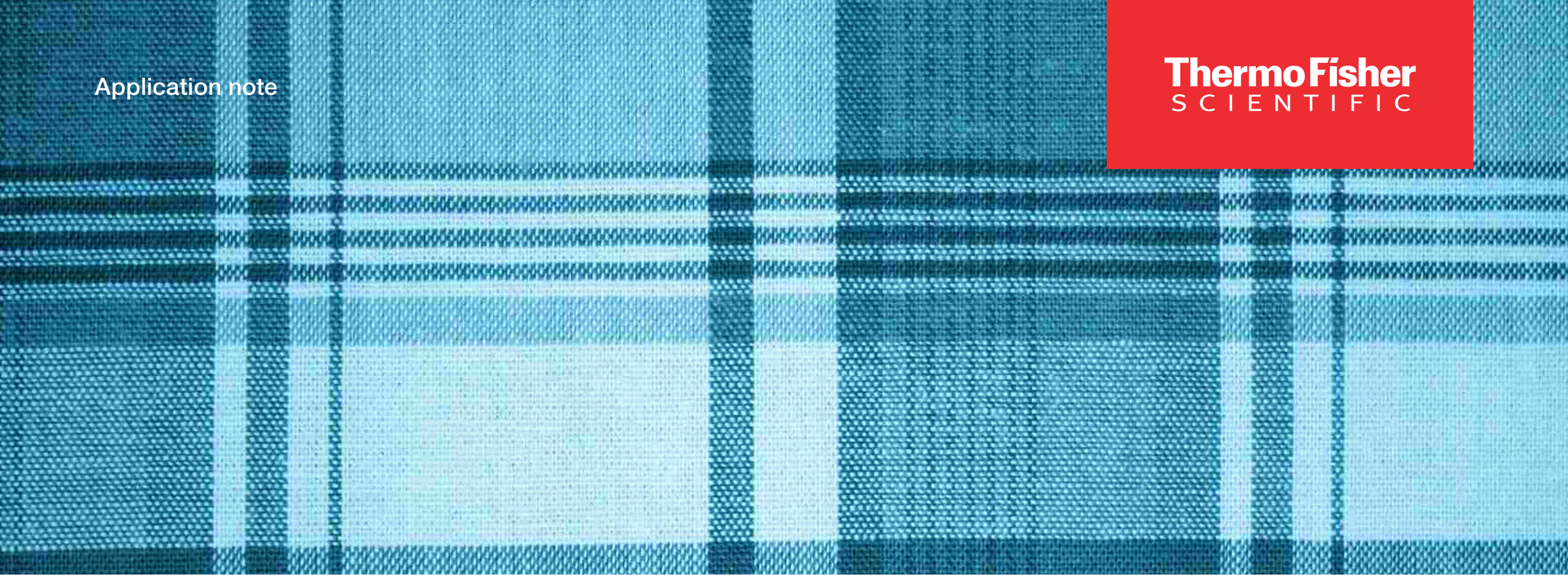

Application note

Thermo Fisher SCIENTIFIC

# Multi-modal analysis of antimicrobial fabrics with the XPS-SEM CISA Workflow

## Introduction

Textiles are ubiquitous across all areas of life, so there is naturally an ongoing interest in their improvement. Functionalization imparts these materials with various desirable properties such as decreased flammability, water repellency, stain resistance, strengthening, and/or antimicrobial properties, just to name a few.

Textiles are particularly important for medical applications, where they are used as part of first aid and hygienic products, as well as in clinical and surgical settings. (I.e., dressings, bandages, gauzes, etc.) This includes personal protective equipment (PPE) such as masks, which were used as a critical tool for the reduction of viral transmission during the coronavirus pandemic.

For medical textiles, functionalization typically focuses on either increasing their antimicrobial properties, increasing their biocompatibility, or both. This can be achieved through a variety of means, including the application of coatings as well as treatment with various additives such as nanoparticles.

