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HEALTH SCIENCES

Promising Nanostructured Materials against Enveloped Virus

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Abstract: The development of self-disinfectant devices is highly needed to prevent and control infections, mainly caused by virus. In the past years, coronaviruses have been a threat to humanity, causing severe epidemics of respiratory infections such as severe acute respiratory syndrome (SARS), in 2003, and Middle East respiratory syndrome (MERS) in 2012, and presently the SARS-CoV2 is causing the COVID-19 pandemic. Previous studies have demonstrated that surface contamination play a significant role in the spreading of viruses. These studies demonstrated that the production of highly reactive species by copper alloys contributes to rapid elimination of viruses. Nanostructured materials such as semiconductors TiO₂, Co₂O₄ CuO, NiO, and TiO₂, and silver nanoparticles can decrease the virus viability on the surfaces when associated with polymers and textiles, especially in conditions of light exposure. In addition, graphene oxide is rising as a promising material for inactivation of viruses due to its capacity of destroying the viral envelope and capsid. The virucidal property of these materials can be enhanced by increasing their functionalization with photosensitizers. The present mini-review brings subsidies for the development of new advanced self-disinfectant materials that can be used in the manufacture of gloves, masks, and a variety of other devices.

Key words: Enveloped virus, SARS-CoV-2, nanostructured materials, semiconductors, metallic nanoparticles, self-disinfecting materials.

INTRODUCTION

Basic aspects about viral infection and structure are important to develop nanostructured materials for rapid elimination of viral particles that contaminate surfaces.

The disease COVID-19

New zoonotic respiratory viruses have emerged in humans in recent years. In 2003, in Guangdong Province, China, a highly pathogenic coronavirus caused severe acute respiratory syndrome (SARS) in more than 8,000 people in 37 different countries with 10% mortality. In 2012, a severe respiratory infection, the Middle East respiratory syndrome (MERS) (Ellis 2009, Chan et al. 2015) affected individuals in the Arabian Peninsula. In this case, a higher percentage of mortality (~ 40%), was observed that resulted from the virus capacity to promote extrapulmonary diseases and the release of viral progeny from apical and basolateral respiratory cell surfaces (Warnes et al. 2015). In late November 2019, cases of novel pneumonia (COVID-19) in Wuhan, Hubei province, China, (Andersen et al. 2020, Jiang et al. 2020) were reported, and the disease spread rapidly throughout the world and attained the status of the pandemic as declared by the World Health Organization (WHO) at 11 March 2020. There is no evidence that SARS-CoV-2 results from a genetic manipulation in the laboratory of a pre-existent virus and there are two possible origins for the virus i) natural selection of a mutant in the animal host before transmission to a human and ii) natural selection in a human host previously infected by a zoonotic transfer (Andersen et al. 2020). SARS-CoV-2 exhibits some differences in comparison with MERS-CoV and SARS-CoV, which also cause severe diseases in humans. The receptor-binding domain (RBD) in the spike protein of SARS-CoV-2 has higher affinity with the human cell receptor (ACE2) (Wan et al. 2020) and the spike protein has a polybasic cleavage site (RRAR) at the junction of S1 and S2, which allows the effective cleavage by furin determining increasing infectivity. Accordingly, patients with COVID-19 have a higher level of inflammatory cytokines that correlates with the severity of the disease (Andersen et al. 2020).

Viral structures and infection mechanisms

Virus particles can be non-enveloped ("naked") or enveloped, the first consisting basically of the genetic material inside a protein coat named capsid, while the second have the capsid containing the viral genome, enclosed by an envelope composed by lipid bilayer associated with glycoproteins (Figure 1). Figure 1 shows



Figure 1. Viral structures represented by two virus types. In the top left it is shown an example of a non-enveloped virus, the Blue Tongue Virus (BTV), sided by the structure of one of its capsid proteins, the VP2. On the bottom right it is shown the open structure of SARS-CoV-2, an enveloped virus. The components of the SARS-CoV-2 represented in the cartoon are: 1- Nucleocapsid proteins (N) and RNA, 2- Spike protein (S), 3- Envelop lipid bilayer, 4- Hematoaglutinin (He), 5- Membrane protein (M), and 6- Envelop Protein (E). The SARS-CoV-2 representation is sided (at center) by the Spike protein (S) structure with a of a top view zoom (left) showing Y351, Y200 and Y741 in red and *N*-acetylglucosamine 1321 in violet. The yellow arrows show the position of Y351, Y200 and Y741 in the complete S protein structure.

the structure of Blue Tongue Virus (BTV) as an example of non-enveloped virus.

