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Gram Scale Synthesis of Cuprous Oxide Nanoparticles: Dip Coating on Cellulose Filter Paper, Antibacterial Activity and Comparison with Commonly Available Face Masks

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Cuprous oxide nanoparticles (Cu_2ONPs) were synthesized on a gram scale *via* bottom-up approach without making use of any hazardous stabilizing agent. The nanoparticles were coated on qualitative cellulose filter paper *via* dip coating method. UV-Visible spectroscopy, powder X-ray diffraction (PXRD) and electron microscopy were used to characterize synthesized Cu_2O NPs and Cu_2O NPs coated filter paper (Cu_2O NPs-FP). The antibacterial activity of Cu_2O NPs-FP was studied against *E. coli* DH5α and compared with commonly accessible face masks.

Keywords: Cuprous oxide, Nanoparticles, Filter paper, Disinfecting layers.

INTRODUCTION

In last few decades, the synthesis of cuprous oxide nanoparticles (Cu_2O NPs) has elicited wide interest due to its functional diversity such as water splitting [1], catalysis [2], solar energy conversion [3], gas sensing [4], wound healing [5], antimicrobial activity [6], *etc*. Easy availability of the copper precursor, low toxicity and cost are the added advantages. Various synthetic methods were developed which could provide nanoparticles at milligram scale. Limited reports discussed the gram scale synthesis of Cu_2O NPs [7,8], however, bulk scale synthesis of Cu_2O NPs with uniform particle size distribution is a challenging task till date.

Since ancient times the outbreak of respiratory infectious diseases witnessed a grave threat to humanity. For example, the Spanish flu in 1918-1919 caused around 500 million morbidities and over 100 million mortalities [9]. Tuberculosis is another example, where the global report says that the total death due to tuberculosis (TB) is 1.4 million only in 2021, double the number of mortalities caused by HIV/AIDS, 0.65 million [10]. Most notably, the world is still struggling with the menacing COVID-19 pandemic with over 757 million morbidities and over 6.8 million deaths till 22nd Feb 2023 [11]. Aerosol or droplets are potential carriers of respiratory infectious diseases. Individuals get infected by direct inhalation of the aerosol containing pathogenic microbes or while interacting with contaminated surfaces or any close contaminated space [12].

The respiratory mask is always considered one of the vital protective gears to control the spread of respiratory infectious diseases. In 2009 to control the spread of influenza virus A (H1N1), face masks played a significant role [13]. Similarly, during COVID-19 pandemic, the use of face masks was one of the vital frontline tools to control the spread of the disease [14]. Disaster and panic in the public caused by the pandemic compelled the researcher to shift their focus in the direction which can control the spread of the infection in a more efficient way which led to the innovation of disinfecting respiratory masks.

As far as disinfecting materials are concerned, copper has always been a center of attraction for many researchers due to its ease of availability and low toxicity. The disinfecting property of copper is known since ancient times [15]. In India, storing drinking water in a copper vessel is an ancient Ayurvedic practice [16]. Later, Sudha *et al*. [17] reported that storing water in copper containers kills diarrhoeagenic bacteria. Similarly, Pandey *et al*. [18] described the antibacterial activities of copper oxide against waterborne bacteria, while Grass *et al*. [19] reported the disinfecting potential of copper surfaces. The copper alloys on stethoscope surfaces efficiently reduce the active bacterial count [20]. The stability of the corona virus on the copper surface was also discovered to be significantly

low compared to its stability on non-disinfecting surfaces [21]. Borkow *et al*. [22] claimed that face masks loaded with copper nanoparticles (Cu-NP) had biocidal properties against both human and avian influenza A viral pathogens.

Numerous studies reported the diverse methodologies to apply metal-based nanoparticles onto various solid surfaces. Dankovich & Smith [23] coated copper on blotting paper by absorbing $[Cu(OH)_4]^{2-}$ on the paper, followed by reduction with ascorbic acid. Yang *et al.* [24] reported the uniform coating of MnO_2 nanoparticles on the filter paper *via* redox reaction. Spray coating methods of copper nanoparticles on face mask was described by Foffa *et al*. [25]. Similarly, the thermal spray coating of copper on wood pieces was achieved by Nejad *et al.* [26] to increase the lifetime of wood. Many other lignocellulose and cellulose-based industrial products were also developed by coating nanoparticles on it [27].

