Antibacterial effect of nanosized silver colloidal solution on textile fabrics

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This paper deals with the antibacterial efficacy of nanosized silver colloidal solution on the cellulosic and synthetic fabrics. Two kinds of Bacteria; Gram-positive and Gram-negative, were used. TEM observation of silver nanoparticles showed their shape, and size distribution. The particles were very small (2–5 nm) and had narrow distribution. SEM images of treated fabrics indicated silver nanoparticles were well dispersed on the surfaces of specimens. WAXS patterns did not show any peak of silver as the fabric had very small quantity of silver particles. However, ICP-MS informed the residual concentration of silver particles on fabrics before/after laundering. The antibacterial treatment of the textile fabrics was easily achieved by padding them with nanosized silver colloidal solution. The antibacterial efficacy of the fabrics was maintained after many times laundering.
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1. Introduction

With the advent of improved human life, a new area has developed in the realm of textile finishing. The control of microorganisms on textile fabrics extends into diverse areas as the hospital environment and everyday household. Although textiles wholly made of natural fibers or synthetic fibers, neither natural nor synthetic fibers have resistance to bacteria or pathogenic fungi. Thus, various antibacterial finishes and disinfection techniques have been developed for all types of textiles. For a long time the chemical agents in use for controlling microorganisms range from the very simple substances such as halogen ions to the very complex compounds typified by the detergents. Many of these agents have been employed for generations, while others represent the latest developments [1, 2]. Several new antibacterial agents of textiles based on metal salt solutions ($CuSO_4$ or $ZnSO_4$) or zinc pyrithione ($Zn(1\text{-hydroxy-2-pyridinethione})_2$) have been developed recently [3, 4]. But pure metals have not been used normally for antibacterial finishing. The wide variety of equipment available for application and the curing limitations of some companies require that the effects of variations in curing conditions be known to obtain the desired quality products. The high level of bacterial resistance obtained by simple application techniques at low processing costs has resulted in commercial interest by many textile finishers. By this reason, we developed new antibacterial finishing with using simple method by taking advantages of nanotechnology.

Nanotechnology is concerned with materials whose structures exhibit significantly novel and improved physical, chemical, and biological properties, phenomena, and functionality due to their nanoscaled size [5, 6]. This raises many issues regarding to new materials for achieving specific processes and selectivity. The uses of nanostructured materials and systems become more widespread. Nanophasic and nanostructured materials are attracting a great deal of attention because of their potential applications in technical areas. As investigations and researches for nanotechnology are inherently multidisciplinary, we have focused nanotechnology to consolidate into bacteriostasis of textile fabrics.

The trend to smaller and smaller structures, miniaturization, is well known in the manufacturing of microelectronics [7]. In the materials area this same trend towards miniaturization is also occurring, but for different reason. Smallness in itself is not the goal. Novel properties of nanoscaled materials will make new breakthroughs in a multitude of technologically important areas. One of the material scientists' particular interests is the fact that nanostructured materials have higher surface area than conventional materials [8]. By this reason, small number of silver nanoparticles can well disperse to the surface of fibers by padding of colloidal solution and inhibit the growth of microorganisms.

Heavy metals are usually toxic and very reactive with proteins [9, 10]. They are believed to bind protein molecules, the cellular metabolism in inhibited, and the microorganism dies. For instance, silver is useful as an antiseptic and disinfectant [11]. Bacterial cells are constantly exposed to stressful situations and an ability to resist those stresses is essential for their survival [12]. The ability of microorganisms to grow in the presence of metal containing might result from specific mechanisms of resistance. Such mechanisms include alteration of chemical structure or and toxicity by changes in the redox state of the metal ions. However, silver has been well known as non-toxic in spite of claimed to kill many different disease organisms. In literatures, silver is skin friendly and does not cause skin irritation [13].

We suppose, the rapid growth of coating and dispersion technology using nanoparticles will improve the properties of their substances as the area of coating and dispersions has seen tremendous advances over the past decades. These advances cover the spectrum from scientific achievements resulting from long-term research to commercial successes. In this research, the nanoscaled silver particles were dispersed on the textile fabrics to be evaluated antibacterial effect and its durability.