The infection by non-enveloped and enveloped viruses involves the following steps, the viral entry, disassembly, viral protein synthesis, production of viral genomes, assembly of viral components, and viral egress. Viral entry involves attachment to the cell followed by specific binding of viral proteins to the cellular receptors (Marsh & Helenius 2006, Brandenburg & Zhuang 2007). Glycans, which are abundant components at cell surfaces, play an important role in facilitating virus ingress in cells (Koehler et al. 2020). The binding of viral particles to receptors can trigger signalling cascades leading to endocytosis or to changes in viral structure that culminate in viral genome release into the cell. Figure 2a shows the principal strategies for viral entry in cells. One mechanism of virus entry involves the canonical endocytosis mediated by clathrin (1), or the non-canonical caveolaemediated endocytosis that activates tyrosine kinase cascade resulting in the traffic of virusloaded caveosome towards the endoplasmic reticulum (ER) through microtubules (2). Viruses can also enter into cells by clathrin- and caveolinindependent mechanisms (3) or direct fusion with the plasma membrane (4). The different viral strategies to enter into the cells result in similar post-endocytic trafficking mechanisms that involve the formation of dynamic and static populations of early endosomes, according to the rapid or slow maturation process (Luxton et al. 2006, Brandenburg & Zhuang 2007). The experimental strategy of single-virus tracking contributed to the mechanism of enveloped virus entry. The virus can be transported by motor proteins, dynein, and kinesin, using direct binding to these proteins or inside a motorbound vesicle. Dynein transport cargos towards the minus extremity of microtubules, whereas kinesin is a plus end-directed motor protein

(5) and (6), respectively. The transport of viral capsids to the nuclear pore (7) to deliver viral genome to the nucleus can occur by kinesin from the microtubule-organizing center (MTOC) (Brandenburg & Zhuang 2007, Zaichick et al. 2013). The completion of viral infection requires the assembly of viral components and the release of viral progeny. Figure 2b shows the mechanisms of viral particle egress from an infected cell that involves the encapsulation of viral genome in capsids to be transported by motor proteins along the microtubules (1) (Rietdorf et al. 2001, Brandenburg & Zhuang 2007). The viral membrane proteins expressed in host cells are transported along microtubules from the endoplasmic reticulum membrane to the Golgi apparatus (2). The viral capsids can bud into an envelope (3) or be encapsulated into multivesicular bodies (4). The motor protein kinesin is used to the transport of viruses- or subviral particles-loaded vesicles to the plasma membrane (5). Exocytosis (6) or budding at the plasma membrane (7) are the mechanisms used for the virus to exit the cells. Direct budding from the plasma membrane and signalling-mediated exocytosis are the more common pathways used to deliver the progeny of enveloped viral particles from cells. These mechanisms do not exclude the occurrence of cell lysis promoted by an enveloped virus. Lysis is the primary mechanism used by the naked virus, which can also take advantage of non-lytic mechanisms to egress from cells. Naked virus can also create new cell compartments to exit the cells by non-lytic secretory mechanisms. Non-lytic mechanisms can secrete virus- or genome-loaded vesicles, naked virus and RNA or a combination of these mechanisms (Bird & Kirkegaard 2015, Staring et al. 2018). Regarding SARS COV-2 there are pieces of evidences that SARSCoV-2 uses endocytosis or fusion at plasma for entry, depending of the cell type (Mahmoud et al. 2020). Therefore, the



Figure 2. Mechanisms of viral entry assembly and exit from cells. a) Viral entrance and transport. Viruses bind to specific receptors on the cell surface and can use canonical and non-canonical endocytic pathways to enter into cells. The canonical endocytic pathways consist of clathrin-coated vesicles with the participation of GTPase dynamin (1); the caveolin-dependent endocytosis (2); the clathrin- and caveolin-independent endocytosis (3), and direct fusion with the cell membrane (4). Virus-loaded vesicles use motor proteins dynein or dynactin for the transport along microtubules on the road to the microtubule-organizing center (5) (MTOC). From the MTOC, capsids can be transported by kinesin towards the replication site of the nucleus (6). Some viruses release their genetic material into the cytosol, whereas others transport lengthways microtubules (1); The viral membrane proteins are packed in capsids for transport lengthways microtubules (1); The viral membrane proteins are synthesized in the endoplasmic reticulum are transported to Golgi apparatus and directed to the site of viral assembly (2); the viral capsids can bud into an envelope (3) or encapsulated into multivesicular bodies (4); viruses- or subviral particles-loaded vesicles, are transported by kinesin along microtubules to attain the plasma membrane (5); the vesicles can egress from the cell by exocytosis (6) or budding (7) at the plasma membrane.

endocytic mechanism of SARS-CoV-2 must be considered according to the host cell type to be studied and understanding the mechanisms of viral entry is important for the finding of effective therapeutic agents in the treatment of COVID-19 (Glebov 2020).

