

Aerosol emission monitoring in the production of silicon carbide nanoparticles by induction plasma synthesis

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Abstract In this study, the synthesis of silicon carbide (SiC) nanoparticles in a prototype inductively coupled thermal plasma reactor and other 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 worker exposure. The purpose of this study was to evaluate the effectiveness of engineering controls and best practice guidelines developed for the production and handling of nanoparticles, identify processes which result in a nanoparticle release, characterize these releases, and suggest possible administrative or engineering controls which may eliminate or control the exposure source. No particle release was detected during the synthesis and collection of SiC nanoparticles and the cleaning of the

reactor. This was attributed to most of these processes occurring in closed systems operated at slight under-pressure. Other tasks occurring in more open spaces, such as the disconnection of a filter assembly from the reactor system and the use of compressed air for the cleaning of filters where synthesized SiC nanoparticles were collected, resulted in releases of submicrometer particles with a mode size of ~ 170 – 180 nm. Observation of filter samples under scanning electron microscope confirmed that the particles were agglomerates of SiC nanoparticles.

Keywords Emission monitoring · Silicon carbide nanoparticles · Inductively coupled plasma · Occupational exposure · Environmental, health and safety effects

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Introduction

Engineered nanomaterial-enabled nanotechnology is experiencing unprecedented growth. In 2010, the global consumption of nanomaterials was 1.7 million metric tons and valued at 5.6 billion US\$ (Schlag et al. 2011). By 2015, this market is predicted to grow to 7.4 billion US\$ (Schlag et al. 2011), with revenues from products incorporating these nanomaterials reaching 2.5 trillion US\$ (Hwang and Bradley 2010) and 2 million workers employed in the nanotechnology sector (Roco 2011). While flame aerosol processes currently are the most widely used in manufacturing

commercial quantities of nanoparticles (Skillas et al. 2011), inductively coupled thermal plasma (ICP) technologies are emerging as a promising alternative.

In an ICP, a current is induced in conductive ionized gas. This electrical energy is converted to thermal energy through resistive heating. Temperatures exceeding 10,000 K can be achieved in ICP reactors, allowing for the evaporation of high melting point precursor materials. Nanoparticles are then formed through gas-to-particle conversion. Unlike a flame reactor, oxygen is not required which permits the synthesis of nonoxide materials. The great flexibility offered by ICP allows for the synthesis of a variety of nanoparticles, including metals, oxides, carbides, and nitrides, as well as complex particles, such as core-shell or hollow nanoparticles (Leparoux et al. 2010; Guo et al. 1997).

With the proliferation of nanotechnology, there has come concern about potential new hazards to human health and the environment (Oberdörster et al. 2005; Maynard and Pui 2007; Wang et al. 2011). To determine whether nanoparticles and nanomaterials pose a risk in the workplace, the National Institute for Occupational Safety and Health (NIOSH) Nanotechnology Research Center has identified exposure assessments as a critical area of research and communication (NIOSH 2012). Although industrial ICP systems can produce a wide variety of nanoparticles at a scale of gram to kilogram per hour (Vollath 2008), there have been few studies conducted assessing the potential for nanoparticle exposure during induction plasma synthesis. One such study was completed at an industrial site housing a large-scale pilot ICP reactor where 20–30 nm silver nanoparticles were produced at a rate of 5 kg/day (Lee et al. 2011). Even though no additional engineering controls beyond natural ventilation were employed, they were unable to detect a nanoparticle release by scanning mobility particle sizer and optical particle sizer (OPS). This was attributed to all production processes being performed under negative pressure. Personal breathing zone (PBZ) and area samples analyzed by ICP optical emission spectrometry contained 0.02–1.02 $\mu\text{g Ag}/\text{m}^3$. Silver nanoparticle agglomerates were also found by transmission electron microscopy. A NIOSH field study was also conducted at a research lab where a pilot scale ICP reactor was used to synthesize 50–80 nm aluminum nanoparticles at a scale of kilograms per day (Methner et al. 2010). The cleaning and brushing down of a plasma torch, filter chamber, and cyclone in a ventilated walk-in enclosure was monitored. Background subtracted condensation

particle counter (CPC) measured concentrations were 7,000–16,000 particles/ cm^3 during cleaning, while OPS measurements exceeded the upper dynamic range of the instrument. Mass concentrations from area and PBZ samples were 40–280 and 160 $\mu\text{g}/\text{m}^3$, respectively. Evidence of aluminum nanoparticles was found on all area and PBZ samples. Clearly more workplace measurements are needed to accurately characterize the risk posed to workers from exposure to engineered nanoparticles during induction plasma synthesis.

In this study, aerosol emissions were monitored during the synthesis of nanoparticles by an ICP reactor prototype and associated production tasks. While highly dependent on the material being synthesized, the reactor prototype is typically capable of producing nanoparticles at a rate of hundreds of grams per hour. This reactor has successfully synthesized tungsten carbide, silicon, copper, and titanium carbonitride nanoparticles (Leparoux et al. 2005, 2010). In this assessment, silicon carbide (SiC) nanoparticles were produced from the in-flight carburization of metallic silicon, where the silicon precursor reacts with the carbon generated from the decomposition of methane in the plasma. While the Occupational Safety and Health Administration (OSHA) regulates SiC under its generic permissible exposure limit (PEL) of 15 mg/m^3 total particulate and 5 mg/m^3 respirable particulate for particulates not otherwise regulated, inductive plasmas are capable of synthesizing materials regulated under more stringent exposure limits, such as silver which has a PEL of 0.01 mg/m^3 (OSHA 2013). Thus, even with its high PEL, it is worthwhile to monitor potential nanoparticle emissions during the synthesis of SiC, as the results may be translated to the synthesis of more hazardous materials. The research objectives of this study were to evaluate the effectiveness of engineering controls and best practice guidelines developed for the production of nanoparticles, identify processes which result in particle emission, characterize these emissions, and suggest possible administrative or engineering controls which may eliminate or control the emission source.