In this study, cuprous oxide nanoparticles (Cu_2O NPs) were synthesized on a gram scale and coated on cellulose filter paper *via* a simple dip and lift-off method. Further, the antibacterial activity of Cu_2O NPs coated filter paper (Cu_2O NPs-FP) was tested against *E. coli* DH5α. The surface disinfecting properties of Cu_2O NPs-FP was also compared with the disinfecting ability of uncoated filter paper and a few easily available face masks (N95, surgical mask and cotton mask). The Cu_2O NPs-FP was employed as external disinfecting layers over a regular surgical mask.

EXPERIMENTAL

Chemicals and reagents were purchased from Merck India and were used without any further purification. Nutrient broth and agar were purchased from HiMedia, India. Whatman cellulose qualitative filter paper (grade 1) was purchased from GE Healthcare, India. Different masks were purchased from the medical store situated in the local market, India. Before disinfection experiments, the control mask sample and uncoated filter paper were sterilized by UV radiation. Double distilled water was used as solvent for the synthesis of Cu_2O NPs.

Characterization: The UV-vis spectra of Cu_2O NPs was recorded using UV-3200 spectrophotometer. The PXRD of filter paper (FP) and Cu_2O NPs-FP was recorded using Bruker D8 Advance instruments with Cu*K*α (λ = 1.5406 Å) radiation in the reflection mode. TEM sample of Cu_2O NPs was prepared by dip and lift-off methods. In a typical procedure, TEM grids were dipped into it with help of forceps in an aqueous suspension of Cu_2O NPs, lifted off and air-dried. The TEM image was recorded using Phillips 120 keV instrument. FE-SEM images of FP and Cu_2O NPs-FP were recorded with a FEG-Quanta 400 equipped with energy dispersive X-ray spectroscopy (EDX).

