Particle Size Measurement for Nanoparticles by Induced Grating Method Applied Dielectrophoresis

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An important method of conducting the particle size analysis of nanoparticles (NPs) in liquid phase relies on the principle of light scattering, such as dynamic light scattering, laser diffraction, and particle tracking analysis. The intensity of scattered light by NPs, however, sharply declines with decreasing particle size; it becomes difficult to measure with accuracy the size below a few tens of nanometer. To overcome this limitation, an alternative approach has been proposed; the method is called Induced Grating (IG). In principle, NPs tend to accumulate near an electrode array by dielectrophoresis when the electric field is applied, and it is inducing the density grating of NPs. Diffracted light due to NPs density grating can then be detected by the sensor. When the electric field is turned off, the diffraction intensity starts to decline due to the NPs diffusion from the accumulated position. During this relaxation time, the diffusion coefficient of NPs is to be obtained from the decay curve of the diffraction intensity and is converted to particle diameter using the Stokes–Einstein equation. In this study, we evaluate the performance of a new system named IG-1000 (Shimadzu) based on this IG principle against various NPs, such as polystyrene latex, colloidal silica and zinc sulfide NPs.

1. Introduction

The functions and performances of products made from fine particles sometimes strongly depend on the particle size and the particle size distribution (PSD) in the field of medicine, semiconductor and cosmetic products and so on. As this size information is important to produce novel materials, there are many particle size analysis (PSA) methods proposed for the range from a few nm to a few μm of particle size [1, 2]. One of them is the electron microscope, that is a transmission electron microscope (TEM) and a scanning electron microscope (SEM) in the vacuum, which can be gotten the particle morphology simultaneously. Regarding NPs dispersed in the gas phase, there is a scanning mobility particle sizer (SMPS) method which consists of differential mobility analyzer (DMA) and condensation particle counter (CPC) is as the standard PSA method ranging from a few

nm to a few μm. On the other hand, many PSA methods for liquid phase are proposed, such as dynamic light scattering (DLS) method, particle tracking analysis (PTA) method, laser diffraction (LD) method, ultra-centrifugal method and so on. In general, DLS can measure the particle size of monodispersed particles, while LD can measure PSD of polydispersed particles. When the particle size is decreasing blow 100 nm, however, the situation changes dramatically. The light scattered intensity for a particle below 100 nm which is called Rayleigh scattering, is proportional to sixth power of the particle diameter, and the scattered intensity becomes to be independent on a scattered angle. Therefore, when DLS or PTA is used for PSA of a few nm size particles, the scattered light intensity is not enough to measure. While, LD is used for PSA on NPs, no dependency of the scattered intensity on a scattered

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angle results in a trouble to measure PSD. That is to say, there is a desire to appear the PSA based on the new principle overcoming these problems.

In order to satisfy this desire, Induced Grating (IG) method was proposed from Shimadzu Corporation and a particle size measurement system IG-1000 was developed [3]. This system utilizes dielectrophoresis (DEP) phenomena for gathering particles and then calculates from the changes of the diffracted light intensity from the accumulated particles. Consequently, it can measure the particles ranging from a few nm to submicron. Kokubo et al. [4] measured successfully the size of fullerenol by IG-1000 and reported the measured size was consistent with the results of DLS and a scanning probe microscopy. In this paper, we used monodispersed polystyrene latex (PSL) particles to check the measurement principle of IG method and also measured polydispersed silica particles and zinc sulfide NPs with a few nm for evaluating the system IG-1000.

2. Theory

When the voltage of alternating electric (AC) field is applied, the NPs suspended in the solution are polarized and they move with the slope of the electric field, that is dielectphoresis (DEP). DEP works whatever the NPs are charged or not. The force of time average of DEP is expressed in Eq. (1) [5, 6].

$$\left\langle \overline{F}_{\text{DEP}} \right\rangle = \frac{\pi}{4} \varepsilon_{\text{m}} x^3 \, \text{Re}\left[K(\omega) \right] \nabla \left| \overline{E}_{\text{rms}} \right|^2 \qquad (1)$$

Where ε_{m} is dielectric constant of solvent, x is particle diameter, $\overline{E}_{\text{ms}}$ is effective electric field, and $\text{Re}\left[K(\omega) \right]$ is the real part of Clausius–Mossotti factor, $K(\omega)$, which is the function of the dielectric constants and conductivities of solvent and particles as well as frequency of applied voltage [7]. The amount of particles accumulated by DEP from Eq. (1) could be proportional to particle volume and square of electric field, and depends on Clausius–Mossotti factor.

