Carbohydrate Polymers 90 (2012) 1557–1563

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

One pot synthesis of polypyrrole silver nanocomposite on cotton fabrics for multifunctional property

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ARTICLE INFO

Article history:
Received 16 May 2012
Received in revised form 25 June 2012
Accepted 9 July 2012
Available online 16 July 2012

Keywords:
Conducting polymer
Silver nanoparticles
Composite
Conductive textiles
Antimicrobial activity

ABSTRACT

Polymer–silver nanocomposites modified cotton fabrics were prepared by in situ chemical oxidative polymerization using pyrrole and silver nitrate. In a redox reaction between pyrrole and silver nitrate, silver ions oxidize the pyrrole monomer and get reduced. This reduced silver as nanoparticles deposited on/into the polypyrrole/cotton matrix layer and the interaction between silver and polypyrrole was by adsorption or electrostatic interaction. The structure and composite formation on cotton fiber was investigated using SEM, FT-IR, XPS and XRD. The results showed that a strong interaction existing between silver nanoparticles with polypyrrole/cotton matrix. FT-IR studies clearly indicated that the interaction between polypyrrole (—N—H) and cellulose (>C—OH) was by hydrogen bonding. It is observed that the conductivity of the composite coated fabrics has been increased by the incorporation of silver nanoparticles. In the synthesized composites, silver content plays an important role in the conductivity and antimicrobial activity rate of the fabrics against gram positive *Staphylococcus aureus* and gram negative *Escherichia coli* bacteria.

1. Introduction

Metal nanoparticles incorporated polymer nano composites found to exhibit improved physico-chemical and biological properties over their single component counterparts, and hence which are potentially useful in a broad range of applications (Abbas, 2011; Lascelles & Armes, 1997). Among the various composites, silver based polymer nanocomposite can be synthesized by simple and efficient methodologies which provide tremendous opportunities in the ever expanding markets of polymer nanocomposites (Paulraj, Janaki, Sandhya, & Pandian, 2011; Wenqin, Wenli, Jian, Ruifeng, & Jianjun, 2010). Different types of polymers were investigated to synthesize and stabilize the silver nanoparticles. Recently the silver nanocomposites composed of conducting polymers have attracted due to their unique characteristics such as conductivity and electro-catalytic activity. Such composites found applications in sensors, electrochemical oxidation, conductive polymer and electronic devices (Kate, Damkale, Khanna, & Jain, 2011; Lee & Liu, 2005; Liu & Yang, 2005; Liu, 2005; Vivekchand et al., 2005; Wang & Zhang, 2009).

Different synthetic approaches are possible for the preparation of conducting polymer silver nanocomposites. Silver containing polypyrrole composites have been demonstrated by impregnating polypyrrole in silver nitrate solution with various dopants (Pinter et al., 2005). Silver/polypyrrole core/shell nanoparticles by UV-induced polymerization would be fabricated in the presence of polyvinylpyrrolidone (PVP) (Yang & Lu, 2005). Tian, Li, Shi, and Yang (2008), have proposed a new method of an electrochemical deposition of silver on polypyrrole film for the preparation of nanocomposites. Kelly, Johnston, Borrmann, and Richardson (2007) characterized the conducting polymer–silver composites prepared by depositing the silver on reduced conducting polymer/fiber composites using excess sodiumborohydride as a reducing agent at room temperature. There are few more reports are also available for silver (I) initiated polymerization of pyrrole leading to polypyrrole–silver composites (Mahesh, Basavaraja, Deshpande, Balaji, & Venkataraman, 2010; Xing & Zhao, 2007). Wet chemical synthesis of silver nanocable wrapped with polypyrrole in a single step redox reaction has also been investigated (Chen et al., 2005). Interfacial polymerization technique can be applied for in situ synthesis of polypyrrole–silver composites in water/chloroform interface to overcome the agglomerization of nanoparticles (Dallas et al., 2007).

Conductive textiles enable development of smart garments, which are desirable both in medical and military applications (Kincal, Kumar, Child, & Reynolds, 1998; Lekpittaya, Yanumet, Grady, & O'Rear, 2004; Wu, Zhou, Too, & Wallace, 2005). Polymerization of conducting polymers like polyaniline, polypyrrole, PEDOT etc. over a textile substrate could make them conductive and are useful in EMI shielding (Akif, Saeed, & Richard, 2008; Firoz Babu, Senthilkumar, Noel, & Anbu Kulandainathan, 2009; Zun-li,

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http://dx.doi.org/10.1016/j.carbpol.2012.07.030

Zhong-li, Hong, Gui-ping, & Hua-feng, 2009). Since these composites found applications in health care, it is necessary to protect them from the microbial attack. Because of the following reasons antibacterial finishes are also applied to textiles: (a) to contain the spread of disease from bacterial infected area, (b) to contain the development of odor from aspiration, stains and soil on textile materials, and (c) to contain the deterioration of textiles caused by mildew, particularly fabrics made of natural fibers (Gao & Cranston, 2008; Lim & Hudson, 2004). The modification of fibers with conducting polymer silver composites provides conductivity as well as reduces the microbial attack. In the present work, we report a detailed study of conductivity and antimicrobial activity of the polypyrrole–silver composite coated cotton fabric with the function of silver content were explored.

