MICRO AND NANO- IMPRINTING OF PEG-BASED HYDROGELS

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The ever-increasing demand for smaller components in electronics and in optical and biological devices has intensified the interest of pushing the resolution limits of lithographic techniques and increased the efforts to develop alternatives to e.g. photolithography or electron-beam lithography without involving complex, expensive equipment. Soft lithography is an important inexpensive, facile lithographic technique based on bas-relief patterns on the surface of soft elastomers (e.g. PDMS).[1] Photocurable fluoropolymers such as PFPE DMA have been proved by the group of DeSimone to be able to successfully replicate naturally occurring objects, which are less than 10nm in size by replica molding.[2, 3]
For potential biomedical applications such as tissue engineering, biosensors or in general for cell behaviour studies, the biocompatibility of the structured substrates is very important. Patterned biomaterials can assist in the better understanding of many biological processes by imitating in-vivo substrates, since they provide cues for cells to attach, migrate and grow into tissues. It is accepted that the topography of the biomaterials' surfaces has an influence on the response of cells or tissue they are in contact with. Therefore, combining cost-effective patterning tools with suitable biocompatible substrates is desired. Patterned PEG based biomaterials are a case in point.

Here we present an easy benchtop method to pattern hydrogels at all length scales relevant for cell studies, that is, from micrometer to sub-10 nm. A PFPE-based fluoropolymer is used as a secondary soft mold material as a better alternative to the commonly used PDMS in replica molding to successfully pattern large areas on PEG-based hydrogels. To remark is the possibility to pattern hydrogels directly from a hard master or via a secondary, soft mold, with easy mold release even without surface treatment.

As shown in Fig. 1 this hydrogel can be structured within the entire length scale relevant for cell studies. When patterning high aspect ratio structures in the nanometer range, collapses on the structure can be observed as previously described (Fig 1b.).[4] Nevertheless, by optimising the mechanical properties of the hydrogel (the elastic modulus can be tuned from several tens of kPa till several MPa), the grooves on the silicon master (100 nm width; 300 nm height) with variable separation (from 100 nm to 4 µm) are successfully replicated as standing ridges on the surface of the hydrogel with no pattern deformation observed. By pushing the limits of surface patterning on these hydrogels, sub-10 nm structures were successfully replicated (gold nanodots ~ 8 nm height)[5] as shown in Fig. 1c.
Hence, we can conclude that structures from micrometers to sub-10 nm in size can be successfully patterned on two biomaterials by means of replica molding. Comparable replication fidelity was obtained for the PFPE based fluoropolymer (a hydrophobic, relatively stiff elastomer with a low surface energy) and StarPEG based hydrogels (a hydrophilic, softer elastomer with a high surface energy). Clean and easy mold release, without any surface treatment can be done from a silicon master and from the respective secondary, elastomeric mold for both of the materials here used. PEG based hydrogels are materials of interest to the nanobiotechnology community due to their nontoxic, biocompatible nature. The exceptionality of this hydrogel permits to topographically pattern large areas not only with micro- but also with nanostructures, which is helpful to understand fundamentals in cell

behaviour. Indeed, first results have shown how the renown non-fouling properties of the smooth hydrogel change drastically when the same material bears microstructures on its surface; cells do adhere to the hydrogel's surface when it is topographically patterned.[6] We expect the nanostructured materials to provide us new insights concerning cell behaviour. Both the simplicity and low cost of this procedure corroborate its potential use in nanomanufacturing as well as the relevance as biomaterials in cell studies, tissue engineering and other bioapplications.

References:

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Figures:

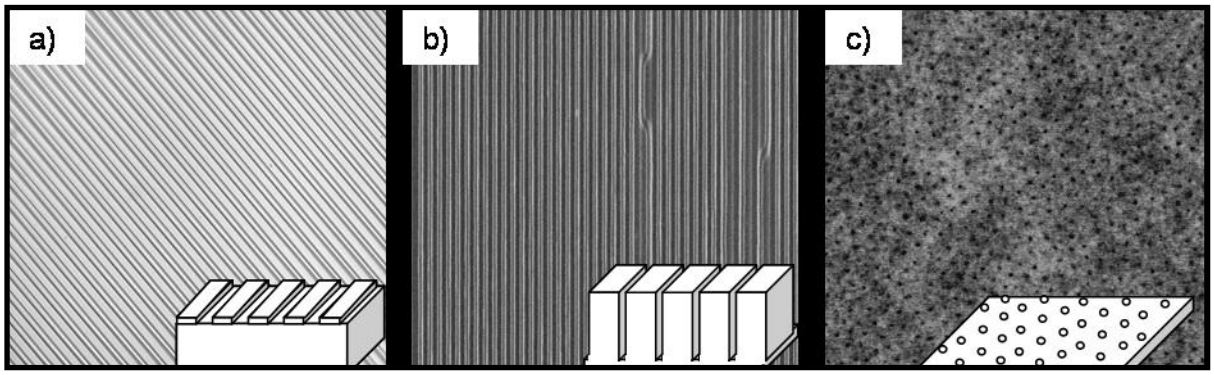

Fig.1 Microscopy images of the structured hydrogels. a) Optical micrograph of micro- lines (10 µm wide; 5 µm high; spaced 10 µm). b) Scanning electron micrograph of nano- ridges (100 nm wide; 300 nm high; spaced 500 nm). c) AFM image of nano- indents (6 nm depth). The corresponding masters used for replication are depicted schematically in the micrographs.