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# Nanostructured copper oxide-cotton fibers: synthesis, characterization, and applications

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## Abstract

Copper oxide nanoparticles were prepared and subsequently deposited onto surface of the cotton fibers by ultrasonic irradiation. The structure and morphology of the coated and un-coated cottons were examined by X-ray diffraction and scanning electron microscopy/energy dispersive X-ray analysis. These methods revealed that of CuO nanoparticles are crystalline and corresponds to monoclinic phase, and that these nanoparticles are physically adsorbed onto the cotton fiber surface. They have an average crystallite size of 10 nm; the physical and chemical properties of the treated cotton fibers are markedly different from those of the untreated cotton fibers. The CuO-cotton fiber nanocomposites were tested against *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive) cultures and showed a significant antimicrobial activity; whereas its analogous CuS-coated cotton material formed by the reaction CuO-coated cotton fibers with H<sub>2</sub>S showed no activity.

**Keywords:** CuO nanoparticles, Sonochemical reaction, Antimicrobial activity, Metal oxide-coated cotton fibers

## Background

Recently, much attention has been paid on the preparation and applications of nanometal oxide and metal sulfide coatings onto cotton substrate due to their promising applications [1-4]. The nanometal oxide films deposited on cotton fabrics have exhibited excellent antimicrobial activity against *Staphylococcus aureus* bacteria [4-7]. The results indicated that the coated fabrics show enhanced protection against ultraviolet radiation [6]. There is a growing awareness of the use of antibacterial fabrics in the form of medical clothes, protective garments, and bed spreads to minimize the chance of the nosocomial infections [3,8]. Nanoparticles are much more active than larger particles because of their higher surface area, and they display unique physical and chemical properties [9]. Textiles coated with silver nanoparticles have become quite common [10]. CuO nanoparticles are very efficient in imparting antibacterial effect to fabric [4,5]. They have been investigated as antibacterial agent both against Gram negative and Gram positive microorganism *Escherichia coli*. These copper oxide plated or impregnated synthetic fibers

possess broad spectrum biocidal properties: they are antibacterial, antifungal, antiviral, and they kill dust mites [11].

Moreover, animal studies demonstrated that these fibers do not possess skin sensitization properties [11]. There were three general routes to impregnate metal oxides nanoparticles onto the cotton fibers. In the first route, the prepared CuO nanocrystals were coated onto cotton fibers simply by pad-dry-cure process [12,13]. The second route was to use the ultrasonic irradiation as an effective method for the deposition of nanomaterials onto the surface of cotton fibers and other substrates [4,5,14,15]. The third route was using thermal chemical treatment [3].

In this research the second method was adopted where the blank cotton fibers before making into textiles was soaked into copper sulfate and sodium hydroxide mixture, and then the mixture was sonicated in one-step reaction. The CuO nanoparticles were impregnated and deposited on/into cotton fibers by irradiation of ultrasound vibrations. Most of the literature was concerned with ZnO nanoparticles-coated cotton and only few articles are concerned with copper and other metal oxides nanoparticles coated onto cotton fibers.

The aim of the present research was to produce CuO nanoparticles coated onto raw cotton fibers and to estimate its antibacterial properties against bacteria *E. coli*.

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CuO nanoparticles act as antibacterial agent, while cotton act as a substrate which can be used to fabricate medical clothes. We aim to have CuO-coated cotton in its natural state so multi-applications could be addressed. It is found that CuO nanoparticles-coated cotton fibers showed high ability to remove H<sub>2</sub>S, forming CuS-coated cotton fibers. The CuS-coated materials do not show any microbial activity with respect to the CuO-coated cotton material. Scanning electron microscope (SEM) was used to reveal information about the sample, including external morphology. Energy dispersive X-ray (EDX) was applied to identify the atomic percentage contents of the main formulation's elements that has been applied in coating using an EDX unit connected to the SEM microscope. X-ray diffraction (XRD) was used to provide information about the crystalline structure and orientation of materials making up the sample.