2. Experimental

2.1. Preparation of polypyrrole silver composite coated cotton fabrics

Polypyrrole silver composite coated fabrics were prepared by admixing at various mole ratios of silver nitrate and pyrrole in presence of cotton fabric. The composition of silver nitrate and pyrrole is given in Table 1. Initially the cotton fabric was impregnated in a solution containing pyrrole for 30 min. Silver nitrate was added into this solution and stirred well for 24 h. After completion of reaction the cotton fabric was washed with methanol and deionized water for several times and finally dried at room temperature. Polypyrrole coated fabrics was synthesized by the similar procedure for PPy–Ag composite using ferric chloride as an oxidant instead of silver nitrate.

2.2. Characterization

Scanning electron microscopy images were obtained using HITACHI Model S-3000H at various magnifications to study the surface morphology of the control cotton and polypyrrole coated cotton fabrics. The control cotton was gold sputtered to get electrical contact. The conductivity of the materials was measured using a four-probe technique connected to a digital multimeter (Keithley Model-2010) having capacity 2400 source meter and 2187 nano voltmeter. X-ray diffraction data sets were collected at room temperature on a PANalytical X'PERT PRO system in Bragg–Brentano geometry using Cu $K_{\alpha 1}$ (1.540 Å) radiation. The powder diffraction covered the $10^\circ < 2\theta > 40^\circ$ range with 0.0170° steps. FT-IR spectra were obtained using BRUKER Optik GmbH FTIR spectrophotometer model TENSOR 27 in the diffuse reflection mode. X-ray photoelectron spectroscopic (XPS) analysis was done using Multilab 2000 (Thermoscientific, UK) photoelectron spectrometer fitted with a twin anode X-ray source using the MgKα (1253.6 eV) radiation. Peak fitting was carried out for high resolution C1 and Ag signals according to Shirley-type background subtraction (Shirley, 1972) using curve fitting XPSPEAK 4.1 program with Gaussian–Lorentzien 60%/40%. Differential pulse voltammetry experiments were carried out at ambient temperature using Eco Chemie Autolab Potentiostat under computer control in order to get the information about silver content in the composite. In three electrodes set up, glassy carbon and platinum were used as working electrode and counter electrode respectively. Silver/silver chloride served as the reference electrode, which is separated from main cell by a salt bridge. The potential scan rate was 20 mV/s and the pulse amplitude was fixed at 50 mV.

Table 1
Chemical composition used for the preparation of polypyrrole–silver composite coating on cotton textile.

S. No	Sample ID	Pyrrole (M)	Silver nitrate (M)
1	PPy	0.05	0.05 ($FeCl_3$)
2	PPy-Ag-1	0.01	0.01
3	PPy-Ag-2	0.02	0.01
4	PPy-Ag-3	0.03	0.03
5	PPy-Ag-4	0.05	0.05

2.3. Antibacterial activity

2.3.1. Bacterial strains and culture conditions

Escherichia coli (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) cultures were used for this study as both are reference strains used for antimicrobial susceptibility testing. Also, both *E. coli* and *S. aureus* are microorganisms that are commonly involved in hospital-acquired infections. The strains were cultured on nutrient agar (Himedia, India) and incubated aerobically at 37 °C overnight.

2.3.2. Agar diffusion plate test

Experiments were conducted according to standard ISO/DIS 20645:2002 (Textile fabrics Determination of the antibacterial activity Agar diffusion plate test). The bacteria tested were *S. aureus* and *E. coli*. Unsterilized textile materials were cut into discs with diameter 5 mm and pressed with sterilized tweezers on the surface of congealed agar with bacteria. Immediately after placing the textiles on the agar the plates were incubated for 24 h at 37 °C. After incubation, textile discs were removed from the agar and the antibacterial effect was evaluated (growth of inhibition zone).

