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Sonochemical Coating of Paper by Microbiocidal Silver Nanoparticles

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Colloidal silver has gained wide acceptance as an antimicrobial agent, and various substrates coated with nanosilver such as fabrics, plastics, and metal have been shown to develop antimicrobial properties. Here, a simple method to develop coating of colloidal silver on paper using ultrasonic radiation is presented, and the coatings are characterized using X-ray diffraction (XRD), high resolution scanning electron microscope (HRSEM), and thermogravimetry (TGA) measurements. Depending on the variables such as precursor concentrations and ultrasonication time, uniform coatings ranging from 90 to 150 nm in thickness have been achieved. Focused ion beam (FIB) cross section imaging measurements revealed that silver nanoparticles penetrated the paper surface to a depth of more than 1 μm, resulting in highly stable coatings. The coated paper demonstrated antibacterial activity against *E. coli* and *S. aureus*, suggesting its potential application as a food packing material for longer shelf life.

1. Introduction

The enhanced surface to volume ratio attained by nanostructured materials that results in their unique properties has led to ever-growing applications in various fields.[1] These nanoparticles often demonstrate size, shape, and composition dependent variations in properties, and therefore, it is desirable to develop methods of fabricating these nanostructures with tunable properties for specific applications.[2] Metallic silver and silver containing compounds have been well-known and used for their antibacterial properties.[3] Several mechanisms have been proposed for the antimicrobial activities of silver nanoparticles including their inhibition of a large range of bacterial proteins, enzymes, and DNA, cell membrane perforations, and alteration of selective permeability, resulting in the bacteriostatic and bactericidal effects.[4] Such studies have targeted a vast range of common pathogens including bacteria,[5] fungi,[6] and viruses.[7] As a coating material, therefore, silver nanoparticles and their composites have been used to generate antimicrobial surfaces on textiles, fibers, polymers, and metals, leading to biomedical applications such as wound and burn dressings,[8] microbial resistant catheters,[9] surgical masks and tools,[10] and tissue engineering scaffolds.[11] Similarly, various other commercially important applications such as antimicrobial paints[12] and water purification and effluent treatment membranes[13] have also been proposed. Nanoparticle based coatings are also sturdier than organic antimicrobial coatings as they are less prone to destabilization under unfavorable handling, under storage conditions, and upon interaction with biological systems. Moreover, such alternative antimicrobial strategy based on nanoparticles is also capable of overcoming the growing menace of developing resistant microbial strains.[3,14]

In addition to the various substrates described above, paper is yet another surface that could be coated with antimicrobial silver nanoparticles and have significant commercial applications

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beyond biomedical fields. As one of the important packaging materials in food and pharmaceutical industry, paper is susceptible to microbial contamination and damage.[15] Thus, developing coated paper with antimicrobial properties of silver nanoparticles could be an alternative to other food preservation methods employing radiation, heat treatment, low temperature storage, or the introduction of antimicrobial additives.[16] Ionic silver has been previously used as one such antimicrobial additive,[16] but silver nanoparticle coated paper could be useful for preventing microbial growth for longer periods by providing a reservoir for slow releasing of ionic silver form the surface to the bulk as well as preventing growth on the surface itself. Nanomaterial coated papers (based on carbon nanotubes, gold nanoparticles) have been also used recently for developing simple, rapid and disposable biosensors based methods for detection of toxins and antigens[17a,b] as well as antibacterial surfaces (graphene).[17c] Surface Enhanced Raman Spectroscopy (SERS) active behavior of silver nanoparticles makes it an attractive choice of material for such biochemical sensors in form of thin coatings on paper.[18]

Coated paper has several other commercial applications such as in holographic films, high barrier packaging, decorative and printing applications, self-adhesive labels, insulation, and so forth, and several well established coating techniques currently exist. These include dip coating, brush coating, sputtering, mechanical blade or bench coating, rolling, air brush, curtain, spin coating, spray coating, and so forth.[19−21] Many of these methods are specific for the materials that are being coated and have limitations such as defects, nonuniform coating thickness, and energy/cost ineficiencies.[22] However, the field of nanomaterials coatings requires the development of improved coating techniques more adaptive to nanotechnology while still being cost-effective and capable of generating more uniform and highly durable coatings. Furthermore, with the emphasis on ''green chemistry'' being greater than ever, interest has developed in the adoption and implementation of sustainable processes by minimizing the use of toxic chemicals, solvents, and energy.[23−26]

