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# Cuprous oxide nanoparticles incorporated into a polymeric matrix embedded in fabrics to prevent spread of SARS-CoV-2

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Abstract: This paper describes the development of a coating for cotton and polypropylene (PP) fabrics based on a polymeric matrix embedded with cuprous oxide nanoparticles (Cu<sub>2</sub>O@SDS NPs) in order to inactivate SARS-CoV-2 and manufactured by a simple process using a dipassisted layer-by-layer technology, at low curing temperature and without the need for expensive equipment, capable of achieving disinfection rates of up to 99%. The polymeric bilayer coating makes the surface of the fabrics hydrophilic, enabling the transportation of the virus-infected droplets to achieve the rapid inactivation of SARS-CoV-2 by contact with the Cu<sub>2</sub>O@SDS NPs incorporated in the coated fabrics.

**KEYWORDS**: Cuprous oxide hybrid nanoparticles, bilayer coating, fabrics/textile, virucidal activity.

# 1. Introduction

The current pandemic of coronavirus disease 2019 (COVID-19) caused by the etiologic agent Severe Acute Respiratory Syndrome Coronavirus 2, SARS-CoV-2, bring about a great global concern for the rapid spread of new variants that causes the virus SARS-CoV-2, which was adapting and spreading very quickly, leading to more deaths in an unvaccinated population (Meyerowitz et al., 2021). On the other hand, an epidemic turn into a pandemic if infected people and/or objects contaminated with infectious material spread across the globe (Salian et al., 2021), therefore, effective methods for prevention of person-to-person and person-tosurfaces spread out of SARS-CoV-2 are very important to mitigate the virus transmission.

It is now known that respiratory transmission of SARS-CoV-2 is dominant, with proximity and ventilation being determinants of the risk of virus spread (Salian et al., 2021). In this regard, various chemical disinfecting protocols have been approved for this purpose, however, they require repeated applications and are only virucidal during application (Peddinti et al., 2021). Moreover, many of them can negatively impact the environment or human health upon exposure (Dewey et al., 2021).

Sodium dodecyl sulfate (SDS) has also been found to be a broad-spectrum and effective microbicidal and a viral inactivation agent by denaturing both enveloped and non-enveloped virus proteins (Piret et al., 2002; Kumar et al., 2021), for example, SDS can inactivate at non-toxic concentrations, non-enveloped viruses such as human papillomavirus (HPV) (Howett et al., 1999). In particular, Tateyama-Makino (Tateyama-Makino et al., 2021) suggests that some ingredients contained in commercially available toothpaste and mouthwash, such as SDS, might have inhibitory effects on the interaction between SARS-CoV spike protein RBD and

angiotensin-converting enzyme 2 (ACE2) and transmembrane protease subtype 2 (TMPRSS2) activities.

In this work, a novel disinfectant involving a cuprous oxide nanoparticles (Cu<sub>2</sub>O@SDS NPs)/hydrogel-based material is proposed as a low-cost, non-toxic product suitable for industrial-scale application to mitigate virus spread based on Cu<sub>2</sub>O@SDS NPs loading in a chitosan/ascorbic acid (CS/AA) matrix, which was able to inactivate SARS-CoV-2 particles after initial contact and for extended periods of time. The developed material proved to be virucidal, with a durable, and long-lasting disinfection characteristics to fabrics/textiles used for a variety of purposes and in a variety of environments, such as health care, in the context of public transport, hotels, the food industry and also, in domestic situations.