2.3.3. Assessment of antibacterial activity of silver nanoparticle coated cotton fabric

The antibacterial activity of the cotton fiber coated with PPy–Ag composites were quantified according to the procedures of AATCC 100-1999. The fabric was cut into 5 mm diameter circles. Before inoculation of the bacteria, the pieces of fabric were disinfected by ultraviolet C irradiation for 1 min. The circular pieces were divided into 7 groups; one group (tube 1) was seeded with 0.5 mL nutrient broth, this group served as a sterility control. Nine groups (tubes 2–7) were seeded with 0.5 mL fresh *E. coli* or *S. aureus* culture at a concentration of 10^5 colony forming units per mL (cfu/mL). It waits for 20 min and 5 mL of saline was added immediately to all tubes. These tubes were vortexes and incubated at 37 °C for 12 h. The reduction of bacterial efficiency was monitored by total viable counts at various time intervals (3, 6 and 12). All tubes were vortexed. 100 μL samples was drawn from each of the ten groups, spread on to a nutrient agar plate and incubated at 37 °C for 24 h for total viable counts. The percentage reduction in bacterial count was calculated by the formula:

$$\%\,\text{Killing efficiency} = \frac{\text{Viable count (0 h)} - \text{Viable count (time intereval)}}{\text{Viable count (0 h)}} \times 100$$

3. Results and discussion

3.1. Formation of polymer–silver composites

Polymer–silver composites were deposited on to the cotton fabrics through a facile redox reaction between pyrrole monomer and silver nitrate. Initially, washed fabric was introduced into an aqueous solution containing pyrrole. Pyrrole monomer got diffuses into the fiber and polymerization took place inside the fiber when the silver nitrate was introduced into the solution. In a redox reaction process, pyrrole monomer and silver nitrate act as a reducing and oxidizing agent respectively. Since the standard oxidation potential of pyrrole and standard reduction potential of silver (0.8 V vs NHE) is lying in the same region, silver acts as a strong oxidizing agent.

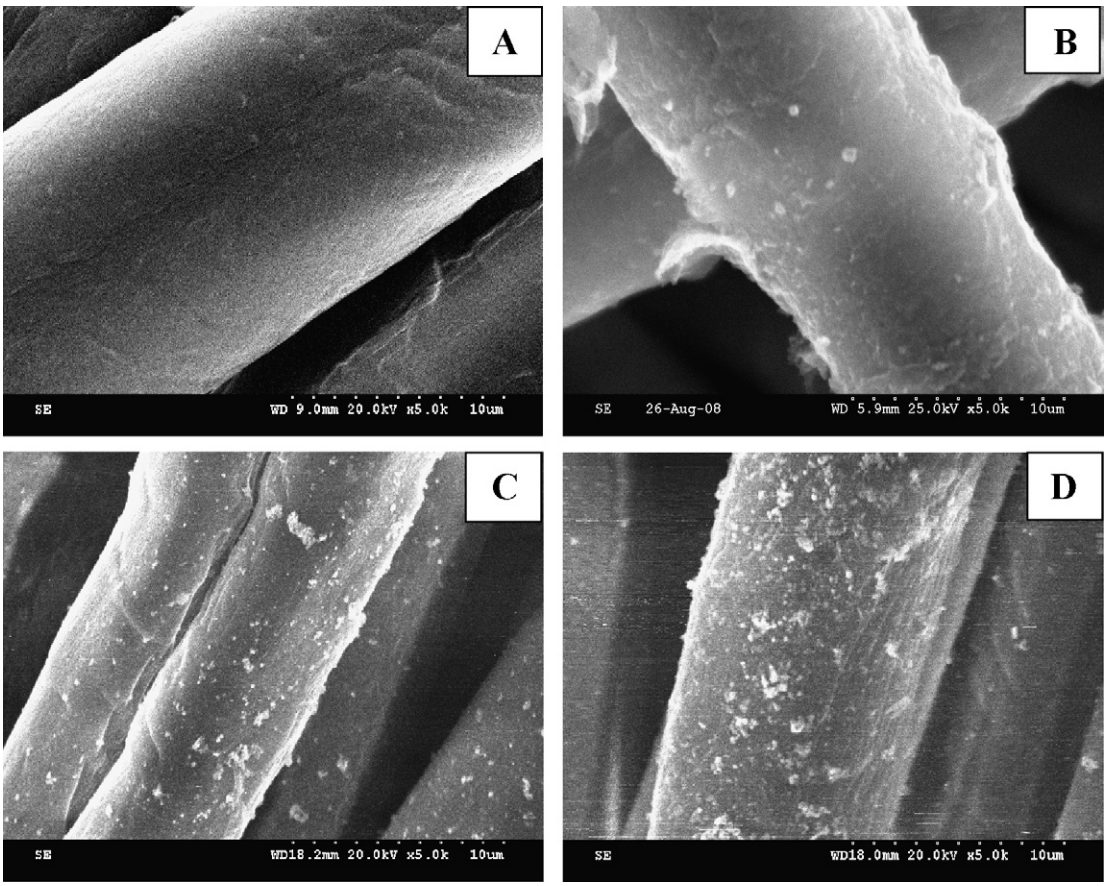
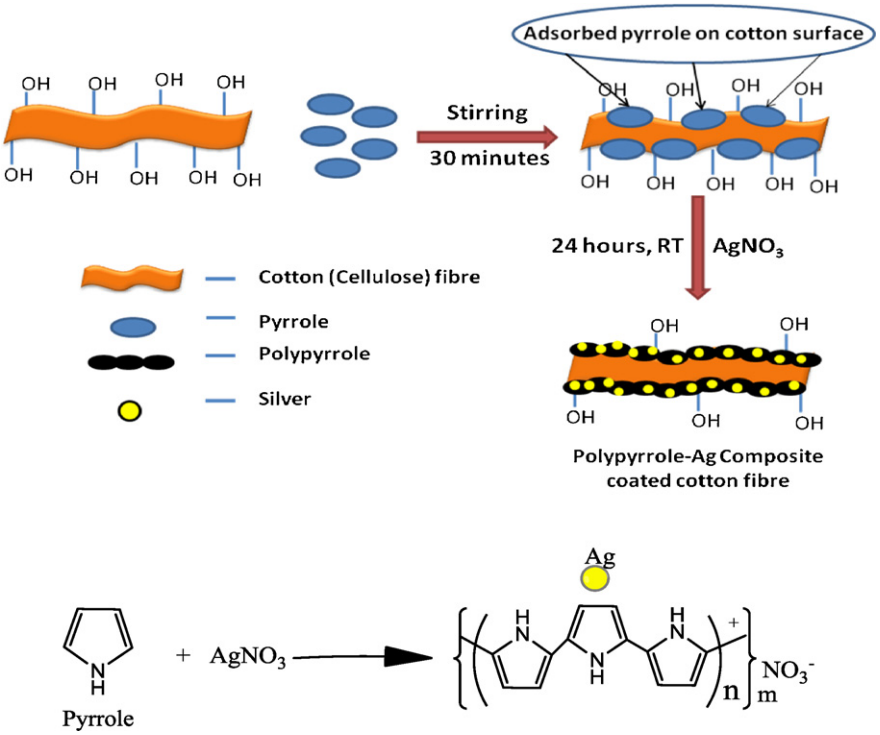


