Emission Monitoring in the Production of SiC Nanoparticles by Induction Plasma Synthesis

Jelena Buha[1,2], Drew Thompson[3], Marc Leparoux[4], Christian Jäggi[4], David Y.H. Pui[3] and Jing Wang[1,2]

[1]*Institute of Environmental Engineering, ETH Zurich, 8093 Zurich, Switzerland;*

[2]*Analytical Chemistry, Empa, 8600 Dubendorf, Switzerland;*

[3]*Particle Technology Laboratory, University of Minnesota, 55414 Minneapolis, USA;*

[4]*Laboratory for Advanced Materials Processing, Empa, 3602 Thun, Switzerland*

Safety of nanomaterials is of growing concern as it becomes more common for consumer goods to utilize them. Key to evaluating the potential health risks posed by nanomaterials is the nature of inhalation exposure to airborne engineered nanoparticles. This is not only needed for establishing safer nanomaterial work practices, toxicology studies also require doses relevant to actual workplace exposures. The few reports[1, 2] of workplace exposures suggest that engineered nanomaterials are released at high mass and/or number concentrations only under unusual circumstances. However, there still exists the need for study of exposure levels to different engineered nanomaterial types in occupational and environmental settings.

In this study aerosol emissions were monitored at a research laboratory during the production of silicon carbide (SiC) nanoparticles by inductively coupled plasma (ICP) synthesis. Regarding the emission studies, the filtration unit was used to collect small quantities of nanoparticles on the surface of a filter. The filter cartridge contained metal filters which were backpulsed to remove caked nanoparticles. This system was used to collect larger quantities of nanoparticles. Further on, real-time aerosol instruments were used to monitor particle concentration and size distribution. By looking for relative changes in size and concentration, while also considering particle sources, it was possible to monitor a nanoparticle release. Instrumentation that was included was: fast mobility particle sizer (FMPS), handheld condensation particle counter (CPC), nanoparticle surface area monitor (NSAM) and aerodynamic particle sizer (APS). Area sampling with track-etched polycarbonate filters was done for particle identification by scanning electron microscopy (SEM).

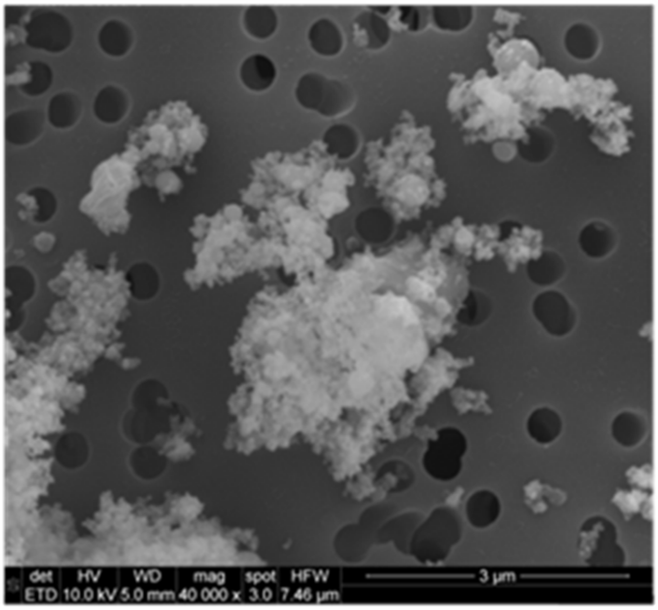

Figure 1. SEM image of SiC agglomerates sampled during the cleaning of the production filter with a compressed air gun

The use of direct-reading particle instruments was found to be effective. No particles were released during the synthesis of SiC nanoparticles due to the reactor being operated in a closed system under slight vacuum. However, aerosol emissions were identified in other related production tasks. A release of submicrometer particles was detected when a nanoparticle collection filter was disconnected from the reactor system. When compressed air was used for cleaning in open spaces, such as the cleaning of the nanoparticle collection filters in a ventilated walk-in enclosure, emissions of submicrometer particles were identified and particle number concentrations exceeded 250,000 #/cm^3. Particle emissions in this facility were found to be largely submicrometer and exhibited a mode size of approximately 170 nm. Observation of filter samples under scanning electron microscope confirmed that the particles released were agglomerates of SiC nanoparticles (Figure 1).

1. Wang, J., et al., *How can nanobiotechnology oversight advance science and industry: examples from environmental, health, and safety studies of nanoparticles (nano-EHS).* Journal of Nanoparticle Research, 2011. **13**(4): p. 1373-1387.

