

Review

Application of Nanomaterials in Personal Respiratory Protection Equipment: A Literature Review

Marzieh Abbasinia ¹, Safoura Karimie ¹, Mojtaba Haghghat ² and Iraj Mohammadfam ^{1,*} 

¹ Center of Excellence for Occupational Health, Occupational Health and Safety Research Center, School of Public Health, Hamadan University of Medical Sciences, Hamadan 65175-4171, Iran; abbassinia.m@gmail.com (M.A.); karimisafoura92@gmail.com (S.K.)

² Department of Occupational Health Engineering, Behbahan Faculty of Medical Sciences, Behbahan 63616-1111, Iran; mo.haghghat1988@gmail.com

* Correspondence: mohammadfam@umsha.ac.ir; Tel.: +98-813-838-1645

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Abstract: Exposure to air pollutants leads to a variety of health effects in humans. Inhalation is one of the most common routes of exposure to poor quality air, mostly in work environments. Respiratory masks are used to prevent breathing in hazardous gases and vapors, especially in the absence of proper controlling measures. This study aims to review the effectiveness of respiratory masks with a nanostructure. The electronic search of the genuine databases, including PubMed, Magiran, Iran Medex, Science Database (SID), Science Direct, Web of Science, and Scopus, was conducted in January and February 2017 in chronological order of publications with the keywords defined in the search strategy. Of all identified papers, nine were collected and included in the study. The results of this study indicated that the use of nanomaterials in the structure of brand new mask filters compared with conventional masks enhances the performance and efficiency of breathing air filtration, improves permeability, increases antimicrobial properties, and offers reasonable comfort to the workers.

Keywords: nanomaterials; personal respiratory protection equipment; PPE (Personal protective equipment), mask; respirator

1. Introduction

Various combinations of air pollutants, their concentration, and the exposure frequencies and durations may affect several aspects of a human's health and well-being [1,2]. Air pollution is defined as a complex blend of airborne particle, biological components and gases that threatens human life, plants, and animals. According to statistics, an estimated number of three million people lose their lives annually due to air pollution and many others suffer from air pollution-related ailments [3]. A large body of literature has already reported epidemiological data indicating the detrimental effects of air pollution [4]. Depending on the levels and duration of exposure, the concentration of substances, and also issues such as individual differences, the various effects of air pollutants on humans include respiratory problems, skin irritation, delayed birth, decreased immune system activity, cardiovascular problems, cancer, etc. [5–7]. Human exposure to various air pollutants mainly occurs through two routes, namely, inhalation and skin contact. Generally, as regards occupational exposure to chemical agents, other routes such as ingestion seem to have a limited contribution and mostly occur only in the case of accidental exposure [8]. Therefore, the entry of substances into the body through the respiratory tract is often identified to be a major concern for occupational hygienists [9,10].

An occupational health hazard to protect them is based on a hierarchy of controls. The first effective control is eliminating the hazard. If eliminating a hazard is not possible, substituting a less hazardous material or process, effective control measures such as engineering controls and

administrative controls, and Personal Protective Equipment are used. Personal Protective Equipment is usually used in the absence of verified controlling measures and as a measure in conjunction with other controls and Respirators are one of the pieces of Personal Protective Equipment which are widely applied to prevent the inhalation of harmful gases, vapors, and particulates in the work environment, especially in the absence of verified controlling measures [11]. There are two categories of respirators, including air-purifying respirators with a filtering element and air-supplied respirators which provide the wearer with fresh air. Currently, the use of purifying masks is one of the most cost-effective and beneficial methods, as well as a practical option on account of its performance in reducing the exposure level of workers to chemical airborne contaminants in the workplace [12]. There is an assortment of air-purifying respirators, ranging from inexpensive single-use, disposable masks to more robust reusable models with replaceable filter containers and face shields extensively used in occupational environments. The replaceable container in which the sorption media is positioned is commonly named a cartridge or canister. Sorption media usually removes the gas or vapor from the breathing air during inhalation [13].

Different strategies, such as applying nanoparticles in their production process, have been employed to enhance the efficiency and performance of respiratory masks in recent years. The use of nanoparticles has received considerable scholarly attention in various fields in a way that a wide range of nanoscale materials are currently being devised to serve various purposes in manufacturing agriculture, electricity generation and storage, and pharmaceutical products, etc. with regard to their unique properties [14,15]. In recent years, many studies have been carried out for incorporating the nanomaterials in the manufacturing of protective masks, but almost no comprehensive data in terms of an increased level of effectiveness of such respirators is yet available.