Fig. 1. Scanning electron microscopic images of (A) cellulose fiber, (B) polypyrrole coated cellulose using $FeCl_3$ and polypyrrole–silver composites coated cellulose (C) PPy-Ag-1 and (D) PPy-Ag-4.



Scheme 1. Schematic representation for the method of formation of polypyrrole–Ag composites.

A schematic representation of polypyrrole–Ag composites coated cotton fiber is shown below (Scheme 1). The monomer bound to the surface gets polymerized with dopant NO_3^- leading to a thin film on the cotton fiber and the reduced silver particles deposited on to the polymer surface.

The morphology of the different molar ratio conditioned polypyrrole–silver (PPy–Ag) composites coated cotton fabrics was observed by scanning electron microscopy (SEM). SEM studies of bare cotton fiber showed a smooth surface, where as polypyrrole coated cotton fiber, prepared using ferric chloride as an oxidant, showed a thin layer coating on the single fiber (Fig. 1A and B). SEM images of in situ polymerized pyrrole on the cotton surface using $AgNO_3$ showed that the each individual fiber was coated with polypyrrole layer and deposited nodules of silver nanoparticles over the polymer layer (Fig. 1C). The reduced silver ion was compounded with polypyrrole layer formed on the cotton fiber through adsorption or electrostatic interaction. The coherent film of polypyrrole silver composite will remain attached to the surface and can withstand several washings. The nodules formed on the surface found to increase with increasing concentration of pyrrole and silver (Fig. 1D).

The interaction of polypyrrole and silver on cellulose fiber in PPy–Ag coated cotton fibers were characterized by Fourier transform infrared (FTIR) spectroscopy. Fig. 2 shows the FTIR spectra of bare cellulose fiber, polypyrrole coated cellulose and polypyrrole–silver composite modified cellulose. When compared to IR spectra of cellulose fabric (Fig. 2A) over all intensity reflected from the polypyrrole and polypyrrole Ag composited showed very low, which is due to the suppression of functional groups from the cotton by coating. The characteristic peaks due to C=C stretching, C=N stretching, C—N stretching and C—H stretching of polypyrrole was observed at 1560, 1482, 1301 and 1045 cm^{-1}. Another peak also found at 1381 cm^{-1} is assignable to the N—O stretching of NO^{3-} counter ion in the PPy–Ag composites (Fig. 2C), which is not available in PPy prepared with ferric chloride as an oxidant (Fig. 2B), indicating that the doping of nitrate in pyrrole.

