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Primary Particle Size Distribution Measurement of Nanomaterials by Using TEM

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Industrial applications of nano-particles are reported in many fields recently. Regulation of nano-materials is also discussed in Organization for Economic Co-operation and Development (OECD). European Union (EU) announced the definition of nano-material in 2012. According to EU definition, nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm. They also announced that particle size should be considered the primary particles in agglomerates or aggregates. For regulatory purposes, it is necessary to measure the size distribution of nano-particles based on the number concentration. European Food Safety Authority (EFSA) recommended using at least two different analytical methods to identify nano-materials for this EU regulation, and one of which should be electron microscopy [1]. Transmission electron microscope (TEM) is the most useful techniques that can give precise information on shape and size of the primary nanoparticles. In this study, for the regulatory use of particle size measurement by TEM, a primary particle size distribution of nano-particles by TEM was performed, and the counted particle number was statistically examined.

Polystyrene latex (PSL) nano-particle dispersion was used as the model material of the mono-dispersed case, and titania (TiO2) nano-particle dispersion was used as the aggregate case. A microgrid with carbon support membrane was used for TEM specimen. The carbon membrane surface of a microgrid was made hydrophilic by plasma-treatment. Filter paper was placed on a hot plate that has been warmed at 100°C, and the hydrophilized microgrid with support membrane was placed on the top of this. The test material dispersion of 12μL was collected using a micropipette, and dripped onto the microgrid with support membrane on the hot plate. Then the microgrid with support membrane was dried. A Carl Zeiss EM-922 TEM was used with acceleration voltage of 200kV. Images of PSL and titania particles were taken at a resolution of 0.1964nm/pixel and 0.1529nm/pixel, respectively. Particle size of each nano-particle was obtained by using Image-J software. Primary particle of titania aggregate was distinguished by tracing manually.

Typical TEM image of PSL was shown in Figure 1. PLS particles are spherical. Small particles with size of 1 nm, which are attaching on a surface of PLS particles are chemical dispersant. An equivalent circle diameter (ECD) was obtained from projection area of each particle. ECD distribution, which was obtained by counting particles of 1130 was shown in Figure 2 (a). Particle size has wide distribution between 25 and 62 nm. Counted particle number dependence of mean diameter, standard deviation, and mean standard error were shown Figure 2 (b), (c), and (d), respectively. Mean diameter shows the value of 44±0.5 nm with the ranging between 50 and 1130 of counted particle number. Standard deviation is converging to the value of 5.7nm with increasing the counted particle number. It is thought that counting more 300 particles is enough to get a sufficient standard deviation. On the other hands, mean standard error decreases rapidly with increasing counted particle number of 300, and that decreases slightly with counted particle number of more than 500 particles. Therefore, counting more than 500 particles is needed for the sufficient accuracy of size distribution.

The same tendency is obtained from aggregated titania case, whose diameter is determined by a manual tracing of each primary particle. We summarize that counting diameter at least 500 particles is requested for the reliable particle size distribution.

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References

[1] E.A.J. Bleeker *et al,* RIVM Letter report 601358001(2012).

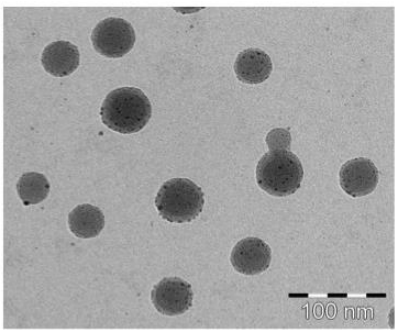

Figure 1. Typical TEM image of PSL particles

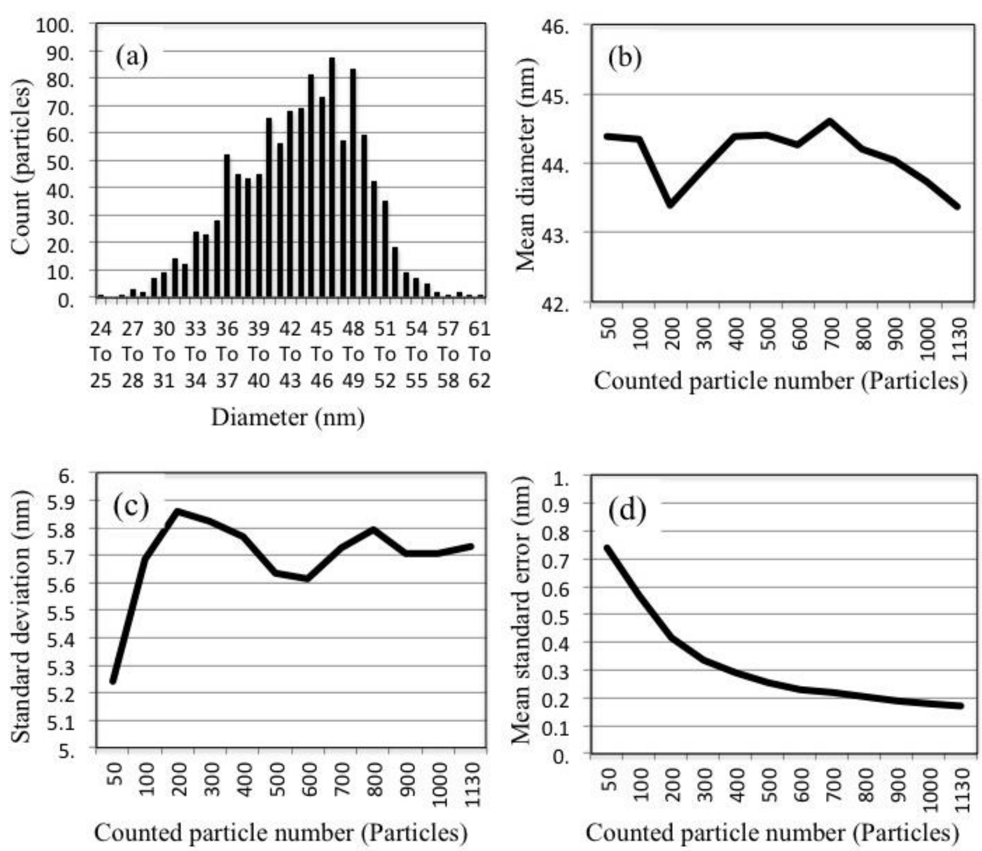

Figure 2. Primary size distribution of PSL particle (a). Counted particle number dependence of mean diameter (B), standard deviation (c), and mean standard error (d), respectively.