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Synthesis of nano Cu_2O on cotton: Morphological, physical, biological and optical sensing characterizations

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ABSTRACT

In this paper, Cu_2O nanoparticles were in situ synthesized on cotton fabric through a new simple and cost-effective chemical reduction method using copper sulfate, sodium hydroxide and ammonia. Cotton fabric participates as a reducing agent in reduction of copper sulfate and facilitates synthesis of cuprous oxide in nano-scale as a stabilizer. The produced cotton/nano Cu_2O composite were characterized by X-ray diffraction, scanning electron microscopy and Energy-dispersive X-ray spectroscopy. Interaction of Cu_2O with cotton fabric in addition to alteration of cotton functional groups were studied by Fourier transforms infrared spectroscopy. The intermediate solution, copper-amine complex, was analyzed by ultraviolet–visible spectroscopy. The mechanical properties of the cotton/nano Cu_2O composite were studied using Instron indicated a higher tensile strain. The antibacterial activity of the fabric samples showed considerable behavior against *S. aureus* and *E. coli*. Further, the treated fabric became highly hydrophobic and sensed ammonia and hydrogen peroxide chromatically.

1. Introduction

Cellulosic cotton fabric consists of many functional hydroxyl groups interact with surrounding inorganic or polymeric nanoparticles. Among inorganic nano structures, metal oxide nanoparticles are highly considered due to their important role in many areas of physics, chemistry and material science (Fernández-García, Martínez-Arias, Hanson, & Rodriguez, 2004). Cuprous oxide as a semiconductor with a narrow direct band gap of 1.9–2.2 eV (Huang, Peng, Yu, & Wang, 2009; Liu, Wang, Wang, & Geng, 2009) is a promising multifunctional metal oxide with application in electronics (Abboud et al., 2013), catalysis (Liu et al., 2009), gas sensors (Abboud et al., 2013), lithium ion batteries (Liu et al., 2009), solar energy conversion (Ogwu, Darma, & Bouquerel, 2007) and magnetic storage (Abboud et al., 2013).

Deposition of Cu_2O nanoparticles on cotton fabric as a metal oxide-polymer nano composite provides many new and improved properties. Cuprous oxide nanoparticles-loaded cotton fabric could be used in medical and textile applications such as medical devices, healthcare, wound dressing, military, protective suits, personal care product, clothing and others (Longano, Ditaranto, Sabbatini, Torsi, & Cioffi, 2012).

Cellulose can be used as a support for nanoparticles (Vainio et al., 2007), reducing agent (Hu, Chen, Yang, Li, & Wang, 2013; Vainio et al., 2007) and stabilizer (Hu et al., 2013). Cellulose determines the size and morphology of nanoparticles, meanwhile acts as a reactor preventing agglomeration (Hu et al., 2013) and limits nanoparticle size in nano scale. Copper and its oxides as antibacterial agents have been known for a long time (Longano et al., 2012). Ancient civilization used copper to sterilized water and wounds, also treated diseases such as sore throats. Namely, Persian people used copper to treat eye infection and even yet as a cooking pot.

Cuprous oxide has been synthesized through different methods such as electro-deposition (Li, Liang, Tao, & Chen, 2008), chemical (Medina-Valtierra, Calixto, & Ruiz, 2004), electro chemical (Zhao et al., 2010), sonochemical (Kumar, Diamant, & Gedanken, 2000) and microwave irradiation (He, Shen, & Gao, 2005). Ma et al. (2013) reported a microwave-assisted ionic liquid method to synthesis cellulose/CuO nano composite. A sonochemical coating of cotton with copper oxide nanoparticles with high quality, stability and fair antibacterial activity was reported by Perelshtein et al. (2013). Monodispersed cuprous oxide nanoparticles were synthesized and embedded into chitosan. Cuprous oxide-chitosan nano composite biosenses and measures total cholesterol level in human serum (Sing et al., 2013). Medina-Valtierra et al. (2004) prepared Cu_2O

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film on fiberglass with a short immersion into the copper solution reported complete coating of Cu_2O on the substrate surface.

In this study, in situ synthesis of cuprous nanoparticles on cotton fabric was carried out by chemical reduction using inexpensive approach. Creating anti-bacterial properties on textile for medical applications with lower production cost and simpler method in comparison with Ag and TiO_2 nanoparticles is one of important purposes of this study. The ability of gas sensing to consider the fabric as chemically sensitive polymer substrate without any additional process and enhancing hydrophobic and mechanical properties of new product are other main fair novel options granted to the fabric. Cu^+ was produced by using cotton fabric as a reducing agent and stabilizer. NaOH and ammonia solution were also used to increase exhaustion efficiency on the cotton fabric. X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–vis diffuse reflectance spectrometry, energy-dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FTIR) were applied to study the crystal shape and size, morphology, presence of elements of nanoparticles and chemical changes. Mechanical properties of the cotton composite were studied and antibacterial activity of treated fabric against *S. aureus* and *E. coli* was considerable. The hydrophobicity of cotton fabric containing cuprous oxide nanoparticles increased due to blocking of some hydroxyl groups of cellulose. Detection of ammonia and H_2O_2 is also possible by the cotton/nano Cu_2O composite due to its efficient optical sensing behavior.

2. Experimental

Copper sulfate ($CuSO_4$), NaOH and ammonia solution (NH_4OH 25%) were purchased from Merck (Germany) without any further purification. 100% bleached cotton fabric with 151 g/m^2 and 25 yarns/cm warp and weft yarn density was prepared from a Tehran (Iran) local market.

Cotton fabric was washed with 1 g/L nonionic detergent to clean dirt and impurities. It was rinsed 3 times with distilled water and dried at room temperature.

8% (w/w) copper salt was added to 100 mL distilled water and the cotton fabric was then introduced into the solution. Temperature was raised to 80 °C with stirring for 1 h. 1.6% (w/w) sodium hydroxide was added to the solution in 5 steps after 5 min and retained for 1 h at boil. The temperature was reduced to the room temperature, and then ammonia solution was added dropwise with vigorous stirring. The process was carried out for 30 min at 40 °C with stirring. The treated fabrics were finally rinsed three times with distilled water and dried at room temperature.

