

# Study of interaction between nitrogen DBD plasma-treated viscose fibers and divalent ions $\text{Ca}^{2+}$ and $\text{Cu}^{2+}$

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**Abstract** Viscose fibers were treated with atmospheric pressure dielectric barrier discharge (DBD) plasma obtained in nitrogen in order to activate the fiber surface prior to sorption of the divalent ions  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$ . Methylene blue sorption was used for estimation of carboxyl group formation on the surface after DBD plasma treatment, through the degree of fabric staining ( $K/S$ ). Sorption of divalent ions was performed from solutions of each individual ion and from solutions of calcium and copper in succession onto untreated and plasma-treated viscose samples. The quantity of sorbed metal was determined from the neutralization and iodometric titration method. Scanning electron microscopy coupled with energy dispersive X-ray analysis was used for fiber morphology and surface characterization before and after plasma treatment, and after metal ions sorption. Experiments revealed copper microparticles formation on the fiber surface when sorption of copper was performed on samples with bonded calcium. Further analysis confirmed that for growth of copper particles, both calcium ions and nitrogen DBD plasma pretreatments are necessary.

**Keywords** Dielectric barrier discharge plasma · Viscose · Sorption of calcium and copper · Copper microparticles

## Introduction

The absorption and interaction of metal ions with textile materials is attracting growing interest because of the many possible applications, especially in the field of biologically active fibers and textiles for special technical uses (Anand and Horrocks 2000; Yudanova et al. 2000; Edwards and Vigo 2001; Zhukovskii 2005). Immobilization of metals in the form of ions and nanoparticles on fibrous substrates has become popular over the years because of the relatively simple immobilization procedures and broad spectrum of achieved effects obtained on textile materials, from antimicrobial (Ag, Au, Cu) and hemostatic (Ca) to UV protection (Zn) and a self-cleaning ability (Ti) (Dastjerdi and Montazer 2010).

As today's most abundant natural, nontoxic, biodegradable polymer, cellulose comes into focus as a suitable textile material for everyday and many special applications. Cellulose macromolecules contain three hydroxyl groups per anhydroglucose unit, which can undergo typical reactions for hydroxyl groups. Chemical modification of cellulose leads to the introduction of new functionalities such are carbonyl and carboxyl groups (Kontturi 2005; Potthast et al. 2006). Through

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active sites, hydroxyl, carbonyl or carboxyl groups, cellulose can bond metal ions and nanoparticles, thus becoming a bioactive material.

The interaction of cellulose with  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions has been thoroughly studied by many authors (Acemioglu and Alma 2001; Druz et al. 2001; Norkus et al. 2004; Saito and Isogai 2005; Sundman et al. 2008; Fitz-Binder and Bechtold 2012; Emam et al. 2012; Ozturk et al. 2009; Nikiforova and Kozlov 2012). According to the literature,  $\text{Ca}^{2+}$  ions react with carboxyl groups of cellulose in a 1:1 ratio through an ion exchange mechanism (Sundman et al. 2008; Ozturk et al. 2009; Fitz-Binder and Bechtold 2012). On the other hand,  $\text{Cu}^{2+}$  ions can interact with cellulose through two different mechanisms, ionic interactions with two COOH groups and van der Waals interaction with OH groups in cellulose (Acemioglu and Alma 2001; Sundman et al. 2008; Cady et al. 2011).

Plasma treatment, among many other applications, can be used to introduce various functional groups on the material surface (Shishoo 2007). Plasma in gases such as oxygen, atmospheric air and nitrogen can be used for the incorporation of COOH, CHO and  $\text{NH}_2$  groups on the fiber surface, and plasma-modified material can be used as a final product with improved sorption properties or as a substrate for further modification (Mather 2009).

Plasma treatment of natural cellulose fibers such as cotton has been thoroughly investigated by many authors, and mostly low pressure plasma or atmospheric pressure oxygen plasma has been used for functionalization of cotton (Malek and Holme 2003; Sun and Stylios 2004; Jun et al. 2008; Karahan et al. 2009; Shahidi et al. 2010; Calvimontes et al. 2011). On the other hand, viscose as a regenerated cellulose fiber has practically been neglected, and there are very few reports about the influence of plasma treatment on viscose (Fras-Zemljic et al. 2009; Peršin et al. 2011; Prysiazhnyi et al. 2013; Kramar et al. 2013).

Even though the plasma discharge obtained in nitrogen is usually more homogeneous than the corresponding discharges in other gases, the treatment of textiles, especially cellulose, using plasma in nitrogen has been poorly investigated. Also, a recent report suggests that nitrogen plasma could induce interesting effects on textile materials, such as the formation of silver nanoparticles after the treatment of viscose and cotton in nitrogen DBD (Prysiazhnyi et al.

2013). As we showed in our previous work, plasma in nitrogen induces changes on the cellulose fiber surface, which serves as both a reducing and stabilizing agent for silver nanoparticle formation.

