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# Functionalized nanoparticles in facemasks for protection of Covid 19

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## Abstract

The literature review of the developments of nanomaterials, application methods, their anti-viral activity confirmed the importance and highlighted the contribution of nanostructures in fighting the corona virus. In order to improve and enhanced the protection function of the facemasks against different viruses, especially last one SARS-CoV-2 (Covid 19), various nanostructures were used, fabricated and modified for that purpose. Among the others, special attention was given on carbon based (carbon nanotubes and graphene) and nano silver, TiO2, iron and cooper with antiviral and antibacterial effects. In this paper, an overview will be presented on several nanostructures used in the facemasks for preventing the spread and protection of Covid 19.

**Keywords:** nanoparticles, facemask, Covid 19, nanostructures,

## Introduction

The Coronavirus disease-19 (Covid 19) pandemic and its rapid spreading has put in the front line the importance of the personal protection equipment (PPE) and protective means such as face masks, gloves, coats. Additionally, the increased environmental awareness and societal pressure have induced the necessity for design and production of new generation of personalized and reusable facemasks with remarkably improved level of filtration and self-sterilization properties that are especially important for the medical persons as well as for the common people. Nanotechnology can help in this process by design of infection-safe facemasks that will be able to inactivate the virus and prevent its spread. Special attention received reusable nano-filtered facemask that would be an economical option for daily usage as disposable masks often end up being very expensive when purchasing it on a regular basis. Further improvement of the facemasks should be done according the guidelines laid out by the National Institute for Occupational Safety and Health. The standard facemasks, N95 where the letter 'N' means "Non-oil" underlined the ban of the use of oil-based particles in the facemask, and 95 stands for the efficiency of filtration. All next research works are mainly related to further improvement of this standard mask. Also, very significant interest received and the method of integration of nanoparticles into the facemask structure. Incorporation of nanostructures into the facemask body resulted in new properties making the facemask materials more efficient, resistant and safer for use.[1–3] Nanomaterials with dimensions less than one micrometer are falling in the nano-scale regime. This nano-size is comparable to the size of the virus itself (Figure 1), endowing nanomaterial with effective functional qualities in combating it. The small size also renders a high surface-to-volume ratio, enabling the nanomaterial to be highly effective against viruses and bacteria. Their unique physical and chemical properties in the nano-size range can be amply utilized in devising strategies against COVID¬19.

According to Campos and his team, application of nanomaterial for facemasks has two positive effects: first one, facemask protection function based on microbicide agent, resulted in blocking and inactivating/killing the pathogens. Second one is related to the management of this material after its use, it becomes safer since the biggest part of pathogens was destroyed in contact with the masks reducing the probability of contamination during the undressing process.[1] Generally, different functionalizing agents of nanoparticles which can meet four important functions in the masks including were used, such as i) incorporation of metal nanoparticles or photosensitizers and boosting the antimicrobial and self-disinfectant characteristics, ii) increasing the self-cleaning properties by using superhydrophobic materials (graphenes or alkyl silanes), iii) design of photo electrothermal properties by combining graphene and metal thin films into the masks, and iv) incorporation of triboelectric nanostructures between the friction layers of masks in order to stabilize the electrostatic charges and to facilitate the recharging of masks.[2] According the published research reports, the mechanism of interaction among the nanoparticles and viruses was divided on indirect and direct. In the indirect interaction, nanoparticles do not directly impact the viruses; but they will intensify the antiviral activity of agents. Mainly, in the indirect mechanism, nanoparticles were used to enhance the bioavailability of antiviral agents. In the direct activity mechanism, the nanomaterials deactivate the virus by altering their viral structure or by changing the genetic structure of materials.[3]

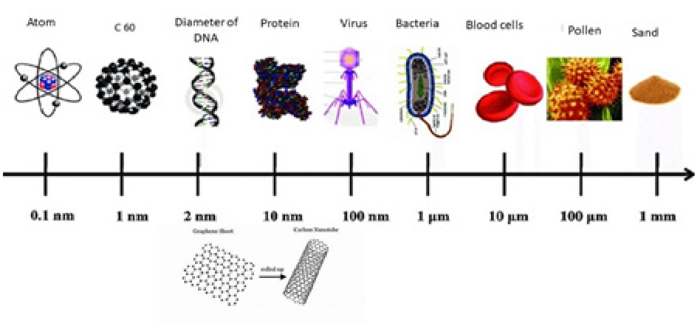


**Figure 1** Nanoscale dimensions of nanomaterials versus viruses and bacteria.

## Carbon nanostructures

Last decades, carbon-based nanomaterials like carbon dots (CD), carbon nanotubes (CNT) and graphene (G), as well as their hybrids