X-ray diffraction determines the type of crystal structure of nanoparticles calculated with Debye Scherrer equation (Eq. (1))

$$\text{Crystal size} = \frac{0.9\lambda}{B_{1/2}\cos\theta} \quad (1)$$

where $B_{1/2}$ is width at half maximum height and λ is X-ray wavelength.

X-ray analysis was determined by X-ray diffractometer (XRD EQuniox 3000, INEL, France) using Cu Kα radiation (λ = 1.540560 Å). To observe the surface changes, presence of nanoparticles on the fabric surface, and also distribution of cuprous oxide particles deposition, SEM and EDX analysis were carried out with VEGA II TESCAN-XMU (Czech Republic) with gold coating. EDX analysis helps to identify copper on the fabric surface and the weight percentages of oxygen, nitrogen in addition to copper. To study the chemical changes in the cellulose functional groups after treatment with nanoparticles, FTIR analysis with a Nicolet spectrometer (France) in the range of 400–4000 cm^{-1} was used. Optical measurements were carried out on a UV–vis spectrophotometer (Raylight UV-2100) using a quartz cell. The solution contains cuprous oxide-amine complex were investigated and the results were recorded on a spectrophotometer. Mechanical properties of the treated fabrics were measured based on the standard BS 1516 using Instron model 5566 (U.S.A).

To assess the antibacterial activities of the treated fabrics qualitatively, AATCC 147 test method was performed. *S. aureous* and *E. coli* bacteria were cultured on the plates containing Hinton agar culture media. Circular fabrics with 30 mm diameter were placed in the plates for 24 h. The plates were then incubated in an oven for 24 h. The inhibition zone around the fabric is indication of antibacterial behaviuor of the fabric.

To assess quantitative antibacterial activity based on AATCC 147, colonies of each Gram (+) *S. aureous* and Gram (−) *E. coli* were suspended in a physiologic saline solution (NaCl 0.9%) with 0.5 McFarland. The vials were then incubated at 37 °C for 2 h. The homogenous bacteria suspensions have 1.5×10^8 colonies/mL. As a control sample, suspensions of 10^8 (CFU/mL) colonies of bacteria were performed on the sample by diluting the suspensions. 0 and 2 h exposure with fabric was considered and 100 mL neutralizing solution were prepared from 1% thiosulfate (Merck), 0.1% tween 80 (Merck) and 100 mL distilled water was added to the contaminated fabrics. Microbial suspension on the sample was poor plated on the cultural medium (3.4% Muller Hinton agar) by dilution of 10^2, 10^1 and 10^0 concentration. The number of colonies was counted and reduction percentage of the bacteria was calculated after 24 h.

To determine the durability of cotton/nano Cu_2O composite, the fabric was washed 10, 20 and 30 times with non-ionic detergent according to AATCC test method 61(2A)-1996. Stability of treated cotton fabric was then studied through antibacterial test.

3. Result and discussion

3.1. In situ synthesis of cuprous oxide on cotton fabric

As copper salt dissolved in water, Cu^{2+} ions were dispersed in the solution. Presence of cotton fabric in the solution led to gradual reduction of Cu^{2+} to Cu^+ that the fabric acted as a reducing agent (Hu et al., 2013; Vainio et al., 2007). Addition of NaOH solution at high temperature led to swelling of cotton fabric structure (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998a). Penetration of water into the cellulose structure and further swelling by destroying intermolecular hydrogen bonds, facilitate the penetration of particles into the fiber structure (Klemm et al., 1998a).

A zero charge complex is essential to continue the polymerization of monomers (Gerko, 2006). By introducing NaOH in the solution, small amount of NaOH was adsorbed onto cellulose fiber resulting in Na-cellulose I formation (reaction 1) (Klemm et al., 1998a).

$$\text{Cell–OH} + \text{NaOH} \rightarrow \text{Cell–O}^-\text{Na}^+ + \text{H}_2\text{O} \quad (1)$$

Cu^+ ions were distributed on the fabric reacted with O^- ions presented in the solution and also on the cellulose surface ionic layer led to formation of Cu_2O precursor according to reaction 2 (Medina-Valtierra et al., 2004).

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O \quad (2)$$

After hydroxylation of Cu_2O nuclei, build-up of Cu_2O molecules leads to supersaturating and nucleation occurs as a result. The supersaturation increases with decreasing of cuprous oxide solubility. Until the supersaturation of solid is reached, further growth of supersaturated solution is possible (Medina-Valtierra et al., 2004). The nucleation sites are evenly placed on the surface of fabric with presence of particles in the solution. However nucleus diffusion into the fiber structure is possible due to presence of NaOH at high temperature, it is difficult to detect inside the fiber. Thus nucleation sites are mostly considered on the surface of the fiber.

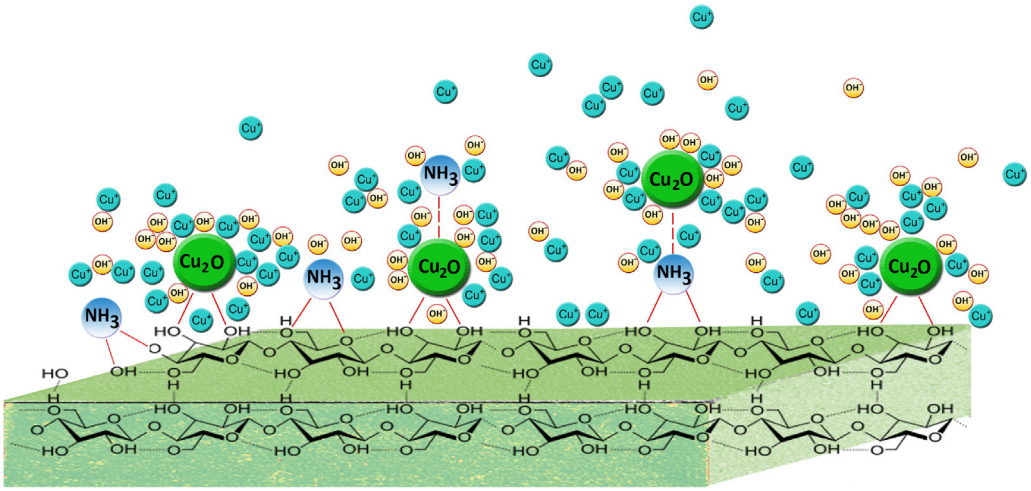

Fig. 1. Schematic of cellulose nucleation and chemisorption of Cu_2O nanoparticles on fabric surface.

