrical force and drag force on the particle; thus, DMAs can separate particles based on electrical mobility.

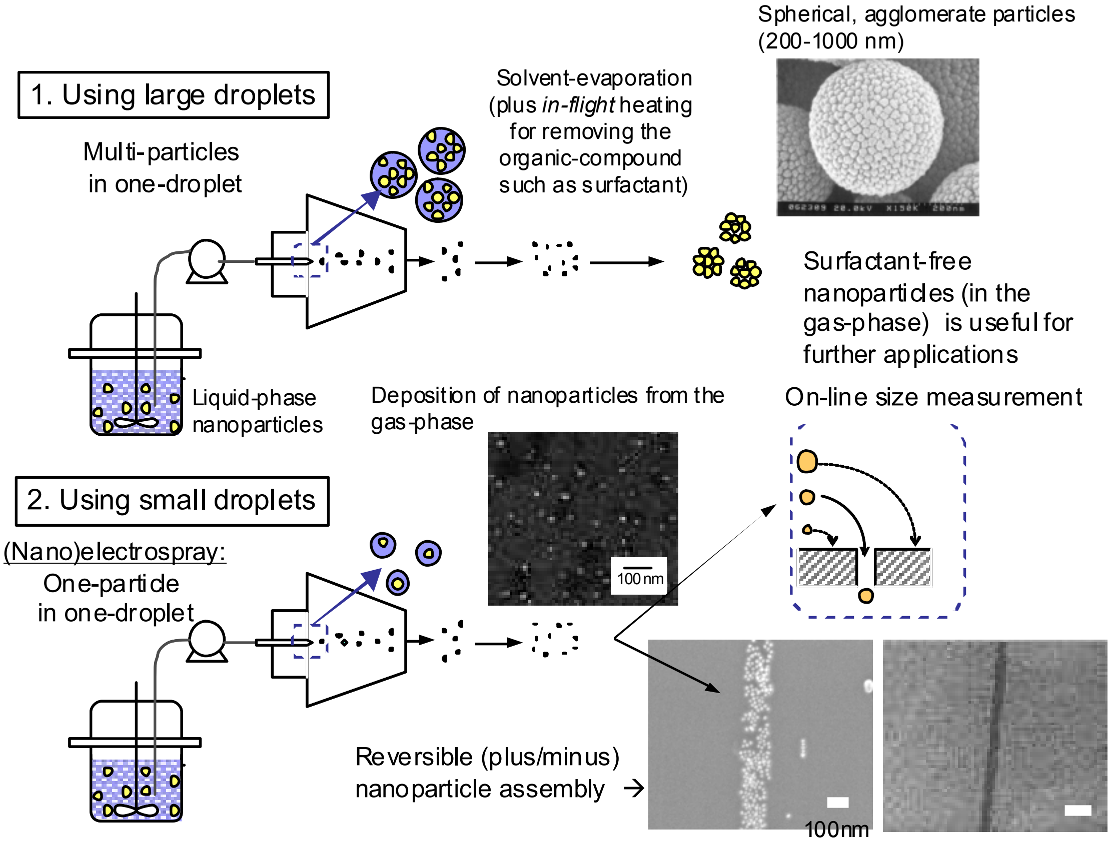


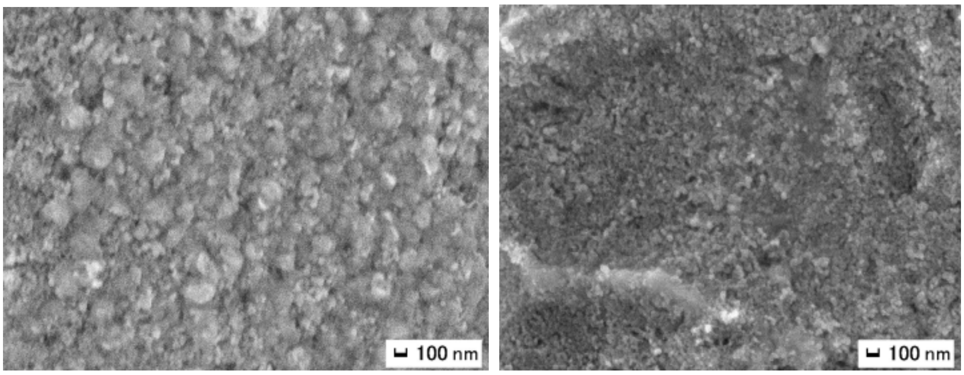
Fig.1 Transferring liquid-phase nanoparticles in to the gas-phase, by (a) large droplets and (b) small droplets, and the morphology of particles derived from the liquid-phase nanoparticles and their further applications. Spherical agglomerate secondary particles can be used for standard-particles application and the individually, non-agglomerate nanoparticles can be used for size measurement and particle-assembly.

