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Carmen Gaidau, Aurora Petica, Madalina Ignat*, Ovidiu Iordache, Lia-Mara Ditu, Marcel Ionescu

Enhanced photocatalysts based on Ag-TiO₂ and Ag-N-TiO₂ nanoparticles for multifunctional leather surface coating

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Abstract: The Ag deposition on TiO₂ nanoparticles (Ag-TiO₂ NPs) and N-TiO₂ nanoparticles (Ag-N-TiO₂ NPs) has been made by electrochemical methodology in view of improved antibacterial properties and enhanced photocatalytic activity under visible light irradiation. The particle size in powder and in dispersion showed similar values and good stability in aqueous medium which made them suitable for use in leather surface covering for new multifunctional properties development. The diffuse reflectance spectra of Ag-TiO₂ NPs, Ag-N-TiO₂ NPs and TiO₂ NPs have been investigated and correlated with their photocatalytic performances under UV and visible light against different silver concentrations. The leather surfaces treated with Ag-N-TiO₂ NPs showed advanced self-cleaning properties under visible light exposure through the hydrophilic mechanism of organic soil decomposition. Moreover the bacterial sensitivity and proven fungitoxic properties of Ag-N-TiO₂ NPs leads to the possibility of designing new multifunctional additives to extend the advanced applications for more durable and useable materials.

Keywords: nanocomposites, silver deposited on titanium dioxide, self-cleaning, antimicrobial, multifunctional properties

***Corresponding author: Madalina Ignat:** Leather Research Department-R&D National Institute for Textiles and Leather-Leather and Footwear Research Institute Division, 93, Ion Minulescu Street, 031215, Bucharest, Romania, E-mail: madalina.fleancu@yahoo.com
Carmen Gaidau, Aurora Petica, Ovidiu Iordache: Leather Research Department-R&D National Institute for Textiles and Leather-Leather and Footwear Research Institute Division, 93, Ion Minulescu Street, 031215, Bucharest, Romania
Lia-Mara Ditu: University of Bucharest, Faculty of Biology, Research Institute of University of Bucharest
Marcel Ionescu: SC Europlastic Ltd, 98E, Timisoara Avn, 6, 061327, Bucharest, Romania

1 Introduction

One of the challenges of large scale application of titanium dioxide nanoparticles is the increased spectral photosensitivity to the visible light domain which can be reached by doping or surface deposition of photocatalysts with metals and/or non-metals. The preparation method for doped photocatalysts is essential for the catalyst's activity performance under visible light [1, 2].

The enhanced self-cleaning or antimicrobial properties of silver doped or deposited titanium dioxide (TiO₂) nanocomposites were shown in different studies in which they were synthesized by physical [3-9] or chemical techniques [10-13].

The improved photocatalytic activity of silver-titanium dioxide nanocomposites (Ag-TiO₂ NP) is explained by the role of silver as an electron trap that inhibits the recombination of electron-hole pairs generated by light on the TiO₂ surface [14-19]. The concentration of silver nanoparticles (Ag NP) was also found to be important for extending the light absorption of nano titanium dioxide in the visible light domain, an effect of electron traps in TiO₂ band gap [20].

Antibacterial activity against *Escherichia coli* under visible light was revealed for 0.15% silver doped titanium dioxide while a concentration of 0.05% dopant exhibited the highest decomposition efficiency of Rhodamine B [21]. Improved properties against bacteria and Rhodamine B were also registered for a filtration membrane treated with silver doped titanium dioxide [22]. Ag/TiO₂ nanofibers prepared by combining electrospinning technology and the solvothermal route also showed excellent properties for Rhodamine B photo-decomposition [23].

Recently, the heterogeneous catalyst based on silver and copper nanoparticles, deposited by dipping on cotton fabric showed excellent self-cleaning properties against organic matters. This marked the beginning of the era of multifunctional consumer goods treated

with photocatalysts, active in visible light [4, 24]. The antimicrobial properties of textiles can be induced by a large number of inorganic based nanoparticles which require facile manufacturing techniques for scale-up at industrial level [25].

Silver nanoparticles proved to be effective across a wide antibacterial spectrum both in solution and in different nanocomposites for applications to medical products [26, 27]. Silver nanoparticles' antibacterial mechanism was demonstrated through the release of a low concentration of silver ions [28] which were able to generate reactive oxygen species resulting in oxidative damage to bacteria cells [29]. In other studies, the excellent antimicrobial properties of Ag-TiO₂ nanocomposites [6] and films [30] were attributed to the synergistic generation of zero valent nanosilver [31,32].

Our research should be viewed in light of the development of materials with multifunctional properties and the reduction of volatile organic compounds used as biocidal or dry cleaning chemicals. This paper presents new photocatalysts based on Ag-TiO₂ and Ag-N-TiO₂ nanoparticles synthesized by via the electrochemical route and their application to leather surface coating. The electrochemical synthesis method is recognized as a versatile low temperature approach which is easy to scale up. This synthesis method allows the control of the final product characteristics by varying parameters such as potential, current density, temperature and pH [33].

2 Experimental

2.1 Materials

TiO₂ and N-TiO₂ nanopowders of 99.5% purity were supplied by TitanPE Technologies, Inc., China (surface area of 115 m²/g and average pore size of 130 Å).