2. Experimental

Cotton fabric weighting 109 g/m^2, Polyester fabric weighting 89 g/m^2, polyester/cotton blended fabric (ratio of 65/35) weighting 80 g/m^2, and polyester/spandex blended fabric (ratio of 92/8) weighting 85 g/m^2 were desized, scoured, bleached. Experiments were performed on samples with maximum dimensions 97 cm × 97 cm.

The ethanol based nonosilver colloids was supplied from Nano EnC. Co. Ltd., at the concentration of 2,000 ppm. This colloidal solution was diluted with distilled water by 50 ppm and 25 ppm at RT for our experimentation. Padding was performed at the constant pressure for all samples after wet pickup of 83% through of colloids bath.

Cotton and polyester fabrics were padded through 25 ppm and 50 ppm silver colloids. First eight pieces of cotton and polyester samples were padded before dyeing, respectively. Thereafter, other eight pieces of cotton and polyester fabrics were padded after dyeing, respectively. Some samples were rinsed in water after padding at 25°C and the others were not. We detected bacterial reductions on all occasions and compared them to find out the optimal process of antibacterial finishing. Printed wovens which were made polyester and polyester/cotton blended, were padded through 50 ppm silver colloids before printing. Polyester/spandex blended knits were padded through 50 ppm silver colloidal solution before bleaching or dyeing. We also measured bacterial reduction of printed wovens and stretchable knit after antibacterial treatment.

Three kinds of fabrics—cotton wovens treated after dyeing, cotton wovens treated before printing, and polyester wovens treated after dyeing – were tested laundering durability of antibacterial effect after 5 cycles, 10 cycles, and 20 cycles washing. We laundered our samples with the machine set for warm water (40 ± 3°C) at normal cycle. After each laundering the fabrics were tumble dired in an electric dryer at 70°C.

The antibacterial properties were quantitatively evaluated against *Staphylococcus aureus* (*A. aureus*), ATCC6538, a Gram-positive bacterium and *Klebsiela pneumoniae* (*K. pneumoniae*), ATCC 4352, a Gram-negative bacterium, according to KS K 0905-1996 test method. The specimens were placed on germ containing agar plates, inoculated with *S. aureus*, and *K. pneumoniae*, then incubated in an agar media. The sample diameter was 4.8 ± 0.1 cm. Inoculum concentration was $1.3–1.6 \times 10^5$/ml. 0.5% non-ionic agent was used to wet the fabric samples with inoculum solution.

Bacteriostatic activity of colloidal solution was evaluated after certain contact time and calculated percent reduction of bacteria. Using the following equation

$$R\,(\%) = \frac{A - B}{A} \times 100$$

Where $R =$ the reduction rate, $A =$ the number of bacterial colonies from untreated fabrics, and $B =$ the numbers of bacterial colonies from treated fabrics.

Morphological observations of shape, size, and its distribution of nano-scaled silver particles were carried out with transmission electron microscope (TEM) on JEOL 2000FX operated at 200 kV and employed with up to 200,000 magnification. The specimen on the grid was shadowed with platinum in order to increase contrast of image [14].

For the surface observation of treated fabrics, the scanning electron microscope (SEM) was operated at 5 kV on JEOL JSM-6330F with up to 20,000 magnifications.

Wide-angle X-ray diffraction (WAXD) measurements were carried out on Rigaku Denki X-ray generator using Cu K_α radiation operated by 40 kV and 100 mA. Scan region and speed was $5° \leq 2\theta \leq 35°$ (2θ is scattering angle, θ is Bragg angle) and 5°/min, respectively.

Inductively coupled plasma-Mass spectroscopy (ICP-MS) was used on Perkin-Elmer Sciex ELAN-5000 to measure the remained quantity of silver particles. We compared the concentration of silver particles on fabrics before washing to the particles on them after 5, 10, 20 times washing.

3. Results and discussion

The morphological appearance of nano-sized silver particles was observed by TEM (Fig. 1). The shape of particles was spherical. The diameter of particles was estimated at 2–5 nm.

