Synthesis of Copper Nanoparticles on Cellulosic Fabrics and Evaluation of their Multifunctional Performances

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Research Article

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Abstract

Two different kinds of copper nanoparticles (CuNPs) (brown colour and greenish colour) were synthesised by using simple solution route and applied on cotton by exhaust method to achieve multidimensional functionalization on one of the most popular cellulose materials e.g., cotton fabric. The synthesised CuNPs imparted different colours to cotton textile due to different conditions of synthesis and localized surface plasmon resonance. Physico-chemical characterizations of the synthesized nanoparticles were performed by using scanning electron microscope (SEM) and EDX analysis whereas the optical properties of the nanoparticles were studied using UV-visible spectroscopy. The prepared CuNPs of both the types demonstrated very good antimicrobial activity up to 97%. In addition, cotton fabric treated with CuNPs showed very high catalytic activity for reduction of 4-nitroaniline in presence of sodium borohydride to phenylene diamine. Washing durability and rubbing fastness of the treated fabric have also been measured by following standard testing methods and found to be very good with a rating 4.

Introduction

Recent advancement in nanomaterials plays a major role in science and technology. Nanomaterials have been used in various applications such as sensor, catalyst, energy storage, energy harvesting and many more (Sharma et al. 2016; Chawla et al. 2017; Bairagi et al. 2019, Bairagi et al. 2020, Bairagi et al. 2020, Bairagi et al. 2020;). Numerous techniques have been used in the recent past to apply nanomaterials on different natural substrate for useful value addition. Treatment and functionalization of cotton with natural material and application of nanomaterial to textile attracted extensive attention, with the aim of imparting various functional properties such as flame retardancy using bulk as well as nanomaterial (Shukla et al.2019; Alongi et al. 2014; Alongi and Malucelli et al 2015; Sharma et al.2018; Durani et al 2020), hydrophobicity (Leng et al. 2009), ultra-violet-protection (Dhineshbabu et al. 2016; Shaheen et al. 2016) and antimicrobial (Sedighi et al. 2014; El-Shishtawy et al. 2011; Mohamed et al. 2017) properties. Different methods of application have been developed to achieve different functionalities by exploring different nanoparticles. Among them, electrostatic assembly, chelation by active groups, plasma treatment and in situ synthesis are most common and much explored process route for generation or synthesis of nanoparticles (Alongi et al. 2014; Cady et al. 2011; Dong and Hinestroza et al. 2009; Gorjanc et al. 2010; Tang et al.2012, 2013).

Among the mostly available and explored nanoparticles, copper nanoparticles (CuNPs) attract more attention due to their low production costs and they are free from toxicity. Copper complexes and metallic copper have been used from centuries in various processes such as disinfection of liquid, solid, and human tissues, etc. (Perelshtein et al. 2013). Copper based materials have been used in heat transfer systems (Eastman et al. 2001) as antimicrobial agents (Esteban-Cubillo et al. 2006; Cioffi et al. 2005a, b), sensors (Kang et al. 2007; Male et al. 2004; Xu et al. 2006), as an excellent-resistant material (Wang et al. 2002; Kang et al. 2007) and as catalysts. Recently, various types of nanoparticles have been applied on the fabric to impart multifunctionalities on cellulose (like catalyst, antimicrobial, coloration, self-cleaning, ultraviolet ray protection, etc.). In the same way, cellulosic materials also attract more attention for the application of nanoparticles due to their exceptional biocompatibility, no or low toxicity, and potential biological activities (Mary et al. 2009). Various scientific techniques have been reported on the synthesis route of copper nanoparticles including gas-phase evaporation, vacuum vapor deposition, chemical–mechanical, hydrothermal radiation, ultrasonic, reverse microemulsion, electrolysis, electron beam irradiation, sol–gel, and mostly used chemical reduction methods, (Cheng et al. 2006) etc. As per report, chemical reduction technique used for the synthesis of nanoparticles has certain advantages of tuning the process parameters such as the pH, temperature, stabilizing agent, reducing agent, and solvent quantity. As a result, particle size of the synthesized material can be controlled in a proper manner and also the process provides a grip for addressing the aggregation challenge of nuclei (Wang and Gao et al. 2007). ZnO nanoparticles were used in organic Knoevenagel reaction in coumarins synthesis as a single pot green synthesis (Vinay et al.2011) whereas silver nanoparticles were used as catalyst in reduction, coupling and various aspects in synthesis of a variety of fine chemicals (Dong et al.2015). So, nanoparticles are also gaining a lot of interest in synthesis and transformation of various organic moieties as emerging field.

In present method, CuNPs were synthesised and applied on commodity cotton textile by using exhaust process. On the other hand, copper salt used for the nanoparticle formation is cheaper (as compared to silver and gold salt) and thus the entire process is an affordable and sustainable approach for value added product development. Nanoparticles like $Ni/ZnSn(OH)_{6,}$ Nickel/Zinc hydroxy stannate were used for reduction of 4 nitroaniline to phenylene diamine (Mohamed et al. 2014) but the concerned nanoparticles are quite expensive and have adequate effect on environment. Contrary, CuNPs play a major role in electro catalysis of p-nitro aniline and reduces 4 NA efficiently to 4 PD. Two types of copper nanoparticles were synthesised in the present study and both have showed remarkable efficiency to reduce 4 NA. This may be due to smaller size of the synthesized CuNPs which exhibit large surface area for the catalysis and render higher catalytic activity than other ones. Synthesized CuNPs also have showed very good antimicrobial activity, good coloration on cotton textiles having wonderful washing and rubbing fastness properties.

