Distribution of Nanoparticle Number Concentrations at a Nano-TiO₂ Plant

Yi Yang*, Ping Mao, Zheng-Ping Wang, Jin-Hua Zhang

School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

ABSTRACT

Nanoparticle number concentration distributions were measured at various sites in a plant manufacturing nano-sized titanium dioxide powder. It was found that aerosol nanoparticles suspended in the air were mainly in the form of agglomerated particles, and had the average diameters of 124.2 nm and 524.4 nm, respectively. The number concentration of aerosol particles increased with source height, but decreased with distance from the source. The concentration was highly affected by the dispersive forces of the discharging port, and the suspension and the agglomeration of particles. The aerosol particles accumulated after a long working time, and the concentration was reduced at large suspending distances. In contrast, the concentration of primary particles was higher for a working time of less than 2 hours, and returned to normal levels after 3 hours, due to the accumulation and agglomeration effects experienced by the primary particles. Motivated by these findings, an aerosol enclosure was developed in this study, and it showed excellent control over the distribution of aerosol particles, including the agglomerated and primary particles. This is thus a promising approach to achieve effective and efficient personal protection in the workspace.

Keywords: Aerosol nanoparticles; Aerosol control technology; Workshop; Number concentration; Titanium dioxide.

INTRODUCTION

Nanomaterials are regarded worldwide as one of the key materials of the 21st Century. The outstanding performance of nanomaterials has motivated research in a variety of fields, resulting in many nanotechnological applications, and acceleration in the manufacturing of nanomaterials (Ashby et al., 2009; Woskie, 2010). Nanoparticles (NPs) can be generated in the process of handling engineered nanomaterials (ENMs), and from high-temperature combustion and reaction processes, or incidental sources (Tsai et al., 2012). As one of the most widely used ENMs, nano-sized titanium dioxide (nano-TiO₂) has been manufactured in large quantities; it is therefore essential that useful occupational health and safety recommendations are developed for those who work with ENMs, at both the laboratory and the manufacturing levels. That is, workers in the nanotechnology-based industry deserve more attention as they may have the greatest risk of exposure to ENMs that may lead to adverse health effects (Tsai and Pui, 2009; Tsai et al., 2012). However, to the authors' knowledge, no equipment currently exists to effectively protect these workers from aerosol NPs. Although epidemiological studies have not found a direct relationship between TiO₂ doses and lung cancer in manufacturing workers (Fryzek et al., 2003; Boffetta et al., 2004), and insufficient evidence exists to designate many nanomaterials—including TiO₂—as a potential occupational carcinogen (Gilbert, 2009; ILSI, 2000), dose-response data are already available in rats for both cancer (lung tumors) and early non-cancer (pulmonary inflammation) endpoints. To minimize any risks that might be associated with the development of pulmonary inflammation and cancer, the National Institute for Occupational Safety and Health (NIOSH) has recommended an exposure limit for ultrafine (smaller than 100 nm) TiO₂ of 0.1 mg/m³, based on the international definitions of respirable dust (ISO, 1995). A respiratory tract model developed by the International Commission on Radiological Protection (ICRP) (publication No. 66) showed that particles deposited in the tracheal bronchus and alveoli were mostly smaller than 100 nm (Bair, 1991; Kuo et al., 2005; Oberdörster et al., 2005). These studies also suggested that aerosol particles of various diameters may lead to different health risks to workers, and may therefore require different aerosol protection methods. Hence, the knowledge of the size and number distribution of aerosol nanoparticles is of great importance if aerosol nanoparticle protection methods are to be established for workshop workers (Mädler and Friedlander, 2007). This knowledge would also help in the assessment of aerosol nanoparticles in the environment by the relevant enterprises and organizations for environmental health.

Due to their high surface energy and small size, nanoparticles tend to form aggregates or big particles, to reduce the surface energy (Cao, 2004). High concentrations...
of aerosol particles are of significant concern in many nanomaterial-related workplaces in China, because of insufficient protection for workers and ill-equipped manufacturing lines (Song et al., 2009). The aggregation of aerosol particles at high concentrations is better reflected in the number concentrations in the workshop, in contrast to mass aerosol concentration. However, current human lung dosimetry models (Flagan, 2001) and the occupational exposure limits for most airborne particulates (including TiO₂) are all mass-based (Tsai et al., 2011). A mass-based personal nanoparticle sampler, which enables the collection of both respirable particulate mass (RPM) and nanoparticles (NPs) simultaneously, was developed recently by Tsai et al. (2012) which may be used to sample large agglomerated NPs as RPM in workplaces.

