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Hydrophobic cellulose-based and non-woven fabrics coated with mesoporous TiO$_2$ and their virucidal properties under indoor light

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Keywords:
Nanoparticles
Textiles
Virucidal effect
Supercritical CO$_2$ nanoparticles
Sol–gel synthesis

ABSTRACT

Antiviral hydrophobic cellulose-based cotton or non-woven fabrics containing mesoporous TiO$_2$ particles were developed for potential use in healthcare and in other contaminated environments. Hydrosols made with the sol–gel method using two different amounts of the Ti precursor were applied to cotton and non-woven fabrics and their virucidal effect on Murine Coronavirus (MHV-3) and Human Adenovirus (HAdV-5) was evaluated under indoor light irradiation. The results show 90% reduction of HAdV-5 and up to 99% of MHV-3 in non-woven fabric, and 90% reduction of MHV-3 and no reduction of HAdV-5 in cotton fabric. The antiviral activity was related to the properties of the TiO$_2$ powders and coatings characterized by BET surface area, DRX, DLS, FTIR, DRS, SEM, TEM and water contact angle. The hydrophobic characteristic of the treated fabrics and the high surface area of the TiO$_2$ particles favor interaction with the virus, especially MHV-3. These results demonstrate that non-woven fabric and cotton, coated with TiO$_2$, can be highly effective in preventing contamination with MHV-3 and HAdV-5 viruses, particularly for applications in healthcare indoor environments.

1. Introduction

Nanoparticles are among the studied materials in the area of antimi-crobial applications, having demonstrated a great potential for the disinfection/inactivation of harmful pathogens, including bacteria, viruses, and fungi (Hamouda et al., 2021; Hosseini, Chin, Behzadinasab, Poon & Ducker, 2021; Park et al., 2014; Rodríguez-González, Obregon, Patrón-Soberano, Terashima & Fujishima, 2020; Uyguner Demirel, Birben & Bekbolet, 2018; Za, Fa, Peng & Gong, 2007). Among different nanoparticles, TiO$_2$ has demonstrated biocidal effect for numerous microorganisms (Hosseini et al., 2021; Park et al., 2014; Rodríguez-González et al., 2020; Uyguner Demirel et al., 2018; Za et al., 2007) including gram-positive and gram-negative bacteria (Dicastillo, de, Correa, Martínez, Streit & Galotto, 2020; Ibrahim et al., 2018; Ibrahim, Eid, El-Aziz, Abou Elmaaty & Ramadan, 2017; N. A. Ibrahim, Eid, Khalil & Almetwally, 2018), various viral species and parasites (Rodríguez-González et al., 2020).

The antiviral behavior of TiO$_2$ nanoparticles is, however, less documented than its antibacterial properties. In particular, the antiviral activity of TiO$_2$ has been investigated against the influenza virus (H3N2) and against bacteriophages such as MS2, PRD1 or ΦX174 (Gerrity, Ryu, Crittenden & Abbaszadegan, 2008; Mazurkova et al., 2010; Syngouna & Chrysikopoulos, 2017). Increasing concerns about the spread of epidemic and pandemic viral diseases have drawn the attention towards the development of photocatalytic nanotechnologies particularly for application in hospital settings. Recently, Khaioullina, Uppal, Dhabarde, Subramanian and Verma (2020) reported that surfaces coated with titanium dioxide, a thin, nontoxic layer applied as paint, can enhance surface disinfection of human coronaviruses, under UV light. Similarly, Moon, Lee, Rok and Ha (2020) demonstrated that viral particles of HuNoVs could efficiently be disinfected using Cu/TiO$_2$-treated non-woven fabric under UVA-LED.

Mechanistically, it has been reported that photocatalytic viral disinfection occurs through three possible steps: (1) particle shape...
rupture of the viral capsid proteins, and possibly leading to gene efflux. In parallel, the oxidation of proteins by reactive oxygen species (ROS) distort the virus first step, the adsorption of a virus on the photocatalytic surface could distortion, (2) protein oxidation, and (3) gene leakage or damage. In the activity. The virucidal effects of the coatings were correlated to the irradiation encountered in healthcare indoor environments and ac

The material used to support TiO$_2$ can significantly contribute to promoting the interaction between viruses and particles. Cellulose-based fabrics such as cotton and non-woven fabrics have been widely studied for the application of titanium dioxide hydrosols, resulting in fabrics with photocatalytic and self-cleaning properties (Ahmad et al., 2019). The physical and chemical properties of the TiO$_2$ coatings to gain a deeper understanding of the impact of catalyst properties on the inactivation of MHV-3 and HAdV-5 in coated fabrics.