Sodium hydroxide concentration is a very important factor in this process. The concentration of NaOH should be low enough to precipitate a very small amount of $Cu(OH)_2$ (reaction 3) (Qing, Kai, Sujie, Yunsheng, & Weixin, 2011).

$$CuSO_4 + NaOH \rightarrow Cu(OH)_2 + Na_2SO_4 \quad (3)$$

The pH of solution should be lower than 6. Increasing NaOH leads to the irreversible formation of CuO in the solution as illustrated in reaction 4 (Qing et al., 2011).

$$Cu(OH)_2 + 2OH^- \leftrightarrow [Cu(OH)_4]^{2-} \rightarrow CuO + H_2O + 2OH^- \quad (4)$$

When this process was occurred without cotton fabric, using low NaOH leads to more $Cu(OH)_2$ precipitation. Cotton fabric not only acts as a reducing agent, but also behaves as a substrate with numerous active sites for adsorption of Cu^+ ions (Cu_2O sediments) facilitates the nano synthesis by generating nucleation sites (Hu et al., 2013).

The surface chemistry is an important parameter was used to control the particle size distribution (Medina-Valtierra et al., 2004). Since the exhaustion of cuprous oxide on the fabric is low, it can be claimed that the movement of nucleation sites which are located close to the surface of cellulose are reduced due to vacant orbitals of copper and formation of complexion with cellulose surface functional groups. Therefore the possibility of joining nuclei and formation of aggregates is diminished. This is due to the degrees of free motions of particles close to the surface, which reduces the possibility of collision between nuclei drastically.

During the growth process, Cu_2O nuclei formed hydrogen bonds with hydroxyl groups of cellulose or van der Waals interaction with cellulosic chains (Hu et al., 2013). Thus cellulose controls the size of the synthesized nanoparticles as a stabilizer.

Despite the loading of nanoparticles on cotton fabric surface, exhaustion was low. Introduction of ammonia solution to the bath, produces $Cu(OH)_2$ sediment dissolved in the solution and $[Cu(NH_3)_4]^{2+}$ complex was formed as shown in reaction 5 (Qing et al., 2011).

$$Cu(OH)_2 + 4NH_4OH \rightarrow [Cu(NH_3)_4]^{2+}(OH)_2 + 4H_2O \quad (5)$$

Ammonia also makes Cu_2O particles dissolved in the solution and even on the surface of fabric which are physically attached to create $[Cu(NH_3)_4]^+$ complex according to reaction 6 (Qing et al., 2011).

$$Cu_2O + 8NH_3 + H_2O \rightarrow 2[Cu(NH_3)_4]^+ + 2OH^- \quad (6)$$

The amount of cuprous oxide nanoparticles bonded through hydrogen bonding or strong van der Walls attraction was low. Thus remaining particles attached physically or weakly bonded with van der Walls attractions dissolved in ammonia. Cu^+ and Cu^{2+} ions available in the solution produce complexes with nitrogen of ammonia. On the other hand, nitrogen bounds with cellulose by breaking O–H. . .O bonds replacing them with O–H. . .N (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998b) leading to binding copper ions to cellulosic chains. This also helps to load copper ions on the cellulosic fabric through physical attractions. Thus, the composition of copper–amine complex increases the yield of cuprous oxide on fabric (Vainio et al., 2007). Through the nitrogen complex on the fabric surface, the color of fabric turned blue similarly to the solution. Washing the fabric breaks some ammonia-copper ligands turned fabric color turned to green again. The schematic of interaction between cotton fabric and Cu_2O nanoparticles is illustrated in Fig. 1.

3.2. XRD and EDX

XRD pattern of Cu_2O nanoparticles synthesized on cotton fabric is shown in Fig. 2a. XRD pattern indicated crystalline Cu_2O with face centered cubic shapes. Well-defined peak at $2\theta = 36.2$, 42.2, 61.3 and 73.6, corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively. The XRD pattern well matches with standard data (JCPDS file no. 05-0667). The obtained peak intensity of nanoparticles in XRD pattern was reasonable. Nevertheless the overlap of the cellulose peak in 34° and Cu_2O in 36° cannot be ignored.

The crystal size of nanoparticles was calculated using Scherrer's equation (Eq. (1)). The average crystallite size of cuprous oxide nanoparticles was 20.7 nm.

Chemical composition of treated fabric was checked by EDX analysis (Fig. 2b). The final product contains Cu, O and N confirming presence of nitrogen on the fabric surface due to ammonia processing withstanding even after rinsing. Therefore, the nitrogen attachment to the fabric is strong and links between cuprous oxide and cellulose substrate act as a ligand.

The amount of nitrogen on the fabric is considerable and even more than Cu. Loading of noticeable amount of cuprous oxide nanoparticles on cellulosic cotton fabric was confirmed in EDX pattern indicated cuprous oxide synthesis.