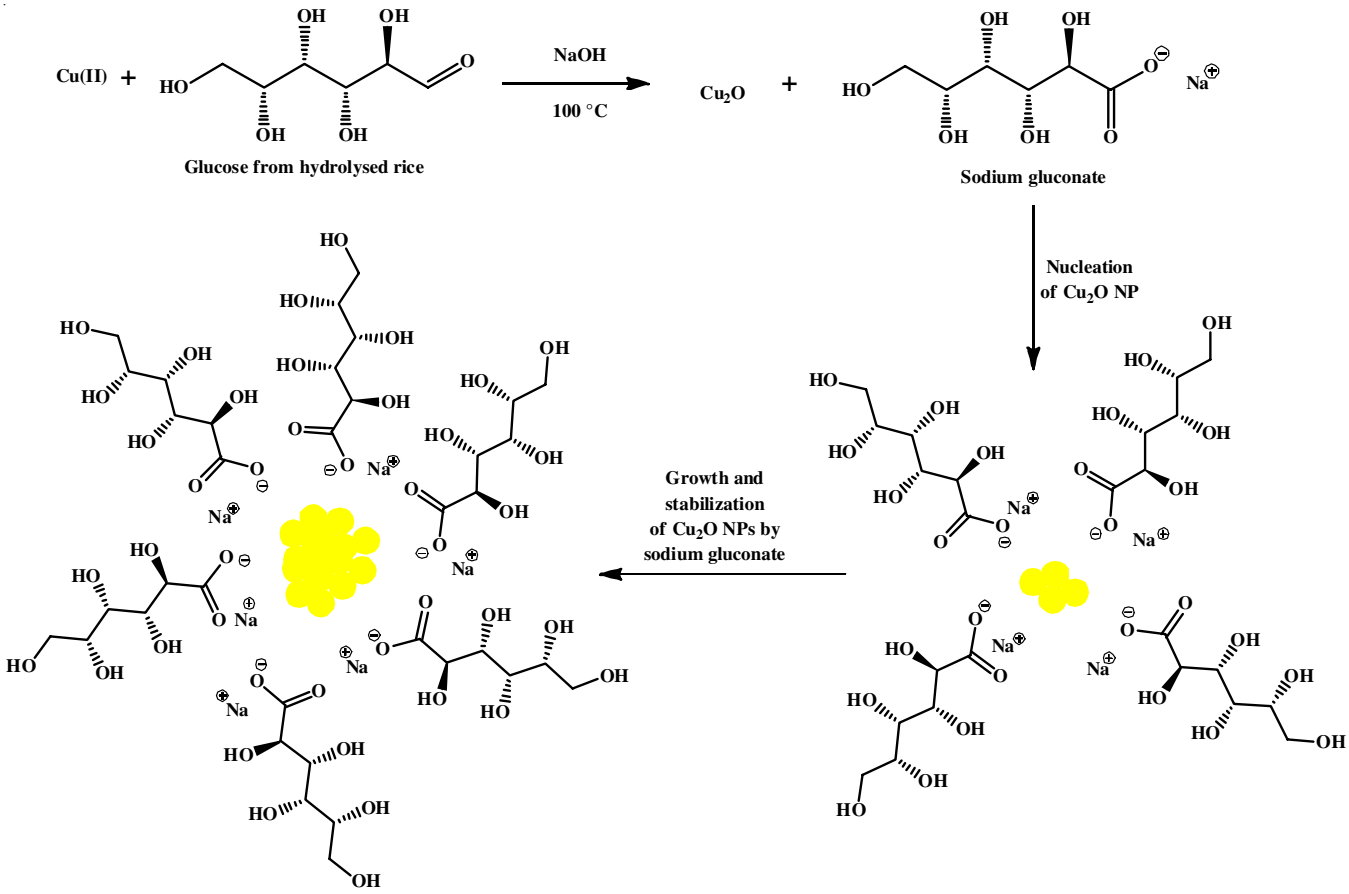
Preparation and coating of Cu_2O NPs on the surface of filter paper (FP): The Cu_2O NPs was prepared by small modification as mentioned in the reported procedure [28]. In a 250 mL round bottom flask containing 20 mL of water, 10 g of rice was added followed by a dropwise addition of 1 mL conc. H_2SO_4. The reaction mixture was heated at 100 ºC for 2 h with continuous stirring and then 10 mL of freshly prepared 5 N NaOH (aq.) was added dropwise to neutralize the acid. Now, 12.5 g of $CuSO_4{\cdot}5H_2O$ dissolved in 100 mL water was added to the above reaction mixture followed by the addition of 25 mL of 5 N NaOH. The stirring process continued for another hour at the same temperature, resulting in the formation of a yellow-colored product (Cu_2O NPs). The reaction mixture was then cooled to room temperature and the product was collected by centrifugation for 10 min at 5000 rpm at 25 ºC. The collected solid was redispersed in 100 mL of deionized water by sonication. The procedure was repeated two more times to wash the nanoparticles and to remove the undesired ions adsorbed on the surface of the nanoparticles. After a third cycle, Cu_2O NPs were dispersed in 1000 mL water and kept in a plastic tray. A piece of filter paper (23 cm × 14 cm) was dipped into the Cu_2O NPs suspension with the help of forceps for around 5 s and lifted. Finally, the Cu_2O NPs coated filter paper was air-dried and used for further study.

Preparation of liquid nutrient and agar nutrient medium: To prepare the liquid nutrient medium, nutrient broth (1.3) g was dissolved in 100 mL water. Around 20 test tubes were taken and 5 mL of dissolved liquid media was transferred to each and the mouth of these test tubes was closed with cotton plugs. To prepare the agar nutrient medium, 200 mL of liquid medium was added to a 500 mL conical flask containing 3 g agar. The mouth of the conical flask was closed with a cotton plug. All these liquid nutrient medium and agar nutrient medium was sterilized in an autoclave at 121 ºC for 15 min.

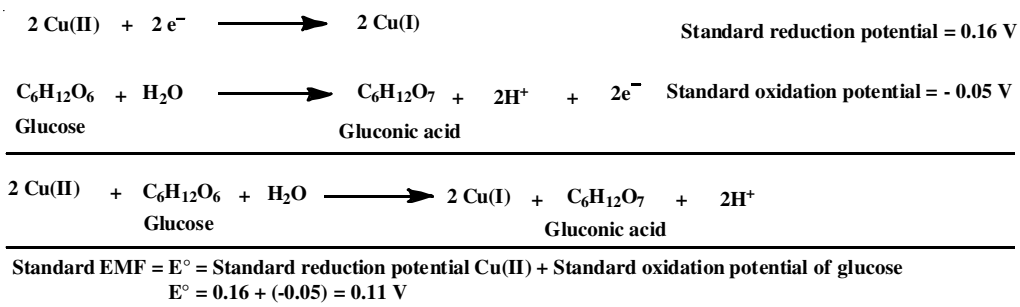
Antibacterial activity: In this work, *E. coli* DH5α was chosen as the test bacterial species. Colonies of *E. coli* DH5α was picked up from the nutrient agar plate with a sterile inoculating loop and inoculated separately in 5 mL of sterile liquid nutrient medium. The inoculated liquid nutrient media was incubated overnight in a rotary incubator shaker at 180 rpm and 37 ºC. About 50 mL of sterile water was taken in a 100 mL sterile beaker and then contaminated with 10 µL of freshly cultured *E. coli* DH5α. With the help of sterile forceps, a small portion of different masks, sterile FP and Cu_2O NPs-FP (each with dimension 2 cm × 2 cm) was dipped in the contaminated water and kept as such for 30 s for bacteria to get adsorbed on their surface. The contaminated mask, FP and Cu_2O NPs-FP kept outside for 20 min were gently pressed on an agar nutrient plate for 30 s and then removed. The plates were then incubated for 24 h at 37 ºC and the antibacterial activity of Cu_2O NPs-FP was observed.