2. Experimental

2.1. Materials

Cellulose-based cotton (166 ± 5 g m$^{-2}$) and polypropylene non-woven (40 ± 4 g m$^{-2}$) fabrics were purchased from a local market in Santa Catarina (Brazil). Titanium butoxide was provided by Sigma – Aldrich (97%). The acetic acid (99.5%) and ethanol (99.8%) were obtained from Lafan (Brazil) and Neon (Brazil), respectively. The fabrics and reagents were used without prior treatment/purification.

2.2. Synthesis of TiO$_2$ hydrosol and textile treatments

The titanium dioxide hydrosol synthesis were conducted as proposed by Wang et al. (2018). Initially, 5.54 ml of titanium butoxide [Ti(OBu)$_4$] and 2.46 ml of ethanol were added to a beaker and stirred for 1 h (solution 1). Subsequently, 5.72 ml of acetic acid and 36.14 ml of deionized water (solution 2) were added to another beaker and the pH was measured (pH ~ 1.96). Solution 1 was added dropwise to solution 2 and agitated for 3 h. The resulting hydrosol solution (TiO$_2$ hydrosol-S1, solids concentration 33.02 mg L$^{-1}$) was stored at room temperature for 10 days. Further, another TiO$_2$ hydrosol sample (TiO$_2$ hydrosol-S2, solids concentration 17.28 mg L$^{-1}$) was prepared using the same procedure but half the amount of [Ti(OBu)$_4$], i.e. 2.77 ml. Translucent yellowish-white colloidal hydrosols were obtained. After the preparation of the hydrosols, pristine cotton and polypropylene non-woven fabrics (2 × 2 cm) were then submerged for 5 min into the TiO$_2$ hydrosols, and subsequently, the impregnated fabrics were cured in an oven at a temperature of 100 °C for approximately 12 h. The amount of TiO$_2$ per square centimeter loaded on each fabric sample was calculated by mass balance. Untreated fabric samples (without TiO$_2$ deposition) were also subjected to the same protocol and further used in the photocatalytic tests, as controls. The fabric samples were designated as shown in Table 1.

The physical and chemical properties of the TiO$_2$ coated onto the fabric were obtained after drying TiO$_2$ hydrosols in an oven at a temperature of 105 °C for 24 h to obtain white colored TiO$_2$ powders denoted TiO$_2$-S1 and TiO$_2$-S2.

2.3. Testing and characterization of TiO$_2$ particles and TiO$_2$ coated fabrics

The crystalline structure of the sample was evaluated by X-Ray diffraction (XRD) analysis using a MiniFlex600 DRX apparatus (Rigaku, Japan), at a scanning speed of 10 ° min$^{-1}$ with step size of 0.05°. The crystallite sizes, based on the average of all the peaks of the XRD standards, were calculated using the Scherrer equation:

$$D = \frac{K \lambda}{βocosθ}$$

where $D$ is the size of the crystallites, $K$ is the Scherrer constant (0.9), $λ$ is

Table 1

| Fabric | Impregnation | TiO$_2$ loading, mg cm$^{-2}$ |
|--------|--------------|------------------------------|
| Untreated cotton (white) | none | 0.0 |
| Non-woven fabric (NWF) | none | 0.0 |
| TiO$_2$-S1-cotton | TiO$_2$ hydrosol-S1 | 1.40 |
| TiO$_2$-S1-NWF | TiO$_2$ hydrosol-S1 | 1.07 |
| TiO$_2$-S2-cotton | TiO$_2$ hydrosol-S2 | 1.03 |
| TiO$_2$-S2-NWF | TiO$_2$ hydrosol-S2 | 1.04 |
the wavelength of the radiation used (0.15406 nm), \( \theta \) is the full width at half maximum (FWHM) of selected peak and \( \beta \) is the Bragg’s angle of diffraction for the peak.