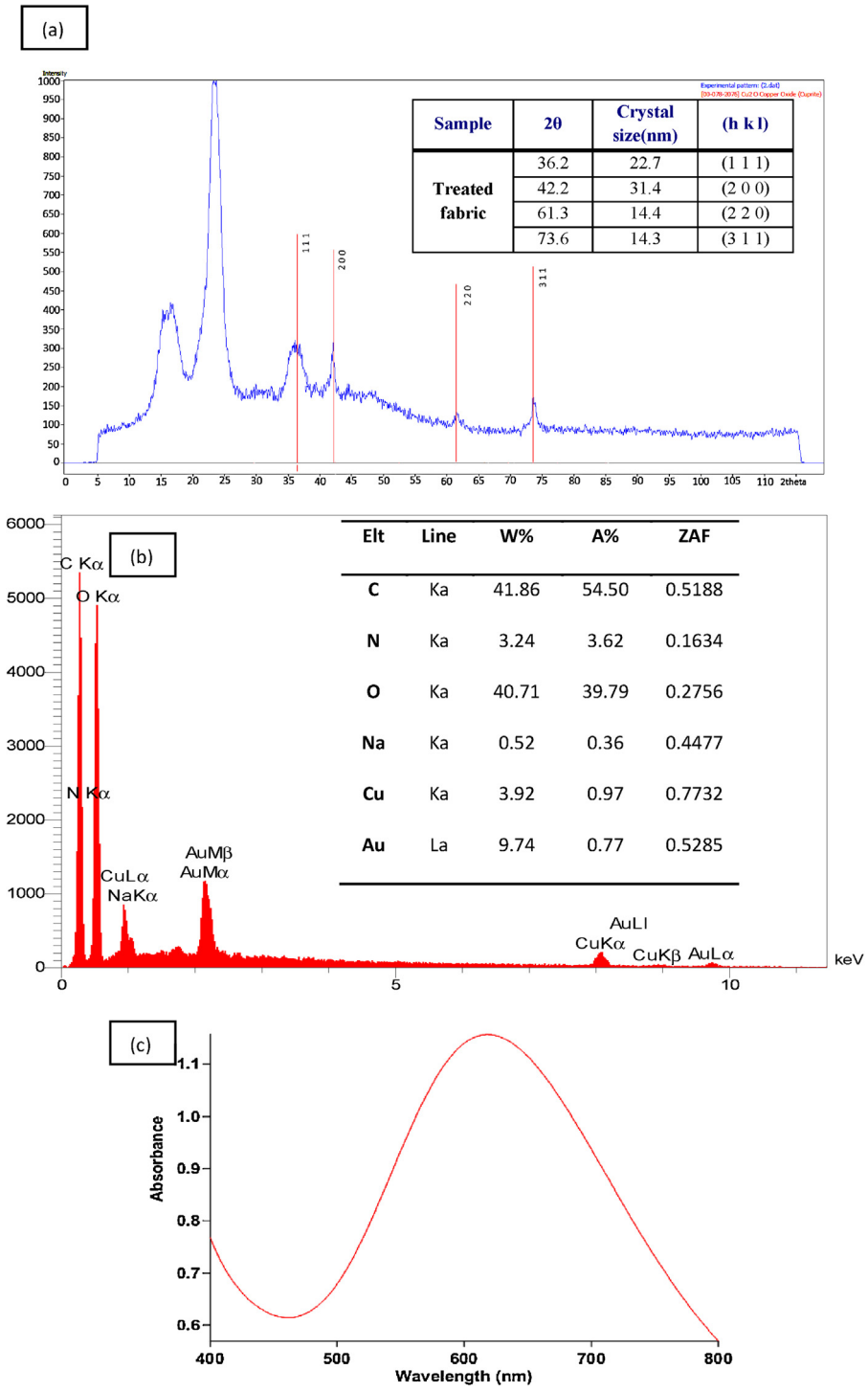

Fig. 2. (a) XRD patterns of cuprous oxide nanoparticles on cotton fabric and crystal size of nanoparticles. (b) EDX spectrum of cotton/nano Cu_2O composite. (c) UV–vis absorbance of cuprous oxide/ammonia complex solution formed in the bath.

3.3. UV–vis spectra

UV–vis absorbance spectra of cuprous oxide/ammonia complex are shown in Fig. 2c. The complex presents an absorbance maximum at 620 nm (Liorens, Lioret, Picouet, & Fernandez, 2012). A broad peak in the spectra confirms the formation of $[Cu(NH_3)_4]^{2+}$ complex in the solution at final stage of the processing and dissolution of the remaining cuprous oxide and other particles or compounds containing copper.

3.4. SEM images

The morphology and dispersion of cuprous oxide nanoparticles deposited on the fabric surface is illustrated in Fig. 3a. Cotton as a stabilizer is able to retain the size of particles in nano-scale and prevents agglomeration.

Average random particle size of cuprous oxide nanoparticles synthesized on cotton surface was 93 nm. Generally the excessive agglomeration of nanoparticles can be reduced by lowering

