IDENTIFYING AND MANAGING THE HEALTH AND SAFETY HAZARDS OF NANOMATERIALS IN LABORATORIES

A Thesis

by

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ABSTRACT

In the last decade, nanomaterials have been increasingly researched as the result of the rapid development in nanotechnology due to novel properties and behavior of nanomaterials different from their bulk materials. However, the development of nanomaterials results in unexpected impacts on humanity and the environment. Exposure to nanomaterials causes potential health and physical hazards to researchers handling nanomaterials in laboratories. In addition, specific standards and guidelines on the safe handling of nanomaterials' hazards in laboratories are very scarce compared to the handling of bulk materials. With this concern in mind, this paper describes efforts toward the development of applicable and appropriate guidelines with the objective of identifying and managing the health and safety hazards of nanomaterials inside laboratories.

Two main areas of research are studied: 1) Identification of nanomaterial hazards in laboratories, and 2) Mitigation of nanomaterial hazards in laboratories. For the first task, the control banding approach should be recommended to identify the health hazards of nanomaterials rather than the occupational exposure limits because toxicological data of nanomaterials is not sufficient. Dust explosion classes based on dust explosion deflagration index (K_{St}) are used for identifying the physical hazards of nanomaterials using the dust explosion test apparatus. For the second task, control methods dedicated for nanomaterials such as Nano-glovebox, Local Exhaust Ventilation (LEV), and

Personal Protective Equipment (PPE) should be used to protect researchers in laboratories from the hazards of nanomaterials.

Finally, in order to accomplish the objective, this paper focuses on both developing a control methods selection flowchart and developing hazard controls during the whole life cycle of nanomaterials.

DEDICATION

To my wife: Boyoun Kim

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NOMENCLATURE

ANSES	Administracion Nacional de la Seguridad Social (National Social Security Administration)
APR	Air-purifying Particulate Respirator
ASTM	American Society for Testing and Materials
BAuA	Bundesanstalt fur Arbeitsschutz und Arbeitsmedizin (Federal Institute for Occupational Safety and Health)
BM	Bulk Material
BSI	British Standards Institution
CB	Control Banding
DOE	United States Department of Energy
$(dP/dt)_{max}$	Maximum Rate of Pressure Rise
EOR	Enhanced Oil Recovery
EPA	US Environmental Protection Agency
FFR	Filtering Facepiece Respirator
GEV	General Exhaust Ventilation
HEPA	High Efficiency Particulate Air
K_{St}	Deflagration Index
LEV	Local Exhaust Ventilation
MKOPSC	Mary Kay O’Connor Process Safety Center
MEC	Minimum Explosive Concentration
MIE	Minimum Ignition Energy

MPPS	Most Penetrating Particle Size
MWCNT	Multi-walled Carbon Nanotube
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
NM	Nanomaterial
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
P_{max}	Maximum Explosion Pressure
PPE	Personal Protective Equipment
SCBA	Self-Contained Breathing Apparatus
SWCNT	Single-walled Carbon Nanotube
TEM	Transmission Electron Microscope
ULPA	Ultra Low Particulate Air

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CHAPTER I

INTRODUCTION

The word “nano” in the Greek language means “dwarf” [1]. Nano is a unit of measurement corresponding to one thousand millionths (10^{-9}), and a single nanometer (nm) is one thousand millionth of a meter. Nanoscale is a range in size from around 1 nm to 100 nm. The diameter of virus and DNA is included in the nanoscale. The substances of nanoscale are invisible to the naked eye.

ISO/TS 27687:2008 [2] defines a nano-object as a material with one or more external dimensions on the nanoscale. A specific term of nano-objects is the nanoparticle, which is a particle with all three external dimensions on the nanoscale. Ultrafine particles are naturally occurring particulates of nanoscale, whereas nanomaterials, which are a main term of this paper, are defined as engineered nano-objects including nanoparticles [3].

Most currently, the accelerated development in nanotechnology causes an increase of a production of nanomaterials to fulfill the demands of particular applications, especially within chemical/petroleum industries, textile industries and medical sciences. Applications of nanomaterials, categorized by their chemical composition, are shown in Section 3.2.

As the demands of research related to nanomaterials have risen, the number of researchers and research papers associated with nanomaterials has significantly increased in the last decade. This rapid growth of nanomaterials research is reflected in the graph shown in Figure 1, which summarizes a literature search of papers having selected keywords (nanotube, graphene, nanowire, and quantum dots) in their titles during the last decade (2004-2013) [4].

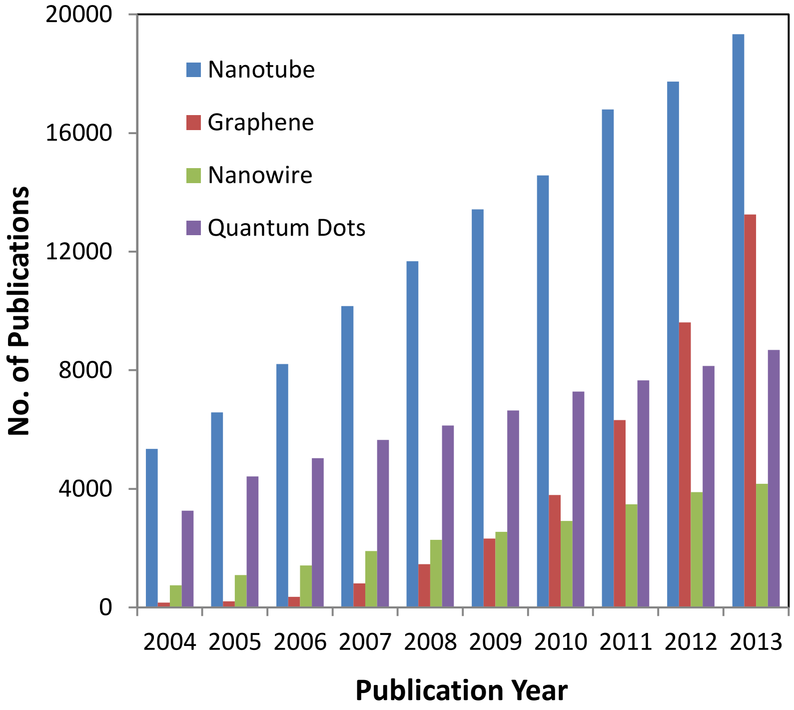


Figure 1. Number of Papers Published During the Last Decade (2004-2013) [5]

However, the explosive increase of nanomaterials could result in unwanted impacts on humanity and the environment. Exposure to nanomaterials causes potential health and safety hazards. Therefore, many researchers working with nanomaterials in laboratories are at risk of serious diseases or explosions. To protect the researchers against hazards of nanomaterials, this paper looks into identifying and managing the health and safety hazards of nanomaterials in laboratories.

CHAPTER II

RESEARCH BACKGROUND

2.1 Applications of Nanomaterials

Nanomaterials are categorized by their chemical compositions. Many nanomaterials are divided into one of five classes listed in Table 1 [6].

Table 1. Categorization of Nanomaterials and Their Applications [6]

Categories	Major Items	Applications
Carbon-based Nanomaterials	Carbon Nanotubes, Fullerenes, Graphene	Optical electronics, Photovoltaic cells, Energy storage, Ultrafiltration, and Composite materials
Metal-based Nanomaterials	Silver, Gold, Iron, Copper, Aluminum	Anti-microbial wound dressings and Biosensors
Metal Oxide Nanomaterials	Titanium Dioxide, Zinc Oxide, Cerium Oxide	Enhanced oil recovery, Well stimulation fluids, Sunscreen filters, Self-cleaning and antibacterial surfaces, and Electrocatalysis
Quantum dots	Cadmium Selenide, Cadmium Telluride	Agents for medical imaging, Transistors, Solar cells, and LEDs
Polymeric Nanomaterials	Hydrocarbon Polymers	Drug delivery devices

2.1.1 Carbon-based Nanomaterials

Carbon is one of the most common elements. Carbon-based nanomaterials, such as fullerenes, nanotubes, and graphene, are more usable when compared with other conventional materials. Fullerene is composed of more than 60 carbon atoms connected to form 20 hexagonal and 12 pentagonal rings as shown in Figure 2(c) [7]. Carbon nanotubes consist of a graphene sheet rolled up into a tubular structure. Depending on the number of layers, carbon nanotubes with a single layer are called single-walled carbon nanotubes (SWCNTs) as shown in Figure 2(a), and carbon nanotubes with multiple layers are called multi-walled carbon nanotubes (MWCNTs) as shown in Figure 2(b) [8]. Current uses and applications of carbon-based nanomaterials are optical electronics, photovoltaic cells, energy storage, ultrafiltration, and composite materials.