The optical properties of the samples were evaluated using the data from the diffuse reflectance spectroscopy (DRS) obtained in a UV/Vis/NIR Lambda 750 spectrometer (PerkinElmer, USA), equipped with a 60 mm integrating sphere. The reflection (R) data were converted to adsorption through the Kubelka–Munk function, \( F(R) = \frac{(1 - R)^2}{2R} \) (2).

Infrared spectra were obtained using a Fourier transform infrared (FTIR) spectrophotometer (model Cary 660 Series, Agilent, USA). The samples were analyzed directly with the crystal (ZnSe, 45°) by attenuated total reflection (ATR), averaging 10 scans in the range of 4000–550 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). The Brunauer–Emmett–Teller (BET) surface area, Barrett–Joyner–Halenda (BJH) pore volume and pore size distributions of the samples were determined via \( N_2 \) adsorption–desorption isotherm measurement at 77 K after degassing at 300 °C for 2 h. The isotherms were obtained in a Autosorb-1 gas sorption analyzer (Quantachrome Instrument, USA). The particle size distribution was obtained by the dynamic light scattering (DLS) technique using a Zetasizer Nanozizer particle size analyser (Malvern Instruments, UK). Before analysis, TiO\(_2\) samples (TiO\(_2\)-S1 and TiO\(_2\)-S2) were dispersed in distilled water (0.1 mg mL\(^{-1}\)) using an ultrasonic bath for 1 h. The morphology and microstructures of TiO\(_2\) powdered were characterized by Scanning Electron Microscopy-FEG using a FEG-SCIOS (FEI, USA) and by Transmission Electronic Microscopy using a JEM-1011 (JEOL, Japan) equipment.

The surfaces of treated and untreated fabrics were analyzed by scanning electron microscopy (SEM) using a JEOL JSM-6390VL microscope (JEOL, Japan). The contact angle between liquid and solid surfaces of the treated fabrics was conducted with a Goniometer model 250 (Ramé-Hart Instrument, USA). Measurements were performed in triplicate and the angles were determined by the mean of the values obtained. In these analyses, drops of 3 µL of deionized water at room temperature were deposited over each fabric sample.

2.4. Virucidal activity

Coated and uncoated fabrics were previously evaluated for their cytotoxic characteristics. For this, mouse fibroblast cells (L929, ATCC® CCL-1) were maintained in a minimal essential medium (MEM; Thermo Fisher Scientific, Poland) supplemented with 10% heat-inactivated fetal bovine serum (FBS; Thermo Fisher Scientific, Poland), then sown on plates (96-well format plates, 2.5 × 10\(^5\) cells/well) maintained for 24 h at 37 °C in an atmosphere containing 5% CO\(_2\). Tissues were washed with 5 mL of 1% phosphate-buffered saline and the eluate was added to the cell culture for 48 h.

The virucidal activity of the materials and fabrics were assessed according to the ISO 18,184:2019 and standard method for determination of antiviral activity of textile products (International Organization for Standardization, 2019). Information about the light indoor irradiation is supplied in the Supplementary Information (Figure S1). This method measures the concentration of 10\(^6\) plaque-forming units (PFU) of human adenovirus type 5 (HAdV-5) and murine coronavirus MHV-3 strain (MHV-3), previously propagated in cell lines A549 (human lung carcinoma - CL185) and L929 (murine fibroblasts - CCL-1), respectively.

Tests were performed with 30 min viral exposure against the tested surfaces at 25 °C under indoor light irradiation. Similar control experiments were performed in the absence of light irradiation by exposing the samples to the viruses inside a dark chamber. Both impregnated and pristine fabrics were used. After 5–7 days of in vitro infection with the respective viruses tested, the amount of PFU was quantified and the viral reduction was expressed in percent reduction (%) (International Organization for Standardization, 2019). Triplicate experiments were performed for all trials.

To assess the absence of viral replication, in addition to the cell culture test, assays based on detection of the viral genome after 5–7 days of infection in cell culture were performed. This test was carried out to verify whether or not there was entry and exposure of the viral genome in permissive cells, as well as whether these genomes were replicated. In summary, after 5–7 days of incubation the cells with HAdV-5 and MHV-3 fluids after exposure to tissues with and without TiO\(_2\), were washed 3 times with PBS 1X and subjected to extraction of genetic material (DNA / RNA). The extraction of viral nucleic acid was performed with the commercial mini kit RTP DNA / RNA Virus® II (Invitrogen) and a RT enzyme and primers (Sensiscript RT Kit - QIAGEN®). Real-time quantitative PCR (qPCR) was performed as described by Hernroth, Conden-Hanson, Rehnstan-Holm, Girones and Allard (2002) and Besselsen, Wagner and Loganbill (2003), for HAdV-2 and MHV-3, respectively. The limit of quantification is ten copy gene (CG) per cm\(^2\).