Aerosol particles are also characterized by surface area concentration, which can be measured off-line for bulk materials, using the BET method (Kuempel and Tran, 2002; Tsai et al., 2011). However, instruments capable of measuring aerosol surface areas in the field are not widely available. In addition, only a few research efforts are focused on the study of particle number concentrations (Tsang et al., 2008; Hussein et al., 2011; Yang et al., 2011). By measuring the number concentration distribution of aerosols in the workshop and the diameter of the primary particles, it is easy to display the agglomeration status of the aerosol particles, and to convert to the other two characteristics of the aerosol; i.e., the mass concentration and the surface area concentration.

In this work, the number concentration distributions of aerosol nanoparticles were measured to investigate the dispersion and suspension behavior and the aggregation and deposition status of aerosol particles in a workshop producing nanometer-scale titanium dioxide powder. The nano-aerosol number concentration in the workplace exhibited a strong dependence on the distance and height from the aerosol source, and variations in the working time. An aerosol enclosure was developed to control aerosol particles effectively in the workspace.

EXPERIMENTS AND METHODS

The sampling experiments were carried out in the pulverization workshop (dimensions: 15 m length × 8 m width × 7.5 m height) of a nano-TiO₂ factory. As shown in Fig. 1(a), high-speed compressed air passed into the pulverization cavity through the supersonic speed nozzle. Stock powder carried by the airflow was broken into nanoparticles under the action of crushing, friction and extrusion forces. Following the airflow, uniform nano-TiO₂ products were carried into the cyclone collector, and were discharged from the outlet with an average rate of 1 kg/min. From the leaking points of the discharge port with charge bucket, the aerosol nanoparticles were dispersed mainly out of the discharge port outlet by the compressed air; the discharge port was thus regarded as the aerosol source, which was at a height of one meter above the ground. To suppress the influence of airflow on this study, all workplace windows and doors were closed during the sampling processes. The samplers were located at various distances from the discharge port and various heights above the ground. The background tests were performed each morning before the working day began, and the background corrections of the concentrations were carried out based on the referenced background data. To minimize experimental errors, each measurement was performed for 5 min at every sampling location. Mean values were calculated and are reported in this study.

A wide-range particle spectrometer (WPS 1000XP-A, MSP corp., USA) with a sampling flow rate of 1.0 L/min was employed to characterize the nano-TiO₂ nanoparticle number concentration in the workplace. N-butyl alcohol (butanol) was used as the working solvent for the condensation particle counter (CPC) in the instrument. The microstructure of the nano-TiO₂ particles was characterized.
using field emission scanning electron microscopy (FESEM, UltraPlus, Carl Zeiss, German). The commercial software ImageJ was used to measure the particle diameters from the FESEM images.

RESULTS AND DISCUSSION

SEM Micrographs of Aerosol Particles

Fig. 2 shows a typical SEM image of the nano-TiO₂ product. From the SEM images, the average diameter of these primary particles was calculated to be 36.7 nm. This average value corresponds exactly to the distribution peak for small-sized aerosol particles observed in the aerosol distributions (see Figs. 3–5). This result suggested that the aerosol particles, which ranged in size from 20–50 nm, were mostly composed of primary particles of the nano-TiO₂ product.

Aerosol Distributions in the Workshop Space

To ensure stable aerosol nanoparticle suspension conditions, the sampling processes were started after a working time of 3 hours. Fig. 3 shows the particle number concentrations for aerosols sampled at a fixed height of 1.0 m, at distances ranging from 1 to 5 m. All of the curves in Fig. 3 exhibited the typical distribution of the nano-TiO₂ aerosol in the workplace. The inset in Fig. 3 shows an enlargement of the size distribution of particles in the diameter range 0–200 nm. The number concentrations and distributions of aerosols are summarized in Table 1, for heights of 1–2 m and distances of 1–5 m.

No obvious differences in number concentration or distribution were observed for the aerosols sampled at 1–5 m. It was found that two peaks were dominant; these were at diameters of 124.2 and 524.4 nm, with number concentrations ranging from 20.8 k to 23.6 k #/cm³, and 1.6 k to 2.3 k #/cm³.
Yang et al., Aerosol and Air Quality Research, 12: 934–940, 2012

Table 1. Aerosol particle number concentrations and distributions.