RESULTS AND DISCUSSION

Synthesis and coating of Cu_2O NPs on filter paper (FP): In the synthetic procedure as reported herein, the use of additional stabilizing agents such as PVC, surfactant and ligands were completely avoided. However, the synthesis of Cu_2O NPs was performed by using acid-hydrolyzed rice as a source of reducing and stabilizing agents [28]. The glucose formed from the acidic hydrolysis of starch, a major component of rice, serves as the reducing agent. Glucose and Cu^{2+} undergo redox reactions in the alkaline conditions and resulting in the formation of Cu_2O and gluconate. It is important to mention that glucose acts as a reducing agent and the produced gluconate serves as a stabilizing agent (**Scheme-I**). The redox reaction between Cu(II) and glucose can be understood *via* redox chemistry [29]. The



Scheme-I: Proposed reaction mechanism for the formation of gluconate stabilized Cu_2ONPs



Scheme-II: Redox reaction between Cu(II) and glucose

reduction potential of gluconic acid to glucose and Cu(II) to Cu(I) are 0.05 V and 0.16 V, respectively. The following redox reaction takes place between Cu(II) and glucose (**Scheme-II**). The E°_{cell} for production of Cu_2O is 0.11 V.

Characterization studies: The Cu_2O nanoparticles was characterized by recording UV-Vis absorption spectra and surface plasmon resonance peak at 480 nm was observed (Fig. 1a), which is consistence with the reported data [28,30]. TEM image (Fig. 1b) reflects the homogeneous distribution of particle size. The quantity of copper was analyzed by ICP-OES and found to be 71.9 ± 1.5 μg/cm^2 area of Cu_2O NPs-FP.

The powder X-ray diffraction (PXRD) of filter paper (FP) and Cu_2O NPs-FP was recorded. In comparison, the 2θ peak corresponding to cellulose was observed for both samples while the 2θ peak corresponding to Cu_2O was observed only for Cu_2O NPs-FP (Fig. 2). Scanning electron microscope (SEM) images describe the surface feature of the filter paper (FP) and Cu_2O NPs-FP (Fig. 3) whereas EDEX data of filter paper and Cu_2O NPs-FP were compared and the presence of copper was observed on Cu_2O NPs-FP (Fig. 4).

Antibacterial activity: A small portion (each of dimension 2 cm × 2 cm) of different masks, filter paper (FP) and Cu_2O NPs-FP (Fig. 5) after contamination with active bacterial cells was left for 20 min. The experiments were performed in triplicate and consistency in the results was observed. Reducing the contact time between bacteria with Cu_2O NPs-FP for 10 min, was found to be insufficient to kill all the bacteria. Hence, the designed materials can be used as an external layer on regular masks during an outbreak of any air-communicable microbial infectious diseases (Fig. 6). The material being cellulose based, when discarded doesn't pose threat to the environment. In fact, copper can act as a micronutrient for plants too.