In this work, we investigated the interaction between nitrogen DBD-treated viscose and divalent metal ions. Viscose samples were prepared by treatment in DBD in nitrogen using different plasma energy densities, i.e., different treatment times. Sorption of divalent ions was performed on both untreated and plasma-treated samples. Viscose morphology and surface analyses were performed together with determination of the ion sorption quantity as a function of the different energy densities used during plasma treatment, i.e., different plasma treatment times.

## Materials and methods

### Experimental material

Commercial, untreated viscose fabric was used for the experiments. Fabric parameters were: plain weave,  $150 \text{ g m}^{-2}$  weight and  $0.460 \pm 0.004 \text{ mm}$  thickness. All used chemicals were of pro analysis purity.

### DBD plasma treatment

A DBD plasma source with plane-parallel electrodes operating at atmospheric pressure was used (Kostic et al. 2009; Prysiazhnyi et al. 2013; Kramar et al. 2013). The discharge was generated between two aluminum electrodes ( $5 \text{ cm} \times 5 \text{ cm}$ ) covered by a 0.65-mm-thick alumina layer ( $10.5 \text{ cm} \times 10.5 \text{ cm}$ ). The distance between the covered electrodes was fixed by glass space holders with 0.5 mm thickness. The DBD was assembled in a chamber with gas injected into the discharge volume through ten equidistant holes to ensure homogeneous gas flow. Nitrogen (purity 99.995 %) was used as a plasma gas with a flow rate of  $6 \text{ l min}^{-1}$ . Viscose samples ( $4 \text{ cm} \times 4 \text{ cm}$ ) were treated using energy densities of 0.1, 0.25, 0.5 and  $1 \text{ J cm}^{-2}$ , i.e., time of treatment 18, 45, 90 and 180 s, which corresponds to a 0.14 W power of plasma discharge.

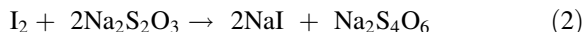
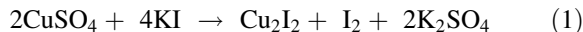
### Sorption of $\text{Cu}^{2+}$ and $\text{Ca}^{2+}$

Viscose samples (0.1 g) were immersed in 100 ml of 0.01 M solution of  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$  for 4 h. After

sorption, samples were removed from solution, squeezed and dried at room temperature. These conditions were chosen for comparison with our previous work, which involved spontaneous formation of Ag particles of nanometer size from silver solution onto viscose after nitrogen DBD treatment (Prysiashnyi et al. 2013).

For  $\text{Ca}^{2+}$  sorption, the standard method for carboxyl group determination was used as sorption method (Praskalo-Milanovic et al. 2010) since it enables maximum ion exchange of H in COOH groups of cellulose with calcium ions. On this basis, the following method was applied. Viscose samples (0.5 g) were

0.01 M  $\text{Na}_2\text{S}_2\text{O}_3$  until it became light yellow in color. At that point, 2–3 ml of 5 % starch indicator solution was added and titration carried on until complete discoloration of the blue solution was achieved. During titration, the following reactions (1) and (2) occurred:



Titration was performed for the blank and samples. The amount of  $\text{Cu}^{2+}$  ions in the sample was calculated from the following equation:

$$[\text{Cu}^{2+}] = \frac{100/20 \times C(\text{Na}_2\text{S}_2\text{O}_3) \times (V_0(\text{Na}_2\text{S}_2\text{O}_3) - V(\text{Na}_2\text{S}_2\text{O}_3))}{m_s}; \quad \frac{\text{mmol}}{\text{g}}$$

treated with 0.01 M HCl for 1 h and washed thoroughly with water. In the next step, 50 ml distilled water and 30 ml (0.25 M) calcium acetate solution were added to the samples. Samples were in a solution for 2 h, after which samples were removed from the solution and the remaining solution was investigated.

Three different experimental routes were used on untreated and plasma-treated samples. In the first route, treated samples sorbed only  $\text{Cu}^{2+}$  ions, in the second route the samples sorbed only  $\text{Ca}^{2+}$  ions, and the third route included samples with consecutive sorption of both ions, first  $\text{Ca}^{2+}$  then  $\text{Cu}^{2+}$ .

## Characterization

### Quantity of $\text{Cu}^{2+}$ ions in samples

The amount of  $\text{Cu}^{2+}$  ions in samples was determined by standard iodometric titration of sorption solution adapted for use when sorption of Cu is performed by sorbent material.

From 100 ml of sorption solution, a 20 ml portion of liquid was transferred to a dry flask in which 2 g of solid KI was added along with 2–3 drops of 0.1 M  $\text{H}_2\text{SO}_4$ . This flask needed to be held in the dark for 5 min. After that time, the solution was titrated with

where  $C(\text{Na}_2\text{S}_2\text{O}_3)$  is the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for titration,  $V_0(\text{Na}_2\text{S}_2\text{O}_3)$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for blank titration (ml),  $V(\text{Na}_2\text{S}_2\text{O}_3)$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for sample solution titration (ml), and  $m_s$  is the weight of the absolutely dry sorbent sample (g). For each sample, titration was performed in triplicate.