# 2. Materials and Methods

#### 2.1 Materials

Chitosan (Todo Droga, Argentina), Ascorbic acid (Anedra), Copper salt (Todo droga), Sodium dodecyl sulfate (Cicarelli), African green monkey kidney cells (*Cercophitecus aethiops*, Vero cl 76 ATCC), Eagle's minimal essential medium (E-MEM, Gibco, USA), Fetal Bovine Serum (FBS, Natocor, Argentina), L-glutamine (Sigma-Aldrich, USA), Gentamicin (Sigma-Aldrich), formalin (Anedra, Argentina), crystal violet (Anedra, Argentina). SARS-CoV-2 (hCoV-19/Argentina/PAIS-G0001/2020, GISAID ID: EPI\_ISL 499083). A Millipore Milli-Q Water Purification System generated the water used in these studies. Commercially available cotton (100% cotton, 144 threads, referred to cotton fabric) and polypropylene (100% polypropylene, PP, Friseline® 40 GSM) fabrics were obtained from a local dealer (Córdoba, Argentina). Chitosan (CS) was of food grade and its deacetylation degree (DD) determined by <sup>1</sup>H-NMR and ATR-FTIR techniques was found to be 75%, respectively (Domszya et al., 1985; Lavertu et al., 2003).

#### 2.2 Methods

#### 2.2.1 Preparation of Cu<sub>2</sub>O(a)SDS NPs and BL Self-Assembly Process

The procedure for obtaining the cuprous oxide nanoparticles ( $Cu_2O@SDS$  NPs) and the coating process in order to manufacture the cotton and polypropylene (PP) fabrics with Cu<sub>2</sub>O@SDS NPs embedded into a matrix of chitosan and ascorbic acid (CS/ASS) was carried out by following the manufacturing procedures described in the Argentine patent application: "Nanocomposite coatings with antiviral activity against SARS-CoV-2" (National Institute of Industrial Property (INPI), Argentina. PATENT BULLETIN No. 1238 - August 31, 2022. AR122227 A1. ISSN: 0325-6529. Boletín de Patentes de Invención y Modelos de Utilidad – INPI https://portaltramites.inpi.gob.ar. Briefly, the Cu<sub>2</sub>O@SDS NPs were obtained by dissolving 250 mg of CuSO<sub>4</sub> 5H<sub>2</sub>O in 25 mL of Milli-Q water. Then, an aqueous solution of surfactant sodium dodecyl sulfate (SDS, 280 mg in 13 mL of Milli-Q water), as the stabilizing agent, was added to the previous solution and stirred for 30 min at room temperature. After, 5 mL of 1 M NaOH aqueous solution was added dropwise into the CuSO<sub>4</sub>.5H<sub>2</sub>O and SDS solution. The light blue coloration of the solution turns to intense blue due to a blue precipitate of  $Cu(OH)_2$  was produced. After stirring the last mix for 30 min at room temperature, 3.5 mL of an aqueous solution of 5% (p/v) ASS was added dropwise into the blue Cu(OH)<sub>2</sub> precipitate solution, with constant stirring. The Cu(OH)<sub>2</sub> precipitate gradually turned into an orange-yellow color. After, 53.5mL of Mill-Q water was added into the mixture, which was kept under constant stirring at room temperature for 24 h.

The CS solution (2.5 mg/mL) was prepared by dissolving 250 mg of CS in mL of an aqueous solution of ASS (50 mg/mL). After, 0.4 mg of NaCl was added to the solution. The coating was built on fabrics with a layer-by-layer (LBL) strategy in order to self-assemble a bilayer (BL) coating in which  $Cu_2O@SDS$  NPs and CS/AA alternately were assembled on cotton/PP fabrics via electrostatic attraction. Briefly, the fabric was first immersed in the CS/AA solution for 30 min, rinsed with Milli-Q water and then, immersed in the  $Cu_2O@SDS$  NPs dispersion for 60 min, resulting in one  $Cu_2O@SDS$  NPs and CS/AA bilayer on fabric. After that, the coated fabric was dried in an oven at 60°C.

### 2.2.2 Characterization

SEM images were obtained in LAMARX Laboratory, by using a FE-SEM  $\Sigma$ igma analytical scanning electron microscope on a Carl Zeiss Sigma at an intensity of 5 kV, which was employed to observe the morphologies and distribution of the coated samples. The morphology of Cu<sub>2</sub>O@SDS NPs was observed by transmission electron microscopy (TEM) (Zeiss Leo 906-E electron microscope. Oberkochen, Germany). The crystal phases of Cu<sub>2</sub>O@SDS NPs were detected by X-ray diffraction (XRD, Philips-PW1800) and the surface elemental composition of the Cu<sub>2</sub>O@SDS NPs was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientifics K-alfa).