Sodium polyacrylate (Na-PAA) with average Mw of 2100, Orange II (OII), Methylene blue (MB) dyes were of analytical grade and supplied by Sigma-Aldrich Chemie GmbH, Germany. The deionized water used had a resistivity of 18 µΩ·cm and a pH value of 5–7.

Sheepskin leathers were manufactured in the Leather Research Department's pilot plant according to the ecological technologies available on the market.

2.2 Synthesis of doped titania nanoparticles

The method of obtaining Ag-TiO₂ and Ag-N-TiO₂ composite nanopowders consisted of *in situ* electrochemical synthesis of Ag nanoparticles in a disperse aqueous suspension of TiO₂ NPs or N-TiO₂ NPs in the presence of Na-PAA using deionized water whilst stirring vigorously. The electrochemical method used is also known as “sacrificial anode method” which results in anodic solubilisation of Ag electrodes in aqueous medium [34, 35]. The electrochemical synthesis setup consisted of a cell with two Ag electrodes of 99.999% purity. The electrode plates (155x27x0.5 mm) were connected to a constant current generator in the range of 1-5 mA. Current densities between 0.01-0.06 mA·cm⁻² were applied for 5 h by a constant current pulse reversed generator with a mechanical stirrer. Work parameters were: 10g/L TiO₂ NPs or N-TiO₂ NPs dispersions, 1g/L Na-PAA, at 20 °C and shaking speed of 500 rotations/min. Ag-TiO₂ NPs and Ag-N-TiO₂ NPs dispersions were centrifuged and the separated slurries were dried in oven. The obtained powders were milled and finely ground by using a Specamill grinding mixer. Nanocomposites of Ag-TiO₂ NPs and Ag-N-TiO₂ NPs with 0.53%-1.3% Ag concentrations were synthesized via the electrochemical method. After the characterization, the selected nanopowders were used for leather surface finishing (Figure 1).

2.3 Chemical-physical characterizations of Ag-TiO₂ NPs and Ag-N-TiO₂ NPs

Chemical-physical characterizations of Ag-TiO₂ NPs and Ag-N-TiO₂ NPs were performed for silver concentration by *Inductively Coupled Plasma - Optical Emission Spectrometry* (ICP – OES, Agilent 725) according to ASTM E 1479 - 99(2011) standard. Powder morphology and surface composition analysis were determined by *Scanning Electron Microscopy* coupled with *Energy Dispersive X-Ray spectroscopy* (SEM, EDX, Quanta 250 GEI). Measurement of particle size in powder form were performed by *Transmission Electron Microscopy* (TEM, Philips EM 410). Particle size and Zeta potential evaluation in water dispersion of 0.1% NPs were measured by *Dynamic Light Scattering* (DLS, Zetasizer Nano ZS, Malvern). UV-Vis diffuse reflectance spectra measurements (JASCO V 570 spectrophotometer, equipped with integrating sphere) and photocatalytic activity of Ag-TiO₂ NPs, Ag-N-TiO₂ NPs and TiO₂ NPs in dispersion were tested on OII solution after exposure to UV and Vis light and by UV-Vis spectra recording at λ=365 nm.

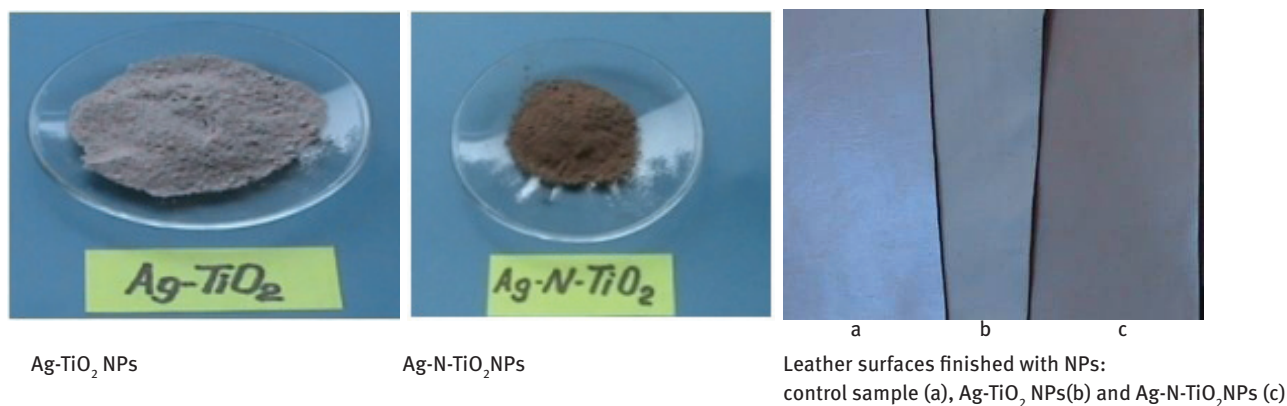


Figure 1: Ag-TiO₂ NPs and Ag-N-TiO₂ NPs powders and leather surfaces covered with NPs.