### Quantity of $\text{Ca}^{2+}$ in samples

The carboxyl groups of the cellulose react with the salts of weaker acids, i.e., calcium acetate, forming a salt of the cellulose,  $\text{COO}^- \text{Ca}^{2+} \text{X}^-$ , and releasing an equivalent amount of the weaker acid. On this basis, the solution after sorption was investigated when a 20 ml portion of the solution was titrated with 0.01 M sodium hydroxide, using a phenolphthalein indicator. The amount of weaker acid in a solution was equivalent to the amount of  $\text{Ca}^{2+}$  ions in samples and calculated using the following formula (Praskalo-Milanovic et al. 2010):

$$[\text{Ca}^{2+}] = \frac{80/20 \times 0.01\text{M} \times V(\text{NaOH})}{m_s}; \quad \frac{\text{mmol}}{\text{g}}$$

where 0.01 M is the concentration of NaOH,  $V(\text{NaOH})$  is the volume of NaOH solution used for titration (ml), and  $m_s$  is the weight of the absolutely dry sample (g). The results are given as the mean value of three titrations per sample.

#### *Methylene blue test for carboxyl groups*

The methylene blue test was used for estimation of carboxyl group formation on the surface after DBD plasma treatment, through the degree of fabric staining ( $K/S$ ) (Malek and Holme 2003). In this test, the untreated and plasma-treated viscose samples (0.25 g) were put in flasks containing 25 ml of 1 % methylene blue dye solution of pH 5.1 and shaken for 5 min at room temperature. They were then rinsed thoroughly in tap water for 5 min and air dried, and their reflectance was measured using a SF300 (Datacolor, USA) reflectance spectrophotometer under illuminant D65 with a 10° standard observer. Reflectance was measured on four different spots on the sample. The degree of fabric staining ( $K/S$  value), which normally is dependent on the presence of carboxyl groups, was calculated using the Kubelka-Munk equation from reflectance values ( $R$ ) obtained at 660 nm wavelength:

$$K/S = \frac{(1 - R)^2}{2R}$$

where  $K$  is the absorption coefficient,  $S$  is the scattering coefficient, and  $R$  is the measured reflection for monochromatic light.

The same instrument was used for measuring the color difference value ( $\Delta E^*$ ) between the untreated and plasma-treated sample.

#### *Surface analysis using SEM/EDX*

Investigations of samples morphology were carried out with scanning electron microscopy (SEM) using a JEOL JSM-840A instrument. The samples investigated were coated with gold using a JFC 1100 ion sputterer. The elemental composition was analyzed by an INCAPentaFETx3 energy dispersive X-ray (EDX) microanalyzer.

SEM photographs were analyzed using Infinity Analyze software. SEM/EDX analysis was also used to investigate the stability of copper microstructures on the fiber surface toward wet treatment (washing

**Table 1** Staining degree ( $K/S$ ) and color difference ( $\Delta E^*$ ) between untreated and nitrogen plasma-treated viscose samples

Samples	$K/S$	$\Delta E^*$	Description of color difference
Untreated	6.2	4.1	Darker, more blue
Plasma treated (1 J cm <sup>-2</sup> )	7.9		

with distilled water at room temperature for 30 min with a material-to-liquor ratio of 1:1,000).

## Results and discussion

### Methylene blue test for the carboxyl group

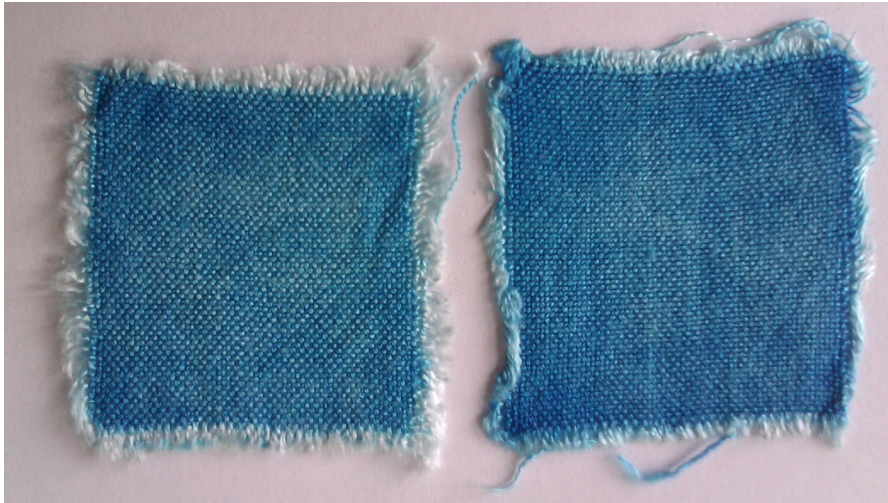
Methylene blue sorption has been frequently used for determination of the quantity of carboxyl groups in cellulose (Klemm et al. 1998; Frasc et al. 2002; Fitz-Binder and Bechtold 2012). Due to the fact that in this case the surface is modified by DBD, the staining effect on the DBD-treated sample after dye sorption should be pronounced, and the difference in coloration between plasma-treated and untreated samples should be a good indicator of surface changes. Therefore, the  $K/S$  value as a degree of staining and  $\Delta E^*$  as a level of the difference between coloration of untreated and treated viscose could serve as indicators of carboxyl group change on the material surface. Results of these parameters are shown in Table 1.