Methods

Facility and process descriptions

The ICP reactor prototype was housed in an approximately 170 m^2 laboratory building at the Laboratory

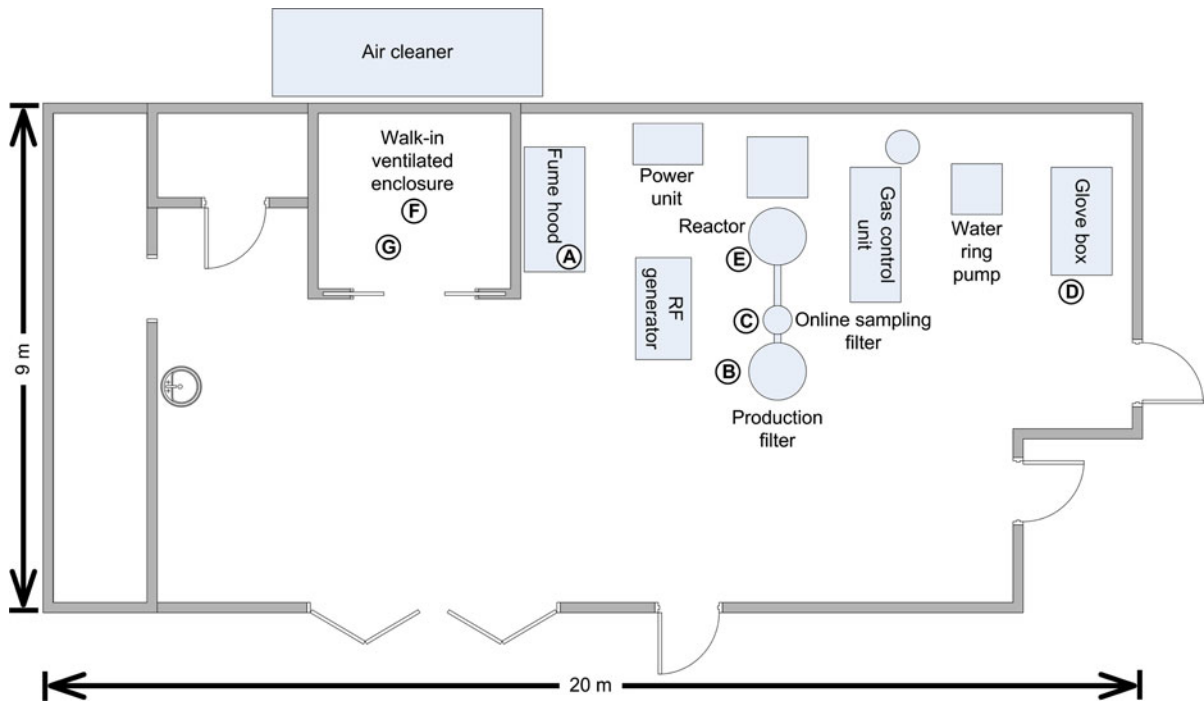


Fig. 1 A schematic of the facility housing the ICP reactor prototype where sampling locations corresponding to those listed in Table 1 are given by letters

for Advanced Materials Processing, Empa – Swiss Federal Laboratories for Materials Science and Technology located in Thun, Switzerland. This lab is dedicated solely to the reactor and contains no office space. The building is kept under slight negative pressure. All ventilation exhaust and aspiration lines pass through two air cleaners (EBS P.4.160, LWK Innofil GmbH, Germany) operating in parallel, with each having a filtration surface of 160 m² and handling an airflow of 6,000 m³/h. The makeup air entering the lab is not filtered. The outside ambient temperature and dew point ranged from −2 to 6 °C and −5 to 3 °C, respectively, during the assessment. The temperature and humidity in the laboratory was uncontrolled, with the indoor temperature being ~20–22 °C during the study. A schematic of the laboratory is given in Fig. 1.

The tasks monitored included the handling of powder precursor, the synthesis of nanoparticles, the disconnection of the sampling filter used to capture these nanoparticles, the collection and packaging of the nanoparticles captured on the filter, and the cleaning of the reactor and filters. The details of these tasks will be presented in the following sections. For safety, all tasks are performed by at least two trained

persons. Nanoparticles are passivated for at least 24 h under static vacuum before any cleaning. After this passivation step, the nanoparticles are normally no longer reactive. If it is known that there is no risk of the nanoparticles reacting with air, as is the case for SiC, alumina or other stable oxides, the cleaning can be done after a few minutes or hours. For all but two tasks, plasma synthesis and cleaning of the production filter, the personal protective equipment (PPE) worn at this facility included a filtering facepiece respirator which provides at least 99 % filtration efficiency (FFP3), lab coat, nitrile gloves, and safety glasses. During plasma synthesis, the safety glasses worn were protective against ultraviolet (UV) and infrared (IR) radiation. This was because the plasma was visible through view ports on the reactor, which were also equipped with green UV glass filters. During the cleaning of the production filter, the PPE worn included a supplied air, hood type respirator, a Tyvek jumpsuit, nitrile gloves, Tyvek sleeves worn over the seam between jumpsuit and gloves, and shoe covers. A summary of the tasks monitored, the duration and frequency of these tasks, and the engineered controls and PPE employed for each task is given in Table 1.