To use DMA system to measure colloidal particles, an appropriate method is necessary to convert particles from the colloid phase to the aerosol phase while preserving the particle size distribution. Traditional atomizers and nebulizers used in spray-drying processes with nanoparticle sols typically produce nanoparticle agglomerates where the agglomerate size is primarily dependent on the spray-drying conditions and are not effective in preserving nanoparticle size distributions. Electrohydrodynamic atomization, more commonly referred to as electrospray, is the only known technique capable of producing monodisperse, submicrometer and nanometer sized droplets, and can effectively transition nanoparticles from the liquid-phase to gas/aerosol phase. The use of aerosol instrumentation to measure the size distribution of colloidal particles using an electrospray to create aerosol particles from colloidal particles was proposed (Fig.1).

We have been used a spray (an aerosol method based on the droplets-to-particles conversion) method for preparing spherical particles of a variety of materials. We have extensively investigated the preparation of nanoparticles (particles having size below 100 nm). From submicron droplets, one can expect the generation of aerosol dry particle with size in the order of ten nanometers. To achieve this goal, the electrospray (ES, an electrostatic-assisted spray) system was designed and built to generate droplet with size below one micrometer.

Possible applications - *For Environment & Energy: Selective-deposition method for liquid-phase nanoparticle*

Beside the electrostatic-assisted gas-phase/aerosol process (i.e. electrospray), an electrostatic-assisted liquid-phase approach, a pulse electrophoresis method, was designed for depositing TiO_2 nanoparticles on a metal substrate inside an aqueous suspension. The suspension was prepared by mixing the commercially available nanometer-sized TiO_2 powders (P25, Degussa) with an organic surfactant in water. A suspension with relatively high concentration (30 wt%) is stable for a few months; therefore it was not necessary to place an additional mixing during the deposition process. We have developed a pulse direct current (PDC) charging type electrophoretic and found that the PDC-mode could narrow the particle size distribution (or dispersity) of TiO_2 particles depositing on the surface of a stainless steel electrode. The morphology of the TiO_2 nanoparticles layer deposited by PDC-mode was finer than those was deposited by a direct current (DC) charging mode (Fig.2). Since the TiO_2 particles used have made by a gas-phase synthesis method and, therefore, having high photocatalytic function, one may expect that a solar-cell device with higher energy-efficiency may be possible fabricated from particle layers (with finer morphology) made by our approach.



Direct Current **Pulse Current**

Fig.2 Morphologies of TiO_2 nanoparticle-layers made by electrophoresis deposition with conventional direct-current (left) and the newly-developed pulse-current (right) methods. Both structure were obtained from the same sample (P-25, Degussa) with the same deposition time. Note that the pulse-current made finer morphology.

Possible applications - *For Healthcare -* ***Measuring the non-spherical nanoparticles in the gas-phase***

Electrospray served as a stepping stone to further development and application of aerosol nanoparticles. I have been developed a technique for online measurement of liquid-phase nanoparticles (Fig.1). Liquid-phase nanoparticles is necessary to be measured real-time and in high resolution. We dispersed individually the liquid-phase nanoparticles into the gas phase as an aerosol via electrospray followed subsequent evaporation of the solvent. The size distribution of the generated aerosol particles was then determined by a differential mobility analyzer combined with a counter. The measured values (10–100nm) were comparable to results obtained by electron microscope. We also demonstrated the potential of the electrospray technique in analyzing the structure of non-spherical colloidal particles (Fig.3).