SURFACES AS A SOURCE OF VIRAL INFECTION

Surface contamination has been recognized as an essential contributor to the spread of diseases. Infected and symptomatic individuals promote constant recontamination of surfaces that are then touched by non-infected persons leading to a rapid dissemination of the disease (Figure 3). Similarly to the previous coronaviruses of high infectious potential, MERS-CoV and SARS-CoV, and considering the unprecedented capacity of SARS-CoV-2 spread, it is likely that prolongated virus viability on contaminated surfaces has a significant contribution in viral spread. (Warnes et al. 2015). Firquet et al. (2015) determined the viability of non-enveloped and enveloped viruses on surfaces under repetitive cycles of drving and resuspension (Firguet et al. 2015). The viruses that were used in their study were the naked minute virus of mice (MVM) and coxsackievirus B4 (CVB4) and the envelopedviruses influenza A virus (H1N1) and herpes simplex virus type 1 (HSV-1). In the case of CVB4, the influence of the initial protein and sodium chloride concentrations was also studied. The results demonstrated that enveloped viruses were less resistant than the naked viruses. The presence of proteins increased the impact of drying, while sodium chloride had a protective effect. Recently, van Doremalen et al. (2020) compared the stability of SARS-CoV-2 with that of SARS-CoV-1 in aerosol and surfaces and showed that both have similar stability in the assayed conditions (van Doremalen et al. 2020).

The study aimed to investigate whether the differences in the epidemiologic characteristics of these viruses arise from significant differences in the resistance on surfaces and aerosols. The authors concluded that the epidemiologic differences likely result from other factors related to the capacity of infected asymptomatic individuals to spread the virus and the presence of high viral load in the upper respiratory tract



Figure 3. Mechanisms of viruses' dissemination by surface contamination. Fluid droplets containing virus from an infected and symptomatic person can be spread by a cough or sneeze and attain a surface directly or by the touch of the contaminated hand. Other non-infected persons can be contaminated by touching the contaminated surface and leading viral particles to the face. (Bai et al. 2020, van Doremalen et al. 2020). As illustrated in Figure 2, the authors concluded that similarly to SARS-CoV, the virus SARS-CoV-2 can easily be propagated via respiratory droplets spread by cough, sneeze, speech, and aerosol of the nosocomial environment. The virus present in droplets can remain viable on surfaces up to several days leading to dissemination by touching dirty/contaminated surfaces with subsequent self-inoculation by touching eyes, nose, and mouth (Bai et al. 2020, van Doremalen et al. 2020). SARS CoV-2 has higher transmission rates compared to the other human coronavirus, such as SARS-CoV and MERS (Liu et al. 2020, Sportelli et al. 2020). The high transmission rates associated with the absence of preexisting immunity of the population, lack of specific and efficient treatments, and vaccines make the prevention as the most effective way to combat the COVID-19 (Sportelli et al. 2020). Social confinement is efficient and mandatory to prevent rapid dissemination of SARS-CoV-2, but it is not possible for the entire population since essential services such as food, medicine, and hospital care should be available. Furthermore, at the initial period of return to work after confinement, it is imperative to have sufficient availability of efficient personal protective equipment (PPE) (Sportelli et al. 2020). Therefore, besides the search for anti-SARS-CoV-2 drugs and vaccines, another critical aspect of the combat of viral epidemics is the development of personal protective equipment such as masks and gloves with biocidal properties provided by different additives. Self-decontaminating surfaces constitute an additional strategy towards preventing transmission in a diversity of situations. The chemical and photochemical biocide activity can result from the intrinsic properties of the material or by association with organic molecules with biocide properties (Zhou et al. 2010, Hodek et al. 2016, d'Amora &

Giordani 2018). A recent study performed by van Doremalen et al. (2020) investigated the capacity of SARS-CoV-2 to remain viable on different material surfaces, and the results were similar to the previous work performed with Human Coronavirus 229E (Warnes et al. 2015. van Doremalen et al. 2020). Plastic and stainless steel are materials that preserve the virus viability for longer times, whereas copper surface was most favourable for virus inactivation. The virucidal property of copper is assigned to the production of reactive oxygen species. The virucidal activity of the oxygen reactive species led to an increased interest in the use of nanostructures to produce materials for disinfection purposes. The nanostructured materials can provide biocide action through chemical and photochemical activity.