When the comb-like electrodes are used, a space of each electrodes is located alternately as shown in Fig. 1, whose pitch is a. The alternating electric field is applied among the electrodes, and then a strong electric field gradient is foamed between the different polar electrodes. NPs gathered by DEP force are located periodically at the pitch of $2a$ (= Λ). This periodic accumulated particles distribution works as the induced grating, and makes the diffracted light. Although the electrodes themselves work as the induced grating, the grating pitch of the particle concentration distribution (Λ) is twice as much as the grating pitch of the electrodes (a), that is the diffracted light intensity results in getting independently, as shown in Fig. 1.

When the applied voltage for DEP is turned off, the diffraction intensity by NPs decreases, because accumulated particles diffuse into uniform particle concentration due to the particle concentration gradient made by DEP. The decreasing process of the diffraction intensity can be measured, and then the diffusion speed of NPs, that is the particle diffusion coefficient, could be calculated. The diffraction intensity for time $I(t)$ can be expressed as a following Eq. (3).
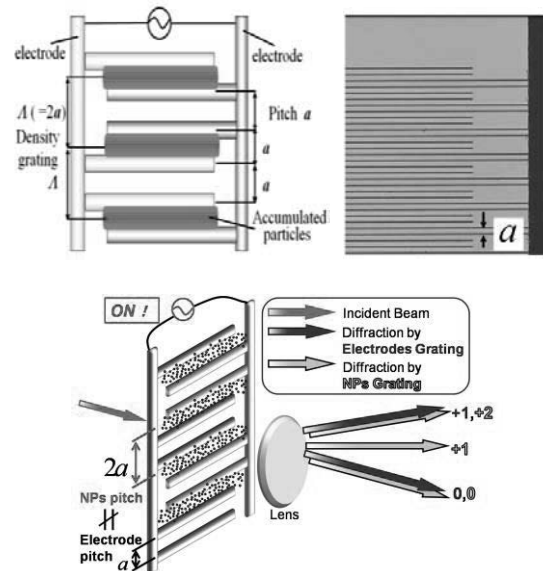

Fig. 1. Schematic diagram (left) and optical microscope photograph (right) of comb-like electrodes and image of accumulated particles and diffracted beams (bottom).

$$I(t) = I_0 \exp\left\{-2Dq^2(t-t_0)\right\} \qquad (2)$$

Where t_0 is the time when DEP is turned off after the particle accumulation process, I_0 is the initial diffraction intensity when DEP is turned off, D is diffusion coefficient of particle, q is defined using the pitch of electrode or of accumulated particles as expressed by Eq. (3).

$$q = 2\pi / \Lambda = \pi / a \qquad (3)$$

Then particle diameter x can be calculated by the Stokes–Einstein relationship, if each particles diffuse only by Brownian motion.

$$x = (k_B T) / (3\pi\eta D) \qquad (4)$$

Where k_B is Boltzmann constant, T is absolute temperature and η is viscosity coefficient. When the initial time t_0 is equal to zero, Eq. (2) is expressed as Eq. (5).

$$\ln\sqrt{I/I_0} = -Dq^2 t \qquad (5)$$

In order to compare Eq. (5) to experimental results, the relationship between $\sqrt{I/I_0}$ and t was shown as Fig. 2. The diffraction intensity increased during the time gathering NPs due to DEP as shown as the shadow area in Fig. 2. When the voltage was turned off after this period, i.e. the measurement time in Fig. 2 is zero, the diffraction intensity decreased gradually where the plotted keys are measured values and the lines are
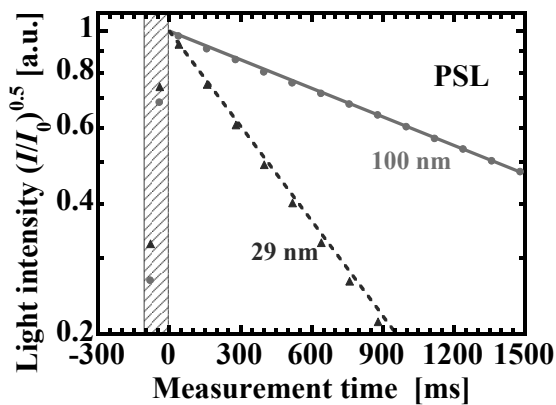