Experimental

Materials

Copper sulphate ($CuSO_4.5H_2O$), phenylene diamine, sodium hydroxide (NaOH, Assay-98%), 4-nitroaniline, and sodium borohydride ($NaBH_4$ 98%) were purchased from Merck, India. All chemicals used for the experimental purposes were of analytic-grade reagents and further purification was not required. Entire study was carried out on pure cotton cellulosic fabric of density of 118 g/m^2. Deionised water was used throughout the process.

Synthesis Of Cunps On Cotton Fabric

Synthesis of CuNPs on cotton fabrics was done by using direct solution route. Two types of CuNPs were prepared separately by addition of 240 mg of disodium citrate, 0.01 molar solution of sodium borohydride to 100 ml 0.01 molar solution of copper sulphate in continuous stirring in one formulation and in second formulation additional 150 mg of sodium hydroxide was added before addition of sodium borohydride solution. Disodium citrate was used as capping agent in both the cases, otherwise the synthesized CuNPs became agglomerated very fast and precipitated out. Afterwards, two pieces of cotton fabric (25 cm*15 cm) were dipped into two formulations separately with a continuous stirring at 30^0C for 10 min. After that, the temperature of the reaction mass was increased to 80-90^0C for 30 min. Two types of colours were found to be developed on the fabric; one was light brown wherein there was no content of NaOH and second one was greenish copper nanoparticles where NaOH was added. The treated fabrics were rinsed with running deionized water twice and dried at room temperature. Thereafter the treated materials were finally dried further at oven at 100^0C for 2 hrs. Samples obtained were named as Cot-Cu-1 (brown colour, without addition of NaOH) and Cot-Cu-2. (greenish brown colour, with addition of NaOH). Copper nanoparticles (CuNPs) were synthesized by reduction of copper sulphate solution using sodium borohydride solution wherein sodium borohydride acts as reducing agent. In case of gold nanoparticles, cellulose itself acts as reducing agent (Bin Tang 2017). It was also observed that at basic pH, particles size of formed copper nanoparticles also gets decreased because sodium hydroxide itself acts as stabilizing agent. Light brown particles were formed when only sodium borohydride was used, while greenish coloured nanoparticles were formed when sodium borohydride was used in presence of sodium hydroxide at basic pH which is supported by SEM data.

Functional Group Analysis Of The Fabric Treated With Cunps

Functional group analysis of treated and untreated sample was accomplished using a Fourier Transform IR spectroscopy (Thermofisher Scientific instrument, Model: Nicolet is50 FTIR). The samples were scanned in the range of 500 to 4500 cm^{-1} wave number.

Surface Morphology Of Nanoparticles And Treated Cotton Fabric

The surface morphology of CuNPs prepared by both the routes and the treated cellulosic fabric with these nanoparticles was investigated by scanning electron microscope (SEM) (made by ZEISS EVO).

Colourfastness To Washing

Washing fastness of the treated fabric samples was analysed in accordance with standard test. Cotton fabrics treated with CuNPs were washed at 50°C for 45 min in presence of ECE reference detergent (4 gL^{-1}) using a Launder-o-meter. Gregteg Color i7 7000 spectrophotometer was used to record the values of lab colour coordinates (L*, a*, and b*) for the CuNPs treated samples before and after washing where L* represents the lightness/darkness, a* value corresponds to the red or green chroma, and b* corresponds the chromaticity coordinate for yellow/blue.

Colourfastness To Rubbing

Rubbing fastness of CuNPs incorporated fabrics was analysed as per standard (AS 2001.4.15–2006). Fabric treated with CuNPs was rubbed using a ready for dyeing (RFD) cotton cloth. Grey scale was used to evaluate the staining on RFD cotton cloth.

Catalytic Activity

Catalytic activity of the CuNPs treated cotton fabric was analysed by monitoring the conversion of 4-nitroaniline (4-NA) to 4-phenylene diamine (4-PD) in presence of $NaBH_4$. Catalytic activity was performed in presence of untreated and treated fabric by using Shimadzu 2450 UV spectrophotometer. In a typical experiment, 2.0 mL NaBH4 solution (3.0 M) was added into 30 mL 4-NA aqueous solution (0.025 mM). Subsequently, 30 mg cotton fabric (Control cotton, Cot-Cu-1 to Cot-Cu-2) was added into the mixed solution of 4-NA and $NaBH_4$ under vigorous stirring. UV–Vis absorption spectra were monitored during the conversion of 4-NP to 4-PD. Catalytic efficiency of treated fabrics was analysed using UV-Vis spectrophotometer.

Tensile Strength Of The Fabric

ASTM D5034, grab test method was used to evaluate the tensile strength of control and copper treated cotton fabrics using tensile testing machine (Tinius Olsen, Model: H5KS). Treated and untreated samples of dimension 200 mm*50 mm were analysed at a speed of 300 mm/min.