VIRUCIDAL NANOSTRUCTURED MATERIALS

Literature data have reported that different nanostructured materials exhibit virucidal activity provided by the intrinsic properties of the materials such as the production of reactive oxygen species, by the capacity to act as drug delivery or to potentialize the action of some pharmaceuticals. Typical materials that can contribute to virus destruction are silver nanoparticles (AgNPs) (Lara et al. 2010, 2011), metal oxides mainly, copper and iron oxide (Borkow et al. 2010, Kumar Mishra et al. 2013, Kumar et al. 2019), hybrid materials (Hodek et al. 2016), organic polymeric nano/microstructures, (Ciejka et al. 2017) and nanostructured carbon materials (d'Amora & Giordani 2018, Pedrosa et al. 2019). Many studies involving gold and silver nanoparticles have focused on the use as carriers of drugs, potentiating the medication. However, the purpose of this review is to discuss the use of nanostructures to prevent viruses,

materials. Another aspect of prevention that can count on the help of nanostructured materials is the development of faster and more efficient diagnostic platforms, that requires approaching in a specific review.

Gold and silver nanoparticles

The materials acquire specific properties at the nanoscale, as depicted in Figure 4. The decrease in the size of a bulk metallic material to the nanoscale changes the electronic structure of the conduction band, replacing the continuum density of states by a set of discrete energy levels and opening a bandgap.

There is an increase of bandgap energy accompanying the size decrease of a material to the nanoscale, and the nanostructured metals can behave as a semiconductor (Gleiter 2000, Steinhart 2004, Roduner 2006, Aneesh et al. 2014, Charra et al. 2018, Brito et al. 2019) (Figure 4). The effect of resonance resulting from the interaction of conduction electrons of metal nanoparticles with incident photons is the surface plasmon resonance (SPR) (Jana et al. 2016). The interaction is dependent on the size and shape of the metallic nanoparticles as well as on the composition and nature of the medium used for dispersion (El-Sayed et al. 2006, Austin et al. 2014, Kabb et al. 2015, Jana et al. 2016). Figure 4 shows, on the right side, the events associated with direct excitation of metallic nanoparticles that can be used for virus inactivation (González-Béjar et al. 2013, Jana et al. 2016). The plasmon relaxation of metallic nanoparticles produces very high temperatures (González-Béjar et al. 2013, Riedinger et al. 2013) that can inactivate the virus by inducing chemical and supramolecular changes. The plasmon excited particle can donate holes or electrons directly to virus biomolecule or water and molecular oxygen leading to the production of reactive species for the pathogen inactivation. The antenna effect can, for instance, raise the excitation rates of a quantum dot (QD) leading to higher yield of fluorescence and reactive species (Holzinger et al. 2014). Thus, AgNPs and AuNPs, when associated with different



Figure 4. Specific optoelectronic properties and applications of metallic nanoparticles. On the left side, is shown the increase of the bandgap energy and the density of states associated with the diminution of the number of atoms constituting a particle with the representation of material valence and conduction bands (*vb* and *cb*). On the right side, possible events after plasmon excitation of metallic nanoparticles: thermal, redox reactions, and antenna. The figure is inspired by the references (González-Béjar et al. 2013, Brito et al. 2019).

matrices such as polymers and textiles, can give virucidal properties for these materials (Simoncic & Tomsic 2010, Gadkari et al. 2020). Films of poly (3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV) associated with AgNPs revealed an efficient virucidal activity. The material inactivated feline calicivirus (FCV) and 86% of murine norovirus (MNV) within 24 h exposure at 37°C (Castro-Mayorga et al. 2017). In textiles, AgNPs are used mainly against bacteria, and nowadays, these nanoparticles have also been recognized as virucides. Regarding the production of silver nanoparticles, they can be produced in situ by a photochemical method and remain decorating the surface of polymers as the example that is shown in Figure 5. The events of hyperthermia and the production of reactive oxygen species metallic nanoparticles have been extensively used for anti-tumor therapies. In this regard, the absorption of red light is desirable because the deep penetration in tissues. Many green, rapid, and one-pot methods are currently available for Au and Ag NPs synthesis, such as those that have been developed by our research group (Miranda et al. 2016, Tofanello et al. 2016, Cruz et al. 2018, Santos et al. 2020). The spectral range of light absorption can be modulated by the size, shape, and aggregation state of the nanoparticles. To achieve virus inactivation, it is crucial to have the production of reactive species by absorption of UV and visible light from sun and artificial light sources. Therefore, the combination of different nanoparticles regarding their size, shape and composition is an interesting strategy for best use of UV and visible spectra to produce reactive species against virus.