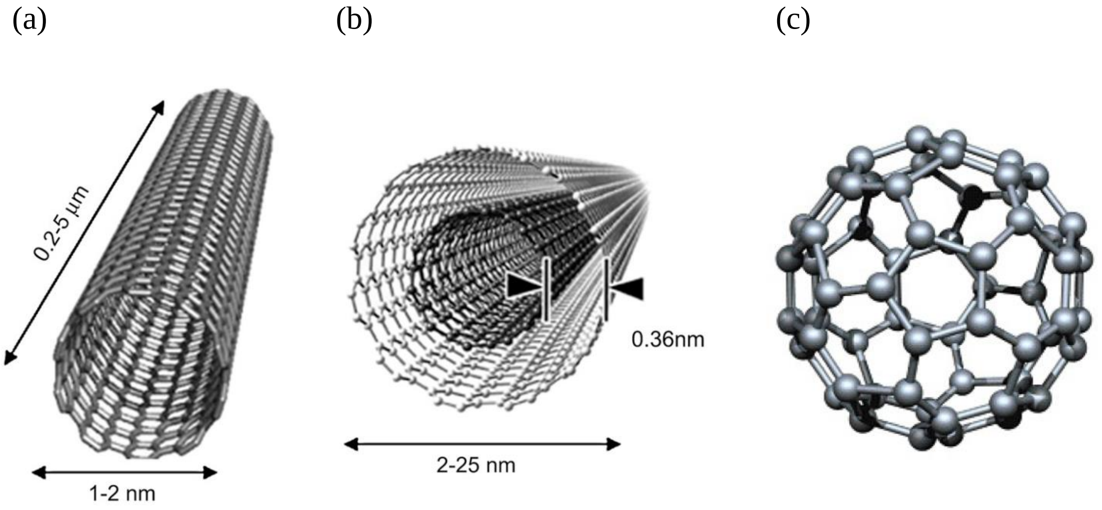


Figure 2. (a) Diagram of Single-walled Carbon Nanotube (SWCNT), (b) Multi-walled Carbon Nanotube (MWCNT), and (c) Fullerene (C60) [6], [9]

2.1.2 Metal-based Nanomaterials

Some of the notable known metal-based nanomaterials are gold, silver, copper, and iron. These metals have unique physical and chemical properties, which determine their application. Of the metal-based nanomaterials in use today, the most commercially used nanomaterial is nanosilver, which has anti-microbial properties. Metal-based nanomaterials are used in many medical applications, such as anti-microbial wound dressings and biosensors [10].

2.1.3 Metal Oxide Nanomaterials

Metal oxide nanomaterials cover all kinds of metal oxides, such as Titanium Dioxide (TiO_2), Zinc Oxide (ZnO), and Cerium Oxide (CeO_2). More importantly, these materials have wider applications [11].

Recent research projects have shown that the nanotechnology has the potential to solve or manage several problems in the petroleum industry. The researched areas of application, for example, are enhanced oil recovery (EOR) and well stimulation fluids. These areas are especially important now because of the recent rise in global energy demand. The ability of nanomaterials to alter certain properties of oil can be used advantageously with EOR and well stimulation. N.A. Ogolo et al. [12] experimentally showed that oxides of Aluminum, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin, and Silicon are selected as good agents for EOR.

2.1.4 Quantum Dots

A quantum dot is a nanometer-scale semiconductor crystallite, which confines the electron-hole pair in all three dimensions [13]. One of the main advantages of quantum dots is that the size and shape are easy to control precisely. This benefit allows semiconductor quantum dots to be customized for various uses, such as transistors, solar cells, LEDs, and size-dependent optical and optoelectronic devices, including agents for medical imaging [14]. Figure 3 shows the typical structure of quantum dots.

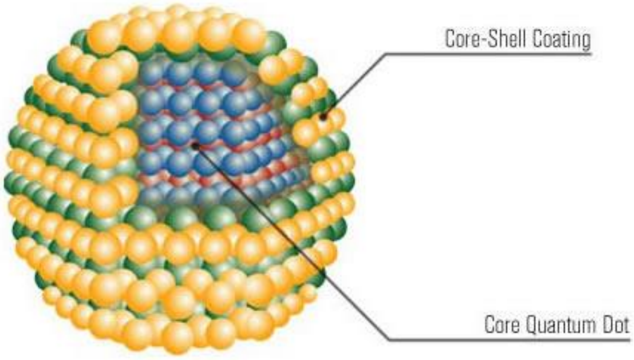


Figure 3. Structure of Quantum Dots [14]

2.1.5 Polymeric Nanomaterials

Polymeric nanomaterials are prepared from hydrocarbon polymers. Polymeric nanomaterials can be used to deliver the drug to the precise location due to the drug’s ability to target particular organs and tissues. Dendrimers are one of the polymeric nanomaterials [15].

2.2 Motivation

It is widely known that nanomaterials exhibit novel properties and functions different from their bulk materials, such as extremely small size, high reactivity, and large surface area [16]. As explained in the previous section, this novelty of nanomaterials has developed many applications over time. However, these special properties could result in unexpected impacts on humans and the environment. If someone is exposed to nanomaterials in the air, nanomaterials can access that person's body through four potential routes, such as inhalation, dermal, ingestion, and injection. Many studies related to toxicology of nanomaterials have reported that nanomaterials can cause serious diseases, including cancer, Crohn's disease, Alzheimer's disease, asthma, and different kinds of lung diseases [17].

Figure 4 shows a specific example regarding the toxicity of nanomaterials. In Figure 4(a), a researcher synthesizes single-walled carbon nanotubes (SWCNTs) from a carbon arc reactor. Figure 4(b) illustrates that carbon nanotubes were collected in his personal breathing zone during the synthesis of carbon nanotubes. These pictures show that a large amount of carbon nanotubes exposed in the laboratory were deposited in his lungs [18].

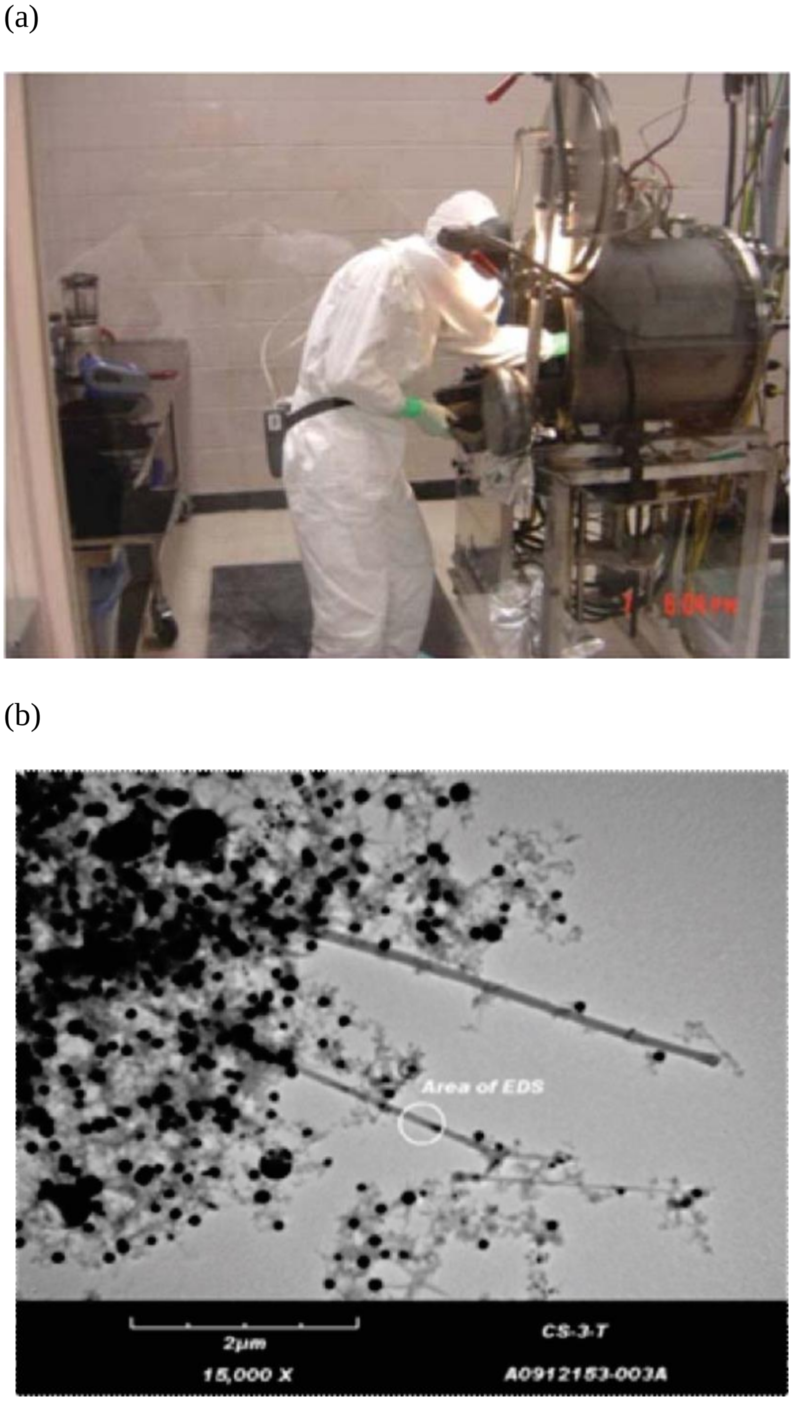


Figure 4. (a) A Researcher Harvests SWCNT from a Carbon Arc Reactor. (b) A TEM Image of Nanotubes Collected in the Researcher's Personal Breathing Zone During Nanotube Harvesting. [18]

Figure 5 is another specific example regarding the toxicity of nanomaterials. Recently, researchers at the National Institute of Occupational Safety and Health (NIOSH) implemented a study of mice to see how inhalation of multi-walled carbon nanotubes (MWCNTs) affects the development of a lung tumor. Group 2 mice receiving both a cancer initiator and exposure to MWCNTs significantly increased the incidence of developing tumors and created on average more tumors per mouse lung than Group 1 mice, who only received the cancer initiator. Therefore, MWCNTs increase the probability of cancer in mice when they were exposed to a cancer initiator, which is a carcinogen. Furthermore, it is concluded in this study that MWCNTs are a cancer promoter [19].