Evaluation Of Antimicrobial Activity

Antimicrobial activity of copper treated cotton samples was tested using standard colony counting method (AATCC 100). Digital colony counter was used to calculate the number of colonies of control and treated cotton fabrics and bacterial cell reduction (BCR) was calculated by using following formula:

BCR %= (No. of colonies in untreated sample - No. of colonies in treated sample) / No. of colonies in untreated sample

Results And Discussion

FTIR analysis

FTIR spectra of raw and treated cotton fabric with copper nanoparticles were analysed. It was observed from the curve that some new peaks have been formed in the FTIR curve of the treated fabric, at about 1500 to 1700 cm^{-1}. This phenomenon has been occurred may be because of the oxidation of cellulose due to reduction of copper ion. Cu nanoparticles treated cotton fabric (Cot-Cu-2) in presence of sodium hydroxide, shows less intense peak near this region. Tensile strength also follows the same order as strength got decreased due to oxidation of the treated cotton while the strength loss is even more in absence of sodium hydroxide. This observation substantiates that Cu nanoparticles get attached to cellulosic structure physically as well as chemically. Stretching observed around 1500–1700 cm^{-1} in the treated samples is due to oxidation of cellulose whereas OH stretching was observed in all three samples in region of 3,200–3,500 cm^{-1} (Sedighi et.al 2014.)

Surface Morphology Of Copper Nanoparticles And Treated Fabric

Synthesis of CuNPs on cotton fabric was performed by using direct solution route. As mentioned earlier, two types of CuNPs (cu nanoparticles) were prepared by addition of 100 mg of disodium citrate, 0.01 M solution of sodium borohydride to 100 ml 0.01 m solution of copper sulphate in continuous stirring in one formulation and in second formulation additional 100 mg of sodium hydroxide was added. Disodium citrate was used as capping agent for restricting the agglomeration or precipitation of synthesised nanoparticles. Thereafter, two pieces of cotton fabric were added to above mentioned formulation with continuous stirring at to 30°C for 10 min. Thereafter, the reaction mass was heated to 80°C for 30 min. At the end, the CuNPs (copper nanoparticles) treated fabrics were washed with running deionized water twice and dried at 30°C temperature for 10 min. Further the treated fabric was dried at oven at 100°C for 2 hrs and samples obtained by following the method was Cot-Cu-1 and Cot-Cu-2. Average particle size of 400 nm was found to be formed on Cu-1 samples while average dimension of 300 nm particles was formed when sodium hydroxide was used which is mainly responsible for fast reduction of p nitro amine to p-phenylene diamine.

From the surface morphology analysis, the uniform covering of the fabric surface by in-situ formation of nanoparticles was observed as depicted in Fig. 3. SEM figure clearly shows the uniform coating on both the treated fabrics with copper nanoparticles.

The cotton fabric treated in first formulation (Cot-Cu-1) was light brown and in second formulation (Cot-Cu-2) was greenish, implying presence of CuNPs on the cotton fabric. The colour of the cotton fabric treated with CuNPs (Cot-Cu-2) has been changed from light brown to red to dark greenish brown as the sodium hydroxide was added to second formulation.

Edx Analysis Of The Treated Sample

Elemental analysis of both the treated samples was done using EDX analysis. It was observed that copper content gets increased on the fabric which was treated at basic pH. This may be due to more swelling of the treated cotton at basic pH which helps to penetrate more copper nanoparticles inside the cotton fabric and supports faster reduction in Cot-Cu-2 sample than Cot-Cu-1 sample. Copper nanoparticles percentage was 1 in Cot-Cu-1 sample and 3% in Cot-Cu-2 when applied at basic (pH 11) pH using sodium hydroxide. SEM EDX image also shows smaller particles in Cot-Cu-2 image than Cot-Cu-1 image in single thread which also justifies SEM analysis of the formed particles.

Influence Of Ph Value

The original pH value of the $CuSO_4$ aqueous solution at 0.01M was around 2.8. It has been investigated that pH plays an important role in the formation of copper nanoparticles as without sodium hydroxide treated sample showed more strength loss than the sample treated in presence of sodium hydroxide. The pH value of the reaction systems of Cot-Cu-1 was around 2.8 as such and the Cot-Cu-2 was 11 by addition NaOH aqueous solution. Two different colours have been generated after addition of sodium borohydride solution to above solutions due to the formation of different size nanoparticles.

Assessment Of Colourfastness Of The Copper Treated Cotton

Colourfastness is one of the important aspects to assess the properties and performance of the textile products. Cot-Cu-1 and Cot-Cu-2, both the treated fabric samples were tested for colourfastness to washing. Treated samples were washed by using Lissapol N detergent at 50°C for 45 min. L, a*, b*, c*and h* values of the treated fabric were measured before and after washing and the concerned data is represented in Table 1. Value obtained after wash clearly demonstrates that both the cotton fabrics coloured with CuNPs possess reasonably good colourfastness to washing. Treated fabrics also were examined for colour fastness to rubbing. The grey scale rating was used to demonstrate the DE values of Cot-Cu-1, Cot-Cu-2, under dry and wet rubbing conditions. The dry rubbing colour fastness was rated as 4 for both the treated fabrics whereas wet rubbing data for Cot-Cu-1 and Cot-Cu-2 are 3 and 3.5, respectively. Therefore, from the fastness data it could be confirmed that the copper treated fabrics retain copper particles even after laundering and rubbing.