Through this study, we can see that the organic surfactant coated on nanoparticles can be removed, and the non-spherical metal particles became spherical on elevating the ambient temperature during the gas-phase dispersion. The thickness of organic-surfactants was estimated by comparing the theoretically and experimentally obtained mobilities. The combination of electrospray and the mobility information by a DMA can also be applied for predicting the molecular weight distribution and/or density of water-soluble polymer and for determining non-volatile residue (ratio) in water sample (as a novel monitoring tool).

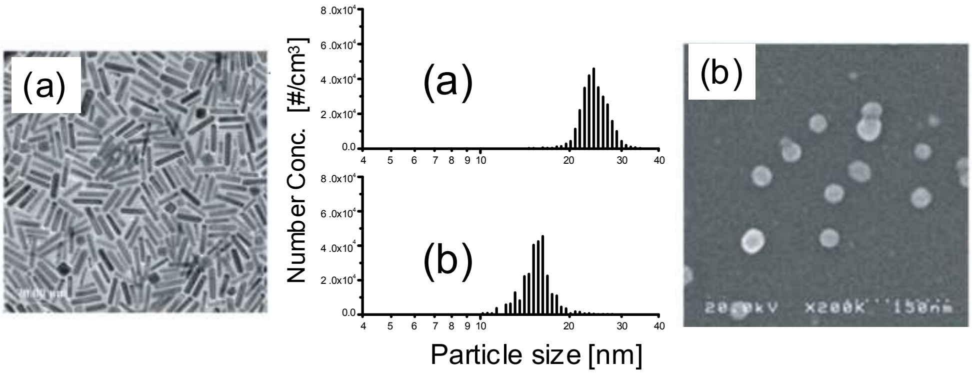


Fig.3 Morphology and size distribution of aerosol particles of gold (Au) after transferring the liquid-phase nano-rods in to the gas-phase with (a) room-temperature drying and (b) in-flight heating (800°C). *Note:* Non-spherical morphology of the gold became spherical through in-flight heating and its "smaller" particle size could be detected well by the newly-developed aerosol measurement system.

There is only a few studies concerning about the determination of size of non-spherical particles in the gas-phase (as well as in the liquid-phase). Our approach for sizing the non-spherical particles has being received a lot of citations from the other researchers in Japan and abroad. This is maybe also because the non-spherical gas-phase material such as asbestos is now becoming one of the most important issue for the human health related to the work environment.

In 2006-2007, we have been involved to the national project on Health Risk Assessment of Nanomaterials (Project Leader: Dr. Junko Nakanishi at AIST), and have been charged on the development of a novel spray method for converting the liquid-phase nanoparticles into the gas-phase in high concentration. We have succeeded to transfer the liquid-phase particle having average size of 120 nm in to three chambers (with 20 rats for each chamber) via gas-phase and our medical collaborator (at the University of Occupational and Environmental Health) had detected the existence of sample particles inside the rat and calculated the residence time of particles in the lung. This was the first study using the particles transferring via gas-phase and the rat had sucked the particles via its respiration route. Right now we are designing a novel spray generator for another inhalation exposure system.

