



## Functionality and chemical stability of plasma polymer films exhibiting a vertical cross-linking gradient in their subsurface



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### ABSTRACT

Preserving the amount of amine groups in a plasma polymer film (PPF) immersed in water is crucial for biomedical applications such as, e.g., bio-sensing or tissue engineering. In this study, nanometer thick PPFs were deposited on a substrate by activation of NH<sub>3</sub>/C<sub>2</sub>H<sub>4</sub> gaseous mixtures in a low pressure plasma. In particular, plasma deposition conditions were adjusted during film growth to create a vertical gradient in amine group functionality and cross-linking degree extending over a few nanometers of the PPF near its surface. As a result of the vertical gradient structure, undesired changes in wettability, in chemical composition, in surface charge and in topology of the 'gradient' NH<sub>2</sub>-PPF were strongly reduced as observed over one week in water. In comparison, 'conventional' coatings, i.e. deposited at constant plasma conditions yielding the same chemical composition as the top layer of the gradient structure, revealed distinct surface restructuring effects. Albeit oxidation of the coatings was found to be inevitable, the gradient structure significantly decreased these aging effects of the NH<sub>2</sub>-PPF. To further highlight the benefits of the stabilizing structure in the coating's subsurface, investigations were carried out under flowing water conditions demonstrating the reduced degradation of the NH<sub>2</sub>-PPFs with vertical cross-linking gradient for realistic conditions.

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### 1. Introduction

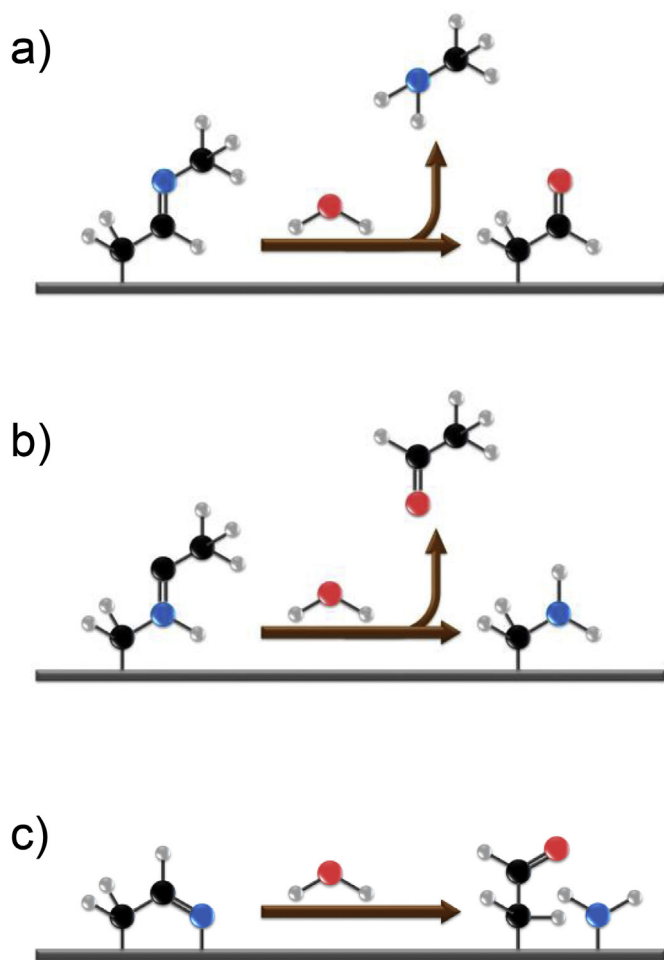
Engineering of biointerfaces typically requires soft materials with enhanced surface mobility and defined surface functionality; in terms of plasma polymer films, this translates into limited cross-linking [1], which, however, also raises questions about their surface stability [2,3]. Organic polymer thin films deposited by means of plasma polymerization hold the prospects of tuning surface functionality and cross-linking [4,5]. Over the last decades, in particular, the use of amine-containing plasma polymer films (NH<sub>2</sub>-PPFs) has increased for various applications in the biomedical field, such as bio-sensing, tissue engineering, cell culture, etc. due to the high functionality of aminated surfaces [2,6–9]. Among the variety of nitrogen-containing groups stochastically formed in a NH<sub>2</sub>-PPF, particularly the primary amine groups yield a positive surface charge in aqueous solutions at physiological pH values that electrostatically attracts negatively charged biomolecules such as

proteins and supports cell attachment [9–11]. Furthermore, the chemical reactivity of NH<sub>2</sub> groups can be used for the immobilization of biomolecules in aqueous environments [6,10]. However, plasma polymers containing –NH<sub>2</sub> groups are well-known for their low stability, compared to most of the oxygen-containing PPFs currently used for biomedical applications. More specifically, NH<sub>2</sub>-PPFs undergo fast degradation processes such as hydrolysis and dissolution in aqueous environments [9,12]. In view of their application, there is thus a need to provide stable NH<sub>2</sub>-PPFs [13].