In Fig. 1, a photograph of untreated and plasma-treated samples dyed with methylene blue is presented.

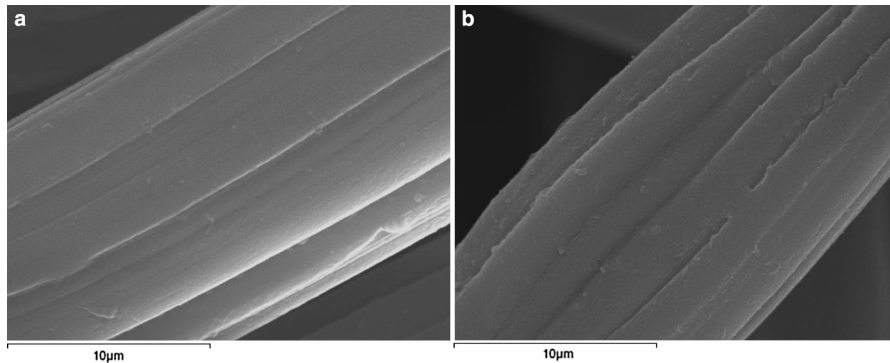
The higher  $K/S$  value of the nitrogen DBD-treated sample indicates much stronger, darker coloration, which was confirmed by the higher  $\Delta E^*$ , which can be seen in Fig. 1. These results indicate better sorption of methylene blue after DBD treatment by the surface carboxyl groups available to interact with the dye molecules. This is also confirmed by the results of the improved Ca<sup>2+</sup> sorption by plasma-treated samples, which are given in the “Sorption of Ca<sup>2+</sup> and Cu<sup>2+</sup>” section.

### Fiber morphology after nitrogen DBD

Surface analysis before and after plasma treatment was performed using SEM (Fig. 2).



**Fig. 1** Photograph of untreated (*left*) and plasma-treated ( $1 \text{ J cm}^{-2}$ ) samples (*right*) dyed with methylene blue

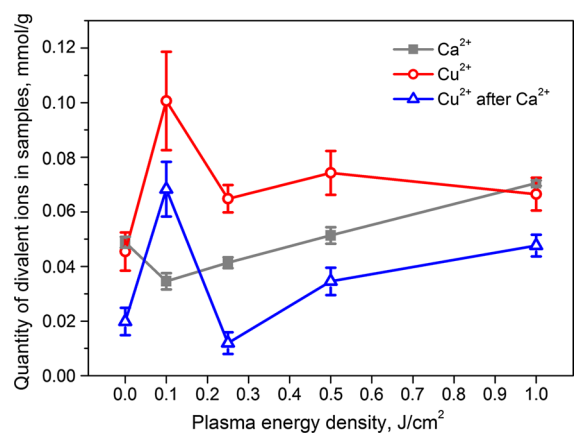


**Fig. 2** Viscose fibers **a** before and **b** after plasma DBD treatment (energy density used is  $1 \text{ J cm}^{-2}$ , i.e. 180 s) ( $\times 3,000$  magnification)

The surface of the untreated fiber (left) is fairly smooth with some defects that could be seen periodically throughout the sample. After plasma treatment in nitrogen, the surface has more roughness and fiber fragments that can be seen on the plasma-treated sample (right) occurring because of plasma etching. EDX analysis (results not shown) showed the presence of only C and O on the fiber surface without the presence of any other peaks except Au peaks from the gold coating.

#### Sorption of $\text{Ca}^{2+}$ and $\text{Cu}^{2+}$

On untreated samples and after DBD treatment in nitrogen, sorption of divalent ions was performed in



**Fig. 3** Quantity of sorbed divalent ions as a function of plasma energy density during the treatment

aqueous solutions. The quantity of  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ions in untreated and plasma-treated samples is presented in Fig. 3. As can be seen, there is an increase in the quantity of  $\text{Ca}^{2+}$  ions with treatment time, which confirms the increase in carboxyl group content due to nitrogen DBD treatment. The amount of calcium ions in fibers decreased compared to the untreated sample, from  $0.049 \pm 0.002$  to  $0.037 \pm 0.003 \text{ mmol g}^{-1}$  when treatment was performed with an energy density of  $0.1 \text{ J cm}^{-2}$ . With prolonged treatment time, an increase in the quantity of  $\text{Ca}^{2+}$  ions was detected, up to  $0.070 \pm 0.001 \text{ mmol g}^{-1}$  in fibers treated using an energy density of  $1 \text{ J cm}^{-2}$ . Considering this together with the results of improved dyeing with methylene blue of the DBD-treated samples (energy density  $1 \text{ J cm}^{-2}$ ), a definite conclusion could be reached that the quantity of COOH groups is increasing on the fiber surface because of nitrogen DBD plasma treatment using an energy density of  $0.5 \text{ J cm}^{-2}$  or higher (90 s of treatment or longer).