In this study, a simple, one-step process of coating paper with antimicrobial colloidal silver using ultrasonic radiation is presented. Ultrasonication is one of the most attractive methods for coating applications involving nanomaterials.[27] This method has been successfully used to deposit various nanomaterials (metals, metal oxides, semiconductors) on the surfaces of fabrics, ceramics, and polymeric fibers,[28−30] resulting in the formation of a smooth homogeneous coating on the surfaces. The nanoparticles are anchored strongly to the surface either by physically embedding them in the surface or by forming chemical bonds or other interactions with the substrate, and form a remarkably sturdy coating. In a typical sonochemical procedure, the nanoparticles generated in the reaction chamber are thrown by the microjets of the fluid onto the substrate's surface. These microjets are formed after the collapse of the acoustic bubble near a solid surface, leading to the formation of a homogeneous layer composed of nanoparticles.[27]

Unlike other substrates, sonochemical coating of paper largely remains unexplored. To best of our knowledge, the only other such report involves coating of ZnO on paper by sonochemical deposition of preformed nanoparticles.[31] The current study, on the other hand, involves in situ generation of nanoparticles in the reaction vessel and simultaneous deposition on the paper as a substrate. The results presented here show that, by varying the precursor concentrations and reaction times, the thickness of the silver nanoparticle coating and the particle size can therefore be controlled to a great extent. Further, these silver nanoparticle coated papers have been shown to possess microbiocidal properties against the Gram-negative *Escherichia coli* (*E. coli*; strain 1313) as well as against the Gram-positive *Staphylococcus aureus* (*S. aureus*; strain 195) bacteria. Moreover, formation of a robust coating as a result of ultrasonication results in long lasting coating with extended lifetime and antibacterial properties. We believe that such coated paper has potential application in the food industry as a packing material with a long shelf life and antifouling properties. At the same time, the sonochemical process used in the current study can be extended to other nanomaterials on similar substrates to achieve different functionalities for various other applications. The simplicity of the procedure means that such a method could be easily scaled up to meet the requirements of large scale coatings.

2. Experimental Section

2.1. Coating of Paper via Ultrasonication. In order to test best conditions of coating, precursor concentration and ultrasonication times were varied. In a typical reaction, solutions of 25, 50, or 100 mM $AgNO_3$ (Sigma Aldrich, St. Louis, MO) in 176 mL of absolute ethanol (Bio Lab, Israel), 20 mL of ethylene glycol (EG) (J.T. Baker, Phillipsburg, NJ), and 4 mL of ultrapure water (Milli-Q) were purged under Ar for 30 min in order to remove traces of O_2/air. The purging was done in the presence of the paper (8×3.5 cm^2 of parchment paper, purchased from Casa, Israel). The paper was held immersed in the solution with a Teflon disk to prevent it from floating (Figure 1A). In the next stage, the solution was irradiated for

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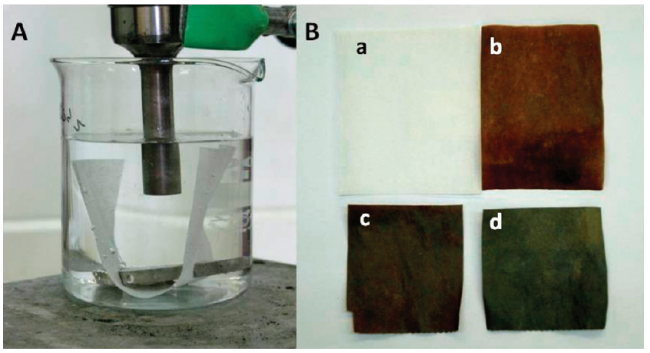

Figure 1. (A) Experiment setup for the ultrasonication reaction. The paper was held immersed in the solution with a Teflon disk to prevent it from floating. (B) Changing appearance of the coated papers: (a) uncoated paper; (b) 25 mM/30 min coated paper; (c) 25 mM/60 min coated paper; (d) 100 mM/30 min coated paper.

30 or 60 min with a high intensity ultrasonic horn (Ti horn, 20 kHz, 600 W at 40% efficiency, Sonics and Materials VCX600) under a flow of Ar. A 25% aqueous solution of ammonia (Bio Lab, Israel) (molar ratio $NH_3/AgNO_3$ = 2:1) was added to the reaction slurry during the first 5 min of sonication. The temperature inside the ultrasonication flask was measured to be 80 °C during the reaction. Similar experiments were also carried out with identical silver concentrations in aqueous solutions. After the ultrasonication, the paper was washed thoroughly with Milli-Q water to remove residual ammonia and then with ethanol and dried under vacuum for 24 h. These samples have been designated henceforth as 25 mM/30 min, 25 mM/60 min, 100 mM/25 min, 100 mM/60 min, and 100 mM/120 min coated papers, indicating the initial precursor concentration and the duration of ultrasonication.