## Methods

### Materials and apparatus

Copper sulfate, sodium hydroxide and ethanol were purchased from Merck (Merck & Co., Inc., Whitehouse Station, NJ, USA) and used without further purification. Egyptian cotton material was purchased from the local market and pretreated before used.

Chemical analysis of the CuO-coated cotton fibers was obtained by EDX using an Oxford on X-Max (area: 20 mm<sup>2</sup>) detector installed on a Hitachi S3400N SEM (Hitachi High-Technologies Europe GmbH, Krefeld, Germany). Calibration of the instrument was performed on Ti Ka at 4.509 KeV. The XRD study was performed on a Bruker D8 advance diffractometer (Bruker Corporation, Billerica, MA, USA) using Cu-K $\alpha$  radiation ( $\lambda = 15,418 \text{ \AA}$  at 45 KV and 40 mA, 0.05 step size, and 60 s step time over a range from 0 to 80°.

### Coating procedure

Cotton fibers were first washed in a water bath containing 5% of sodium dodecyl sulfate at 40°C for an hour. After rinsing with distilled water, the fibers were dried in vacuum at 60°C for 24 h.

The CuO-coated cotton material were prepared as follows: 0.05 g dry cotton was first soaked into 10 ml of aqueous solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (4.8 × 10<sup>-4</sup> M) solution in a sonicated flask and irradiated for 10 min with Ultrasonic generator model US-150 Ti-horn (20 kHz, output 10 Turning 7). Then 0.06 g of NaOH was added to the mixture while stirring. The mixture was then resonicated at 35°C to 40°C for 1 h; a strong blue color was gradually converted into brown after 15 min. The bath temperature was kept at a constant temperature around 40°C. The product was then washed thoroughly several times with distilled water to remove any excess hydroxide and dried in vacuum at 60°C overnight. The copper

concentration in the fiber was determined by titration method and found (3 to 5 wt.%). The CuS-coated cotton material was prepared by soaking the CuO-coated cotton materials into water containing H<sub>2</sub>S.

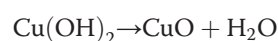
### Antibacterial activity screening

The antimicrobial activity of cotton coated with CuO nanoparticles was tested against Gram negative and Gram positive bacteria. A small piece of cotton coated with CuO nanoparticles was added to a tube containing 5 ml of freshly prepared brain heart infusion broth (BHIB) (HiMedia, Mumbai, India) that is inoculated with *E. coli* and *S. aureus* (these clinical isolates were kindly provided by the Microbiology laboratory of Al-Shifa Hospital). The tubes were incubated at 37°C for 24 h. The turbidity of the test tubes was compared visually to an uninoculated (control) BHIB tube. A 100  $\mu$ l of each tube was diluted and fractions were plated on nutrient agar plates and incubated at 37°C for 24 h. The colony-forming units/ml was calculated by multiplying the number of colonies by the dilution factor.

## Results and discussion

### Synthesis

The CuO-coated cotton fiber was obtained by deposition of CuO nanoparticles onto the cotton fibers via the ultrasound irradiation of metal hydroxide according to the reaction in a similar way previously reported [5]:



During the formation process, a blue fresh product Cu(OH)<sub>2</sub> is formed immediately after the addition of OH<sup>-</sup>, which turns into brown color of copper oxide after a few minutes of sonication. The CuO nanoparticles produced by the reaction were probably physically adsorbed onto

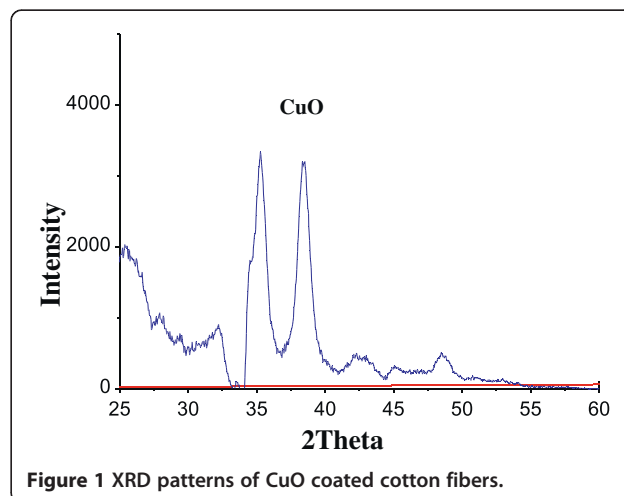
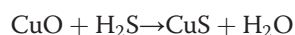