The amount of  $\text{Cu}^{2+}$  in the untreated samples was  $0.045 \pm 0.007 \text{ mmol g}^{-1}$  and very close to the amount of  $\text{Ca}^{2+}$  ions, which could indicate that Cu binds to COOH groups in a 1:1 ratio; however, due to the fact that the  $\text{COO}^{-}\text{Cu}^{2+}$  form is thermodynamically unstable (Sundman et al. 2008) and that for ionic interaction  $\text{Cu}^{2+}$  requires two close COOH groups, it can be concluded that in untreated viscose, a mechanism of Cu bonding is based on van der Waals interaction with OH groups. In DBD-treated samples, when very low energy density was used during plasma treatment of  $0.1 \text{ J cm}^{-2}$ , the lowest amount of  $\text{Ca}^{2+}$  was sorbed, but the amount of sorbed  $\text{Cu}^{2+}$  ions was maximal,  $0.101 \pm 0.020 \text{ mmol g}^{-1}$  and almost two times higher compared to untreated sample. This could be the consequence of the etching effect on the viscose surface when it is affected by plasma particles that break the intermolecular hydrogen bonds between cellulose chains; new OH groups become available for interaction with  $\text{Cu}^{2+}$  ions. At the same time, etching of fibers leads to a decrease of the COOH groups' content, which affects  $\text{Ca}^{2+}$  ion sorption. When plasma energy density is higher ( $0.5 \text{ J cm}^{-2}$  or above), the quantity of  $\text{Ca}^{2+}$  increases, i.e., the quantity of COOH groups introduced is increasing, but the quantity of  $\text{Cu}^{2+}$  is decreasing. This indicates that available OH groups are being oxidized to COOH groups during plasma treatment.

An overall increase in quantity of both  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ions after DBD in nitrogen compared to untreated samples was present if the deposited energy density was  $0.5 \text{ J cm}^{-2}$  or higher, which is important for those applications of viscose that require improved sorption of divalent ions.

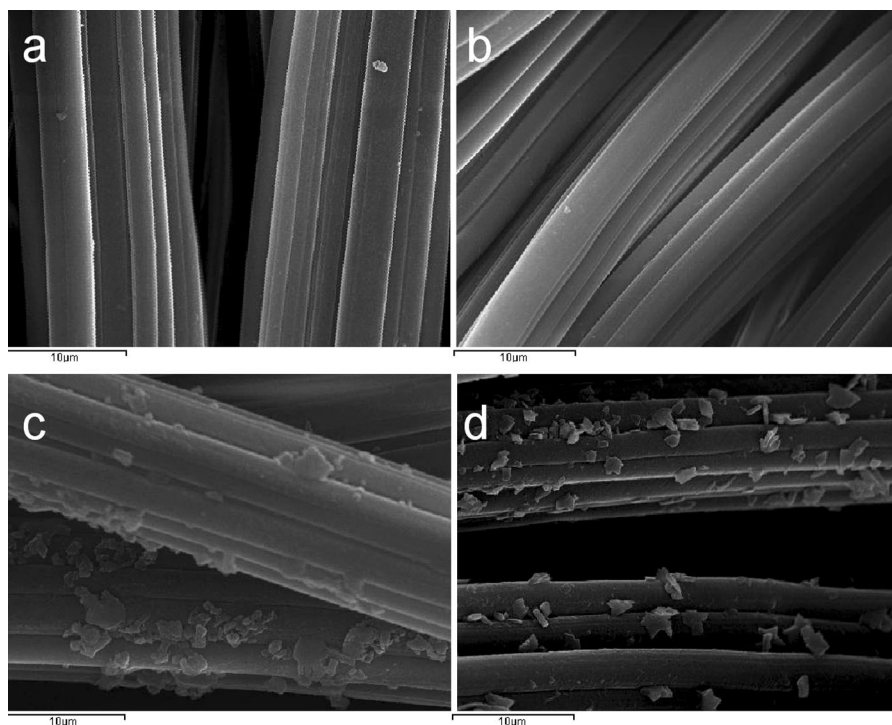
Different effects occurred when the sorption of  $\text{Cu}^{2+}$  ions was performed on fibers that already contain bonded calcium. The dependency of ion quantity on plasma energy density (or treatment time) is almost the same regardless of the presence of  $\text{Ca}^{2+}$  on material (Fig. 3), except the overall quantity of  $\text{Cu}^{2+}$  ions, which is lower by about 1.5–2 times compared to the amount of sorbed ions without bonded  $\text{Ca}^{2+}$ . This means that sorption of copper is affected and reduced by the presence of  $\text{Ca}^{2+}$ , which is in agreement with previous work by Huang et al. (2009). Furthermore, COOH is already occupied by  $\text{Ca}^{2+}$  ions. This also confirms that copper bonds with  $\text{N}_2$  DBD-treated cellulose through both OH and COOH. The maximum amount of  $\text{Cu}^{2+}$  was again found in samples treated with plasma of  $0.1 \text{ J cm}^{-2}$  energy density,  $0.068 \pm 0.010 \text{ mmol g}^{-1}$ .

However, ion exchange or the van der Waals interaction mechanism cannot fully support the obtained results of copper sorption for samples treated with plasma and with bonded calcium, because, as will be seen in the “Fibers morphology after nitrogen DBD and sorption of  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$ ” section, not all copper bonded directly with cellulose.