All amplifications were performed in a StepOne Plus® Real-Time PCR system (AppliedBiosystems). Each sample was analyzed in triplicate. Ultrapure water was used as a non-template control for each assay.

3. Results and discussion

3.1. Characterization of pristine TiO\(_2\) particles and of the impregnated and pristine fabrics

The crystalline structure of the TiO\(_2\) powders obtained from hydrosols (TiO\(_2\)-S1 and TiO\(_2\)-S2) was evaluated by X-ray diffraction (Fig. 1). The crystal phase of all samples coincides with the standard data for anatase -TiO\(_2\) (JCPDS 01-178-6999) without impurities (Klee et al., 2013). The values of crystalline sizes of TiO\(_2\)-S1 and TiO\(_2\)-S2 were similar and below the 10-nanometer range (Table 2).

The particle size distribution of TiO\(_2\)-S1 was non uniform and ranged from 50 to 1700 nm with a maximum peak at 142 nm, a second peak with a maximum at 532 nm (Fig. 2(a)) and average particle size of 284 nm (Table 2). In contrast, TiO\(_2\)-S2 had a uniform particle size distribution (Fig. 2(b)) but in the range of 300 – 1000 nm and a maximum peak at 255 nm, with the average particle size of 263 nm (Table 2). The samples have size distributions in the characteristic range of microspheric particles, that is, 100 nm – 100 µm, indicating that TiO\(_2\) nanoparticles formed aggregates in the aqueous dispersion.

The scanning electron microscopy (SEM-FEG) of powdered TiO\(_2\)-S1 and TiO\(_2\)-S2 analysis showed the preparation of spherical-shape TiO\(_2\) nanoparticles (Figure S2). The transmission scanning microscopy (TEM) images exhibited aggregated nanoparticles while the selected area diffraction (SAED) patterns endorsed the polycrystalline nature (Figure S2). Particle dimensions obtained from TEM images were 9.7 ± 6.0 nm.
5.0 nm and 6.5 ± 2.1 nm for TiO$_2$-S1 and TiO$_2$-S2, respectively. As largely known, the particle size increases with increasing precursor concentration due to enhanced coagulation and sintering, resulting from the large concentration of TiO$_2$ nuclei generated at high Ti precursor concentrations (Nyangumakamba, Okoh, Mungondori, Taziwa & Zinya, 2018). Moreover, a more uniform particle size distribution was observed for powdered TiO$_2$-S2 than TiO$_2$-S1. The particles size calculated from TEM micrographs were slightly different from the average crystallite size obtained from XRD pattern (Table 2), although these were within the experimental deviation.

The optical properties of the uncoated and coated fabrics (cotton and NWF) and TiO$_2$ powders were evaluated by diffuse reflectance spectroscopy (Fig. 3 and Figure S3). The uncoated fabrics (cotton and NWF) did not show a significant photoresponse, Fig. 3. Conversely, in coated fabrics, reported remarkable absorption in the UV range ($\lambda < 400$ nm). The TiO$_2$-S1-cotton and TiO$_2$-S2-cotton curves were integrated in the range below 400 nm, and the areas were 693 and 757, respectively. For the TiO$_2$-S1-NWF and TiO$_2$-S2-NWF curves, the areas were 284 and 329, respectively. According to the areas and intensities in the TiO$_2$ absorption range, the photoresponse of tissues impregnated with TiO$_2$ hydrosol-S2 was greater than that presented by tissues impregnated with TiO$_2$ hydrosol-S1, and gravimetric measurements showed that the amounts of TiO$_2$ in the coated fabrics were very similar, Table 1. Therefore, the differences in the optical absorption was attributed to larger particle sizes of TiO$_2$-S2 (Fig. 2), which results in lower scattering coefficients and higher K-M function values when they have the same absorption coefficient (Jiménez Reinosa, Leret, Alvarez-Docio, del Campo & Fernández, 2016; Tan et al., 2013).