A further justification for the formation polypyrrole–Ag composites was shown from the X-ray diffraction analysis. The X-ray diffraction pattern of the PPy–Ag composites coated cotton fibers is shown in Fig. 3. It reveals that the incorporation of silver nanoparticles on to the polypyrrole matrix in the composites. The pristine cotton has three diffraction peaks at 15°, 16.4° and 22.6° are assigned to (1 0 1), (1 0 2) and (2 0 0) planes, respectively (Parikh, Thibodeaux, & Condon, 2007). The percentage of crystallinity of the cotton is reduced in polypyrrole coated cotton. Amorphous

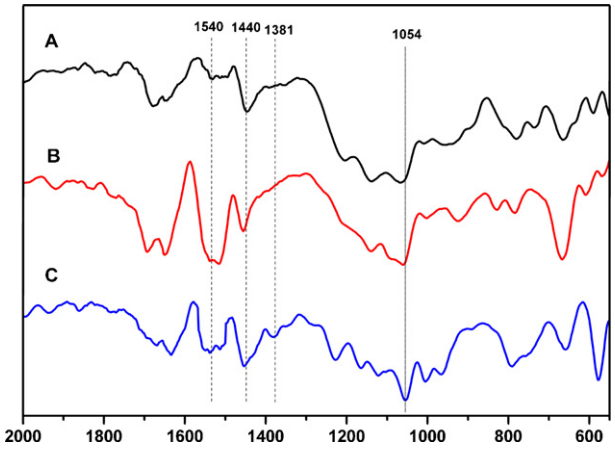


Fig. 2. FT-IR spectra of (A) cellulose fiber, (B) polypyrrole coated cellulose using $FeCl_3$ and polypyrrole–silver composites coated cellulose (C) PPy-Ag-4.

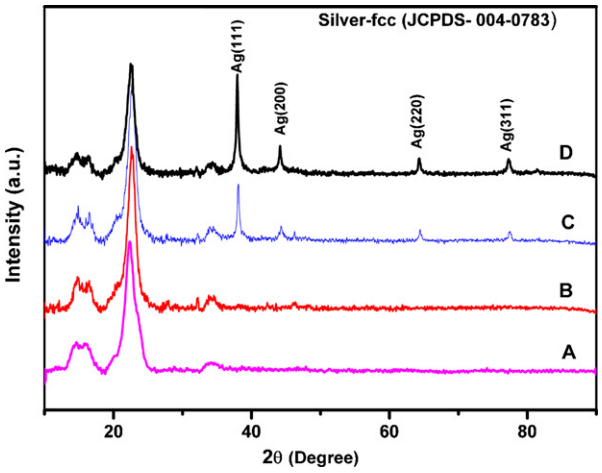


Fig. 3. X-ray diffraction pattern of (A) cellulose fiber, (B) polypyrrole coated cellulose using $FeCl_3$ and polypyrrole–silver composites coated cellulose (C) PPy-Ag-1 and (D) PPy-Ag-4.

polypyrrole showed only a reflection at 21°. However apart from the cotton peaks, the PPy–Ag coated fabrics showed another four peaks with 2θ values of 37.9°, 44.1°, 64.3° and 77.3° are correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes respectively. These brags reflections of silver are in good agreement with the JCPDS file No. 004-0783. Average crystalline size obtained from the Ag (1 1 1) diffraction line using Scherrer's equation is about 20 nm.

To investigate the chemical state of silver in the PPy–Ag composite, X-ray photoelectron spectroscopy (XPS) measurements were made. Neat cotton showed XPS signals at binding energy (BE) of 285 and 532 eV which are attributed to C1s and O1s respectively, whereas PPy–Ag composite finished cotton showed an extra peak for N1s at 402 eV. The nitrogen signal is observed only in PPy–Ag composite (from polypyrrole ring). The oxygen/carbon (O/C) atomic ratio of the cellulose and modified cellulose are calculated from the survey spectrum and given in Table 2. The O/C atomic ratio of native cellulose is 0.81, which is very near to the theoretical value (0.83) reported in the literature (Tatjana et al., 2007). But there is a decrease in O/C ratio after the modification of cellulose with polypyrrole, indicating the interaction of polypyrrole on to the cellulose. Fig. 4 shows the C1s high resolution XPS spectrum of the cellulose and PPy–Ag composite modified cellulose. The high resolution XPS of the C1s core-level obtained for cellulose is decomposed to three peaks with binding energy (BE) of 284.8 eV (C—C or C—H), 286.5 (C—OH) and 288.2 (O—C—O). Whereas in the case of PPy or PPy–Ag composites modified cellulose are decomposed to four signals. Apart from the cellulose signals, a new signal was observed at BE of 285.9 eV (C—N). The atomic ratios of these C1s signals are given in Table 2. The high resolution spectra of Ag3d of the PPy–Ag modified cellulose shows two XPS signals at BE of 368 and 374 eV with 6.0 eV separations, corresponding to $Ag3d_{5/2}$ and $Ag3d_{3/2}$ binding energy of Ag^0, respectively (Fig. 5). Therefore it is clearly evident that silver ions are reduced to silver nanoparticles in presence of pyrrole.