Nanosized silver particles in colloidal solution had excellent antibacterial effect on all specimens against Gram-positive and Gram-negative bacteria. Table I shows the antibacterial effect of nanosized silver colloidal solution on cotton and polyester wovens. We tried to compare the antibacterial effect of our samples which were padded through colloidal solution before dyeing with the padded samples after dyeing. In the result, bacterial reductions of all specimens were very excellent against *S. aureus* and *K. pneumoniae*. The bacterial reduction was more effective when the specimens were treated with silver colloids after dyeing than when treated before dyeing. The fabrics padded through 50 ppm silver colloidal solution also had better bacteriostasis than the samples treated with 25 ppm solution. Rinsing after padding reduced the antibacterial efficacy of treated fabrics. But the numerical differences of bacterial reductions are not significant as shown in Table I.

The fiber surfaces of antibacterial treated fabrics were observed by SEM micrographs. In Fig. 2, SEM

TABLE I Antibacterial effect of nano-silver colloids on cotton and polyester fabrics

S. aureus			RAT 25[a]	NAT 25[b]	RAT 50[c]	NAT 50[d]
Samples		Start	1.3×10^5	1.3×10^5	1.3×10^5	1.3×10^5
Cotton	TBD[e]	After 24 hrs.	<10	<10	1.5×10^5	<10
		% reduction	99.9	99.9	99.8	99.9
	TAD[f]	After 24 hrs.	<10	<10	1.6×10^5	<10
		% reduction	99.9	99.9	99.8	99.9
Polyester	TBD[e]	After 24 hrs.	<10	2.4×10^5	3.8×10^6	<10
		% reduction	99.9	99.7	95.3	99.9
	TAD[f]	After 24 hrs.	<10	<10	1.6×10^5	<10
		% reduction	99.9	99.9	99.8	99.9
K. pneumoniae			RAT 25[a]	NAT 25[b]	RAT 50[c]	NAT 50[d]
Samples		Start	1.5×10^5	1.5×10^5	1.5×10^5	1.5×10^5
Cotton	TBD[e]	After 24 hrs.	1.9×10^5	<10	<10	<10
		% reduction	99.7	99.9	99.9	99.9
	TAD[f]	After 24 hrs.	<10	<10	1.2×10^5	<10
		% reduction	99.9	99.9	99.8	99.9
Polyester	TBD[e]	After 24 hrs.	6.8×10^5	1.3×10^5	3.1×10^5	1.9×10^5
		% reduction	98.9	99.8	99.5	99.7
	TAD[f]	After 24 hrs.	<10	<10	<10	<10
		% reduction	99.9	99.9	99.9	99.9

[a]Rinsed after antibacterial treatment with 25 ppm nanosized silver colloidal solution.
[b]Not rinsed after antibacterial treatment with 25 ppm nanosized silver colloidal solution.
[c]Rinsed after antibacterial treatment with 50 ppm nanosized silver colloidal solution.
[d]Not rinsed after antibacterial treatment with 50 ppm nanosized silver colloidal solution.
[e] Antibacterial treated before dyeing.
[f]Antibacterial treated after dyeing.

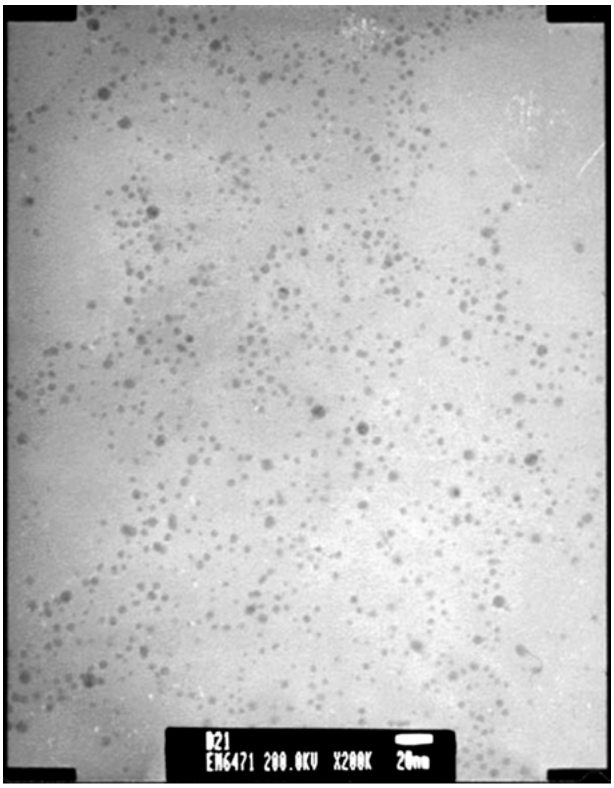


Figure 1 HR-TEM picture of nano-silver particles (×200 K).