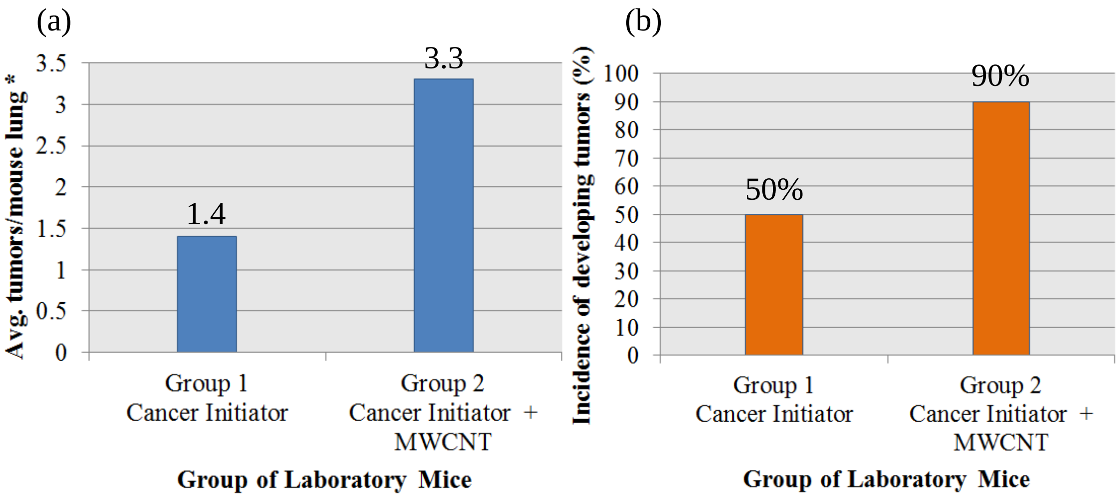


Figure 5. Tumor Formation in Laboratory Mice Lung Exposed to MWCNTs [19]

Therefore, it is important for the researchers to know how dangerous they are and which proper engineering control methods and personal protective equipment (PPE) should be used in laboratories to protect them from nanomaterial hazards. In addition, specific standards and guidelines for identifying and safely handling hazards caused by various nanomaterials in laboratories are too scarce compared to the handling of bulk materials. In conclusion, understanding, predicting, and managing the health and safety hazards of nanomaterials in laboratories is urgently needed for the health and safety of researchers.

2.3 Objectives

The purpose of this study is to propose a proper guideline for researchers to be able to identify and control the health and physical hazards related to nanomaterials in laboratories. Occupational exposure limits (OELs) and control banding approaches are suggested to identify nanomaterial's health hazards and the dust explosion classes are proposed to identify nanomaterial's physical hazards. Above all, this research focuses on three contributions as stated below:

- Selecting proper control methods and PPEs dedicated for nanomaterials
- Developing control methods selection flowchart
- Developing hazard controls during the whole life cycle

2.4 Research Scope

Nanomaterial hazards can be divided into three groups. The three hazard groups are diagrammed in Figure 6. This research is concerned about health and physical hazards of nanomaterials because this is limited to inside laboratories.

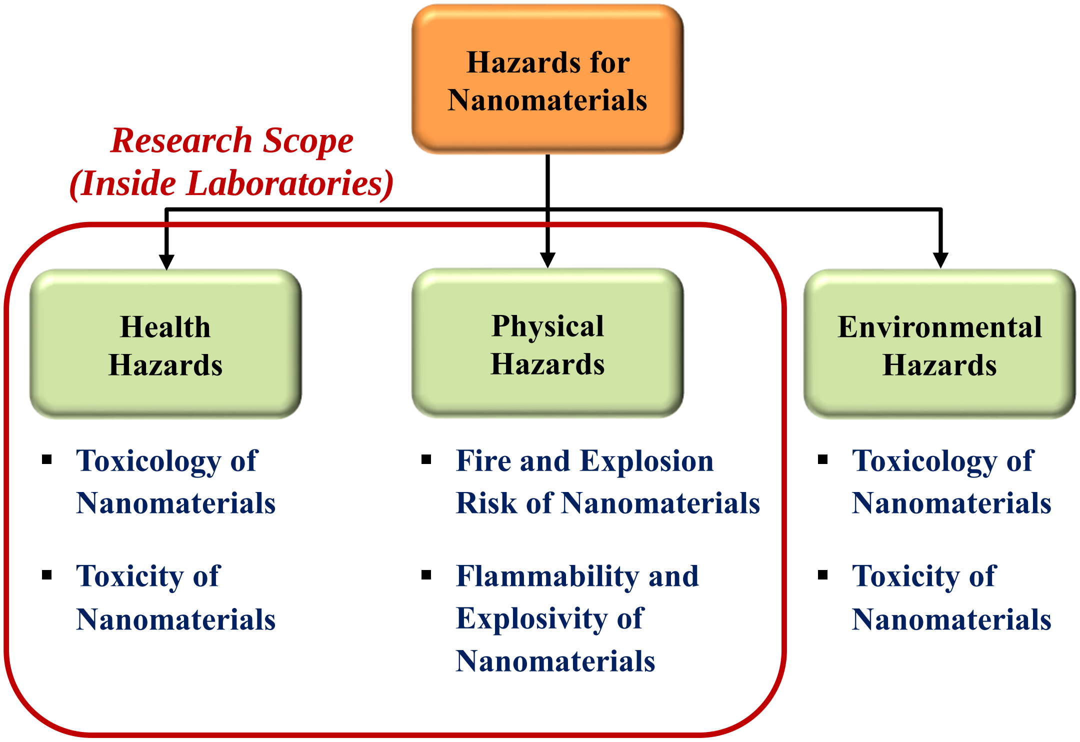


Figure 6. Classifications of Nanomaterial Hazards

CHAPTER III

METHODOLOGY

3.1 Identification of Health Hazards

Before identifying the health hazards of nanomaterials, it is important to recognize the potential routes of nanomaterials when a person is exposed to them. Potential routes of nanomaterial exposure include inhalation, dermal, ingestion, and injection as shown in Figure 7 [20].

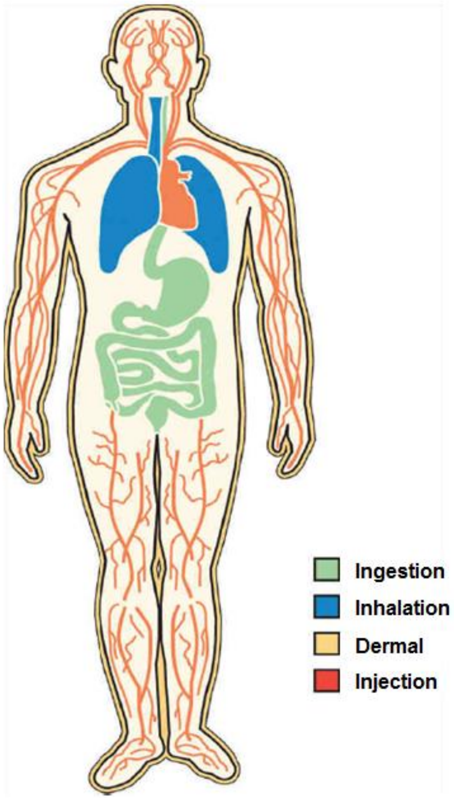


Figure 7. Potential Routes of Nanomaterial Exposure [20]

In order to determine the occupational exposure limits and the health risk levels of control banding, various types of laboratory animal studies have been conducted with several nanomaterials using the four different potential routes of nanomaterial exposure to get the toxicological data [21].

Figure 8 shows how the level of toxicological data of nanomaterials can determine the nanomaterials hazard identification. Occupational exposure limits (OELs) are the most robust type for identifying hazards of nanomaterials when the toxicological data is adequate. But the currently available toxicological data for nanomaterials would be considered limited. Therefore, the most practical approach is the control banding method, which is the lower level type [22].

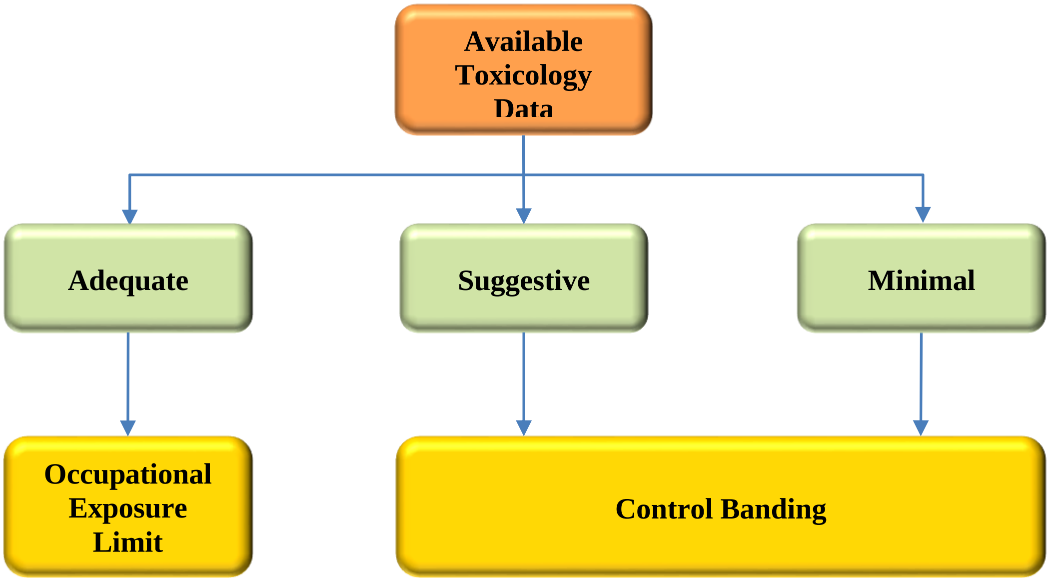


Figure 8. Flowchart of the Level of Toxicological Data [22]

3.1.1 Current OELs for Nanomaterials

OELs are one of the main methods for preventing exposure to occupational health hazards. In the case of nanomaterials, OELs play an essential role in determining the risk of hazards caused by nanomaterials and determine if engineering controls, for example, glovebox and local exhaust ventilation, need to be used by researchers. [22].

