



Distribution Characteristics of nano-TiO₂ Aerosol in the Workplace

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ABSTRACT

In this study, the distribution characteristics of nano-TiO₂ aerosol have been studied to get insight of the suspension, agglomeration and depositing performances of aerosol nanoparticles in the workplace. The number concentration and mass concentration of the aerosols have been characterized by using a wide-range particle spectrometer and cascade impactor samplers, respectively. Water based wet aerosol samplers, as well as its corresponding analysis approaches based on ultraviolet spectrometry, have also been developed to investigate the mass concentration and present an efficient sampling performance with the quite shorter sampling time than that by cascade impactors. To get a comparison of the test results with each other, sampling points have been set at the heights of breathing zone (1.0, 1.5 and 2.0 m) and at the distances of 1 to 5 m away from the discharge port of the assembly line. It is found that all the number concentration curves exhibit two peaks at the ranges of 10–200 nm and 500–900 nm. The aerosol particles with distance of 3 m exhibit the highest number concentration at all the diameter range except for the diameter less than 20 nm. While, aerosol at the distance of 5 m presents the highest number concentration, up to 18000 particles per cm³, in the diameter less than 20 nm. It is attributed to the spray forces of the discharge port and the suspending and depositing of aerosol nanoparticles in the air. The mass concentration and particle weight percentage at different diameter tested by cascade impactor show a strong dependence on the number concentration, which is well consistent with the results obtained by wet method.

Keywords: Aerosol nanoparticles; Mass concentration; Number concentration; Titanium dioxide, Workplace.

INTRODUCTION

Nanoproducts and processes hold an enormous economic potential for the markets of the future. This prompts a focus on the development of occupational health and safety recommendations for those working with engineered nanomaterials at both the laboratory and the manufacturing levels. Although the epidemiologic studies on lung cancer have not shown a dose-response relationship in TiO₂ workers (Fryzek *et al.*, 2003; Boffetta *et al.*, 2004), dose-response data are already available in rats, for both cancer (lung tumors) and noncancer (pulmonary inflammation) endpoints. Song *et al.* (2009) has reported that the exposure to nanoparticles in the workplace is related to death and several kinds of illness of workers, such as pleural effusion, pulmonary fibrosis and granuloma. Although it is hard to pin down nanoparticles as the cause of the ill health (Natasha, 2009) and these possible risks have still not been investigated to the fullest extent, lots of efforts are still

being made in on the research of aerosol nanoparticles in work places. A respiratory tract model proposed by the International Commission on Radiological Protection (ICRP) has shown that particles deposited in the tracheal bronchus and alveoli mostly are less than 100 nm in diameter (Bair, 1991; Kuo *et al.*, 2005, Oberdörster *et al.*, 2005). Thus, special methods on the control or protection of the aerosol particles less than 100 nm would be necessary to avoid the potential adverse health effects associated with aerosol nanoparticles exposure. Therefore, it is really essential to know the size and mass distributions and transport of nanoparticles in the workplace to establish nanoparticles protection methods for workers (Mädler and Friedlander, 2007). It is also very important for the assessment on aerosol nanoparticles in the environment by the relevant enterprises and organizations for environmental health.

Ensemble aerosol characterization and monitoring methods can respond to many particles simultaneously, either in real-time or using off-line analysis (Flagan, 2001; Alonso and Alguacil, 2008; Intra and Tipayawong, 2011). However, it is difficult to find an instrument or method could characterize all the features of aerosol particles. In general, the critical parameters to describe the aerosol particles are mass concentration, surface area concentration

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and number concentration. Although the available evidence suggests that mass concentration is not an appropriate exposure metric for many nanoparticles, mass-based techniques are still widely researched and used as a basic and conventional method. When the particle diameter is smaller than 100nm, the active surface is a function of the square of particle diameter. Normally, the critical doses are mostly derived using particle surface area, which is estimated from the mass lung burden data and from measurements or estimates of specific surface area (i.e., particle surface area per mass). However, these critical particle surface area doses are converted back to particle mass dose when extrapolating to humans because the current human lung dosimetry models (used to estimate airborne concentration leading to the critical lung doses) are all mass-based (Kuempel and Tran, 2002), and because the current occupational exposure limits for most airborne particulates including TiO₂ are also mass-based.