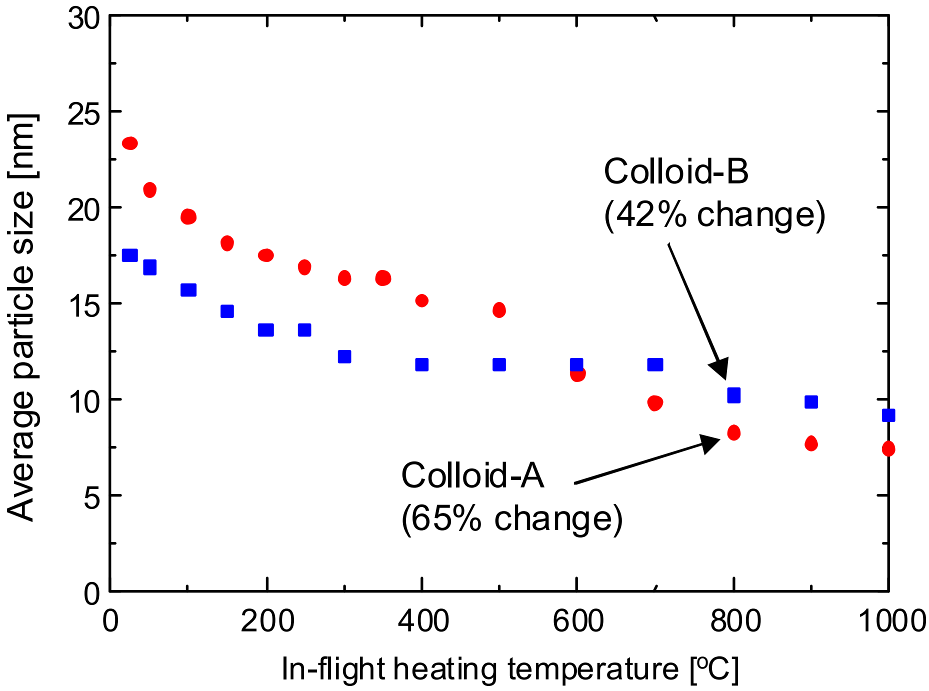


Fig. 4 Changes in sizes of two colloidal particles as a function of temperature. At 800°C, size decreases are 65% and 42% for A and B, respectively (the conventional thermal-analysis system can not detect this difference). From these results, it is clear that colloid-B has high thermal resistance comparing with that of colloid-A.

Potential impact on the environment

Development of the "world-first" and "the only" thermal analysis method for nanoparticle

An electrospray–furnace–scanning mobility particle spectrometer (SMPS) system was developed which is capable of rapidly and accurately measuring the size distributions of colloidal nanoparticles. Many colloidal suspensions require the use of nonvolatile surfactants to stabilize the suspensions. Nonvolatile materials coat colloidal particles and form residue particles during the electrospray process. A tubular furnace reactor is used to evaporate residue nanoparticles and coatings, which allows for correct nanoparticle size measurement. Test suspensions of silver, gold, and SiO_2 nanoparticles were measured in the electrospray–furnace–SMPS system. SMPS measurements and field emission scanning electron microscopy measurements were in excellent agreement for all test suspensions. High-temperature heating in the furnace was used to evaporate the nanoparticles themselves, which shifted the nanoparticle size spectra to smaller sizes, allowing for thermal analysis to be performed on colloidal suspensions in addition to size measurement (Fig.4).

For example, by comparing the results obtained from two different colloidal particles (Fig.4), it is clear that colloid-B has high thermal resistance comparing with that of colloid-A. This means that a device made by colloidal-B has more excellent performance (electrical, etc.) comparing with device-A. Without using a lot of "raw-materials" colloidal samples for measuring the performance of a device (made by materials from the colloids), through our approach with only a small volume of colloid, one can detect and understand the quantitative difference between several samples.

