Onsite aerosol measurements for various engineered nanomaterials at industrial manufacturing plants

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Abstract. Evaluation of the health impact of and control over exposure to airborne engineered nanomaterials (ENMs) requires information, inter alia, the magnitude of environmental release during various industrial processes, as well as the size distribution and morphology of the airborne ENM particles. In this study, we performed onsite aerosol measurements for various ENMs at industrial manufacturing plants. The industrial processes investigated were the collection of SiC from synthesis reactors, synthesis and bagging of LiFePO$_4$, and bagging of ZnO. Real-time aerosol monitoring using condensation particle counters, optical particle counters, and an electrical low-pressure impactor revealed frequent increases in the number concentrations of submicron- and micron-sized aerosol particles, but few increases in the number concentrations of nanoparticles. In the SEM observations, a large number of submicron- and micron-sized agglomerated ENM particles were observed.

1. Introduction
Although engineered nanomaterials (ENMs) have many potential benefits for society, there is growing concern about their potential impact on health [1]. A significant exposure route is inhalation of airborne ENMs during manufacture and handling. Information on airborne ENMs, such as the magnitude of release and the industrial processes involved, as well as particle size distribution and morphology, is required in order to evaluate and control ENM exposure [2].

In this study, we performed onsite aerosol measurements for various ENMs at industrial manufacturing plants. The processes investigated were the collection of silicon carbide (SiC) from synthesis reactors, synthesis and bagging of lithium iron phosphate (LiFePO$_4$), and bagging of zinc oxide (ZnO). The investigations were conducted in collaboration with the National Institute of Occupational Safety and Health, Japan (JNIOSH). However, this paper presents only the results obtained by the National Institute of Advanced Industrial Science and Technology (AIST).

2. Methods

2.1. Real-time aerosol monitoring
The number concentrations and size distributions of aerosol particles were measured using real-time aerosol monitoring instruments, viz., condensation particle counters (CPCs; model 3007; TSI Inc., USA; 10 to >1000 nm), optical particle counters (OPCs; Handheld 3016; Lighthouse Worldwide Solutions Inc., USA; optical diameters of >300, >500, >1000, >3000, >5000, and >10000 nm), and an
electrical low-pressure impactor (ELPI; Dekati Ltd., Finland; aerodynamic diameters of 7–10000 nm, 12 channels). A stainless pipe and conductive silicone tubing were used to transmit the particles from the sampling point around the work area to the measuring instruments. The sampling flow rates of the CPC, OPC, and ELPI were 0.7, 2.8, and 10 L/min, respectively, and the average time was 10 s per sample.

2.2. Filter sampling and electron microscope observation
The aerosol particles were collected on a Nuclepore membrane filter (diameter of 25 mm; pore size of 0.080 µm; Nomura Micro Science Co. Ltd., Japan) with a stainless steel filter holder (available filtration area of 380 mm²; KS-25F; Advantec Toyo Kaisha Ltd., Japan) for electron microscopy analysis. The sampling flow rate was set at approximately 1–2 L/min. A stainless pipe and conductive silicone tubing were used to transmit the particles from the sampling point around the work area to the sampling filter.

The aerosol particles collected on the Nuclepore filters were observed using a field-emission scanning electron microscope (SEM; S-4300; Hitachi High-Technologies Corporation, Japan) under an accelerating voltage of 1 kV. Before the SEM observation, the samples mounted on SEM grids were coated with platinum–palladium (approximately 1 nm) to avoid image charging.

2.3. Processes investigated
We performed onsite aerosol measurement for ENMs at industrial plants manufacturing ENMs during the following processes.

2.3.1. Collection of SiC from synthesis reactors. During the collection of SiC from two reactors after synthesis by thermal plasma chemical vapor deposition, the aerosol particles at a site near to the work area (approximately 50–100 cm) and at a site far from the work area (approximately 5 m) were measured simultaneously. Because the room had a ventilation system with a high efficiency particulate air (HEPA) filter, the aerosol particle concentrations in the room during nonworking periods were generally low. The representative characteristics of SiC provided by the manufacturer are as follows: the average primary particle diameter is 30 nm and the specific surface area is 50 m²/g.

2.3.2. Synthesis and bagging of LiFePO₄. LiFePO₄, which is used as the cathode materials in lithium-ion batteries, is synthesized by sintering a precursor material; the nature of this material is confidential. Aerosol particles were measured at a distance of approximately 60 cm from the work area where the synthesized LiFePO₄ was being bagged (11:00–13:20) and approximately 100 cm from the work area where the precursor material was being filled into containers and weighed (13:20–15:20). In addition, the aerosol particles in the air entering through the outside air intake were simultaneously measured. Both LiFePO₄ and precursor material mainly consist of the primary particles with a diameter of approximately a hundred to a few hundred nanometers.

