Research Article

Decontamination of Surfaces Exposed to Carbon-Based Nanotubes and Nanomaterials


1 FM Global, Norwood, MA 02062, USA
2 Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, USA

Received 10 October 2013; Accepted 12 December 2013; Published 16 January 2014

1. Introduction

Nanomaterials (NMs) are becoming more involved in an increasingly wide range of applications such as in composites, electronics, and automotive, biomedical, and personal care products due to their novel properties and functions [1–3]. Over the last decade, the global production of NMs has experienced a huge growth. For instance, the global production of carbon nanotubes (CNTs) was increased from ca. 280 metric tons in 2006 [4] to ca. 1000 metric tons in 2010 [5] and is anticipated to reach thousands of metric tons in the following decade [4, 6, 7]. The increasing production and application of NMs highlight the need for development of preventive measures and regulations to minimize NM exposure in case of accidental release inside the workplace [2, 8–14].

The potential toxicity of nanomaterials has raised concern about health and safety issues related to the production and use of NMs and their environmental impact as well as potential for contaminated property damage or business interruption due to accidental release of nanomaterials [2, 8–21]. Preliminary toxicology studies on nanomaterials, including in vitro cytotoxicity [22–24], small animal toxicology [25], and extrapolation of these data to the human scale, reveal the potentially toxic nature of these materials to human biological systems [26–29]. There are several inherent physiochemical factors including NM size, shape, chemical composition, surface charge, surface modifications, and adsorption capacity that can possibly affect the toxicity of nanomaterials [12]. Physical and environmental phenomena such as dissolution, agglomeration, and disagglomeration are the other factors that determine the toxic interaction of nanomaterials with biological systems [28–30]. The three exposure possibilities to NMs are respiration, dermal penetration through skin contact with contaminated surfaces, and digestion [31, 32]. Thus, effective decontamination measures for removal of nanomaterials from contaminated surfaces, air, and possibly water supplies are needed. With regard to NM air decontamination, high efficiency particulate air (HEPA) filters can trap air suspended NMs with high efficiency through various filtration mechanisms [33, 34]. As a first attempt to introduce approaches to remove NMs from contaminated water, Yang et al. reported that the CNTs suspended in the aqueous
environment can be transformed into large micron size aggregates in the presence of calcium ion (Ca$^{2+}$) and then effectively removed via paper filtration [35]. Concerning the removal of NM from surfaces of solids, the strong attachment of NMs to substrates by van der Waals forces [36–45] and also their increased contact area make it difficult to remove NMs [46, 47]. Their removal has to be through a physical force that could be applied directly (wipe or brush) or through a fluid (such as ultrasonic, megasonics, or a fluid jet) [48–59]. A few studies [9, 34, 60–62] have provided some basic surface cleaning recommendations for research laboratories and workplace in case of accidental release and spillage of nanomaterials. These recommendations include using vacuum cleaners fitted with HEPA filters on the exhaust to collect the NMs and prevent their dispersion in the air [63]; cleaning the liquid spills by applying absorbent materials/liquid traps [60, 61]; use of walk-off mats such as a clean room mat or “sticky mats” at access/egress points to limit propagation of particles outside the premises [34, 60, 61]; and avoiding the use of energetic methods such as dry sweeping and compressed air for removing the deposited nanomaterials [60–62]. After any visible NM contamination is removed, it is suggested to use wet or electrostatic microfiber cleaning cloths to remove residual NMs from the surfaces while causing minimal dispersion into the air [64].

In this paper, we focus on the surface decontamination of carbon-based NMs which are regarded as one of the most common types of NMs. We propose chemical (solvents, surfactants, etc.) cleaning as a potential method for surface decontamination of carbon-based NMs. In Section 2, we provide an overview of the current state of literature for common categories of solving media and summarize the solubility data for most carbon-based NMs. In Section 3, we discuss our preliminary results on surface decontamination of silicon wafers covered with single- and multiwalled CNTs using a simple wiping procedure and we quantify the removal efficiency of different solvents using scanning microscope imaging of samples before and after cleaning. Finally, conclusions will be derived and the need for further studies will be discussed in Section 4.