The DRS curves (Fig. 3 and Figure S3) also showed cutting wavelengths for samples TiO$_2$-S1, TiO$_2$-S2, TiO$_2$-S1-cotton, TiO$_2$-S2-cotton, TiO$_2$-S1-NWF and TiO$_2$-S2-NWF equal to 380, 377, 368, 357, 401 and 402 nm, respectively. This different values indicated that the absorption of TiO$_2$ varied when this was impregnated in the fabrics due to the interaction between the particles and the substrate (Kisch & Weiβ, 2002; Tan et al., 2013; Zhang et al., 2020). Moreover, all DRS curves of the impregnated fabrics showed a slight tail wavelength larger than 400 nm, which was attributed to the presence of defects or surface impurities.

### Table 2

Specific surface area (S$_{\text{BET}}$), average pore diameter, pore volume and average particle size for TiO$_2$ samples.

| Sample         | Crystallite size (nm) | Band gap energy (eV) | $S_{\text{BET}}$ ($m^2 g^{-1}$) | Average pore size (Å) | Pore volume (cm$^3 g^{-1}$) | Average aggregated particle size (nm)** |
|----------------|-----------------------|----------------------|----------------------------------|------------------------|-----------------------------|---------------------------------------|
| TiO$_2$-S1     | 7.0 ± 1.3             | 3.16                 | 293.1                            | 43.87                  | 0.3292                      | 284                                   |
| TiO$_2$-S2     | 9.0 ± 1.0             | 3.17                 | 342.4                            | 37.29                  | 0.3221                      | 263                                   |
| Uncoated cotton| *                     | *                    | < < 1                            | *                      | 0.010                       | *                                     |
| Uncoated NWF   | *                     | *                    | 0.9                              | 938                    | 0.021                       | *                                     |
| TiO$_2$-S1 cotton | *                  | *                    | 10                               | 69                     | 0.020                       | *                                     |
| TiO$_2$-S1 NWF | *                     | *                    | 51                               | 44                     | 0.057                       | *                                     |
| TiO$_2$-S2-cotton | *                  | *                    | 9                                | 29                     | 0.006                       | *                                     |
| TiO$_2$-S2-NWF | *                     | *                    | 110                              | 40                     | 0.111                       | *                                     |

* Not measured.
** Obtained by the dynamic light scattering (DLS) technique in aqueous dispersion.

Fig. 2. Particle size distribution of (a) TiO$_2$-S1 and (b) TiO$_2$-S2 dispersed in distilled water. [TiO$_2$] = 0.1 mg mL$^{-1}$.

Fig. 3. Diffuse reflectance spectra UV–visible curves (a) for untreated cotton, TiO$_2$-S1-cotton and TiO$_2$-S2-cotton and (b) for non-woven fabric, TiO$_2$-S1-NWF and TiO$_2$-S2-NWF.
over the less crystallized TiO$_2$ nanoparticles (Jiang, Long, Wu & Cai, 2011).

Additionally, the band gap energies of TiO$_2$-S1 (3.16 eV) and TiO$_2$-S2 (3.17 eV), Figure S3, were close to the value assigned for the indirect band gap of the anatase phase (3.20 eV) (Lin et al., 2006; Lopez & Gomez, 2012). It is worth mentioning that the indoor light used to evaluate de virucidal effect of coated fabrics presented a very small amount of irradiation at wavelength $\lambda < 400$ nm (Figure S1), and could lead to poor photoactivation of the TiO$_2$ particles (Rodriguez-Gonzalez et al., 2020).