Figure 6 shows the snapshot and the corresponding spectra of the colloidal dispersion of nanorods (NRs) with increasing aspect ratio. At left, the flask with the brownish solution is the seed suspension used for preparing the NRs. Other promising metallic nanostructures for the fabrication of materials with virucidal properties are the Ag/Halogens-NPs (Araújo et al. 2017, 2018, Cruz et al. 2018) that exhibited efficient photocatalytic activity on the removal of dyes. Considering that the bleaching of dyes is associated with the production of reactive oxygen species, these nanoparticles are promising for virus inactivation.

Carbon nanostructured materials

The electronic, mechanical, and magnetic properties of carbon nanostructures (CNSs) have been extensively studied (Chand 2000, Zhu & Xu 2010, Kukovecz et al. 2013, Ahn & Hong 2014, Lim et al. 2015, Champi et al. 2016, Karousis et al. 2016, Acatay 2017, Liu et al. 2018, Ferreira et al. 2018, Pochkaeva et al. 2020).

The CNSs have a diversity of applications including to act as powerful microbicide agents. Complex mechanisms respond for the capacity of CNSs to inactive virus, fungi and bacteria that is dependent of type of microorganism, the intrinsic material properties and environmental conditions.(Al-Jumaili et al. 2017). The physical interaction of CNSs is able to promote structural changes in the microorganisms biomolecules causing damages in bacteria membranes, virus capsid and envelope.(Kholmanov et al. 2012, Dizaj et al. 2015, Al-Jumaili et al. 2017). As an example, graphene oxide conjugated with a nonionic polymer, polyvinylpyrrolidone (PVP) showed potent anti-viral activity which did not occur when combined with a cationic polymer, polydiallyldimethylammonium (PDDA). Also, GO promoted structural destruction of the virus before cell entry supporting GO as a novel promising anti-viral agent. (Ye et al. 2015). Table I summarizes structural features and general and microbicide properties of CNSs and Figure 7 illustrates virus inactivation by GO.



Figure 5. Field Emission Scanning Electron Microscopy (FESEM) of organic polymer decorated with AgNPs produced photochemically by using the reducing power of a thiazinic dye irradiated with visible light according to an adaptation of the method described in the literature (Santos et al. 2020).



Figure 6. Spectra and colloidal suspension of gold nanorods (NRs). In the snapshot, the NR aspect ratio increases from left to right. The peaks of the lower energy band are redshifted with the increase of the NR aspect ratio.

Table I. Structure and Applications of CNSs.

CNS	Structure	Usual Potential Applications	Microbicide capacity
Carbon black	Spherical particles of carbon aggregated and fused together. Carboxylic groups can be present (Tofighy & Mohammadi 2019).	Rubber or polymer fortification, catalysis, pigments and electrodes (Ali et al. 2017, Tofighy & Mohammadi 2019).	Against bacteria. Composite with chitosan and metallic nanoparticles Carbon black (Ali et al. 2017)
Carbon fiber	Graphene sheets twisted, folded and shattered upon each other (Acatay 2017).	Aerospace and nuclear engineering for devices submitted high damping, extreme temperatures and corrosive environments. Template for nanostructure growing.(Chand 2000, Acatay 2017, Liu et al. 2018)	Against bacteria. Fibers impregnated with silver (Le Pape et al. 2002)
Fullerene	Closed cage Structure with icosahedral symmetry formed by 20 hexagonal and 12 pentagonal rings. (Pochkaeva et al. 2020).	Electrocatalysis in fuel cells, diversity of biomedical applications (Pochkaeva et al. 2020)	Against HIV Water-soluble fullerene derivatives with carboxy, hydroxy groups, derivatives with amino acids, peptides and proteins. (Arts & Hazuda 2012, Strom et al. 2015, d'Amora & Giordani 2018, Pochkaeva et al. 2020)
Graphene	Crystalline allotrope in the form of a 2D, atomic-scale, structured as a hexagonal lattice with carbon atoms with sp2 hybridization.(Novoselov 2004)	Graphene has potential to be applied from flexible electronics to DNA sequencing. Few graphene-based products have reached the market that requires large-scale production. (Torrisi & Coleman 2014, Ahn & Hong 2014, Böhm 2014, Drndić 2014, Kostarelos & Novoselov 2014, Siochi 2014).	Against bacteria and virus Microbicide activity is associated to physical contact and oxidative stress. (Ye et al. 2015, Perreault et al. 2015)
Carbon nanotubes	Carbon nanotube (CNT) is formed by graphene wrapped in the shape of a cylinder and bonded together to form a carbon nanotube. This material exists as single- and multiwalled forms.(Nanot et al. 2013, Kukovecz et al. 2013)	The applications are reported for energy conversion and storage, electronics, semiconductor devices, capacitors, hydrogen storage, catalysis, composite materials of owned of high- strength and conductive properties, batteries, several sensors; field emission displays, interconnects and others. There are some products using carbon nanotubes such as bicycle frame, antifouling CNT paints, printed electronics, electrostatic discharge shielding reported for Juno spacecraft uses, CNT ESD shield. (Baughman et al. 2002, Sun et al. 2002, Schnorr & Swager 2011, Zhi et al. 2013, De Volder et al. 2013)	Against bacteria and HIV, more common use in filters against virus and bacteria (Cheng et al. 2010, Vecitis et al. 2011, Rahaman et al. 2012, Banerjee et al. 2012, Al-Jumaili et al. 2017)

