Extended Abstract of PSA-19

P-13

Detection method for ring-shape agglomerations formed by drying nanoparticle-dispersed droplet

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The detection method for the ring-shaped agglomerations of nanoparticles (NPs) on a microgrid surface is described. The ring distribution of NPs is typically formed by naturally drying the droplet of nanoparticle-dispersed water. Fluorescent (FL) NPs dispersed in water and an FL microscope were used for the identification of the ring formation. With this method, the reduction of the ring formation was observed by a freeze-drying specimen preparation. The comparison with the transmission electron microscope image showed that this method gives not only for ring-shape detection but also for the evaluation of the particle-density homogeneity.

1. Introduction

The size distribution of manufactured nanoparticles (NPs) is one of the most important properties because it controls their material characteristics and the reproducibility of the product. According to the EC recommendation of the nanomaterial definition [1], we need to measure particle-size distribution to determine if they are nanomaterial. The scanning electron microscope (SEM) and transmission electron microscope (TEM) have enough spatial resolution to identify a single nanoparticle, therefore, they have been expected to be effective measurement tools to derive a reliable size distribution.

To observe NPs dispersed in water with the electron microscope (EM), typically, one drop of the liquid is put on an EM microgrid and is dried out naturally. The problem of this specimen preparation method is that NPs tend to make a ring-shape agglomeration, known as a 'coffee ring effect' [2]. The ring is the stack of NPs, and its formation disturbs appropriate EM observations. Therefore, ring-free specimen preparation is necessary. We have studied a freeze-drying method to prepare EM specimen [3].

The freeze-drying method has many parameters, such as the temperature and the surface treatment of EM microgrid, volume and NP concentration of the droplet, and dispersant, etc. For optimizing these parameters, we need a series of trial and error experiments until no ring-formation was observed. But EM analysis is a rather precise and a time-consuming method. This is because EMs need high magnification to identify several tens of nanometer-sized particles, while the droplet area has nearly several hundred micrometers in diameter.

Therefore, a better observation method was needed to determine if the ring was formed. In this study, we have proposed a fluorescent (FL) maker method to identify the ring-shaped agglomeration.

2. Experimental methods

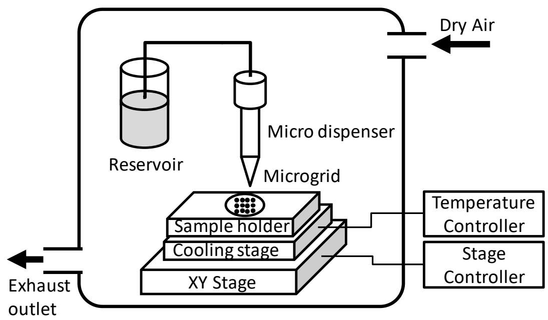
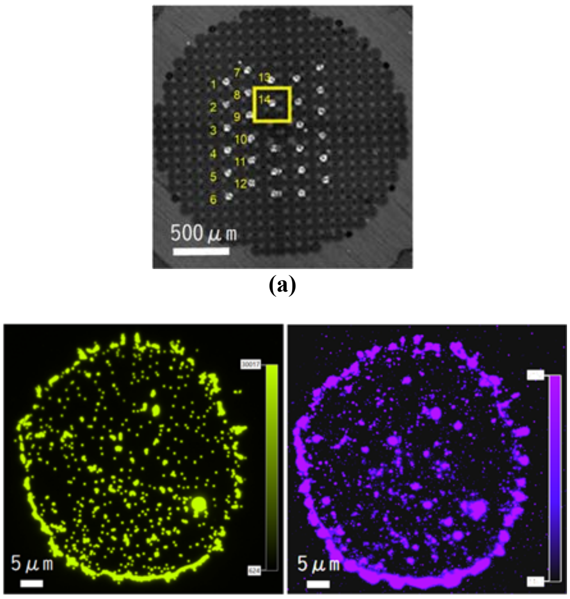


Fig. 1 Schematic view of the specimen fabrication system. The box was filled with dry air.



(a)

(b) (c)

Fig. 2 FL image of freeze-dried droplets on an EM microgrid. The droplet of No.14 (in square) shows the distribution of particles with the diameter of 150 nm in (b) (green color) and that of 70 nm in (c) (blue color).

The specimen of the freeze-drying droplet was fabricated using the equipment as shown in Fig. 1., which was equipped with a micro dispenser head to drop a tiny droplet of NP suspension with a volume of 70 pL. An EM microgrid covered with a high polymer film (ELS-C15, STEM Co., Ltd, Japan) was plasma-cleaned and was put on a cooling stage. The sample holder could be cooled down to about –40°C in a low-humidity environment. The dropping points on the microgrid were controlled by an XY moving system. After fabrication of frozen droplets by dropping on the cooled microgrid, the air in the chamber was pumped out to sublimate the ice of the droplets leaving NPs on the microgrid.

The liquid sample of the NP suspension was water-dispersed polystyrene microspheres (Estapor, Merck KGaA, Germany) with diameters of 70 nm (F-U007, blue fluorochrome) and of 150 nm (XC-015, green fluorochrome). The mixture of these microspheres with the mix ratio of 1:1 in number concentration was prepared. Their number concentrations were 3×10^{10} NP/mL. The FL images with four million pixels were derived by an FL microscope (BX53, Olympus Co, Japan). Typical image acquisition time was 5 sec.

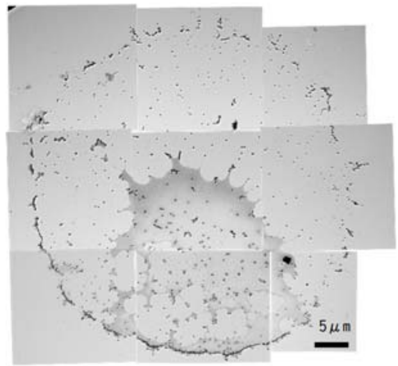


Fig. 3 TEM image of the freeze-dried droplet in Fig. 2(b). Accelerating voltage was 120 kV.

3. Results

The 29 droplets were put on an EM microgrid and freeze-dried. Their FL images are shown in Fig. 2. Both images of the NPs with a diameter of 70 nm and of 150 nm indicate nearly the same ring shape. It was not like conventional natural-drying methods which form the different particle distribution for the different particle diameter. Thus, the freeze-drying method will give benefit to EM analysis.

The TEM result of Fig. 3 showed the particles accumulated at ring position made up 40% of the total, and Fig. 2 showed FL microscope was able to detect this ring formation. The bright spots in Fig. 2 almost assigned to the particles in Fig. 3. Then the homogeneity of the particle-density inside a ring is possibly evaluated from the FL image.

4.Conclusion

We described the FL marker method to detect a ring-shaped NP agglomeration formed by drying a droplet of NP suspended water. This method will be useful to optimize the parameters of freeze-drying methods.

Homogeneously distributed NP specimen will be useful for NP analysis methods with surface sensitivity such as XPS since the stack of NPs will be reduced.

5. References

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