Table 1 Summary of tasks monitored in the production SiC nanoparticle by ICP synthesis

Task	Sampling location (Fig. 1)	Duration/frequency	Engineering controls	Personal protective equipment	Observations
Handling of powder precursor	A	1 min/daily	Enclosing hood	FFP3, lab coat, nitrile gloves, safety glasses	Release of both fine (~ 250 nm) and coarse (~ 2.1 μm) particles (measured inside enclosing hood w/o ventilation to simulate worst case scenario)
ICP synthesis of nanoparticles	B	4 h/daily	Reactor under 30–75 kPa depression	FFP3; lab coat; nitrile gloves; IR and UV safety glasses	No particle emissions
Disconnection of online sampling filter	C	10 min/daily	Two valve system, flanged opening capturing hood	FFP3; lab coat; nitrile gloves; safety glasses	Release of ~ 180 nm particles from dead volume in two valve system
Collection of nanoparticles on online sampling filter	D	30 min/daily	Glove box, gloves worn on interior of glove box	FFP3; lab coat; nitrile gloves; safety glasses	No particle emissions
Cleaning of reactor	E	2 h/weekly	–	FFP3; lab coat; nitrile gloves; safety glasses	–
Windows of view port opened and wiped, interior walls cleaned w/compressed air	–	60 min	Reactor under 0.4 kPa depression, connected to aspiration	–	No particle emissions
Reactor opened and separated into two sections	–	2 min	Connected to aspiration	–	No particle emissions
Two reactor sections cleaned w/compressed air	–	30 min	Connected to aspiration, lid w/slit opening	–	No particle emissions
Interior walls of top reactor section wiped w/damp cloth	–	30 min	Connected to aspiration	–	No particle emissions
Cleaning of online sampling filter w/compressed air	F	10 min/weekly	Walk-in ventilated enclosure	FFP3; lab coat; nitrile gloves; safety glasses	Particle release
Cleaning of production filter w/compressed air	G	3 h/yearly	Walk-in ventilated enclosure	Supplied air, hood type respirator; Tyvek coveralls; Tyvek sleeves; nitrile gloves; shoe covers	Particle release, number concentrations exceeded 226,000 particles/cm ³ , particles had mode size of ~ 170 nm, SiC agglomerates found on filter sample by SEM

Handling of silicon metal powder precursor

Before the synthesis of SiC nanoparticles, the powder precursor, silicon metal (SIMET 993, Keyvest Belgium SA, Belgium), was handled in an enclosing hood. The

manufacturer's specifications of the precursor list a mass median diameter (MMD) of 11 μm . This powder was poured back and forth from its original container into the vessel which empties into the powder feeder. To simulate a worst case scenario, the ventilation of the

hood was not turned on. Normally, the ventilation is always on. This simulated work practice was done to determine whether nanoparticles would become airborne in the handling of materials which, from mass-based measurements, were assumed to consist of micrometer-sized particles. Since there was no ventilation engaged in the hood, this was in no way considered a measure of hood effectiveness. To properly evaluate the effectiveness of the enclosing hood, the approach of Tsai et al. (2012), where the capture velocity at the particle release site is measured and/or calculated, should be used.

Synthesis of SiC nanoparticles

The nanoparticle synthesis prototype consisted of an induction plasma torch coupled to a radio frequency (RF) power supply, a powder feeder, a synthesis chamber, a flow control system, a filtration unit, and a vacuum system (Leconte et al. 2008; Leparoux et al. 2005). A schematic of the ICP reactor is given in Fig. 2a. Precursors, carrier gas, and reactive gas were introduced axially into the induction plasma torch (PL-35, Tekna Plasma Systems Inc., Canada), while the plasma gas (Ar) is introduced with a swirl. Silicon metal powder was used as a precursor and was fed into the torch by a dense phase convey powder feeder (PowderCube, DACS, Switzerland) which was able to transport non- or poor-flowable powders (Dvorak and Dietrich 2001). The induction coil was connected to a RF power supply (Elgotec AG, Switzerland). The torch was mounted atop a stainless steel, water cooled synthesis chamber. Quenching gas was introduced through a quenching ring positioned below the torch. Quenching permitted tailoring of the temperature profile in the reaction chamber which resulted in the control of the particle size distribution. In this case, a quenching rate exceeding 10^8 K/m resulted in SiC particles with a mean diameter of ~ 30 nm. The synthesis chamber was equipped with view ports which allowed for in situ process visualization and characterization.

The synthesis chamber was connected to a specially designed filtration unit. This consisted of an online sampling filter and a production filter. The larger production filter was composed of regenerable metallic high-efficiency particulate air (HEPA) filters and had a filtration surface of 2 m^2 . Nanoparticles can be accumulated in the powder collector at the base of the production filter after regeneration. The online sampling

filter can be used to bypass the production filter and collect small quantities of nanoparticles on a membrane filter without halting production. A two valve system was employed at the filter inlets and outlets, allowing both the online sampling filter and the production filter to be disconnected while the filters and the reactor remained sealed (Leparoux and Siegmann 2003). Nanoparticles were drawn from the synthesis chamber to the filtration unit by a water ring pump with a pressure regulation system which typically maintained a constant process pressure of 15–60 kPa. The pump exhaust is also connected to the external air cleaners. For this assessment, nanoparticles were collected primarily on the online sampling filter with flow directed to the production filter at the beginning and end of the synthesis.

Disconnection of online sampling filter

After nanoparticle production was halted and appropriate time had elapsed for passivation of nanoparticles, the online sampling filter was disconnected from the reactor prototype, as shown in Fig. 2b. While the two valve system employed did prevent air movement from or into the filter and reactor, a dead volume existed in the transport line between the valves. Because of this dead volume, local exhaust ventilation (LEV) with a flanged opening capturing hood ~ 5 cm in diameter was used in this process. LEV captures contaminants near their source, which is more effective and results in lower equipment and operation costs in comparison with dilution ventilation.