As evidently higher in concentration than in the atmosphere, aerosol nanoparticles are tending to aggregate in the workplace. In this paper, to investigate the agglomeration and distribution of aerosol nanoparticles in the workplace, the number concentrations and mass concentrations of nanoparticles have been studied within the breathing zone with various distances away from the discharge port. In addition, a novel home-made wet sampler and its relevant analytical method have also been developed to characterize the mass concentration of nano-TiO₂ aerosol in the workplace.

EXPERIMENTAL METHODS

A workplace (dimensions: 15 m length × 8 m width × 7.5 m height) manufacturing nanometer titanium dioxide (nano-TiO₂) powder was employed to study the nano-TiO₂ aerosol suspending in the space. In this plant, the nano-TiO₂ products are conveyed by the forces of air stream and discharged from the outlet in an average rate of 1 kg/min. The aerosol nanoparticles are spraying out to all the directions at the outlet by the pressure of compressed air because of the semitight of the discharge port. The discharge port (1 m high from the ground) was set as the aerosol source since the aerosol in the space was mainly released from the unit. To investigate the suspension, agglomeration and depositing performances of the aerosol particles without the interference of air flow, all the windows and doors of the workplace were closed during the sampling procedures. The locations of samplers varied in distance from the discharge port and height from the ground. The background tests were operated each day before working time and the background corrections on the concentrations were carried out based on the background data. Unless otherwise noted, all the data in this paper were the mean values of three times of repeat measurements.

A wide-range particle spectrometer (WPS 1000XP-A, MSP Corp., USA) was used to test the number concentration of the nano-TiO₂ aerosol in the workplace. The spectrometer combines differential mobility analyzer (DMA), condensation particle counter (CPC) and laser particle spectrometer (LPS)

technology into one single system. Seventy percent of the sampled flow of the instrument is sampled directly into the LPS for particle sizing and counting by laser light scattering. Simultaneously, thirty percent of the sampled flow is directed into the DMA for size classification and particle counting by the CPC. With integrated software, the spectrometer can present particles distributions from 10nm to 10μm. Isopropanol was used as the working solvent for CPC of the instrument.

As an efficient sampler for aerosol nanoparticles, cascade impactor was widely used and researched in recent years (Tsai *et al.*, 2009; Furuuchi *et al.*, 2010). Cascade impactor uses the principle of inertial separation to size segregate particle samples from a particle laden gas stream. Particulate matter is withdrawn isokinetically from the air in the workplace and segregated by size in a cascade impactor at the sampling point. In this study, the mass concentration distributions of nanoparticles were characterized by an eight stage cascade impactor sampler (Model 20-800, Tisch. Environmental, Inc.). During working time, two cascade impactors were placed individually and sample simultaneously at 3 and 5 meters away from the aerosol source at the height of 1.5 meters and keep sampling for 6 hours at 28.3 L/min. Before and after the sampling process, numbered glass fiber filters were put into a glove box with a stable temperature and moisture for 24 hours. Weighting processes were also operated in the glove box at the same temperature and moisture. To minimize the errors during the weighing processes, the eight stages of the instrument (10, 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65, and 0.43 μm) were divided into three parts, 1.1 to 10.0 μm, 0.43 to 1.1 μm and less than 0.43 μm, since the mass of each size fraction was determined gravimetrically.

A water or liquid based wet nanoparticles sampler was designed and developed to measure the mass concentration as well. The collection efficiency of the wet sampler was ranged from 95 to 99.5% which was evaluated by using an eight stage cascade impactor sampler with an assumed collection efficiency of 99.5%. The schematic diagram of the sampler is shown in Fig. 1. The working principles are as following: Under the negative pressure by vacuum pumping, nanoparticles is sampled through the sampling orifice along with the air and passes into the spray tower. Subsequently, aerosol nanoparticles mix with the liquid drops sprayed from the top nozzle of the tower, and pass through the sieve trays in the tower together with the fluid. As approaching to the fluid reservoir, most aerosol particles are washed out and collected into the liquid. Those particles which still suspended in the air are blended violently with the micro droplets down to 20 μm in diameter which sprayed out of the spray nozzle at high speed. The blending of liquid aerosol (micro droplets in the air) with nanoparticle aerosol in the limited space promotes the collection process of nanoparticles effectively. Eventually, the cleaning air goes out of the instrument through the liquid seal and the vacuum pump.

