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ORIGINAL PAPER

# Thermal preparation and stabilization of crystalline silver particles in $SiO_2$-based coating solutions

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**Abstract** $Ag/SiO_2$ coating solutions for antimicrobial functionalisation can be prepared by a thermal reaction (reflux or solvothermal conditions) of mixtures of tetraethoxysilane, alkylamine compounds and $AgNO_3$. These coating solutions are especially useful for antimicrobial refinement of temperature sensitive materials like textiles or wood. Moreover coating application onto substrates such as glass or metal, as well as preparation of micrometer sized bulk particles by using a spray-drying process is also feasible. The efficiencies of $AgNO_3$ reduction in the presence of different amine compounds like triethanolamine, triethylamine or diethanolamine are compared. $SiO_2$ nanoparticles are formed by basic hydrolysis of tetraethoxysilane and stabilize the crystalline silver particles in the solution. The antimicrobial effect of silver containing coatings on textile fabrics is investigated.

**Keywords** Silver · Solvothermal · Antimicrobial · $Ag/SiO_2$-composite · Alcoholamine · Amine

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## 1 Introduction

Nanosized silver particles and coatings containing these particles are of high scientific and economic interest due to a broad range of application in several technological fields, like preparation of antimicrobial materials, prevention of biofilm formation and utilisation as optical filter material as well as for nonlinear optics [1–4]. One advantage of silver particles used as antimicrobial agents is their high biocidal efficiency, even at low concentration, against a broad range of germs like bacteria, fungi and yeast [1, 5, 6]. Furthermore, avoiding microbial growth and therefore prevention of infections, silver particles are also used to refine textile fabrics for the medical treatment of atopic dermatitis or for skin-therapy of patients with diabetes [7]. To provide thermal sensitive materials like textiles or wood with antimicrobial properties and for therapeutic purpose sol–gel technology is an appropriate method [8–11]. The embedding of nanosized silver in inorganic sol–gel matrices can be used for stabilisation of silver particles and their fixation and immobilisation onto thermal sensitive substrates [12–18]. In principle several methods of preparing silver particles by reduction of silver salts can be distinguished [4, 19–21]. These are:

(a) The thermal decomposition of silver salts like $AgNO_3$ [22–26]. However, this procedure is not useful for common textile materials or wood which are destructed at temperatures above 120 °C [8–10].
(b) The photolytic decomposition of precipitated AgCl [27].
(c) The chemical reduction of solved $AgNO_3$ with reductive agents like $NaBH_4$, hydrazine or ascorbic acid [28, 29].

Beside the addition of reductive agents also the reduction of $AgNO_3$ by the solvent ethanol is reported. However this reaction is slow and has to be performed under thermal treatment with reflux or solvothermal conditions at temperatures up to 180 °C [30–33]. Nanosized silver particles are mostly gained as precipitates and powders. In order to apply silver particles to different surfaces it is most beneficial to have a liquid solution of stabilized silver particles which could be easily applied by dip-coating or spraying. Therefore, the thermal preparation of Ag/$SiO_2$ coating solutions in the presence of amine compounds, as reported in the present work, could be advantageous. The thermal preparation is performed under reflux or solvothermal conditions. As stabilizers several amine compounds like triethanolamine or diethanolamine are used, which are also known as stabilizing chelating agent for the preparation of $TiO_2$ sols [34–36], ZnO sols [37] or $LiNbO_3$ particles with tunable shape [38]. These amine compounds catalyze the basic hydrolysis of tetraethoxysilane to $SiO_2$ particles, stabilize the $Ag^+$ ions in the basic medium and enable the reduction to crystalline silver particles. The presence of $SiO_2$ particles is of importance, since they are observed to be necessary to prevent aggregation of the as-formed silver particles in the solution. In addition a silica matrix develops after coating deposition which could be important to fix the silver particles onto different substrates. Due to the commercial interest in antimicrobial coatings, the antimicrobial effect of as-prepared silver containing coatings on textile fabrics is investigated. However, coating other materials like wood, glass or metal is also possible. Furthermore, a spray-drying process can be performed with the coating solutions leading to bulk materials. These bulk materials are micrometer sized powders, useful for example in spinning processes or as additive in inorganic coatings [39].