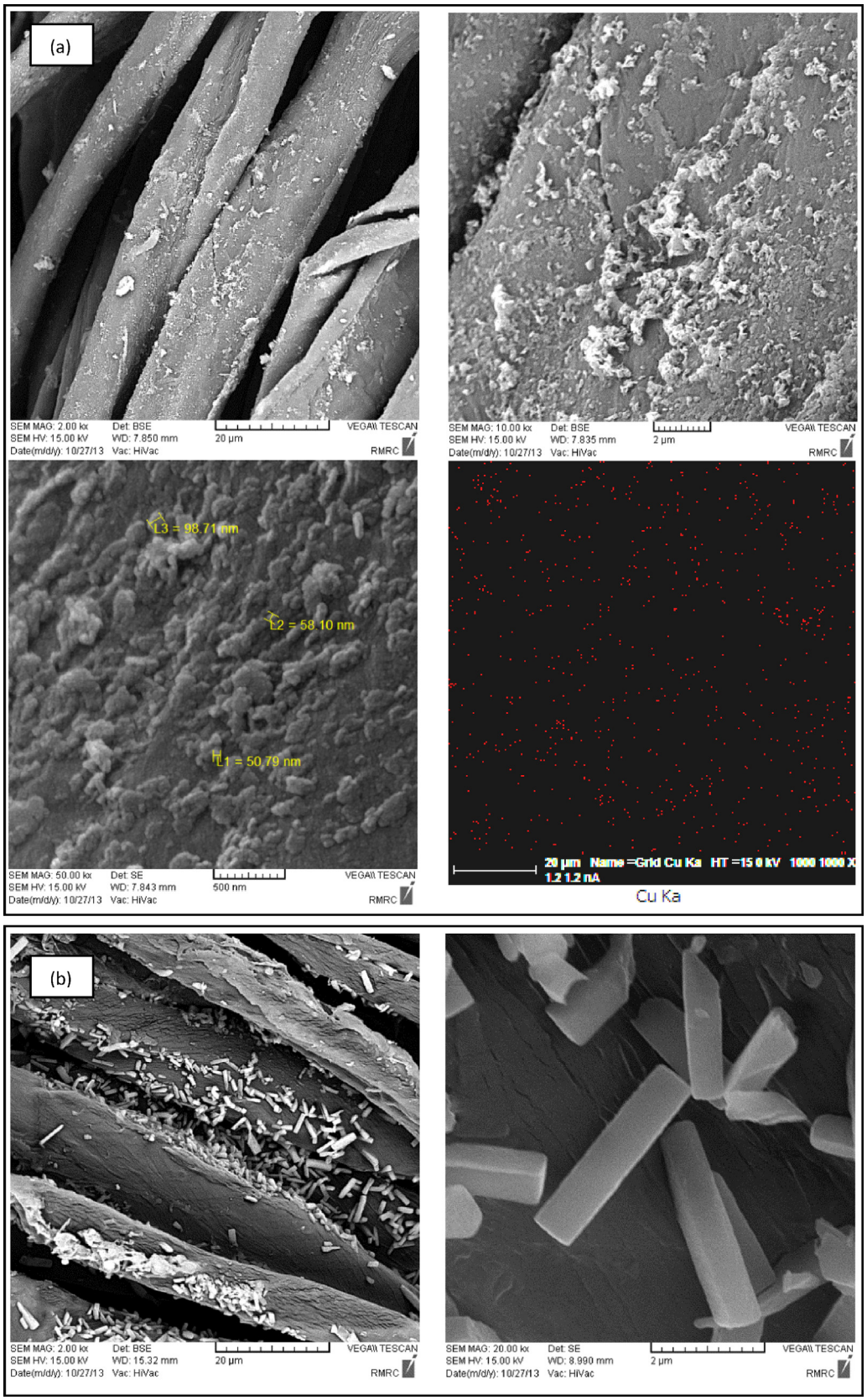

Fig. 3. SEM pictures of cotton fabric containing cuprous oxide nanoparticles synthesized (a) without CTAB, (b) with CTAB.

Table 1
Mechanical properties of cotton fabric containing cuprous oxide nanoparticles.

Fabric sample	Max. load (cN)	Tensile strain (%)	Modulus (gf/tex)	Tenacity (gf/tex)	Tenacity CV%
Raw	249.82	17.86	11219.61	17.732	4.34
Treated	196.44	18.16	10175.99	15.88	9.13

surface energy using stabilizers such as surfactants (Hu et al., 2013). Cetyl trimethyl ammonium bromide (CTAB) as a surfactant stabilizes the growth of nanoparticles nuclei in the solution. Fig. 3b shows the SEM pictures of the synthesized cuprous oxide nanoparticles with CTAB. Rod-like shape particles are loaded on the fabric surface. CTAB usually controls the shape and size of nanoparticles in the solution by electrostatic and steric stabilizing effect (Exerowa et al., 2003). Here, in situ synthesis of cuprous oxide has been carried out on cotton fabric, thus CTAB is not able to cooperate in synthesis process of particles in nanoscale. Cellulosic chains of cotton fabric having numerous active sites act for adsorption of Cu_2O facilitate the nano synthesis by generating nucleation sites. Thus, CTAB as cationic surfactant can be linked with anionic surface of cotton fabric preventing the linkage of Cu_2O nanoparticles to the cellulosic chains of cotton by surrounding nanoparticles and thus reducing creation of Cu_2O nuclei. As a result, the action of CTAB here was different from its usual action in synthesis of nanoparticles in the solution. This does not help to reduce the particle size and contributes to synthesis cubic microparticles.

3.5. Water droplet adsorption time

The hydrophobicity of the treated cotton fabric was compared with raw fabric through measuring the time of water droplet adsorption on the fabric surface. The average time of water droplet adsorption on the raw and treated fabrics was 17 s and 2248 s, respectively. The hydrophilicity of raw fabric is much higher than treated one. Cu_2O hydrogen bonding with hydroxyl groups of cellulose reduced hydrophilic properties of fabric. Substitution of easily accessible surface hydroxyl groups by amine groups on the fabric surface, reduced the fabric hydrophilicity due to lower hydrophilic properties of $-NH_2$ compared with –OH groups (Gourianova, Willenbacher, & Kutschera, 2005). The wettability decreased drastically while the hydrophobicity of the treated cotton surface highly increased confirmed the chemical changes occurred at the fabric surface and changed the surface characteristics to more hydrophobic. Also, the presence of cuprous oxide clusters and their agglomeration do not allow water to penetrate easily into the fabric.