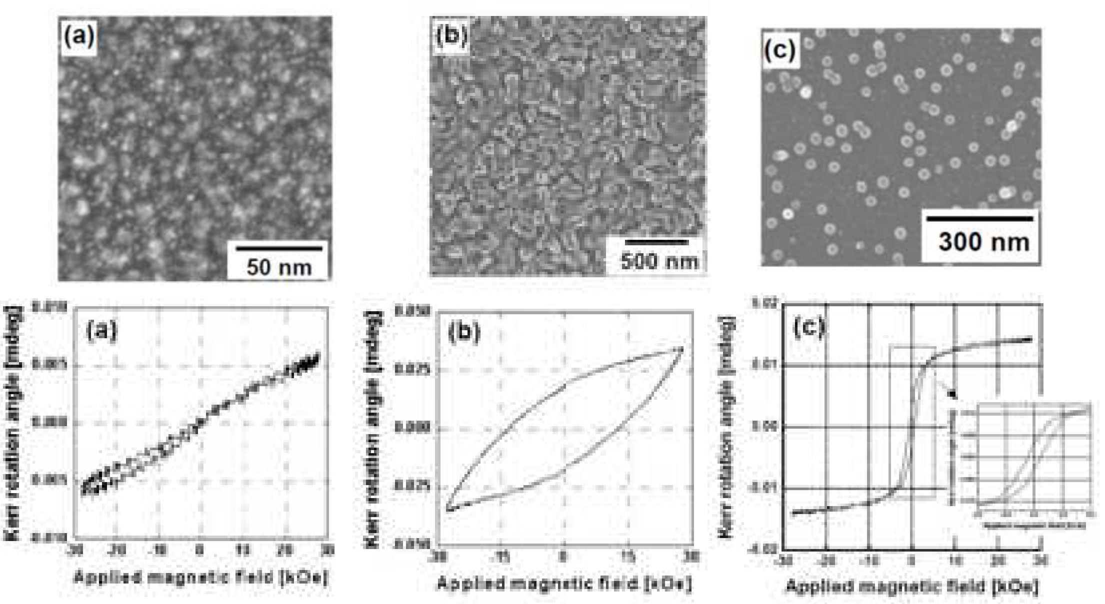


Fig.5 Morphology and magnetic properties of FePt colloidal particles prepared by different routes: (a) Pasting the colloids and then drying at room-temperature, (b) pasting the colloid and heating up to 800°C, (c) *in-flight* heating the colloid and deposition from the gas-phase. Note that (c) has the highest magnetic property.

Direct assembly method of nanoparticle layer with high-crystallinity

Because nanoparticles generated by electrospray are highly charged, one of the available applications is the formation of nanoparticulate thin film. I have been proposing two novel methods, (i) electrospray-preheating-deposition method and (ii) Electrospray-based selective deposition method for one-step formation of patterned area of nanoparticles in the flat surface.

The deposition monolayers of magnetic FePt nanoparticles via an electrospraying method and the magnetic properties of the deposited film were studied. FePt nanoparticles in a size of around 2.5 nm in diameter, prepared by a liquid process, were used as a precursor. The size of the deposited particles can be controlled up to 35 nm by controlling the sprayed droplet size that is formed by adjusting the precursor concentration and the precursor flow rate. The droplets were heated in a tubular furnace at a temperature of up to 900°C to remove all organic compounds and to transform the FePt particles from disordered face centered cubic (fcc) to an ordered FCT phase (this phase has magnetic property). Finally, the particles were deposited in the form of a monolayer film on a silicon substrate by electrostatic force. The monolayer of particles was obtained by the high charge on particles obtained during the electrospraying process. After measuring the magnetic properties of the monolayer, it is clear that this route has low energy-consumption comparing with the previous, conventional method (i.e. heat-treatment after pasting the colloidal materials on the substrate) as showed in Fig.5.

Direct-patterning of nanoparticle without using a vacuum system

Using the electrospray, a selective deposition of metal (Au) and oxide (SiO_2) nanoparticles with a size range of 10–30 nm on patterned silicon (wafer) substrate was performed. Electrical charging characteristics of particles produced by the electrospray and patterned area created by contact charging of the electrical conductor with non- or semi-conductors were investigated. Colloidal droplets were electrosprayed and subsequently dried as individual nanoparticles which then were deposited on substrates, and observed using field emission-scanning electron microscopy. The number of elementary charge units on particles generated by the electrospray was 0.4–148, and patterned area created by contact charging contained sufficient negative charges to attract multiple charged particles (Fig.6). Locations where nanoparticles were (reversibly) deposited depended on voltage polarity applied to the spraying colloidal droplet and the substrate, and the existence of additional ions such as those from a stabilizer (or a surfactant). Through this "writing technology" of nanoparticles, it is clear that here it is not necessary to use a vacuum system which needs also an extra energy for maintaining the vacuum (pump) environment. Also, our techniques did not need a "mask" or a template for patterning, therefore a mask-less technology is possible.