Contact angles (CA) of the surface of fabrics were measured via the sessile drop method using a video contact angle (VCA) system. A  $2\mu$ L water droplet was placed on the fabric surface and stabilized for 0.6 s before the measurement. Four randomly selected spots were tested on each specimen, and the results from at least three similar specimens were averaged for each fabric sample.

The concentration of copper from  $Cu_2O@SDS$  NPs incorporated into the chitosan matrix was determined by atomic absorption spectrophotometry (AAS, Thermo Fisher iCE 3000), according to the methods described previously by Turalija et al., 2015.

#### 2.2.3 Laundering durability assay

It was following the standard method of AATCC-61 without using steel balls. Briefly, pieces of 2 x 2 cm of each fabric were placed in 50 mL of wash water (50  $\mu$ L of household laundry detergent in 50 mL of milliQ water). Fabrics were placed in the wash water for 30 min and dried in an oven at 60°C for 15 min between washes cycles. The washes cycle was repeated 1, 2, 3 and 5 times for the cotton fabric and 1 and 3 times for the PP fabric. The remaining copper embeds into fabrics was extracted from the fabrics using the methodology described by Turalija et al., 2015.

#### 2.2.4 Mechanical characterization

Stress-strain assays were performed on a universal tensile machine (Instron Emic 23-5s) with testing method ISO 13934-1 and a 50 N load cell. At least four specimens with rectangular shapes of 10 cm in length and a cross section of 20 mm x 0.2 mm were tested at an elongation rate of 10 mm/min. Both tensile strength (TS) and elongation at break (%E) were determined in addition to the materials' toughness defined as the area under the curve.

#### 2.2.5 Water vapor permeability test (breathability)

The water vapor permeability rates (WVTR, breathability) of the coated and uncoated fabrics (controls) were evaluated by following standard ASTM E-96 (cup method) with modification (Quan et al., 2020). Media glass bottles (50 mL, diameter 3.8 cm) were filled with 30 mL of deionized water, sealed with the coated and uncoated fabrics and placed in a hot plate to maintain a constant water temperature of 90 °C under a typical laboratory environment. The

WVTR were determined by measuring the weight of water evaporated over time by the following equation:

$$WVTR = \frac{\sub{m1 - m2 \supset}}{A \, x \, time}$$
 Eq.1

where WVTR is the water vapor transmission rate,  $(m_1 - m_2)$  is the water weight changes, and A is the test area.

#### 2.2.5 *Antiviral experiments*

#### 2.2.5.1 *Cell cultures and viruses*

VERO cells were used as host cells for SARS-CoV-2. They were grown in a humid atmosphere at 37 °C with 5% CO<sub>2</sub>. Eagle's minimal essential medium supplemented with 10% (v/v) Fetal Bovine Serum, L-glutamine (30  $\mu$ g/mL), and gentamicin (50  $\mu$ g/mL), was used as a growth medium (GM), E-MEM plus 2% FCS containing the same formulation as that described above was used as a maintenance medium (MM).

#### 2.2.5.2 Viruses

SARS-CoV-2 live wild-type strain (WT) B.l lineage was used (Blanco et al., 2022). The viral stock was obtained and titrated employing the plaque-forming units (PFU) reduction method (del Barrio and Parra, 2000) establishing a viral titer of 2.5 x 10<sup>6</sup> PFU/ml.

# 2.2.5.3 Plaque reduction assay

This methodology was used to quantify viable viruses in all trials below according to the methods described previously (Cheng et al., 2008). Thus, the ability of the SARS-CoV-2 to produce lysis plaques in VERO cells was seized to quantify viral inhibition by performing the technique of plaque -forming units (PFU). This technique consists of covering the monolayer of cells (infected or not, treated or untreated) with a semisolid medium. The scientific

justification for this assay is to consider that when a virus infects a cell, its offspring can only migrate to the immediate neighboring cells, and not to the remote ones, since the semisolid medium limits their mobility. Thus, each plate is considered initiated by a simple viral particle, so it constitutes a clone (del Barrio and Parra, 2000).