## 2 Experimental part

### 2.1 Sample preparation

For preparation of the coating solution (CS 1–6) a mixture 19 mL of tetraethoxysilane (TEOS), 77 mL water and 3.8 mL of an amine A1–A6 (cp. Table 1) compound is stirred for at least 2 days until the solution becomes clear. To this solution a mixture of 0.1 g $AgNO_3$ in 5 mL of water is added under vigorous stirring. Two types of thermal treatments are performed with this solution, a treatment under reflux (TR) for 5 h and a solvothermal treatment (ST) for 1 h at 120 °C and 2.5 bar pressure under stirring in a commercially available autoclave with teflon vessel (Berghof instruments GmbH; Hochdruck-Laborreaktor BR-500). A solvothermal processing cycle comprises a temperature raise for 45 min starting from room temperature up to an aimed final temperature and subsequent cooling down to room temperature for the duration of 2 h. As reference samples for the particle size determining methods applied, both $SiO_2$ sols without addition of $AgNO_3$ and silver sols without tetraethoxysilane using the composition of 19 mL ethanol, 77 mL water and 3.8 mL amine compound are prepared analogously. The application onto textile is performed by dipping and withdrawing viscose fabrics from the solution. After dipping, the textile samples are first dried at room temperature and afterwards annealed for 30 min at a temperature of 120 °C.

**Table 1** Investigated amine compounds together with related pKa values and peak potential $E_p$

| Amine | Amine compound | Formula | pKa [50, 61] | $E_p$ [V] |
|---|---|---|---|---|
| A1 | Triethanolamine | $N(C_2H_4OH)_3$ | 7.9 | 1.21 |
| A2 | Ethyldiethanolamine | $NC_2H_5(C_2H_4OH)_2$ | 9.0 | 1.13 |
| A3 | Diethylaminoethanol | $N(C_2H_5)_2C_2H_4OH$ | 10.1 | 1.07 |
| A4 | Triethylamine | $N(C_2H_5)_3$ | 10.7 | 1.05 |
| A5 | Diethanolamine | $HN(C_2H_4OH)_2$ | 8.9 | 1.39 |
| A6 | Pyrrolidine | $C_4H_8NH$ | 11.3 | 1.28 |

### 2.2 Methods

The UV-VIS transmission spectra of as-prepared solutions are measured using an UV-NIR spectrometer Zeiss MCS 501 UV-NIR. For these measurements the solutions have been diluted with water in a ratio of 1:50. The silver ion concentration in the coating solution is measured potentiometrically using a Silver/Sulfide Combination Electrode Ag/S 800 (WTW GmbH, Weilheim, Germany). The peak potentials for the oxidation of the used amine compounds are determined by cyclic voltametry (sweep rate 50 mV/s; potential range 0 to 1.5 V) with a potentiostat VSP from BIOLOGIC. As working electrode a glassy carbon disk electrode is used (shrouded in PTFE, active area 0.28 $cm^2$). The counter electrode is a platinum sheet, and the reference electrode is an Ag/AgCl in saturated LiCl in acetonitrile. All potential values in this paper are quoted with reference to this reference electrode. The measurements are performed in acetonitrile containing 0.1 M $NaClO_4$ (supporting electrolyte) and 0.005 M of the corresponding amine.