2. Walser, T., et al., *Exposure to engineered nanoparticles: Model and measurements for accident situations in laboratories.* Science of The Total Environment, 2012. **420**(0): p. 119-126.

Emission Monitoring in the Production of SiC Nanoparticles by Induction Plasma Synthesis

Jelena Buha[1,2], Drew Thompson[3], Marc Leparoux[4], Christian Jäggi[4], David Y.H. Pui[3] and Jing Wang[1,2]

[1]Institute of Environmental Engineering, ETH Zurich, 8093 Zurich, Switzerland; [2]Analytical Chemistry, Empa, 8600 Dubendorf, Switzerland; [3]Particle Technology Laboratory, University of Minnesota, 55414 Minneapolis, USA; [4]Laboratory for Advanced Materials Processing, Empa, 3602 Thun, Switzerland

Introduction

Environmental Health and Safety of nanomaterials are of growing concern as it becomes more common for consumer goods to utilize nanomaterials. For a risk to be posed, both hazard and exposure need to be present. The hazard is determined by toxicology studies. Exposure is determined by exposure assessments. Key to evaluating the potential health risks posed by nanomaterials is the nature of inhalation exposure to airborne engineered nanoparticles. This is not only needed for establishing safer nanomaterial work practices, toxicology studies also require doses relevant to actual workplace exposures. In this study aerosol emissions were monitored at a research laboratory during the production of silicon carbide (SiC) nanoparticles by inductively coupled plasma (ICP) synthesis.

Methods

By looking for relative changes in size and concentration, while also considering particle sources, it is possible to monitor for a nanoparticle release. Following real-time aerosol instruments were used to monitor particle concentration and size distribution:

Fast Mobility Particle Sizer (FMPS) [5.6 – 560 nm];

P-Trak Ultrafine Particle Counter 8525 [1 – 1000 nm];

Handheld Condensation Particle Counter (CPC) [10 – 1000 nm];

Nanoparticle Surface Area Monitor (NSAM) [10 – 1000 nm];

Aerodynamic Particle Sizer (APS) [0.5 – 20 µm].

Additionally, area sampling with track-etched polycarbonate filters was done for particle identification by electron microscopy.

Figure 1. Left: An image of the ICP setup; ***Right***: A photograph demonstrating that the cleaning of the production filter resuspended high concentrations of SiC particles

Results

In this study the synthesis of SiC nanoparticles in a prototype ICP reactor and supporting processes, such as the handling of precursor material, the collection of nanoparticles, and the cleaning of equipment, were monitored for particle emissions and potential exposure. Task based area sampling was conducted using a suite of direct-reading particle instruments. NSAM was used to measure the particle number concentration and lung deposited surface area, respectively, in the 0.5 to 1 µm size range every second. FMPS and APS were employed to measure particle size distributions. A time series approach was used to distinguish released engineered nanoparticles from the background. It was assumed that concentrations and size distributions measured during no work activity was the background.

Task	Duration / Frequency	Engineering controls	Personal protective equipment	Results
ICP synthesis of nanoparticles	2 h / weekly	Reactor under 30 - 75 kPa depression	Filtering facepiece; lab coat; nitrile gloves; IR and UV safety glasses	No particle emissions
Handling of powder precursor in enclosing hood	1 min / weekly	Enclosing hood	Filtering facepiece; lab coat; nitrile gloves; safety glasses	Handling of powder precursor released both fine (~ 200 nm) and coarse (~ 2.1 µm) particles
Disconnection of online sampling filter	1 min / weekly	Two valve system, LEV	Filtering facepiece; lab coat; nitrile gloves; safety glasses	Release of 170 nm particles from dead volume in two valve system
Collection of nanomaterials in online sampling filter in glove box	15 min / weekly	Under controlled atmosphere in glove box, glove worn on interior	Filtering facepiece; lab coat; nitrile gloves; safety glasses	No particle emissions
Cleaning of online sampling filter w/ compressed air	5 min / weekly	Ventilated walk-in enclosure	Filtering facepiece; lab coat; nitrile gloves; safety glasses	Release of smaller particles
Cleaning of production filter w/ compressed air	10 min / yearly	Ventilated walk-in enclosure	Supplied air, hood type respirator; Tyvek coveralls; Tyvek sleeves; nitrile gloves; shoe covers	Particle release, number concentrations exceeded 250,000 #/cm^3, mode size of 170 nm, SiC agglomerates found on filter sample by SEM
Windows of view port opened and wiped, interior walls cleaned w/ compress air	30 min	Reactor under 0.4 kPa depression, connected to aspiration	Filtering facepiece; lab coat; nitrile gloves; safety glasses	No particle emissions
Reactor open and separated into two sections	1 min	Connected to aspiration	Filtering facepiece; lab coat; nitrile gloves; safety glasses	No particle emissions
Two reactor sections cleaned w/ compressed air	10 min	Connected to aspiration, cover w/ slit opening	Filtering facepiece; lab coat; nitrile gloves; safety glasses	No particle emissions
Interior walls of top reactor section cleaned w/ damp wipe	5 min	Connected to aspiration	Filtering facepiece; lab coat; nitrile gloves; safety glasses	No particle emissions