The FTIR spectra obtained for both synthesized TiO$_2$ samples (TiO$_2$-S1 and TiO$_2$-S2), Figure S4, were very similar and presented the same absorption bands at 3384, 2920, 1625, 1527, 1427, 790, 663 and 484 cm$^{-1}$. The broad band centered at 3384 cm$^{-1}$ and another band at 1630 cm$^{-1}$ was assigned to the vibrations of the O–H stretch and OH bend, respectively, demonstrating the presence of water physically attached to the surface of the samples (Z. Wang et al., 2020). Additionally, characteristic peaks of the O–H wagging; 1160 and 1101 cm$^{-1}$ (asymmetric bridge C–O–C); 1026 cm$^{-1}$ (C–O stretch) and 896 cm$^{-1}$ (asymmetric stretching of C1–O–C4 of cellulose) (Ahmad et al., 2019; Nam et al., 2016; Tudu, Sinhamahapatra & Kumar, 2020); 3600–3000 cm$^{-1}$ (O–H stretching vibration of H-bonded hydroxyl groups); 1641 cm$^{-1}$ (O–H stretching vibration of adsorbed water); 2901 cm$^{-1}$ (C–H asymmetric stretching of alky chain); 1426 cm$^{-1}$ (C–H bending); 1311 cm$^{-1}$ (C–H wagging); 1160 and 1101 cm$^{-1}$ (asymmetric stretching of C1–O–C4 of cellulose) (Ahmad et al., 2019). The spectra of TiO$_2$-coated cotton presented the same bands of uncoated cotton and more two new peaks at 1535 cm$^{-1}$ and 791 cm$^{-1}$. These peaks related to the O–COO– symmetric stretching and O–Ti–O bonds (see the TiO$_2$ FTIR spectra in Figure S4) indicated the attachment of TiO$_2$ on the cotton fabric surface.

As expected, the uncoated NWF fabric, Fig. 4b, showed the characteristic peaks of polypropylene (Cabello-Alvarado et al., 2019; Cerkez, Worley, Broughton & Huang, 2015; Nam et al., 2016). In the range from 3000 to 2800 cm$^{-1}$, the bands corresponded to the asymmetric and symmetric C–H stretching vibration of methylene (CH$_2$) and methyl (CH$_3$) groups (Cabello-Alvarado et al., 2019). The peaks corresponding to bending of CH$_2$ and CH$_3$ bonds were localized at 1453 cm$^{-1}$ and 1376 cm$^{-1}$, respectively (Cabello-Alvarado et al., 2019). Both coated NWF fabrics (Fig. 4(b)) presented a new band at 1530 cm$^{-1}$ related to –COO– symmetric stretching, an important functional group that can indicate the presence of TiO$_2$ on the fabric surface.

The surface area analysis of TiO$_2$-S1 and TiO$_2$-S2 particles (Figure S5) generated type IV adsorption/desorption isotherms with an hysteresis loop, typical of mesoporous adsorbents according to the IUPAC classification (Burwell, 1977). The average pore size calculated due to the presence of the high surface area TiO$_2$ nanoparticles (Table 2), on the cotton fabric surface.

Chemical surface modification of the cotton and NWF fabrics by coating with TiO$_2$ hydroxyl S1 and S2 was studied by FTIR-ATR analysis, Fig. 4. Pristine cotton, Fig. 4(a), presented a spectra characteristic of cellulose (Ahmad et al., 2019; Nam et al., 2016; Tudu, Sinhamahapatra & Kumar, 2020): 3600–3000 cm$^{-1}$ (O–H stretching vibration of H-bonded hydroxyl groups); 1641 cm$^{-1}$ (O–H stretching vibration of adsorbed water); 2901 cm$^{-1}$ (C–H asymmetric stretching of alky chain); 1426 cm$^{-1}$ (C–H bending); 1311 cm$^{-1}$ (C–H wagging); 1160 and 1101 cm$^{-1}$ (asymmetric bridge C–O–C); 1026 cm$^{-1}$ (C–O stretch) and 896 cm$^{-1}$ (asymmetric stretching of C1–O–C4 of cellulose) (Ahmad et al., 2019). The bands observed at 1427 and 1527 cm$^{-1}$ were related to –COO– antisymmetric and symmetric stretching, respectively (Z. Wang et al., 2020). These bands were assigned to the carbonyl groups present on the surface of the TiO$_2$ samples provenient from the acetic acid used in the synthesis of hydrosol (Liao, Lien & Lin, 2001). The small peaks centered on 2930 and 2850 cm$^{-1}$ were attributed to the asymmetric stretching vibrations of aliphatic C–H, the existence of organic species adsorbed on the surface of TiO$_2$ particles, such as residues of acetic acid originating from the synthesis method. These results indicated that the surface of TiO$_2$ obtained from hydrosol presented functional important groups such as –OH and –COOH, which facilitated the retention of the particles within the fibers of the fabrics. Although the TiO$_2$ particles showed traces of adsorbed residual organic species, the virucidal effect caused by these was below the detection limit both under indoor illumination and dark conditions as shown in Section 3.2.