In this case study, the Thermo Scientific™ Correlative Imaging and Surface Analysis (CISA) Workflow is used to analyze polypropylene fabrics modified with copper nanoparticles. CISA combines X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to provide both chemical characterization and imaging of sample surfaces. For functionalized textiles, it is critical to understand the changes that occur at the surface during treatment. XPS provides clear, unambiguous chemical identification of material surfaces, and is an ideal technique for such studies.


**Figure 1. Example applications of textiles in the medical field.**

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## Functionalization of medical textiles

Polypropylene (PP) is a common synthetic resin that can be spun into a non-woven fabric; this material is frequently used in disposable medical products such as surgical gowns, shoe covers, face masks, and more. While practical and easy to produce, PP fabrics lack any significant antimicrobial properties that would enhance their utility in contemporary medical settings.

There have been various attempts to modify the surface of PP fabrics to improve their antimicrobial behavior, including the application of nanoparticles, biopolymers, and even herbal extracts. Nanoparticles are particularly promising due to their high reactivity, meaning that the desired antimicrobial behavior can be achieved with extremely small amounts of material. In this case study, novel green methods were investigated for the in situ functionalization of PP non-woven fabrics with copper nanoparticles.

## Methods

Researchers at the University of Belgrade produced PP fabric functionalized with copper-based nanoparticles; copper was chosen as it has excellent antimicrobial activity while still being a relatively inexpensive precursor.

Here, ex-situ XPS was used to determine the surface characteristics of antimicrobial functionalization, which were then paired with high-quality SEM visualization. This correlative approach can reveal and monitor the chemical changes introduced by various surface modifications, which can be useful for improving and optimizing medical textile engineering.

## Functionalization of polypropylene textiles

The chemically inert and hydrophobic nature of the PP fibers means that it is essential to activate the surface to improve its wetting and adhesion properties. This is necessary for in situ nanoparticle creation as it enables surface interaction with alginate molecules, which display high affinity towards Cu(II) ions and can be used for crosslinking with the metal ions.

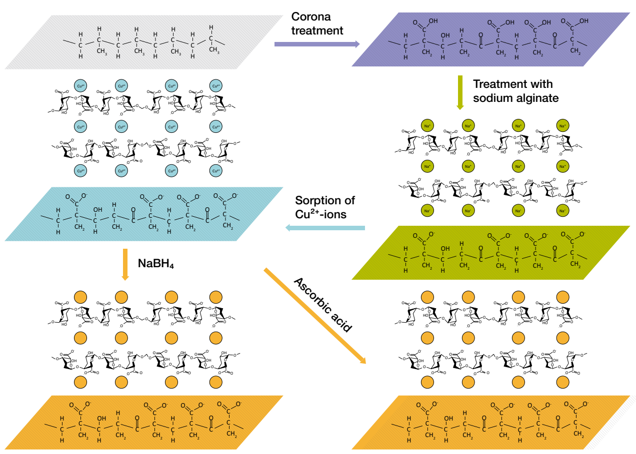



**Figure 2. Schematic showing functionalization of a polypropylene fabric surface by copper nanoparticles.**

The nanoparticle-doped PP fabric was prepared using the following general procedure:

- Polypropylene fibers are exposed to a corona discharge in air.
- The material is treated with sodium alginate ($C_6H_9NaO_7$) and immersed in a copper sulphate solution. This step exchanges the sodium ions for copper ions on the surface of the fabric.
- Cu(II) ions are reduced to copper metal.

Two different reduction methods were compared, using either $NaBH_4$ or ascorbic acid. While $NaBH_4$ is a more efficient reducing agent, it is also less environmentally friendly than a gentler reduction step with ascorbic acid. Researchers were hoping to determine if the greener ascorbic acid reduction produced sufficient nanoparticles for antimicrobial activity.