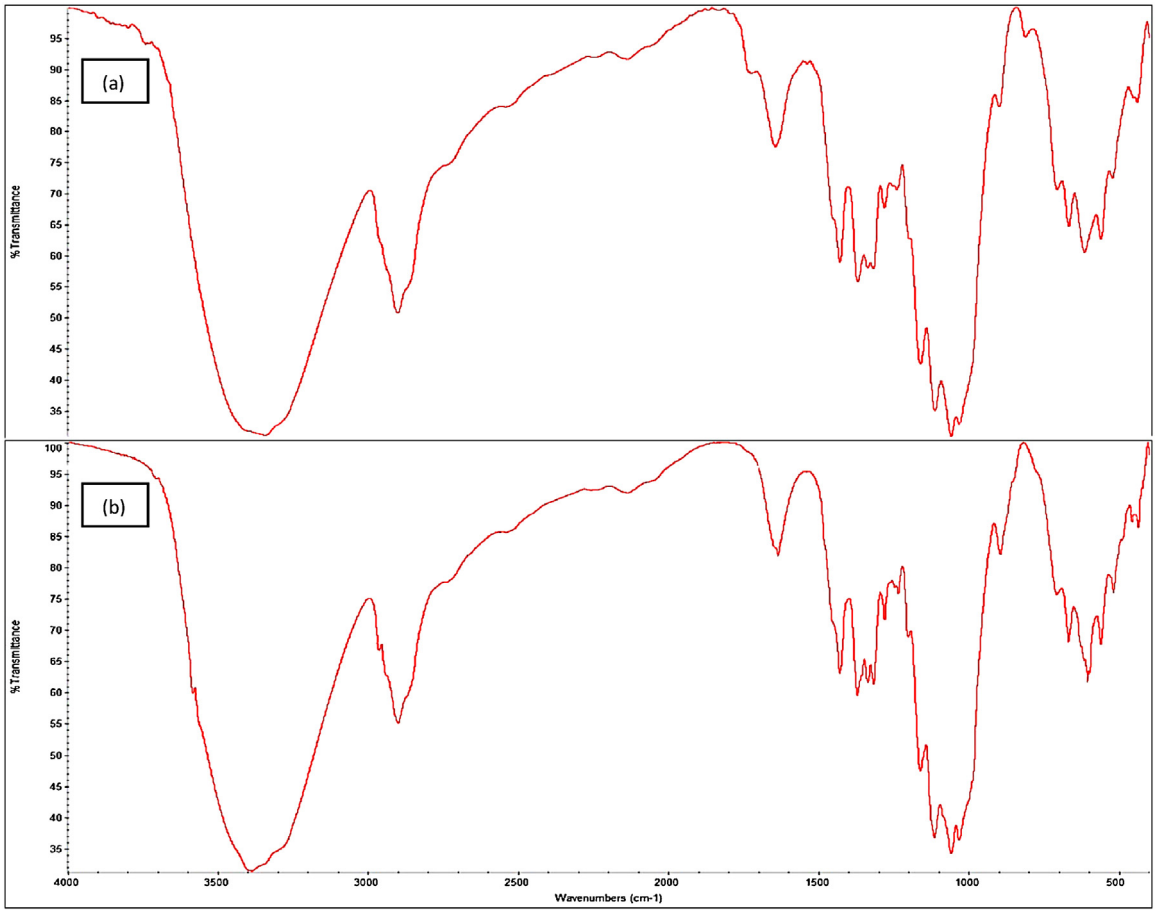

Fig. 4. FTIR spectra of (a) raw cotton (b) cotton/nanocuprous oxide composite.

3.6. Mechanical properties

Table 1 shows the mechanical behaviors of pure cotton fabric and cotton/nano Cu_2O composite. Introduing Cu_2O nanoparticles on the fabric leads to lower tensile strength and Young's modulus. Since the crystalline of cellulose is subjected to change and dissolution by forming copper-amine complex, tensile strength reduction is one of the possible consequences of the treatment. This can also be attributed to lower cross-linking and hydrogen bonding between cellulosic chains in fibers. This possibly relates to the reduction of cotton hydrogen bonding or crystalline structure through exposure to alkaline solution (Yang et al., 2012).

The elongation at break of cotton/nano Cu_2O composite was higher than raw fabric due to the higher frictional force of fibers. Breaking of the chains and slight dissolution of the crystalline of cellulose possibly leads to higher tensile strain. Placing cuprous oxide nanoparticles between cellulosic fibers reduced the hydrogen bonding between functional groups of cellulosic chains led to freedom of cellulosic chains movement.

3.7. FTIR

FTIR analysis was performed to reveal the reactive site during in situ synthesis and examine the interaction between Cu_2O nanoparticles and cotton fabric. The FTIR spectra of raw cotton and cotton/nano Cu_2O composite are presented in Fig. 4. A weak band at 458 cm^{-1} is assigned to the metal-oxygen vibrational bond (Nakamoto, 1978). The peak at 606 cm^{-1} is related to Cu(I)–O vibration of Cu_2O nanoparticles (Gopalakrishnan, Ramesh, Ragunathan, & Thamilselvan, 2012). Two weak new peaks at 1204 cm^{-1} and 1236 cm^{-1} in treated fabric spectrum corresponds to C–O vibration of cellulose that was changed after treatment (Ghule, Ghule, Chen, & Ling, 2006) and 1336 cm^{-1} (symmetric) indicates the presence of carboxylate ions ($-COO^-$) responsible for reducing Cu^{2+} (Gopalakrishnan et al., 2012). The peak at 1645 cm^{-1} arises from the absorbed water of cellulose fibers (Yang et al., 2012; Ghule et al., 2006), attributed to –OH deformation vibration that moved to lower wavenumbers (1638 cm^{-1}) (Yang et al., 2012).

The band at 1735 cm^{-1} in raw cotton fabric is characteristic of C=O stretching bond (Hu, Chen, Xu, & Wang, 2011). The weak band at 2901 cm^{-1} is assigned to C–H stretching vibration of cellulose (Ghule et al., 2006). The strong band at 3349 cm^{-1} is corresponding to stretching vibrations of hydroxyl groups of cellulose transferred to higher wavenumbers (3388 cm^{-1}) (Ghule et al., 2006; Yang et al., 2012). The hydroxyl groups are the active site during synthesis processing and produce a strong interaction between the cotton and Cu_2O nanoparticles. Also, Ghule et al. (2006) reported the weak peak at 3587 cm^{-1} related to hydroxyl functional groups which are occupied with Cu_2O nanoparticles.

3.8. Antibacterial activity

3.8.1. Qualitative method

The antibacterial properties of raw cotton fabric and cotton/nano Cu_2O composite were examined against both Gram-negative and Gram-positive bacteria using disc diffusion method (zone of inhibition test). The hale size of treated fabric is 45 mm against *S. aureus* while 18 mm against *E. coli* (Fig. 5). The raw fabric showed no zone of inhibition. Cu_2O nanoparticles exhibited efficient antibacterial activity due to their large surface area which leads to better contact with microorganisms (Abboud et al., 2013). Nanoparticles provide higher environmental mobility and improve disinfecting effect by interacting closely with bacteria membranes (Longano et al., 2012). Copper and copper oxides generate reactive hydroxyl radicals oxidize proteins, cleavage DNA and RNA molecules and damage membrane due to oxidation of lipid (Pena, Koch, & Thiele, 1998). Copper ions inside bacteria cells also disrupt biochemical processes (Kim, Cho, Ryu, & Choi, 2000). Also, oxygen free-radical created from excited electrons of Cu_2O particles surface are powerful oxidizing agents, break the cell wall of microorganisms through oxidation–reduction reactions (Samal, Jeyaraman, & Vishwakarma, 2010).

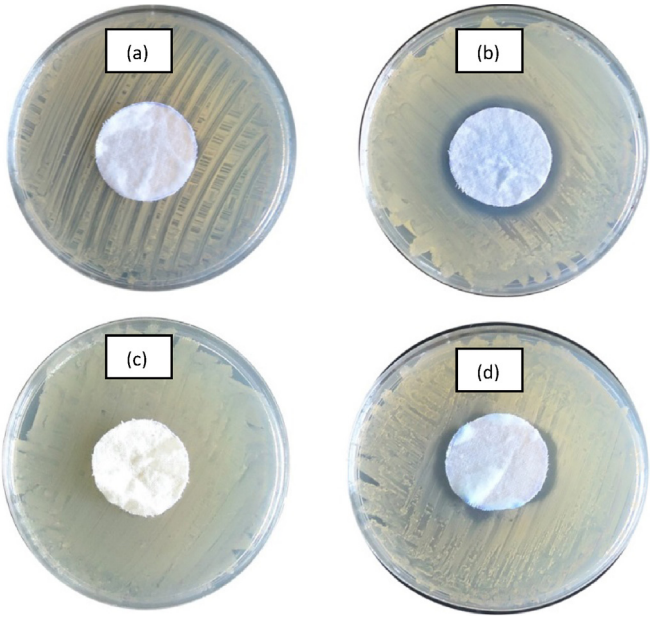

Fig. 5. Zone of inhibition of (a) raw cotton fabric, (b) cotton containing Cu_2O nanoparticles against *S. aureus* and (c) raw cotton fabric, (d) cotton containing Cu_2O nanoparticles against *E. coli* after 24 h.