2.2. Characterization of Coatings. The silver content on the paper was determined by thermogravimetric analysis (TGA) using a TA TGA Q500 instrument, model Thermostar, Pfeiffer. The X-ray diffraction (XRD) patterns of the coated paper were measured with a Bruker D8 diffractometer (Karlsruhe, Germany) with Cu Kα = 1.5418 Å radiation. The morphology and the size of the noble metal nanoparticles were studied with a high resolution scanning electron microscope, HRSEM (JEOL-JSN 7000F). Measurements of the coating thickness and nanoparticle penetration depth into the paper's bulk were done by focused ion beam (FIB) using a FEI Helios 600 system. Determination of silver leached from the coated paper was carried out via inductively coupled plasma (ICP) mass spectrometry using an ULTIMA JY2501 instrument.

2.3. Antibacterial Assay. The antibacterial activities of Ag-coated papers, 25 mM/30 min and 100 mM/60 min, were tested against the Gram-negative *Escherichia coli* (*E. coli*; strain 1313) as well as against the Gram-positive *Staphylococcus aureus* (*S. aureus*; strain 195) bacteria. Both strains were obtained from the Bacteriological Laboratory of the Meir Hospital, Kfar Saba, Israel. A typical procedure was as follows: cultures of the bacteria were grown overnight on nutrient agar (Difco, Detroit, MI). These cultures were then transferred into a flask containing nutrient broth (NB) at an initial optical density (OD_{660}) of 0.1 and allowed to grow at 37 °C. When the cultures reached OD_{660} = 0.3 (the beginning of the logarithmic phase), they were centrifuged and washed twice with a saline solution (NaCl 0.145 M, pH 6.5) to yield a final bacterial concentration of approximately 10^8 colony forming units (CFU mL^{-1}). Samples of Ag-coated paper (1 cm^2) were suspended in an initial bacterial load of 10^7 CFU mL^{-1} in saline (in vials with an inner diameter of 2.5 cm) and incubated at 37 °C for under constant shaking at 180 rpm for up to 4 h. To ensure that any decrease in the number of bacteria was due to exposure to a coated-paper treatment, two controls were included in the experiment, one with bacteria and without a paper sample (negative control), and the second with the bacteria at the appropriate concentration in saline with the presence of an uncoated paper (positive control). Samples of 100 μL, from each, were taken at a specified times (t = 0, 1, and 3 h), diluted 10-fold in saline, and then transferred onto nutrient agar plates (Difco). The plates were incubated for 24 h at 37 °C, and then the viable bacteria counts in terms of CFU mL^{-1} were recorded using a colony counter from the appropriate dilutions. The survival fraction, N/N_0, was determined by comparing the colony count from the culture exposed to coated paper (N) and the colony count from the control bacterial culture (N_0) for a given duration of treatment.

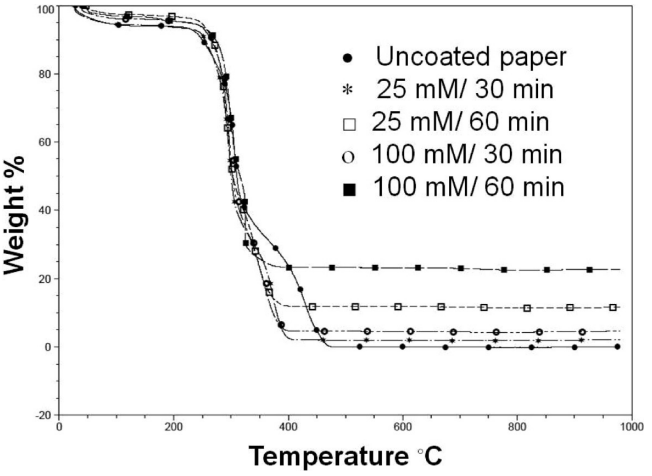

Figure 2. TGA analysis of different paper samples depicting variation in weight losses that were used to calculate the amount of deposited silver on each sample.