The presence of crystalline silver is determined by means of X-ray diffraction (XRD). These investigations are performed on dried powder samples, which are obtained by evaporation of the solvent at room temperature for a minimum of 24 h. The XRD patterns are recorded using Cu-Kα radiation at an X-ray diffractometer URD-6 (Seifert FPM) equipped with a secondary Johannson-type graphite-monochromator and scintillation detector. The diffraction patterns are analysed qualitatively using the PDF-2 [40] and ICSD databases [41]. Furthermore, in order to obtain detailed information about the mean size of nanocrystalline silver particles in the sols a quantitative phase analysis of the diffraction patterns is performed using the computer program TOPAS [42]. X-ray emission profile and instrumental parameters of the diffraction experiment are determined beforehand by analysing the diffraction pattern of a Silicon standard powder (NIST SRM 640c). The reflection profiles in the diffraction patterns of the sol powders are analysed using a *Fundamental Parameters Approach* convolution algorithm [43] which includes the refinement of the full-width-at-half-maximum (FWHM) of a Lorentzian profile to account for sample induced diffaction line broadening. For all refinements, a crystal structure of silver according to ICSD 64706 [44] is applied. For the fit of sample C3 an $R_{wp}$ value of 8.25% was obtained whereas for the fits of all other samples the $R_{wp}$ values ranged from 4.1% to 5.3%. With respect to serial correlation effects of the parameters refined standard deviations of the mean crystallite size are corrected according to [45]. Dynamic light scattering (DLS) is used to determine the particle size distribution in the prepared coating solutions. These measurements are performed with a device Zetasizer 1000 HSa/Malvern Instruments. For DLS measurements the liquid samples have been diluted with water in a ratio of 1:10. High-resolution transmission electron microscopy (HRTEM) is used to determine the size of crystalline silver particles in the $Ag/SiO_2$ composites. For sample preparation copper grids with a graphite membrane (Plano GmbH) have been chosen. The silver containing solutions have been applied to the copper grids by dip-coating. After dipping the coatings have been dried at room temperature for at least 24 h. As-prepared samples are investigated with a Philips CM30 transmission electron microscope. The antimicrobial activity of the silver containing textile samples against gram-negative *Escherichia coli* bacteria is determined as described in reference [15]. The wash fastness of silver treated textiles is tested with a commercial washing machine according to DIN EN ISO 6330. An ECE washing powder (according to ISO 105-C08/C09, supplied by EMPA) is used. The washing cycles are 5 times repeated at 40 °C. After washing, the textile fabrics are dried at room temperature and their antimicrobial activity is determined.

## 3 Results and discussion

By using the ternary amine compounds A1–A4 (cp. Table 1) as additives in the $AgNO_3$ containing $SiO_2$ sol, immediately after starting the thermal reflux treatment the reaction solutions turned to a red–brown coloration which got more intense with increasing reaction duration (see Fig. 1). Even after 15 min of reflux these solutions are coloured and the maximum of the optical absorption at around 420 nm indicates the formation of nanosized crystalline silver particles in the solution [46–48].

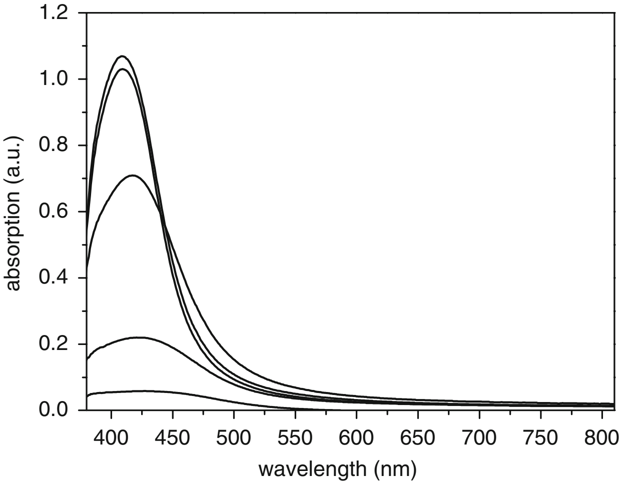

**Fig. 1** Absorption spectra of CS1 with increasing process duration (upward 15 min, 30 min, 1 h, 2 h, 5 h). For the measurements the solutions are diluted with water in the ratio of 1:50