(Figure 2) were used as a drug-carriers for the drug-delivery systems in the pharmacy, and has remarkably helped in effective treatment of many disease.[4,5] These days, when the people are facing the highly danger and rapid spreading of SARS-CoV-2 virus, carbon nanostructures are attractive also to be used in order to increase the protection levels of the human life and in the same time to provide greater security and freedom for people to carry out usual daily activities without any fear of being infected by the virus.[4,5,6] Actually, various carbon nanomaterials, like fullerene, CD, CNT and G can be applied as antiviral agents due to their capability of inhibiting RNA type virus, biocompatibility and low toxicity. Namely, carbon based nanostructures should increase the filtration efficiency of the personal face- masks and to reduce the viruses transmission (Figure 3). Researchers have found that by the increasing CNT loading content and the filtration efficiency of the biological aerosol in CNT filters was significantly greater than total aerosol.[6]

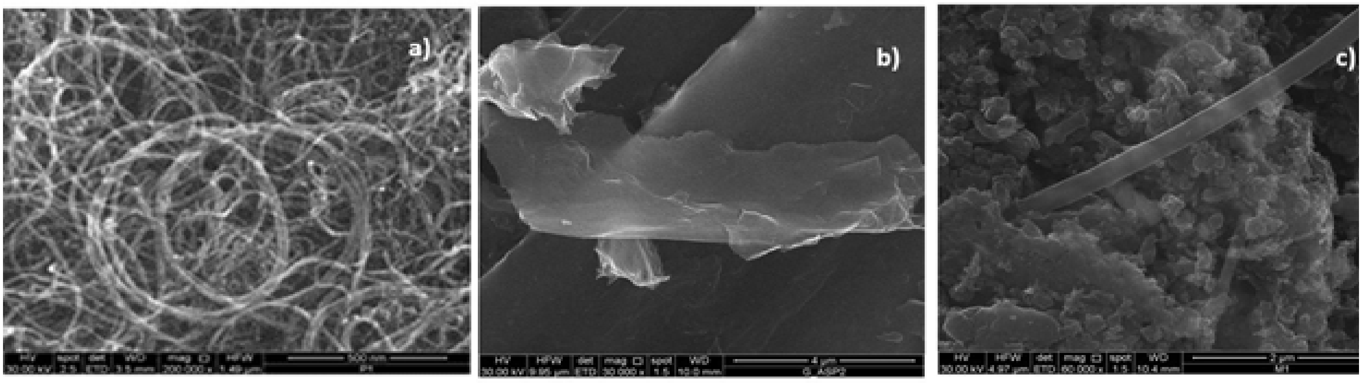


**Figure 2** Carbon based nanomaterials: A) MWCNT, B) Graphene, C) Hybrid MWCNT-G.

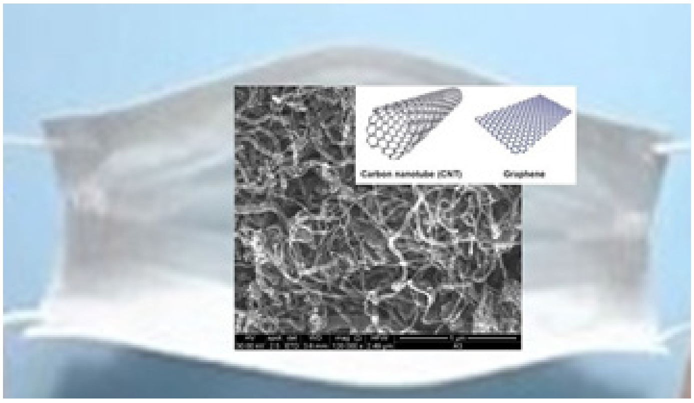


**Figure 3** Incorporation of nanostructures in facemasks.

It was reported that primary obtained carbon dots were with lower activity against viruses in vivo, but after their functionalization, they offered some opportunities for improved antiviral efficiency. Ting et al.[7] have created stable cationic carbon dots from curcumin.[7] They produced carbon nanoparticles that suppress viruses by the synthesis of negative-strand RNA with the formation of interferon-stimulating genes and pro-inflammatory cytokines. Namely it was supposed that the virus inhibition was possible due to the interaction between CQDs functional groups with entry receptors of the virus and the positive charge of carbon dots surface disjointed the spike protein of the virus and then react with negative RNA of COVID-19.[7–9] Literature survey has shown that there were published a number of surface modifications of carbon dots by using functionalization moieties such as 2,2′ -(ethylene dioxy) bis (ethylamine) (EDA), 3-ethoxy-propyl-amine (EPA), boronic acid and amino phenylboronic acidic.[8,9]