Collection of nanoparticles in online sampling filter

Once disconnected, the online sampling filter was transported to a glove box. The SiC nanoparticles were collected by hand, transferred to well-labeled bottles, and then sealed in tight plastic bags under an argon atmosphere. A new pair of nitrile gloves was worn on the interior of the glove box to prevent cross contamination. After the nanoparticles were collected from the surface of the membrane filter, the online sampling filter was reassembled and the outer surface wiped clean.

Cleaning of reactor

It was necessary to clean the interior of the reactor to avoid contamination when one wants to synthesize different products. In cleaning the reactor, first, two

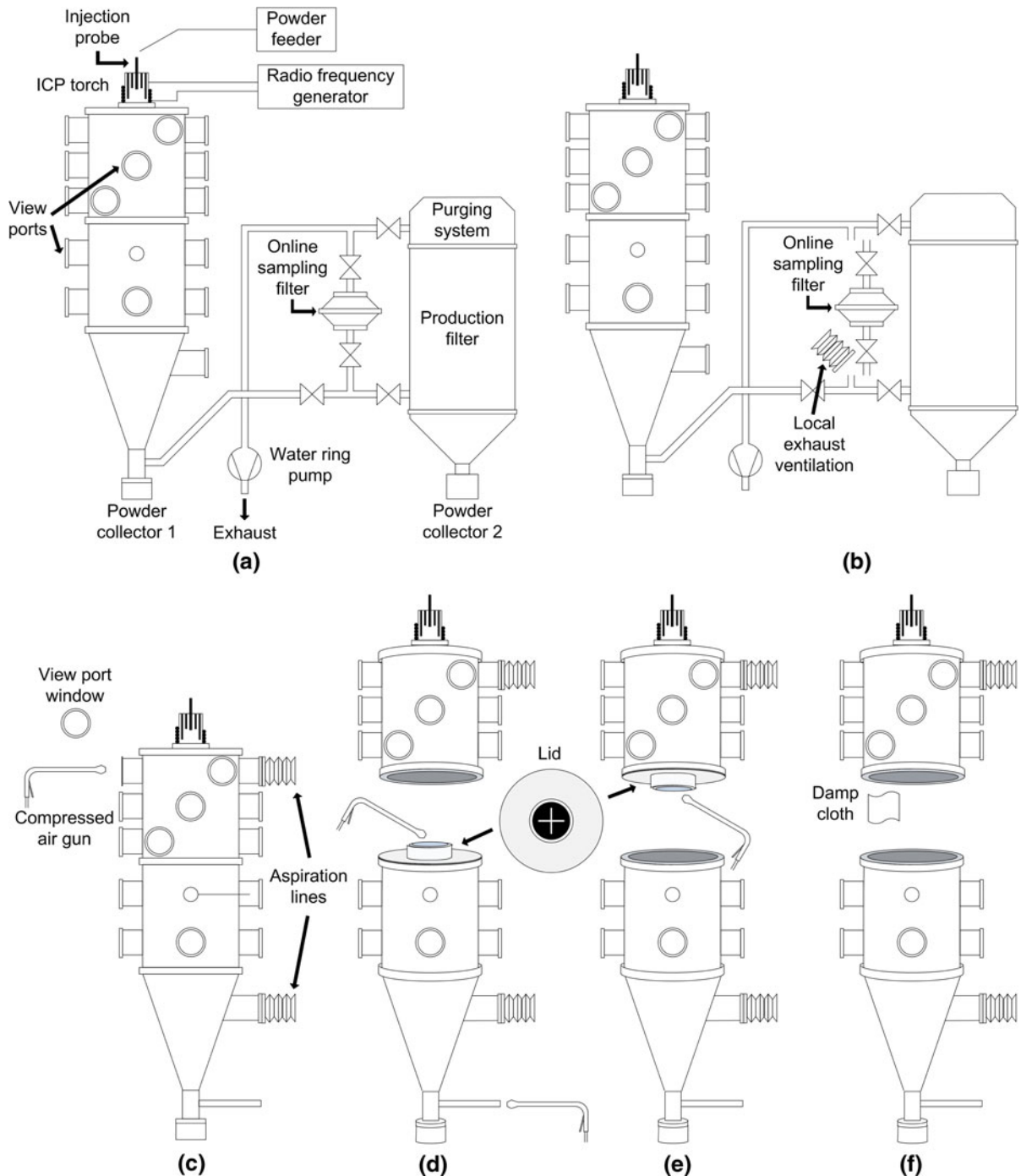


Fig. 2 A schematic of **a** the ICP reactor prototype adapted from Leconte et al. (2008), **b** the disconnection of the online sampling filter, and **c–f** the steps taken in cleaning the ICP reactor. **c** An individual view port window was removed and wiped clean. The compressed air gun was used to clean the inside walls of the reactor through the open view port. This was repeated at all viewports. **d** The reactor was split open and a lid with a slit

plastic membrane at its center was attached to the bottom section. Compressed air was used to clean the interior of the reactor, first through the particle transport line at the base of the reactor and then through the slit in the lid. **e** The lid was attached to the top section of the reactor and compressed air was applied through the slit in the lid. **f** The lid was removed and a damp cloth was used to clean the interior of the top section of the reactor

aspiration lines were attached to the reactor. When connected to these aspiration lines, the reactor was under 0.6 kPa depression. Then, view ports were opened, one at a time. With one open view port, the reactor was under 0.4 kPa depression. The window was then wiped clean directly in front of the opened view port. Thus, any particles released in this cleaning would be captured by the suction of the opened view port. Next, a compressed air gun was inserted through the open view port and used to blow off particles which deposited on the interior walls of the reactor, as shown in Fig. 2c. This process was performed at each view port, proceeding from the top of the reactor to the bottom. Because particles tend to redeposit during cleaning, this process may need to be repeated.