To confirm the experimental results obtained by the cascade impactor, the home-made wet sampler was operated at the height of 1.5 meters for 2 hours in the rate

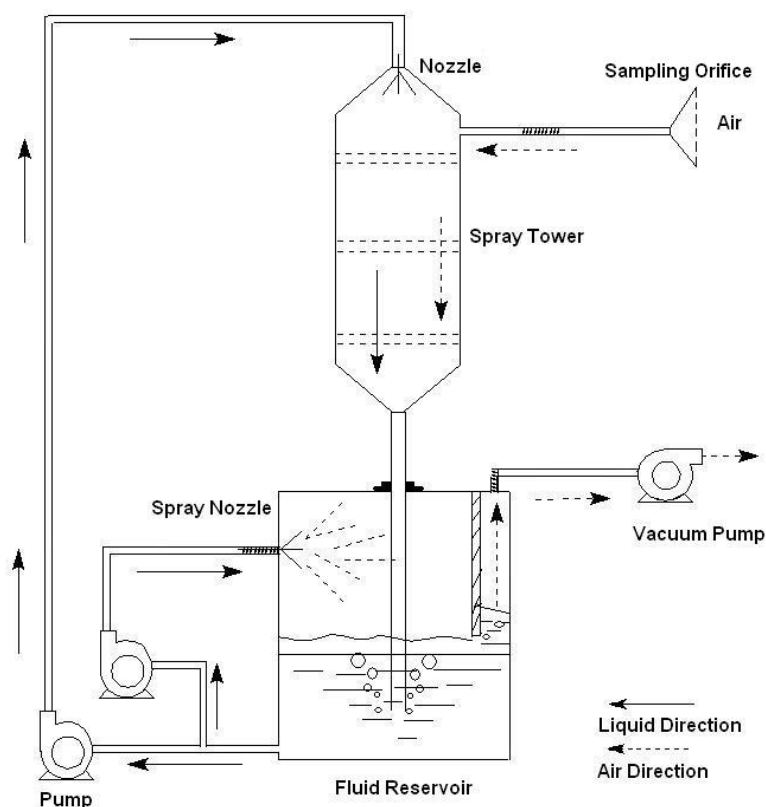


Fig. 1. The schematic diagram of the wet sampler.

of 400 L/h with 1.0 L diluted water. Two wet samplers were placed in the workplace at 3 and 5 meters away from the discharge port, respectively. After sampling for 2 hours, the nano-TiO₂ liquid suspension was taken out of the sampler and fully dispersed by ultrasonic, then tested by using an UV-Vis spectrometer (UVS) (Cary 100, Varian, Inc). The principle of the analytical method was based on the linear relationship of the ultraviolet wave absorption with the concentration of nano-TiO₂ suspension. To obtain the linear equation, the dispersions of nano-TiO₂ in various concentrations, from 0.2 to 2.0 mg/L, were fully dispersed by ultrasonic and tested by employing an UVS at the wave length of 330 nm. The linear equation of the ultraviolet absorption (Y) and the concentration (X) was built as: $Y = 0.01694X - 5.72519 \times 10^{-5}$, with a related coefficient $R = 0.99904$. The detection limit of the method by using UVS was 0.00102 mg/L. With the indication of UVS, the concentration of the sampled suspension could be drawing out from the linear equation. Based on the sampling flow rate, sampling time and volume of water, the relationship of the concentration of suspension (C_L , mg/L) and aerosol (C_A , mg/L) was described as: $C_L = 800 C_A$.

A field emission scanning electron microscopy (FESEM, UltraPlus, Zeiss, German) and a laser particle sizer (Zetasizer 3000HS_A, Malvern, UK) were employed to characterize the microscope images and the diameter distributions of the collection suspension and nano-TiO₂ products, respectively. Commercial software named ImageJ was used to analysis the particle diameters of the microscope images. Before the testing of the laser particle

sizer, the samples were dispersed thoroughly by ultrasonic to minimize the aggregation of nanoparticles.