Carbon nanohorns	Carbon nanohorns are similar to carbon nanotube but it is shaped as a conical single- walled tip. Carbon nanohorns are constructed from an sp ² carbon sheet (Zhu & Xu 2010, Karousis et al. 2016)	Carbon nanohorns have potential applications in capacitors, gas adsorption, catalysis, sensing, and drug delivery. One of the most auspicious applications is in the biological area.(Zhu & Xu 2010, Zhang et al. 2015, Karousis et al. 2016)	Carbon nanohorns produces reactive oxygen species and can eliminate microorganisms. It is described photo-induced inactivation of virus by carbon nanohorns.(Miyako et al. 2008)
Carbon quantum dots	Carbon quantum dots are described as quasi-spherical nanostructures including amorphous to nanocrystalline centers. The cores have predominance of sp ² carbon or sheets of graphene and graphene oxide bonded by diamond-like sp ³ hybridised carbon insertions.(Lim et al. 2015)	Carbon quantum dots are materials with tunable fluorescence and have potential application in chemical sensing, biosensing, bioimaging, nanomedicine, photo and electrocatalysis (Wang & Hu 2014, Lim et al. 2015, Fernando et al. 2015)	Against microorganisms including vrus JEK, ZIKV, DENV, PPV, AAV, PK-15, MARK-45 and others. (Huang et al. 2019, Dong et al. 2020)



Figure 7. Representation of a GO layer with a virus before and after inactivation with RNA liberation. RNA is represented as a red curled line, virus envelope in yellow, oxygen in red, and carbon in blue.

Nanostructured metal oxides

Nanostructured metal oxides hematite (α -Fe₂O₃), goethite (α -FeOOH), magnetite (Fe₃O₄), amorphous iron(III) hydroxide (Fe(OH)₃), titania nanostructures (anatase nanoparticles and titanate nanotubes) and zinc oxide (ZnO), are also efficient for the fabrication of textiles with virucidal properties (Sang et al. 2007, Dias et al. 2012, Nakano et al. 2012, Nieto-Juarez & Kohn 2013, Ruales-Lonfat et al. 2015, Zeedan et al. 2020, Menezes et al. 2020). The well-known production of reactive oxygen species by these materials under illumination is promising for a large scale use in the fabrication of self-disinfecting materials (Yan et al. 2009, Menezes et al. 2019, 2020).

Semiconductors such as iron oxides, ZnO and TiO, are well known for the capacity to produce, under irradiation, and even in the dark, oxidative species such as hydroxyl radical (OH^{\cdot}), superoxide ion, hydrogen peroxide (H₂O₂), and singlet oxygen $({}^{1}\Delta_{\sigma}O_{\gamma})$ (Rao et al. 1980, Macyk et al. 2006, He et al. 2014) that can promote oxidative damages in biomolecules like proteins (Estevam et al. 2004, Rodrigues et al. 2007). The irradiation of the semiconductor generates the superoxide ion (O_2^{-}) by electron transfer from cb to molecular oxygen. Singlet oxygen can also be produced by energy transfer to molecular oxygen that occurs associated with the $h^+/e^$ recombination (Macyk et al. 2006). Therefore, semiconductors are materials with high potential for virus inactivation. Importantly, our research group has developed green methods for the production of nanoparticles of metal oxides, including magnetite nanoparticulated (Nantes-Cardoso & Tofanello de Souza 2019) and Co₂O₄ (unpublished results). The association with metallic nanoparticles can also improve the property of self-disinfection. In the case of hematite (α -Fe₂O₃), it is possible to produce