images show the nanoscaled silver particles on cotton (a) and polyester (b) fabrics. The silver nanoparticles are well dispersed on fiber surfaces in each fabric.

Table II explains the antibacterial effect of nanosized silver colloids on printed fabrics those were padded through 50 ppm colloidal solution before printing. The antibacterial effects of printed fabrics were also excellent whether the samples were made of pure cotton or cotton blended with polyester.

We tried same treatment on knitted fabrics. Table III shows the antibacterial effect of nanoscaled silver colloidal solution on knitted stretchable single span fabrics which were padded through 50 ppm colloidal solution

TABLE II Antibacterial effect of nano-silver colloids on printed fabrics

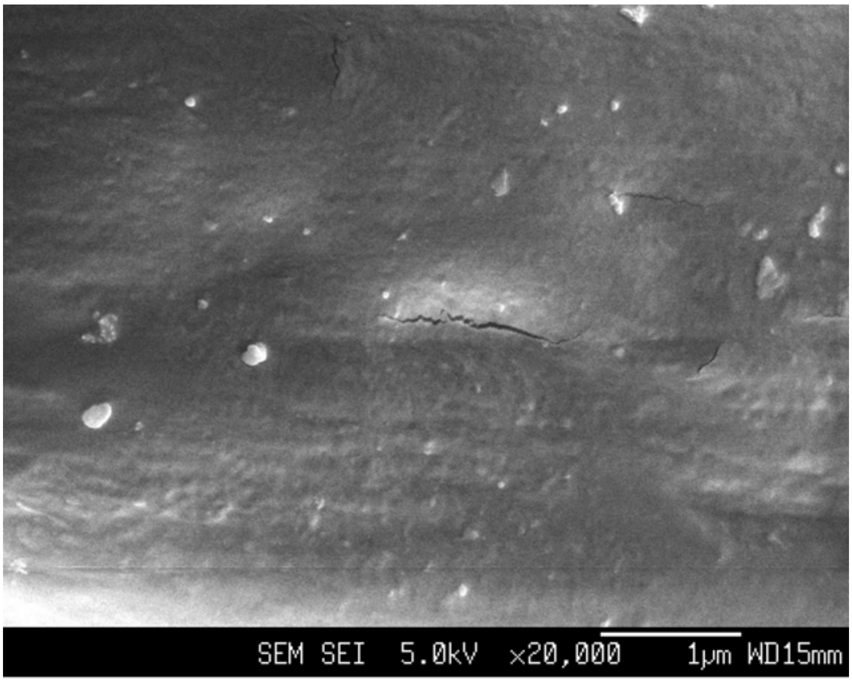
		CBP[a]	CPBP[b]
S. aureus	Start	1.6×10^5	1.6×10^5
	After 24 hrs.	<10	<10
	% reduction	99.9	99.9
K. pneumoniae	Start	1.4×10^5	1.4×10^5
	After 24 hrs.	<10	<10
	% reduction	99.9	99.9

[a]Padded 50 ppm nanosized silver colloidal solution on cotton wovens before printing.
[b]Padded 50 ppm nanosized silver colloidal solution on cotton/polyester blended wovens before printing.