Table 1
Color value of the treated and washed cotton fabric

Sr No		L	a*	b*	c*	H
1	Pure Cotton	81.78	-0.11	2.85	2.85	92.27
2	Cot-Cu-1	71.41	1.26	9.67	9.75	82.59
3	Cot-Cu-2	38.44	-0.33	5.45	5.56	93.45
4	Cot-Cu-1 after wash	77.13	1.69	7.07	7.27	76.53
5	Cot-Cu-2 after wash	41.26	-0.34	5.33	5.34	93.63

Investigation Of Catalytic Activity Of The Treated Fabric

Metal and metal oxide nanoparticles have widely been used as catalyst in various applications from long back (Sharma et al. 2017). Metals have been used as reducing agent and its oxide have been exploited as oxidising agent (Sharma et al. 2017). Recently, silver (Ag), gold (Au) nanoparticles have been widely used by the researchers as catalyst in various organic reactions (El Shistawy et al. 2010, Tang et al. 2017). In the present research, CuNPs are bound to cotton fabrics after their synthesis at higher temperature and for the first time it has been used in the reduction of p-nitroaniline to p-PD as a model reaction, depicted in Fig. 4. UV absorption of standard 4NP and 4PD was also recorded. From the experimental analysis, it was clear that 4PD and 4NA absorb at different wavelength i.e., 300 and 380 nm. Cellulose acts as support and after reaction CuNPs remain with cellulosic fabric and this copper functionalized cellulosic fabrics were again used for reduction.

CuNPs treated cotton samples showed catalytic activity which was monitored by UV–Vis absorption spectra of aqueous solution during reduction of 4-NP using $NaBH_4$ using a UV-visible spectrophotometer. There was a change in colour of the 4-NP solution from light yellow to brown after reduction. In general nitro compounds are inert to $NaBH_4$ in absence of catalyst. However, metal nanoparticles on cellulose fabric have acted as an electron transfer agent from $NaBH_4$ to nitro compound to accelerate the reduction reaction (Barnes et al. 2003). Absorption peak observed at 300 nm in UV–vis absorption may be assigned with 4-PD and 380 nm in UV-Vis absorption may be denoted for 4-NP. It has also been observed that the absorption peak intensity at 300 nm was increased and peak intensity at 380 nm was decreased during the reaction in presence of the treated fabric. However, peak intensity remains almost same whatever has been observed for only 4-NP in presence of untreated sample. Further, it also has been observed that CuNPs treated sample in presence of sodium hydroxide shows more activity than without sodium hydroxide treated samples.

The absorption peak observed at 380 nm due to 4 nitroaniline was rapidly decreased due to excellent catalytic activities of CuNPs treated cotton fabrics. However, Cot-Cu -2 reduced 4 nitroaniline faster than the Cot-Cu-1 system whereas no reduction was observed in case of control cotton even after 24 hours. 4-

NA reduction is generally considered to be a pseudo-first-order kinetic reaction on account of excess $NaBH_4$ used. (Ai et al. 2012; Tang et al. 2017.

Figure5. UV-Vis spectra of (A) 4-nitroamine, 380 nm, (B) phenylene diamine, 300 nm, (C) (4-nitroamine (380 nm) and phenylene diamine (300 nm), (D) cellulose-Cu-1 nanoparticles used reduction at initial, 1, 3, 5, 10, 20, 30, 45, 60 min, (E) cellulose-Cu-2 nanoparticles at initial, 1, 3, 5 min.

Mechanical Properties Of Treated Cotton Fabric

Physical effect of copper nanoparticle integration on cotton fabrics was analysed by studying the tensile strength of control cotton and treated cellulosic fabrics. Pristine cellulosic fabric showed the tensile strength of around 635 N whereas CuNPs treated cotton fabric showed the tensile strength of around 314 N (Cot-Cu-1) and 614 N (Cot-Cu-2). CuNPs treated samples have adverse effect on the strength of the treated fabric while the treatment has been carried out in absence of sodium hydroxide (Cot-Cu-1 in this case). However, the tensile strength has remained almost same in which the treatment was performed in presence of sodium hydroxide (Cot-Cu-2 in this case). It also has been reported in literature that cellulosic fabric if treatment is done in basic pH, then there should not be any detrimental effect on the fabric properties (Sharma el.at 2018). However, strength falls to remarkable extent is a known phenomenon once the treatment is done in acidic pH. It is obvious that cotton gets degraded at acidic pH due to depolymerisation due to acid attack on chain of cellulose. In our case FTIR analysis also supports the same wherein there is a significant loss in tensile strength due to degradation of cellulosic structure as represented by increased formation of aldehyde groups after the treatment process (in case of Cot-Cu-1).

Antimicrobial Activity Of The Treated Fabrics

It is well known that the cellulosic materials are prone to attack by microorganisms, usually they act as accumulator, spreader, and multiply microorganisms in nearby environment (Dastjerdi and Montazer et al. 2010). It has already been reported in literature that cellulosic fabrics treated with various metal, metal oxide nanoparticles exhibit antibacterial properties (Sedighi et al. 2014.) The results of the antibacterial tests, represented in Table 2, demonstrate the excellent antibacterial efficacy of the cotton fabrics containing copper nanoparticles. Both the treated fabric samples exhibited an efficient antibacterial effect against Gram negative, *E. coli* bacteria. Table 2 represents the reduction of colonies of treated sample [Cu-Cot-1 and Cu-Cot-2] and BCR percentage with respect to control cotton sample.