#### Fiber morphology after nitrogen DBD and sorption of $\text{Ca}^{2+}$ and $\text{Cu}^{2+}$

After sorption of  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$ , viscose fibers were observed under the scanning electronic microscope, and their surface was analyzed using EDX. Untreated fibers with sorbed copper ions (Fig. 4a) were clean, and surface EDX analysis (spectrum not presented) showed the presence of small Cu peaks. The fiber treated by plasma of the lowest energy density and with sorbed copper has the same appearance (Fig. 4b). Samples treated using other plasma energy densities and with sorbed copper were also clean and without any impurities or structures.

Untreated viscose fibers with both bonded copper and calcium (Fig. 4c) have many precipitates. When plasma treatment is applied before sorption of calcium and copper, the afterwards formed precipitates obtain



**Fig. 4** SEM photographs of viscose fibers under  $\times 1,000$  magnification. **a** Untreated with sorbed  $\text{Cu}^{2+}$ , **b** treated in plasma using energy density of  $0.1 \text{ J cm}^{-2}$  and with sorbed

$\text{Cu}^{2+}$ , **c** untreated with sorbed  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$ , **d** treated in plasma using energy density of  $0.1 \text{ J cm}^{-2}$  and with sorbed  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$

a certain shape (Fig. 4d). Deeper analysis revealed that precipitates formed on plasma-treated fibers (Fig. 5c) are in fact three-dimensional trigonal and star-like copper structures. EDX analysis showed strong multiple Cu peaks (Fig. 5d). At the same time, on fibers that are not plasma treated and that contain some precipitates (Fig. 5a), EDX analysis shows peaks of both Ca and Cu (Fig. 5b).

It should be pointed out again that in all EDX spectra Au peaks originated from the gold coating.

In all plasma-treated fibers with previously bonded  $\text{Ca}^{2+}$ , after the sorption of copper, three-dimensional particles were found regardless of the plasma energy density used; the highest number of microparticles and highest distribution density were found on fibers treated using a maximal energy density of  $1 \text{ J cm}^{-2}$ . Almost the entire sample investigated with SEM was covered with these microparticles (Fig. 6a, b). Furthermore, these fibers were still covered with microparticles after washing (Fig. 6c), which suggests good stability of the formed copper structures.

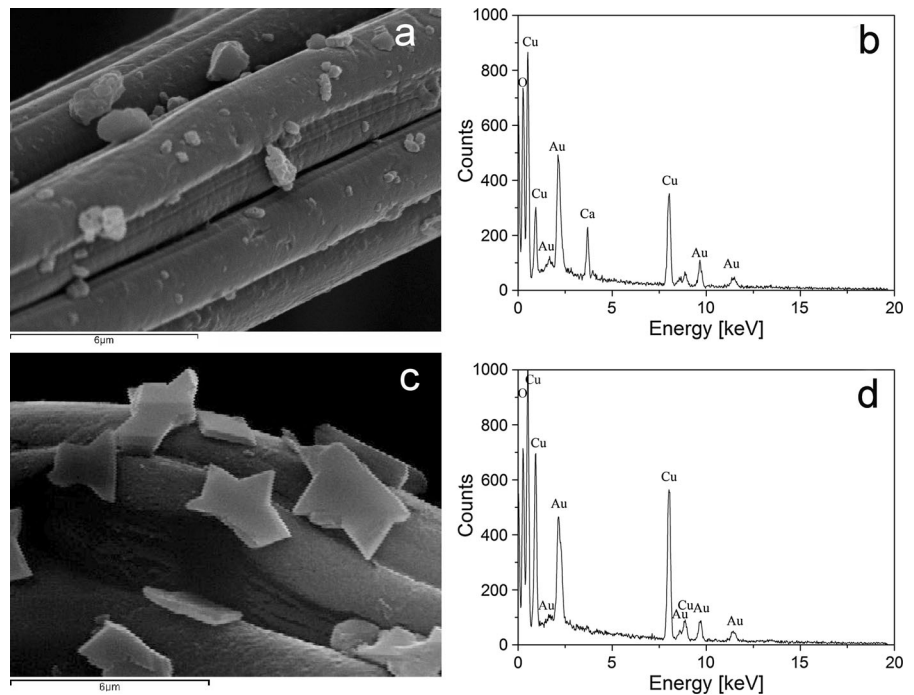
Size distribution (Fig. 6d) shows that the average size of microparticles, measured at the longest edge of

the structure, was within the range of 2.0–2.5  $\mu\text{m}$ . Average thickness of the particles, measured on SEM photographs where some of the particles were placed perpendicular to fiber surface, was found to be  $380 \pm 150 \text{ nm}$ .