Fig. 2.   Diffracted light intensity of PSL particles with 29 or 100 nm diameter.   In the shaded area, the applied voltage was turned on, while the voltage was not applied in the other region.

calculation by Eq. (5). To compare the PSL particles of 29 nm and 100 nm diameter, the decreasing speed of 100 nm PSL was slower than that of 29 nm, because the diffusion coefficient of 100 nm PSL is smaller than that of 29 nm.

3. Experimental

All samples were dispersed in ultrapure water passed though ultrafiltration filter (pore size 0.22 μm, MILLIPAK 20, USA) and its particle concentration was prepared as about 0.01 – 0.3 wt%.   Sample solutions was prepared using the ultrasonication for 5 minutes with 28 kHz and 100 W (VS-100 III Sunpar, Iuchi, Tokyo, Japan) for dispersion and then sampled 0.3 mL by syringe for measuring.

3.1 Polystyrene latex particles

In order to check the performance of IG-1000 based on IG principle, we used monodispersed polystyrene latex (PSL) particles (STADEX, JSR, Tokyo, Japan).   Their nominal diameter were 29, 48, 76, 100, or 178 nm (STADEX SC-0030-A, SC-0050-D, SC-0075-D, SC-0100-D, SC-017-S), and sample concentration was 0.1 wt% of 29, 48, and 76 nm, 0.025 wt% of 100 nm, and 0.01 wt% of 178 nm. KCl solution was added to suspension to adjust the solution conductivity.

3.2 Colloidal silica particles

Colloidal silica particles of 0.2 wt% concentration with 10 – 20, 20 – 30 and 40 – 50 nm size were used, which were supplied form Nissan Chemical (Snowtex 20, 50, and 20L, Tokyo, Japan).   Spherical silica particles with much broad PSD (20 – 200 nm diameters) were also used as a polydispersed sample, and their concentration were changed from 0.15 to 0.3 wt% at the measurement. Fig. 3 shows the SEM image (inbox) and number-based PSD of polydispersed silica particles, which was obtained by the image analysis method from SEM photographs for counting about 100,000 particles. The volume-based PSD also indicates in Fig. 3, where a volume of each particle was calculated as the particle shape was assumed with

spherical.

3.3 *ZnS nanoparticles*

For the sample of smaller NPs, we prepared zinc sulfide NPs of about 2 nm size, and classified them by size using the size-selective precipitation technique [8, 9]. The samples were indicated by No. 0 (before classification) and were labeled from No. 1 to No. 8, which were corresponding with the cycle number of the classification operation. ZnS particles of No. 0, No. 2 and No. 5 were used, and the sample concentration was 0.2 wt%. The particle diameters by TEM image and an optical absorbance method [10] (Tight-binding, TB, method) were compared with the IG results.

4. Results and Discussion

4.1 *PSL particles*

The electric conductivity of suspending solution is one of the most critical parameters in the IG method, since it has a strong influence on the particle mobility under DEP. Fig. 4 shows the effect of solution conductivity on the average particle size x_S (from IG software) for a series of sample suspensions of 29 nm PSL with various conductivity and its Debye length λ_D calculated by assuming KCl concentration n_0 corresponding with solution conductivity.

$$\lambda_D = \sqrt{\left(\varepsilon_r\,\varepsilon_0\,k_B\,T\right)\big/\left(2\,n_0\,e_0^2\right)} \qquad (6)$$
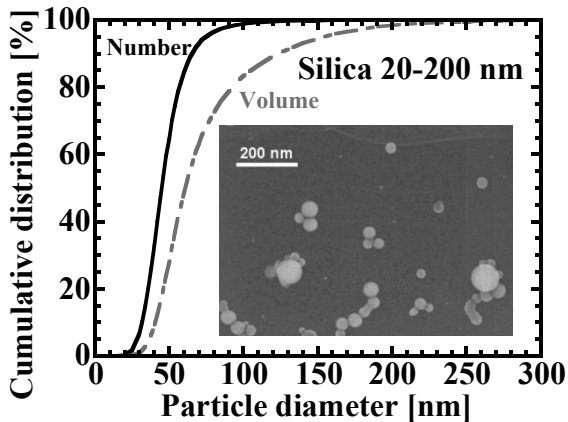