Table 2
Antimicrobial results of the control and the treated cotton fabrics

Antimicrobial test results against *E. coli* bacteria			
Sr. No	**Sample Description**	**No. of Colonies**	**BCR %**
1	UNTREATED	780	
2	Cot-Cu-1	18	97.69
3	Cot-Cu-2	24	96.92

Antimicrobial activity of metal nanoparticles is a proven phenomenon which occurs in multiple mode as these can penetrate inside the cell wall of bacteria due to its very small size and eventually inhibit the activity of bacteria to multiply. Nano copper showed antibacterial activity due to various aspects as they can adhere to the cell wall of Gram-negative bacteria because of electrostatic force, disturb cell membrane protein structure, accelerate the process of denaturation of protein, etc. (Ali Sedighi 2014).

Conclusions

This research work represents in-situ synthesis of the two types of CuNPs on cotton fabrics. The fabric became coloured by application of the synthesized CuNPs. Two different types of colours (light brown and greenish) were obtained on the treated fabric. Both the fabrics treated with CuNPs showed catalytic activity, as measured by reduction of 4-NA to 4-PD. Greenish coloured cotton fabric showed more catalytic activity toward reduction of 4- nitroaniline. The mechanical property of cotton fabrics treated with CuNPs in absence of sodium hydroxide showed remarkable decrease in tensile strength of fabric treated (in acidic pH), due to degradation of cellulosic structure. Both the treated fabrics showed an excellent antimicrobial efficacy against *E. coli* bacteria. SEM investigations showed homogeneous distribution of CuNPs on cotton fabric. The treated fabric also demonstrated good rubbing and colour fastness properties.

Declarations

Competing financial interest

The authors declare no competing financial interest.

Human And Animal Rights

This research article does not involve any human participants and/or animals for studies by any of the authors.

