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Gradient Structures Enhancing Stability and Functionality of Plasma Polymer Films

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Functional plasma polymer films (PPFs), e.g. containing carboxyl or amino groups, typically reveal limited stability in aqueous media due to swelling and degradation. In particular, amine-functional PPFs were found to be prone to oxidation and hydrolysis reactions. To improve the stability of PPFs while maintaining a suitable amount of available functional groups, vertical chemical gradients in PPFs were thus explored based on a crosslinked structure that gradually becomes more functional towards the surface. Thus, migration and degradation processes can be effectively hindered.
A comprehensive study involving plasma diagnostics (OES) and surface characterization methods (XPS, ToF-SIMS, AFM, contact angle, zeta potential) was performed to define a suitable vertical gradient structure on the nanoscale. The stability in water was compared for carboxyl- and amine-containing PPFs, with and without vertical gradient structure. Highest stability combined with functionality was achieved for 1-2 nm thick terminal layers of higher functional group density. Thereby, the initial number of functional, e.g. amino, groups can be preserved in aqueous environments, while a reference layer lost all $–NH_2$ groups after the first day of immersion in water. Chemical processes to support the stabilization of the functional surfaces are discussed. Finally, lateral gradients as well as combinations of N and O functional layers were investigated revealing important aspects with respect to protein adsorption.
Adjusting the thin film architecture of plasma polymer films thus provides an additional parameter to modulate surface properties of materials offering unique opportunities for biomaterials and chemical engineering.

Keywords
plasma polymer
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subsurface structure
protein adsorption