2.3.3. Bagging of ZnO. When the synthesized ZnO was being bagged, aerosol particles at a distance of approximately 50–100 cm from the work area and outdoors were measured simultaneously. Although the hoppers of ZnO were automatically emptied into drums, which were lined with plastic bags, the processes of disconnecting the bags containing the synthesized ZnO from the hopper outlets, sealing the bags, and connecting the empty bags in the drums to the hopper outlets were performed manually. The bagging began at 10:00 and ZnO was filled into ten drums during a period of three hours, i.e., till 13:00. The primary particle diameter was a few tens of nanometers as observed through the SEM (see section 3.2).
3. Results

3.1. Particle number concentrations and size distributions of released airborne ENMs

3.1.1. Collection of SiC from synthesis reactors. Figure 1 shows the changes in the particle number concentrations measured by the CPCs and OPCs. When collecting SiC from the two synthesis reactors (first: 10:54–11:05 and second: 11:10–11:17), the number concentrations of micron-sized particles increased, whereas those of nano- and submicron-sized particles did not.

Figure 2 shows the particle size distributions during the SiC collection (highest 10-s-average concentration at 11:10) and before it (i.e., the average concentration in the period 10:42–10:54) at the site near to the work area measured by the ELPI and OPC. Figure 2 indicates that the number concentrations of particles with a diameter greater than a few hundred nanometers were higher during the collection process than before.

Figure 1. Changes in the particle number concentrations at a site near to and at a site far from the work area where SiC was collected from the synthesis reactors.
3.1.2. Synthesis and bagging of LiFePO₄. Figure 3 shows the changes in the particle number concentrations measured by the CPCs and OPCs near the work areas where the synthesized LiFePO₄ was bagged (11:00–13:20) and where the precursor material was filled into containers and weighed (13:20–15:20) and outdoors (11:00–15:20). The number concentrations of submicron- and micron-sized particles increased when a bag containing LiFePO₄ was being disconnected from the hopper outlet and sealed (11:35 and 12:50) and when filling and weighing the precursor material (11:40–11:52, 14:00–14:24).

Figure 4 shows the particle size distributions during the bagging of LiFePO₄ (highest 10-s-average concentration at 11:35) and before it (i.e., the average concentration in the period 11:20–11:34) near the work area measured by ELPI and OPC. Figure 5 shows the particle size distributions during the filling and weighing of the precursor material (i.e., the average concentration in the period 14:00–14:24) and before it (i.e., the average concentration in the period 13:50–14:00) near the work area measured by the ELPI and OPC. Figures 4 and 5 indicate that the number concentrations of particles with a diameter greater than several hundred nanometers increased when LiFePO₄ was being bagged and when filling and weighing the precursor material.
Figure 3. Changes in the particle number concentrations near the work areas where synthesized LiFePO$_4$ was bagged (11:00–13:20) and where the precursor material was filled into containers and weighed (13:20–15:20) and outdoors (11:00–15:20).

Figure 4. Particle size distributions during and before the bagging of LiFePO$_4$. Particle sizes are expressed in terms of aerodynamic diameter for ELPI and optical diameter for OPC.
3.1.3. Bagging of ZnO. Figure 6 shows the changes in the particle number concentrations measured by the CPCs and OPCs near the work area and outdoors during the bagging of ZnO (10:00–13:00). The number concentrations of micron-sized particles were slightly higher near the work area than outdoors.

Figure 7 shows the particle size distributions during the bagging of ZnO (highest 10-s-average concentration at 11:15) and before it (i.e., the average concentration in the period 9:55–10:00) near the work area measured by the ELPI and OPC. The number concentrations of micron-sized particles during the bagging of ZnO were slightly higher than those before.
Figure 6. Changes in the particle number concentrations near the work area and outdoors during the bagging of ZnO.

Figure 7. Particle size distributions during and before the bagging of ZnO. Particle sizes are expressed in terms of aerodynamic diameter for ELPI and optical diameter for OPC.
3.2. Morphology of released airborne ENMs

Figure 8 shows the SEM images of the aerosol particles collected during each process. A large number of submicron- and micron-sized ENM aggregates/agglomerates were observed.

![SEM images of the aerosol particles collected during each process.](image)

**Figure 8.** SEM images of the aerosol particles collected during each process. A: Collection of SiC from synthesis reactors, B: Synthesis and bagging of LiFePO₄, C: Bagging of ZnO

4. Conclusions

In onsite aerosol measurements for ENMs at industrial manufacturing plants, increases in the number concentrations of submicron- and micron-sized aerosol particles were generally observed, whereas few increases in the number concentrations of nanosized particles were observed. Although the relatively high background concentration of nanosized aerosol particles may have prevented the detection of a small amount of released nanosized aerosol particles, we can at least be certain that the number concentration of nanosized particles released during these processes was substantially lower than the background concentration. In the SEM observations of the aerosol particles collected during each process, a large number of submicron- and micron-sized ENM aggregates/agglomerates were observed.

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References

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