This study therefore sets out to review the previous research conducted on the effectiveness of respirators and respiratory masks containing nanomaterials in their structure. Throughout this paper, the terms “mask”, “cartridge”, or “canister” will be used to refer to “mask filter” or “sorption media”.

2. Method

A comprehensive literature review was performed from multiple databases in English and Persian languages in January and February 2017 based on the chronological order of publications on the use of nanotechnology in the production of respirators. Data used in this review were obtained from Persian databases, including Magiran, Iran Medex, and Science Database (SID), using keywords such as nanomaterials, nanoparticles, nanotubes, nanocomposites, cartridge, protective mask, and mask. English papers retrieved from Biomedcentral, PubMed, Scimedirect, Web of Science, and Scopus databases were also reviewed.

The following list of keywords was used for searching the related publications:

Nano* OR “nano composite” OR “nano clay” OR “nano material” OR “nano particle” OR “nano structure” OR “nano wire” OR “nano tube” OR “nanofiber” OR “CNT (Carbon Nanotube)” OR “carbon nano tube”

AND

“Respiratory protection device” OR “personal respiratory protection” OR “mask”, respirator* OR “cartridge” OR “half mask”

All studies identified through the database searches were placed in a “user defined field” of an Endnote database by only one researcher. Subsequently, duplicated articles were removed from the library and two researchers independently evaluated and reviewed the articles and removed the irrelevant ones. Then, the abstracts from the remaining papers were reviewed. Ultimately, the full texts of the remaining articles were examined so that all the papers were specified in line with the entry criteria.

Having extracted the related papers in accordance with the objectives of the study, a highly detailed examination revealed which articles were consistent with the objectives of the present study.

Similarly, all the relevant sources of the articles were taken into account, and the related articles were extracted and re-examined as well.

The principal inclusion criterion in this study was the use of nanomaterials within the structure of the respirators media in order to protect people against hazardous substances in occupational environments. Therefore, the use of nanoscale materials in safety equipment other than respirators and non-occupational applications was excluded.

Figure 1 presents a flowchart related to the study selection process, including the exclusion of studies.