Figure 1 XRD patterns of CuO coated cotton fibers.

the surface of the natural cotton fibers by the sonochemical microjets resulting from the collapse of sonochemical bubbles [5]. These nanoparticles are strongly physically adsorbed onto the cotton substrate, since these particles are not removed by several washing. They are also very stable at pH 3 to 6, but they are less stable at pH < 3, where most CuO particles reacted with the acidic solution. So this method was used to determine the content of CuO which was found to be 3 to 5 wt.%. The CuO-coated cotton could be used as sensor for low concentration for H<sub>2</sub>S. It reacts with hydrogen sulfide to

give copper sulfide [16]; this reaction is used commercially to remove H<sub>2</sub>S (e.g., as deodorant).



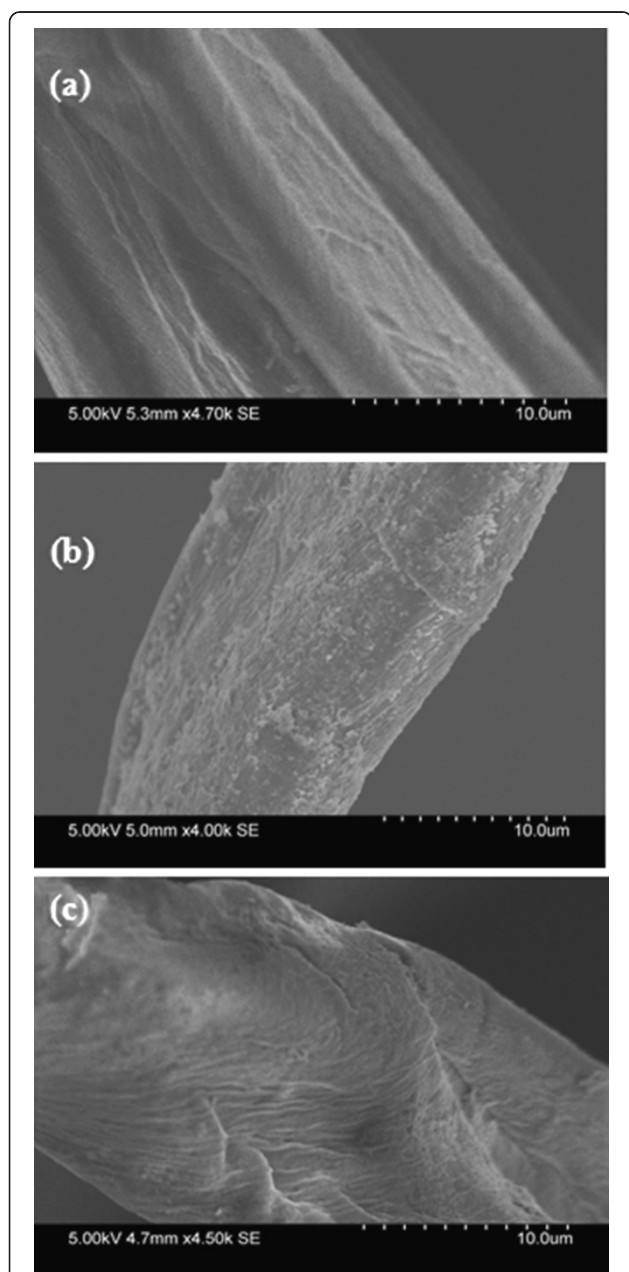
The CuS-coated cotton was formed in two ways: either passing H<sub>2</sub>S gas onto the CuO-coated cotton material or by soaking the CuO-coated cotton sample into water containing H<sub>2</sub>S.