## Sample mounting

Samples from each step of the process were analyzed with CISA. Chemical changes on the surface of the sample were first identified with XPS, followed by SEM analysis, which showed how the fibers changed during processing as well as the distribution of the copper nanoparticles.

| Position | Sample |
|---|---|
| A | Polypropylene |
| B | After corona treatment |
| C | After treatment with sodium alginate |
| D | After reduction with $NaBH_4$ |
| E | After reduction with ascorbic acid |

**Figure 3. Left) Description of samples analyzed with the CISA Workflow. Right) Sample positions on the CISA sample holder.**

## XPS results

The XPS survey spectra show that the initial PP material has the expected composition; mostly carbon with a small amount of surface oxygen. After corona processing in air, the surface is significantly oxidized, with a small amount of nitrogen incorporation (Figure 4). The corona-processed material was subsequently exposed to sodium alginate; the resulting survey spectrum shows the presence of sodium as well as small amounts of chlorine and phosphorous contamination.

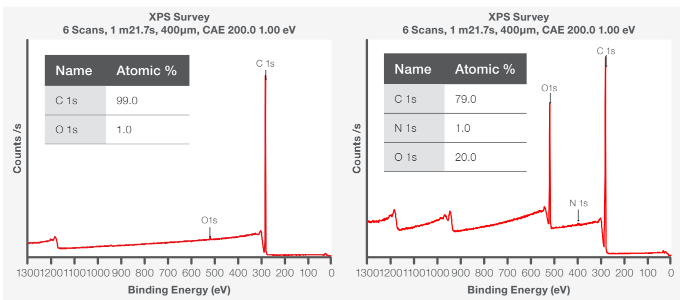
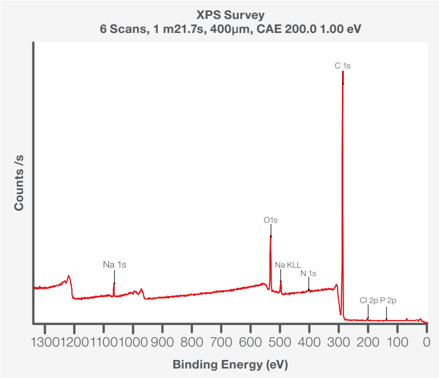



**Figure 4. XPS survey spectra of the PP material before (left, Sample A) and after (right, Sample B) corona treatment in air.**




| Name | Atomic % |
|---|---|
| C 1s | 87.4 |
| O 1s | 9.8 |
| N 1s | 1.1 |
| Na 1s | 1.0 |
| Cl 2p | 0.4 |
| P 2p | 0.3 |

**Figure 5. XPS survey spectrum of the PP material following corona treatment and subsequent exposure to sodium alginate (Sample C). Atomic composition (right) shows the presence of sodium as well as small amounts of chlorine and phosphorus contaminants.**

## High-resolution XPS analysis of surface hydrophobicity

High-resolution XPS analysis provides additional information about surface chemistry. For the initial polypropylene, XPS sees just a single chemical state in the C1s region, as expected (Figure 6). Following the corona treatment the polymer has clearly been oxidized and new carbon-oxygen chemical states are present. These are more apparent in the C1s spectrum, where they overlap less than in the O1s spectrum (Figure 6, top right). After the addition of sodium alginate, the C1s and O1s spectra show that the surface has been functionalized and is ready to be treated with the $CuSO_4$ solution (Figure 6, bottom right). Overall, the shifts in the C1s spectrum clearly indicate that the surface has increased hydrophilicity, both after corona discharge and sodium alginate functionalization.