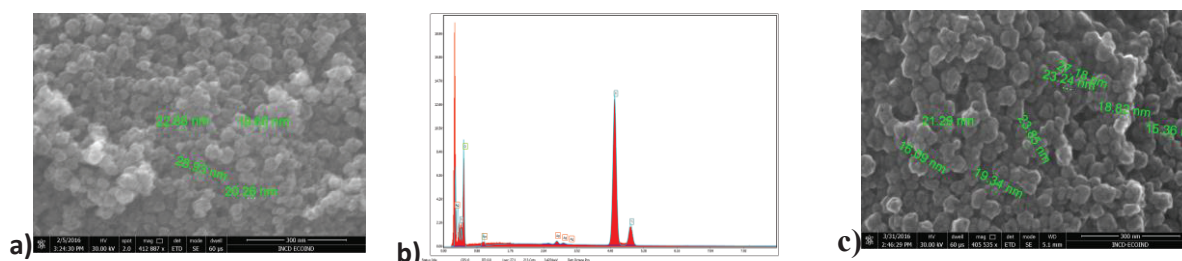


Figure 2: SEM images of Ag-N-TiO₂(a) and Ag-TiO₂(c) nanopowders and identification of Ag doping on N-TiO₂ NP surface(b) by EDX.

2.4 Leather surface finishing with Ag-TiO₂ NPs, Ag-N-TiO₂ NPs and TiO₂ NPs and characterisation

The selected Ag-TiO₂ and Ag-N-TiO₂ nanopowders were embedded in finishing layers based on film forming polymers. This followed classical technologies based on spraying the aqueous composites on leather surface [36, 37].

The leather surface was investigated for finishing film morphology characterization and Ag identification using SEM/EDX (Quanta 200 FEI). Self-cleaning properties under UV (VL 204 lamp with irradiation at 365 nm) and Vis light (500W halogen lamp with irradiation between 400-700 nm) exposure of simulated stains (ball pen ink, OII, MB dyes) were recorded by photography. The antimicrobial sensitivity and resistance against *Epidermophyton floccosum*, *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923, *Candida albicans* ATCC 26790, *Candida albicans* 1726 and *Candida albicans* 1760 strains were tested according to EN ISO 20645 and ISO 20743. The dynamic contact angle modification for water drop on leather surface was measured using a contact angle analyzer (VGA Optima XE).

3 Results and Discussion

The powder morphology showed that the grains of Ag-N-TiO₂ and Ag-TiO₂ nanopowders were round, with uniform shape and size under 30 nm. The doping Ag was identified by EDX analysis proving a successful loading of silver on the surface of TiO₂ NPs and N-TiO₂ NPs (Figure 2).

TEM analyses of Ag-N-TiO₂ and Ag-TiO₂ nanopowders showed higher particle sizes as compared to N-TiO₂ and TiO₂ nanopowders indicating that electrochemical deposition occurred on the particle surface. According to literature, the inclusion of silver nanoparticles inside titania crystallite would decrease the particle sizes of nanocomposites [38]. In Figure 3 are presented the TEM images for TiO₂ NPs with particle size of 25 nm, N-TiO₂ NPs with 28 nm, Ag-TiO₂ NPs with 31 nm and Ag-N-TiO₂ NPs with 40 nm.

As the nanopowders are used in leather finishing aqueous composites, the particle size and the Zeta potential were measured for Ag-TiO₂ NPs and Ag-N-TiO₂ NPs by DLS. In Figures 4a and 4c it can be seen that the average particle sizes of Ag-TiO₂ NPs and Ag-N-TiO₂ NPs are 50 nm and of 55 nm respectively, similar values to those measured by TEM. It is known that Zeta potential below

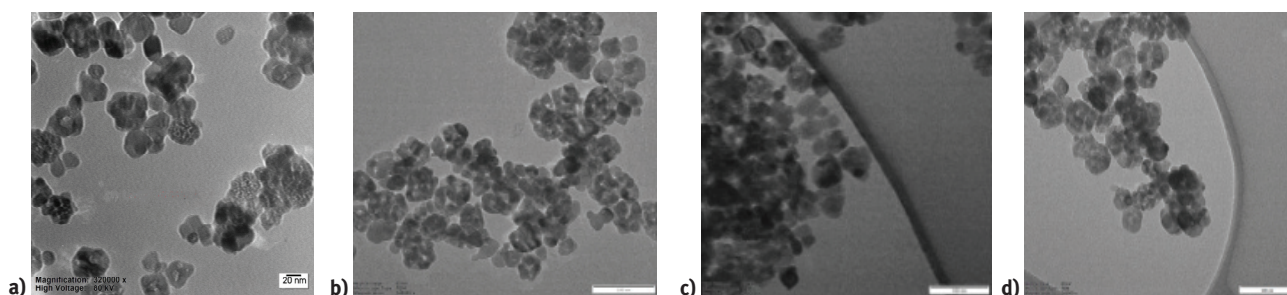


Figure 3: TEM images of: a) TiO_2 NPs; b) N-TiO_2 NPs; c) Ag-TiO_2 NPs and d) Ag-N-TiO_2 NPs.