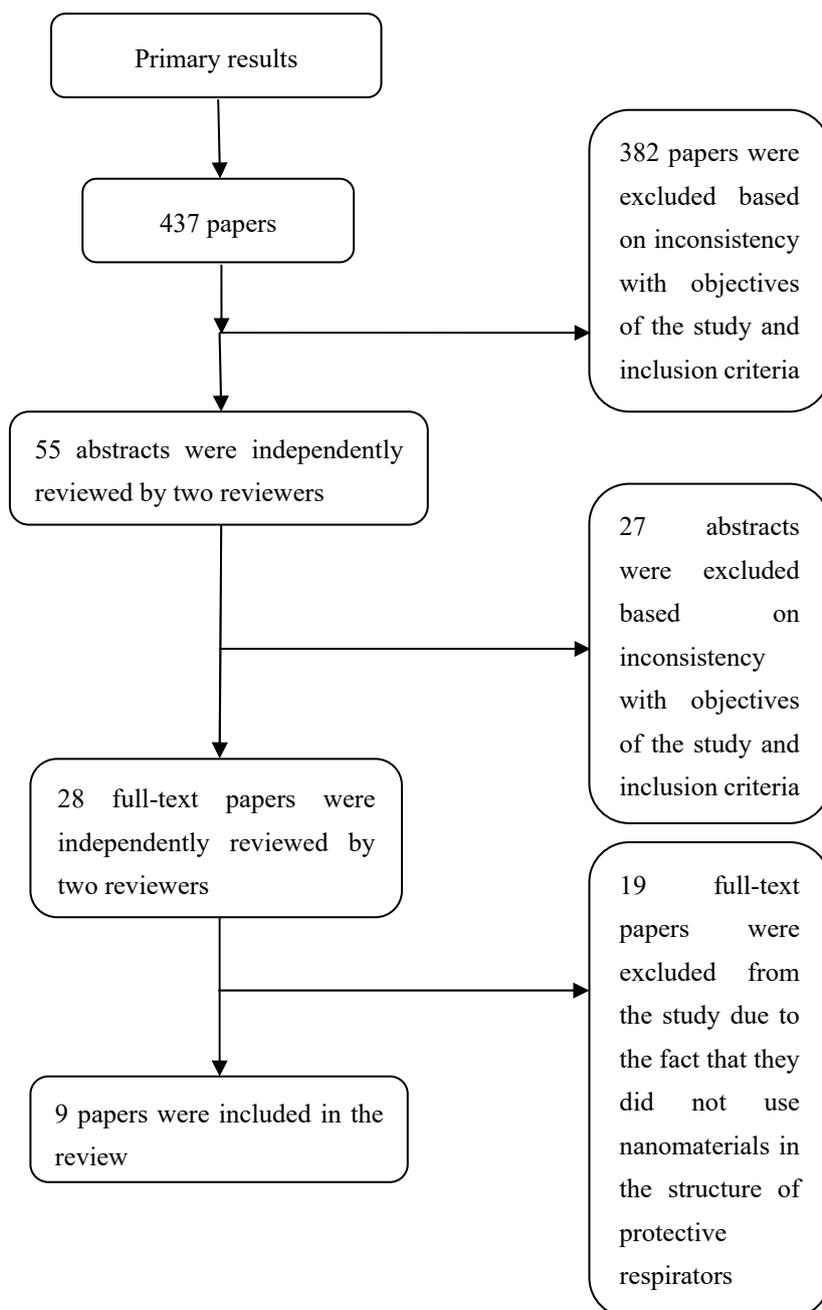


Figure 1. Flowchart showing selecting process.

3. Results

Details from the extracted papers such as the name and affiliation of the lead author, year of publication, the type of nanoparticles under study, the use of nanomaterials in the structure of the respirators or cartridges, and key findings from each article were specified. Lack of consistency in the results obtained by the first two researchers was resolved through deliberating with the third reviewer.

A brief overview of selected papers that were reviewed in this study is outlined in Table 1.

Table 1. The summary of study samples.

No.	Author (year)	Application	Protection Provided	Applied Nanomaterials	Results in Brief
1	Y. Li (2006)	Surgical masks	Against infectious agents	Mixture of silver nitrate, titanium dioxide, Ca ²⁺ , Mg ²⁺ and oleophobol C	Nanoparticle-coated fabrics show promising result for producing protective clothes that reduce transmission of infectious agents.
2	X. Li (2015)	Gauze masks	Prevent inhaling the PM _{2.5} (particulate Matter 2.5) fine particles	Polysulfone-based nanofiber	Nano-fiber masks efficiently filter out the PM _{2.5} particles along with maintaining an acceptable breathability.
3	M. Jahangiri (2012)	Cartridge	Against organic vapors	AC/CNF (Activated Carbon and Carbon nanofiber) composite	The results showed that nanofibers can be used effectively in the development of PPE against organic solvents.
4	AK. Selvam (2015)	Protective mask filter	Anti-bactericidal filter	PAN (Polyacrylonitrile) nanofibres with Ag nanoparticles	Anti-bactericidal activity and also 99% BFE (Bacterial Filtration Efficiency) is suitable in production of protective mask.
5	M. Jahangiri (2013)	Respirator cartridge	Organic-vapor	Activated carbon and carbon nanofiber (AC/CNF)	The results showed this composite has lower weight and higher adsorption capacities and is a very effective alternative adsorbent for respirator cartridges.
6	A. Rengasamy (2015)	Facepiece respirators	Bioaerosol	Three types of carbon nanotube (CNT) filters+ different densities SWNTs (single-walled carbon nanotube) onto round polypropylene filters	Significant improvements were observed in filtration performance of higher CNT loaded filters, also higher biological aerosol particle filtration efficiencies than the total aerosol particles.
7	SD. Skaria (2014)		Polydisperse aerosols	Face mask with nanofiber filter media	Low airflow resistance and effortless exhalation through mask filter made by nanofiber filter media, making it suitable for surgical mask production.
8	TK. Lin	Water filters, masks, protective clothes and wound dressing	Inhibition of bacterial growth	Silver nanoparticle-loaded activated carbon	Results showed proper disinfectant properties and using the hydro-gel formula provided a large surface area.
9	Y. Li	Nano-masks	Water repellency and antibacterial function	Coating with antibacterial nano-materials	Nano-masks can yield extra protection in stopping capillary diffusion and antibacterial activities.