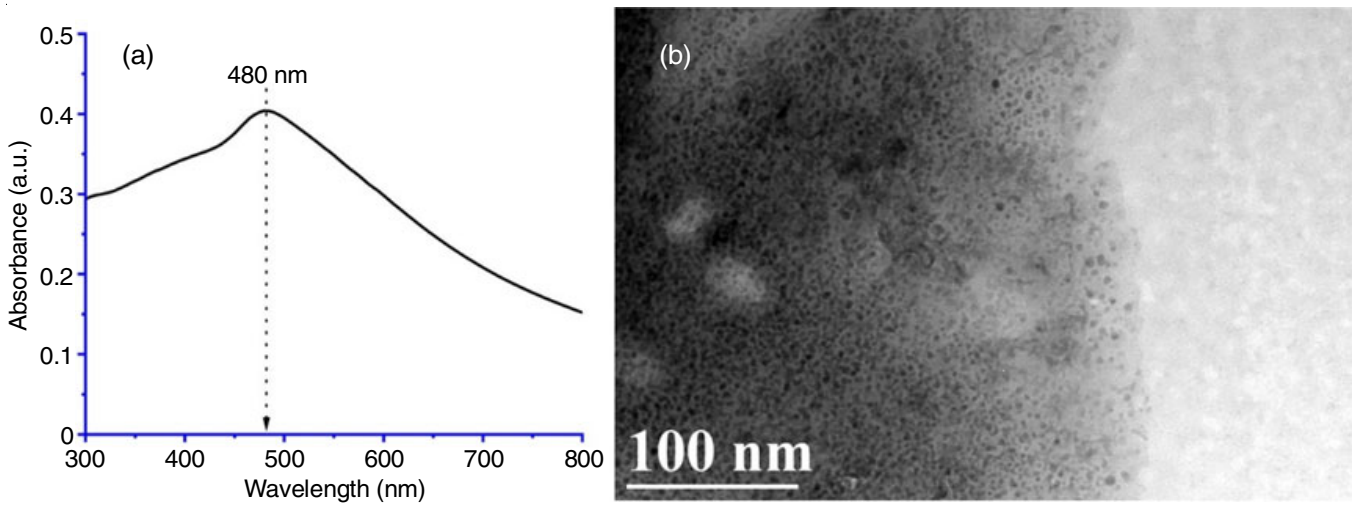


Fig. 1. (a) UV-Vis spectra of Cu_2O NPs, (b) TEM image of Cu_2O NPs

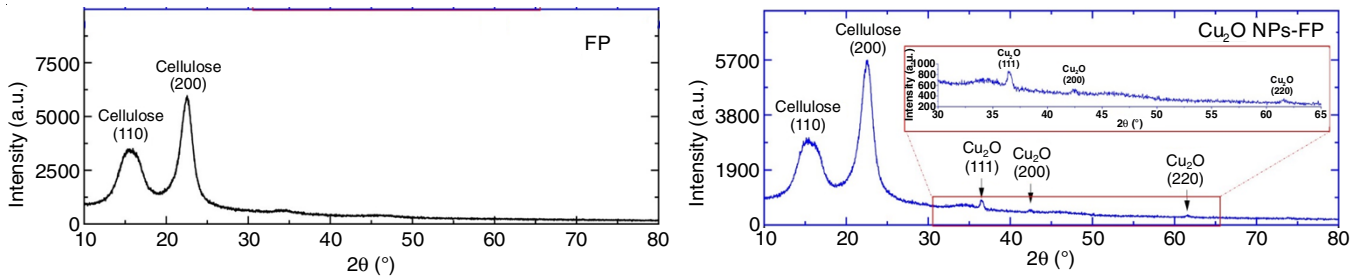


Fig. 2. Powder X-ray diffraction of FP and Cu_2O NPs-FP (for Cu_2O NPs-FP, 2θ region between 30 to 65 is enlarged and provided in the inset)