OELs generally minimize the probability of negative effects that come from exposure to potentially hazardous substances. OELs are established based upon results from animal studies and observing researchers exposed to substances [22].

OELs for nanomaterials are scarce, whereas those for their bulk materials are abundant. Certain nanoparticles have different properties from larger particles of the same substance. Therefore, using existing OELs for bulk materials may not be useful for protection from their nanomaterials. Nevertheless, a few relevant agencies have proposed some specific occupational exposure limits for certain nanomaterials as shown in Section 4.3 [23].

3.1.2 Control Banding Methods for Nanomaterials

The level of available toxicology data for most nanomaterials could be considered suggestive or minimal. The control banding method usually offers simplified solutions in the absence of nanomaterials toxicological data [24].

There are several tools for control banding such as Precautionary Matrix, CB Nanotool, ANSES, Stoffenmanager Nano, Nanosafer, and Guidance [25]. However, the

CB Nanotool proposed by Paik et al. could be strongly recommended because of usability and specialty for nanomaterials. [26]. This CB Nanotool is based on four risk levels and each level has a proper engineering control method for dealing with certain nanomaterials. These four overall risk levels are determined using both severity and probability scores in the risk level matrix as seen below in Table 2.

Table 2. Risk Level Matrix for the CB Nanotool [26]

Probability

Severity

	Extremely Unlikely (0-25)	Less Likely (26-50)	Likely (51-75)	Probable (76-100)
Very High (76-100)	RL 3	RL 3	RL 4	RL 4
High (51-75)	RL 2	RL 2	RL 3	RL 4
Medium (26-50)	RL 1	RL 1	RL 2	RL 3
Low (0-25)	RL 1	RL 1	RL 1	RL 2

Degrees of the engineering control method are determined by each risk level [26].

- Risk Level 1: GEV
- Risk Level 2: LEV or Fume hoods
- Risk Level 3: Full Containment
- Risk Level 4: Inquire expert advice

Calculating scores for the CB Nanotool has been the biggest challenge faced in development. The severity and probability scores are determined by the sum of points by answering questions about the following factors in Table 3. The calculated points for each severity or probability factor decide the overall risk level in the risk level matrix [26].

Table 3. Severity and Probability Factors and Maximum Points per Factor [26]

Severity factor	Maximum points	Probability factor	Maximum points
Surface Chemistry of NM	10	Estimated amount of nanomaterial	25
Particle shape of NM	10	Dustiness/mistiness	30
Particle diameter of NM	10	Number of employees with similar exposure	15
Solubility of NM	10	Frequency of operation	15
Carcinogenicity of NM	7.5	Duration of operation	15

Table 3 Continued

Severity factor	Maximum points	Probability factor	Maximum points
Reproductive toxicity of NM	7.5	-	-
Mutagenicity of NM	7.5	-	-
Dermal toxicity of NM	7.5	-	-
Toxicity of BM	10	-	-
Carcinogenicity of BM	5	-	-
Reproductive toxicity of BM	5	-	-
Mutagenicity of BM	5	-	-
Dermal hazard potential of BM	5	-	-
Total	100	Total	100

(NM: nanomaterial, BM: bulk material)

3.2 Identification of Physical Hazards

Nanoparticles tend to explode more than larger particles with the same concentration, because the specific surface area increases as a particle size decreases [3].

Several properties of flammability and explosivity of various carbon nanotubes, carbon blacks, and zinc and aluminum nanomaterials have been studied using a 20 liter or 36 liter dust explosion test apparatus. These studies were conducted in accordance with current practices such as the ASTM Method E 1226 [27] and the NFPA Standard

68 [28]. This apparatus consists of an explosion chamber, dispersion system, ignition system, sensor system, data acquisition system, and vacuum system [29]. The Mary Kay O'Connor Process Safety Center (MKOPSC) has a 36 liter dust explosion test apparatus in the dust explosion laboratory to study various kinds of sample nanomaterials, including carbon nanofibers. Firstly, as shown in Figure 9, the nanomaterial sample is loaded into the dust container linked to the dust explosion chamber. The vessel is vacuumed to a certain level and compressed air is stored in the air reservoir. Then, the fast acting valve (FAV) is opened to allow a certain amount of high-pressure air into the air reservoir. This helps the loaded nanomaterial sample to enter the explosion chamber to form a dust cloud at the atmospheric pressure. Finally, the data acquisition system records the evolution of the explosion pressure of the nanomaterials [30].

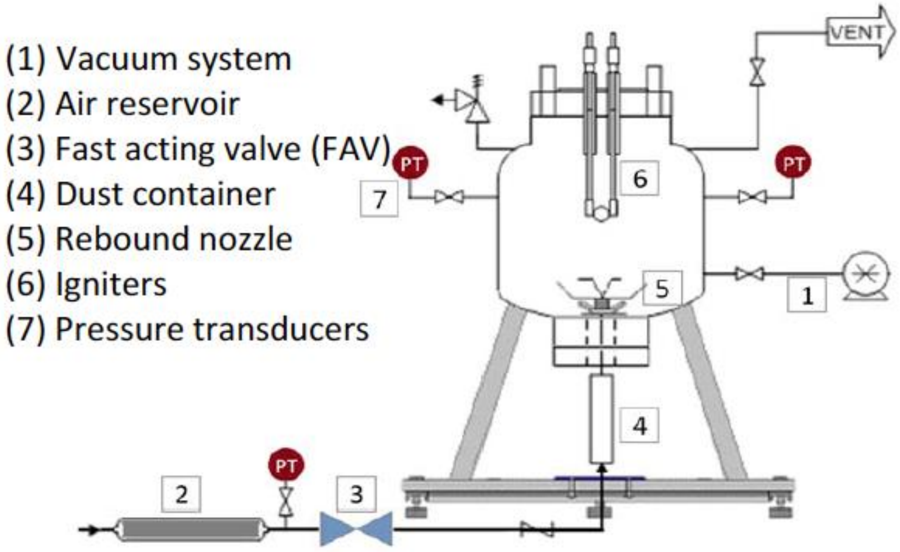


Figure 9. Schematic Diagram of the 36 L Dust Explosion Vessel [30]

According to the ASTM Method E 1226, dust explosion classes are categorized into four levels according to the deflagration index (K_{St}), which is a main explosion property as shown below in Table 4 [27].

Table 4. Dust Explosion Classes determined by Deflagration Index (K_{St}) [31]

Dust Explosion Class	K_{St} (bar m/s)	Characteristics
St-0	0	No explosion
St-1	1 - 200	Weak explosion
St-2	200 – 300	Strong explosion
St-3	> 300	Very strong explosion

Bouillard et al. [32][33], Wu et al. [34] and MKOPSC have implemented research about the flammability and explosivity of various nanomaterials to determine the relationships between a nanoparticle’s size and its explosion characteristics. The results of the research are shown in Section 4.3.

3.3 Concept of Engineering Control Methods

To protect researchers from nanomaterial hazards, there is a hierarchy of exposure hazard controls. The hierarchy consists of elimination, substitution, engineering control, administrative control, and personal protective equipment. In the hierarchy, engineering control methods and personal protective equipment are the fundamental methods to mitigate nanomaterial hazards [35].

3.3.1 Mechanisms of Air Filtration

Control methods specialized for nanomaterials, which are local exhaust ventilation (LEV), Stoffenmanager Nano-glovebox, and PPE, are used. Because most of these control methods are equipped with a fibrous filter to capture particulates in the air, being able to understand mechanisms of air filtration is very important.

Air filtration gets rid of unexpected particulates in the air. Figure 10 illustrates four primary filter collection mechanisms related to fiber materials that affect filter performance [7].

- Diffusion: This happens when a particle’s random (Brownian) movement results in that particle to contact a fiber.
- Interception: The particle trajectory meets a fiber and is then attached by that fiber.
- Inertial impaction: Air flow is deviated around a fiber, denser particles cannot follow air curvature.
- Electrostatic attraction: This is affected by electrostatic charge and more effective as a particle becomes smaller.

By diffusion phenomena, the smaller the particles, the higher efficiency of filtration. Therefore, fibrous filters are efficient in capturing airborne nanomaterials.