In accordance to the increased coloration and therefore the formation of crystalline silver, the concentration of the ion $Ag^+$ in the reaction decreased as determined potentiometrically (Fig. 2). The decrease of $Ag^+$ concentration starts in the first 15 min and after 2 h of reflux the $Ag^+$ concentration of the solutions CS1 to CS4 is reduced to <1%. The speed of decrease of $Ag^+$ strongly depends on the ternary amine additives used. With amines A1 to A3 the $Ag^+$ concentration is drastically reduced in the first 30 min to values less than 20% compared to the starting concentration. After 1 h the $Ag^+$ concentration with A2 and A3 is <1%, in presence of A1 the reaction is slower and <1% is reached not before 2 h. In contrast, with A4 the decrease of $Ag^+$ is slower at the beginning of the reaction and only after 1 h a reduction to <20% is gained. In addition, for all samples the formation of crystalline silver is confirmed by means of XRD as shown in Fig. 3. The mean size of silver crystallites for all samples prepared under reflux is $\leq$3 nm (Table 2). Surprisingly, with the secondary amines A5 and A6 the decrease of $Ag^+$ concentration is significantly decelerated, so that even after 5 h of reflux about more than 10% $Ag^+$ is left in the solution (Fig. 2b). Accordingly, the change of colouration of the solution CS5 and CS6 to red–brown is slower compared to CS1–CS4 as demonstrated by the absorption of light at $\lambda = 420$ nm (Fig. 2a). However, from XRD the presence of crystalline silver in the solutions CS5 and CS6 is also

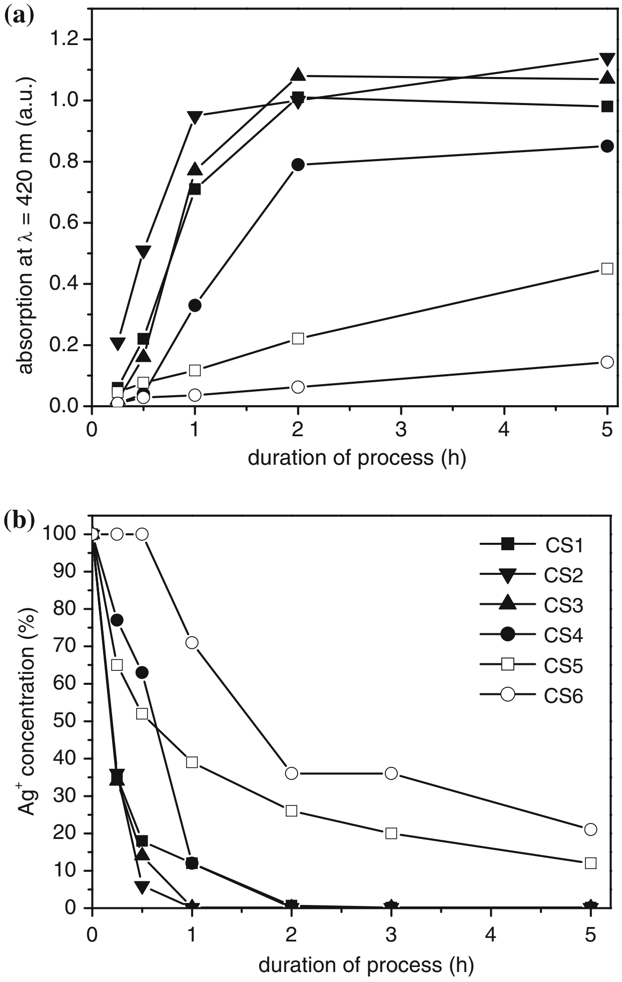

**Fig. 2** Change of absorption at $\lambda = 420$ nm of the sols CS1–CS6 (**a**) and the rate of the $Ag^+$ reduction (**b**), i.e. remaining $Ag^+$ concentration compared to a system without thermal treatment of the sols CS1–CS6 during reflux