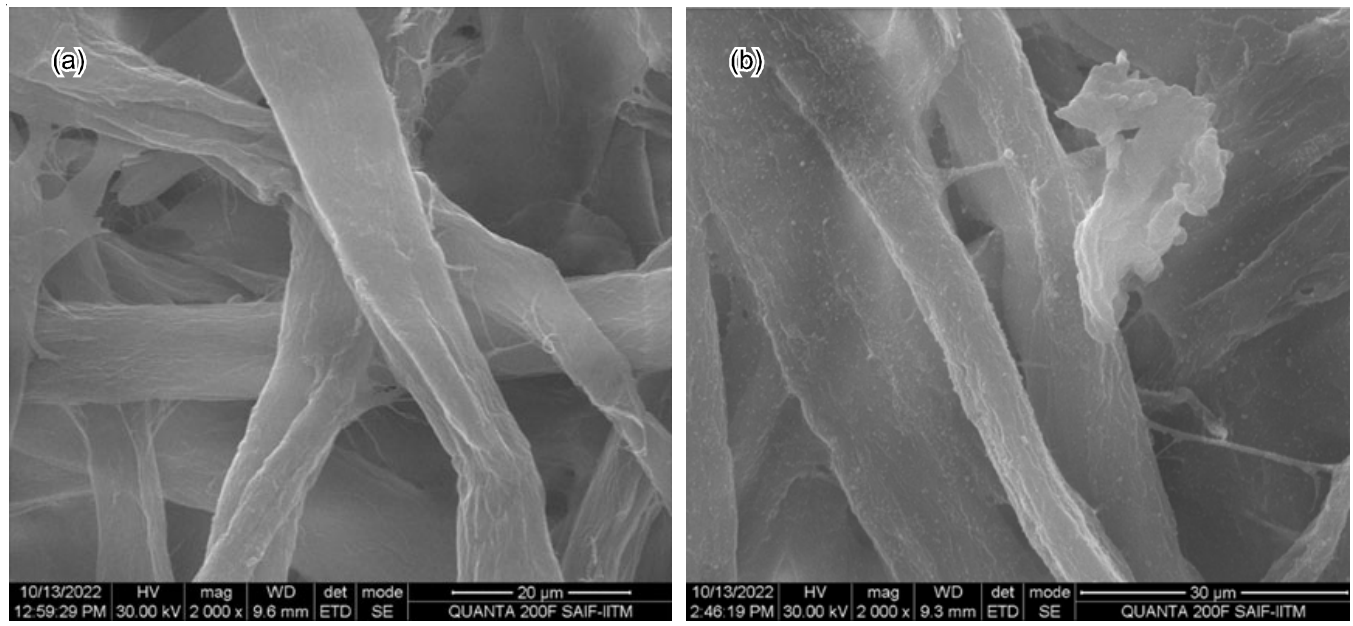


Fig. 3. SEM image of (a) FP and (b) Cu_2O NPs-FP

Conclusion

In this work, cuprous oxide nanoparticles (Cu_2O NPs) were synthesized in gram scale without using any environmentally hazardous stabilizing agent, such as PVP or any surfactant or ligands. The Cu_2O NPs were coated on cellulose filter paper by dipping it into the aqueous suspension of the nanoparticles. Cu_2O NPs-FP was found to possess excellent antibacterial activity. The designed materials have a scope for use, as an external disinfecting layer on regular masks, which can play a key role in preventing the transmission of respiratory infectious microbial diseases.

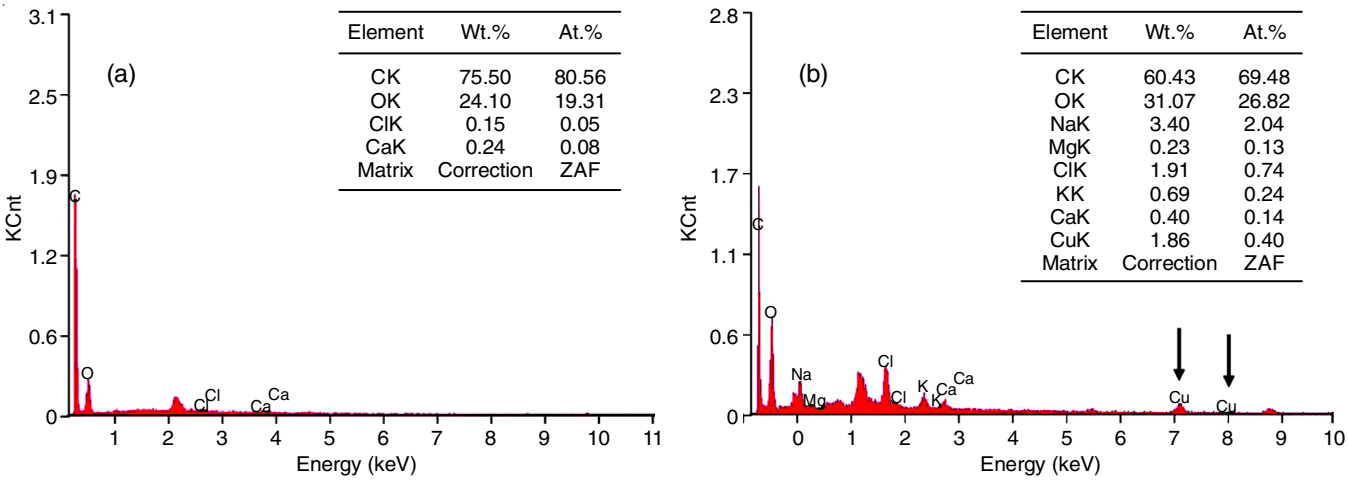


Fig. 4. EDX data of filter paper (FP) (a) and Cu_2O NPs-FP (b) describing atomic percentage of different atoms