### 2.2.5.4 In vitro virucidal activity of $Cu_2O(a)SDS$ NPs

To evaluate the effect of Cu<sub>2</sub>O@SDS NPs on SARS-CoV-2 viral particles, the viral stock (2.5 x 10<sup>6</sup> PFU/ml) was incubated with Cu<sub>2</sub>O@SDS (2.5 mg/mL) NPs in 1:1 proportion (T: treatment), which was compared to the viral control (VC) that contains viral stock in sterile MilliQ H<sub>2</sub>O (1:1). After 2, 5 y 60 min of incubation room temperature (RT), T and VC were subjected to a series of dilutions at 1:10. Each dilution (100  $\mu$ L) was incubated (n=3) on a confluent monolayer of VERO cells (3.5 x 10<sup>5</sup> cells/wells) at 37 °C during 1 h before the addition of the semi-solid medium (MEM 4% SFB, 0.3 gr/L glutamine y 0,5% agarose) and incubated for 96 h at 37°C, 5% CO<sub>2</sub> in a humid atmosphere. After fixing the cell monolayer with 10% formalin for 2 h, the semi-solid medium was removed, and PFUs were revealed with 1% crystal violet.

Results were expressed as Inhibition percentage (I%) compared to VC (100% of viable virus) (Nikesh et al.; 2005) according to equation 2:

Inhibition percentage (I%) = 
$$\left(1 - \frac{number \ of \ PFU/mL \ treatment}{number \ of \ PFU/mL \ VC)}\right) x \ 100\%$$
 Eq. 2

The Logarithm Reduction Value (LRV) of the infective titer of VC was obtained through equation 3:

Logarithm Reduction Value 
$$(LRV) = lg(VC) - lg(T)$$
 Eq.3

where, LRV is the antiviral activity value, lg(VC) is the common logarithm average of 3 infectivity titer values (PFU) at different exposure times of the viral control and lg(T) is the

common logarithm average of 3 infectivity titer values (PFU) at different exposure times of the virus with the  $Cu_2O@SDS$  NPs.

#### 2.2.5.5 In vitro virucidal activity of treated cotton and polypropylene (PP) fabrics.

The effect of coating different cotton and PP fabrics with Cu<sub>2</sub>O@SDS NPs embedded in a chitosan/ascorbic acid (CS/ASS) on the viral inactivation of SARS-CoV-2, was evaluated by cutting 20 x 20 mm pieces of fabric from each type of fabric, placed in individual glass Petri dishes and decontaminated by irradiating them with UV light for 30 min per side. Then, each sample was inoculated with 200  $\mu$ L of a viral suspension containing 1.2 x 10<sup>6</sup> PFU/mL (T) and incubated for 5, 15, 30, 60 and 90 minutes in independent tests (n=3) at room temperature. Cotton and PP fabrics (negative control, NC), virus + Cu<sub>2</sub>O@SDS NPs (1:1) (positive control, PC) and viral suspension (1.2 x 10<sup>6</sup> PFU/ml) (200  $\mu$ L) (VC) were used as controls. Subsequently, inoculates were taken up with 800  $\mu$ L of culture medium and viral titration was carried out as described above. Absence of microbial growth from the uncoated fabrics subjected to the same decontaminated process as the coated fabrics after incubation in the culture medium confirmed that the UV radiation was effective.

Results were expressed as: Inhibition percentage (I%) compared to VC (100% of viable virus): Eq. 2 and Logarithmic Reduction Value (LRV) of the infective title of VC:

## Logarithm Reduction Value (LRV) = lg(VC) - lg(T) Eq.4

where, LRV is the antiviral activity value; lg(VC) is the common logarithm average of 3 infectivity titer values (PFU) at different exposure times of the viral control, lg(T) is the common logarithm average of 3 infectivity title values at different exposure times of the virus with the fabric Cu<sub>2</sub>O@SDS NPs:CS/ASS coated.