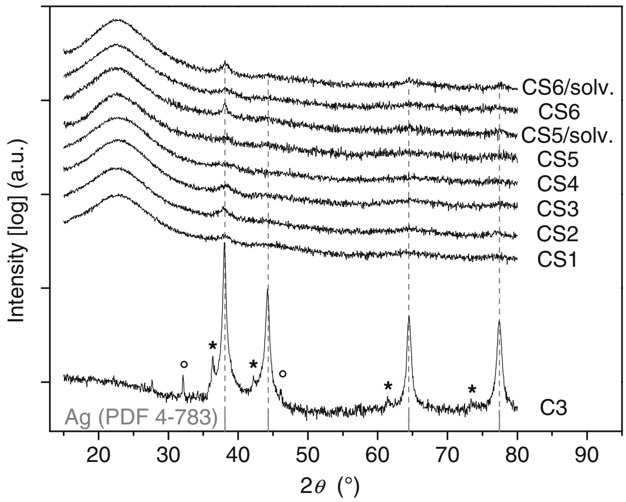

**Fig. 3** XRD measurements of powders obtained by solvent evaporation from C3 (same sol as CS3 but without $SiO_2$), CS1–CS6 after 5 h of reflux, CS5 and CS6 after solvothermal treatment at 120 °C for 1 h (CS5/solv., CS6/solv.). Reflections marked with open circle (o) are attributed to traces of $AgNO_3$ (PDF Card No. 43-649) and those marked with an asterisk (*) correspond to parasitic W-Lα radiation present in the X-ray tube emission spectrum

**Table 2** Mean crystallite size of silver nanoparticles as obtained by quantitative analysis of the diffraction patterns (drawn in Fig. 3) of powders obtained by solvent evaporation from C3 (same sol as CS3 but without $SiO_2$), CS1–CS6 after 5 h of reflux, CS5 and CS6 after solvothermal treatment at 120 °C for 1 h (CS5/solv., CS6/solv.)

| Sample | Mean crystallite size (nm) |
|---|---|
| C3[a] | 27 ± 0.7 |
| CS1–CS6[b] | ≤3 |
| CS5/solv. | 8 ± 0.9 |
| CS6/solv. | 4 ± 0.4 |

[a] Obtained by only fitting the last 3 reflections in the 2θ- range of 40–80°

[b] All refinements yielded a mean crystallite size of 3 nm, which is the minimum value to be obtained using the TOPAS software for refinement

confirmed (Fig. 3). The formation of a solution with strong red–brown coloration and a decrease of $Ag^+$ concentrations to values lower than 1% with the amines A5 and A6 is only achieved by a solvothermal treatment in an autoclave at 120 °C with 2.5 bar (Fig. 4). Beside the full reduction of $Ag^+$ concentration by solvothermal treatment also the mean size of silver crystallites increases (Table 2). Therefore, by harsher solvothermal reaction conditions the growth of larger silver crystallites is favoured while under reflux the whole $AgNO_3$ is consumed to build up smaller silver crystallites.

An explanation for this different behaviour in presence of different amines could be given by the peak potential $E_p$ of the amines investigated (compare Table 1). Roughly speaking higher values of $E_p$ correspond to more "noble" amines, i.e. amines that are more difficult to oxidise. However it must be borne in mind that the values reported in Table 1 are no redox potentials (the cyclic voltammograms were not reversible) and are for the oxidation of the amines at glassy carbon in acetonitrile. Nevertheless they allow a first estimation of the "ease of oxidation" of the corresponding compounds. As observed by Mann the potential $E_p$ of secondary amines is significantly higher than for corresponding ternary amines [49]. A higher $E_p$ value could be the reason for a slower reductive reaction as reported by Coelhan and Parlar for the reduction of water [50]. This probably is the reason, why with both secondary amines A5 and A6 the reaction is decelerated under reflux and a complete reduction of $Ag^+$ is only gained under harsher solvothermal conditions. By this, the slightly slower reaction of A1 compared to the other both ethanolamines A2 and A3 could be explained, too.