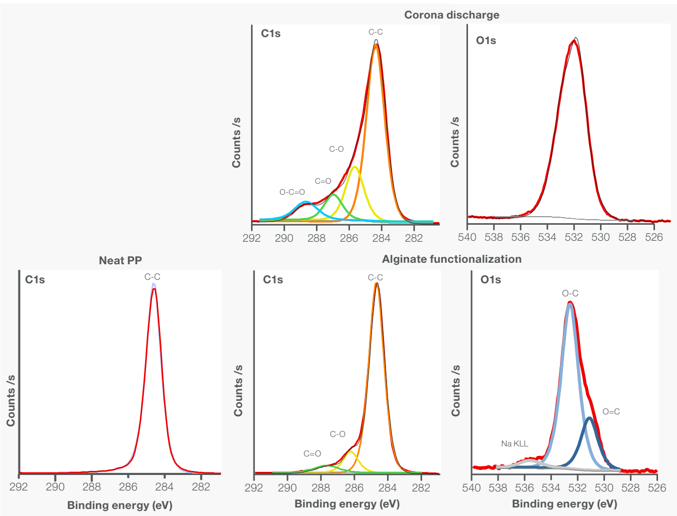



**Figure 6. High-resolution XPS spectra of carbon and oxygen signal in Samples A-C (untreated PP, corona-treated PP, and alginate-functionalized PP).**

## SEM results

SEM images of Samples A-C show how the polypropylene fibers change throughout the functionalization process. The smooth surface of the initial PP fibers becomes rougher following corona discharge. The application of sodium alginate leaves the fibers visibly coated with residue.

Energy-dispersive X-ray spectroscopy (EDS) analysis with a Thermo Scientific™ Axia™ ChemiSEM confirms that this is sodium alginate, through the presence of sodium.

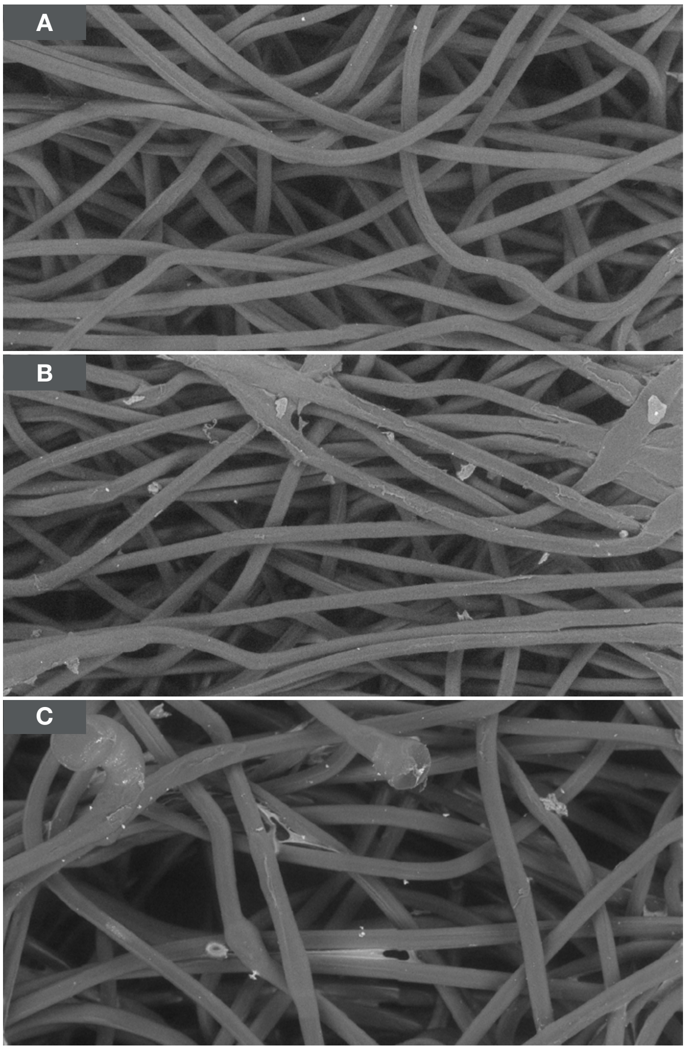



**Figure 7. Polypropylene Samples A-C imaged with scanning electron microscopy.**

## Evaluation of copper nanoparticle formation

SEM and XPS data were collected following treatment with either $NaBH_4$ or ascorbic acid (Samples D and E, respectively). Large area XPS SnapMaps were used to determine the distribution of copper across the sample surface; data was then collected from points on each sample that showed either high or low amounts of copper.