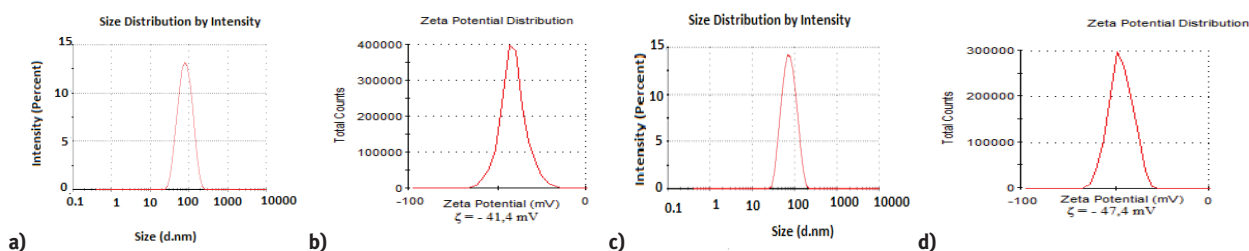


Figure 4: Size distribution and Zeta potential for Ag-TiO_2 NPs (a,b) and for Ag-N-TiO_2 NPs (c,d) in aqueous dispersions.

-25 mV and above +25 mV indicates a stable nanoparticles surface without aggregation tendency. Lower values of Zeta potential suggest aggregation of nanoparticles due to Van der Waals forces. In Figures 4 b and 4 d, Zeta potential values of -41.4 mV and -47.4 mV for Ag-TiO_2 NPs and Ag-N-TiO_2 NPs can be seen, corresponding to stable water dispersions. The stability of NP dispersions represents an important characteristic for uniform distribution on leather surface and surface contact increase.

UV-Vis diffuse reflectance spectra (DRS) of Ag-TiO_2 NPs, Ag-N-TiO_2 NPs and TiO_2 NPs showed an increase of photocatalytic activity in the visible range. This is due to the influence of silver and especially of silver and nitrogen elements which shift the absorbance from the UV to visible domain in accordance with data from the literature [32]. As can be seen in Figure 5, 0.5% Ag and N enhance the absorbance value and generate the shifting of the so-called tail band to the visible domain as compared to other concentrations of Ag and with TiO_2 NPs. It can be estimated that the photocatalytic activity is increased due to electron acceptor role of Ag and the facilitation of more holes to be transported at the surface. The results suggest that the Ag concentrations of 1.3% and 0.8% blocked the light from the TiO_2 NPs surface with the decrease in photo-induced electrons-holes and catalytic efficiency, in accordance with literature [39, 40].

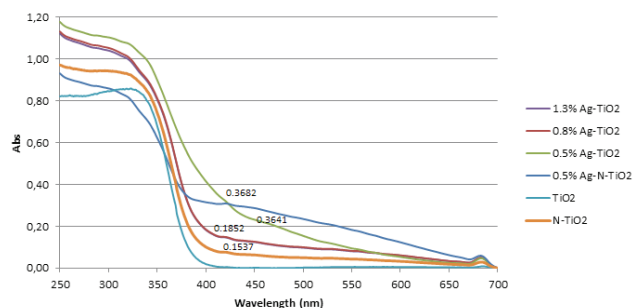


Figure 5: UV-Vis diffuse reflectance spectra of Ag-TiO_2 NPs and Ag-N-TiO_2 NPs compared with TiO_2 NPs and N-TiO_2 NPs.

The photocatalytic activities of Ag-TiO_2 NPs and Ag-N-TiO_2 NPs were tested on solutions of 20 ppm OII with 0.5 g/L nanopowder exposed to UV and visible light. The photocatalytic activity under UV light was evaluated depending on Ag concentration with the aim of selecting the most efficient nanocomposite. Figure 6 shows the improved efficiency of OII dye photocatalytic decomposition recorded at $\lambda=365$ nm after 60 minutes of UV exposure under the influence of doped TiO_2 NPs. The concentration of 0.5% Ag deposited on TiO_2 NPs surface was shown to be more effective as compared to 1.3% and 0.8% Ag concentrations, in agreement with DRS spectra (Figure 5) and literature data [32]. Ag electrochemically

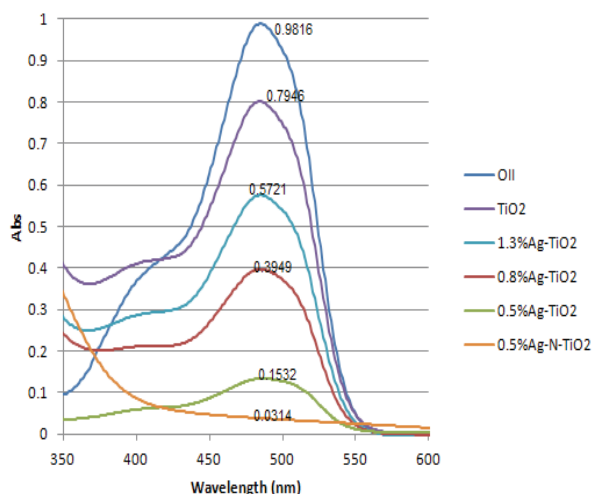


Figure 6: OII dye photocatalytic decomposition under UV exposure in presence of different concentrations of Ag deposited on TiO₂ NPs.