#### XRD analysis

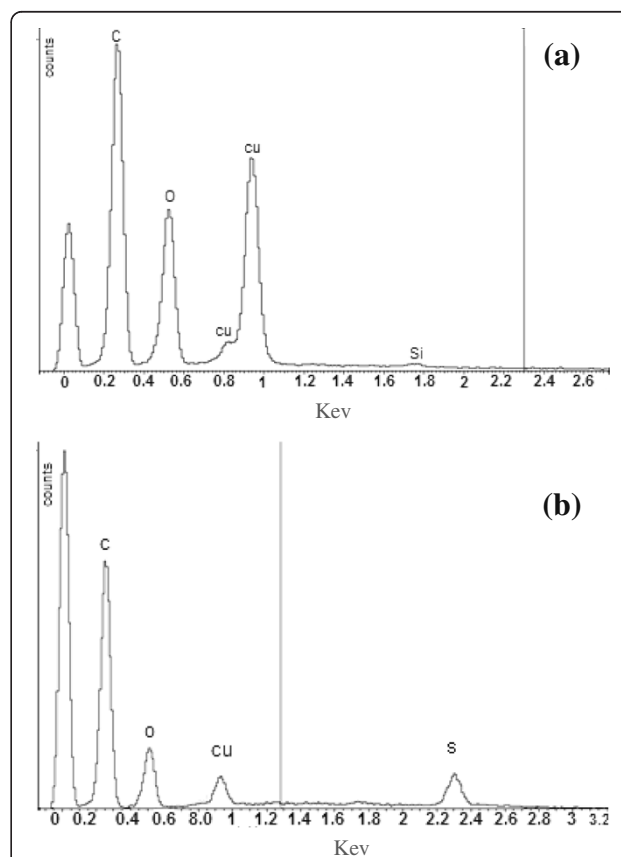
The XRD pattern of the coated cotton (Figure 1) reveals that copper oxide is present in crystalline form onto the cotton fibers. The pattern corresponds to the monoclinic phase of CuO; the diffraction peaks matches very well with the PDF file 80–1916. The peaks at  $2\theta = 35.53$  and  $38.37$  are assigned to the (-111) and (111) reflection lines of monoclinic CuO particles. Scherer's equation was used to estimate mean size of nanoparticles [17].

$$P = \frac{0.9\lambda}{\beta \cos\theta},$$

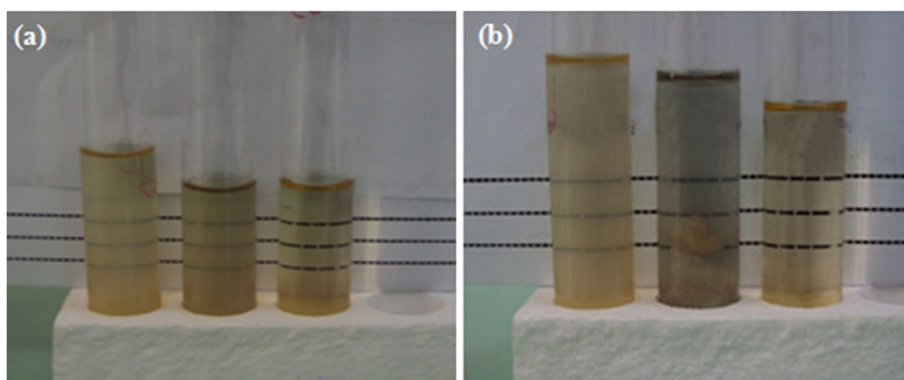
where  $P$  is the mean diameter of nanoparticles,  $\lambda$  is the wavelength of X-ray radiation source, and  $\beta$  is the



**Figure 2** SEM image of (a) blank cotton, (b) nanoparticles of CuO-coated cotton, and (c) CuS-coated cotton.



**Figure 3** EDX atomic compositions of (a) CuO coated cotton and (b) CuS-coated cotton.



**Figure 4** Photos of antimicrobial activity (a) CuS-coated cotton and (b) CuO-coated cotton (left, positive control; middle, sample; right, negative control).

angular full width at half maximum of the X-ray diffraction peak at the diffraction angle. The average mean crystallite size of copper oxide estimated by XRD data was 10 nm which is very close to the reported value of 10 to 15 nm of similar CuO-coated cotton material [4,5]. But these values are much smaller in size compared with the reported average size of 50 nm of copper oxide nanoparticles impregnated onto cotton using pad-dry-cure method [12]. The reason for this significant change is probably that in this method of preparation, the cotton fibers could cap the growth of particle size after the formation of metal oxide.