The disc diffusion result depends on the releasing capability and ion-exchange properties of polymer containing Cu_2O nanoparticles. Utilizing cellulosic fabric as a substrate and stabilizer provides better control over ion release properties of Cu_2O nanoparticles, especially in interaction with cellulose fibers (Anyaogu, Fedorov, & Neckers, 2008).

3.8.2. Quantitative method

The results of quantitative antibacterial activity of cotton/nano Cu_2O composite test through counting the number of bacteria colonies shows 89% and 100% antibacterial reduction against *S. aureus* and 67% and 90% against *E. coli* for 0 and 2 h exposure, respectively.

E. coli bacteria are more resistant to Cu_2O nanoparticles than *S. aureus* bacteria. The results of qualitative and quantitative antibacterial test methods are similar and in agreement with earlier studies claimed Cu_2O nanoparticles have better anti-bacterial behavior against Gram-positive bacteria (Zarrindokht & Chehrazi, 2011).

Gopalakrishnan et al. (2012) suggested a possible mechanism for Cu_2O nanoparticles effect on *E. coli* bacteria. When Cu_2O nanoparticles are absorbed on the cell surface, impair the cell wall and damage the membrane. The permeability of the membrane increased and as a result the viability of the bacteria decreased in the Cu_2O solution (Gopalakrishnan et al., 2012). Hrenovic, Milenkovic, Daneu, Kepcija, and Rajic (2012) reported Cu_2O strong antibacterial and antibiotic activity against *S. aureus*.

3.9. Washing fastness

Treated fabric was subjected to 0, 10, 20 and 30 wash cycles and antibacterial activities of sample on Gram-negative and Gram-positive bacteria were investigated after 2 h exposure. The results exhibit that increasing washing cycles insignificantly decrease the

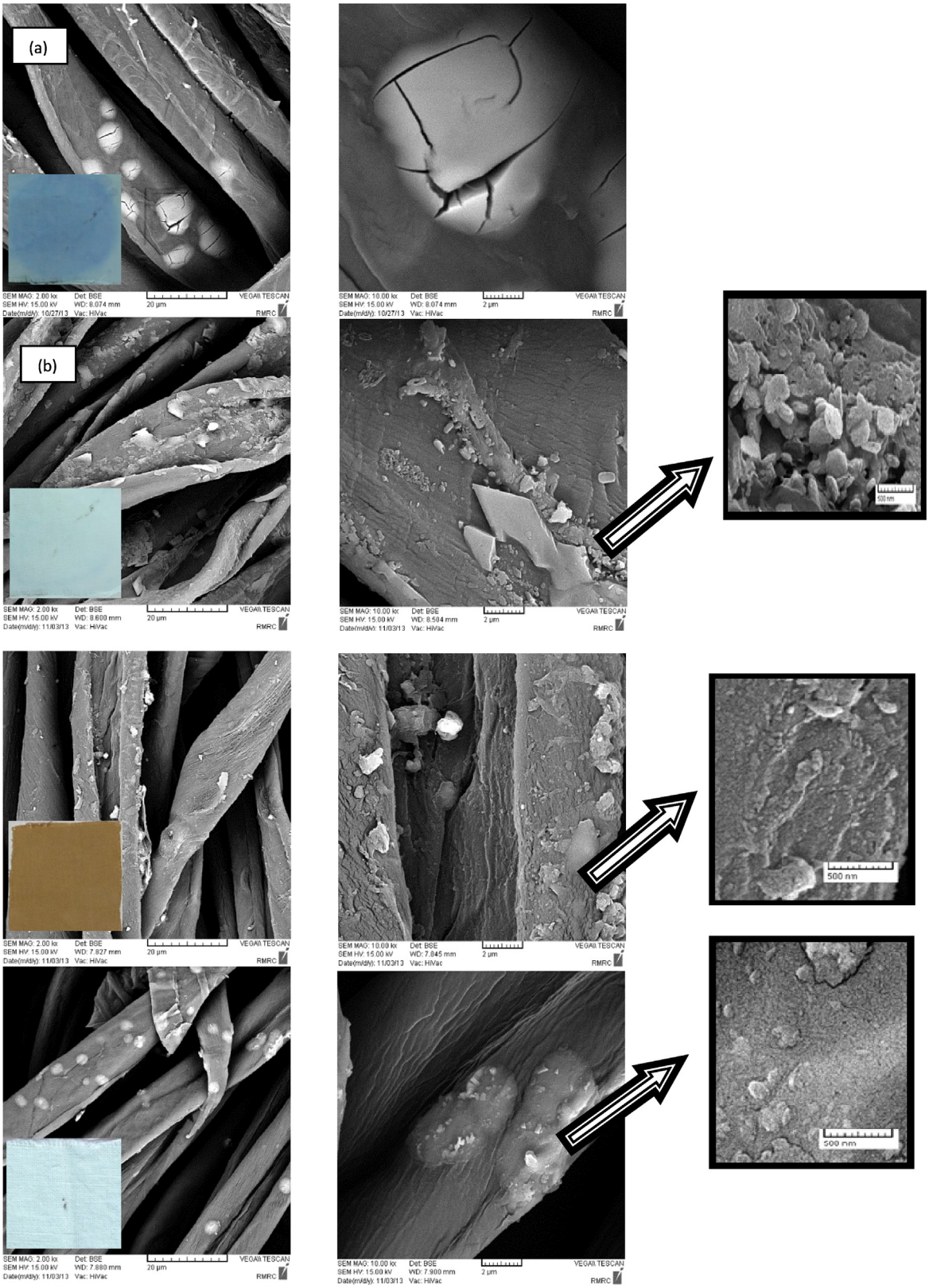

Fig. 6. (a) Cotton/nanoCu_2O composite exposed to ammonia, (b) after reduction with acetic acid. (c) cotton/nanoCu_2O composite exposed to H_2O_2, (d) after reduction with acetic acid

bacteria reduction percentages by cotton/nano Cu_2O composite (Table 2).