Table 1. Summary of tasks monitored in the production SiC nanoparticle by ICP synthesis and respective results

Most of the measured processes had no emission of the particles, as summerized in Table 1. However, the cleaning of the production filter was a very dusty process. Particle number concentrations measured by the FMPS/P-Trak exceeded 100,000/250,000#/cm^3, respectively. The concentrations in the enclosure returned to background levels approximately 5 min after cleaning began. Size distribution measured by FMPS showed the average size of 170 nm. What appears to be a mode at 0.7 µm was thought to only be a result of APS counting inefficiencies.

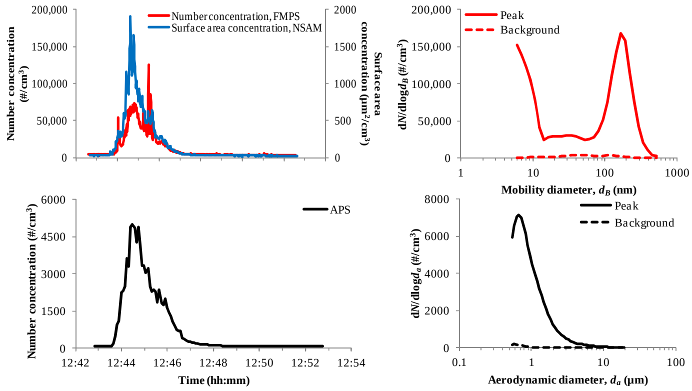

Figure 2. Real-time particle measurements of the cleaning of the production filter with a compressed air gun. ***Top left***: FMPS and NSAM number concentrations; ***Top right***: The size distributions measured by FMPS for peak concentration and background conditions. ***Bottom left***: APS number concentration time series. ***Bottom right***: Peak and background size distributions measured by APS.

Inspection of the filter sample collected during the cleaning of filters processes by SEM revealed the presence of SiC agglomerates. The average size estimated from the scanning electron micrographs was in good agreement with the real-time particle measurements of the respective processes.

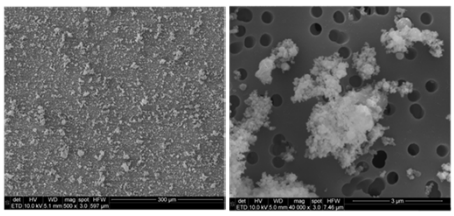

Figure 3. SEM images of SiC agglomerates sampled during the cleaning of the production filter with a compressed air gun.

The FMPS measured a size mode of 170 nm for the airborne SiC particles for both cleaning of the production filter (Figure 2, top right) and disconnection of the sampling filter (Figure 4, left) from the ICP reactor. What was believed to be a false peak at 10 nm was measured by the FMPS for both cleaning and disconnection of the sampling filter, as shown in Figure 4.

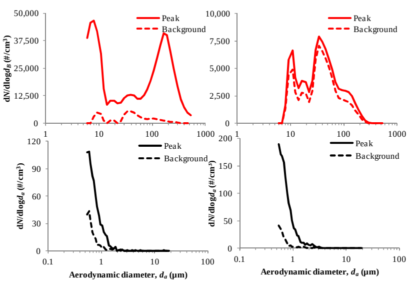

Figure 4. The size distributions measured by FMPS (***top***) and APS (***bottom***) for peak concentration and background conditions.
Left: disconnection of the online sampling filter from the ICP reactor
Right: cleaning of the online sampling filter with a compressed air.

Conclusions

A particle release was not detected during the synthesis of SiC nanoparticles. Particles were released when nanoparticles or nanoparticle contaminated equipment were handled in the open air. Compressed air was found to resuspend nanoparticles when it was used in inadequately ventilated areas. The use of compressed air in workplaces containing nanoparticles should be avoided.

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich
Institute of Environmental Engineering
Air Quality & Particle Research Laboratory

EMPA
Materials Science & Technology
Analytical Chemistry
Air Quality & Particle Research Laboratory