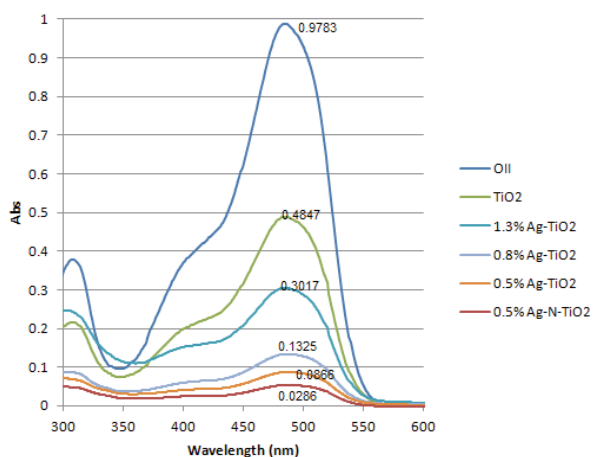


Figure 7: OII dye photocatalytic decomposition under visible light exposure in the presence of TiO₂ NPs, Ag-TiO₂ NPs and Ag-N-TiO₂ NPs.

deposited on N-TiO₂NPs improves the photocatalytic efficiency of OII decomposition under UV light.

The photocatalytic activity of Ag-TiO₂ NPs, Ag-N-TiO₂ NPs and TiO₂ NPs under visible light was measured after 30 minutes of exposure to visible light (Figure 7) and showed the best photocatalytic decomposition of 20 ppm OII dye in solution in the presence of 0.5g/L Ag-N-TiO₂ NPs.

The selected NPs for leather surface finishing were Ag-TiO₂NPs and Ag-N-TiO₂NPs with 0.5% Ag concentration. The morphology of leather surfaces and the identification of silver were performed using SEM/EDX analyses and are presented in Figure 8. The images showed a uniform distribution of NPs clusters and concentrations of 0.2% Wt Ag to 0.6% Wt Ag on the leather surface.

The self-cleaning properties of leather surface treated with Ag doped TiO₂NPs were tested after the simulation of model staining with ball pen ink, MB and OII dyes and by monitoring the organic stain degradation over time under exposure to UV and visible light.

In Figure 9 are presented the photos of organic stains degradation after 70 hours of exposure to visible light and 100 hours of exposure to UV light. The ball pen ink, MB and OII stains were degraded only after the visible light exposure of the leather surface treated with Ag-N-TiO₂NPs. The improved self-cleaning effects on leather surface were recorded in the case of treatments with Ag-TiO₂ NPs and mostly with Ag-N-TiO₂NPs under visible light exposure, thus enhancing the leather durability and consumer comfort. The results are consistent with information in the literature regarding the photocatalytic enhancement of Ag-N-TiO₂ NPs under visible light exposure against methyl orange dye or methylene blue decomposition. This was explained by the decrease in rate of electron-hole pair recombination on TiO₂NPs surface [41, 42] and increased surface area [43]. The Fermi levels of silver and nitrogen are lower than those of TiO₂, and photoexcited electrons can be transferred from the conduction band to the dopant particles deposited on the surface of TiO₂, while photogenerated valence band holes remain in the TiO₂. These activities greatly reduce the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reactions [44, 45]. The mechanism of improved visible light activity (VLA) of TiO₂ NPs doped with noble metal nanoparticles is attributed to the promotion of interfacial charge separation by electron attraction and increase of lifetime of the charge separated species [46].

The results showed clearly that the enhanced photocatalytic activity of Ag-N-TiO₂NPs against organic matters was successfully transferred not only in aqueous dispersion but also to leather surface treated with film forming polymers which are innovative approaches as compared to the literature [36, 47].

The possibility to avoid solvent use for dry cleaning and restoring of leather items is an important ecological issue of NPs use in leather surface finishing. Moreover in the last decades the demand for light colors, the most sensitive to soiling, have increased [48].

The photocatalytic activity of NPs on leather surface in the presence of H₂O leads to a modification of the contact angle due to the generation of hydroxyl radicals (•OH) and superoxide anions (•O₂⁻) after exposure to UV and visible light. The modification of the contact angle of a water drop under the treated leather surface was evaluated over time after exposure to UV and visible light. The hydrophilicity