Fig. 3. Particle size distribution and SEM image of 20-200 nm silica particles. The solid line is number based PSD and the dash line is volume based PSD.

where e_0 is elementary charge, ε_0 is vacuum permittivity, and ε_r is relative permittivity of solution. At lower conductivities, the diameter of monodispersed particles sample was calculated considerably smaller than the nominal particle diameter. As the electrostatic repulsive forces due to the thick electric double layer (Debye length) strongly increased the particle motion, the diffusion rate or coefficient was overestimated, and then the particle diameter calculated by the Stokes–Einstein equation was underestimated. Increasing the conductivity, the electrostatic repulsion decreased due to the thin Debye length, and then x_S reached to the nominal particle diameter which was indicated as dotted line in Fig.4. However, when the conductivity of the solution became much higher conductivities, NPs could not accumulated near the electrode due to the weak DEP force, and IG method could not measure the particle diameter. There exists therefore an optimal conductivity range of sample solution for attaining reliable PSA.

Monodispersed PSL particles with various sizes from 29 to 178 nm were analyzed to give their sizes under the proper solution conductivity condition. Fig. 5 and Table 1 demonstrate that IG-1000 has the excellent performance system based on IG principle. Here, x_n is the nominal diameter reported from the manufacturer, x_S is obtained from the software mounted in IG-1000, and x_C is calculated from the slope of the decay curve of the diffraction intensity with Eq. (5). Both diameters
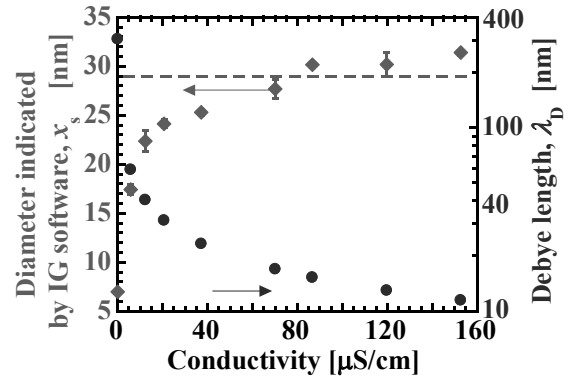

Fig. 4. Effect of solution conductivity on measured diameters and Debye length of the electric double layer.

estimated from IG method were agreed well with the nominal diameter within 5 % error.

4.2 *Silica particles*

Fig. 6 shows PSDs of colloidal silica samples measured by IG-1000 and comparing with the results measured from TEM images. The medium diameter of Snowtex 20 (10 – 20 nm), 50 (20 – 30 nm) and 20L (40 – 50 nm) was obtained as 14.4, 22.4, 41.2 nm from IG

Table 1.   Particle diameters of PSL obtained by various method.

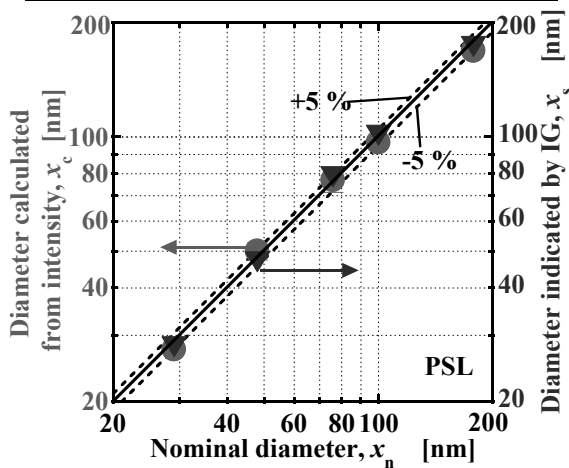| x_n [nm] (nominal)	x_C [nm] (calculated)	x_S [nm] (IG software)
29	27.5	28.0
48	50.0	46.9
76	77.0	78.5
100	96.8	101
178	169	173