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Figures

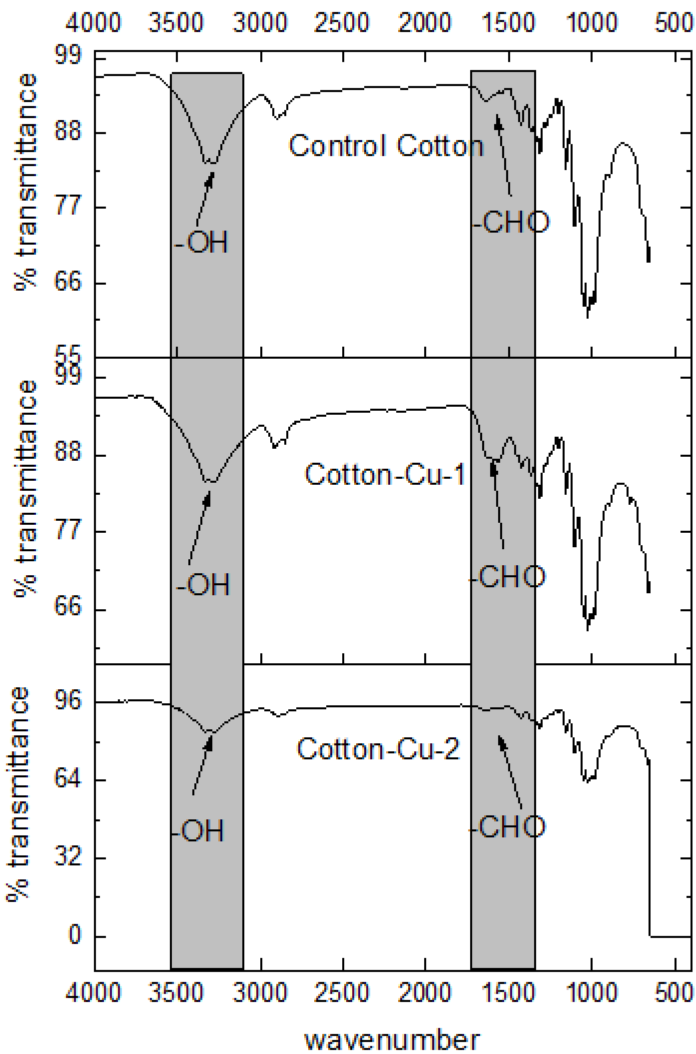

Figure 1

FTIR spectra of (A) control cotton, (B) Cot-Cu-1,(C) Cot-Cu-2

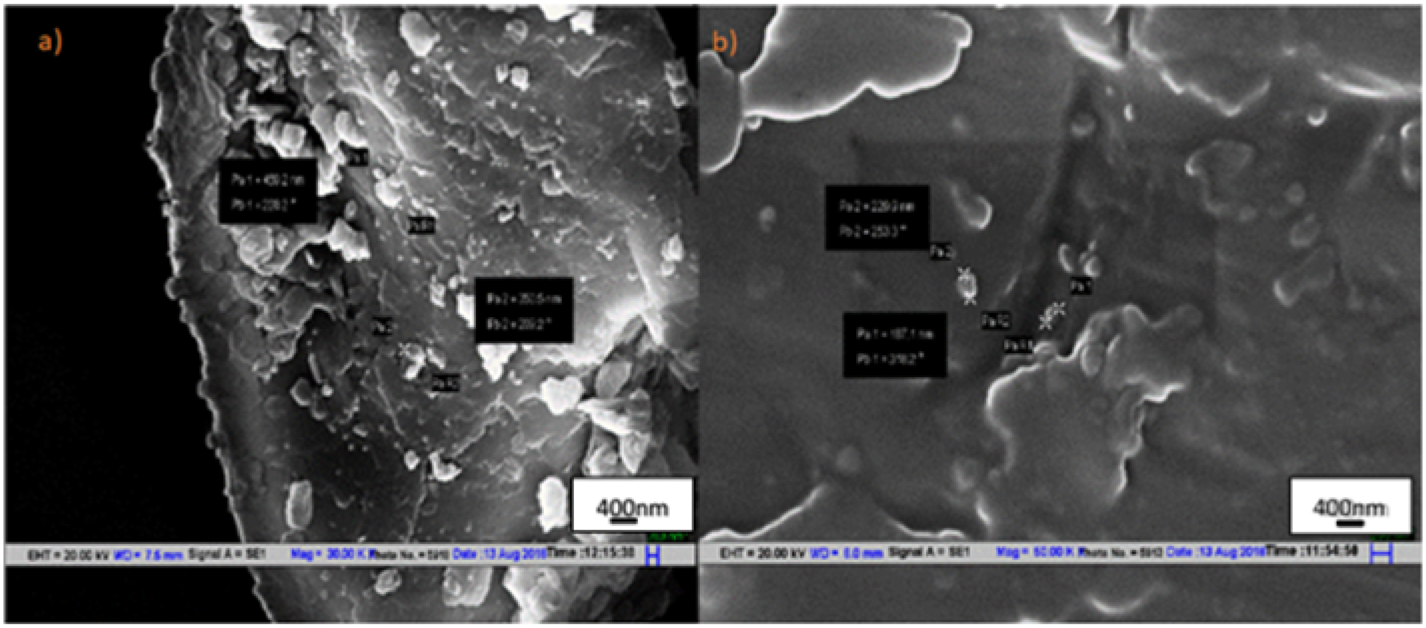

Figure 2

SEM image of (a) Cu-1 and (b) Cu-2 particles

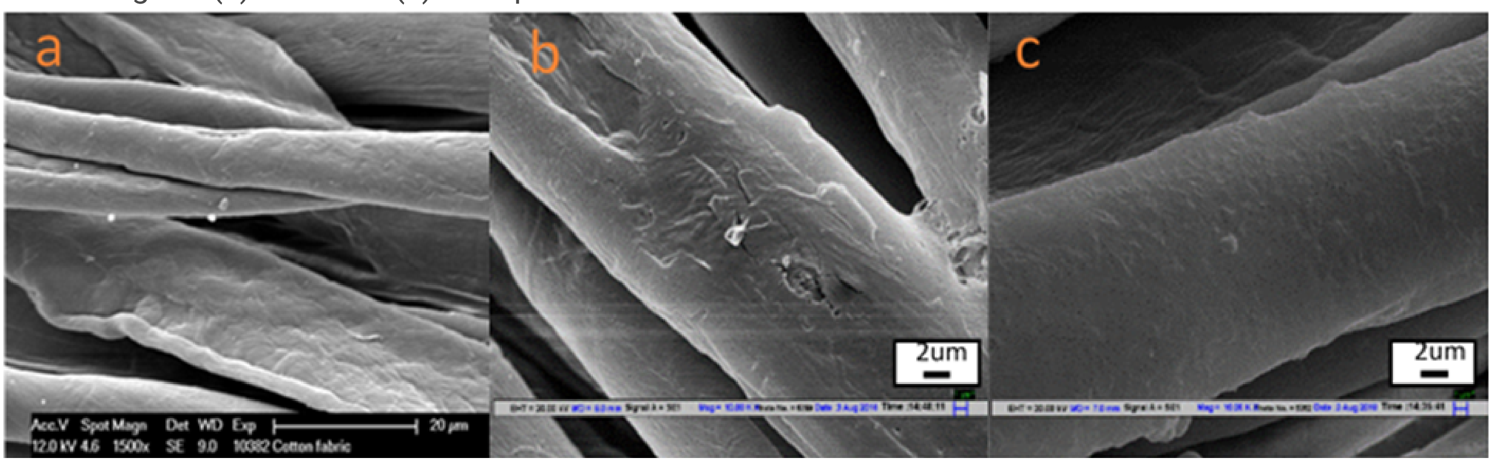

Figure 3

SEM images of (a)untreated cotton at magnification 1200x(b) Cot-Cu-1 at magnification 1000x and (c) Cot-Cu-2 at magnification 1000x

