Nanopatterned surfaces via colloidal lithography and plasma processing applied to selective protein immobilization and superhydrophobicity

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Colloidal lithography, based on the close-packed self-assembly of colloidal microparticles over large surface areas, is a versatile, fast, and low cost, mask-less lithographic method to reach successfully the nanometer scale. This method has been extensively used as a patterning technique, with the colloidal particles acting as masks in plasma etching. Here we present a simple, rapid and high throughput generic method to obtain ordered nano-rough islands or posts using colloidal lithography combined with short plasma treatments to generate surfaces appropriate for selective protein immobilization or liquid repellence.

A well-ordered, colloidal polystyrene (PS, 1μm in diameter) particle assembly is created by spin-coating on Si/glass/polymer substrates. After a step of plasma treatment, a desirable reduction in particle size is performed, while at the same time, roughening of the microparticle surface is observed. Subsequently, the modified particles are exploited either as islands for selective immobilization of proteins with respect to the surrounding substrate area (route A, Fig. 1) or as masks for transferring the pattern to the underlying polymer substrate, in which case after deposition of a hydrophobic coating, superomniphobic surfaces are demonstrated (route B, Fig. 1). A periodic arrangement of rough PS particles (shrunk diameter d=450 nm) on Si/glass substrate is depicted in Fig. 2a. These substrates were then immersed in a b-BSA (biotinylated Bovine Serum Albumin) protein solution and model binding assays were performed based on biotin-streptavidin interaction with fluorescently labeled streptavidin. The highly selective protein immobilization on the nanotextured islands with respect to the substrate surrounding area was confirmed by epifluorescence and atomic force microscopy (AFM) and subsequent image analysis Fig. 2b. The implementation of such surfaces for biosensing with enhanced sensitivity is envisioned. Alternatively, this method allows the fabrication of dual scale pillars (Fig. 2c) of controlled height and diameter depending on etching time and bias voltage, with excellent liquid repellent properties (Fig 2d). Such surfaces can be used as "smart" passive valves in microfluidics and in other practical applications.

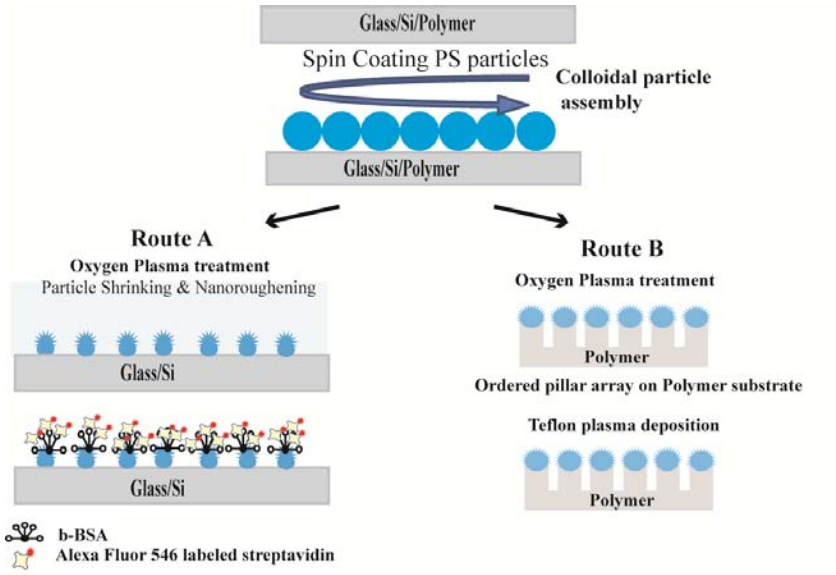

Figure 1: Schematic of the colloidal particle assembly and nanopatterning through O_2 plasma treatment. Route A: selective protein immobilization on plasma-textured/modified particles (left). Route B: plasma-induced dual scale microcolumns for superomniphobic surfaces (right).

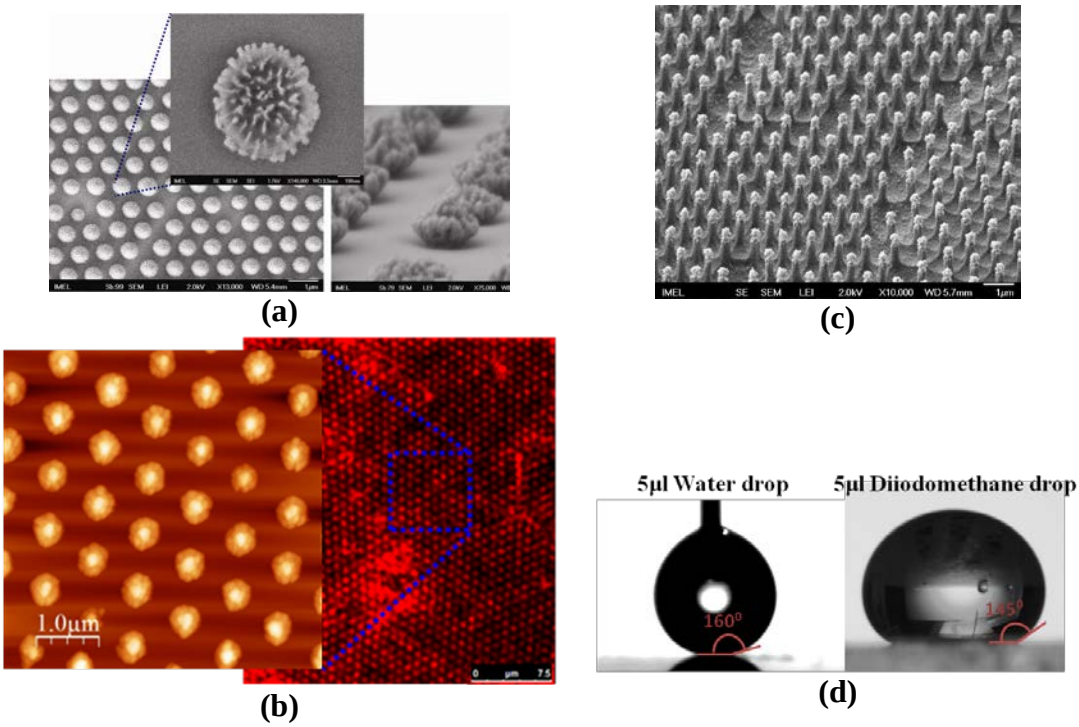

Figure 2: (a) SEM images of colloidal particles after plasma-induced size reduction and nanotexturing. (b) AFM and epifluorescence images of the surface in (a) after protein immobilization (red spots: streptavidin). (c) Highly ordered array of nanotextured PMMA micro-pillars after 2 min O_2 plasma etching. (d) Water (160^0) and diiodomethane (145^0) drops on the surface in (c).