The reactor was then opened. Once opened, both aspiration lines were in operation with each section of the reactor having its own aspiration line. The two sections of the opened reactor were separated and a lid with a slit plastic membrane at its center was attached to the bottom section. The compressed air gun was then used to clean the bottom section of the plasma reactor. The compressed air was applied into the particle transport line at the base of the reactor and through the slit in the lid attached to the reactor section, where in the latter instance the particle transport line was closed, as seen in Fig. 2d. This lid was then attached to the top section of the reactor. Again, the compressed air gun was inserted through the lid and the walls were cleaned, as shown in Fig. 2e. Finally, the lid was removed from the top section of the reactor and the interior walls were wiped with a damp cloth, which is demonstrated in Fig. 2f.

Cleaning of online sampling and production filters

It was also necessary to clean the online sampling and production filters to avoid contaminating future synthesized nanoparticles with the current product. The online sampling filter was cleaned with a compressed air gun in a walk-in ventilated enclosure with flow aligned with the side wall. The worker was upstream of the filter during the cleaning. For this assessment, the production filter was also cleaned in the enclosure using a compressed air gun. While only a small quantity of SiC nanoparticles was collected in the production filter during this assessment, its filtration surface had not been cleaned after prior production runs.

Monitoring strategy

Task-based area measurements were conducted using a suite of direct-reading particle instruments. A handheld CPC (Model 8525, TSI Inc., USA) and Nanoparticle Surface Area Monitor (NSAM) (Model 3550, TSI Inc., USA) were used to measure the particle number concentration and lung deposited surface area concentration, respectively, in the 10 nm to 1 μm size range every second. A Fast Mobility Particle Sizer Spectrometer (FMPS) (Model 3091, TSI Inc., USA) and Aerodynamic Particle Sizer Spectrometer (APS) (Model 3321, TSI Inc., USA) were employed to measure particle size distributions. The FMPS measured electrical mobility diameters in the range of 5.6–560 nm every second. The APS measured aerodynamic diameters from 0.5 to 20 μm with a possible time resolution of one second. However, an averaging time interval of 5 or 20 s for the APS was used in this assessment. WPS Commander (WPS Commander 3.0, MSP Corp., USA) was used for analyzing and applying fits to the particle size data. 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 were the background. Increases in concentration and changes in size distribution during work activity were attributed to a task (Kuhlbusch et al. 2011). The time series approach was combined with a morphological analysis conducted by scanning electron microscope (SEM) (Nova NanoSEM 230, FEI Co., USA). Samples were collected on 47 mm diameter track-etched polycarbonate membrane filters with 0.4 μm pore size (Cat. No. 111107, Whatman plc, UK) housed in an open-faced 47 mm stainless steel filter holder with filter support screen (Cat. No. XX5004710, EMD Millipore, USA).

Instruments and sampling equipment were typically placed on carts and positioned as close to the task being monitored as possible without disrupting the work and were generally within 1 m of the task. The sampling locations corresponding to the tasks listed in Table 1 are given in Fig. 1. In the monitoring of some tasks, ~ 1 m of conductive silicon tubing with a 7.9 mm inner diameter was connected to the inlets of the FMPS and NSAM. This conductive tubing acted as a sampling probe. Being conductive, the electrostatic losses in the tubing were negligible. Diffusion was the major loss mechanism in particle transport through the

tube. The nanoparticle diffusional losses calculated by the Gormley and Kennedy (1948) formula were less than 6 % for the size ranges of particles measured by the FMPS and NSAM. Thus, no corrections were made for these minimal diffusional losses in the results.

Results and discussion

Tasks

Handling of silicon metal powder precursor

When the silicon metal precursor, with a MMD of 11 μm , was handled, a bimodal lognormal size distribution was measured by the FMPS and APS inside an enclosing hood, with one mode, or geometric mean, μ_g , at an electrical mobility diameter, d_B , of 252 nm (geometric standard deviation, σ_g , of 1.45 and coefficient of determination, R^2 , of 0.991) and the other at an aerodynamic diameter, d_a , of 2.10 μm ($\sigma_g = 1.70$, $R^2 = 0.996$), as shown in Fig. 3. The size distributions measured by the FMPS and APS are presented as a function of electrical mobility diameter and aerodynamic diameter, respectively. No effort was made to

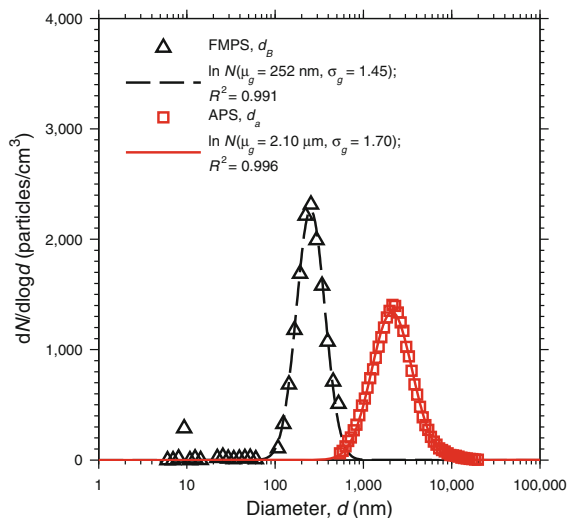


Fig. 3 Background subtracted particle size distributions measured by FMPS (in terms of mobility diameter, d_B) and APS (in terms of aerodynamic diameter, d_a) inside an enclosing hood during the handling of metal silicon powder precursor. A 20 s averaging interval was used for the instruments

relate electrical mobility diameter and aerodynamic diameter using an effective density (Kelly and McMurry 1992) since this property is material and size dependent (Rao et al. 1995) and its implementation would introduce extra uncertainties.