![Fig. 4. FTIR-ATR absorbance spectra of coated and uncoated cotton (a) and non-woven (b) fabrics.](image-url)
Virus reduction in textile surfaces treated with TiO$_2$-S1-NWF and TiO$_2$-S2-NWF.

**Fig. 5.** Image of water droplets from tissue samples (a) TiO$_2$-S1-cotton, (b) TiO$_2$-S2-cotton, (c) TiO$_2$-S1-NWF and (d) TiO$_2$-S2-NWF.

Table 3

| Samples          | HAdV-5 PFU/cm$^2$ | MHV-3 PFU/cm$^2$ | Indoor light HAdV-5 reduction (%) | MHV-3 Reduction (%) | Dark conditions HAdV-5 reduction (%) | MHV-3 reduction (%) |
|------------------|-------------------|-----------------|----------------------------------|---------------------|-------------------------------------|---------------------|
| TiO$_2$-S1-Cotton| $1.5 \times 10^9 \pm 1.1 \times 10^4$ | $1.5 \times 10^7 \pm 1.1 \times 10^4$ | NR                               | $97.69 \pm 0.16$    | *                                   | *                   |
| TiO$_2$-S2-Cotton| $1.4 \times 10^{5} \pm 2.3 \times 10^{4}$ | $2.8 \times 10^{5} \pm 2.3 \times 10^{4}$ | NR                               | $95.69 \pm 0.34$    | *                                   | *                   |
| TiO$_2$-S1-NWF   | $1.1 \times 10^4 \pm 1.2 \times 10^3$ | $1.1 \times 10^5 \pm 1.2 \times 10^3$ | 90.83 ± 1.00                     | 99.98 ± 0.19        | NR                                  | NR                  |
| TiO$_2$-S2-NWF   | $1.1 \times 10^4 \pm 1.2 \times 10^3$ | $3.2 \times 10^5 \pm 1.2 \times 10^3$ | 90.83 ± 1.00                     | 99.94 ± 0.19        | 90.00 ± 1.00                       | 90.00 ± 1.00        |
| Untreated/Control Cotton | $1.5 \times 10^9 \pm 2.0 \times 10^4$ | $6.5 \times 10^9 \pm 2.0 \times 10^4$ | NR                               | *                   | *                                   | *                   |
| Untreated/Control NWF | $1.2 \times 10^9 \pm 1.3 \times 10^5$ | $6.2 \times 10^9 \pm 1.3 \times 10^5$ | NR                               | *                   | *                                   | *                   |

NR: No reduction.

* Not measured.
Although the amount of TiO$_2$-S1 and TiO$_2$-S2 particles deposited on the fabrics were similar (Table 1), the virucidal activities on NWF fabric were higher than those measured on cotton, due to more uniform distribution of TiO$_2$ particles on the NWF fabric solid surface, as shown in Figs. 7 and 8. These results implied that viral particles of HAdV-5 and MHV-3 could be efficiently inactivated using TiO$_2$ under indoor light.

Although several polysaccharides such as chitosan (Modak, Jha & Kumar, 2021), an acid polysaccharide from Laminaria japonica (Yue et al., 2017), and polysaccharides from algae (Harden, Falshaw, Carnachan, Kern & Prichard, 2009) have shown virucidal activity, cellulose-based fabric alone did not present virucidal activity (Table 3). However, cellulose can strongly attach TiO$_2$ particles through the formation of intermolecular hydrogen bonding between the hydroxyl group of cellulose and the hydroxyl group in the TiO$_2$ surface (Chai,
Pang, Lim & Chong, 2021; Zong et al., 2021) even those produced using a hydrolysis-precipitation method (Zong et al., 2021), and the materials exhibited antibacterial properties.