The comprehensive search yielded a total of 437 relevant articles. A total of 382 articles were excluded because they were duplicates or not in line with the objectives of this study and the inclusion criteria. Afterwards, 55 abstracts from the papers were independently reviewed by two reviewers and the irrelevant studies were excluded. In total, 28 full texts papers were also independently reviewed by two reviewers. Following this, 19 full texts papers were excluded because the researchers did not make use of nanomaterials in manufacturing respirators and protective cartridges.

4. N95 Respirators

Fine particles can cause various short- and long-term effects on human health, including allergies, asthma, pneumoconiosis, and cancer, as well as bio-aerosol-related infectious diseases, such as tuberculosis, fever Q, measles, and influenza [16].

N95 particulate filtering face piece respirators (FFRs) are widely used as cheap, accessible, and effective masks to reduce the inhalation of harmful particles.

These types of respirators are approved by the Food and Drug Administration (FDA) as a surgical mask to protect patients and health care workers against the transmission of microorganisms, body fluids, and classified particles [17,18]. Although the respirators have been designated as protective devices [19], several studies have shown that the N95 mask and also the ordinary surgical mask do not provide adequate protection against bacteria and viruses [20].

Surgical masks are broadly used in hospitals and healthcare centers in order to protect the staff. According to many studies, N95 masks and surgical masks may not provide sufficient protection against ultra-fine particles such as viruses [16,20,21]. Hence, more attention should be paid to the overall efficiency and effectiveness of these respirators [22].

Today, various methods have been put forth to increase the effectiveness of such respirators. The use of nanomaterials in the structure of the respirator has been specifically studied in several cases.

Skaria et al. illustrated that the use of a nanofiber prototype would reduce the weight ($0.02\text{--}0.5\text{ g m}^{-2}$ versus $5\text{--}200\text{ g m}^{-2}$ for melt-blown filter), enhance the surface area, and minimize micropores of the respirators' filter [23]. As opposed to commercial surgical masks, the nanofiber prototype has lower resistance to the airflow, even in cases where it is totally sealed. Thanks to this lower resistance to the airflow, the likelihood of leakages and breakthroughs was minimized and resulted in more particles being trapped. The results of this study demonstrated the relative effectiveness of the nanofiber prototype over N95 masks [23].

The proper use of the respiratory protective equipment (RPE) is one of the most important factors for efficient protection, whereas statistics indicate that, in most cases, such a goal seems to be unattainable [24–27]. Moreover, wearing a respirator may contribute to overall discomfort via excessively increasing the user's heart rate, facial skin temperature, fatigue, breathing resistance, etc. [28]. Several factors, such as being unfitted, permeability to water and moisture, improper usage [29], and facial discomfort [24,30], along with resistance to the airflow [23], may considerably reduce the effectiveness of the respirators [31]. The harmful agents might find their way into the respirator if its surface becomes contaminated. In order to prevent this problem, the sorption media in the respirator filter was covered with a thin layer of antimicrobial nanoparticles.

In Li et al.'s study, nanoparticles of silver and titanium dioxide were used as a coating on the surface of the mask to protect the respirator wearers against infectious agents. The results showed a 100% decrease in *E. coli* and *S. aureus* activity after 48 h [31].

In Rengasamy et al., the study resistance of airflow and biofiltration performance of CNT filters and conventional facepiece respirators were compared. In this study, CNT that is known to have antimicrobial properties was applied to filtering facepiece respirators (FFRs) and its pressure drop and biological aerosol filtration performance were compared with other commercially available masks using a manikin-based protocol. The studied masks were:

N95 FFRs (three types), medical masks (two types), doctor mask (one type), and activated carbon mask (one type).

The purpose of this study was to incorporate CNT materials into the mask to increase breathability and protection efficacy. They showed that except for the active carbon mask, all other respirators provided at least 80% protection from particles. Increasing CNT loading content indicated a better performance, and the filtration efficiency of the biological aerosol in CNT filters was significantly greater than total aerosol [22].