RESULTS AND DISCUSSION

Number Concentration Distributions of Nanoparticles

As the breathing zone of workers is close to the height of 1.5 meter, the distributions of number concentration at 1.5, 1.0 and 2.0 m height were studied in this paper, as shown in Fig. 2–4, respectively. The sampling sites varied in distance from 1 to 5 meters away from the aerosol source. The insert graphs in Fig. 2–4 enlarged the distribution characteristics within the diameter range of 0–200 nm.

Fig. 2 presents the number concentrations of nano-TiO₂ aerosol at 1.5 meter high above the ground in the workplace. It is found that there are two broad bands around, 10–200 nm and 500–900 nm with the number concentrations of more than 4000 and 1000–2000 particles per cm³, respectively. Aerosol particles located in the area of 500–900 nm in diameter are probably agglomerates since the primary particle diameter of the product is about 70 nm based on the images of SEM (Fig. 5). Distinct peaks located within the range of 10 to 70 nm can be observed in the insert graph and the peak values of number concentration are higher than 8000 particles per cm³. It suggested that the primary particles always present the highest number concentration at various distances in the workplace in spite of the transformation or agglomeration of the aerosol nanoparticles. Aerosol particles with diameter ranging from 70 to 200 nm are the secondary

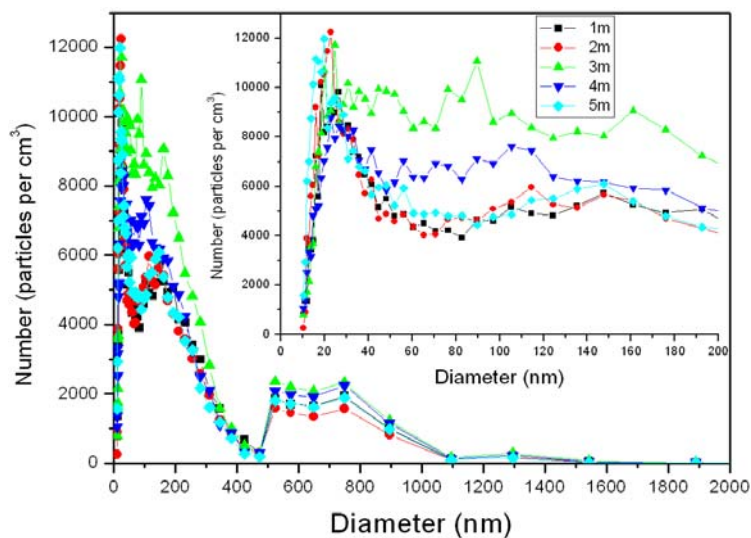


Fig. 2. Number concentrations of nanoparticles sampling at 1.5 m high.

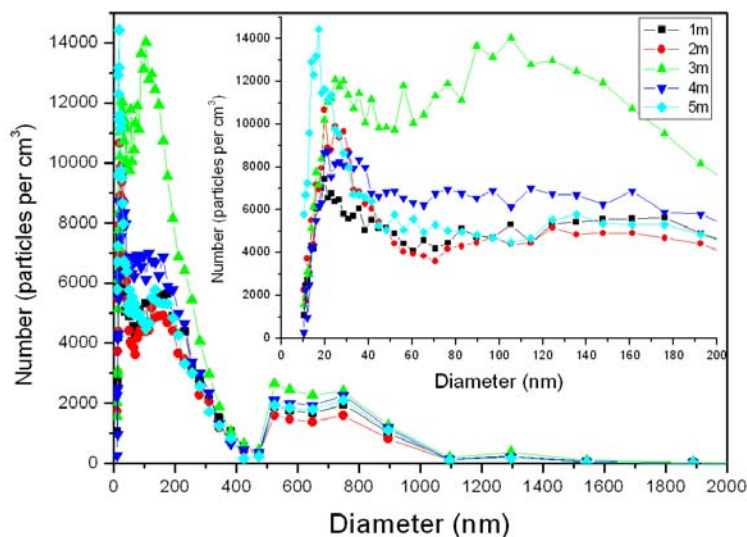


Fig. 3. Number concentrations of nanoparticles sampling at 1.0 m high.

