Finnish Institute of
Occupational Health

Best practices for safe graphene work

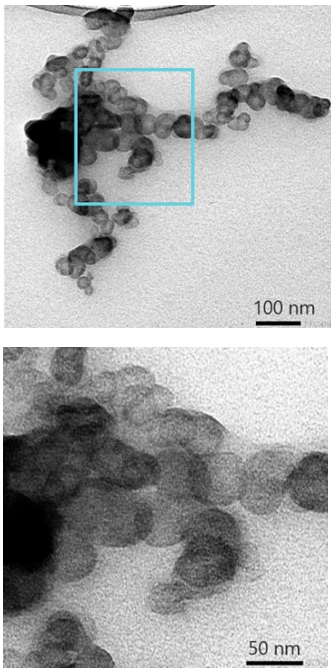
Use of graphene-based materials is increasing. New technologies and materials can have safety concerns in the working environment. Worker's exposure in new or under development processes should be assessed carefully to reduce health risks.

Graphene and graphene-based materials (GBMs)

Graphene, a two-dimensional material, consist of a monolayer of carbon atoms arranged in a honeycomb-like structure, with a high surface area on both sides of the planar axis. Since its isolation in 2004 by mechanical exfoliation of graphite, the interest in graphene has increased over the years due to its unique physicochemical properties.

Being 100 times stronger than steel, graphene is yet flexible, electrically conductive, and impermeable to all gases. Oxidation and/or functionalization can generate a wide family of graphene-based materials (GBMs), such as graphene oxide (GO), reduced graphene oxide (rGO), few-layer graphene (FLG), graphene nanosheets and flakes, and graphene ribbons and dots.

In addition, the planar surface of graphene can be functionalized with, e.g., carbonyl, hydroxyl, and epoxy groups, or capping agents or coatings (e.g., polyethylene glycol). Therefore, GBMs exhibit a variety of extraordinary properties making them compatible and attractive for a multitude of applications, like energy storage devices, solar cells, advanced food packaging, foldable touch screens and protective coatings for wind turbines and ships, as well as biomedical applications, such as drug delivery systems, tissue engineering, and imaging.



Transmission Electron Microscopy image of graphene (GO) in an air sample collected from worker's breathing zone.

The increasing use of GBMs calls for a thorough evaluation of their possible impact on human health, as the unique physicochemical properties may also guide graphene's interaction with biological systems, affecting the toxic response.

The main risk posed by GBMs to human health appears to be associated with occupational exposure through inhalation during their production, use, and waste disposal.

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A dust drum containing graphene powder is emptied and cleaned in a fume hood. The worker is using a filter protector (TH3P) with a fan and a hood, type 5 protective clothing and nitrile gloves.

Hazard and exposure assessment

Hazard assessment

Toxicity studies in cultured cells show that harmful effects of GBMs depend on their physicochemical characteristics. Therefore, hazard potential of each GBM must be assessed separately.

The main mechanism of graphene toxicity is the generation of reactive oxygen species that can cause cellular and DNA damage. Fine graphene particles easily become airborne and pose inhalation hazard.

The inhalation toxicity studies show pulmonary inflammation, fibrosis, and bio-persistence in rodents. Studies also suggest that graphene particles can translocate from the lungs to other organs such as lymph nodes and liver, but health effects of particle translocation are still under investigation.

Occupational exposure

In the case of nanomaterials, including graphene, the respiratory tract is considered the most important route of exposure, as it leads to a higher internal dose in the body. Skin exposure is also possible in many work tasks. Undamaged skin is an effective protection against external exposures.

Health hazards posed by longer term low level occupational exposure to graphene are not yet known, therefore it is advised to follow precautionary principle and avoid exposure whenever possible.

Exposure assessment

Exposure assessment for inhalation exposure route should be carried out according to OECD and CEN standards approach (OECD 2015, CEN 2018). The widely harmonized multi-metric approach for workplace exposure measurement demonstrates guidance for three tiers of assessment.

Tier 1: Initial assessment

- Relevant workplace, process and production activity information is gathered structurally, according to best practices in occupational hygiene.
- Together with detailed material information, the potential for release and emission of nanomaterial (including 2D-materials) into the workplace air can be considered.
- Control and/or risk banding tools can be used to examine the exposure potential.

Tier 2: Exposure assessment

- The exposure to nano-objects is investigated using suitable measurement equipment to detect the airborne nanomaterial (nanoparticles, aerosol) levels in real time during the work processes.
- The off-line sampling and analysis of workplace air to characterize the possible nanomaterials (e.g., using electron microscopy) is combined to the real time assessment.