5. Nanoparticles Application to Increase the Filtration Performance of PM_{2.5}

Several studies have revealed that airborne particles lead to respiratory, cardiovascular, and pulmonary abnormalities [32–34]. Particles with a diameter of 2.5 μm or less (PM_{2.5}) may penetrate to the deepest part of the lungs, such as the alveoli, mainly due to their small size, and cause chronic diseases such as asthma [35] and cancer in humans [28], decrease average life expectancy [36], and lead to other diseases [37].

In Xingzhou Li's study, 18 wt % (dissolved in DMAc (Dimethylacetamide)/acetone) polysulfone-based nano-fibers were used to prevent the inhalation of PM_{2.5} particles. Due to the higher porosity of the mask materials, regular gauze masks are not able to remove PM_{2.5} particles, and masks with such features have poor breathability, which makes respiration difficult [38]. Nanofibers were used to produce high-performance and low-cost respirators. The results of this study revealed that nanofiber respirators effectively filter out PM_{2.5} particles and provide acceptable breathability [39].

Various studies have shown that the use of carbon nanofibers improves the filter absorption properties of materials such as SO_x and NO_x [40], as well as the removal of metals from water [41]. Active carbon granules are mainly used in air-purifying respirator cartridges or canisters to absorb organic vapors [42]. Nonetheless, several limitations, such as poor selectivity [43] and limited absorption capacity, have already been attributed to this type of filter [44].

Jahangiri et al. used carbon nanofiber and granulated activated carbon in respiratory mask cartridges to absorb and remove volatile organic vapors from breathing air. They made use of CO₂ for sample preparation and recovering the surface area and micropores of the cartridge. The results of this study showed that the breakthrough time for this type of cartridge was more extended than other types. Similarly, the carbon fiber and activated carbon nanofiber composite was determined to be a very suitable alternative for respiratory cartridges because of its lower weight and acceptable absorption capacity [45]. Another study by Jahangiri et al. showed that an activated carbon and carbon nanofiber (AC/CNF) composite which was impregnated with a nickel nitrate catalyst precursor has lower weight and higher adsorption capacities, and is a very effective alternative adsorbent for respirator cartridges [46]. Consequently, carbon nanofibers are likely to be suitable materials for absorption and catalyst supports on account of their unique properties, including their purity, mechanical strength, and larger surface area [40,47–49].

6. Antibacterial Nanoparticles

Recently, there have been numerous reports on the levels of resistance that bacteria have developed towards antibiotics and antibacterial agents. Several antimicrobial agents are highly stimulating and have even proved to be toxic, so researchers are seeking new types of safe and cost-effective materials to eliminate such harmful microorganisms [50]. Moreover, the performance of surgical masks used in healthcare centers against infectious agents is still open to debate [51].

Some antimicrobial formulations and nanoparticles have been identified as effective antibacterial agents [52,53], which have unique properties, including a large aspect ratio and unique chemical and physical properties [54,55]. For instance, Borkow used copper oxide to eliminate influenza viruses in the mask filter, and the results showed that the mask's performance was more than 99.85% [51].

This is similar to the combination of silver sulfadiazine which has been applied for half a century to treat chronic wounds [56–58], including Gram-positive, Gram-negative, yeast, and fungi [59].

Several studies have also used silver ions as an antibacterial agent [60–64]. Annually, about 500 tons of silver nanoparticles are produced and consumed worldwide [56]. Silver ions and silver-based compounds are known to be highly toxic to microorganisms [57,58]. Hence, these compounds are used as an antimicrobial agent with [65] biocide effects for 16 types of bacteria [66]. Such a compound leads to the destruction of the bacterial cell wall and cell membrane [67] when positively charged silver ions interact with the negatively charged cell wall of the bacterium [68]. However, most studies have argued that the precise mechanism of the antibacterial activity of silver is still unknown.

Klabunde's study highlighted that some metal oxides nanoparticles (Cl_2 , Br_2) are very effective antibactericidal agents against gram-positive and gram-negative bacteria [53]. After discovering the antimicrobial properties of these metal oxides, numerous studies were conducted to more objectively find similar properties in other metal nanoparticles. Considering that the toxic properties of silver ions for microorganisms have already been recognized [57,58,67], and only a few species are resistant to silver nanoparticles [15,58,69], various studies have demonstrated promising results related to the antimicrobial properties of this nanoparticle. Also, studies have found a successful and cost-effective way to produce silver nanoparticles, which is used for antibacterial properties of silver nanoparticles [59,67].