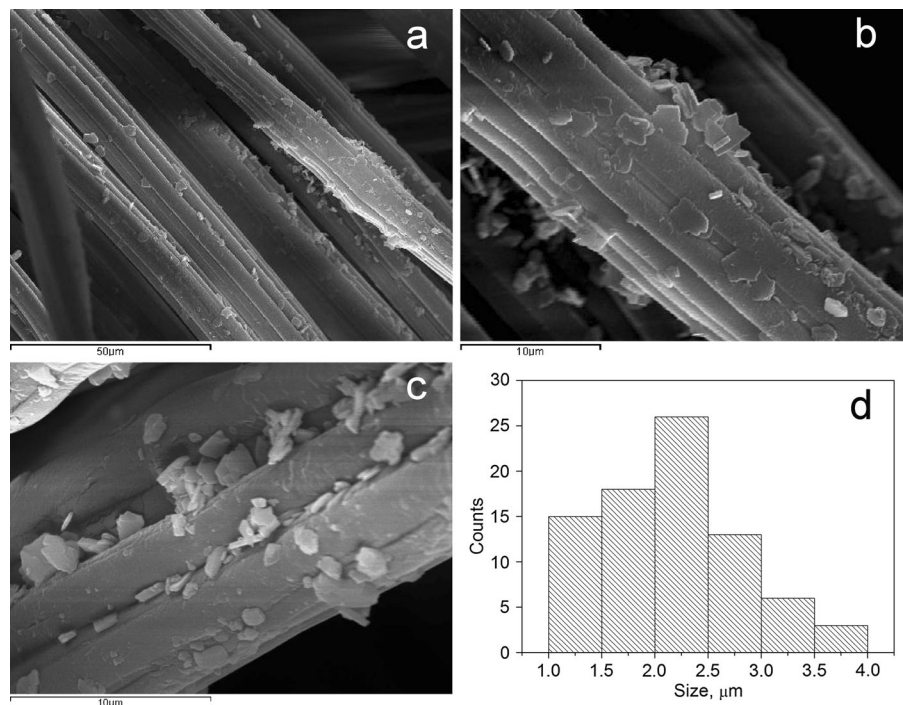
#### Formation and growth mechanism of copper microparticles

The mechanism of microparticle formation lies first in the nature of the substrate. It is known that cellulose can serve as a good stabilizing agent for metallic nanoparticles formation. The activated surface of fibers can be a perfect platform for nanoparticles and microparticle formation because of the presence of functional groups on the cellulose surface, aldehyde and carboxyl, which can serve as reducing and stabilizing agents, respectively. However, in the literature reports, mostly those functional groups serve as only reducing or only stabilizing agents and usually with the use of some reducing chemical agent such as  $\text{NaBH}_4$  (Vainio et al. 2007; Wu et al. 2008; Cady et al. 2011; Song et al. 2012).

**Fig. 5** **a** SEM of untreated fibers with sorbed  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ( $\times 5,000$  magnification). **b** EDX analysis of precipitates on untreated fibers with sorbed  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$ . **c** SEM of fibers treated in plasma using energy density of  $0.1 \text{ J cm}^{-2}$  and with sorbed  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ( $\times 5,000$  magnification). **d** EDX analysis of formed structures on the fiber surface after  $\text{N}_2$  DBD treatment ( $0.1 \text{ J cm}^{-2}$ ) and sorption of  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$



**Fig. 6** Viscose fibers treated in nitrogen DBD of  $1 \text{ J cm}^{-2}$  energy density and with formed copper particles at magnifications of **a**  $\times 500$ , **b**  $\times 1,000$ , **c** after washing at  $\times 1,000$  magnification and **d** size distribution of microparticles measured along the longest edge of the particle

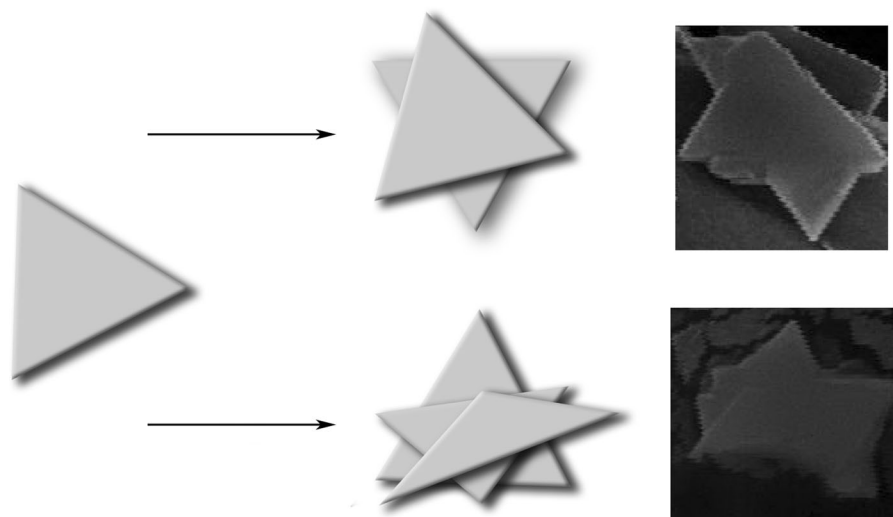


In our previous work, viscose, only functionalized in nitrogen DBD, served as an instrument for in situ synthesis of silver nanoparticles, for both the reduction and stabilization of the formed nanoparticles

(Przyaszny et al. 2013). However, in this case, plasma treatment alone could not influence the formation of microparticles, as is obvious from the photograph where a smooth fiber with sorbed copper



**Fig. 7** Schematic illustration of trigonal microplates assembling into a star-like copper superstructure



ions without any structures is present (Fig. 4b). This is most likely because, opposite to  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  is not so easily reduced to metallic copper using only reducing groups of cellulose.