### 2.3 Statistical Analysis

The values reported are the average  $\pm$  standard deviation. Statistical analyses were performed with the one-way analysis of variance (ANOVA) test. Values of p < 0.05 were considered statistically significant.

#### 3. **Results and discussion**

Figure 1 shows a schematic representation of the coating process of the different types of fabrics tested with a single bilayer (BL) involving a pair of positively CS/AA and a negatively Cu<sub>2</sub>O@SDS NPs charged layers assembled by successively depositing each ink on commercial cotton and PP fabrics by dipping-assisted layer-by-layer technique (LbL).

Other authors have also proposed fabric coatings containing Cu<sub>2</sub>O NPs. For example, Errokh et al., 2016 proposed to generate Cu<sub>2</sub>O NPs *in situ* on cotton fibers at room temperature and using water as solvent. However, before generating the Cu<sub>2</sub>O NPs by using hydrazine monohydrate (NH<sub>2</sub>NH<sub>2</sub>-H<sub>2</sub>O) or hydroxylamine (NH<sub>2</sub>OH) as reducing agents for the precursor CuSO<sub>4</sub>, prior oxidation of the cotton fibers was required by using sodium chlorite (NaClO<sub>2</sub>) and a sodium hypochlorite solution at 60 C, followed by a 2-wash cycle. The proposed method is not only laborious but also requires the use of toxic chemical agents. Copper NP-coated fabrics were also proposed by Gonçalves et al., 2022 by spray coating copper dispersions and a commercial plastic adhesive solution into 55/45% cellulose/polyester fabric blend, 70/30% rayon/polyester fabric blend and a glossy vinyl sheet (AIVA). This strategy has the disadvantage that it requires the use of toxic organic solvents to dissolve the adhesive.

Other authors have also suggested a coating consisting of cuprous oxide (Cu<sub>2</sub>O) particles bound with polyurethane on glass or stainless steel. However, the proposed coating applied to

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various solid surfaces requires a cleaning with argon plasma to remove excess polyurethane (Behazadinasab et al., 2020). Likewise, Purniawan et al., 2022, proposed a resin-based paint (CuNP/paint) consisted in a mix of copper nanoparticles (CuNPs) with an acrylux AAC955 acrylic resin water-based paint sprayed on the surface of stainless steel.

This work proposes a strategy for coating cotton and PP fabrics based on a natural polymeric matrix embedded with  $Cu_2O@SDS$  NPs manufactured by a simple process using a dip-assisted layer-by-layer technology, at low curing temperature and without the need for expensive equipment or toxic chemicals.

The Scanning electron microscopy (SEM) images of BL coating fabrics show that  $Cu_2O@SDS$  NPs were highly dispersed within the polymeric layer onto fabrics (Figure 2).

The treated commercial fabrics exhibited a high contact angle (CA),  $70.8 \pm 14.1$  for cotton and  $91.3 \pm 5.2$  for PP fabric, respectively, with reversible surface wettability making the surfaces of both types of fabrics superhydrophilic, contact angle ~ 0° (Figure 3).

Cu2O@SDS NPs embed into fabrics were characterized by different techniques. TEM images showed that Cu<sub>2</sub>O@SDS NPs appeared with rough and no uniform spheroidal shapes and polydisperse sizes, which ranged between ~11 nm to ~500 nm (Figure 4). The surface composition of the Cu<sub>2</sub>O NPs investigated by X-ray photoelectron spectroscopy (XPS) was found to be in good agreement with the reported binding energies for Cu<sub>2</sub>O (Figure 5 A) (Nikesh et al.; 2005). The structure and phase of the obtained Cu<sub>2</sub>O@SDS NPs characterized by XRD displayed three main diffraction peaks, which can be related to the diffractions of the (111), (200) and (220) crystalline planes of Cu<sub>2</sub>O powder (JCPDS, No. 05-0667). Also, no strong peak from impurities was detected; indicating that the major number of particles was pure cuprous oxide (Figure 5 B) (Feng et al., 2012). Also, the copper content embedded within the BL nano-

coating onto the commercial fabrics, determined by atomic absorption spectrophotometry (AAS) as atomic species, were  $370.54 \pm 78.20$ ,  $295.28 \pm 81.49$  and  $341.20 \pm 47.38 \ \mu\text{g/cm}^2$  for cotton, at 30, 60 and 90 min of soaking time respectively, and  $335.31 \pm 75.55$ ,  $280.70 \pm 72.20$  and  $286.73 \pm 88.43 \ \mu\text{g/cm}^2$  for PP fabric at 30, 60 and 90 min of soaking time, respectively (Figure 6).