3. Results and Discussion

The polyol reduction method has been used previously for the preparation of finely dispersed silver nanoparticles. This process involves the reduction of soluble silver species by ethylene glycol or another polyol. When the reaction is carried out in the presence of the suitable protective agents (e.g., polyvinyl alcohol, polyacrylate, polyvinyl pyrrolidone), the polymers can prevent the agglomeration of the silver nanoparticles at relatively low temperatures, 60−120 °C.[28,29] Here, EG was used as a polyol reducing agent for the reduction of silver ions to metallic silver. Addition of ammonia leads to the formation of the $[Ag(NH_3)_2]^+$ complex. The equilibrium constant for the formation of $[Ag(NH_3)_2]^+$ is large, $\sim 10^7$, which dictates a small amount of Ag^+ in equilibrium with the complex. Thus, the concentration of ammonia in the reaction mixture is a key parameter in the control of particle size of resulting nanoparticles.[32] In this study, therefore, the Ag^+/NH_3^+ ratio was kept constant and the only variables were the concentration of Ag^+ and the sonication time.

At the end of the reaction, deposition of silver is indicated by the change in the color of the paper. The variation in color of coated papers from white to brown and to gray indicated variation in the particle size/aggregation or the amount of silver deposited with changing concentration of the precursors and sonication time (Figure 1B, a-d).

The amount of deposited silver in terms of weight percentage was determined using TGA measurements (Figure 2). It is evident from the TGA results that the amount of metallic silver deposited on the paper is dependent on the precursor concentration and sonication

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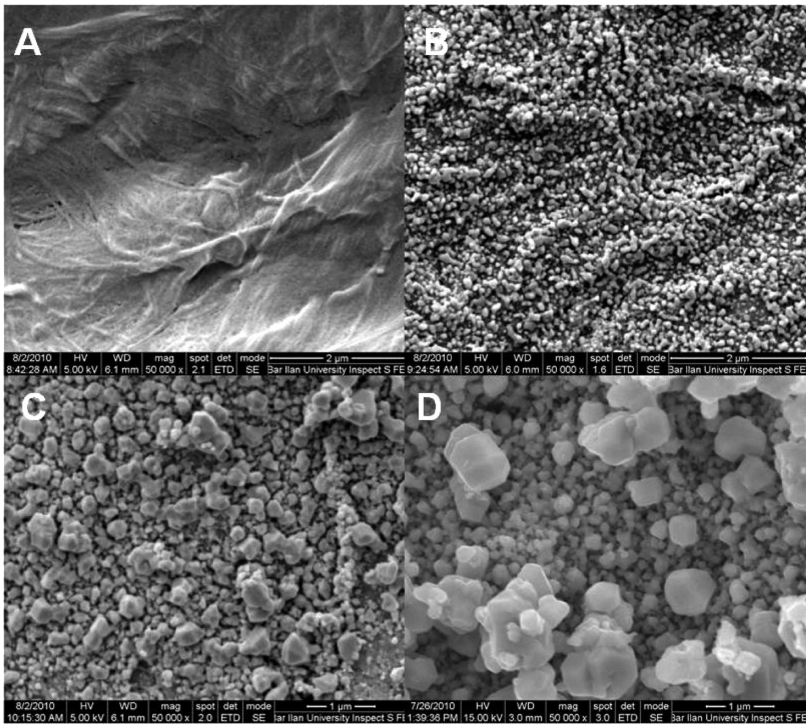

Figure 3. SEM images showing general growth in silver nanoparticles sizes for a 100 mM silver nitrate concentration as a function of sonication time: (A) Uncoated paper, (B) 30 min sonication, (C) 60 min sonication, and (D) 120 min sonication. The scale bar in (A) and (B) corresponds to 2 μm, while in (C) and (D) it corresponds to 1 μm.

time. Thus, the weight percentage of silver varies as 2%, 4.5%, 11.9%, and 23.9% for $AgNO_3$ concentrations of 25 mM/30 min, 25 mM/60 min, 100 mM/30 min, and 100 mM/60 min, respectively.

In addition, SEM results also support this observation. It was shown that there is a direct correlation between precursor concentrations and sonication times with particle size of the coated sample. Figure 3 shows the comparison between SEM images of uncoated paper (A) and coated papers (B−D) with varying sonication time as the precursor concentration remained unchanged (100 mM), It is evident that the nanoparticles grow in size as the sonication time is increased, consequently resulting in higher weight percentage of the coatings (B−D). This phenomena is similar to the previous studies where other substrates such as glass, fabrics, and plastics were coated using ultrasonication.[28−30,33]