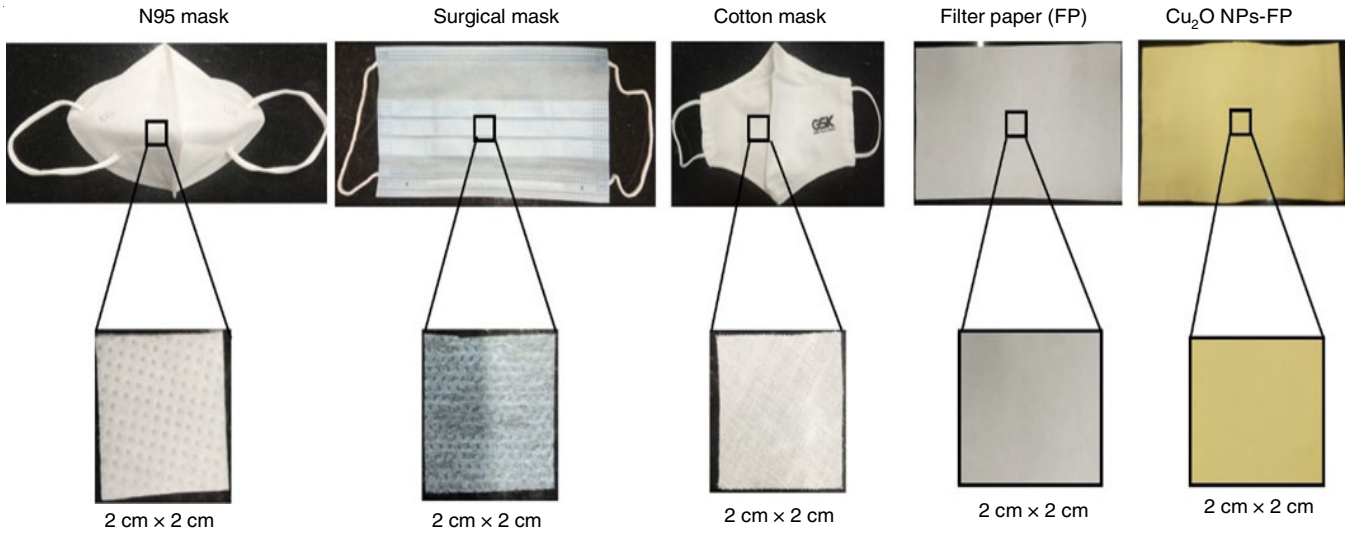


Fig. 5. Image of different masks, FP and Cu_2O NPs-FP and its portion (2 cm × 2 cm) used

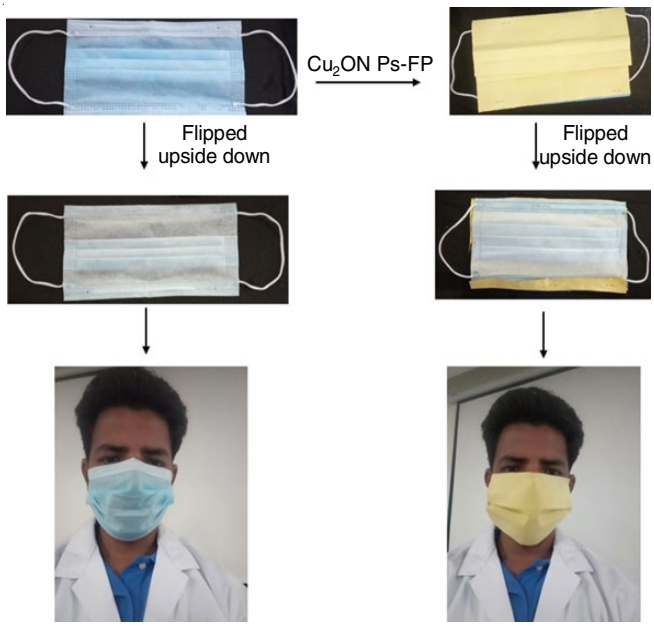


Fig. 6. Fixing of Cu_2ONPs-FP on a surgical mask and its possible use

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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