<table>
<thead>
<tr>
<th>Sampling height</th>
<th>Peak location</th>
<th>1.0 m</th>
<th>2.0 m</th>
<th>3.0 m</th>
<th>4.0 m</th>
<th>5.0 m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
<td>FWHM</td>
<td>NC</td>
<td>FWHM</td>
<td>NC</td>
<td>FWHM</td>
</tr>
<tr>
<td>1.0 m</td>
<td>124.2 nm</td>
<td>23288</td>
<td>92.6</td>
<td>21541</td>
<td>81</td>
<td>22544</td>
</tr>
<tr>
<td></td>
<td>524.4 nm</td>
<td>1756</td>
<td>109.4</td>
<td>1648</td>
<td>116.2</td>
<td>1985</td>
</tr>
<tr>
<td>1.5 m</td>
<td>124.2 nm</td>
<td>23371</td>
<td>70.3</td>
<td>22207</td>
<td>79.1</td>
<td>22824</td>
</tr>
<tr>
<td></td>
<td>524.4 nm</td>
<td>1854</td>
<td>112.8</td>
<td>1609</td>
<td>119.3</td>
<td>2260</td>
</tr>
<tr>
<td>2.0 m</td>
<td>124.2 nm</td>
<td>23508</td>
<td>83.1</td>
<td>22103</td>
<td>68.6</td>
<td>23004</td>
</tr>
<tr>
<td></td>
<td>524.4 nm</td>
<td>1882</td>
<td>116.7</td>
<td>1793</td>
<td>129.1</td>
<td>1895</td>
</tr>
</tbody>
</table>

Note: (1) The units used for number concentration (NC) were #/cm³. (2) FWHM represents the full width at half maximum of the number concentration peaks. (3) Data from peaks located in the diameter of 0-30 nm are absent in Table 1, since most of the peaks were too small to be noted, as shown in Fig. 3.

respectively. Since the average diameter of the primary particles was approximately 36.7 nm (Fig. 2), the particles with a diameter of 524.4 nm were attributed to the agglomeration behavior of nanoparticles, while the particles with a diameter of 124.2 nm could have been agglomerated particles. As shown, the average concentration of the aerosol consisting of 124.2 nm particles showed its highest value of 22.44 k #/cm³ at a height of 2.0 m, with decreased values at heights of 1.5 and 1.0 m, with average concentrations of 22.37 k and 22.21 k #/cm³, respectively. In contrast, there was no similar trend observed in the concentration of agglomerated particles with a diameter of 524.4 nm; this suggested that for the agglomerated particles, the variation of the number concentration peaks. (3) Data from peaks located in the diameter of 0-30 nm are absent in Table 1, since most of the peaks were too small to be noted, as shown in Fig. 3.

The distances and the boundaries of the four transport zones are not very accurate. This is just a simple division in the transport process of nanoparticles in the work place.

The number distribution of the aerosol nanoparticles was highly dependent on the distance and height, as shown in Fig. 3. The full width at half maximum (FWHM) of the peaks for the 524.4 nm particles became larger with increasing sampling height and distance, while the peak for 124.2 nm exhibited a weak dependence on the distance and height, with small FWHM values of 70–93 nm.

Variation of Aerosol Distributions with Time

The aerosol number concentrations were measured after different working times (1, 2, and 3 hours), at a fixed height of 1.5 m, in the breathing zone. As shown in Fig. 4, compared with the sampling height, the sampling time had a more obvious influence on the distribution of the aerosol nanoparticle number concentration. In general, the number concentration of aerosols increased significantly with the working time. It is easy to understand that the increase in the concentration was the result of the accumulation of the aerosol during the working period. The aerosol number concentration showed an overall trend of decreasing gradually with increasing distance. For instance, the number concentration of the 124.2 nm particles sampled at 3 h showed a decrease from 23271 to 20857 #/cm³ in measurements taken at distances of 1 and 5 m, respectively, as summarized in Table 1.

