## Tailorable, ultra-thick hyaluronan polymer brushes: A novel class of interfaces

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Functional interfaces are crucial in many biomedical applications like biosensing, protein purification, anti-bacterial coatings, and tissue engineering. Polymer brushes, or structures of densely organized endgrafted polymers, are of particular interest for dynamic and self-healing bio-interfaces, especially when using biocompatible materials like hyaluronan (HA). We introduce a novel method to generate micronsthick HA polymer brushes using the HA synthase enzyme to synthesize the thickest polymer brushes ever, reaching ~22  $\mu$ m in a matter of hours. Due to this incredible thickness, their characterization and study can be performed in a straight-forward manner with confocal microscopy. The HA brushes offer a unique platform to study surface modification and fundamental polymer physics. We have developed a method to control the topology of the brush with visible light patterning where the underlying grafting density of the HA polymers is modified. In this way, shapes and gradients can be sculpted into the brush. The brush height is tunable through not only synthesis time, but also its stimulus responsiveness. Our brushes exhibit both osmotic and salted brush regimes when exposed to varying salt concentration, as well as collapse in the presence of a poor solvent. These interfaces show promise in a variety of applications from stimulus responsive biomaterials, anti-microbial surfaces, filtration, drug delivery, and the potential for implants or bandages.