The amount of silver deposited in the composites was estimated using differential pulse voltammetry (DPV). In order to extract silver from the composites, the PPy–Ag composites coated fabric (1 cm^2 area) was dipped in 0.5 M HNO_3 solution for 2 h and the extracted silver as silver nitrate was used for the DPV analysis. In the DPV analysis −0.2 V vs Ag/AgCl was fixed for the deposition potential for silver. Stripping peak for the silver was observed at 0.28 V vs Ag/AgCl. To estimate the silver concentration, a calibration graph was constructed for stripping peak current against the known concentrations of silver nitrate solution in 0.5 M HNO_3.

Table 2
XPS analysis of the cellulose and modified cellulose.

S. No.	Sample ID	O/C ratio	Binding energy (eV)			
			284.8 C—C or C—H (at.%)	285.6 C—N (at.%)	286.5 C—OH (at.%)	288.1 O—C—O (at.%)
1	Cellulose	0.81	58 ± 2	–	36 ± 2	6 ± 2
2	PPy	0.72	48 ± 2	10 ± 2	38 ± 2	4 ± 2
3	PPy-Ag-1	0.79	52 ± 2	4 ± 2	35 ± 2	9 ± 2
4	PPy-Ag-2	0.68	46 ± 2	8 ± 2	39 ± 2	7 ± 2

Table 3
Conductivity and antimicrobial activity of the modified cellulose fabrics.

S. No	Sample ID	Silver conc. DPV ($\mu g\,cm^{-2}$)	Conductivity ($S\,cm^{-1}$)	Antimicrobial inhibition (mm)	
				E. coli	*S. aureus*
1	PPy	–	1.03×10^{-3}	5.6	5.6
2	PPy-Ag-1	10.74	0.75×10^{-3}	6.9	6.7
3	PPy-Ag-2	11.04	0.93×10^{-3}	8.1	7.7
4	PPy-Ag-3	14.61	2.14×10^{-3}	9.5	8.3
5	PPy-Ag-4	19.26	4.82×10^{-3}	11.2	9.8

The stripping current vs silver nitrate concentration was linear in the range of 2–60 μM with linear correlation coefficient (R^2) 0.996 (Fig. 6, inset). Differential pulse voltammetry of the extracted silver solution is shown in Fig. 6. From the calibration graph, the average concentration of the silver present in the composite coated cotton was calculated and presented in Table 3. While increasing

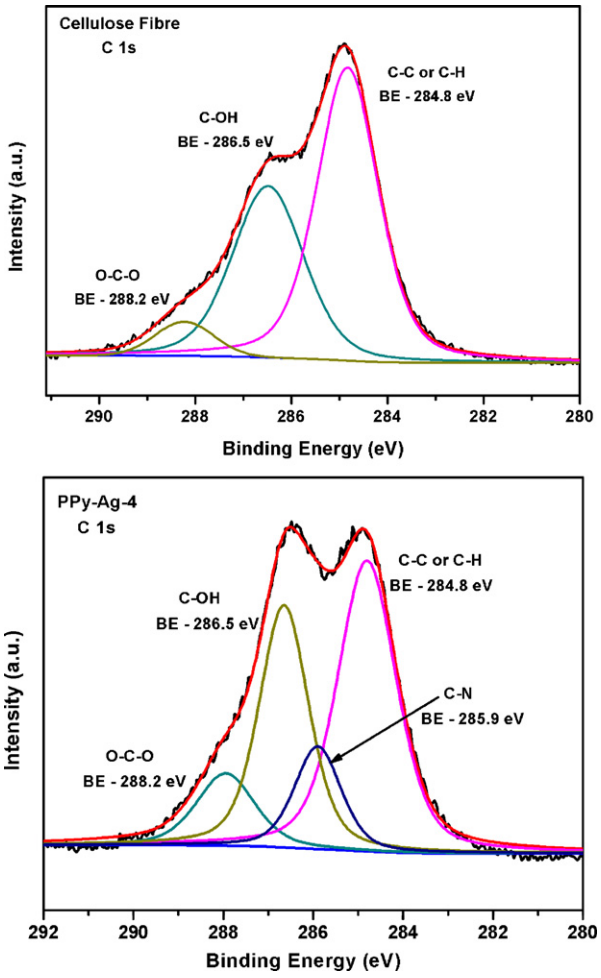


Fig. 4. Deconvoluted XPS graph of the cellulose and polypyrrole–silver composites coated cellulose (PPy-Ag-4) high resolution signals from C1s region.