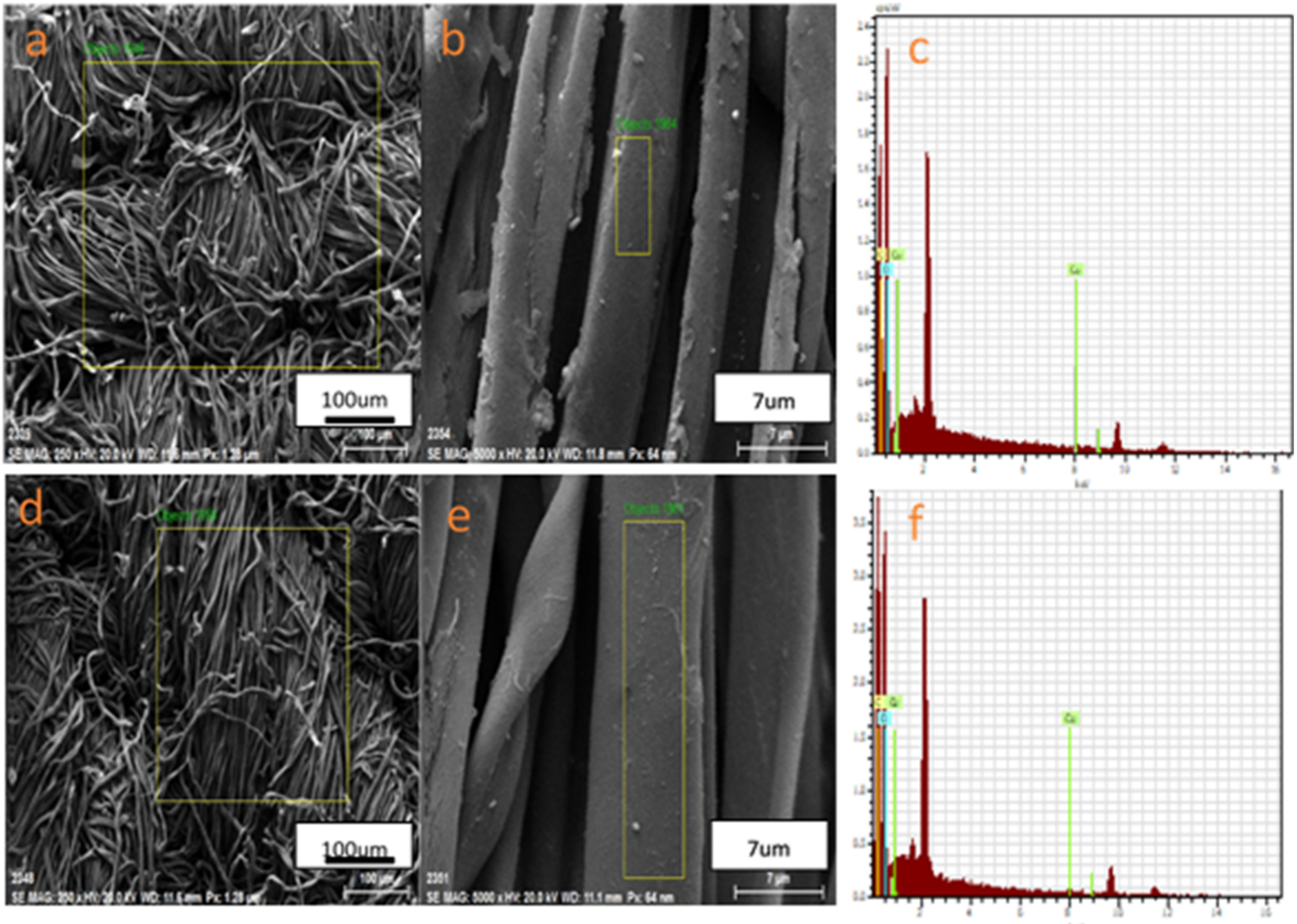

Figure 4

(a), (b), (c)show EDX of Cot-cu-1 taken at larger area and on single thread and (d), (e), (f) show EDX of Cot-cu-2 at larger area and single thread