In a study by Li et al., a combination of nanoparticles of AgNO_3 and TiO_2 was applied to produce antibacterial respiratory masks. For this purpose, related compounds with sizes in the order of 100 nm were used to increase the aspect ratio and improve the microbicidal process. They had used *E. coli* and *S. aureus* as test microorganisms. One side of the mask was covered with nanoparticles of 0.4 mg/cm^2 . Antibacterial activity of mask coated with nanoparticles was examined using the AATCC 100–1999 method (Antibacterial Finishes on Textile Materials). The results showed that modified masks at low concentrations exerted effective antibacterial activity and after 48 h of incubation, 100% of bacteria were killed [31].

Respirators with uncoated nanoparticles not only did not prevent the bacterial growth, but the number of bacteria (*E. coli* and *S. aureus*) increased by 25% and 50%, respectively [31].

The effects of nanoparticles on human skin were also examined by the case-control group and according to the results that indicated whether volunteers had signs of skin inflammation or itching [31].

Selvam et al. used electrospun poly acrylonitrile (PAN) nanofibres with different weight percentages of nanosilver particles for assessing the anti-bactericidal activity of *E. coli* and *S. aureus* and bacterial filtration efficiency (BFE). Furthermore, dimethylformamide (DMF) was used as a solvent for PAN and reducing agent for silver ions. In this study, the antibacterial activity of PAN and also PAN with 5, 10, and 15 wt % of silver was investigated.

The results demonstrated that higher antibacterial activity was related to the combination of PAN with 15% weight of silver. Furthermore, it reduced 99% of the activity of this bacterium as well [68].

In another study, a silver nanoparticle loaded on an activated carbon cloth that formed a hydro-gel was used to treat water, produce protective garments and masks, and disinfect wounds. The results from the physical contact showed antibacterial properties that were greater than 99% [59].

In another study, the combination of silver nanoparticles with activated carbon cloths coated on a respirator was used to increase its performance to provide protection against antimicrobial agents. The results from this study indicated that although the referred respirators did not show a significant impact on air and vapor permeability in comparison with N95 and surgical masks, their antibacterial activity was found to be much more satisfactory [70].

It is worth mentioning that due to unknown effects for nanoparticles, the use of such material in the mask structure can lead to skin irritation and itchy skin in people with sensitive skin.

In addition to the advantages of these particles, they can also cause adverse effects in people. For example, studies have shown that Titanium dioxide nanoparticles can dissolve in human sweat and can enter stratum corneum and epidermis through the skin. Also, due to prolonged exposure, these nanoparticles can cause toxic effects in humans [71].

In the case of silver nanoparticles, there are different opinions about the probability of penetrating through skin in different studies [72]. Some studies have shown that silver nanoparticles can enter the human body through intact skin, and that damaged skin can also cause these particles to penetrate into the body [73,74]. A review study also showed that “Intact skin is observed to pose an efficient barrier against silver. Mucosal surfaces, including in the eye, are observed to pose a less efficient barrier. When skin is compromised by burns, scalds, or wounds, it is observed to be more penetrable. Following exposure, silver has been detected in all organs investigated. Detection in the brain indicates that silver crosses the blood–brain barrier” [73].

Some studies also reported allergic contact dermatitis, irritation of the skin and eyes, and genotoxicity, upon exposure to nanosilver [73,75].

Therefore, in addition to the positive effects of the use of nanoparticles in the structure of personal protective equipment, the less-known effects of these nanoparticles should also be considered in the exposed work force.

7. Conclusions

In recent years, nanotechnology has displayed rapid progress and has been extensively applied in many areas of science and technology. According to previous studies, the application of nanomaterials in the structure of protective respirators compared with conventional masks has numerous plus points, such as increasing the efficiency and performance of breathing air filtration, along with boosting antimicrobial properties.

Often, in the working environment, other particles exist, the effects of the nanoparticles used in the protective respiratory structure of these particles should be taken into account. Additionally, skin allergy of the facial skin of people who use these masks should be more carefully examined. Therefore, along with the positive effects of using these particles, the unknown or lesser known effects of these particles also require further investigation.

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