Graphene belongs to the family of 2D carbon based nanostructures with extraordinary physiochemical and mechanical characteristics who was widely used in biomedical applications demonstrating very good biocompatibility. Besides antibacterial activity (trapping or deactivation of bacteria), also it's antiviral activity was confirmed and graphene received active role against Covid 19.[10–12] It was discussed that the mechanism of interaction among the graphene flakes and the viruses was based on hydrogen bonding, electrostatic interactions, and redox reaction.[11] What is very important for the great antiviral efficiency of graphene is the fact that antibody-conjugated graphene sheets can quickly recognized targeted proteins of the virus and it is stable at higher temperatures who destroy the bacteria and disease agents. Due to these facts, graphene oxide films were successfully used as a coating of fabrics as the breathable barrier for the bacteria and viruses.[13] Ye et al.[14] compared the antiviral efficiency of several derivatives of graphene such as: graphite (Gt), graphite oxide (GtO), graphene oxide (GO), reduced graphene oxide (rGO), graphene oxide/poly(diallyldimethyl-ammonium chloride) composite (GO-PDDA), and graphene oxide/polyvinylpyrolidone composite (GO-PVP). PDDA was added as cationic polymer, while PVP as nonionic polymer. The obtained results of the antiviral activity followed the order: GO ≈ rGO > GO-PVP > GtO. Gt and GO-PDDA did not show antiviral activity. The researchers pointed out that the obtained results were associated to the nanosheet structure of the materials tested; better antiviral activity was registered for GtO, GO, and rGO as a result of their nano sheet structures.[14] Zhao et al.[15] immobilized GO onto the cotton fabrics using three different methods to provide the fabrics antibacterial and antiviral for fabrication of facemasks.[15] Ramaiah et al.[16] reported two types of graphene based facemasks: Polygreen and Nanene that were certified and proved by the international graphene council. These masks were constructed by 4-layers with composition: the graphene outer protective layer forms

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28.6%, Polypropylene non-woven fabric makes 14.2% and the melt-blown fabric is 28.6%.[16] Ruquan and his research team from City University of Hong Kong has successfully produced graphene masks with an anti-bacterial efficiency of 80%, which can be enhanced to almost 100% with exposure to sunlight for around 10 minutes. Initial tests also showed very promising results in the deactivation of two species of coronaviruses.[17] Since the literature survey suggested that COVID-19 would lose its infectivity at high temperatures, the researchers performed experiments to test if the graphene's photo thermal effect (production of heat after absorption of light) can enhance the anti-bacterial effect. The obtained results showed that the anti-bacterial efficiency of the graphene material could be improved to 99.998% within 10 minutes under sunlight, while activated carbon fiber and melt-blown fabrics only showed an efficiency of 67% and 85% respectively.[17] Besides graphene, carbon nanotubes demonstrated also very high antiviral efficiency against Covid 19. It was confirmed that CNT and fullerene have a very high binding affinity towards the protein component of the coronavirus. Research experiments, also demonstrated that carbon nanotubes coupled with metal complex compounds exhibited very high anti-viral activity and can deactivate the RNA virus-like the coronavirus. Literature survey show that there were reported a lot of different methods of synthesizing multiwall carbon nanotubes for anti-viral applications, among them a spark plasma sintering technique.[16] They produced a nanocomposite of higher fracture toughness and improved wear resistance. They have also synthesized multiwall carbon nanotubes using acetylene ($C_2H_2$) gas and Fe/MgO as a catalyst.[16] Research papers demonstrated that the hybrid structures of CNT, graphene oxide and other nanoparticles such as silver exhibited antiviral performances to block and killed the SARS-CoV-2 viruses.