2. Chemical Cleaning

Chemical cleaning (or solvent cleaning) is used conventionally for the removal of residues, contaminants, or soils deposited on or attached to a substrate surface. The basic concept of chemical cleaning is to dissolve or suspend the contaminants and to eliminate them by the removal of the cleaning media. Studies on the solubility of nanomaterials have shown that many engineered NMs have minimal solubility and dispersibility in water or many common solvents [65–68]. For example, CNTs are shown to be neither soluble nor wettable by water or many other solvents, making them hard to be physically dispersed which in addition to cleaning is critical for obtaining individual CNTs for research and other applications [69–71]. Therefore, various surfactants [65, 69, 72–76], solvents [77–82], and polymers [83–85], as well as DNA [86–88] have been explored to noncovalently dissolve and disperse CNTs into a liquid phase. Figure 1 summarizes the solubility of single-walled CNT in various solvents as reported in the literature. In general, surfactants (short for surface active agents) are more effective for dissolving higher quantities of single-walled and multiwalled CNTs in water compared to most available solvents. The use of surfactants for the cleaning process is particularly of high interest for a number of reasons; water is a safe and convenient substance and surfactants are cheap, commercially available, and easy to use. The highest solubility is currently reported for an aqueous solution of gum arabic (15% wt), where 3% wt. (∼30 mg/mL) solubility was obtained using sonication at 50 W and 43 kHz for a relatively short duration of 15–20 minutes [85]. We have also explored the available data on solubility of other common carbon-based NMs. In Figure 2, we have summarized the available results on the solubility of C$_{60}$ fullerene in different solvents. Motivations for studying the solubility of fullerenes in solvents include exploring chemical reactions pathways for fullerene, their purification methods, and extracting higher fullerenes [66, 89–101]. Also, the aqueous solubility of fullerenes with the use of surfactants has been investigated for potential biological applications and the results are included in Figure 2 [102–106]. The differences in the reported solubility of fullerenes in a specific solvent in different studies can be attributed to the effects of temperature, illumination, or sonication during the solving process. Extraordinary temperature dependence is observed in the solubility of fullerene C$_{60}$ in some solvents, reaching its maximum magnitude near 280 K and decreasing remarkably by increasing the temperature above this value [97, 107, 108]. In addition, there are studies investigating the solubility of higher-order fullerenes [90, 91, 93, 96–98] or combinations of different-order fullerenes [93] in various solvents. Studies performed on the solubility of fullerenes in aqueous media suggest that the solubility rates of fullerene in water-surfactants are several orders of magnitude less than the solubility rates obtained by successful solvents.

Since CNTs are one of the most common carbon-based NMs, we have discussed the efficiency of different solvents for dissolving CNTs in the following sections in more details.

2.1. Surfactants as the Cleaning Media. Surfactants can weaken the strong bond between particles and substrate by reduction of the surface tension, prevention of particle readhesion by creating a repulsive zone between the particles and substrate, and suspension of the particles in the solution by their amphiphilic mechanism [110]. When surfactants are available in adequate concentrations in the solution, they get adsorbed on the surface of CNTs, forming cylindrical micelles or hemimicelles which make CNTs soluble in water [111]. It is necessary that the amount of surfactant dissolved in the aqueous media should be far exceeding the surfactant critical micelle concentration to ensure that enough surfactant molecules can be absorbed onto the surface of the nanotubes to make them suspended and dissolved in water. For example, Sun et al. [76] obtained the optimum concentration of some surfactants for suspending CNTs as equal to 10 mg/mL. However, critical micelle concentrations for these surfactants from the literature are far less than...
10 mg/mL [76]. In the use of surfactants as the cleaning media combined use of surfactants and mechanical removal might be necessary to fully overcome the adherence of NMs to substrates [110, 112].

