Plasma-enhanced Synthesis of Bactericidal Quaternary Ammonium Groups

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The need to combat microbial infections in materials and devices for medicine drives interest in developing surfaces with antimicrobial functional groups. Free polycationic structures are known to exhibit antibacterial characteristics in water-based environments, but suffer from residual toxicity, leaching out and low efficiencies. Cold plasma technologies open up novel and efficient routes to tailor the surface characteristics without altering the bulk of a material, facilitating the covalent implantation of structure- and functionality-controlled chemical groups under selected discharge parameters. The work describes surface layers that kill bacteria on contact by using low pressure, non-equilibrium plasma (LP-NEP)-enhanced synthesis and deposition of bactericidal quaternary ammonium (QA) thin layer macromolecular structures onto stainless steel surfaces.

The bottom-up chemical synthesis of QA groups from the surface was integrated with top-down plasma thin film depositions. The plasma-polymerized films are deposited in capacitively-coupled parallel plate reactor equipped with 13.56 MHz RF power source. A pretreatment of SS substrates to stabilize the top bioactive structure is done with O_2 plasma (200 mTorr, 200 W, 5 min) and hexamethyldisiloxane plasma (200 mTorr, 200 W, 1 min). Ethylene diamine (ED) plasma films were deposited at 100 mTorr, 100 W at 13.56 MHz RF power for 10 min. The plasma-modified substrates are alkylated with various alkyl bromides in amyl alcohol and KOH for 12 h. After rinsing with methanol, the substrates are further reacted with iodomethane in amyl alcohol for another 6 h. Electron Spectroscopy for Chemical Analysis (ESCA) and Fourier Transform Infrared Spectroscopy (FTIR) are used to determine the chemical composition at all steps in the process. The bactericidal properties of these surfaces are evaluated against Gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae* using standard colony counting procedures.

The survey ESCA spectra of quaternized SS is shown in Fig 1(a). The presence of iodine peaks from various core levels in survey ESCA confirms the reaction between amine groups on ED-plasma-modified surface and alkyl halides to form QA groups on the surface. The high resolution ESCA C 1s spectrum of SS coated with QA functionalities is shown in Fig 1(b). The I $3d_{5/2}$ peak at 619.6 eV was used to determine the binding energy shift associated with surface charging in the high resolution spectrum. The C 1s spectrum was fitted with peaks corresponding with *C—C, *C—N, *C—N^+—R (R=H, C), *C—O/*C=N, *C=O, *C(O)=O at 285.0, 285.6, 286.2, 286.7, 288.0, and 289.1 eV respectively. The ED-plasma films deposited on top of O_2 and HMDSO plasma do not laminate during washing with water or acetone in an ultrasonicator for 10 min. The FTIR spectra of films deposited in ED-plasma on potassium bromide pellets show bands around 1100, 1627, and 3434 cm^{-1} and substantiate the presence of amine functionalities. A shoulder at 3680 cm^{-1} reveals the presence of imine functionalities and the bands in the region 1850-1700 cm^{-1} confirms the carbonyl group in the macromolecular structure. Hence, the IR spectrum of plasma deposited films co-ordinates with the ESCA data.

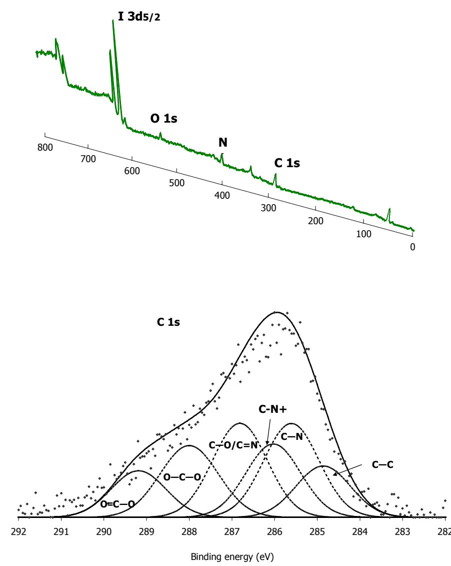

Fig 1. (a) Survey and (b) High resolution C 1s ESCA spectrum of quaternized SS

Compared to unmodified SS, quaternized substrates showed about 99% decrease in *S. aureus* attachment at 24 h contact time. The quaternized substrates were not very effective against gram-negative *K. pneumoniae*. The effect of chemical architecture of quaternary ammonium groups with varying alkyl chains was optimized for antibacterial efficacy.

This cold plasma-mediated deposition of quaternary ammonium groups provides a promising technique to synthesize bactericidal surfaces with end use application in medical devices and biomaterials. The plasma-aided technology is a clean and alternative way to develop controlled and robust bioactive surfaces with potential applications in biomedical devices, sensors, MEMS etc.