Upon storage the surfaces of commonly explored NH<sub>2</sub>-PPFs not only undergo hydrophobic recovery (mainly in air) [14–16] and post-plasma oxidation (in air and in water) [17–19], but also major surface restructuring and film loss (mainly in water) [12,19] – effects referred to as 'aging' of PPFs. Namely, loss of low molecular weight fragments (or oligomers) of the PPF in aqueous environments occurs due to potential hydrolysis reactions, resulting in a loss of fragments that contain amine groups as well as progressive oxidation of the PPF. These hydrolytic reactions lead to changes in chemical composition as well as morphological changes such as modification of the micro- or nano-structuring, formation of voids in the film, and change of porosity [12,19,20]. This degradation

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**Fig. 1.** Scheme of the main scenarios occurring after hydrolysis reaction of the imine group in  $\text{NH}_2$ -PPF: a) direct release of the amine-containing fragments due to a low cross-linking degree; b) direct release of the carbonyl-containing fragments (in this case, the amine groups would be lost later by successive hydrolysis in the low cross-linked network); and c) no release of the carbonyl and the amine groups in the case of a secondary imine (mainly in a highly cross-linked network). Note that carbon atoms are represented in black, oxygen atoms in red, nitrogen atoms in blue and hydrogen atoms in grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

process, also known as hydrolytic degradation, is a four-step process: i) diffusion of water molecules into the polymer film, often accompanied by swelling; ii) hydrolysis reactions in the polymer film, which can be auto-catalyzed by degradation products; iii) mass loss due to dissolution and diffusion of some film fragments; and iv) formation of a porous structure that will homogeneously degrade over time until the polymer layer is fully dissolved [21].

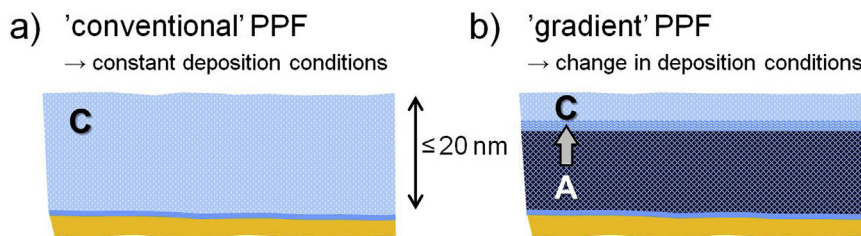
Thus, the degradation of common ('conventional')  $\text{NH}_2$ -PPFs in water is a crucial problem as the initial functions provided by the plasma deposition process are rapidly lost, which is unwanted for typical applications like bio-sensing.

According to literature,  $\text{NH}_2$ -PPFs contain various chemical groups, such as amine, imine, nitrile or isonitrile groups [22]. By immersing a  $\text{NH}_2$ -PPF in water, amine groups are expected to remain largely unchanged, but nitrile or isonitrile groups are known to oxidize which, however, proceeds slowly due to their low reactivity. Imine groups, on the other hand, are more sensitive to water molecules: in presence of water molecules, imine groups hydrolyze to parent carbonyl (see supplementary information, Figure S1), leading to the release of an amine-containing fragment. Three main scenarios can thus be considered according to the cross-linking degree in the plasma-based coating (Fig. 1).

If the coating is less cross-linked, there are actually two possibilities: amine-containing fragments (Fig. 1a) or carbonyl fragments (Fig. 1b) can be directly released from the PPF. Note that, even if the amine groups stay inert, they could easily be released by the subsequent hydrolysis occurring in the structural vicinity, since the polymer cross-link density is reduced by chain scission [23]. If the coating is initially more cross-linked (mainly via carbon-carbon bonds), carbonyl and amine groups preferentially survive near the surface of the coating, leading to a slight increase of the number of amine groups at the surface (Fig. 1c).

The improvement of the stability of the PPF is thus possible by selecting deposition conditions leading to highly cross-linked PPFs near the surface: such highly cross-linked PPFs are stable for an extended time in air and water, but naturally contain a lower amount of the functional groups, whereas a higher amount would be preferred, e.g., for bio-sensing applications [5,6]. Furthermore, enhanced cross-linking to achieve stable  $\text{NH}_2$ -PPFs affects mechanical properties typically resulting in a Young's modulus in the range of a few GPa that might also influence cell interaction [24–28], whereas softer PPFs tend to dissolve in aqueous environments [27,29]. To circumvent those difficulties a recently developed method to obtain stable yet soft and functional  $\text{NH}_2$ -PPFs consists in preparing a vertical chemical gradient during film growth from a highly cross-linked/less functional to a less cross-linked/highly functional plasma polymer film within an overall film thickness  $\leq 20$  nm as depicted in Fig. 2 [30–33]. A strong reduction of the aging process is expected by the more cross-linked base-layer, which would also hinder water penetration as well as migration and restructuring processes in general [34]. As an additional advantage the chemical composition of the base-layer can be controlled so as to limit the number of chemical groups that could undergo hydrolysis reactions in the first place.

This study aims to further elucidate and understand the physico-chemical mechanisms involved in the enhanced stability found with such gradient-stabilized  $\text{NH}_2$ -PPFs, by systematic examination of the surface properties via a variety of macroscopic measurements and discussion of plausible underlying molecular



**Fig. 2.** Scheme of plasma polymer films deposited on a substrate with a) constant deposition conditions (named 'C') and b) change in deposition conditions ('A' to 'C') during film growth resulting in a transition (gradient). Note that slightly different initial growth conditions can be expected due to plasma-substrate interaction.

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