Further, SEM analysis of samples with different precursor concentration and ultrasonication times highlighted the significant differences between particle sizes of deposited silver nanoparticles (Figure 4). With the 25 mM silver nitrate concentration, ultrasonication for 30 and 60 min (25 mM/30 min and 25 mM/60 min) resulted in silver nanoparticles with average sizes of 27 ± 7 and 41 ± 8 nm, respectively (Figure 4A,B). On the other hand, for 100 mM silver nitrate concentration, similar ultrasonication times of 30 and 60 min (100 mM/30 min and 100 mM/60 min) resulted in silver nanoparticles with average sizes of 89 ± 20 and 142 ± 37 nm, respectively (Figure 4C,D). It should be noted that these particle sizes correspond to the silver nanoparticles deposited on the surface of the paper only. The nanoparticles left over in the solution after the sonication showed largely aggregated morphology when observed though TEM (data not shown), which could be attributed to the absence of surfactant during the coating procedure.

XRD measurements showed the presence of crystalline silver on the coated papers. As evident from Figure 5, the increase in the silver content (weight percentage) is reflected in the increasing intensity of the XRD diffraction peaks (Figure 5a−d). The strongest diffraction peak is detected at a 2θ value of 38° corresponding to the (111) plane of metallic silver (PDF 03-065-2871). The coated paper 100 mM/120 min shows the highest XRD peak intensities (Figure 5d) which results from the high weight percentage of coated silver (39.6%, data not shown), while the 100 mM/60 min coated sample has relatively lower intensities for the same peaks (Figure 5c). Both of these samples showed electrical conductivities (data not shown), confirming the metallic nature of the deposited silver. The 25 mM/30 min sample (Figure 5b) showed a similar XRD pattern as the uncoated paper (Figure 5a). However, the SEM results did show the presence of a silver coating consisting of small silver nanoparticles (Figure 4A). The presence of silver on the paper is also confirmed by the color change after coating (Figure 1B-b) and its antibacterial properties as discussed later. It should be noted that a very low intensity peak corresponding to AgCl at $2\theta = 32°$ (PDF 01-085-1355) was also observed.

The formation of AgCl could result from the presence of residual chlorine in the paper, the origin of which is attributed to the manufacturing process of parchment paper that specifically employs chlorine and chlorine dioxide for the removal of lignin during processing.[34] It is established that inextractable organochlorine traces could be detected in cellulosic substrates post-bleaching with chlorine.[35] We confirmed the presence of chloride in uncoated paper using Mohr's titration method[36] (results not shown).

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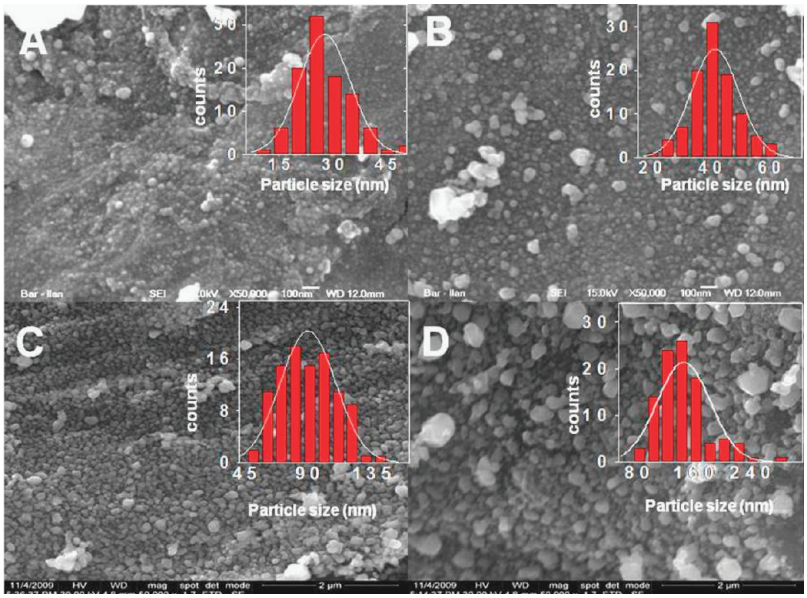

Figure 4. SEM images and particle size distribution of coated papers: (A) 25 mM/30 min, (B) 25 mM/60 min, (C) 100 mM/30 min, and (D) 100 mM/60 min. The particle size distribution was measured using the Scion Image software where $n = 100$. The scale bar in (A) and (B) corresponds to 100 nm, while in (C) and (D) it corresponds to 2 μm.