While this powder was considered to consist of coarse particles, during handling, both fine and coarse airborne particles were detected. The modes of this size distribution were comparable to those observed in dustiness tests, $d_B \approx 100\text{--}200$ nm and $d_a \approx 0.8\text{--}2.5$ μm , for various nanopowders (zinc oxide, Bentonite, nanoclay, titanium dioxide, talc, fumed silica, Goethite, and Y-zirconia) using a rotating drum (Jensen et al. 2008; Schneider and Jensen 2008; Tsai et al. 2009). The peak measured by the FMPS at around 10 nm was believed to be an artifact of the instrument. Particles of this size would suggest a particle generation event, which one would not associate with the handling of powders. This peak measured by the FMPS has been observed by other researchers in ambient and indoor measurements (Jeong and Evans 2009) and when challenged with sodium chloride particles (Asbach et al. 2009). They, too, concluded that this may be an artifact of the instrument.

Synthesis of SiC nanoparticles

No particle emissions were detected by direct-reading particle instruments during the synthesis of SiC nanoparticles. This was a result of the entire ICP reactor prototype, from powder feeder to filtration unit, being under negative pressure. These results were similar to those in the exposure assessment performed by Lee et al. (2011) at an industrial site where an ICP reactor synthesized silver nanoparticles.

Disconnection of online sampling filter

A particle release was detected when the online sampling filter was disconnected from the ICP reactor prototype, as shown in Fig. 4a. These emitted particles were believed to have originated from the dead volume present in the two valve system which sealed off both the reactor and online sampling filter. The capturing hood, which was held near this dead volume as the online sampling filter was disconnected, was inadequate for containing the particle release. The FMPS and NSAM, whose probes were held near the online sampling filter as it was disconnected, and the APS, which was adjacent to the reactor, all detected this event. The FMPS

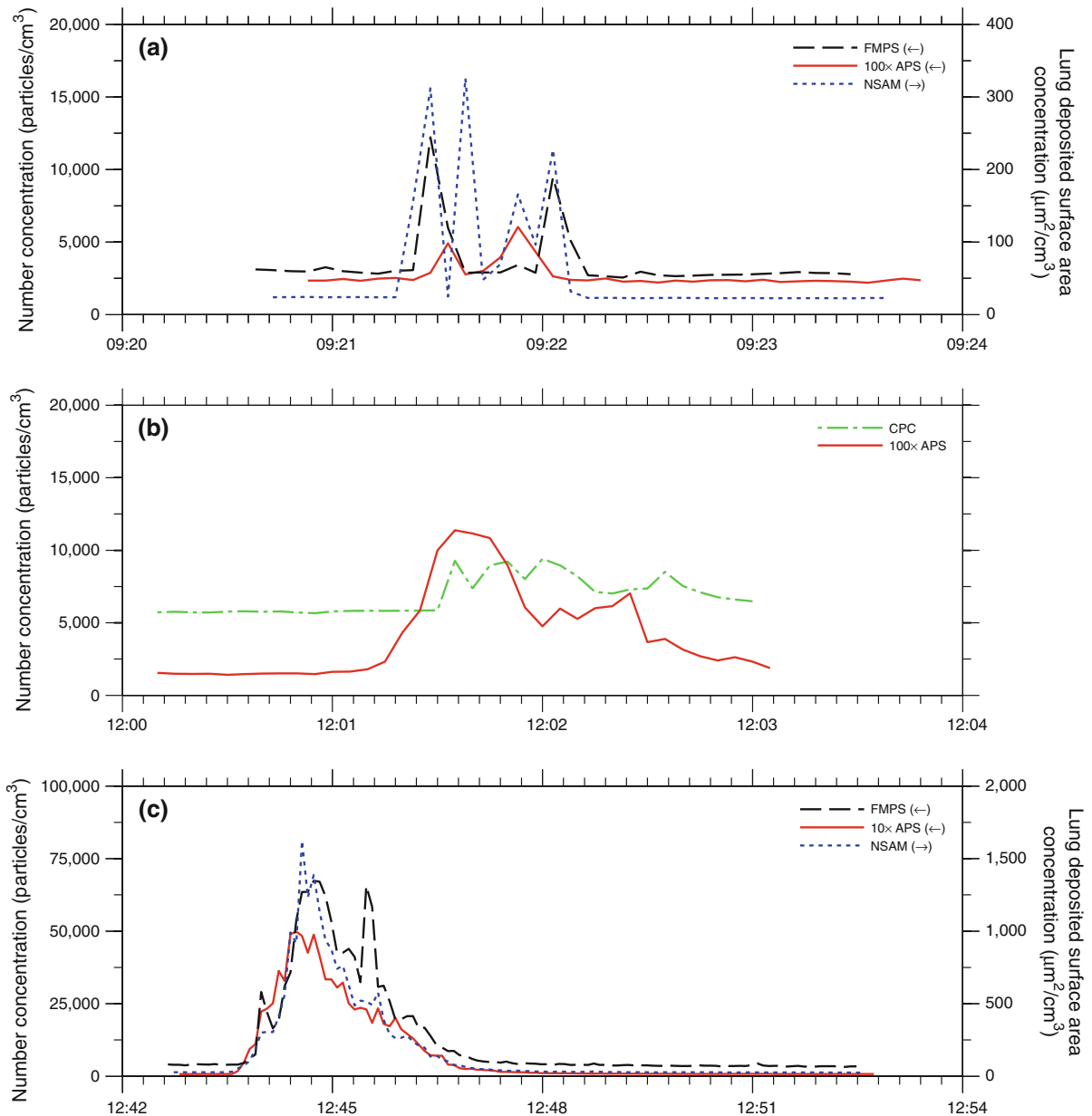


Fig. 4 Real-time particle measurements, where the instrument averaging interval was 5 s. **a** Particle number concentrations measured by the FMPS and APS and lung deposited surface area concentrations measured by the NSAM during the disconnection of the online sampling filter. **b** Particle number