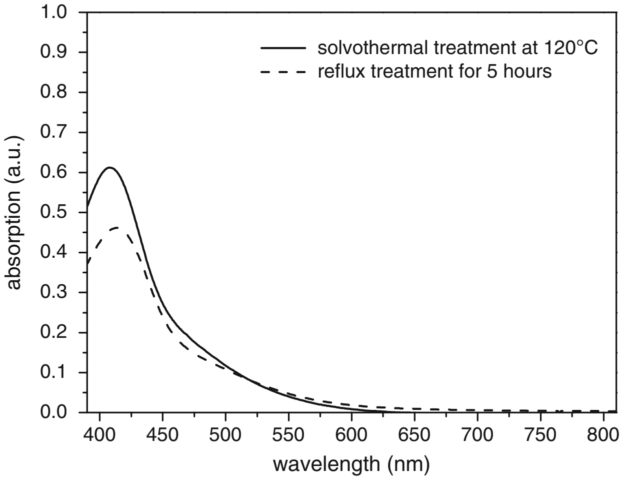

**Fig. 4** Absorption spectra of CS5 prepared with a solvothermal treatment at 120 °C for 1 h and under reflux for 5 h. For measurements the solutions are diluted with water in the ratio of 1:50

However, the amine A4 with lowest $E_p$ exhibits a slower initial reaction compared to A1. This reaction behaviour could be explained by a higher stability of $Ag^+$ ion complexes formed with the amine A4 compared to the stability with A1 {log$K_2$ for $[Ag(A4)_2]^+$ of 4.40 compared to log$K_2$ for $[Ag(A1)_2]^+$ of 4.08 [51, 52]}. The redox potential for $Ag^+$ ions is strongly related to the stability of formed $Ag^+$ complexes. With increased complex stability the reduction of $Ag^+$ to elementary silver is limited [53].

For the silver reduction it could be assumed that the reaction of $AgNO_3$ to crystalline silver particles is caused by reaction with ethanol which is present in the solution as product of the hydrolysis of TEOS [30]. A similar reduction of $AgNO_3$ by ethanol in presence of modified silica particles under reflux is reported elsewhere [30]. In this study the modification of $SiO_2$ particles was done with epoxy groups containing silanes which are supposed to stabilize the formed silver particles in solution and support the reductive reaction. In the now presented study, the stabilisation and support of reduction is achieved by the amine additives instead of the epoxy groups. The evidence that silver reduction by amine compounds is possible can also be found in [54] where the reduction of $AgNO_3$ by triethanolamine or triethylamine is reported. The amine acts as complexing agent keeping the $Ag^+$ ions in solution, even under basic conditions, and thus preventing the precipitation of AgOH. It is further supposed that these complexes are decomposed under the formation of elementary silver, i.e. the amine acts as both complexing and reductive agent. This reaction works even in aqueous solution without any organic solvent like ethanol, so the presence of ethanol as reductive agent should not be necessary [54–56]. Accordingly, the use of ternary amine compounds for preparation of silver particles is described in several patents [57, 58] but usually larger silver particles which precipitate as black powder from the solution, are gained. In contrast, the preparation presented here results in the formation of stable solutions containing silver particles which can be immediately applied as coatings to substrates like glass or textiles. The reason for this different behaviour probably is the presence of $SiO_2$ particles in the solution stabilizing the Ag particles and preventing further aggregation. Confirming this assumption, Ag particles with significantly smaller diameter are observed by HRTEM when the reaction is performed in presence of $SiO_2$ particles, while silver agglomerates up to several hundred nanometers in diameter are detected in solutions without $SiO_2$ (see Fig. 5). For the mean size of silver crystallites, as obtained by XRD, the same tendency is observed but compared to HRTEM smaller values are obtained (Table 2). Neglecting strain induced line broadening this can lead to the assumption that the particles to be seen in the HRTEM images are either polycrystalline in nature or agglomerates. At this point it is also worth mentioning, that the silver crystallites in the right image of Fig. 5 (sample