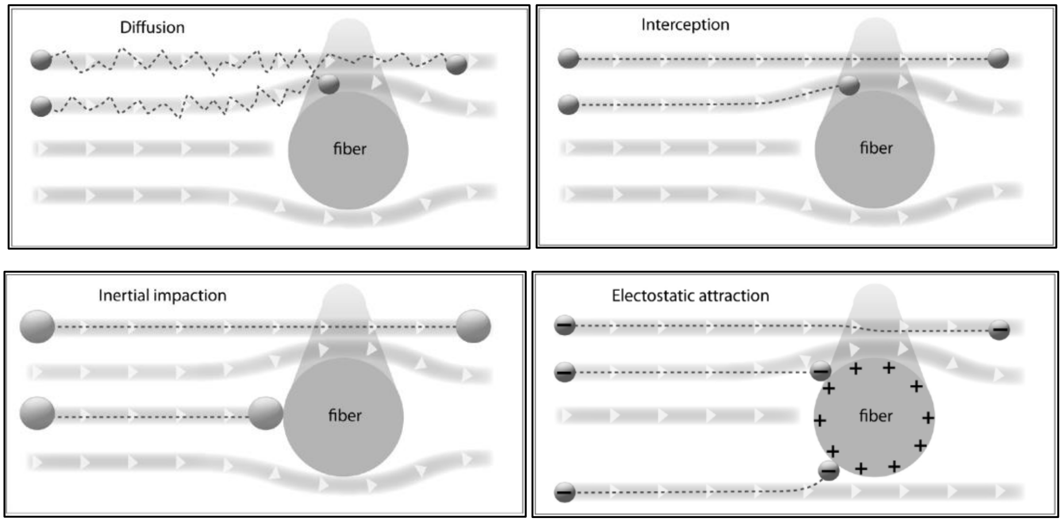


Figure 10. Four Primary Filter Collection Mechanisms related to Fiber Materials [36]

These four air filtration mechanisms are applied to mechanical filters. If the particle size is larger than 0.2 μm, inertial impaction and interception are dominant. Otherwise, the diffusion and electrostatic attraction are dominant [37].

In the Figure 11 shown below, this collection efficiency curve shows the combined effects of these four air filtration mechanisms and the most penetrating particle size (MPPS) of 0.3 μm [37].

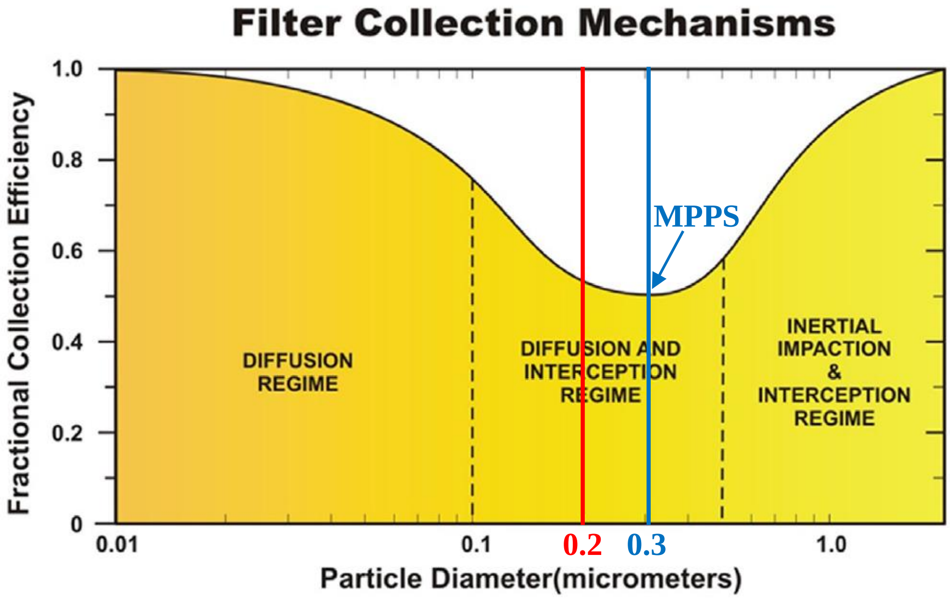


Figure 11. Collection Efficiency Curve [37]

3.3.2 High Efficiency Particulate Air (HEPA)

High efficiency particulate air (HEPA) is a type of air filter requiring high filtration. The filter must meet the HEPA standard set by the United States Department of Energy (DOE). To satisfy the HEPA standard, the filter must remove 99.97% of the particle at the MPPS of 0.3 μm, which is the most difficult-sized particle to filter [38].

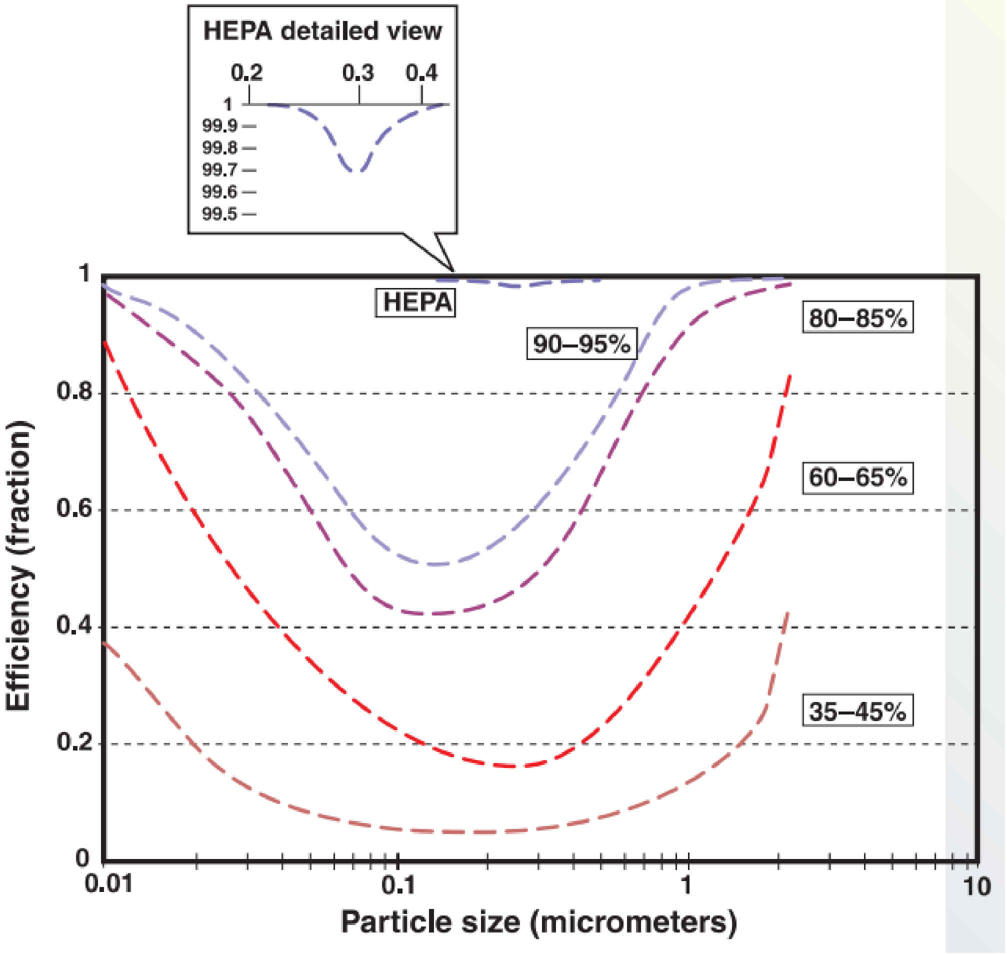


Figure 12. Comparison of Collection Efficiency and Particle Size for Different Filters [37]

Figure 12 illustrates how a HEPA filter performs when compared to lower efficiency filters. Different grades of the HEPA filters have different efficiencies in the particle size classified as EN1822-1:2009 as shown in Table 5. For example, the HEPA filter H14 is designed as 99.97% efficient at the MMPS of 0.3 µm, and the ultra low particulate air (ULPA) filters are designed as 99.999% efficient (U15 – U17) [39].

To capture nanomaterials in laboratories, the HEPA filters should be properly sized and installed for local exhaust ventilation systems and respirators.

Table 5. Various Classifications of High-efficiency Filters [39]

	Integral Value		Local Value	
Filter Class	Collection Efficiency %	Penetration %	Collection Efficiency %	Penetration %
E10	85	15	-	-
E11	95	5	-	-
E12	99.5	0.5	-	-
H13	99.95	0.05	99.75	0.25
H14	99.995	0.005	99.975	0.025
U15	99.9995	0.0005	99.9975	0.0025
U16	99.99995	0.00005	99.99975	0.00025
U17	99.999995	0.000005	99.9999	0.0001

CHAPTER IV

RESULTS AND DISCUSSION

4.1 OELs Proposed by Agencies for Various Nanomaterials

Recently NIOSH has proposed OELs for carbon nanotubes, carbon nanofibers, and titanium dioxide. European agencies have also established more OELs for various nanomaterials than the United States. Some companies have proposed OELs for their products. Table 6 lists their proposed OELs for certain nanomaterials [22].

Table 6. OELs Proposed by Agencies for Various Nanomaterials

Nanomaterial	OELs	Reference
CNTs and nanofibers	1 µg/m^3	NIOSH [21]
Titanium dioxide	0.3 mg/m^3 ultrafine 2.4 mg/m^3 fine	NIOSH [40]
General dust	3 mg/m^3	BAuA [41]
Photocopier toner	0.06 mg/m^3	BAuA [42]
Fibrous (3:1 aspect ratio, length 75,000 nm)	0.01 fibers(f)/ml	BSI [43]
MWCNTs (Bayer product only)	0.05 mg/m^3	Bayer [44]
MWCNTs (Nanocyl product only)	0.0025 mg/m^3	Nanocyl [45]

4.2 Overall Risk Level for Various Nanomaterials Using CB Nanotool

Paik et al. [26] shows the results of several nanomaterials calculated by the CB Nanotool as below in Table 7. The nanomaterials' risk levels are calculated using severity and probability scores. Carbon nanotubes' overall risk level is determined to be risk level 3 in the risk matrix, which means full containment is recommended as an engineering control method according to the CB Nanotool.

