**Novel sample preparation to improve the accuracy of nanoparticle size distribution measurement by electron microscopies**

Kumagai, K.[1], Akai, S.[2], Handa, N.[2], Kitamura, S.[2], Manabe, H.[2] and Kurokawa, A.[1]

[1] National Institute of Advanced Industrial Science and Technology, Japan, [2] JEOL Ltd., Japan

Size distribution of nanomaterial is increasingly important property for the regulations based on "nanomaterial" definition as well as a quality index of products. While there are many possible techniques to obtain the size distribution, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are regarded as one of the most realistic solution, due to their capability to visualize individual particles. In the size distribution measurements by these microscopies, the specimen preparation is the key to achieve reliable result because of their nature as imaging methods. To minimize ambiguity in the measurement, particles should be (1) uniformly placed over a specimen holder with no localization in particle size and number, or (2) placed only in a small area without agglomeration or overlapping that allows us to count all particles in the area. To achieve these conditions is, however, not so easy due to localization and agglomeration of nanoparticles in preparation process. Thus, we have worked on the development of the sample preparation techniques.

This paper presents a new sophisticated sample preparation instrument for nanoparticle observation by SEM/TEM. We adopted a combination method of inkjet and freeze-drying to realize the specimen preparation satisfying the condition (2) above. The instrument consists of a movable inkjet head attached to x, y and z-axis manipulator and a vacuum chamber, in which a specimen holder is placed on a cooling unit (Fig. 1). The inkjet head can eject droplets, as small as several tens of picoliter, of water suspension of nanoparticles onto specified positions of a cooled substrate. The droplets get immediately frozen after landing keeping the dispersing state of the suspension, and then dried in vacuum by evacuating the chamber so that dispersed particles are deposited on the substrate.

Figure 2 shows a SEM image for an example of specimen preparation for a suspension of calcium carbonate nanoparticle. As shown in Fig. 2a, droplets were ejected one by one at the center of holes of a TEM grid with support film in good reproducibility. The particles are uniformly spread in the area about 100 m in diameter, not forming either ring-shaped localization, so-called "coffee ring" effect (Fig. 2b) or serious overlapping (Fig. 2c). Since the particles are confined only in the limited area, it is possible to measure all particles in single droplet by stitching observation within a realistic time frame (only several hours) as shown in Fig. 3. Furthermore, the number concentration of nanoparticle in suspension can be obtained by determining the volume of single droplet via gravimetry.

We have demonstrated that our technique is effective to transfer nanoparticles in suspension to a substrate keeping their dispersion state. These specimens enable us to observe clearer images and to perform more reliable size distribution measurement of nanoparticles by electron microscopies.

**Acknowledgement** This research was supported by the "Bridging R&D and Business Promotion for Small and Medium-Sized Enterprises Project" in New Energy and Industrial Technology Development organization (NEDO), Japan.

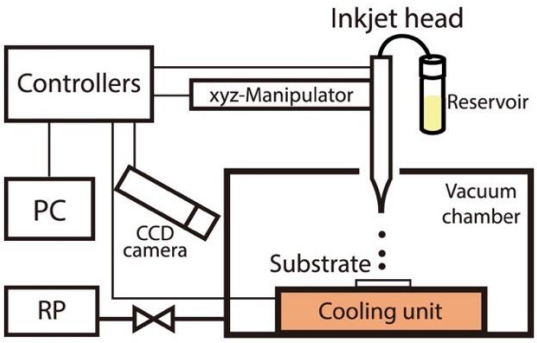


Figure 1 The schematics of the sample preparation instrument

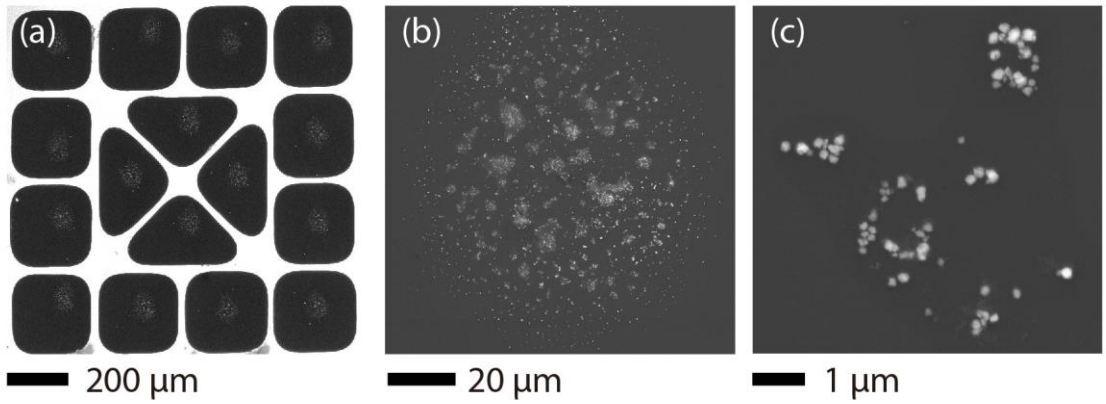


Figure 2 Secondary electron images for calcium carbonate nanoparticle prepared by the sample preparation instrument

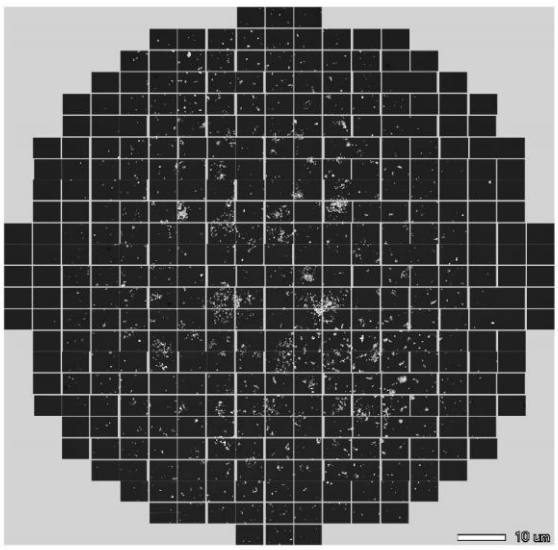

Figure 3 An example of stitching SEM observation for the whole area of a droplet.