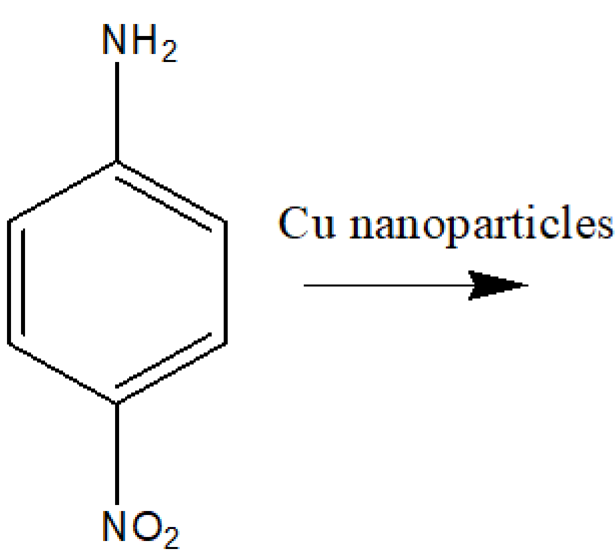

Figure 5

Representation of reduction reaction of 4-nitroaniline to phenylene diamine

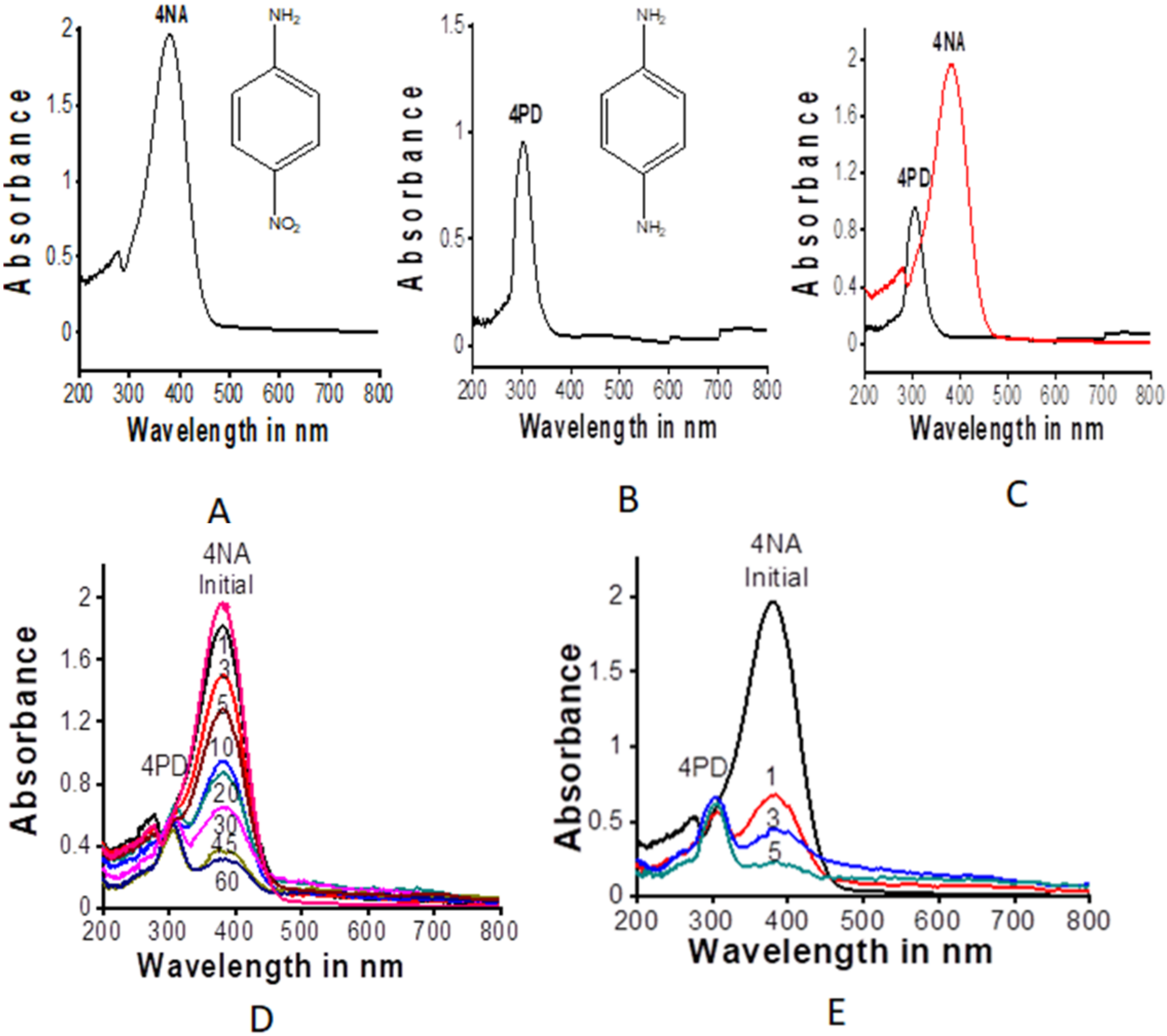

Figure 6

UV-Vis spectra of (A)4-nitroamine,380nm,(B)phenylene diamine,300nm,(C)(4-nitroamine(380nm) and phenylene diamine(300nm), (D) cellulose-Cu-1 nanoparticles usedreduction at initial,1,3,5,10,20,30,45,60 min,(E) cellulose-Cu-2 nanoparticles at initial,1,3,5min.

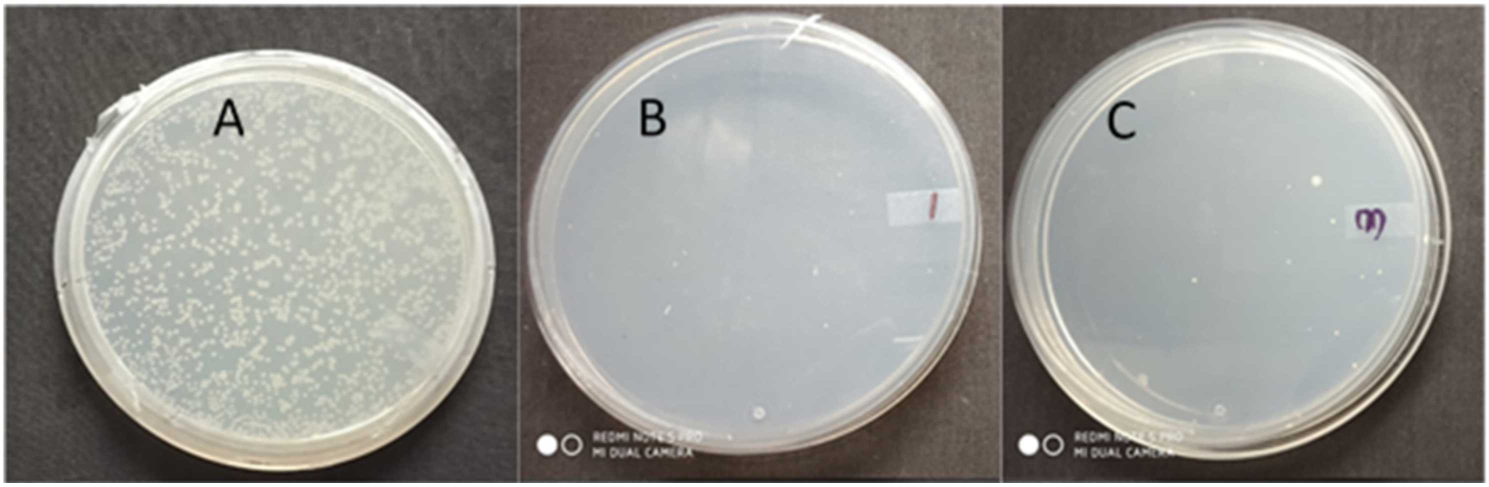

Figure 7

Bacterial colony growth onAgar plate (A)control cotton, (B) Cot-Cu-1, (C) Cot-Cu-2

Supplementary Files

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- GraphicalAbstract.bmp