As largely known, TiO$_2$ particles inactivate influenza virus (Nakano et al., 2012), human coronavirus (Tong et al., 2021), bovine coronavirus (Yoshizawa et al., 2020), human norovirus, murine norovirus (Park et al., 2016), SARS coronavirus (Han et al., 2004), and bacteriophage (Syngouna et al., 2017), among others. These effects may involve reactive oxygen species that can damage viral surface proteins, what in turn may impair of even abolish the adsorption of the viruses to host cells as well as to damage the viral genome, preventing the replication process. So, the attachment of TiO$_2$ particles on cellulose fibers could be useful to produce virucidal fabrics. Hospital supplies made with non-woven fabric are usually disposable. However, hospital cotton items are usually washed and reused. In the latter case, the cotton fabric covered with TiO$_2$ generally presents a low level of wash resistance due to the poor adhesion between the TiO$_2$ particles and the fibers (Dastjerdi, Montazer & Shahsavan, 2009; Wang et al., 2018).

The virucidal activity was also performed after one cycle washing of TiO$_2$-coated fabrics. The TiO$_2$-treated cotton and TiO$_2$-treated NWF were submerged in pure water under magnetic stirring for 1 h. After this, the samples were dried and submitted to virucidal tests, resulting in similar virus inactivation.

The results in this study collectively reveal the photocatalytic inactivation mechanism of HAdV-5 and MHV-3 by TiO$_2$ under standard indoor light irradiation. The high surface area of TiO$_2$ and the hydrophobicity of coated fabrics could contribute to the antiviral properties. Proteins oxidation by ROS formed under indoor light irradiation also contributes to virus inactivation, although the interaction of MHV-3 and HAdV-5 on TiO$_2$-S2 coated fabrics would be enough for some virus inactivation. The hydrophobic characteristic of the treated fabrics and the high surface area of TiO$_2$ particles favor interaction with the virus, mainly MHV-3.

Although the sol-gel based TiO$_2$ particles of large area have been applied for various biological applications (Amanulla et al., 2019; Chegeni, Pour & Dizaji, 2019; Dinesh, Suresh Yadav, Kannadasan & Rasool, 2017), a deeper study about cytotoxic effect should be performed to guarantee their potential impact on environmental health and safety (Rashid et al., 2021).

4. Conclusions

High surface area and mesoporous TiO$_2$ particles were successfully prepared using the sol-gel method. The study found that non-woven fabric, coated with high surface area TiO$_2$ particles, exhibited remarkable virucidal effects on both the human adenovirus type 5 (HAdV-5) and the murine coronavirus MHV-3 strain under indoor light and room temperature. Inactivation of the MHV-3 virus (a lipid bilayer enveloped virus) occurred more efficiently than that of the HAdV-5 virus. The virucidal effect increased as the surface area of the particles was increased and the average particle size was decreased. These observations indicate that hydrophobic interactions with the TiO$_2$ particles and/or adsorption on the TiO$_2$ immobilized particles are important for developing effective virucidal fabrics. The TiO$_2$ hydrosol can, thus, be regarded as an effective photocatalytic agent for producing virucidal fabrics, with higher efficiency when applied on non-woven fabric than on cotton. Photocatalytic TiO$_2$-based nanomaterials are nowadays restricted to research laboratories, but the results obtained in this work
are likely to represent a significant contribution to their industrial and operational application.

Associated content

Supporting information

Spectrum of LED lamp used in this work (Figure S1); SEM-FEG and TEM images (Figure S2); diffuse reflectance spectroscopy analysis of powdered TiO2 (Figure S3); FTIR absorbance spectra of powdered TiO2 (Figure S4); adsorption-desorption isotherms of powdered TiO2 (Figure S5) and tissue samples (Figure S6); images of water droplets from tissue samples under dark conditions (Figure S7).

Author contributions

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Rafael D. Cadamuro: Formal analysis; Investigation; Visualization
Gianluca Li Puma: Formal analysis; Investigation; Writing - Review & Editing.
Rosane M. Peralta: Formal analysis; Writing – Review & Editing.
Gianluca Li Puma: Formal analysis; Writing – Review and Editing.
Regina de FP M Moreira: Conceptualization; Methodology; Formal analysis; Resources; Writing - Review & Editing; Supervision; Project administration

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This research was supported by the Coordination for the Improvement of Higher Education Personnel (CAPES-PRINT) Project number 88887.310560/2018-00 and CAPES Finance code 001), National Council for Technological and Scientific Development (CNPq/Brazil), and by other partners at UFSC (LINDEN, LCME and the Central of Administration at EQA/UFSC).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.carpta.2021.100182.

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