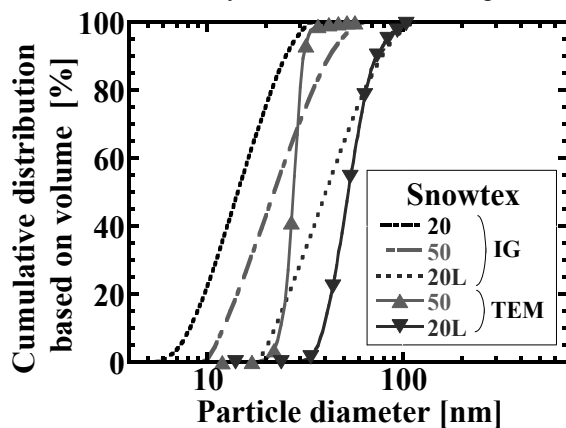Fig. 5. Comparison of nominal diameters with diameters measured by IG-1000 for each PSL particles.

Fig. 6. Particle size distribution of colloidal silica particles with size range of 10 – 20 nm (Snowtex 20), 20 – 30 nm (Snowtex 50), or 40 – 50 nm (Snowtex 20L).

software, respectively. These values were within their nominal size ranges. Compared PSD from IG with that by TEM, the medium diameter from IG was estimated as 5 nm smaller than that of TEM, besides the range of the distribution obtained by IG method was wider than nominal size range. These silica particles had not a complete sphericity, thus the particle diameter is the equivalent projected area diameter. Additionally, when it converts to the equivalent volume diameter, there is an assumption of a complete-spherical shape. Even though these assumptions can cause the discord of the 50 % diameter, it is impossible to explain the broadening particle size distribution from IG. Despite the monodispersed PSL particles have smaller CV values, it results that they have some of the distribution. From these results, IG software tends to calculate a relatively-narrow sample as a wider distribution, and this is one reason of the discord between IG results and TEM ones.

Fig. 7 shows PSD based on volume of spherical colloid silica particles with wider PSD (20 – 200 nm) by IG method together with the result of image analysis method used SEM images. IG method could be measured with reasonable accuracy as well, in close agreement with the SEM results. Besides it was also found that there was few effect of the particle concentration on the measurement results. From the results of Figs. 6 and 7, it seems that IG software could estimate a proper PSD for actual sample powder or colloid with wide size distribution.

4.3 *ZnS Nanoparticles with a few nm*

Zinc sulfide nanoparticles (ZnS NPs) of about 2 nm size were prepared by zinc acetate and sodium sulfide in dimethylformamide with 1-thioglycerol. ZnS NPs was classified by size using the size-selective precipitation technique [11]. Fig. 8 shows the average sizes of as-prepared sample (No. 0) and classified samples (No. 2, No. 5) measured by IG, TEM and an optical absorbance method based on the quantum size effect [12]. From these results, it was found that the size-selective precipitation

technique was able to classify ZnS NPs by their size. Additionally, we could also confirm that No.2 sample was larger than No. 0 and No. 5 was almost same as size as No.0, which indicated the IG method can measure the difference with sub-nanometer size. Since there was not so huge discord between IG and the others, it was found that IG method can measure the particle size with a few nm in liquid phase.

5. Conclusions

The new principle of PSA was proposed as the IG method. PSL particles with various uniform sizes from 29 nm to 178 nm could be analyzed their size by IG method, which could be indicated this method works with principle. When solution conductivity was low, however, particle size could be underestimated due to the