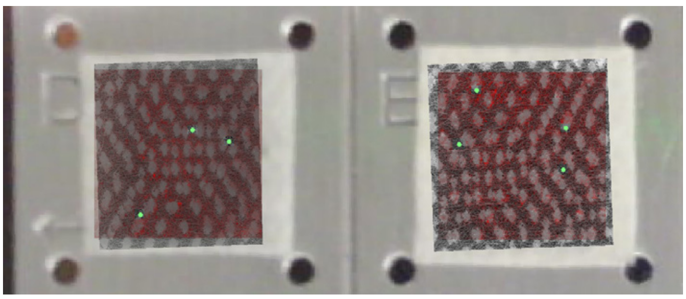
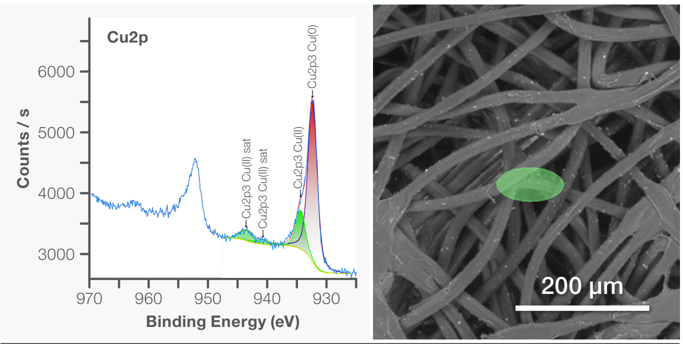


**Figure 8. Polypropylene Samples D and E, imaged using both the Axia ChemiSEM (to illustrate the structure) and the SnapMap functionality of the Thermo Scientific™ Nexsa™ G2 Surface Analysis System (to identify variation in copper concentration across the sample surface). Resulting data was correlated using Thermo Scientific Maps Software. Points with high/low concentrations of copper are marked; additional XPS data and SEM imaging were performed at these positions.**

## Copper nanoparticle formation

Following $NaBH_4$ reduction, the XPS data shows that metallic copper is present, but it also indicates that there is still some remaining $Cu^{2+}$. SEM data reveals the distribution of the copper nanoparticles, which are seen as bright features in the backscatter images (Figure 9). EDS confirms that these features are copper (Figure 10, blue on the ChemiSEM image). Figure 11 shows the copper nanoparticles formed through the greener ascorbic acid reduction. Similar amounts of copper are seen at the surface of both samples, and their chemistry also appears to be the same, however bulk chemical analysis of the fabrics shows that the amount of copper on Sample D is around 2x greater than on Sample E.




| Name | Peak BE | Atomic % |
|---|---|---|
| C 1s | 285.38 | 87.9 |
| O 1s | 532.74 | 9.7 |
| Cu 2p | 933.26 | 2.4 |

**Figure 9. Top) SEM image showing the distribution of copper nanoparticles across the PP fabric following reduction with $NaBH_4$. Bottom) XPS atomic distribution data for the highlighted region.**