Table 7. Overall Risk Level for Various Nanomaterials Using CB Nanotool [26]

Nanomaterials	Severity Score	Probability Score	Overall Risk Level	Recommended Engineering Control by CB Nanotool
Carbon Nanotubes	60	likely	RL3	Full Containment
Metal Nanoparticles (Cu, Ni, Ag)	65	75	RL3	Full Containment
Ceramic Particles (Lu_2O_3 and LuAG)	45	75	RL2	Fume hood or LEV
Ceramic Nanoparticles (B_4C, alumina, zirconia, MgO, CaO and carbo wax)	57.5	75	RL3	Full Containment
Uranium dioxide	66.25	65	RL3	Full Containment

4.3 Explosion Test Results of Various Nanomaterials

A few researchers have determined the relationships between the particle diameter of a nanomaterial and its minimum ignition energy (MIE), minimum explosion concentration (MEC), maximum explosion pressure (P_{max}), maximum rate of pressure rise ($(dP/dt)_{max}$), and deflagration index (K_{St}) of various nanomaterials, such as carbon nanotubes, carbon blacks, and zinc and aluminum nanomaterials, using the dust explosion test apparatus.

Bouillard et al. [32][33] have researched the ignition sensitivity and explosion severity of carbon nanotubes, carbon blacks, and metal nanomaterials by using the 20 liter explosion sphere and the modified Hartmann tube. Wu et al. [34] have studied the flammability and explosivity of aluminum nanomaterials using the 20 liter explosion apparatus and the 1.2-L Hartmann apparatus. MKOPSC [46] are conducting ongoing testing of the MEC and K_{St} of carbon nanofibers using a customized 36 liter explosion apparatus, according to ASTM Method E 1226. The results of these researches are listed in Table 8.

The above researches show that, as the particle size decreases, the minimum ignition energy (MIE) decreases. the deflagration index (K_{St}) also tends to increase unless agglomeration/aggregation effects are present [47][48]. In addition, metal nanomaterials are subject to being more flammable and explosible than carbon-based nanomaterials.

According to the dust explosion classifications mentioned in Section 3.2, the four risk levels of nanomaterials' physical hazard can be determined by the deflagration index (K_{St}). Like the established risk matrix of the CB Nanotool, the dust explosion classifications can be classified into four different risk levels, according to K_{St} values.

Table 8. Explosion Severity and Sensibility of Various Nanomaterials [32], [33], [34]

Nano-materials	Particle Size (nm)	Specific Surface Area (m^2/g)	MIE (mJ)	MEC (g/m^3)	P_{max} (barg)	$(dP/dt)_{max}$ (bar/s)	K_{St} (bar.m/s)	Explosi-vity Class St
MWCNTs	10	195	> 1 J	45	6.6	227	62	St-1
Corax N115	23	130	> 1 J	60	7.7	88	88	St-1
Corax N550	75	40	> 1 J	60	7.5	503	136	St-1
Thermal Black N990	330	9	> 1 J	60	6.7	240	65	St-1
Printex XE2	3	950	> 1 J	60	7.2	343	93	St-1
Aluminum (35nm)	35	52.21	< 1	40	7.3	1286	349	St-3
Aluminum (100nm)	100	23	< 1	-	8.2	1340	362	St-3
Aluminum (200nm)	200	10.5	7	-	9.5	2480	673	St-3
Aluminum (40 µm)	40 µm	5.31	59.7	35	5.9	282	77	St-1

Table 8 Continued

Nano-materials	Particle Size (nm)	Specific Surface Area (m^2/g)	MIE (mJ)	MEC (g/m^3)	P_{max} (barg)	$(dP/dt)_{max}$ (bar/s)	K_{St} (bar.m/s)	Explosi-vity Class St
Aluminum 3	-	0.74	14	-	9.8	2090	567	St-3
Aluminum 7	-	0.25	-	-	9.1	1460	396	St-3
Aluminum 27	-	0.11	-	-	7.5	400	106	St-1
Aluminum 42	-	0.08	440	-	7.2	360	98	St-1
Zinc 120 nm	-	19	19	-	3.9	223	61	St-1
Zn 38 μm	-	-	> 1 J	-	3.7	71	19	St-1

4.4 Engineering Control Methods for Nanomaterials

4.4.1 Local Exhaust Ventilation (LEV) for Nanomaterials

To protect researchers from nanomaterial hazards, the local exhaust ventilation (LEV) system is effective in capturing nanomaterials. Figure 13 illustrates how the force of inertia and diffusion affect an efficiency of particle capturing in a ventilation system. Smaller particles with a diameter below 300 nm have the minimum properties of diffusion and the force of inertia. This means the smaller particles are easily captured in a ventilation system. However, inertial behavior of larger particles increases significantly with particle diameter. This means that the larger particles are harder to capture [49].

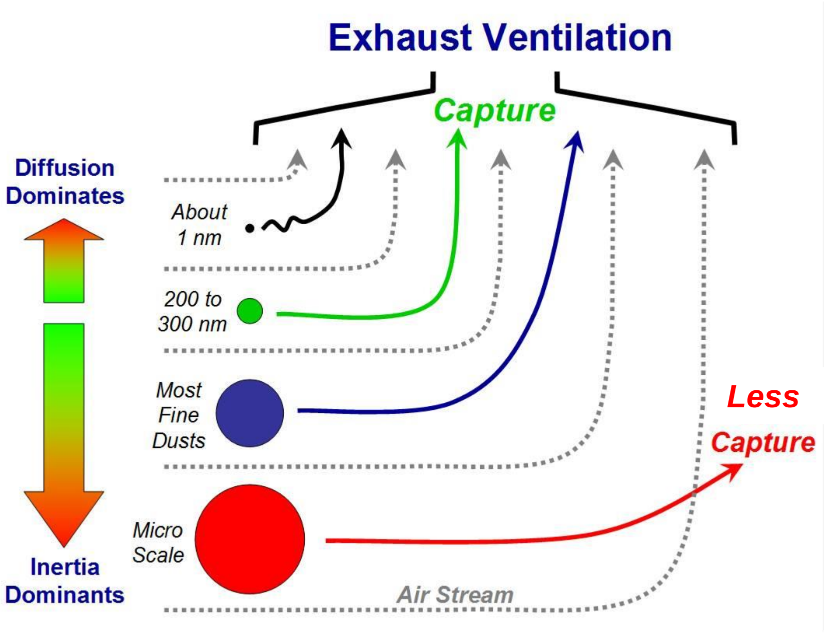


Figure 13. Exposure Control of Particles with LEV [49]

4.4.2 Full Containment for Nanomaterials

Even if local exhaust ventilation is effective, nanoparticles tend to agglomerate and aggregate when the particles are smaller, which means nanoparticles could be as big as micro size. Therefore, agglomerated nanoparticles are less captured in a ventilation system. In this case, the full containment can provide a higher level of protection for handling nanomaterials. Stoffenmanager Nano-glovebox with high efficiency particulate air (HEPA) filter, which is specialized for nanomaterials, should be used for capturing nanomaterials as below in Figure 14 [50].

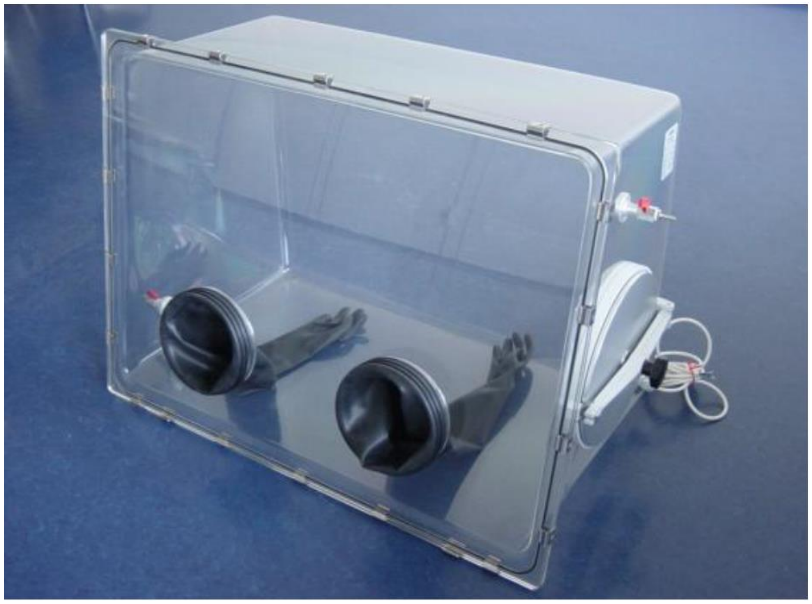


Figure 14. Stoffenmanager Nano-glovebox with HEPA Filter [50]

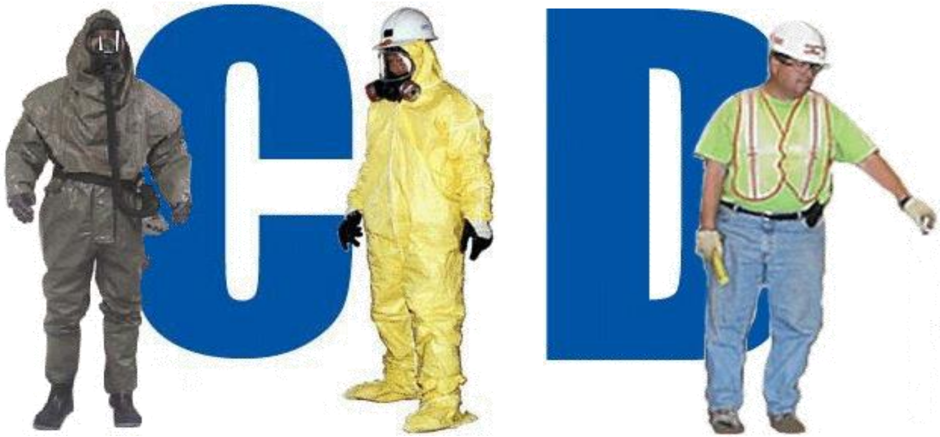
4.5 Personal Protective Equipment for Nanomaterials

4.5.1 Protective Clothing

US Environmental Protection Agency (EPA) and Occupational Safety and Health Administration (OSHA) proposed the four levels of protective clothing for different levels of hazard as below in Figure 15 [51].