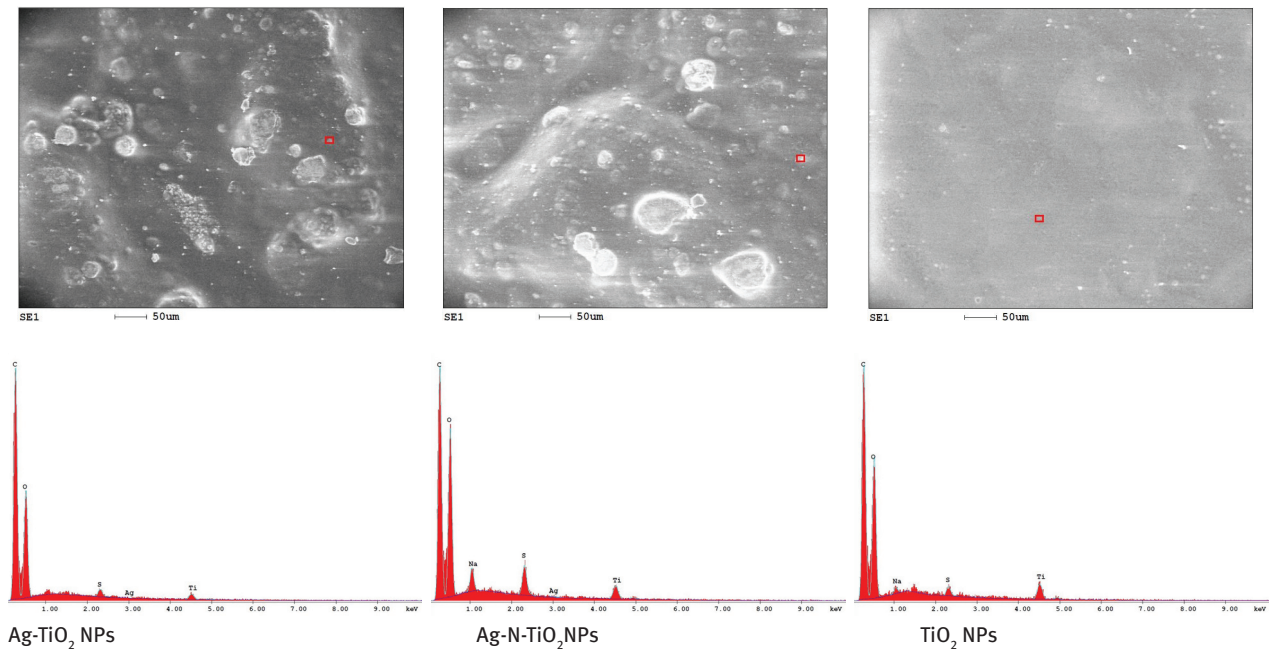


Figure 8: Leather surface morphology and Ag identification by SEM/EDX.

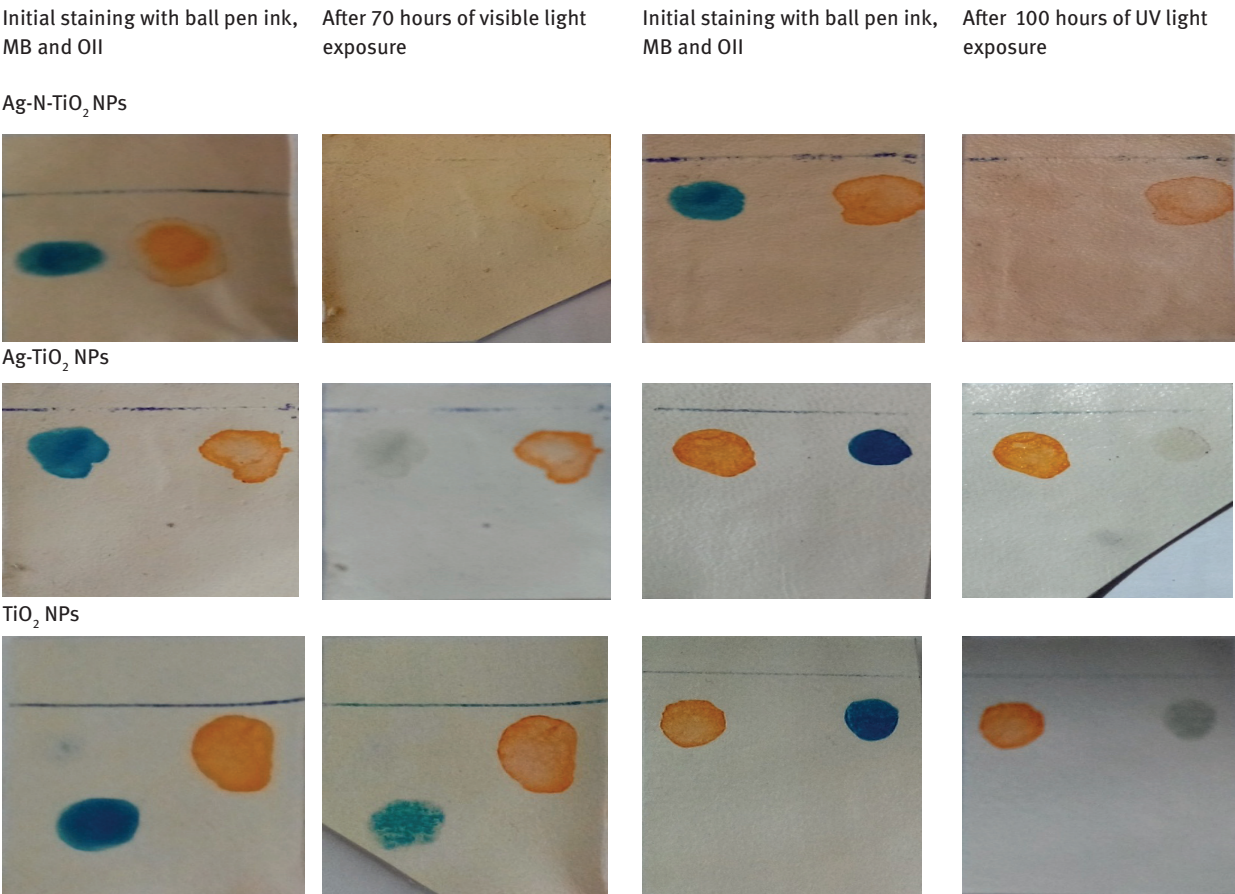


Figure 9: Self-cleaning effect of Ag-N-TiO₂ NPs, Ag-TiO₂ NPs and TiO₂ NPs on leather surface exposed to UV and visible light.