concentrations measured by the CPC and APS during the cleaning of the online sampling filter. **c** Particle number concentrations measured by the FMPS and APS and lung deposited surface area concentrations measured by the NSAM during the cleaning of the production filter

measured a bimodal distribution ($R^2 = 0.973$) with modes present at 6.44 nm ($\sigma_g = 1.63$) and 183 nm ($\sigma_g = 1.55$), as shown in Fig. 5. Again, this sub-10 nm peak was believed to be an artifact of the FMPS. From

Fig. 4a, it can be seen the APS measured an increase in particle concentration, as well. These particles were attributed to the tail end of the peak at 183 nm measured by the FMPS.

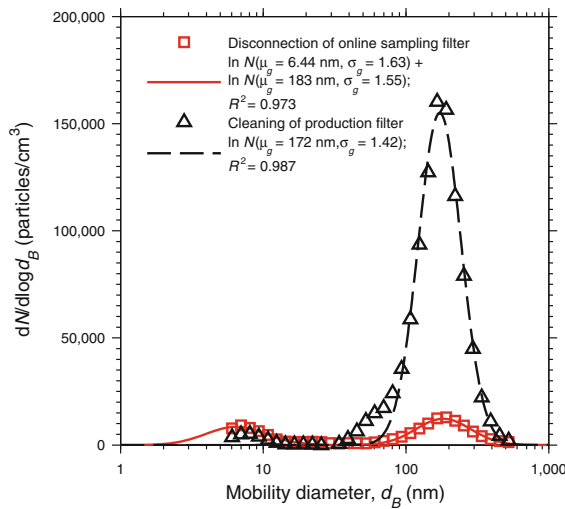


Fig. 5 Background subtracted particle size distributions measured by the FMPS (in terms of mobility diameter, d_B) at the peak particle number concentrations during the disconnection of the online sampling filter and the cleaning of the production filter. A 5 s averaging interval was used for the FMPS

Collection of nanoparticles in online sampling filter

After the online sampling filter was disconnected, it was placed in a glove box where the SiC nanoparticles were collected and packaged in an inert atmosphere. Then, the online sampling filter was wiped clean. No particle release was detected as the online sampling filter was removed from the antechamber of the glove box.

Cleaning of reactor

Direct-reading instruments did not provide evidence of particle emissions during the cleaning of the reactor. Adequate aspiration and enclosure was provided by the engineering controls in place to prevent the release of SiC particles. Although no particle release was detected, in the future, as a precautionary measure, LEV will be used near the slit opening on the lid when compressed air is applied through the particle transport line connected to the bottom section of the reactor, as shown in Fig. 2d.

Cleaning of online sampling and production filters

The cleaning of the membrane filter used in the online sampling filter unit with compressed air in the walk-in

ventilated enclosure was found to resuspend the collected SiC particles. This was to be expected, as the entire purpose of this cleaning was to liberate the SiC particles from the filter surface and have the ventilation in the enclosure capture the aerosol. Unfortunately, during this measurement, the FMPS was positioned upstream of the cleaning and directly behind the worker. Because of this, the FMPS did not measure a particle release. The CPC, which was held near this activity, did measure an increase in particle concentration during cleaning. The APS, too, was able to measure this release, as it was not directly behind the worker. These concentration measurements can be seen in Fig. 4b, where results from the NSAM are not shown due to instrument malfunction.

The cleaning of the production filter was found to be a very dusty process. Particle number and lung deposited surface area concentrations measured by the FMPS and NSAM, respectively, which were transverse to the direction of the ventilation exceeded 67,000 particles/cm³ and 1,600 $\mu\text{m}^2/\text{cm}^3$, as seen in Fig. 4c, while concentrations measured by the CPC placed downstream of the cleaning exceeded 226,000 particles/cm³. The liberated particles had a mode size of 172 nm ($\sigma_g = 1.42$, $R^2 = 0.987$). It can be seen in Fig. 5 that the particle size distribution was similar to that measured when the online sampling filter was disconnected. Again, what was believed to be an artifact of the FMPS was observed below 10 nm. The particles measured by APS were found to belong to the tail of the distribution measured by the FMPS. A filter sample collected during the cleaning of the production filter was inspected by SEM revealing the presence of SiC agglomerates, as shown in Fig. 6. A summary of the observations resulting from monitoring of the production tasks is given in Table 1.