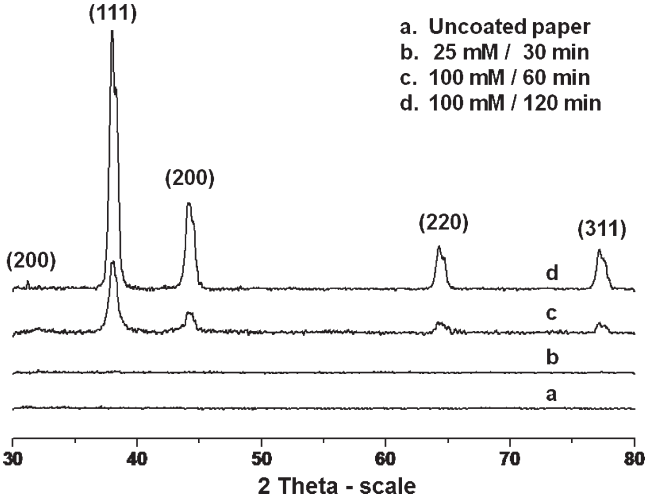

Figure 5. XRD analysis of coated paper showing increasing peak intensities as a function of increasing silver content.

Coating thickness was determined using focused ion beam (FIB) assisted cross-sectional analysis. Since the sample preparation procedures require deposition of platinum over the sample prior to sectioning by FIB, all the samples show a rather smooth metallic layer over the top of the deposited platinum. At the edges of the sections, silver can be seen as the bright regions beneath the platinum layer. The 25 mM/30 min coated paper shows discontinuous silver regions at the edge, measuring up to 50 nm in thickness (Figure 6A1,A2). Both the 25 mM/60 min and 100 mM/60 min coated papers showed more consistent silver coating at the edges (Figure 6B1,B2 and C1,C2, respectively), though the thickness varied from 87 to 123 nm for the former and 85−149 nm for the latter. Also, the 100 mM/60 min coated sample showed the presence of more than one layer of silver (Figure 6C2). It should be pointed out here that both of the 60 min coated samples were found to be electrically conductive (data not shown) whereas the 30 min coating does not lead to any conductivity. This suggests that longer periods of ultrasonication lead to a more closely packed coating, forming continuous layers as depicted in the FIB images also. At a lower magnification, silver nanoparticles were also seen embedded much deeper into the paper (indicated with arrows in Figure 6 B1,C1), which result from the high speed of the microjets impinging on the surface of the paper similar to previously reported studies with other surfaces.[27c]

For applications of coated papers such as those described in the beginning, for example, food packaging, it is important that the nanomaterial coatings are sturdy and stable. Here, to determine the robustness of coatings obtained by the above method, samples of coated papers were treated in an ultrasonic cleaning bath (TPC-15, 30 kHz) in 10 mL of Milli-Q water for 1 h. After the treatment, the washing solution was analyzed for the presence of silver using inductively coupled plasma (ICP) mass spectrometry measurements. As shown in Table 1, it is evident that the amount of leached silver after the treatment depends on the initial loading of silver on the paper. Thus, for the paper with the least amount of silver 25 mM/30 min (2 wt % of Ag), the loss of silver in the ultrasonication cleaning process is the highest (9.5 wt %). On the other hand, as the coating becomes denser and more uniform (also richer in terms of weight percentage of silver), the leaching of silver is minimized, suggesting a more stable coating. Thus, for the 100 mM/120 min sample with the highest coating of silver (39.6 wt %), the amount of silver that came off the paper was the least (0.11 wt %). This could be attributed to better adherence of layers of metallic silver on the primary layer as the coating is continued. When the precursor concentration was low, a non-homogenous and unstable coating was obtained. However, importantly, only a fraction of total coated silver is leached out of the paper, which means that a large reservoir of silver ions is retained which is vital for slow release of ionic silver over a long period of time.

Antibacterial assays were carried out using 25 mM/30 min and 100 mM/60 min coated paper on common bacterial pathogens *E. coli* and *S. aureus*. The results have been summarized in Table 2.

It is evident that the silver nanoparticle coated papers show efficient antimicrobial activity against both *E. coli* and *S. aureus*. While in the case of Gram-negative *E. coli* both coated papers resulted in nearly 100% bactericidal activity within the first hour