Fully encapsulating suit & SCBA

Protective clothing & SCBA



Protective clothing & Respiratory protection

Regular working clothing

Figure 15. OSHA PPE Levels [51]

- Level A is the highest level protection. The workers are completely isolated from their environment in a total encapsulating chemical protective suit equipped with self-contained breathing apparatus (SCBA). This is used in emergency response, which is high toxicity situation.
- Level B is the greatest level of respiratory protection with self-contained breathing apparatus (SCBA), but it offers less skin protection with chemical-resistant clothing.
- Level C is characterized by medium protection. The worker is covered with chemical resistant clothing and uses an air purification respirator. This level occurs when concentration and types of containment are known, and criteria for using respirators are satisfied.
- Level D is minimal protection. The workers do not need respiratory protection and have a regular work uniform [51].

The four levels above of protective clothing can be used for the control methods selection flowchart proposed in Section 4.6.

4.5.2 Glove and Respiratory Protection

NIOSH recommends wearing hand protection when working with nanomaterials. Nitrile gloves are most generally used for nanomaterials [52].

NIOSH recommends wearing respiratory protector with proper HEPA filters with different efficiencies depending on the uses. NIOSH has also developed the 42 CFR, Part 84 Air-purifying particulate respirator (APR) certification for testing and certifying air-purifying respirators. The classification of the respirators based on their minimum efficiencies and test methods are shown in Table 9 [53].

Table 9. Description of Filter Classes Certified under 42 CFR 84 [53]

Minimum Efficiency	NaCl Test (N-Series)	DOP oil Test (R-Series)	DOP oil Test (P-Series)
95%	N95	R95	P95
99%	N99	R99	P99
99.97%	N100	R100	P100

The selection processes of respirators are outlined as following [53][54]:

1) The selection of N, R, and P-series filters are based on the presences of oil particles.
    - N-Series: not resistant to oil mist
    - R-Series: resistant to oil mist
    - P-Series: protective against oil mist
2) The selection of filter efficiency is based on minimum filter efficiency using certified test conditions.

N95 and P100 are the most common for filtering facepiece respirators (FFR) and elastomeric half mask respirators [54]. Currently the P100 respirators are used in the dust explosion laboratory in MKOPSC.

Not only NIOSH but BSI CE and FDA also certifies respirators. The certified respirators based on polydisperse aerosol test and monodisperse aerosol test results by various agencies are listed in Table 10 [54].

Table 10. Percentage Penetration Results of Various Respirators [54]

Approval	Type	Polydisperse Aerosol Test (PAT) (%)	Monodisperse Aerosol Test (MAT) (%)	
			40 nm	300 nm
NIOSH	N95	0.61 - 1.24	2.0 - 5.2	0.20 - 1.56
NIOSH	P100	0.003 - 0.022	0.007-0.009	0.0006 - 0.001
CE	FFP2	0.27 - 0.50	1.45 - 2.22	0.69 - 0.84
CE	FFP3	0.009 - 0.014	0.155 - 0.164	0.06 - 0.07
FDA	Surgical Mask	1.58 - 88.06	8.98 - 72.51	2.14 - 88.95
N/A	Dust Mask	1.00 - 87.02	4.31 – 81.63	0.86 – 95.05

4.6 Control Methods Selection Flowchart for Nanomaterials Health Hazards

This paper suggests the control methods selection flowchart for managing nanomaterials health hazards in laboratories as seen below in Figure 16. Firstly, the four risk levels in the flowchart are determined using CB Nanotool. Second, the four different types of engineering control methods can be used for each risk level. Finally, the four levels of OSHA PPE can be used for each risk level. For example, the overall risk level of carbon nanotubes calculated by the CB Nanotool in Table 7 is risk level 3. This means that a researcher working with carbon nanotubes should work in a laboratory equipped with Nano-glovebox with HEPA filtration, which is a type of the full containment, wearing OSHA Level B PPE, which is chemical-resistant clothing with self-contained breathing apparatus (SCBA).

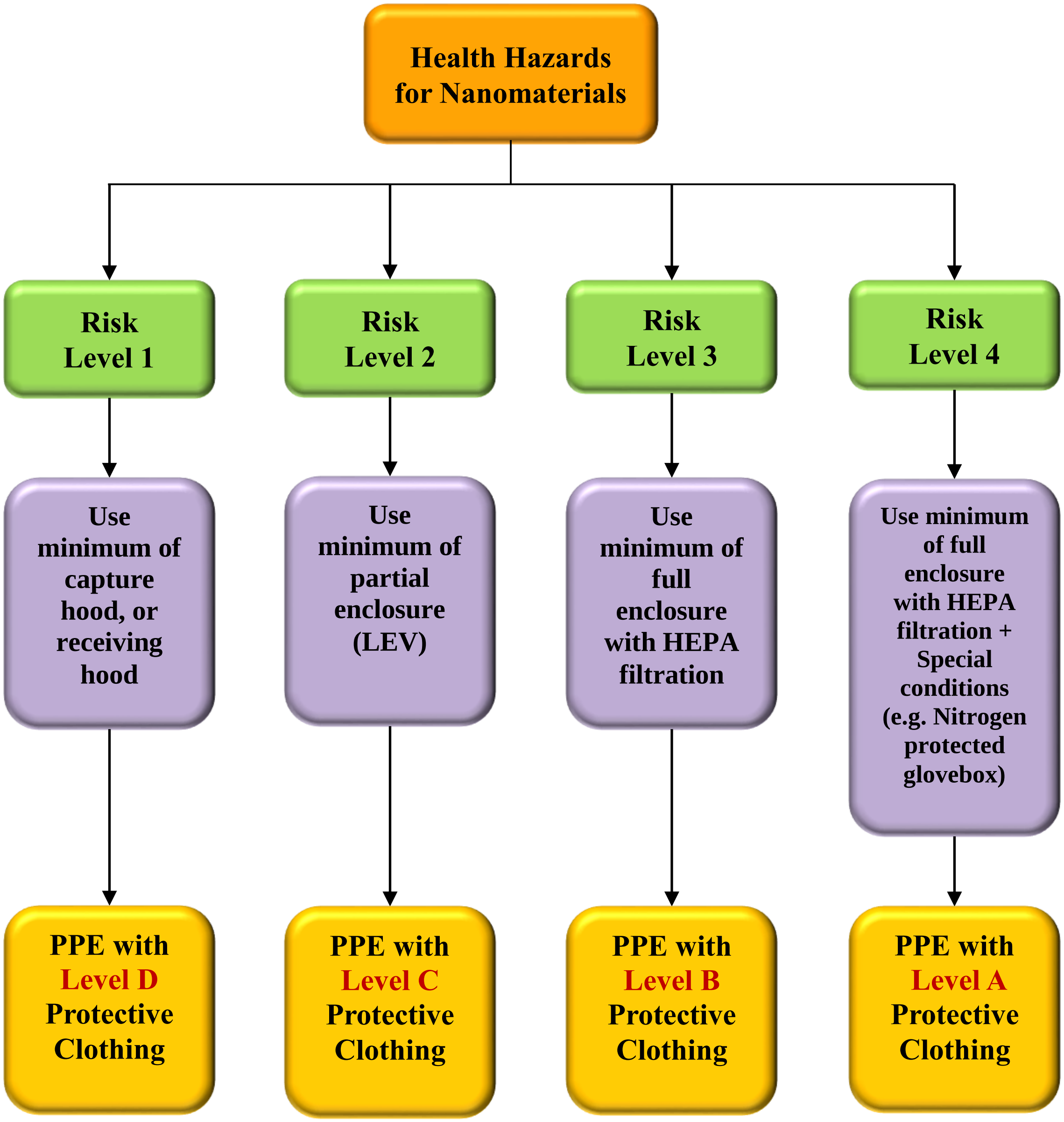


Figure 16. Control Methods Selection Flowchart for Nanomaterials Health Hazards

4.7 Hazard Controls During the Whole Life Cycle of Nanomaterials

During the whole life cycle of nanomaterials, hazards can occur in five steps as shown in Figure 17 [55]. The most important aspect is identifying and managing the health and safety hazards of nanomaterials in each step.