electrostatic repulsive force. Considering the results of the colloidal silica particles measured by IG method, the IG software could estimate as a proper PSD for actual powder or colloid with size distribution, while the software indicated a wider distribution than a true one for monodispersed or sharp size distribution samples. The average sizes of ZnS NPs with a few nm could also be obtained using IG method, and were relatively agreed well with particle size measured by TEM and the optical absorbance method based on the quantum size effect.
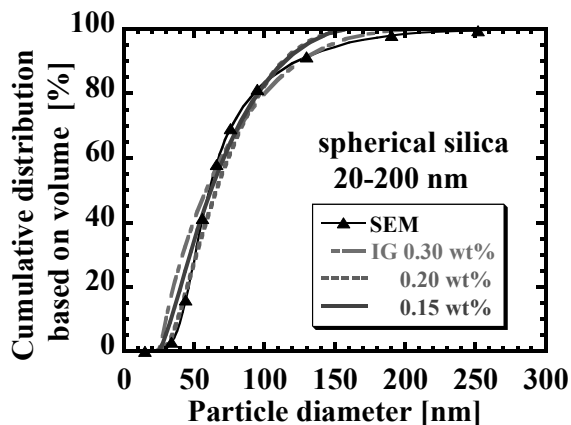
Fig. 7. Particle size distribution of colloidal silica particles with 20 – 200 nm size.
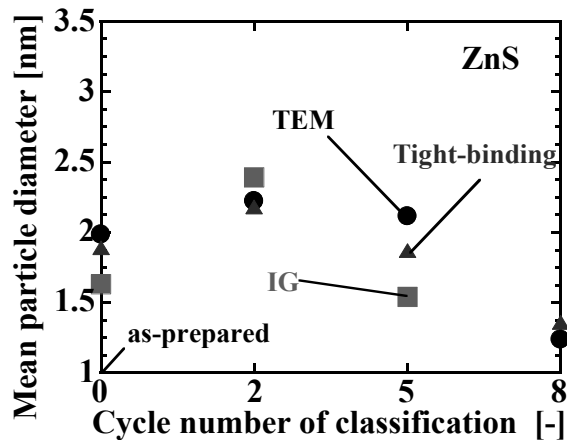
Fig. 8. Mean particle diameter of ZnS from TEM, Tight-binding and IG.

References

1) H. G. Barth, *Modern Methods of Particle Size Analysis*, (John Wiley & Sons.Inc., New York, 1984).

2) H. G. Merkus, *Particle Size Measurements*, (Springer, Alphen aan den Rijn, 2009).

3) Y. Wada, S. Totoki, M. Watanabe, N. Moriya, Y. Tsunazawa, J. Shimaoka, "Nanoparticle Size Analysis with Relaxation of Induced Grating by Dielectrophoresis", *Optics Express*, **14** [12], 5755-5764 (2006).

4) K. Kokubo, S. Shirakawa, N. Kobayashi, H. Aoshima, T. Oshima, "Facile and Scalable Synthesis of a Highly Hydroxylated Water-Soluble Fullerenol as a Single Nanoparticle", *Nano Research*, **4** [2], 204-215 (2011).

5) T. B. Jones, *Electromechanics of Particles*, (Cambridge University Press, Cambridge, 1995).

6) H. A. Pohl, *Dielectrophoresis*, (Cambridge University Press, Cambridge, 1978).

7) P. R. C. Gascoyne, J. Vykoukal, "Particle Separation by Dielectrophoresis", *Electrophoresis*, **23** [13], 1973-1983 (2002).

8) S. Komada, T. Kobayashi, Y. Arao, K. Tsuchiya, Y. Mori, "Optical Properties of Manganese-Doped Zinc Sulfide Nanoparticles Classified by Size Using Poor Solvent", *Advanced Powder Technology*, **23** [6], 872-877 (2012).

9) D. Segets, S. Komada, B. Butz, E. Spiecker, Y. Mori, W. Peukert, "Quantitative Evaluation of Size Selective Precipitation of Mn-Doped ZnS Quantum Dots by Size Distributions Calculated from UV/Vis Absorbance Spectra", *Journal of Nanoparticle Research*, **15** [4], 1486

(2013).

10) Y. Arao, Y. Hirooka, K. Tsuchiya, Y. Mori, "The Structure and Photoluminescence Properties of Zinc Sulfide Nanoparticles Prepared in a Clay Suspension", *Journal of Physical Chemistry, C*, **113** [3], 894-899 (2009).

11) Y. Mori, "Size-Selective Separation Techniques for Nanoparticles in Liquid", *KONA, Powder and Particle Journal*, **32**, 102-144 (2015).

12) S. Sapra, D. D. Sarma, "Evolution of the Electronic Structure with Size in II-VI Semiconductor Nanocrystals", *Physical Review B*, **69** [12], 125304, 1-7 (2004).