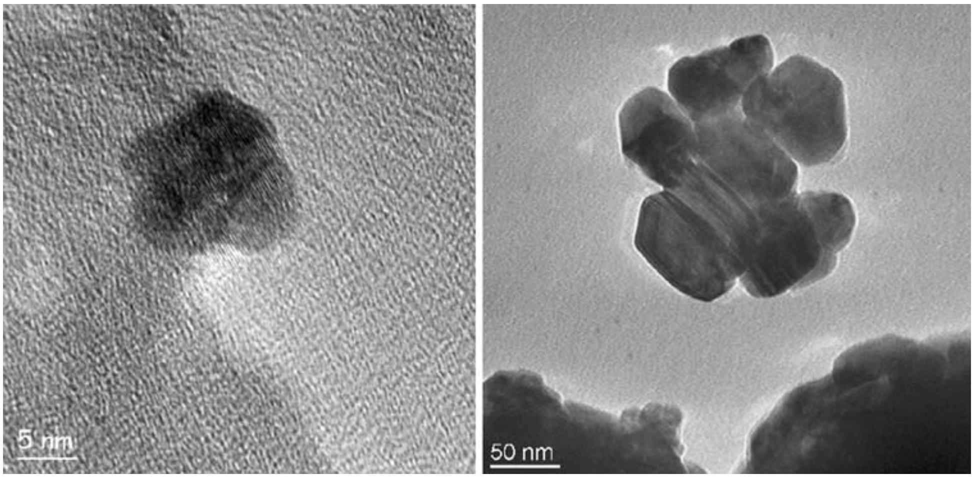

**Fig. 5** HRTEM image of Ag/$SiO_2$ sol CS3 (left) and TEM image of analogously synthesized sol C3 containing Ag particles but no $SiO_2$ (right) both prepared by coating copper grids

C3) exhibit a tabular shape with characteristic angles of facetting crystal faces of 120°. This implies that the extended faces of the silver crystallites are represented by (111) lattice planes. Accordingly, the possibility of constructive interference of X-ray waves diffracted by adjacent crystallites should be higher for the 111 reflection (due to the dispersion of the X-ray diffractometer small misalignments can yield to a vanishing of this effect for reflections at higher diffraction angles). Actually, in the XRD pattern of sample C3 we observed both, an anomalous decrease of the diffraction line broadening and an increase of intensity of the 111 reflection at $2\theta = 38.12°$. A similar effect, also interpreted as coherent scattering of adjacent nanocrystallites, was described by Rafaja et al. [59]. Following this discussion, the value for the mean crystallite size for sample C3 (Table 2) is obtained by fitting the 3 silver reflections in the $2\theta$ range from 40–80°, excluding the silver 111 reflection that would lead to a higher value representing the height of a stack of tabular silver crystallites. Considering a close interaction between metal oxide and silver nanoparticles which was also observed in case of $TiO_2$ [60] it can be assumed that an instantaneous co-deposition of reduced crystalline silver together with amorphous $SiO_2$ nanoparticles occurs with the latter hindering the growth of large silver particles. This aggregation of $SiO_2$ and Ag particles is confirmed by particle size measurements with DLS (Fig. 6). The mean particle size of a pure $SiO_2$ reference sol increases after thermal treatment. An additional increase of particle size is measured in thermally treated systems containing both $SiO_2$ and Ag particles, indicating that in presence of silver a growth of particles in solution occurs. Therefore it can be stated that both the presence of ternary amine and nanosized $SiO_2$ particles are important for the formation of nanosized silver particles in solution by reduction during thermal treatment of the solution.