Use of compressed air in the cleaning of nanomaterials

In recommended work practices published by NIOSH, HEPA vacuum or wet wiping methods are suggested when cleaning nanomaterials (NIOSH 2009). In our study, when compressed air was used for cleaning the inside walls of the reactor, the interior of a semi-closed ventilated system, no particle emissions were detected. When compressed air was used for cleaning in more open spaces, such as the cleaning of the online sampling and production filters in the ventilated walk-

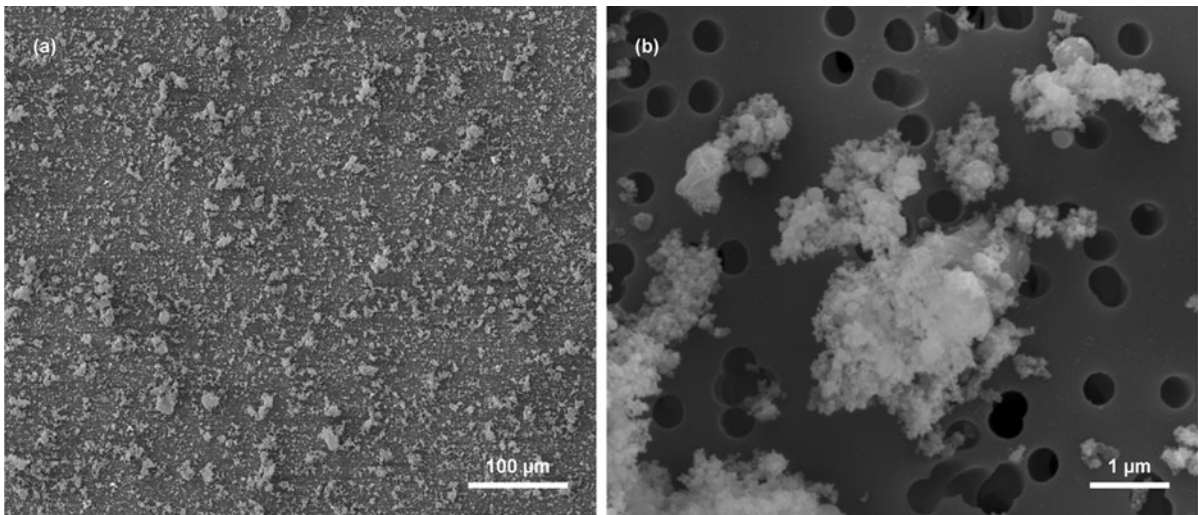


Fig. 6 SEM images of SiC agglomerates sampled on a membrane filter with 0.4 μm pores during the cleaning of the production filter at **a** lower and **b** higher magnifications

in enclosure, emissions of submicrometer particles were identified inside the enclosure. However, the cleaning of the online sampling and production filters only occurs ~ 10 min every week and 3 h every year, respectively. With few opportunities for exposure and adequate engineering controls and PPE used when completing these tasks, it was determined that it is unfeasible to replace the current standard operating procedure with a new procedure employing HEPA vacuuming.

Few other studies have been conducted where particle emissions were measured when compressed air was used for cleaning nanomaterials. Ogura et al. (2010) measured the release of particles from the filter of a cyclone vacuum cleaner used to collect carbon nanotubes from a substrate when this filter was cleaned in a fume hood, first with a spatula and then a compressed air gun. The CPC measured a concentration increase of $\sim 3,000$ particles/ cm^3 , while the optical particle counter exceeded the coincidence loss level of 140 particles/ cm^3 . Zimmermann et al. (2012) measured the emission of nanoparticles in the cleanout of plasma-enhanced chemical vapor deposition (PECVD) equipment used in the production of silicon nanowires. When an air jet was used to clean the equipment, CPCs measured particle number concentrations 10,000 particles/ cm^3 above background with an FMPS measured peak size of 10 nm. In another study, which was conducted at a fullerene factory,

compressed air was used to intentionally disperse an open bag of fullerenes resulting in a release of coarse fullerene agglomerates (Fujitani et al. 2008). Similarly, (Evans et al. 2013) evaluated a novel Venturi device used to aerosolize fine and nanoscale powders. The air flows were expected to resemble energetic dust dispersion activities, such as the use of compressed air for cleaning. The aerodynamic diameters of the dispersed powders ranged from ~ 300 nm to several micrometers, with no modes below 100 nm. The results of our study reinforce the observations made in workplace simulations. Like these workplace simulation studies, the reaerosolized particles were in the form of agglomerates larger than 100 nm. This differs from the results of Zimmerman et al. (2012) where a peak size of 10 nm was reported in the case of cleaning PECVD equipment with compressed air.

Conclusion

The use of direct-reading particle instruments was shown to be an effective means by which to assess efficacy of the engineering controls and best practice guidelines and identify the potential for inhalation exposure in the production of nanoparticles by ICP synthesis. By addressing potential nanoparticle emissions in the design of the engineering controls installed, the work practices performed, and the PPE

worn, the processes conducted in this laboratory were safe along all processing steps from the manipulation of the precursor material to the packaging of the final product. No particle release was detected during the synthesis of SiC nanoparticles. This was attributed to the reactor prototype being a closed system operated under slight underpressure. Similar observations were made during nanoparticle production at industrial sites (Lee et al. 2011), in pilot scale plants (Wang et al. 2012, 2013), and in laboratories (Walser et al. 2012). Tasks related to the synthesis of nanoparticles were also evaluated. A release of submicrometer particles was detected when the online sampling filter was disconnected from the reactor system. Additional LEV has since been installed for this process as a result of this study. The use of compressed air when cleaning nanoparticle contaminated equipment was monitored. When compressed air was used for cleaning the interior of semi-closed ventilated systems, like the inside walls of the reactor, no particle emissions were detected. When compressed air was used for cleaning in open spaces, such as the cleaning of the online sampling and production filters in the ventilated walk-in enclosure, emissions of submicrometer particles were identified. The cleaning of the production filter resulted in particle number concentrations exceeding 226,000 particles/cm³. Particle emissions in this facility were found to be mainly submicrometer with a mode size of ~170–180 nm. Observation of filter samples under SEM confirmed that the particles released in the cleaning of the production filter were agglomerates of SiC nanoparticles.

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