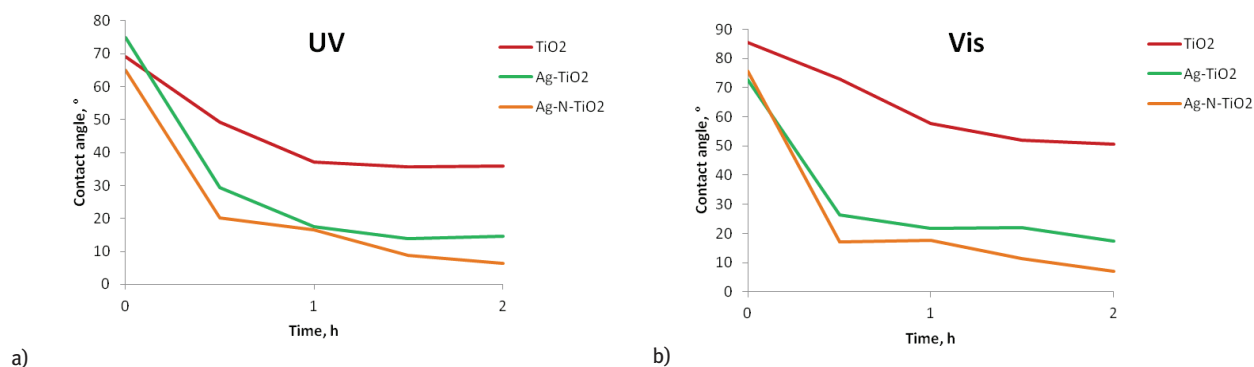


Figure 10: Contact angle of water drop on leather surface treated with TiO₂ NPs, Ag-TiO₂ NPs, Ag-N-TiO₂ NPs and exposed to UV (a) and visible light (b).

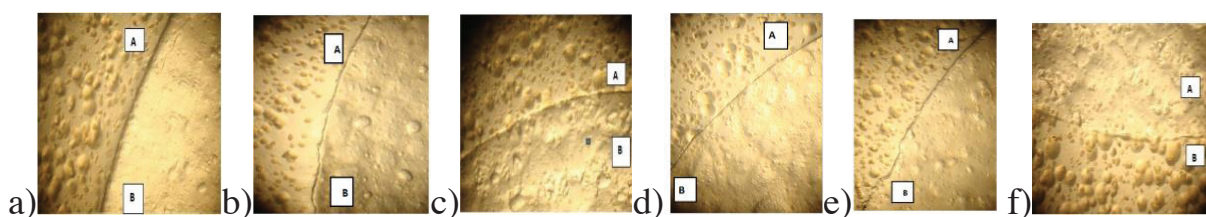


Figure 11: The sensitivity test of leather surfaces against *Escherichia coli* ATCC 25922 (a,b, c) and *Staphylococcus aureus* ATCC 25923 (d,e,f). B areas are leather surfaces (a, b, d and e samples are treated and c and f are untreated samples) and A areas are medium outside leather surfaces.

increased while the contact angle decreased under light exposure of leather surface treated with Ag-N-TiO₂ NPs, Ag-TiO₂ NPs and TiO₂ NPs. After 2 hours of irradiation the contact angle drops for leather surface treated with Ag-N-TiO₂ NPs from 65°-75° to 7°. Ag and N elements act synergistically to increase TiO₂ NPs photoreactivity and surface hydrophilicity. The leather surfaces treated with Ag-TiO₂ NPs and Ag-N-TiO₂ NPs showed the highest hydrophilicity after exposure to UV and visible light as compared to TiO₂ NPs, proving that the self-cleaning effects are generated through photoinduced catalytic effects. In Figure 10 it can be seen that the induced hydrophilicity after exposure to visible light is significantly improved due to the Ag and N elements deposited on TiO₂ NP surface, in accordance with the performances of self-cleaning test results.

The use of silver based NPs as biocides is well-known for treatment of textiles, plastics and other materials for medical [49-51] or every day use. Leather with antimicrobial properties is very important for footwear lining in the case of diabetic patients or in everyday use, taking into consideration the high rate of reported foot mycosis [52]. The other area of application is upholstery leathers with antimicrobial resistance for the furniture or automotive industries.

The leather surface sensitivity at direct contact with *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 25923 was evaluated according to EN ISO 20645 for leather surface treated with Ag-N-TiO₂ NPs and Ag-TiO₂ NPs in comparison to untreated leather surfaces. In Figure 11 there are the optical microscopy images (10X) of colonies from the areas contacted with leather surface (B) and from the media in adjacent areas (A). It can be seen that the treated leather surfaces (Figure 11 a, b, d, e, B areas) are sensitive to tested bacteria as compared to untreated leather surfaces (Figure 11 c, f B areas). A clearer medium after the contact with Ag-TiO₂ NPs treated leather surfaces (Figure 11 a and d) can be seen as compared to the medium after contact with leather surface treated with Ag-TiO₂ NPs (Figure 11 b and e), in correlation to the test results for fungus resistance (Table 1).