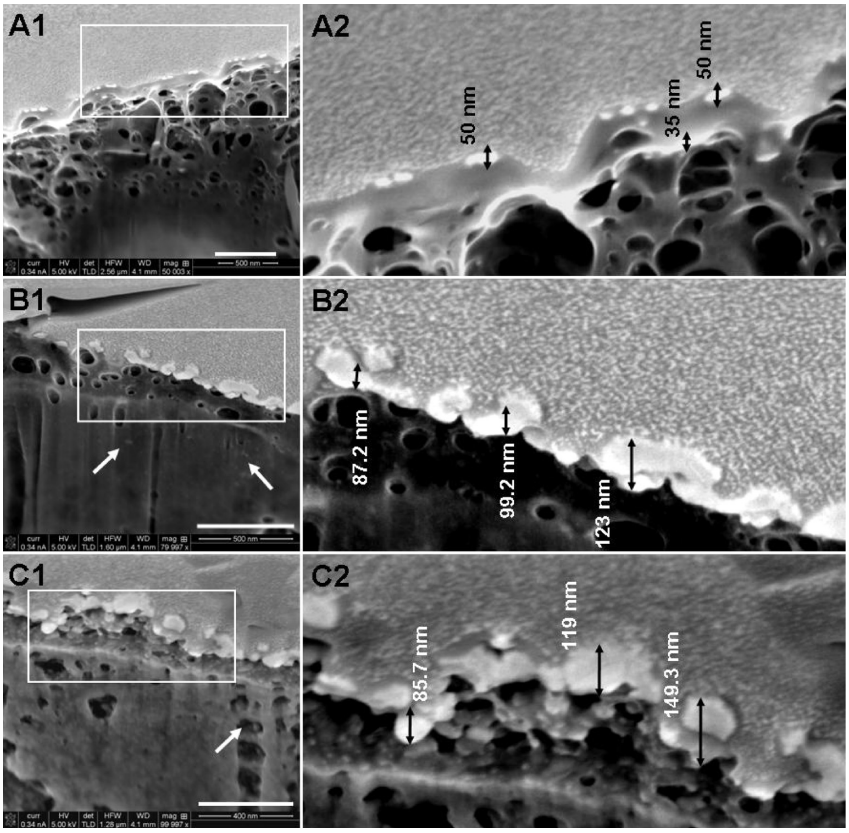

Figure 6. FIB cross-sectional images of silver coated papers: (A1) Cross-sectional image of 25 mM/30 min coated paper; (A2) magnified image of the area marked as box in (A1). (B1) Cross-sectional image of 25 mM/60 min coated paper; (B2) magnified area from (B1). (C1) Cross-sectional image of 100 mM/60 min coated paper; (C2) magnified area from (C1). The scale bars in (A1) and (B1) are 500 nm, while that in (C1) is 400 nm.

Table 1. Coating Stability and Adherence Strength[a]

sample	Ag content on the paper (wt %)	Ag stripped off the paper (wt %)
25 mM/30 min	2	9.5
25 mM/60 min	4.5	2.2
100 mM/30 min	11.9	1.68
100 mM/60 min	23.9	0.62
100 mM/120 min	39.6	0.11

[a] The table compares the amount of silver that came off the different coatings after a 1 h sonication bath treatment. The amount of silver stripped off is reported in percentage of the total silver present on the paper, as measured using ICP analysis.

of incubation, 3 h incubation resulted in total microbial destruction. On the other hand, there is a marginally lower bactericidal activity within the first hour of incubation in the case of Gram-positive *S. aureus* in comparison to *E. coli*, while nearly 100% bactericidal activity is achieved after 3 h of incubation. It is widely accepted now that silver nanoparticles and ionic silver both lead to alteration in the membrane permeability of bacteria and also render several bacterial proteins nonfunctional by attaching to their binding sites.[5] While the Gram-negative bacterial membrane (e.g., *E. coli*) is mostly made of tightly packed lipopolysaccharides (LPS), Gram-positive bacteria (e.g., *S. aureus*) possess additional protection in the form of a dense peptidoglycan cell wall that makes them generally more resistant to several other antimicrobial agents too.[6] These differences could be implicated for the small variation in the activity of the nanosilver coated paper toward the two cultures. However, the coated papers are still effective in inhibiting both *E. coli* and *S. aureus*.

As mentioned earlier, silver nanoparticles have been previously used as antimicrobial agents,[3] and several commercial antimicrobial products based on nanosilver are available.[8−10] Most such studies have attributed the antimicrobial properties to the partial oxidation of coated silver and slow releasing Ag^+ and Ag^0 species from the coated surfaces.[37] The tendency to slowly leach silver from the surfaces, on the other hand, has been reported to be dependent on parameters such as pH, concentration of silver, presence of surfactant and other organic matter,[38] or the predominant presence of specific lattice planes on the silver nanoparticles.[39] Previous studies have also implicated the effect of nanoparticles size on the antibacterial properties and have indicated that smaller silver nanoparticles illustrate improved micobicidal activity over larger particles owing to a higher effective surface area.[40] The two coated samples used in this study, 25 mM/30 min and 100 mM/60 min, differ significantly in the amount of silver contained as indicated by the TGA measurements (2 wt % for the former and 23.9 wt % for the latter, Table 1). However, at the same time, the average particle size of