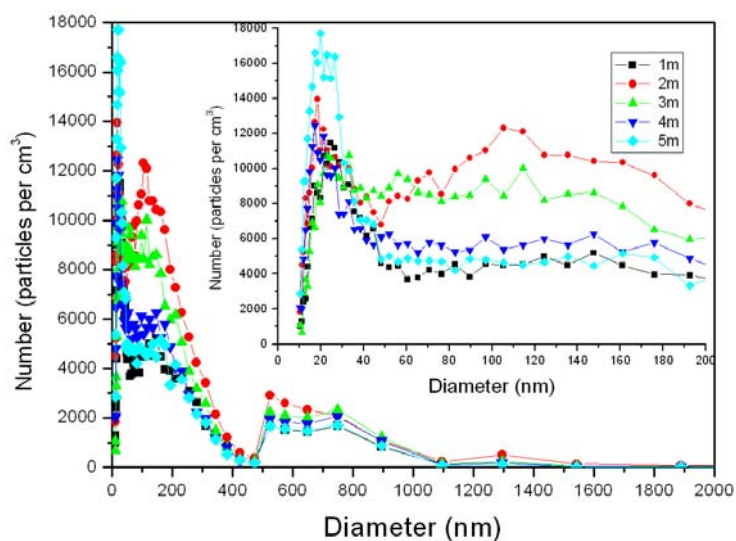


Fig. 4. Number concentrations of nanoparticles sampling at 2.0 m high.

particles. These particles could be the unconsolidated agglomeration aggregated by several primary nanoparticles, which is also called soft agglomerates or loose agglomerates in material field. Similar agglomeration cases of aerosol nanoparticles were noticed by Tsai et al. (2009, 2011) at different workplace. These kinds of agglomeration particles can be de-aggregated by external forces. However, those aerosol particles with diameter of 500–900 nm should mainly be the hard agglomerations which are difficult to be de-aggregated by ordinary forces.

Another interesting feature was observed in Fig. 2 that the aerosol particles at the distance of 3 meters from the aerosol source exhibit the highest number concentration when the particle diameter is larger than 20 nm. It was because that the spray forces of the aerosol source make the aerosol nanoparticles spray out to all directions in a radiate form, and the forces lead to aerosol nanoparticles flying directly about 2 meters in distance from its outlet. However, because of the force of inertia, most of particles start to deposit after flying over 3 meters and the small-sized particles (i.e. less than 20 nm) may keep flying and deposit at the distance of 5 meters.

Fig. 3 shows the distributions of number concentrations as a function of particle diameters of nano-TiO₂ aerosol sampled at 1.0 m high in the workplace. The particle distributions exhibit the similar trending with the case shown in Fig. 2. It also shows that most particles less than 200 nm are floating at 3 m, while particles less than 30 nm are mostly suspending at the distance of 5 meters. However, when nanoparticles were sampled at larger height of 2 meters, the distribution of number concentration is quite different with the former two cases. Although the nanoparticles sampled at 3 meters in distance is still at a high concentration level, the highest number concentration of particles distributed in most diameter range belongs to the aerosol sampled at the distance of 2 meters instead of 3 meters when the sampling height is 1.5 or 1.0 meter. On the contrary, particles sampled at 2 meters in distance exhibit the lowest concentration in both Fig. 2 and Fig. 3.

The distributions of nano-TiO₂ aerosol in the workplace at different heights of 1.0, 1.5 and 2.0 m, are very similar. Most of aerosol particles are concentrated in the diameter less than 200 nm and the number concentration are all higher than 4000 particles per cm³. As the sampling height increases, the number concentrations sampled at 3 meters away from the aerosol source gradually decrease. As shown, the number concentrations of particles with

diameter less than 200 nm at various heights of 1.0, 1.5 and 2.0 m are mostly higher than 1000 particles per cm³, mostly less than 1000 particles per cm³ and totally less than 1000 particles per cm³, respectively. In Fig. 3, when the sample was set at 1.0 m in height and 5 m in distance, the concentrations higher than 12000 particles per cm³ are contributed by the particles less than 18.5 nm in diameter. When at the height of 2.0 m and distance of 5 m, the particles with the diameter of 16–28 nm dominate the distribution feature of number concentration with intensity higher than 14000 particles per cm³. Moreover, when sampled at 1.5 m high and 5 m in distance, two peaks of the primary particles are displayed in the regimes of diameter less than 21 nm and 21–29 nm, respectively. It indicates a simple combination of the two distribution profiles at the height of 1.0 m and 2.0 m in lower peak intensities.