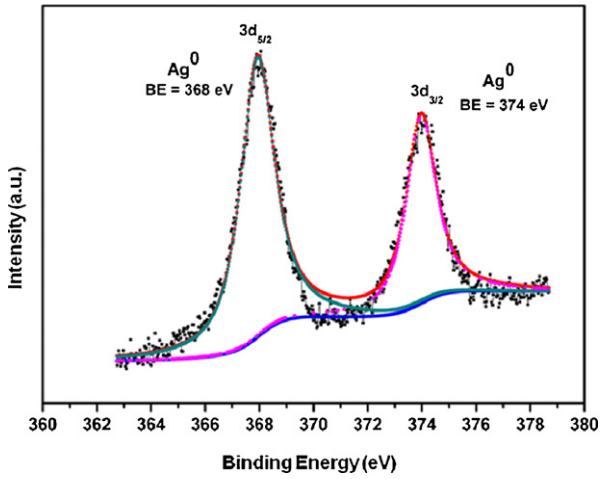


Fig. 5. Deconvoluted XPS graph of the polypyrrole–silver composites coated cellulose (PPy-Ag-1) high resolution signals from silver region.

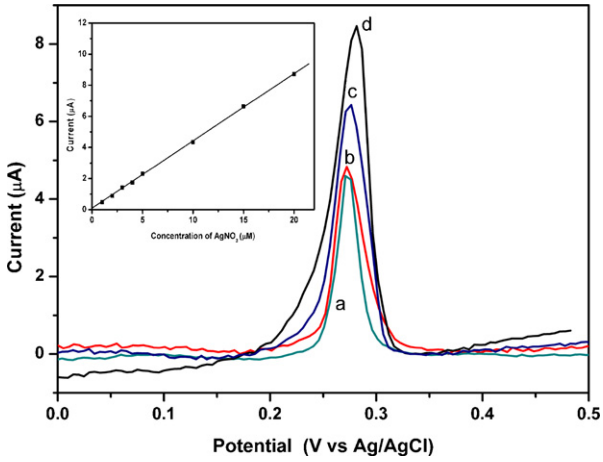


Fig. 6. Differential pulse voltammetry of 0.5 M HNO_3 containing silver ions from polypyrrole–silver composites coated cellulose (A) PPy-Ag-1, (B) PPy-Ag-2, (C) PPy-Ag-3 and (D) PPy-Ag-4. Calibration graph of silver nitrate (2–60 μM) in 0.5 HNO_3 (inset).

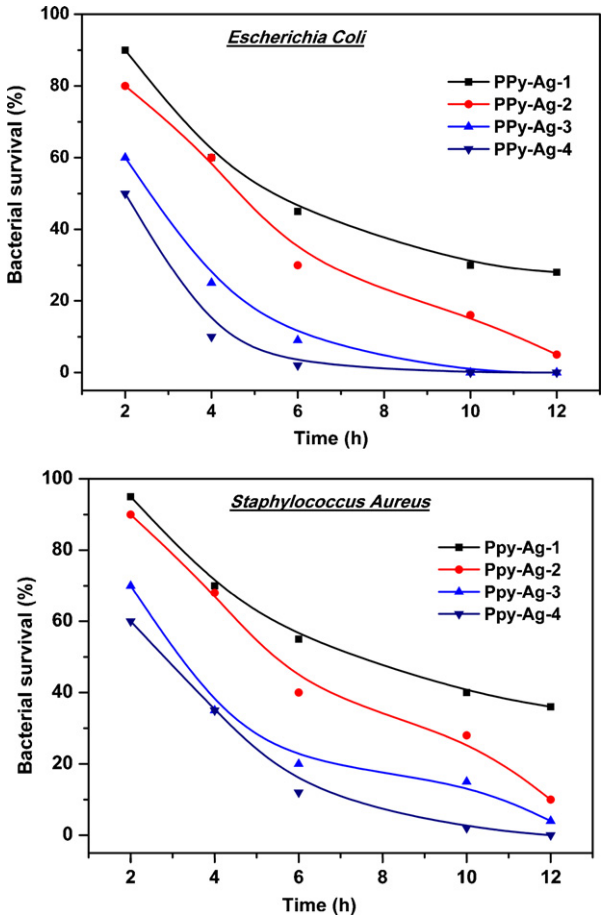


Fig. 7. Antimicrobial kinetics of cotton textile modified with polypyrrole–silver composites.

the concentration of the silver nitrate, the amount of silver also found to increases, whereas the monomer concentration does not influence the reduction of silver, which clearly indicates that silver nitrate oxidizes the pyrrole monomer and get reduced to silver nanoparticles.

