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Double Dielectric Barrier (DBD) plasma-assisted deposition of chemical stabilized nanoparticles on polyamide 6,6 and polyester fabrics

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Introduction

The development of new multifunctional textiles containing nanoparticles (NPs) has a special interest in several applications for pharmaceutical and medical products. Cu, Zn and Ag are the most promising antimicrobial NPs, exhibiting strong antibacterial activities. However, most of antimicrobial textiles coated with NPs are not able to perform a controlled release of NPs because of the high degree of aggregation. The aim of this study is to assess the effect of NPs stabilizers such as citrate, alginate and polyvinyl alcohol (PVA) in Cu, Zn and Ag NPs dispersions. The obtained dispersions were used to develop a new class of antibacterial NPs coatings onto polyamide 6,6 (PA66) and polyester fabrics (PES) by Double Dielectric Barrier (DBD) plasma discharge. Dynamic light scattering (DLS) was used to evaluate the best dispersing agent in terms of size, polydispersity index and zeta potential. Coating efficiency was evaluated by SEM, XPS and FTIR. The DBD deposition in air was compared, in term of NPS deposition, with usually more efficient plasma jets using carrier gas such as N_2 and Ar.

Dynamic light scattering (DLS) analysis

To solve the instability and aggregation problems of Ag, Cu and ZnO NPs suspensions (10 ppm) of citrate, alginate and PVA using water and ethanol as control were prepared in different concentrations (1, 2.5 and 5 wt%) using an ultrasonic bath. Table 1 shows the best results obtained for each NP compared to water as control.

Table 1 - DLS and zeta potential measurements of suspensions tested

	ZnO NPs		Cu NPs		Ag NPs	
	Water	**Citrate 2.5%**	**Water**	**Alginate 5%**	**Water**	**Alginate 2.5%**
ζ (mV)	-17.3±4.2	-38.7±2.5	-0.2±0.3	-32.3±2.7	-19.7±0.8	-28.6±1.4
Size (dnm)	172.6±4.8	176.2±2.3	468.2±22.8	774.8±173.7	239.9±17.6	184.9±8.3

Scanning electron microscopy (SEM) analysis

The SEM images (Figure 1) of the deposited NPs in plasma treated PA66 and PES show a good widespread load of NPs at the expected size but a high aggregation and a not uniform distribution as previously observed at this low NPs concentration (10 ppm)

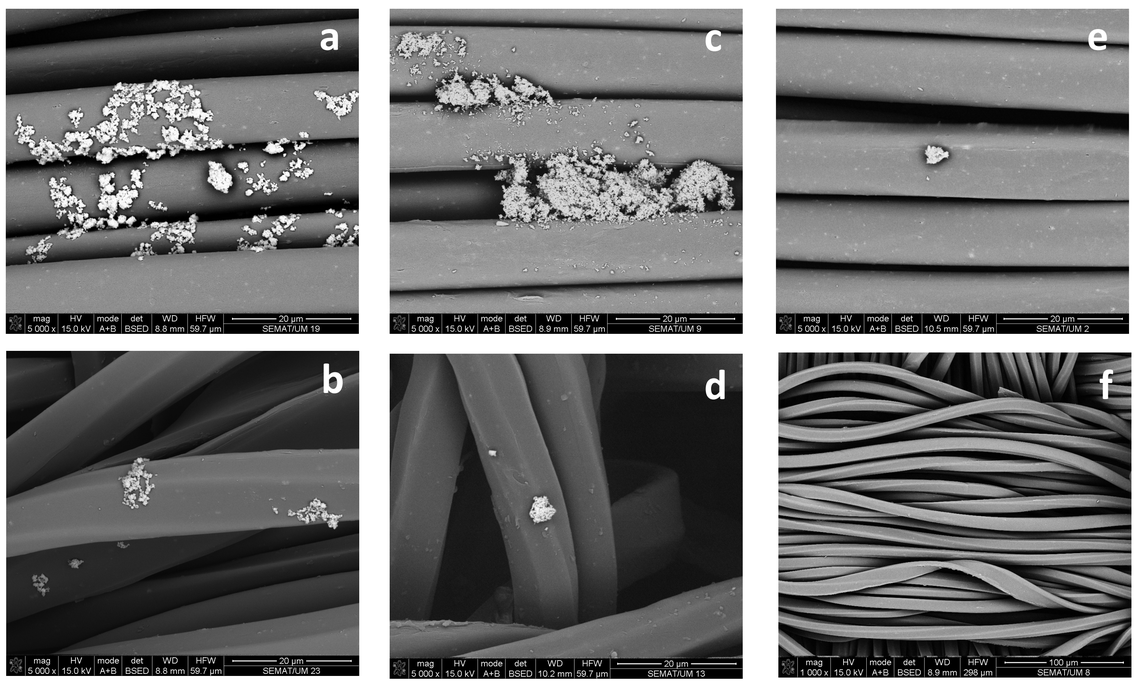

Figure 1 - SEM of Ag (a, b), Cu (c, d) and ZnO NPs (e, f) onto PA66 and PES fabrics, respectively.