Mass Concentration by Cascade Impactor

Table 1 lists the results of nano-TiO₂ aerosol obtained by the cascade impactors. According to the data, the ensemble mass concentration of aerosol at 3 m is much higher than that at 5 m. It is well consistent with the results of the number concentration distribution in which aerosol at 3 m exhibit the highest number concentration. For the particles with diameter smaller than 20 nm, the number of aerosol particles is much more at the distance of 5 m than at 3 m. However, the weight and weight ratio of particles with size less than 0.43 μm at 3 m are both showing a bit heavier and bigger than that of particles at 5 m, as the data listed in Table 1.

Mass Concentrations by Wet Method

Table 2 shows the concentration of nano-TiO₂ in the suspension and in the air. As similar with Table 1, the mass concentration at the distance of 3 meters is much higher than that of aerosol at 5 m, as listed in Table 2. Meanwhile, the concentrations in the two Tables are also very close, which indicates a good consistence of the two methods employed in this study. However, the results obtained by the wet samplers are a little bit lower than that by the cascade impactors. The origin of the deviation might be that the wet samplers start sampling at the first 2 hours of the working time instead of the whole period of working. The concentrations of aerosol particles accumulate and increase gradually with the working process since the windows and doors of the workplace are closed during the

Table 1 Concentrations of nano-TiO₂ aerosol collected by cascade impactors.

Distance (m)	Particle Diameter (μm)	Weight (mg)	Concentration (mg/L) or Weight Ratio (%)
3.0	1.1–10.0 μm	2.256	95.15%
	0.43–1.1 μm	0.112	4.72%
	< 0.43 μm	0.003	0.13%
	Whole range	2.371	2.327×10^{-4} mg/L
5.0	1.1–10.0 μm	1.602	95.19%
	0.43–1.1 μm	0.080	4.75%
	< 0.43 μm	0.001	0.06%
	Whole range	1.683	1.652×10^{-4} mg/L

Table 2 Concentrations of nano-TiO₂ aerosol collected by wet method.

Distance (m)	Concentration in Suspension (mg/L)	Concentration in Air (mg/L)
3.0	0.1586	1.983×10^{-4}
5.0	0.1012	1.265×10^{-4}

sampling procedures, and the concentrations of particles in the last 2 hours are undoubtedly much higher than that of the first 2 hours. Here it is worthy noticing that wet aerosol sampler presents a quick sampling performance with the short sampling time, while cascade impactors always need long sampling time over 6 hours.

Microphotos and Particle size Distributions

Figs. 5(a) and (b) show the micrographs of the suspension sampled at 3 meters in distance and the nano-TiO₂ product, respectively. According to the micrographs, there is no obvious difference on the diameters distribution of particles, and nano-TiO₂ particles in both samples aggregate together

with the primary particle size about 70 nm in diameter. Analyzed with the help of commercial software named ImageJ, the diameters of the primary particles in the micrographs are statistically-calculated and the average size of particles in image (a) and (b) are estimated to be 69.4 nm and 75.5 nm based on the analysis number of 90 and 120 particles, respectively.

The particle diameter distributions of the collection suspension at 3 meters in distance and the nano-TiO₂ product, by using a laser particle sizer, are marked as curve (a) and (b) in Fig. 6. The peak values of curve (a) and (b) are 64.5 nm and 71.8 nm, respectively. The X-axis of Fig. 6 for the diameter is in a logarithmic scale form of the values.