Furthermore, it is obvious that the  $\text{Ca}^{2+}$  ion plays a key role in copper particle formation as a precipitation agent and that the plasma-treated surface influences the morphology and stability of microparticles. The role of  $\text{Ca}^{2+}$  most probably lies within the mechanism of copper precipitation as in Bordeaux mixture preparation for use in agriculture (Dixon 2004). Namely, the so-called Bordeaux mixture is a mixture of  $\text{CuSO}_4$ ,  $\text{Ca}(\text{OH})_2$  and water, used as a fungicide. During preparation of a Bordeaux mixture, a fungicidal precipitate forms, a mixture of copper and calcium compounds or a pure compound, a solid-state greenish–blue copper hydroxide,  $\text{Cu}(\text{OH})_2$  or copper oxide,  $\text{CuO}$ . Which compound will precipitate usually depends on the  $\text{Cu}/\text{Ca}$  ratio in the solution (Butler 1923, 1928; Narayan 1949; Flora 1984).

In this case, a similar mechanism occurred. When untreated viscose fibers with bonded calcium were put in a copper sulfate solution, a mixture of copper and calcium salts precipitated on the fiber surface, which was confirmed with EDX giving strong Cu and Ca peaks (Fig. 5b). After plasma treatment and  $\text{Ca}^{2+}$  bonding, when sorption of copper was performed, the  $\text{Cu}/\text{Ca}$  ratios changed. When plasma-treated viscose fibers with bonded calcium were put in a copper sulfate solution, simultaneous interactions occurred among calcium ions, copper ions and accessible carboxyl and

hydroxyl groups of cellulose. First, certain amounts of calcium ions were discharged from cellulose into the solution, leaving  $\text{COO}^-$  groups now available for interaction with  $\text{Cu}^{2+}$  ions. This explains the absence of Ca peaks in the EDX spectra of viscose fibers with previously bonded calcium and after sorption of copper (Fig. 5d). One part of  $\text{Cu}^{2+}$  ions bonds with cellulose, while the other part of  $\text{Cu}^{2+}$  ions forms  $\text{Cu}(\text{OH})_2$  and precipitates on the fiber surface because of the presence of  $\text{Ca}^{2+}$  ions in solution. Available  $\text{COO}^-$  groups now serve as stabilizers of  $\text{Cu}(\text{OH})_2$  particles on the viscose fiber surface. Similar results of  $\text{COO}^-$  groups being used as nanoparticle stabilizers were reported by Cady et al. (2011) and Song et al. (2012).

Due to orientation and stabilization by functional groups of the plasma-activated fiber surface, formation of copper trigonal microplates occurred. In the next phase, more trigonal microplates were brought together, forming superstructures with various modes of assembly (Fig. 7). This mechanism is similar to the results of copper superstructure formation published by Xia et al. (2010).

It should also be pointed out that the trigonal shape of the copper microplate is dominant, but more different polygonal shapes were noticed in samples as the plasma treatment time increased, i.e., as increased plasma energy density was used for fibers treatment. The shape and size of copper trigonal microplates obtained on viscose fibers in this work were very similar to the Cu microstructures synthesized by Fan et al. (2007) and Cu nanoplates

synthesized by Xu et al. (2010) with the difference that the reported nano- and microstructures of copper were synthesized in solution and in our work the reported Cu microstructures were synthesized in situ on cellulose fibers. Also, the copper microplates formed in this work are probably, based on the proposed mechanism,  $\text{Cu}(\text{OH})_2$ . This is supported by the fact that viscose samples with copper microplates had a pale greenish-blue coloration, which is the color of  $\text{Cu}(\text{OH})_2$ , while if it had been metallic Cu or CuO, the color of the samples would have been dark and gray or red from a  $\text{Cu}_2\text{O}$  precipitate. In conclusion, for in situ synthesis of Cu microplates on viscose fibers, both  $\text{Ca}^{2+}$  and DBD treatments in nitrogen are necessary. An investigation of the possible size, morphology and aggregation control is currently ongoing.

## Conclusion

In summary, trigonal copper microplates were directly produced on cellulose pretreated in nitrogen DBD. Carboxyl groups on DBD-treated cellulose surfaces acted as stabilizing agents, while calcium ions served as a trigger for copper hydroxide precipitation. The investigation confirmed that for copper microplate formation, plasma treatments in nitrogen and the presence of calcium ions,  $\text{Ca}^{2+}$ , are necessary.

The results of this work represent a first step toward the possibility of a fully controllable in situ copper structure growth and immobilization procedure on viscose fibers. This could significantly shorten the usual multistep procedure for immobilization of copper nano- and microparticles on textile materials. Cellulose fibers with immobilized copper can have significant applications in the medical and technical textile fields.

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