Islam et al. [69] investigated the solubility of single-walled CNTs in water with different anionic, cationic, and nonionic surfactants by using a long-duration (16–24 hr) sonication procedure. They showed that the anionic surfactants sodium dodecylbenzene sulfonate (NaDDBS) and the close chemical relative, sodium 4-octylbenzene sulfonate (NaOBS), had high solubility of single-walled carbon nanotubes, with the solubility of up to 20 mg/mL and 8 mg/mL of CNTs, respectively. Using a different solubilization technique, Moore et al. [75] reported the relatively high ability of NaDDBS, and a close relative sodium dodecylsulfonate (SDSA), and sodium dodecyl sulfate (SDS) to individually suspend nanotubes in water [113]. However, of much interest for the purposes of cleaning, they showed that the difunctional block copolymer nonionic surfactants with high molecular weight have high suspendbility (19.2–28.2 mg/mL) but relatively lower individual dispersion quality compared to other surfactants. They concluded that the high dispersion rate of copolymers such as Pluronic F 98 and PEO-PBO-PEO triblock copolymer (EBE) is related to the enhanced steric stabilization by long polymeric groups. The solubility of multiwalled carbon nanotubes in SDS was studied by Zhou et al. [40]. They reported 1.4 wt% (14 mg/mL) as the maximum concentration of multiwalled CNTs that can be homogenously dispersed in the aqueous solution. It is noteworthy that the reported quantities for a single surfactant in different studies might be significantly different due to various factors related to the amount of surfactant used, test temperature, mechanical forcing and CNT type and manufacturing method.

2.2. Polymers as the Cleaning Media. Polymers appear as promising options for dissolving CNTs in aqueous media in high concentrations with relatively low agitation [75, 83–85]. O’Connell et al. [84] studied the solution of SWNTs in water by noncovalently associating them with linear polymers such as polyvinylpyrrolidone (PVP) and polystyrene sulfonate (PSS). They suggested that the high concentration solution of CNTs (2% wt., ~20 mg/mL) can be obtained by the robust association/wrapping of polymer layers with/around the nanotubes.

2.3. Solvents as the Cleaning Media. The use of solvents as cleaning agents to remove nanomaterials is questionable for a number of reasons. First, many of the solvents proposed to disperse nanotubes have some level of toxicity. Second, the solubility/dispersibility of many of the proposed solvents is
below 0.1 mg/mL, far less than the solubility of surfactants. Parra-Vasquez et al. [81] investigated the solubility of SWNTs obtained by different methods of production in superacids (e.g., fuming sulfuric and chlorosulfonic acids) and showed that high concentrations (>100 mg/mL) of SWNTs are spontaneously dispersed in acids within minutes. However, the use of acids as the cleaning media in the cleanup process does not seem reasonable because of the hazards in handling and usage and removal of acids and also the potential damage to the substrate.

3. Experimental Investigation: Removal Efficiency of CNT Chemical Cleaning

In this section, experimental investigations were performed to assess the removal efficiency of CNTs deposited on the surface of silicon wafers using different cleaning media. The CNTs used for this study were combustion chemical vapor deposition (CCVD) grown, acid purified carbon nanotubes dispersed in polyvinylpyrrolidone (PVP) surfactant. The average length and diameter of the MWCNTs used in this study were measured to be 250 nm and 15 nm, respectively. The averaged length and diameter of SWCNTs were 200 nm and 1.2 nm, respectively. In the experiments, carbon nanotubes in the form of pristine liquid solution were deposited on surface of silicon wafers ((III) orientation, nitrogen/phosphorus doped, P/E surface, and with mechanical grading) using the spin coating process. The wafers were 3" in diameter and the spin coating was performed for 1 min at 3000 RPM. After spin coating, the CNT deposited wafers were heated at 105°C for 90 sec. in order to dry the wafer surface completely. A total number of 30 images with equal magnification and resolution were taken from different spots of each wafer surface using scanning electron microscope (SEM) imaging. The CNT surface aerial concentration for each image was then determined using an image processing program incorporated in MATLAB software. Average CNT aerial density from 30 different images of each wafer was obtained and used in the analysis. The average aerial density of the wafers, denoted by AD, was approximately 34% for SWCNTs and 36% for MWCNTs after the spin coating.