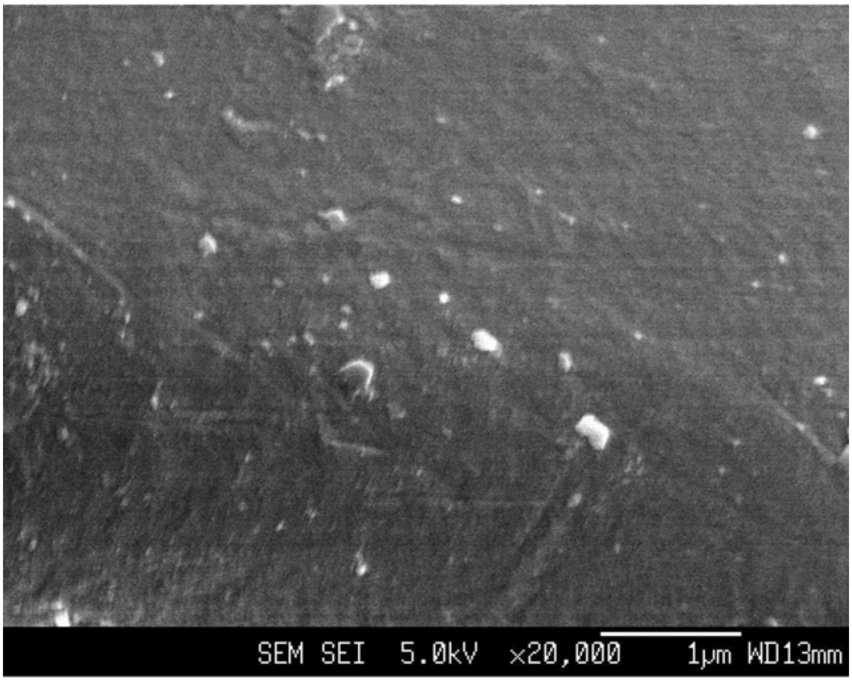
TABLE III Antibacterial effect of nano-silver colloids on knitted stretchable single span fabrics

		KBB[a]	KBD[b]
S. aureus	Start	1.6×10^5	1.6×10^5
	After 24 hrs.	1.4×10^5	<10
	% reduction	95.1	99.9
E. coli	Start	1.4×10^5	1.4×10^5
	After 24 hrs.	<10	<10
	% reduction	99.9	99.9

[a]Padded 50 ppm nanosized silver colloidal solution on polyester/spandex blended knits before bleaching.
[b]Padded 50 ppm nanosized silver colloidal solution on polyester/spandex blended knits before dyeing.



(a)



(b)

Figure 2 SEM images of nano-silver particles on cotton (a) and polyester (b) (×20 K).

before bleaching or dyeing. The antibacterial effect of them was also good as shown their bacterial reduction in Table III. The bacteriostasis against *S. aureus* on dyed sample was better than bleached sample.

Table IV shows excellent laundering durability of bacteriostasis of colloidal silver. Polyester woven fabric had good antibacterial effect against *S. aureus* by 20 times washing, otherwise the bacterial reduction against *K. pneumoniae* was not significant. All cotton fabrics, dyed or printed, had excellent bacteriostasis against *S. aureus* and *K. pneumoniae* by 20 times washing. Only the cotton fabric that was dyed before treatment had not good bacterial reduction after 20 times washing. We need to develop the finishing process to attach silver nanoparticles on fabric dynamically for the excellent laundering durability.

WAXS of pure cotton and polyester fabrics were compared to the samples those were padded through 50 ppm nano-silver colloidal solution and laundered 5, 10, and 20 times respectively after antibacterial treatment. The patterns did not show any peak of silver on all cotton (Fig. 3) nor polyester (Fig. 4) fabrics. We suppose the treated fabrics have too small quantity of silver to affect on WAXS peaks of our samples.

Remained silver particles on fabric before washing or after washing were measured quantitatively with using

TABLE IV Laundering durability of antibacterial effect of nanosilver colloids on fabrics

S. aureus		Cotton I[a]	Cotton II[b]	Polyester[c]
Before washing	Start	1.3×10^5	1.3×10^5	1.3×10^5
After 5 cycles	After 24 hrs.	<10	ND	5.7×10^6
	% reduction	99.9	–	91.6
After 10 cycles	After 24 hrs.	1.2×10^6	<10	7.3×10^6
	% reduction	98.2	99.9	89.3
After 20 cycles	After 24 hrs.	6.3×10^6	$1.9.3 \times 10^7$	1.1×10^7
	% reduction	90.8	97.2	84.3
K. pneumoniae		Cotton I[a]	Cotton II[b]	Polyester[c]
Before washing	Start	1.4×10^5	1.4×10^5	1.4×10^5
After 5 cycles	After 24 hrs.	2.7×10^6	ND	4.6×10^7
	% reduction	96.2	–	36.5
After 10 cycles	After 24 hrs.	5.2×10^6	<10	5.4×10^7
	% reduction	92.8	99.9	24.8
After 20 cycles	After 24 hrs.	5.0×10^7	3,900,000	6.1×10^7
	% reduction	30.4	94.5	15.3