X-ray photoelectron spectroscopy (XPS)

The plasma treatment is able to increase the concentration of polar groups near the surface of the fabric mainly by the incorporation of oxygen atoms from atmospheric air as confirmed by XPS analysis.

Fourier transform infrared spectroscopy (FTIR)

The addition of NPs onto the fabrics surface after plasma treatment change the appearance of low-intensity peaks in ATR-FTIR spectrums in the range between 1700-1750 cm^{-1} and 3500–4000 cm^{-1} attributed to carboxylic acids and hydroxyl groups, respectively. These peaks suggest the interaction of NPs in their oxidized form with the plasma-produced oxygen species onto the PA66 surface.

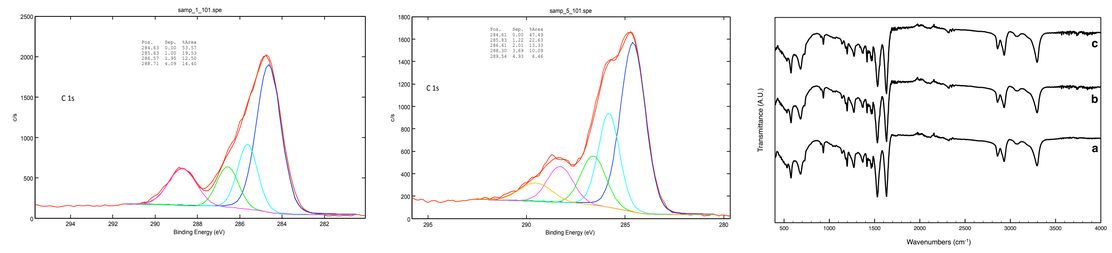

Figure 2 - High-resolution XPS deconvoluted spectra of the C1s envelope of plasma treated PES without (up) and with Cu NPs (down). FTIR spectra of the plasma treated PA66 without NPs (a) and with coated Ag (b) and Cu (c).

Atmospheric DC plasma jet in N_2 and atmospheric RF DBE plasma jet in Ar

For similar NPs concentrations, the DC plasma jet using N_2 shows similar results including a high degree of NPs aggregation (Figure 3-A) while, the RF plasma jet using Ar display a widespread distribution and higher concentration of NPs onto the fabric surface. Overall, the DBD plasma technique showed comparable results despite the absence of a carrier gas and the used lower energies.

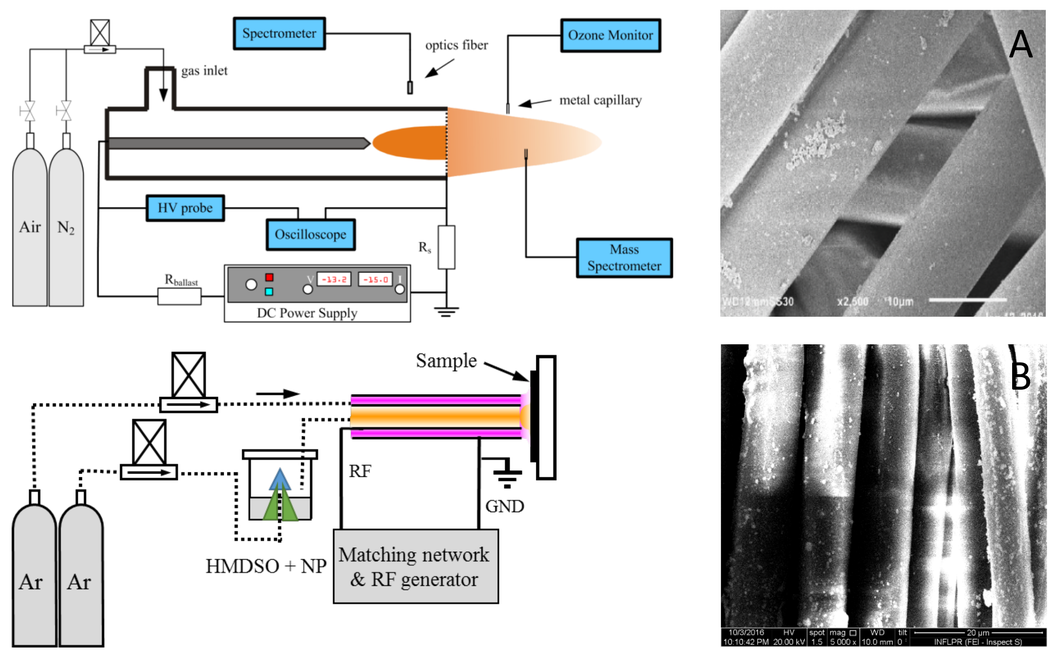

Figure 3 - Schematics of the N_2 DC (A) and Ar RF DBE (B) plasma jets and respective SEM analysis of deposited Ag NPs onto PES fabrics.

Conclusions

The NPs were successfully stabilized improving their deposition onto PA66 and PES fabric surfaces. However, despite the improving in ζ potentials the obtained NPs still show a moderate degree of aggregation.

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