Researchers' activities will be studied to prevent hazards in each step. The step of synthesis is the first step in the whole life cycle of nanomaterials. In this step, the unloading of the reactor and the preparation for the storage are critical steps. This can be worked in full enclosure system like glovebox [56]. The cleaning is also a critical step in the whole life cycle of nanomaterials. For example, many researchers will pay more attention to nanomaterials production than their disposal. When disposing of nanomaterials, it is important to know how to decontaminate the nanomaterials. The nanomaterials' disposal and removal should be managed by all relevant regulations [3].

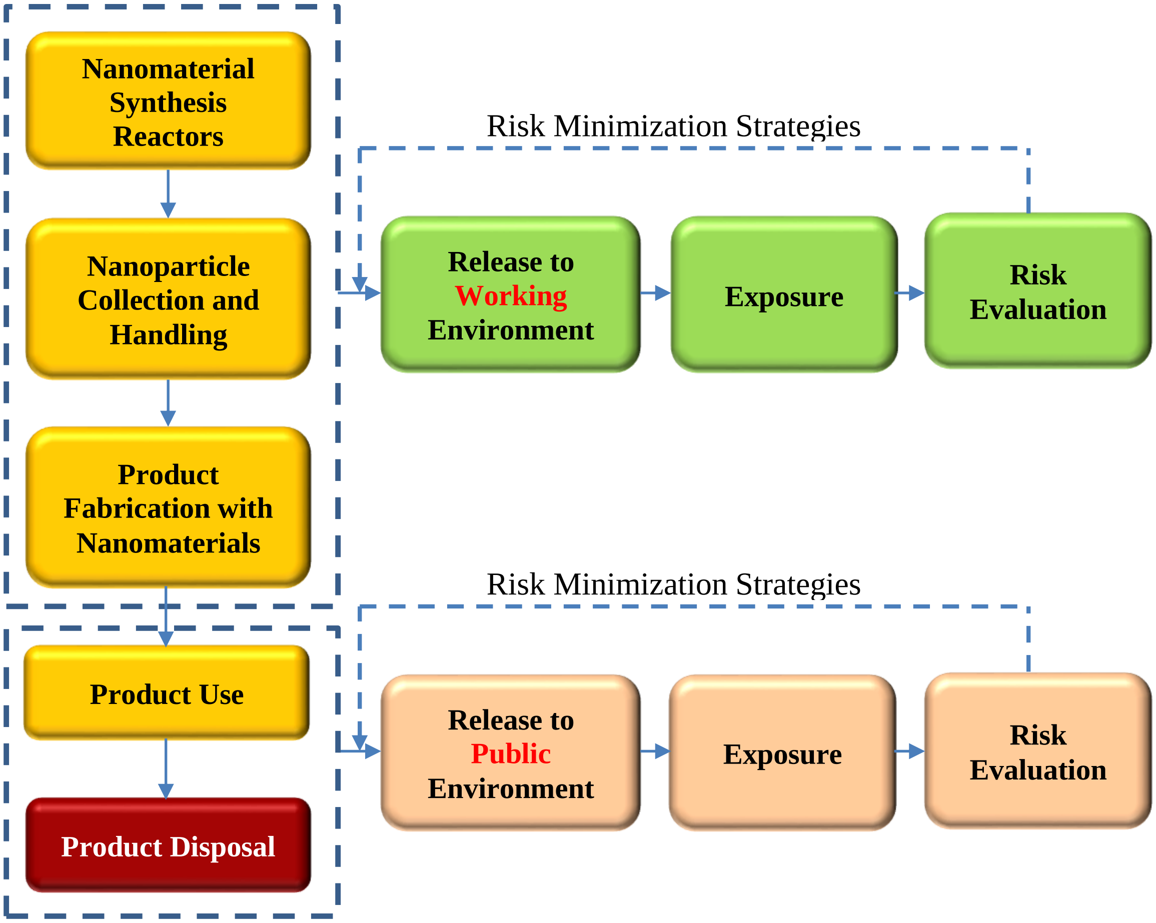


Figure 17. Hazard Control during the Whole Life Cycle of Nanomaterials [55]

4.7.1 Gravity Settling Chamber

When disposing of nanomaterials, it is important to decontaminate the nanomaterials. Cleaning of the deposited micro-sized particles in the local exhaust ventilation (LEV) should be considered. Before particles reach the HEPA filter, large and/or dense particles can be deposited in the system. The simplest mechanical collector is a gravity settling chamber as shown in Figure 18 [57]. The gravity settling chamber is used to control particles greater than 10 µm. The deposited particles are removed by reducing the gas velocity to enable the particles to settle out by gravitational force as a collection mechanism [58]. It is particularly useful for industries that need to cool the gas stream prior to entering the fibrous filter [57]. Therefore, the gravity settling chamber can be considered to clean the deposited larger particles prior to entering the HEPA filter.

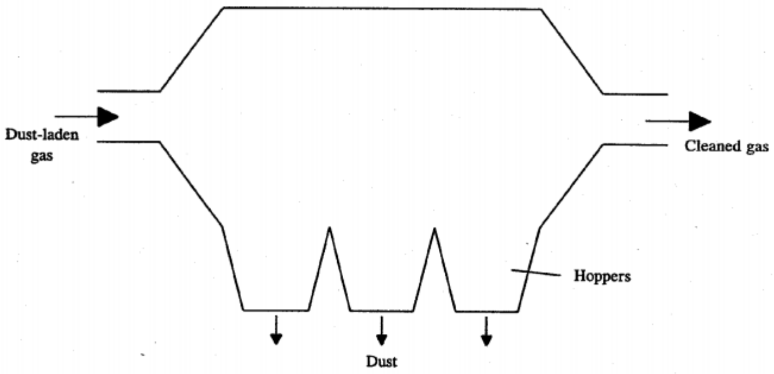


Figure 18. Gravity Settling Chamber [57]

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The demands of research related to nanomaterials have risen due to their novel properties and behavior different from their bulk materials. However, the explosive increase of nanomaterials research could result in potential health and physical hazards to many researchers working with nanomaterials in laboratories. Therefore, it has been important to set up the applicable and proper guidelines for identifying and managing the health and physical hazards of nanomaterials inside laboratories.

There are two main methods to identify nanomaterials' health hazards: the OELs and the control banding method, depending on the level of available toxicological data for nanomaterials. The OELs are the best method for preventing exposure to occupational health hazards of nanomaterials. However, the level of available toxicology data for most nanomaterials is limited. Therefore, the most practical approach is the control banding method. There are several tools for control banding, but the CB Nanotool proposed by Paik et al. [26] is strongly recommended due to its usability and specialty for nanomaterials. The CB Nanotool determines the overall risk level of a certain nanomaterial inside laboratories using both severity and probability scores in the risk level matrix. Calculating scores for the CB Nanotool is the biggest challenge, but it is important to identify and understand the health risk level of nanomaterials in the laboratory where they are working. As indicated in the calculated overall risk levels for various nanomaterials, most of the nanomaterials' overall risk levels were determined to be the level 3 (out of 4) in the risk matrix.

Not only identifying health hazards of nanomaterials but identifying physical hazards of nanomaterials is important. A few researchers have determined the relationships between the particle diameter of a nanomaterial and its MIE, MEC, P_{max}, $(dP/dt)_{max}$, and K_{St} for several nanomaterials using the dust explosion test apparatus, according to the ASTM Test Method. MKOPSC also has tested the explosion properties of carbon nanofibers using a customized 36 liter explosion apparatus, which is still ongoing. The dust explosion classes are classified into four different risk levels, according to K_{St} values, to identify and understand the physical risk level of nanomaterials in the laboratory. According to the explosion test results, as the particle size decreases, the MIE decreases, and K_{St} tends to increase unless agglomeration/ aggregation effects are present. In addition, metal-based nanomaterials are riskier than carbon-based nanomaterials.

To protect researchers from nanomaterial hazards, engineering control methods and PPE are the essential methods. LEV, Stoffenmanager Nano-glovebox, and PPE are used to capture nanomaterials. Most of these control methods recommend the use of HEPA filters because they provide high filtration efficiency. For example, HEPA filter H14, designed as 99.97% efficient at MMPS of 0.3 μm, is the most commonly used filter for capturing nanomaterials. For the PPE, US EPA and OSHA proposed four levels of protective clothing for different levels of nanomaterial hazards. NIOSH recommends wearing a respiratory protector with proper HEPA filters with different grades of filtration efficiencies as per 42 CFR, Part 84. For example, N95 and P100 are the most commonly used against nanomaterial hazards.

One of the main objectives of this thesis is to provide a control methods selection flowchart in order to prevent nanomaterial health hazards among researchers. The control methods selection flowchart is based on the CB Nanotool, the engineering control methods, and the PPE. It is a good guideline for identifying and managing the health and safety hazards of nanomaterials inside laboratories. Another objective is developing hazard controls during the whole life cycle of nanomaterials. Hazards can occur at five different points during this cycle: 1) nanomaterial synthesis reactors, 2) nanoparticle collection and handling, 3) product fabrication with nanomaterials, 4) product use, and 5) product disposal. Studying the potential hazards at each point may help prevent them from occurring throughout the whole life cycle of nanomaterials.

5.2 Recommendation for Future Work

Many researchers have been working with nanomaterials in laboratories, but only a few have provided an overall hazard analysis regarding nanomaterials in their laboratory and have focused only the materials they are using. In addition, current available risk information is still weighted towards carbon nanotubes, metal oxide and metal-based nanomaterials. However, other nanomaterials' demands have arisen. Therefore, comprehensive guidelines that include many nanomaterials will be required.

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