Results show that in contrast to the higher hydrophilicity characteristics of the cotton fabric relative to the PP fabric, manifested through sessile water drops with a static contact angle below  $10^{\circ}$ , both fabrics were able to immobilize about  $232.48 \pm 44.27 \ \mu g/cm^2$  of copper. The BL coating makes the surface of the fabrics very hydrophilic (Figure 3B), so a decrease in the infectivity of the viruses loaded in aerosolized droplets is to be expected as a result of the contact-killing activity with the Cu<sub>2</sub>O@SDS NPs embedded into the hydrogel layer formed on the surface of the fabrics.

Hosseini et al., 2021 pointed out that the wettability characteristics of the polymeric coating containing  $Cu_2O$  NPs affect the course of SARS-Cov-2 virus inactivation. They proposed a coating consisting of  $Cu_2O$  NPs bonded to polyurethane to coat glass or stainless-steel surfaces. Although the polymer coating loaded with  $Cu_2O$  NPs proposed by them is different and is applied on different surfaces than those proposed in this work, these authors found that their coatings with the lowest contact angles were the most efficacious for virus inactivation.

The remaining amount of  $Cu_2O@SDS$  NPs into the fabrics was determined after 1, 2, 3 and 5 wash cycles for cotton and after 1 and 3 washes for the wash cycle for PP fabrics, respectively. A greater amount of copper was soap up in the cotton fabric, which was able to preserve 70% of the initial amount of copper after 5 wash cycles. The PP fabrics, initially impregnated with a smaller amount of  $Cu_2O@SDS$  NPs compared to cotton fabric, after 1 wash cycle lost more

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than 80% of the copper originally embedded in the fabric. The results are presented in Table 3 and show that the majority of the Cu<sub>2</sub>O NPs were washed off from the PP fabric because of the weak interfacial adhesion strength between the polymeric coating containing the copper nanoparticles and the substrate in comparison with the cotton fabric, which had excellent adhesion and long durable properties.

Cotton fabric's TS was increased from 35155 kPa to 39674 kPa after modification while %E decreased from 27% to 15%. This properties' change also affected the material's toughness which decreased from 357922 J/m<sup>3</sup> to 266834 J/m<sup>3</sup> (Figure 7A). This result could be explained by a reduction between the cellulose fibers interactions due to the covering process and the electronically charged layers. This is supported by the rupture in the highly structured fabric's morphology observed in the SEM images (figure 2) after the treatment (Cerkez et al., 2012; Cheng et al., 2014).

On the contrary, PP fabric's mechanical properties were not significantly affected by the coating. Since PP is not able to strongly interact with the electronically charged layers, the natural unstructured morphology of these fabrics did not change after the treatment, leading to statistically similar TS, %E and toughness values (Figure 7B).

The breathability results of the coated and uncoated (controls) fabrics evaluated using the upright cup method from the water vapor transmission test (ASTM E96) are shown in figure 8.

As shown in figure 8, the treatment of the fabrics with the coating did not affect the fabric's respirability properties.

The efficacy of the SARS-CoV-2 viral inactivation of  $Cu_2O@SDS$  NPs upon different virus exposure times (2, 5 and 60 min) is presented in Table 1. Virus contact times were chosen following the European Standard EN 14476, which considers the following minimum

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requirements for virucidal activity of chemical disinfectant and antiseptic products: for the hygienic treatment of hands by friction and hygienic hand washing, a contact time between 30 and 120 seconds, for instrument disinfection, a contact time of no more than 60 min and for disinfection of surfaces close to patients, a maximum contact time of 5 min. The results show that Cu<sub>2</sub>O@SDS NPs were effective in inhibiting SARS-CoV-2, observing a reduction of approximately 5 log in the viral titer, which occurred after 2 min of exposure. Cu<sub>2</sub>O@SDS NP had excellent SARS-CoV-2 inhibition efficacy ( $\geq$  5 LRV).