hierarchically layered Fe₂O₄/Fe₂O₅ microtubes and foils with the respective Fe₂O₃ nanowires (Fe₂O₃NWs) and Fe₂O₃ nanoflakes (Fe₂O₃NFs) vertically protruding at the surface as shown in Figure 8 (Pomar et al. 2018). These materials were used for their self-decoration with gold nanoparticles produced in situ from AuHCl, solutions by using the photochemical properties of Fe₂O₂ (Menezes et al. 2020). Figure 8 shows the FESEM images of Fe₂O₂NWs(NFs) with the surface extensively decorated by gold nanoparticles. A diversity of nanostructured oxides (Figure 9) can be produced using two principal methodologies: (a) electrospinning and (b) hydrothermal synthesis. Oxides such as the electronically related system $RNiO_3$ (R = La, Nd), TiO₂ and the superconductor YBa, (Cu1-,Ni,),O₄ can also be prepared by this electrospinning. (Chiquito et al. 2007, Giraldi et al. 2007, Barbeta et al. 2011, Zenatti et al. 2013, Jardim et al. 2015, Medina et al. 2020a). Hydrothermal synthesis has been used for the synthesis of more complex oxides such as the multiferroic BiFeO₃, the thermoelectric oxide $Ca_3Co_4O_9$, LaNiO₃, and simple oxides such as TiO₂, SnO₂ and Co₂O₄ (Medina et al. 2020b).

Therefore, a diversity of nanostructured materials can be incorporated in different matrices to produce textiles and objects with self-disinfecting properties provided by the production of reactive oxygen species when the materials are exposed to illumination. Figure 10 illustrates the proposal of a mask fabricated with a textile impregnated with a nanostructured semiconductor.

NANOSTRUCTURED MATERIALS FOR BIOSENSOR FABRICATION

Besides the application in self-disinfecting devices, the studies on the interaction of the enveloped viruses with nanostructured



Figure 8. FESEM images of microtube and foil with hematite surface. The 10,000 x magnification image of the hematite surface with nanowires protruding from the surface shows gold nanoparticles decorating the material surface.

materials can also address another critical issue that is the detection of the virus for diagnosis, preferentially at the initial stages of the disease.

Diagnosis is the primary strategy for the control of the viral dissemination and to treat viral infection. Several new approaches based on nanostructured materials have recently been established. Studies have reported the use of gold and silver nanoparticles, magnetic nanoparticles, carbon and polymeric nanostructured materials (Cao et al. 2002, Yang et al. 2010, Theek et al. 2014, Ye et al. 2015, de Souza et al. 2016, Ciejka et al. 2017). Gold nanoparticles are particularly exciting and commonly described to be appropriated for many applications. The photonic, electric, and catalytic properties of gold nanoparticles and particularly the specificity for functional groups present in biomolecule structures, allow designing a wide range of virus detection systems (Rashid & Yusof 2017). Graphene oxide, their derivatives, and in association with metallic nanoparticles have also been applied in

electrochemical biosensors for virus detection (Peña-Bahamonde et al. 2018. ig. 102018, Singh et al. 2019).

HAZARDS FOR THE USE OF NANOSTRUCTURED MATERIALS FOR THE SELF-DISINFECTION OF SURFACES

The growing application of nanotechnology has brought benefits, but also risks to human health and the environment (Joshi & Bhattacharyya 2011, Ferdous & Nemmar 2020, Tortella et al. 2020, Hadrup et al. 2020). The toxicological and environmental risks arising from the application of nanotechnology are present in the stages of manufacture, handling, use and disposal of materials. For the human health, the inhalation is an important via of adverse effects of nanostructured materials. The contamination during fabrication and by unappropriated discard are the principal risks of ecotoxicity. The toxicity of nanomaterials depends on a variety of factors such as composition, shape, size,



Figure 9. SEM images obtained for samples synthesized by the hydrothermal method: (a) LaNiO₃ nanocubes; (b) rutile nanoneedles grown on FTO/ Si (100) (c) rutile nanoneedles grown on Si (100) and (d) rutile nanoneedles.