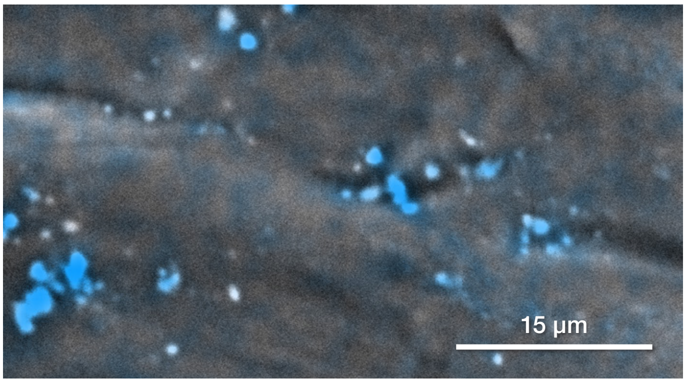
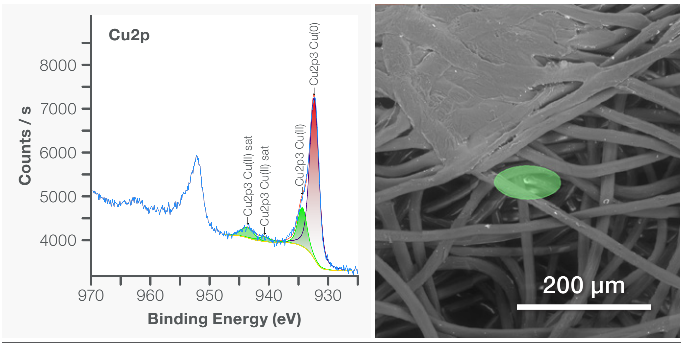



**Figure 10. Close up ChemiSEM image showing copper nanoparticles in blue.**




| Name | Peak BE | Atomic % |
|---|---|---|
| C 1s | 285.26 | 87.4 |
| O 1s | 532.75 | 10.6 |
| Cu 2p | 933.27 | 2.0 |

**Figure 11. Top) SEM image showing the distribution of copper nanoparticles across the PP fabric following reduction with ascorbic acid. Bottom) XPS atomic distribution data for the highlighted region.**

## Antimicrobial activity of synthesized nanocomposites

To evaluate the antimicrobial efficacy of the copper nanoparticles, all five samples were inoculated with a number of common bacteria and the amount of colony forming units (CFU) per milliliter that remained after 24 hours of incubation were measured (Table 1). Base polypropylene, corona-treated PP, and sodium alginate functionalized PP all performed similarly (Samples A-C). Both copper treatments produce excellent antimicrobial activity; the ascorbic acid treatment proved to be equally effective despite having ~50% less Cu loading than the $NaBH_4$ reduced samples. As both fabrics have the same antimicrobial activity, it appears that ascorbic-acid-based metal functionalization of PP fabrics is a viable method for the production of antimicrobial polypropylene textiles.

| Microorganism | Inoculum | Control PP | CPP + ALG + Cu ($NaBH_4$) | CPP + ALG + Cu (Ascorbic acid) |
|---|---|---|---|---|
| **E. coli (ATCC 25922)** | 4.1 × 106 | 1.1 × 106 | <10 | <10 |
| **S. aureus (ATCC 25923)** | 8.0 × 105 | 5.0 × 105 | <10 | <10 |
| **C. albicans (ATCC 24433)** | 6.0 × 105 | 1.0 × 105 | <10 | <10 |

**Table 1. Number of microbial colonies (CFU/mL).**

## Conclusions

The functionalization of textiles is an exciting area of research that promises to improve the performance of fabrics in numerous critical areas. Understanding how these materials react to various treatments requires a multi-scale, multi-modal approach that provides both visual and chemical information. The Thermo Scientific CISA Workflow utilizes combined XPS and SEM analysis to pair chemical identification and quantification with structural visualization.

In this case study, CISA was used to monitor the functionalization of polypropylene fabric and for the unambiguous identification and quantification of copper nanoparticles on the PP textile surface. Researchers were able to determine that a novel “green” approach to antimicrobial nanoparticle treatment was efficient and effective at eliminating bacteria from the material. This exciting collaboration with the University of Belgrade shows how the addition of holistic XPS-SEM characterization can accelerate novel materials research.

## Acknowledgements

We would like to thank our collaborators at the University of Belgrade for including us in their work on functionalized textiles. The full publication described in this case study can be found at DOI:10.1016/j.apsusc.2020.146829

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