Reduction of Cu_2O on the fabric is due to the release of copper ions in washing solutions through removal of Cu_2O nanoparticles attached to the fibers with weak physical bonding. The good antibacterial activity after 20 or 30 cycles of washing proved strong durability of treated fabric due to chemical interaction of cuprous oxide nanoparticles to the fabric.

Table 2
Antibacterial reduction percentages of cotton/nano cuprous oxide composite.

Washing cycles (No.)	0		10		20		30	
Bacteria	*E. coli*	*S. aureus*	*E. coli*	*S. aureus*	*E. coli*	*S. aureus*	*E. coli*	*S. aureus*
Treated fabric	89.9	99.9	80.0	93.8	69.4	90.7	64.6	82.5

3.10. Sensing ammonia and hydrogen peroxide

Cotton/nano Cu_2O composite is an optical sensor. It needs no electrical contact with ability of ammonia gas detection. Ammonia has many applications in chemical industry to produce fertilizers or refrigeration systems (Umar & Hahn, 2010). There is a requirement to detect the chemical substances in many areas including medicine, environmental monitoring, biotechnology, drug and food monitoring, airborne and military biological and chemical agent testing and biological production process monitoring (Umar & Hahn, 2010).

Sensing ability of Cu_2O/cotton composite is due to the short contact with ammonia gas (less than 1 s) changing the fabric color from green to blue. Cu_2O nanoparticles on the cellulose surface interact with ammonia gas as shown in reaction 7 (Lin, Zhou, Zhang, & Sheng, 2010).

$$Cu_2O + 4NH_3{\cdot}H_2O \rightarrow 2[Cu(NH_3)_2]^+ + 2OH^- + 3H_2O \quad (7)$$

$[Cu(NH3)_2]^+$complex is not stable and easily oxidized to $[Cu(NH_3)_4]^{2+}$ as illustrated in reaction 8 (Lin et al., 2010).

$$2[Cu(NH_3)_2]^+ + 4NH_3{\cdot}H_2O + 0.5O_2 \rightarrow 2[Cu(NH_3)_4]^{2+} + 2OH^- + H_2O \quad (8)$$

Fig. 6a shows SEM picture of cotton/nano Cu_2O composite after exposure to ammonia. Ammonia dissolves Cu_2O nanoparticles producing a layer of copper-amine complexes on the fabric surface. Also, the cracks formed on the fiber surface where copper-amine complexes are deposited indicates the influence of the compound on cellulose dissolution and crystalline reduction.

The composite returns back to its primary green color gradually as cotton fabric reduces Cu^{2+} ions to Cu^+ and the complex disappears by exposure of the fabric to air over the time.

The reduction process can be accelerated to seconds by exposure of the fabric to an organic acid such as acetic acid as mentioned in reaction 9 (Prakash, 2005).

$$[Cu(NH_3)_4]^{2+} + 4CH_3COOH \rightarrow Cu^{2+} + 4CH_3COONH_4 \quad (9)$$

Fig. 6b suggests that acetic acid returns the formed complexes to Cu_2O particles. However, fast reduction of nanoparticles by acid led to deposition of irregular and non-uniform particles with various particle sizes on the fabric surface. Further, the particles still remained in both nano-size and micro-scale that can be seen on the fabric surface.

Cotton/nano Cu_2O composite has been investigated as sensitive material for detection of hydrogen peroxide. H_2O_2 is a strong oxidant which interacts with Cu_2O as shown in reaction 10 (Patra & Munichandraiah, 2009).

$$Cu_2O + H_2O_2 \rightarrow 2CuO + H_2O \quad (10)$$

As a result, the original green color of cotton/nano Cu_2O composite turns to brown as illustrated in Fig. 6c. Interaction of cotton/nano Cu_2O composite with H_2O_2 is considered in Fig. 6c. CuO particles were oxidized instantly and uneven particles with different shapes and size formed (often larger than nanometric scale) due to their rapid formation upon exposure to strong oxidant.

The brown colored fabric has never been turned to the prime state when contacted with air, however acetic acid as a reducing agent changes the fabric color as mentioned in reaction 11 (Lewis, 2001).

$$CuO + 2CH_3COOH \rightarrow Cu^{2+} + 2CH_3COO^- + H_2O \quad (11)$$

Produced Cu^{2+} ions on cellulosic fabric reduced to Cu^+ ions and Cu_2O was then formed during exposure to the air (Fig. 6d).

4. Conclusion

Cotton fabric was acted as both reducing agent and stabilizer and successfully synthesized cuprous oxide nanoparticles on its surface. Presence of sodium hydroxide contributes to swelling of cotton fabric and destroys the intermolecular hydrogen bonds, helps easily penetration of the nanoparticles into the fabric. On the other hand, formation of Na-cellulose increases the affinity of positive-charge cuprous oxide ions to negative-charge cotton fiber surface. Also, ammonia forms copper-amine complex increases cuprous oxide exhaustion on the fabric. XRD pattern confirmed synthesis of crystalline cubic Cu_2O nanoparticles with 28 nm crystal size. Moreover, EDX results confirmed presence of copper and nitrogen on the fabric surface. Further, SEM pictures showed nanoparticles distribution on the fabric. The extreme hydroxyl functional groups of cotton acted as nucleation sites prevented nanoparticles from agglomeration and adjusted the size of particles in nano-scale. The hydrophobicity of the treated cotton fabric is much higher than raw fabric due to possible hydrogen bonding of Cu_2O with hydroxyl groups of cellulose. Lower tensile strength and higher tensile strain are also some of the results of introducing Cu_2O nanoparticles to the fabric.The antibacterial behavior of cotton/nano Cu_2O composite is determined remarkable against both Gram-negative and Gram-positive bacteria through disc diffusion test and quantitative method. However, Cu_2O nanoparticles shows higher antibacterial activity against Gram-positive bacteria. On the other hand, durability of treated fabric is fair due to chemical interaction between fabric and nanoparticles. Cotton/nano Cu_2O composite also indicates good reversible behavior and stability as nano optical sensor for detection of ammonia gas and H_2O_2.

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