aggregation, stability, among others. The effects are also varied depending on the species, the degree of development and the tissue affected (Walters et al. 2016, Duhan et al. 2017, Gonzalez & Johnston 2018). In this sense, it is difficult to establish a comprehensive toxicity ranking for all types of nanostructures. Regarding the application of nanotechnology for microbicidal purposes, silver nanoparticles have been the most commonly used. For this reason, a large number of researches have been concerned with determining the toxic effects of silver nanoparticles. (Joshi & Bhattacharyya 2011, Ferdous & Nemmar 2020, Tortella et al. 2020, Hadrup et al. 2020) The available studies about silver nanoparticles toxicity make evident that these nanomaterials are not unharmful and careful is necessary for manipulation and discard of products containing silver nanoparticles. It is important to address carefully the use of silver nanoparticles particularly in textiles that demands frequent wash and discardable materials. The unique properties of CNSs allow the applications of these engineered nanomaterials in the computer, smart textiles,

electronic devices, medicine, aerospace, and others. Therefore, the well-known cytotoxicity of CNSs must be considered for the production of self-disinfecting materials. The CNSs are an optimum example of materials that are inert in the bulk and harmful in the nanostructured form. (Lam et al. 2006). Regarding the use of metal oxide nanoparticles, some studies show a ranking of toxicity that varies according to the parameter that is evaluated (Liu et al. 2015, Ha et al. 2018). Pusyn et al and Mu et al used the quantitative structure-activity relationship (QSAR) method to predict the toxicity of various metal oxides. The authors based on experimental testing obtained for nanotoxicity to bacteria and obtained a good agreement of the theoretical with the experimental data (Table II) (Puzyn et al. 2011, Mu et al. 2016).

Thus, it is very important to give priority to green and sustainable methods of nanoparticle synthesis, to use PPE when handling them, to prefer materials that produce reactive oxygen species rather than those that produce ions to destroy the virus, to choose methods of incorporating nanostructures in fabrics that



Figure 10. A proposed selfdisinfecting mask that is taking advantage of the reactive oxygen species produced by metal oxide nanoparticles that were impregnated in the textile.

Table II. Observed and Predicted Toxicity of Metal Oxides.

Metal Oxide	Observed Log 1/IC ₅₀ (mol.l ⁻¹)	Predicted Log 1/IC ₅₀ (mol.l ⁻¹)
ZnO	3.45	3.30/3.39*
CuO	3.2	3.24/3.35*
V ₂ O ₃	3.14	2.74
Y ₂ O ₃	2.87	3.08
Bi ₂ O ₃	2.82	2.69
In ₂ O ₃	2.81	2.52
Sb ₂ O ₃	2.64	2.57
Al ₂ O ₃	2.49	2.63
Fe ₂ O ₃	2.29	2.35
SiO ₂	2.20	1.99
ZrO ₂	2.15	2.41
SnO ₂	2.01	1.95
TiO ₂	1.74	2.13/1.95*
CoO	3.51	3.38/3.39*
CO ₃ O ₄	-	2.94
NiO	3.45	3.38/3.42*
CrO ₃	2.51	2.52
La ₂ O ₃	2.87	2.85

*According to Mu et al. 2016.

provide strong adhesion of these materials and properly dispose of waste containing nanostructures.

CONCLUSIONS

In addition to the development of anti-viral medicines and vaccines, the combat of viral infections should include the production of self-disinfecting materials. This preventive strategy has the advantage that can be of applied to a diversity of viruses and other pathogenic microorganisms. Nowadays, a diversity of nanostructured materials can be produced, and most of them by green, facile, one-pot methods. The intrinsic capacity of these materials to produce reactive oxygen species under illumination with visible light makes them promissing for the development of a lot of objects and textiles that are able of virus inactivation. However, it is necessary to pay attention to the fabrication, manipulation, and discard of products containing nanostructured materials to avoid hazardous effects to human health and environment.

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Gabriel G. de Toledo – designed and performed experiments and draft the text, Victor H. Toledo – designed and performed experiments and figures, Alexandre J.C. Lanfredi – designed and performed acquisition of scanning electron microscopy and revised the manuscript, Marcia Escote – designed and performed experiments of synthesis and acquisition of scanning electron microscopy and revised the manuscript, Ana Champi – contributed with literature revision about carbon nanostructured materials and revised the corresponding text, Maria Cristina C. da Silva – contributed with text concerning virology and contributed with a extensive revision of the manuscript, Iseli L. Nantes Cardoso – conceived the revision, coordinated the team, wrote the final version of the manuscript and prepared figures.

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