Fig. 4 shows that the samples taken at 2 h exhibited very high concentrations of NPs with diameters of 20–40 nm at distances of 3 and 5 m. This can be attributed to the agglomeration of NPs and the dilution of the distance for the aerosol NPs. Since the agglomeration of NPs, or attachment of NPs to the larger particles, NPs tend to aggregate into large-sized particles in a high-concentration space and contribute to large fraction in the respirable particle mass (RPM) (Tsai et al., 2011). The large-sized agglomerated particles readily deposited within the space close to the discharging port because of the action of gravity of large-sized particles, while the smaller primary particles tended to keep flying and became suspended in the air at longer distances of approximately 3–4 m. The decrease in the concentration in the diameter range of 5 m resulted from the dilution of the aerosol particles in air at longer distances, as mentioned above.
One abnormal feature observed was that distinct concentration peaks dominated the curve at a sampling time of 2 h, but these peaks disappeared and returned to normal concentration levels at 3 h. In the presence of the high concentration of primary nanoparticles observed at 2 h, the ongoing accumulation of aerosol particles would have led to even higher concentrations, and could have easily resulted in the agglomeration of nanoparticles. As a result, a high concentration of agglomerated particles appeared at a working time of 3 h. This was also demonstrated by the slight peak shift to higher diameters, as shown in Fig. 4.

**Distributions with the Use of an Aerosol Enclosure**

An aerosol enclosure (dimensions: 2 m length × 1.5 m width × 2 m height) was designed and installed to control the suspension of aerosol nanoparticles, and to reduce their concentration in the workplace. The aerosol enclosure covered the discharging port in all directions, with the exception of one door that was used for the entrance and exit of the operating person, as shown in Fig. 1(b). When the door was closed, the space within the enclosure became sealed. With the aerosol enclosure, most of the aerosol particles were limited to the space within the enclosure, rather than dispersing throughout the whole workplace.

Since the number concentration values of the aerosol were typically high and stable at a distance of 3 m, the aerosol concentrations were measured at this distance, at a height of 1.5 m. Fig. 5 shows the number concentrations in the presence and absence of the aerosol enclosure, after the working time of 1 h, 2 h, and 3 h, respectively.

It is worthy of note that when the developed aerosol enclosure was used, the aerosol concentrations were significantly reduced for all working times, over the whole range of particle diameters. Moreover, the difference in the concentrations measured before and after enclosure construction increased for a long working time. This indicates that the enclosure provides a promising method for controlling aerosols in the workspace. Fig. 5 shows that the distinct concentration peaks located at 33 nm (2 h) and 124.2 nm (3 h) mode diameters decreased in magnitude—or even vanished—with the use of the aerosol enclosure. Furthermore, with the aerosol enclosure, particles had a mode diameter of approximately 175 nm, rather than smaller mode diameters of 33 or 124 nm. This is beneficial to worker’s protection as larger agglomerates can be separated more easily using proper aerosol protection equipment.

After various working times of 1, 2, and 3 h, the number concentration of particles exhibited a weak enhancement from 8.02 k, to 8.62 k, to 9.66 k #/cm³, respectively. The relationship between the accumulation of particles and the work time weakened greatly compared with the case without enclosure. In Fig. 5, besides the broad distribution at the mode diameter of 175 nm, the aerosol particles gradually became concentrated at a diameter of about 45 nm at the sampling time of 2 h and 3 h. The concentration behavior of particles in this diameter range could have resulted from the accumulation and agglomeration of the primary particles.

**CONCLUSIONS**

The flight and agglomeration behavior of aerosol nanoparticles influenced and limited the number concentration distribution of nano-TiO₂ aerosols in the workplace, while the dispersive forces on the aerosol nanoparticles from the discharging port had a profound influence on the flight and agglomeration of the particles. Agglomerated particles were the most frequently found form of aerosol particles, with a high number concentration in the workplace. Small primary particles of the nano-TiO₂ aerosol reached a relatively high concentration at a height of 1.5 m (in the breathing zone), after a working time of 2 h, but exhibited lower concentrations at other working times. With the aerosol enclosure, a distinct reduction in the aerosol concentrations was observed for all diameter ranges. Furthermore, with the help of the aerosol enclosure, the diameter of agglomerated aerosol particles
increased from the mode diameter of 124.2 nm to 175 nm which is more beneficial to worker protection, as larger agglomerates can be separated more easily using proper aerosol protection equipment.

ACKNOWLEDGMENTS

Financial support by the National Science Foundation of China (NSFC, No. 50876046) and the National Basic Research Program of China (973 Project, No. 2006CB932504) are gratefully acknowledged.

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Received for review, February 28, 2012

Accepted, April 28, 2012