#### SEM/EDX analysis

The morphology of the fiber surface area before and after deposition of CuO nanoparticles was studied by SEM and is presented in Figure 2. On the SEM image of the original cotton fiber (Figure 2a), grooves and fibrils could be easily observed on the surface of the fiber. Figure 2b presents the SEM photographs of CuO nanoparticles coated onto cotton fibers after irradiation of ultrasound vibrations. It is clear to see that cotton fibers were covered homogeneously with CuO nanoparticles. The SEM image of the CuS-coated cotton fibers obtained by the treatment of the CuO nanoparticles with H<sub>2</sub>S is shown in Figure 2c. The SEM analysis revealed that the size of CuO nanoparticles coated onto cotton fibers was in the nanoscale range. From Figure 2a, it is clear that the size of the cotton fibers is in the range of 200 μm, but the size of the CuO nanoparticles coated on the fibers is much smaller at a

nanoscale level about 10 nm as calculated from Scherer's equation, which is consistent with the reported results [5].

Figure 3 shows the EDX spectra of the CuO- and CuS-coated cotton samples. The chemical composition of the CuO- and CuS-coated cotton samples are presented in Figure 3a,b. EDX of the CuO-coated cotton sample showing both Cu and O are present. The presence of Cu atoms in the coated cotton fibers indicates that CuO particles are deposited onto it. The presence of almost equal percentage of S and Cu atoms of the CuS-coated cotton sample indicates that all CuO were converted into CuS. The presence of an oxygen peak at the spectrum of the CuS is probably due to the oxygen of the cellulose units or unreacted CuO.

#### Antibacterial activity

The antibacterial activity of CuO nanoparticles coated onto cotton against *E. coli* microorganisms are shown in Figure 4b. The coated cotton sample displays high activity with a great reduction of bacteria, whereas the coated CuS cotton did not show any antibacterial activity (Figure 4a). No growth was observed in the tube containing the CuO-coated cotton as evidenced by the clear appearance of the tube and the absence of growth from the subcultured samples. Similar results were observed against *S. aureus* (Table 1).

#### Conclusions

Through ultrasonic irradiation, CuO nanoparticles were deposited onto natural cotton fibers. The morphology and structure were examined by XRD and SEM/EDX.

**Table 1** Antibacterial activity of ZnO- and ZnS-coated cotton against *E. coli* and *S. aureus*

| Treatment         | <i>E. coli</i> |                               | <i>S. aureus</i> |                              |
|-------------------|----------------|-------------------------------|------------------|------------------------------|
|                   | Tube           | Subculture                    | Tube             | Subculture                   |
| CuO-coated cotton | No growth      | Negative at 10 <sup>-1</sup>  | No growth        | Negative at 10 <sup>-1</sup> |
| CuS-coated cotton | Growth         | 3.2 × 10 <sup>10</sup> cfu/ml | Growth           | 2.6 × 10 <sup>9</sup> cfu/ml |

The analysis revealed that CuO nanoparticles coated onto cotton fibers are in crystalline form of monoclinic phase. The estimated crystallite size of the CuO nanoparticles was found ca. 10 nm which is consistent with the reported values. These particles were developed onto the cotton fibers and may be dependent on the chemical conditions and physical environment during the growing process. These materials can be used as antibacterial fabrics in the form of medical cloths, protective garments and bed spreads, and many other purposes to minimize the chance of nosocomial infections. Since CuO is used in the form of nanoparticle, it will have a very good absorption, penetration, and availability. It showed a great reduction in the bacterial activity.

#### Competing interests

We declare that we have no competing interests.

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#### Authors' contributions

IM and FK carried out the synthesis the nano-CuO-coated cotton composite. MS, IG and FB participate in examining the morphology and structure by XRD and SEM/EDX. SZ participates in conducting the bacterial activity tests. All authors read and approved the final manuscript.

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