According to the guidelines of the European Chemicals Agency (ECHA), which establish that a reduction in virus titer of  $\geq$ 4 log<sub>10</sub> corresponds to an inactivation rate of  $\geq$ 99.99%, we have sufficient evidence to consider the dispersion of Cu<sub>2</sub>O@SDS NPs is an effective disinfectant.

The percentages of inhibition (I%) of SARS-CoV-2 and the LVR of cotton and PP fabrics embedded with Cu<sub>2</sub>O@SDS NPs contained in a chitosan/ascorbic acid (CS/AA) matrix were greater than 99% and  $\geq$  3.0, respectively, upon 30 min SARS-CoV-2 incubation time (Table 2; Figure 9, A-B). Therefore, according to the ISO 18184 standard that defines the performance of an antiviral activity in tissues as: small effect (3.0 > LRV  $\geq$  2.0) and full effect (LRV  $\geq$  3.0) (INTERNATIONAL STANDARD ISO 18184/2019), both types of treated fabrics tested have full effect activity after 30 min of exposure.

#### 4. Conclusions

This work determined that the coating of cotton and PP fabrics with Cu<sub>2</sub>O@SDS NP embedded in a hydrogel layer provides a reduction in the infectivity of the SARS-CoV-2 virus, capable of inactivating or killing viral particles long after treatment.

Results show that the Cu<sub>2</sub>O@SDS NPs embedded into a hydrogel-adhered coating to the fabric surface were very successful in reducing the infectivity of SARS-CoV-2. The superhydrophilic characteristics of the coating give to the fabric surfaces a substantial advantage because it can enable to speed up the contact between the Cu<sub>2</sub>O@SDS NPs and viruses by attracting the aqueous droplets containing viral particles into the interior of the coating.<sup>17</sup> The fabrics treated with Cu<sub>2</sub>O@SDS NPs supported into a CS/ASS layer introduced here are fabricated with an eco-friendly and cost-efficient method, could provide an easy way for inhibiting human coronavirus infectivity and used for a variety of purposes and in a variety of environments.

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### 6. Conflict of interest

The authors declare that they have no conflict of interest.

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#### LEGEND FIGURES

Figure 1. Schematic preparation of Cu<sub>2</sub>O@SDS NPs.

Figure 2. TEM images of Cu<sub>2</sub>O@SDS NPs.

**Figure 3.** A: XP high-resolution spectra of Cu<sub>2</sub>O@SDS NPs displaying the Cu<sub>2p</sub> region. The binding energies for Cu<sub>2</sub>  $p_{1/2}$  and Cu<sub>2</sub>  $p_{3/2}$  observed at 952.3 and 932.3 eV, respectively, are shown in the figure and B: XRD patterns of a) Cu<sub>2</sub>O@SDS NPs (black) standard Cu<sub>2</sub>O (JCPDS n° 05-0667) (red).

Figure 4. Schematic diagram of dipping-assisted layer-by-layer (LbL) assembler deposition.Figure 5. SEM images of BL nano coating-fabrics process onto fabrics.

Figure 6. Contact angle images.

**Figure 7.** Copper content embedded within the BL nano-coating onto the commercial fabrics determined by atomic absorption spectrophotometry (AAS); Results are statistically equal, p>0.05.

**Figure 8.** Water vapor transmission rate (WVTR) of coated and uncoated (controls) cotton and PP fabrics. \* p > 0.05.

Figure 9. Logarithm of the number of PFUs of SARS-CoV-2 after incubation with A) cotton fabrics or B) PP fabrics with or without coating with  $Cu_2O@SDS$  NPs embedded in a (CS/ASS) matrix, at different exposure times.