## Metals and salts

Among the others nanoparticles (polymers, inorganic self-assembly materials and peptides) used against viruses, nanoparticles of metals and salts exhibited very strong antimicrobial activity towards wide range of bacteria and viruses. Metal nanoparticles such as silver, copper and titanium dioxide are alternatives currently used as chemical disinfectants. A great number of papers were published reporting the biomedical applications of silver, titanium dioxide, copper and zinc.[18–20] The suitable properties and variety of applications of $TiO_2$ nanoparticles are affected by the diversity of crystalline forms in which can exists (Figure 4). One of the most important and essential property of $TiO_2$ is its semiconductivity of n-type with $3d^24s^2$ outer electron distribution,[21] which makes it one of the most popular and most widely used photocatalytic materials (in UV range of light) in the field of environmental protection such as photocatalytic water purification, photocatalytic degradation of toxic, hardly degradable cyclic organic compounds in air and aqueous media, dye degradation, sustainable energy sources such as photocatalytic water splitting, dye sensitized solar cells etc.[21–26] Also, as an oxide compound, it is characterized with high chemical and corrosive stability. Instead of the higher value of the band gap energy (3.2 eV for anatase vs. 3.0 eV for rutile), anatase has been shown as a better photocatalyst than rutile.[27] Due to its excellent photocatalytic activity, TiO2 nanoparticles were recognized as an effective material in destroying bacteria, some viral species and parasites.[28,29] Earlier, the effectiveness of TiO2 against influenza virus has been proved.[30] All previously mentions, indicate that $TiO_2$ nanoparticles can be successfully used in the fight with COVID-19 pandemic as a self-disinfecting surface for personal protective equipment (PPE) disinfection or as a drug carrier.[31]

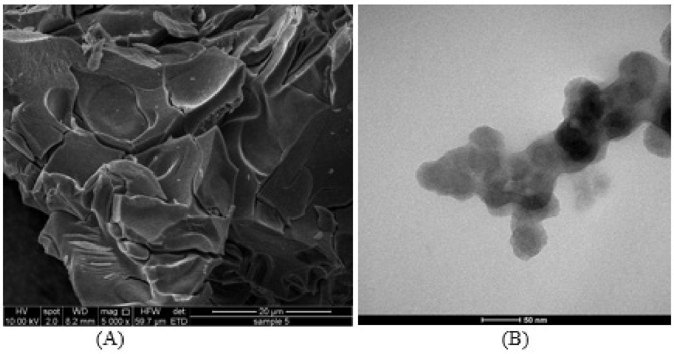

**Figure 4** Characteristic SEM (A) and TEM (B) microphotographs of $TiO_2$.

Hamza et al.[32] reported that $TiO_2$ nanoparticles have potent antiviral activity against SARS-CoV-2 at low concentration with very low cytotoxicity as indicated by their SI value (IC50/CC50 <1) and can generate many free radicals that may cause oxidative stress to SARS-CoV-2.[32] They suggest immobilization of $TiO_2$ nanoparticles with other active compounds such as polyethylene glycated nanoparticles that may reduce this cytotoxicity and enhance its anti-SARS-CoV-2 activity, according to the research of Akhtar et al.[33] Khaiboullina *et al.* tried to determine the disinfection ability of $TiO_2$ nanoparticles using inactivation of human coronavirus HCoV-NL63 (alpha coronavirus) on $TiO_2$ nanocoating and by in-vitro approach.[33] They demonstrated that the $TiO_2$ nanocoating are highly effective in photocatalytic reducing the viral genomic RNA stability and virus infectivity after 1 minute UV light exposure. In-vitro virus inactivation analysis has shown that when the detection of viral RNA by the RT-qPCR is negative (or below the detection limit) the viral genome has been completely collapsed. Matsuura et al.[34] demonstrated the inactivation of SARS-CoV-2 sprayed with nebulizer as aerosols into a 120L acrylic box by photocatalytic reaction using an air cleaner with TiO2 coating and LED light, without toxicity to humans unlike other light-based inactivation methods.[34] Gupta et al.[35] studied the stability of SARS-CoV-2 SARS-CoV-2 Spike pseudotyped virions based on a lent viral system and fully infectious SARS-CoV-2 virus on $TiO_2$ and $TiO_2$/Ag coated ceramic tiles.[35] The nano-coatings were stored 120 day before the use. There was no significant difference between the $TiO_2$ and $TiO_2$/Ag coatings in inactivation of the studied viruses. The coated tiles inactivated SARS-CoV-2 under ambient indoor lighting with 87% reduction in titres at 1h and complete loss by 5h exposure.