[a]Padded 50 ppm nanosized silver colloidal solution on cotton wovens after dyeing.
[b]Padded 50 ppm nanosized silver colloidal solution on cotton wovens before print.
[c]Padded 50 ppm nanosized silver colloidal solution on polyester wovens after dyeing.

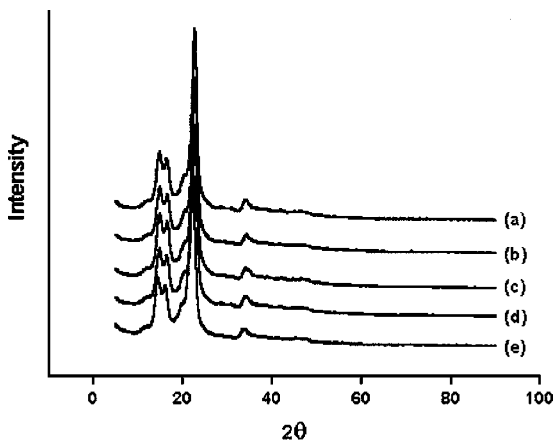


Figure 3 WAXS patterns of cotton (a), cotton padded 50 ppm of nanosilver colloids (b), after 5 times washing (c), after 10 times washing (d), and after 20 times washing (e).

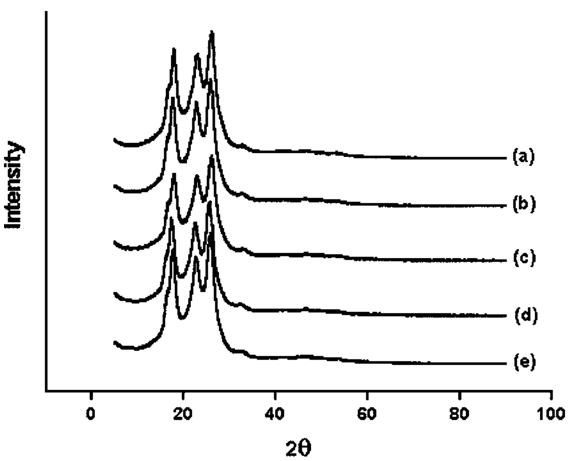


Figure 4 WAXS patterns of polyester (a), polyester padded 50 ppm of nano-silver colloids (b), after 5 times washing (c), after 10 times washing (d), and after 20 times washing (e).

TABLE V Ag concentration on treated cotton fabrics

	Ag concentration (ppm)	
	1st test	2nd test
Before washing	31.8	26.7
After 5 cycles	4.3	3.4
After 10 cycles	2.7	2.2
After 20 cycles	2.2	2.0

ICP-MS. Table V shows the silver concentration on cotton fabrics before washing and that of after washing. The concentrations of silver particles were decreased rapidly after 5 times laundering. The result indicates nano-silver particles were heavy coupled on their substrates and they can have a good bacteriostasis even only small quantity of nano-silver particles exists on fabrics because nanoscaled materials have high ratio of particle number to volume.

4. Conclusion

We investigated the antibacterial effect of nanosized silver colloidal solution against *S. aureus* and *K. pneumoniae* when we padded the solution on textile fabrics. TEM observation of nano-silver particles informed their shape and size distribution. In SEM images, nanosilver particles were well dispersed on their substrate. WAXS patterns did not show any peak of silver on all fabric samples because of small quantity of silver. ICP-MS indicates quantitatively the remained silver concentration of fabrics before/after laundering. Antibacterial efficacy on textile fabrics was easily achieved with using nanosized silver colloidal solution by padding process, and had a good laundering durability.

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