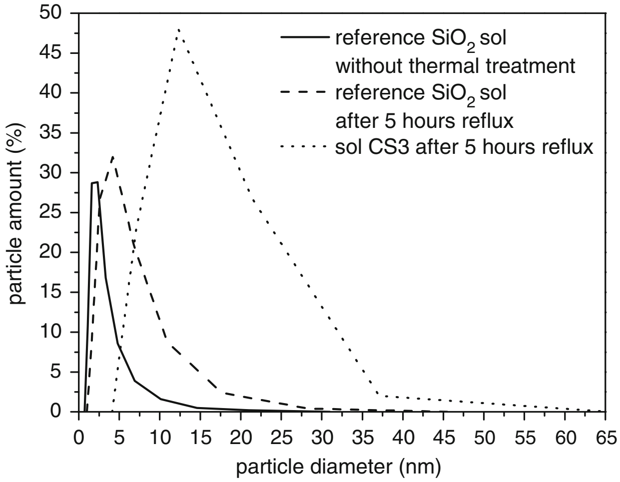

**Fig. 6** Comparison of particle size distribution of two reference $SiO_2$ sols with silver containing $SiO_2$ sol CS3

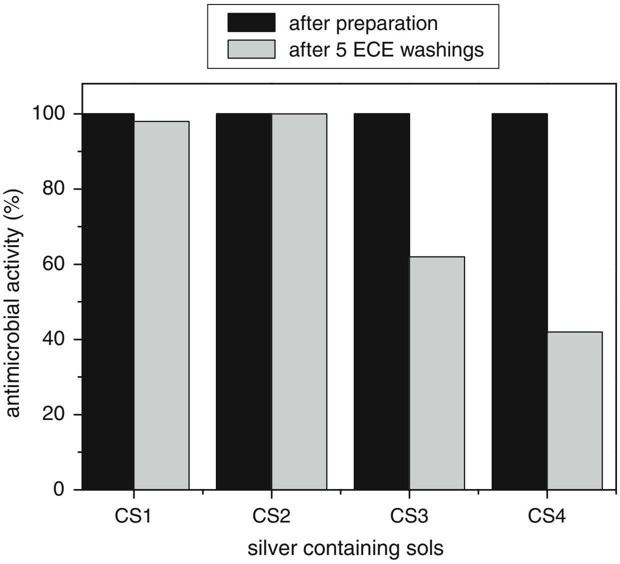

**Fig. 7** Antimicrobial activity against *E.coli* of $Ag/SiO_2$ coated viscose fabrics CS1–CS4 after preparation and after 5 household washing procedures

The prepared solutions of nanosized $SiO_2$ and silver particles are applied to textile fabrics by dipping. After deposition and evaporation of the solvent, a high antimicrobial activity is observed for all coatings investigated. Even after repeated washing procedures under household washing conditions the antimicrobial activity remains significantly high, however, using CS3 and CS4 the antimicrobial activity after 5 washing procedures is reduced to about 50% (Fig. 7).

## 4 Conclusions

The thermal preparation of $Ag/SiO_2$ coating solutions can be realized combining silica sol formation and $AgNO_3$ reduction using reflux or solvothermal treatment. Essentially for the formation of stable nanosized crystalline silver particle in the solution is the presence of both amine compounds and nanosized $SiO_2$ particles. The $SiO_2$ particles prevent the aggregation and further growth of silver particles and thus precipitation does not occur. Beside the presence of $SiO_2$ also the type of amine additive is important. Considering the amines investigated, only with ternary amines a complete reduction of $AgNO_3$ was observed under the reflux conditions chosen, whereas for the secondary amines investigated a solvothermal treatment with a temperature of at least 120 °C is necessary to complete the reduction of $AgNO_3$. The synthesized $Ag/SiO_2$ coating solutions are highly suitable to prepare antimicrobial coatings on textiles.

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