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Nanostructured bioinspired dry adhesives

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INTRODUCTION: The key strategy in many natural attachment systems is the incorporation of patterns, i.e. fibrillar surfaces or subsurface structures. For example, the toes of a gecko have millions of micron-sized fibrils packed closely together and each fibril branches into hundreds of nanosized spatula-shaped structures [1]. We develop nanofabrication processes based on self-assembly, which will allow the fabrication of polymeric nanosized fibrillar arrays (gecko-mimic) or subsurface patterns (grasshopper-mimic) with complex 3D structures, hard to achieve with top-down methods. Here, we developed biomimetic nanostructured surfaces using colloidal self-assembly.

METHODS: Negatively charged polystyrene particles, 1.15 µm in diameter, were synthesized using a surfactant-free emulsion polymerization and spread on an air-water interface, see Figure 1. This monolayer served as a template for polydimethylsiloxane (PDMS). A syringe with a blunt tip needle filled with PDMS was used to apply PDMS to the side of the Petri dish containing the monolayer of particles. PDMS was allowed to crosslink at RT for 2 days, resulting in layers of 0.2-0.6 mm thick. To remove the template particles from the PDMS mold, we first applied Scotch Magic Tape, which removes the largest portion of templating particles. The remaining colloids were removed by soaking the sample in N-methyl-2-pyrrolidone (NMP) for 1 hour, followed by dipping the samples in NMP 30 times in ultrasonic an bath.



Fig. 1: Fabrication of nanopatterned polydimethylsiloxane (PDMS) using colloidal lithography directly at the air/water interface.

RESULTS: Figure 2 shows scanning electron microscopy (SEM) images of a crystalline monolayer of polystyrene particles and the complete removal of the particles after treatment with NMP.



Fig. 2: Scanning electron microscopy (SEM) images of crystalline monolayer and resulting nanostructured surface.

To optimize the order of the colloidal monolayer and to control the immersion depth of the particles, the pH of the subphase was varied systematically. The charges on the particles originate from carboxyl groups with $pK_{a1}=3.85$ and $pK_{a2}=5.44$. The order showed a rapid increase when the pH of the subphase was higher than the first dissociation constant of the carboxyl groups on the surface. This way, different subphase conditions were used to control the topography of PDMS surfaces.

DISCUSSION & CONCLUSIONS: Colloidal lithography directly at the air/water interface resulted in a variety of nanostructured surfaces. We are particularly interested in hour-glass shaped pillars, because this particular fibril size and shape is expected to result in significantly enhanced adhesion, because stress concentrations will be decreased at the pillar edges, thereby increasing the toughness of the system. These biomimetic microstructured surfaces have great potential for a variety of applications such as adhesives, self-cleaning surfaces and anti-fouling coatings.

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