Tier 3: Personal exposure assessment

- The exposure to airborne particles in the breathing zone of the worker is comprehensively characterized by using state-of-the-art techniques and compared to the corresponding reference values currently available.

In the risk and exposure assessment, identifying and verifying graphene particles from the background particles is essential.

Prevention of occupational exposure

Limit values and recommendations

Currently there are no occupational exposure limit (OEL) values for nanosized graphene or any other nanomaterial. For industrially generated nanoparticles, the Finnish Institute of Occupational Health (FIOH) has defined target levels for an exposure time of 8 hours:

- 20000 particles/cm^3 (density > 6000 kg/m^3)
- 40000 particles/cm^3 (density < 6000 kg/m^3)

FIOH's target levels for workplace dust concentrations (8 h). These values can be applied if there is no specific OEL value for the dust in question:

- 0,5 mg/m^3 (general dust, respirable fraction)
- 2 mg/m^3 (general dust, inhalable fraction)

Working environment and risk assessment

In working environment, exposure to graphene and/or other nanoscale 2D-materials is related to the safety and emissions control of processes and activities in the synthesis (e.g., graphite exfoliation, CVD) and manufacturing stages of the product. Also, in the end-of-life scenarios, such as recycling and waste management, occupational exposure can be significant.

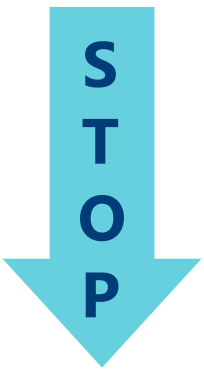
Currently, the production and related handling phases of GBMs are often in the liquid/paste states, and the related emissions and exposure potentials remain low.

The final stages of synthesis/production process, when the raw material, i.e., the produced graphene/2D-material, is dried and packed for further use, are the most critical points regarding the workers' exposure, in addition to the maintenance and cleaning tasks of the process equipment, where dry material can be released uncontrollably or accidentally.

When graphene is handled in liquid or paste state, FFP3 respiratory protective mask, protective clothing and nitrile gloves are recommended.

Exposure prevention

Similar to any other harmful chemical agent in the workplace, minimizing exposure to graphene materials requires utilizing the occupational hygiene principles. According to the hierarchy of control, also known as STOP principle, the control measures should be implemented in the following order below.



Substitution: Use least hazardous material, avoid dry materials, use dosing feeders and disposable packages.

Technical measures: Closed system, negative air pressure, fume hoods, local exhaust ventilation, process automation, filtration in ventilation.

Organisational measures: Minimize exposure (time and number of workers), training for best practices, wet cleaning or vacuum certified for fine dusts, restrict access to risk area.

Personal protection: Respiratory protection (P3 class), protective clothing, gloves, and safety goggles.

Checklists and additional information

Check list for employer

- Has risk assessment been conducted at the workplace?
- Have you identified work processes involving a risk of exposure?
- Have the safety aspects been taken into consideration in the producement plan?
- Are there safety data sheets available for the materials and chemicals?
- Have all workers been sufficiently trained to follow required safety measures?
- Is it possible to avoid handling graphenes in powder form?
- Have you confirmed that the technical measures are efficient and working properly?
- Is the general ventilation sufficient?
- Are all necessary personal protective equipment easily available?
- Are there operating and maintenance instructions for protective equipment and are these instructions followed?
- Are there operating instructions for safe cleaning procedures?

Check list for worker

- Have you read the safety data sheets of the materials and chemicals?
- Are chemicals including nanomaterials stored and handled in appropriate manner?
- Have you been trained to follow required safety measures?
- Are the safety instructions followed at all work stages?
- Do you use the instructed personal protective equipment when required?
- Have you read the operating and maintenance instructions for the protective equipment, and do you follow these instructions?
- Is the workplace clean and tidy?
- Do you know how to operate in unexpected or emergency situations?

Stay updated with the latest scientific information and regulatory guidelines!

Additional information

- Graphene Flagship https://graphene-flagship.eu/
- GrapHazard project https://projects.safera.eu/project/26
- Hazard characterization of graphene based nanomaterials in energy production and storage (SAFERA) project https://www.ttl.fi/en/research/projects/hazard-characterization-graphene-based-nanomaterials-energy-production-and-storagegraphazard-safeura
- EUON study report of the potential health and environmental effects of GBMs https://euon.echa.europa.eu/documents/2435000/3268573/echa_2021_286_graphene_study.pdf
- The European Chemicals Agency (ECHA) REACH registration dossier of graphene https://echa.europa.eu/it/registration-dossier/-/registered-dossier/24678