The fungistatic activity of leather surfaces treated with Ag-N-TiO₂ NPs and Ag-TiO₂ NPs was evaluated according to ISO 20743 using the absorption method by direct inoculation of fungi (*Epidermophyton floccosum*, *Candida albicans* ATCC 26790, *Candida albicans* 1726 and *Candida albicans* 1760) on leather surface and quantification of viable colonies after 24 hours. The results are presented in Table 1 and show that leather surface treated with Ag-N-

Table 1: The resistance of leather surfaces against *Epidermophyton floccosum*, *Candida albicans* ATCC 26790, *Candida albicans* 1726 and *Candida albicans* 1760.

Fungus strain	T ₀ CFU/ml Ag-N-TiO ₂ NPs	T ₂₄ CFU/ml	Reduction %	T ₀ CFU/ml Ag-TiO ₂ NPs	T ₂₄ CFU/ml	Reduction %
<i>Epidermophyton floccosum</i>	3.42x10 ³	8x10 ¹	97.66	3.42x10 ³	1.8x10 ³	47.37
<i>Candida albicans</i> ATCC 26790	6.6x10 ³	0	100	6.6x10 ³	6.6x10 ³	0
<i>Candida albicans</i> 1726	173x10 ³	13.3x10 ³	92.3	173x10 ³	46.6x10 ³	73
<i>Candida albicans</i> 1760	56x10 ³	0	100	56x10 ³	20x10 ³	64.3

TiO₂ NPs has excellent resistance against *Candida albicans* ATCC 26790, *Candida albicans* 1760 and good resistance against *Epidermophyton floccosum*, specific fungus for footwear interior.

Ultrastructural analyses elucidating the interaction between Ag NPs with *Candida spp* have not been reported. In 2014, TEM analysis achieved by Vazquez-Muñoz *et al.*, revealed a high accumulation of Ag NPs outside the cells but also smaller nanoparticles localized throughout the cytoplasm [53]. These results suggest that the mode of action of Ag NPs is to aggregate outside the fungal cells, releasing silver ions and thus inducing cell death through the reduction process resulting from the interaction of cell components with ionic silver. As the Ag NPs' mechanisms of action are not clear yet, is difficult to explain the comportment of the different *C. albicans* strains. Both strains, *Candida albicans* 1726 and *Candida albicans* 1760, are clinical isolates that probably become more sensitive to different antimicrobial substances *in vitro*. The behavior of the *C. albicans* ATCC 26790 strain with respect to the interaction with Ag NPs is unknown, therefore further investigation is necessary to elucidate this effect.

The improved behavior of leather surfaces treated with Ag-N-TiO₂ NPs is attributed to the higher hydrophilic surfaces favorable for the contact of NPs with bacteria and fungus. The results suggest that the increased surface contact [54, 55] and the generation of reactive oxygen species on leather surface treated with electrochemically nano Ag deposited on N-TiO₂ NPs can explain the antimicrobial effectiveness. The improved resistance of Ag-N-TiO₂ NPs against bacteria strains was also confirmed by other studies [56, 57]. In our work the resistance against bacteria and fungus strains of Ag-N-TiO₂ NPs was successfully transferred on leather surface coating.

4 Conclusions

Silver nanoparticles were deposited on TiO₂ NPs and N-TiO₂ NPs by electrochemical method and showed advanced photoinduced catalytic properties in the visible domain. The particle size increased by silver deposition from 20 nm and 25 nm for TiO₂ NPs and N-TiO₂ NPs to 31 nm and 40 nm for Ag-TiO₂ NPs and Ag-N-TiO₂ NPs according to transmission electron microscopy analyses. The water dispersions of Ag-TiO₂ NPs and Ag-N-TiO₂ NPs were stable with Zeta potential of -41.4 mV to - 47.4 mV. Diffuse reflectance spectra of Ag-TiO₂ NPs and Ag-N-TiO₂ NPs shifted to the visible domain as compared to TiO₂ NPs. Photocatalytic properties of silver deposited on TiO₂ NPs and N-TiO₂ NPs tested on Orange II dye solution under UV and visible light exposure were investigated for different silver concentrations and resulted in the selection of the 0.5% concentration as the most efficient in visible light. The enhanced photocatalytic properties in the visible light domain were confirmed under leather surface through self-cleaning stains of ball pen ink, Orange II and methylene blue dyes that were recorded for treated leather surfaces with Ag-N-TiO₂ NPs. The antimicrobial resistance of leather surface treated with Ag-N-TiO₂ NPs was excellent against *Candida albicans* ATCC 26790, *Candida albicans* 1760 and good against *Epidermophyton floccosum*. The leather surface sensitivity tests at direct contact with *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 25923 proved to be resistant for both treatments based on Ag-TiO₂ and Ag-N-TiO₂ nanoparticles. The improved antimicrobial sensitivity and resistance as well as the self-cleaning effects under visible light were attributed to the photocatalytic induced hydrophilic properties on leather surface treated with silver electrochemically deposited on N-TiO₂ NPs.

The leather surface covered with Ag-N-TiO₂ NPs showed enhanced self-cleaning and antimicrobial properties, increasing the leather durability and usability and paving the way for designing new nanoparticles with multifunctional functionalities.

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