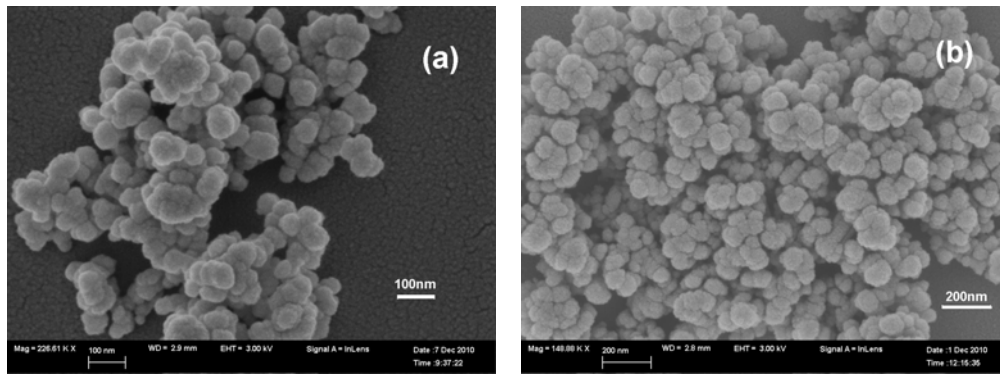


Fig. 5. SEM images of (a) collection suspension and (b) nano-TiO₂ product.

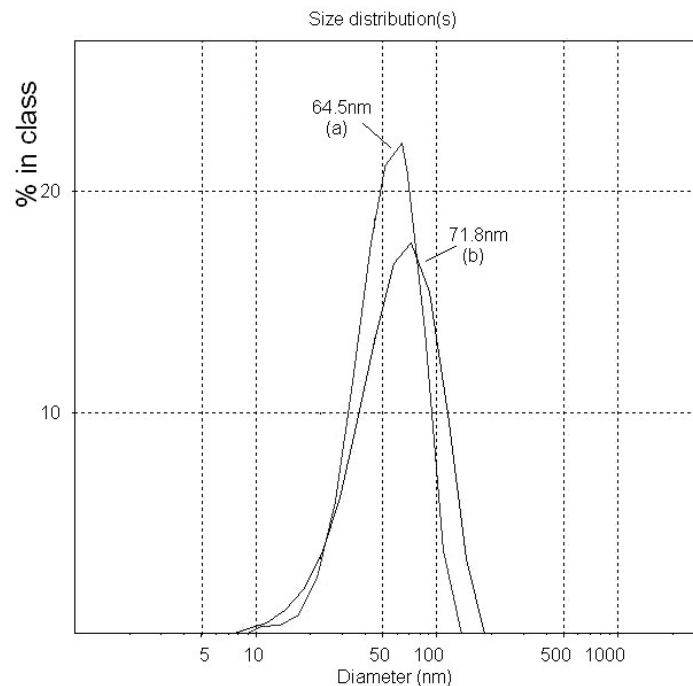


Fig. 6. Diameter curves of (a) collection suspension and (b) nano-TiO₂ product.

The microscope images and the particle diameter distribution feature of the samples indicate that the aerosols suspending in the air are the same particulate matter with the product and the discharge port is the main aerosol source in the workplace. However, there still exists a little gap between the diameter of the collection suspension and nano-TiO₂ product. The particle diameter of the aerosol suspending in the air is always less than that of the nano-TiO₂ product as a whole. It is partially because that the particles with small size can fly further in distance under the same spray forces of the aerosol source and aerosol nanoparticles suspending at 3 m are less in diameter than those particles at the original source.

CONCLUSIONS

Two peaks of nano-TiO₂ aerosol in the diameter range of 10–200 nm and 500–900 nm in the workplace are presented in the distribution profiling of number concentration curves with the number concentration of more than 4000 particles per cm³ and 1000–2000 particles per cm³, respectively. Owing to the spray force of the aerosol source and the inertia force of flying aerosol particles, the number concentration at 3 meters in distance shows the highest concentration than other sampling distance at the height of breathing zone. Mass concentrations tested by cascade impactor and the home-made wet nanoparticles sampler exhibit a good agreement with each other, and the wet sampler presents a quick sampling performance with high collection efficiency. The particle diameter distributions of aerosol suspension exhibit a dependence on the sampling distance. Furthermore, aerosols suspending in the workplace air are slightly less in diameter than the product. This work would shed some light on the research in the field of environmental evaluation and the aerosol protection in the workplace.

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