First, we have assessed the multiwalled CNT removal efficiency of two surfactants (i.e., SDBS (sodium dodecyl benzene sulfonate) and SDS (sodium dodecyl sulfate)), one polymer (gum arabic), and pure water in a simple wipe cleaning method. The concentrations of SDBS, SDS, CaCl₂, and gum arabic (GA) were 1.5%, 4%, 11%, and 10% wt, respectively. The mineral salt calcium chloride was specifically chosen since it was shown to be capable of transforming dispersed CNT in aqueous environment into aggregates [35]. The CNT-coated wafers were first treated by different cleaning media and then cleaned with a piece of nonwoven polyester/cellulose fabric. In the experiments, first the cleaning medium was sprayed on the surface of the wafer. After 2 minutes, the wafer was manually wiped once unidirectionally. The estimated hand pressure and wiping duration were 2 kPa and 5 sec., respectively. The wafer was dried using nitrogen gas after the cleaning. After cleaning, the wafers were imaged using SEM and the average final area density for each wafer was obtained by postprocessing the images as explained above. The removal efficiency was defined as the difference between the initial and the final average CNT aerial densities. Figure 3(a) shows the quantitative comparison of MWNT surface removal efficiency by different cleaning media used in this study. Figure 3(b) shows the SEM images of MWCNT-coated wafer surfaces before and after cleaning using different cleaning media. The two surfactants used in the experiments, SDS and SDBS, showed the highest MWCNT removal rates among all the solvent cleaning media with removal efficiency greater than 95%. The high removal efficiency in using the surfactant as the cleaning media can be attributed to the role of
surfactant micelles in suspending the CNTs in aqueous media and increasing the soaking ability of water by decreasing the water surface tension. Pure water has the removal efficiency of almost 65% on the silicon wafer substrate. Gum arabic and CaCl$_2$ have comparable removal efficiency of approximately 76% and 80%, respectively, standing between the removal efficiency of pure water and that of surfactants solutions.

As the next step, we measured the single-walled CNT removal efficiency of two surfactants (i.e., SDBS (sodium dodecylbenzene sulfonate) and SDS (sodium dodecyl sulfate)), and pure water in the same wipe cleaning method. The two surfactants were chosen since they showed the highest efficiency for the removal of MWCNTs from the surface of silicon wafer in the last section. The same deposition and wiping methods were used. In Figure 4(a) a quantitative comparison of SWNT surface removal efficiency by different cleaning media is given. The two surfactants showed high SWCNT removal capability with efficiency greater than 90%. Wiping after pure water spray resulted in a removal efficiency of approximately 61%. Figure 4(b) shows sample SEM images of SWCNT-coated wafer surfaces before and after cleaning.

4. Conclusions

We proposed solvent cleaning as a technique for surface decontamination of carbon-based NMs such as CNTs, which can potentially be used for removal of nanomaterial adhered to surfaces caused by unwanted spillage and release or the gradual accumulation during the processing or handling. The role of cleaning media (i.e., surfactants, solvents, etc.) in facilitating the mechanical removal of single- and multiwalled CNTs from contaminated surfaces was discussed. The challenges associated with this technique include the high levels of agglomeration of CNTs and extremely low solubility in water and many common solvents, which tend to lower the efficiency of this method. Based on our pilot study presented in Section 3, the removal efficiency of single- and multiwalled carbon nanotubes using two different water-surfactant solutions from a highly smooth surface of a silicon wafer through wiping is greater than 90% and 95%, respectively. The higher removal efficiency for multiwalled carbon nanotubes can be attributed to the larger value of the binding energy density holding the nanotube aggregates together for MWCNTs compared to SWCNTs [114]. Surfactants are economical, commercially available, and easy to use. These factors make surfactants a good candidate for the removal of CNTs deposited on surfaces. However, more studies are needed to determine the effectiveness of CNT removal using the solvent cleaning technique for CNTs obtained by various production methods, with different chemical modifications or attached on different substrates.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this article.

Acknowledgments

The authors thank Dr. Sivasubramanian Somu for the insightful discussion and Ms. Joy McNally for assistance in providing the journal articles referenced in this work. This work was supported in part by FM Global and by the U.S. Air Force.
Office of Scientific Research under AFOSR YIP Grant Award, #FA FA9550-10-1-0145, under the technical supervision of Dr. Joycelyn Harrison. The authors also acknowledge the support of the Center of High-Rate Nanomanufacturing at Northeastern University for the experimental part of the study.

References


Y. N. Yamakoshi, T. Yogami, K. Fukushima, S. Sueyoshi, and N. Miyata, “Solubilization of fullerenes into water with polyvinylpyrrolidone applicable to biological tests,” *Journal of


Submit your manuscripts at http://www.hindawi.com