Improve of the $TiO_2$ nanoparticles performances and to shift the photocatalytic activity to the visible region of light, can be achieved through decrease of the band gap energy by the following approaches: i) doping of anions (N, C, F, B) or cations (Co, Ni, Au, Pt, Ir, Pd), generating lattice defects, mainly oxygen vacancies, shifting the photocatalytic activity in the visible range of light; iii) treatment of TiO2 by hydrogen plasma or iv) irradiation of $TiO_2$ by ionizing radiation (electron-beam, x-ray or γ-ray).[36-38] Usually, metal and salts nanoparticles were embedded in the textile fabric structures creating the antimicrobial fabrics. Many reports were presented embedding of such a metals like Ag nanoparticles and Ag nanowires on cotton textile fabrics, Ag/ZnO embedded on cotton/polyester hybrid fabric.[39,40] Silver particles (Ag°) deposited on surfaces of the MWCNT coated nonwovens by means of cyclic voltammetry.[40] Incorporation of these metals in various forms into the structures of respiratory facemasks resulted to ensure the masks with increased antimicrobial/antiviral activity.

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Jeremiah *et al.* studied the Ag-antiviral properties and effects of inhibition of SARS-CoV-2.[41] They compared Ag-nanoparticles of different sizes and concentration and find out nanoparticles of diameter around 10nm were effective in inhibiting extracellular SARS-CoV-2 at concentrations ranging between 1 and 10ppm. The cytotoxic effect was measured at higher concentrations of 20ppm and above. The obtained results show that Ag-nanoparticles exhibited very high potential of microbicides against SARS-CoV-2 but should be used with caution due to their cytotoxic effects and their potential to derange environmental ecosystems if they will be improperly disposed. Balagna et al. demonstrated that silver nanocluster/silica composite coating deposited on facial masks exhibit antiviral effect.[42] They reported that this coating can be practically applied on any kind of filtering media and various types of surfaces (metallic, ceramic, polymeric and glasses surfaces). Other type of metal nanoparticles used in facemasks were Cu-based nanostructures. According the theory, copper has long-established antimicrobial properties that include killing the COVID-19 virus within four hours. The proposed mechanism was that positively charged copper ions attract and trap bacteria and most viruses, which are negatively charged.

The copper ions then penetrate the microbes and destroy their ability to replicate, significantly reducing the number of infectious particles that might get through the pores of the mask. It was well known that also, oxide form - CuO possesses both antiviral and antibacterial behaviors. They have demonstrated excellent bactericidal properties when Cu nanoparticles were obtained by the ligand-assisted method in the presence of antibiotic molecules such as the tannic acid or the bacitracin used directly in situ as NC stabilizing agents.[43] The synergistic effect between Cu nanoparticles and the antibacterial organic molecule essentially consists of the damaging of the cell membrane of a Gram-positive bacteria (*Bacillus subtilis*) and in the increased reactive oxygen species (ROS) production.[43] Highly efficiency of CuO nanoparticles impregnation in respiratory masks that provide effective minimization of viral contamination was confirmed also by Leung et al.[44] For anti-viral and anti-Covid-19 activity were tested and magnetic nanoparticles (MNPs) of zinc ferrite because of its high chemical stability, soft magnetic behavior and biocompatibility. Somvanshi et al.[45] proposed a MNP's assisted RNA-extraction protocol for potential extraction and RT-PCR-based diagnosis of COVID-19.[45] Due to the surface functionalization of MNPs with silica and carboxyl-modified polyvinyl alcohol, very strong interactions in the interface among nucleic acids and carboxyl groups were registered that facilitate speedy and potential adsorption of viral RNA.[46]

## Conclusion

In order to find out the most effective protection and response to the SARS-CoV-2 global health outbreak, researchers all over the world have done a lot and they widely, disseminate their work. We have summarized some of the current state of knowledge regarding the application of nanostructures in the construction facemasks. The present article concerned the antiviral performances of the main nanoparticles, with the accent on carbon based (CNT and graphene), metal and salts, and their potential for incorporation into facemasks to combating coronaviruses including COVID-19. The reported results clearly confirmed that carbon based nanostructures, both CNTs and graphene, $TiO_2$ and nanosilver demonstrated very high efficiency of facemasks.

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## Conflicts of interest

Authors declare that there is no conflict of interest.

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