The conductivity of the polypyrrole–Ag composite coated textile was studied using four probe conductivity measurements and the results are given in Table 3. Conductivity obtained for the polypyrrole layer formed with ferric chloride was 1.03×10^{-3} S cm^{-1} (Table 3, Expt. No. 1). The polypyrrole–Ag composites showed conductivity higher than the polypyrrole alone coated cotton fabrics (Table 3, Expt. No. 2). When increasing the concentration of silver in the composite, the electrical conductivity of the coated fabrics was found to increase.

3.2. Antibacterial activity

The antimicrobial activity of the silver nanoparticles in polymeric matrix proved to be of great interest for the prevention of adherence and proliferation activities of some bacteria on the materials surface (Saha et al., 2010; Tran et al., 2010).

The antimicrobial efficacies of neat cotton, PPy coated cotton and polypyrrole Ag composite coated cotton were examined against two representative microorganisms *E. coli* and *S. aureus* under identical conditions. *E. coli*, the most characterized bacterium, has been used as a model bacterial system for various antimicrobial testing programs (Lim & Hudson, 2004). *S. aureus* is responsible for a wide range of infectious diseases ranging from benign skin infections to life threatening endocarditis and toxic shock syndrome. The degree of antimicrobial activity of PPy–Ag composites against representative bacterial systems is determined by measuring the assessment test as well as agar diffusion test. The small amount of silver released from cotton surfaces is evaluated against bacterial culture through agar diffusion method and the assessment test would be an efficient method to understand the prevention of bacterial attachment and proliferation.

The contact antimicrobial property of PPy–Ag composites can be measure by the clear zone of inhibition around the fabric after incubation of 24 h in agar plate method and the zone inhibition in diameter (millimeter) for all samples with respect to the silver concentration estimated from the DPV is presented in Table 3. The normal cotton, which was used as a control, did not show any antimicrobial activity against both bacteria. Moreover, the bacteria were grown over the surface after 24 h. The polypyrrole coated cotton alone shows a low zone inhibition, whereas in PPy–Ag composites coatings the zone inhibition was found to increase with increasing concentration of silver nitrate in the composites. The diameter of zone inhibition obtained for the higher concentration of composites is ca 11.2 and 9.8 mm against *E. coli* and *S. aureus*, respectively.

The activity of the PPy–Ag composites coated cotton fabric was then evaluated according to their antibacterial rate. Fig. 7 shows the assessments of antibacterial activity of the composites by means of bacterial killing efficiency vs time against *E. coli* and *S. aureus* as compared with raw cotton textile. The PPy–Ag composites coated cotton fabric is shown that gradually increased bacterial reduction efficiency (%) with respect to time period. The antibacterial rate was found larger with higher concentration of silver present in PPy–Ag composites coated cotton textile. It is found that count for viable colonies of both bacterial is decreased and reaches likely 100% within 6 h against *E. coli* and 12 h taken for *S. aureus*. This implies that the resultant cotton textile finished with PPy–Ag composites have excellent antibacterial activity against both gram positive *S. aureus* and gram negative *E. coli*.

4. Conclusions

The conducting polymer coated textiles are very important in various technical applications such as electromagnetic interference shielding, biomedical applications and sensors. Microbial growth reduces the efficiency of the processes and also leads to deterioration of the coated textiles. In summary, we explored the one pot synthesis of silver nanoparticles incorporated polypyrrole/cotton matrix and studied its conductivity as well as antimicrobial properties. Nodules of silver nanoparticles deposited over polypyrrole layer were observed by SEM studies. Polypyrrole–silver composites coating on cotton fabrics were confirmed by FT-IR and XRD studies. XPS analysis revealed that the silver ions were reduced to silver nanoparticles and composited with polypyrrole. Increasing the silver content in the composites was quantified by differential pulse voltammetric techniques. The conductivity of the polypyrrole/cotton matrix was found to increase by the incorporation of silver nanoparticles and the composites showed good antimicrobial property against microorganisms such as *S. aureus* and *E. coli*.

Acknowledgment

CSIR-HRDG, New Delhi is gratefully acknowledged for the Senior Research Fellowship of Firoz Babu. K.

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