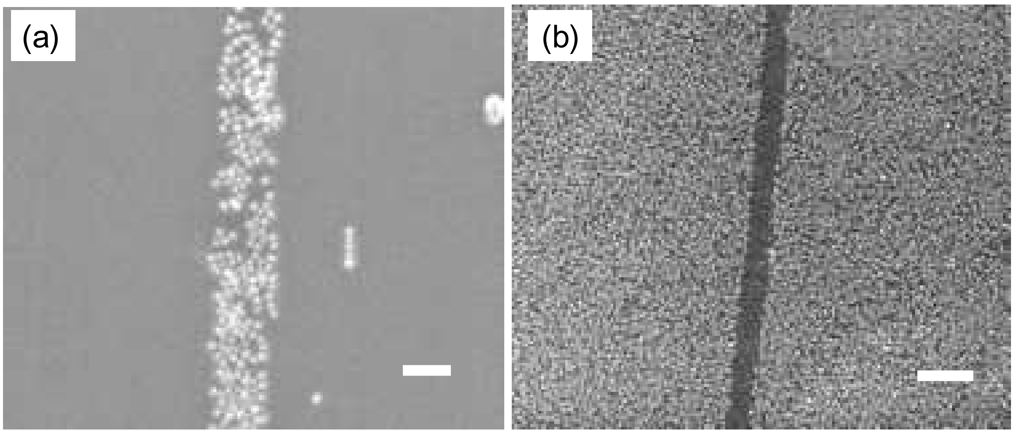


Fig.6. Colloidal nanoparticles can be dispersed in the gas-phase and deposited selectively and reversibly on a patterned substrate, by "plus/minus" electrospray and contact charge of the substrate. Bar length: 100nm (a) and 2μm (b)

Expected impact on society

We have combined chemical engineering, aerosol technology, and materials science to develop new strategies for environment/energy-particulate materials processing. Some novel methods have been developed, based on the electrospray-assisted transport and assembly of the nanoparticles from a liquid-sample in to the gas-phase, and by introducing the aerosol measurement technique which has high-resolution (sub-nm) for measuring *real-time* the size distribution of the particles. Through our studies on the "good" nanoparticles as advanced/functional materials and the "bad" nanoparticles as a size-controlled material for health-effect study, we hope the future study will enable us to control nanoparticles in the gas- and liquid-phase for more understanding the related (physical, chemical, biological) phenomena, and also to open the opportunities for innovative technology as well as fundamental science.

ACKNOWLEDGMENTS

Hiroshima members (K. Okuyama, W. N. Wang, Widiyastuti, H. Widiyandari, H. M. Lee, S. G. Kim, I. Matsui, T. Iwaki, F. Iskandar); Fukuoka members (T. Oyabu, Y. Morimoto, I. Tanaka); USA members (J. Fernandez de la Mora, P. Biswas, C. Hogan Jr.); Tokyo members (M. N. Naim, M. Kuwata, H. Kamiya); Korea members (T. O. Kim)

SPONSORS

New Energy and Industrial Technology Development Organization (NEDO);
Ministry of Economy, Trade and Industry, Japan (METI);
Japan Society for the Promotion of Science (JSPS);
Ministry of Education, Culture, Sports, Science and Technology.

REFERENCES

Deposition of TiO_2 nanoparticles in surfactant-containing aqueous suspension by a pulsed DC charging-electrophoresis	M. N. Naim, M. Kuwata, H. Kamiya, I. W. Lenggoro	Journal of the Ceramic Society of Japan, 2008
Colloidal nanoparticle analysis by electrospray size spectrometry with a heated flow	I. W. Lenggoro, H. Widiyandari, C. Hogan, Jr., P. Biswas, K. Okuyama	Analytica Chimica Acta, 585(2),193-201, 2007
Biopersistence of inhaled nickel oxide nanoparticles in rat lung	T. Oyabu, Y. Morimoto, M. Shimada, W. Lenggoro, K. Okuyama, I. Tanaka	Inhalation Toxicology, 19(S1), 55-58, 2007
Photoluminescence optimization of luminescent nanocomposites by spray pyrolysis of a colloid-solution precursor	W. N. Wang, W. Widiyastuti, I. W. Lenggoro, T. O. Kim, K. Okuyama	Journal of the Electrochemical Society, 154(4),J121-J128, 2007
Monolayer deposition of L10 FePt nanoparticles via electrospray route	H. M. Lee, S. G. Kim, I. Matsui, T. Iwaki, F. Iskandar, I. W. Lenggoro, K. Okuyama	Journal of Magnetism and Magnetic Materials, 313, 62-68, 2007
Nanoparticle assembly on “plus/minus” surfaces from electrospray of colloids	I. W. Lenggoro, H. M. Lee, K. Okuyama	Journal of Colloid Interface Science, 303, 124-130, 2006