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Table 2. Antibacterial Activity Assay with Silver Nanoparticles-Coated Paper against *E. coli* and *S. aureus*[a]

E. coli				*S. aureus*			
25 mM/30 min				25 mM/30 min			
duration of treatment (h)	CFU mL^{-1} ($\times 10^6$)	N/N_0	reduction in viability (%)	duration of treatment (h)	CFU mL^{-1} ($\times 10^6$)	N/N_0	reduction in viability (%)
t_0	10.2	100	0	t_0	5	100	0
t_1	0.3	0.25	99.97	t_1	3	2.4	97.9
t_3	0	0	100	t_3	3	0.4	99.5
100 mM/60 min				100 mM/60 min			
duration of treatment (h)	CFU mL^{-1} ($\times 10^6$)	N/N_0	reduction in viability (%)	duration of treatment (h)	CFU mL^{-1} ($\times 10^6$)	N/N_0	reduction in viability (%)
t_0	10.1	1	0	t_0	5	100	0
t_1	0.2	0.07	99.98	t_1	3	2.4	97.9
t_3	0	0	100	t_3	0.6	0.09	99.91

[a] The viable bacteria were monitored by counting the number of CFUs. Reduction in viability was measured by calculating the surviving fraction (N/N_0). See text for details.

the coating of 25 mM/30 min paper is significantly smaller than that of 100 mM/60 min paper (~27 nm against ~142 nm) as is evident from the SEM images (Figure 4A and D). As is evident from the results of antimicrobial activity (Table 2), similarities between the antimicrobial activities of the two samples despite the difference in the amount of coated silver could therefore be attributed to the smaller particles present on the 25 mM/30 min coated paper. These results corroborate the earlier reports on the size dependent microbicidal activity of silver nanoparticles.[40]

Also, it has been recognized that dual functional bactericidal surfaces bearing both chemical-releasing bacteria-killing capacity and contact bacteria-killing capacity have added advantages over any method consisting of either function alone.[41] The sturdy coating of silver on the paper resulting from the ultrasonication could be advantageous, as it acts as a reservoir for slow releasing ionic silver over a long period. Moreover, the defectless coated surface of the paper achieved using the ultrasonication method would be highly effective in killing bacteria upon contact and prevent any growth of pathogens on the surface. As indicated in the ICP measurements, the 25 mM/30 min paper showed a higher leaching of silver (9.5 wt %) from the coating upon the sonication treatment than the 100 mM/60 min paper (0.62 wt %). Thus, it is possible that this difference in the leaching silver is contributing to the mostly similar microbicidal efficiency of the two coatings. In this study, it was shown that the coated surfaces minimize any effect of nanoparticle sizes on their antibacterial properties as the significant difference in their leaching properties compensates for these size differences. This could be reason that our results show that there is no difference in the antibacterial activity when compared to previous studies where the nanoparticles size had a significant impact on the activity.[40] Importantly, antibacterial tests carried out on coated papers stored at room temperature for over 6 months under ambient light conditions showed similar results, suggesting that the coatings are stable and their activity is unaffected by the prolonged storage periods. Variation in parameters such as precursor concentration and ultrasonication time, therefore, could lead to significantly different coatings with varying amounts of deposited nanosilver and dissimilar leaching properties. Thus, the choice of coating based on the requirement for different functionalities could be a key factor in selecting these parameters.

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4. Conclusions

The current paper demonstrates a new method of depositing silver nanoparticles on the surface of paper using a one step, simple, and efficient utrasonication process. By varying parameters such as precursor concentration and ultrasonication time, excellent control of the extent of coating has been achieved. It has been demonstrated that the coatings thus obtained are remarkably stable and the loss of silver from the coated surfaces is minimal, which is crucial for a longer lifetime of such coated papers in an active state. The coated paper demonstrated highly efficient antibacterial activity against both Gram-positive and Gram-negative bacteria, suggesting potential application as a food preservation material for longer shelf life and prevention of cross contamination. The uniform coating of metallic silver also demonstrated conductivity which could be utilized to develop paper based biosensors for rapid and portable biochemical detection procedures. The coating method employing utrasonication can be efficiently extended to other nanomaterials in order to acquire desirable properties such as hydrophobicity and varying degrees of conductivity and roughness on paper and could lead to interesting applications.