Exposure (minutes)	time	PFU ( <sup>1</sup> )	Treatment	PFU VC ( <sup>2</sup> )	Inhibition percentage (I %)	LRV ( <sup>3</sup> ) (log)
2			0	$(1.1 \pm 0.8) \times 10^5$	99.9	5.04
5			0	$(2.3 \pm 0.3) \times 10^5$	99.9	5.36
60			0	$(1.3 \pm 0.1) \text{ x} 10^5$	99.9	4.11

Table 1: Disinfectant	effectiveness of the	Cu <sub>2</sub> O@SDS NPs (2.	.5 mg/mL) against	t SARS-CoV-
2.				

Values obtained from three independent experiments performed in triplicate

<sup>1</sup>PFU treatment: Plaque-forming units counts in treatment

<sup>2</sup>PFU viral control: Plaque-forming units count in untreated controls.

<sup>3</sup>LRV: Log Reduction Value. This is the reduction in viral titer with treatment compared to the viral control titer.

Fabrics		Exposure time (minutes)	I% (1)	LRV <sup>(2)</sup> (log10)	Antiviral performance <sup>(3)</sup>
		5	99.40	2.22	Small effect
Cotton fabric Cu <sub>2</sub> O@SDS NPs coated		15	99.64	2.44	Small effect
	Cu <sub>2</sub> O@SDS NPs	30	99.99	4.16	Full effect
	60	99.99	3.97	Full effect	
		90	99.99	3.97	Full effect
		5	99.61	2.41	Small effect
PP fabric Cu <sub>2</sub> O@SDS coated		15	99.67	2.49	Small effect
	Cu <sub>2</sub> O@SDS NPs	30	99.96	3.43	Full effect
		60	99.96	3.34	Full effect
		90	99.94	3.22	Full effect

**Table 2**: Viral inhibition percentage (I%) and logarithmic reduction value (LRV) of cotton and PP fabrics coated with  $Cu_2O@SDS$  NPs (2, 5 mg/mL) in a chitosan/ascorbic acid (CS/AA) matrix after different exposure times with SARS-CoV-2.

(1) I %: Percentage inhibition of treatment compared to viral control (100% viable virus).

(2) LRV: Logarithmic reduction value. It is the reduction of the viral titer of the treatment compared to the viral titer of the viral control.

(3) Antiviral textile products may be evaluated as small effect  $(3.0 > LRV \ge 2.0)$  and full effect  $(LRV \ge 3.0)$  according to ISO 18184.

Fabric	Wash	Copper remaining after washing (%)		
	1	97.38 ± 9.31		
Cotton fabric Cu <sub>2</sub> O@SDS NPs	2	91.81 ± 7.63		
coated	3	86.10 ± 15.88		
	5	$73.59 \pm 8.30$		
DD fabria Cu. O@SDS NDs control	1	$18.45 \pm 13.01$		
FF Tablic Cu <sub>2</sub> O( <i>w</i> SDS NFS coaled	3	$10.14 \pm 7.31$		

**Table 3**: Percentage of copper remaining after washing of cotton and PP fabrics coated with<br/> $Cu_2O@SDS$  NPs (2, 5 mg/mL) in a chitosan/ascorbic acid (CS/AA) matrix.



Figure 1



Figure 2



Figure 3





Figure 5



Figure 6



Figure 7







Figure 9

# Graphical abstract



# Cuprous oxide nanoparticles incorporated into a

# polymeric matrix embedded in fabrics to prevent

# spread of SARS-CoV-2

# Highlights

- Cotton and PP fabrics coated with a chitosan matrix containing Cu<sub>2</sub>O@SDS NPs were developed.
- The coating of the fabrics was carried out by using a dip-assisted layer-by-layer technology.
- Low curing temperature and without expensive equipment or toxic chemicals were requirement.
- The coating of fabrics developed provides a reduction in the infectivity of the SARS-CoV-2

virus.

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#### **Declaration of interests**

□ 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.

⊠ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Gladys Ester Granero has patent #Nanocomposite coatings with antiviral activity against SARS-CoV-2 pending to AR122227 A1.