Single-colloidal-particle microcontact printing†‡

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Received 8th June 2007, Accepted 12th July 2007
First published as an Advance Article on the web 30th July 2007
DOI: 10.1039/b708722e

We have utilized colloidal probe atomic force microscopy (AFM) in conjunction with microinterferometry to study the forces acting in the microcontact printing process. The procedure we have developed yields well defined asymmetric imprints on colloidal probes, which could find further application in interaction force measurements between Janus-type particles and surfaces.

Controlling surface properties of colloidal particles is one of the oldest and at the same time most vital topics in physical chemistry. Comparatively few procedures still exist that allow producing colloidal particles which are asymmetric in their surface properties/interactions.[1–11] Recently, there has been much interest in such particle types, since they would offer several new perspectives for both applications and fundamental science. Asymmetric interactions are expected to give rise to surface activity[12,13] or novel colloidal phases, like (liquid) colloidal crystals[15,16] with new symmetry classes.[14] Such structures, as well as the asymmetric single particle properties are expected to lead to interesting applications in optics (especially photonics), electronics, biosensing or emulsion stabilization.[14,17–20]

One of the most established routes for production of asymmetric particles is the use of microcontact printing on colloidal monolayers. Microcontact printing was originally developed for patterning flat surfaces.[21,22] The method comprises two steps, *i.e.* "inking" of an elastomeric stamp with a solution of the molecules of interest, and pressing the stamp onto the substrate to be patterned. If suitable molecules are used, only a molecularly thin layer is formed in the contact region on the substrate. The technique was originally developed for thiols and silanes which form self-assembled monolayers, but has since been demonstrated for various molecules including macromolecules and even proteins,[23–27] see ref. 28 for a recent review article. If the flat substrate is replaced by a supported monolayer of colloidal particles, the particles are partially coated and can afterwards be released. The process is highly versatile with regard to the type of functionalization. For example, asymmetric particles with insoluble surfactant layers[5] or with macromolecular coatings[9] have been reported. Still, so far little is known about the forces acting during the stamping process and control of the coated area is rather limited. We aim to solve these problems by studying the printing process for individual colloidal particles using the AFM colloidal probe technique. In the colloidal probe technique colloidal particles are attached to an atomic force microscope cantilever and their interaction with surfaces can thus be probed as a function of distance using an atomic force microscope in force spectroscopy mode.[29,30] We have recently combined this technique with microinterferometry,[31] which allows observing particle-substrate contact areas with sub-micron lateral resolution during pressing particles against surfaces.[32] Here we use this technique to monitor a microcontact printing process for individual colloidal particles and to discuss the forces involved in the printing process. Also, we demonstrate that by controlling the applied force, the coated area of the particle can be accurately controlled.

In our experiment we prepared soft and deformable PDMS (polydimethylsiloxane) Sylgard 184 (Dow Corning, USA) (polymer-crosslinker ratio 10 : 1) with microscope cover slides as solid support. To obtain smooth stamps the PDMS was deposited on the slides by spin-coating of a 1 : 1 mixture of the pre-cured polymer and heptane. Structured stamps were fabricated with PDMS cast from hydrophobised silicon masters (GeSim, Großerkmannsdorf, Germany). After curing, the PDMS was inked with a 3.5 mg ml^{-1} solution of Rhodamin labeled poly(allylamine-hydrochloride)[34,35] by spreading it on the surfaces, incubating for 15 min and rinsing with water followed by drying in a nitrogen jet. The colloidal probe is prepared by gluing, a silica bead with epoxy to an AFM cantilever (7–28 N m^{-1}, tipless NSC 12, Micromash, Estonia). The spring constant of the contact cantilevers was determined by a method introduced by Sader.[33] With the AFM (Nanowizard 1, JPK, Germany) and its feedback controls the colloidal probe can now be pressed onto the PDMS surface with a defined load, which is recorded. A recently developed method of combining colloidal probe AFM and interferometry makes it possible to observe the contact areas while pressing the probe onto the sample (see Fig. 1 and ESI‡).[32]

As shown in Fig. 1 the contact area increases with increasing the load. The dotted line in the images shows the radius of the largest adhesion area at a maximum applied load (right) and shows the growth of the area when pressing the colloid further against the surface, thus allowing precise adjustment of the contact area. If the PDMS substrate is now coated with a suitable ink, like fluorescently-labeled polyelectrolyte as in this paper, the contact area is mapped on the colloidal probe. The ink is transferred to the contact area of the colloid, as shown in

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Preparation of probe and substrate, instrumental details, materials. See DOI: 10.1039/b708722e

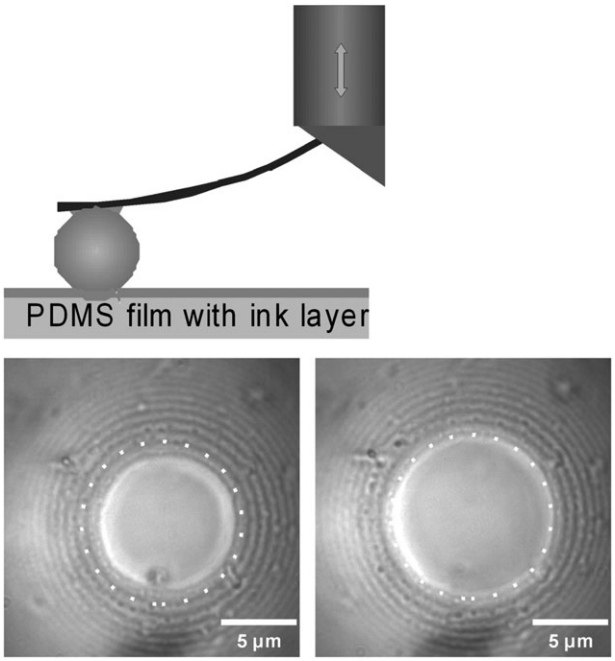

Fig. 1 Top scheme: driving the colloid on the substrate; bottom: RICM images adhesion area for different loads; left: 0.5 μN, right: 1 μN.

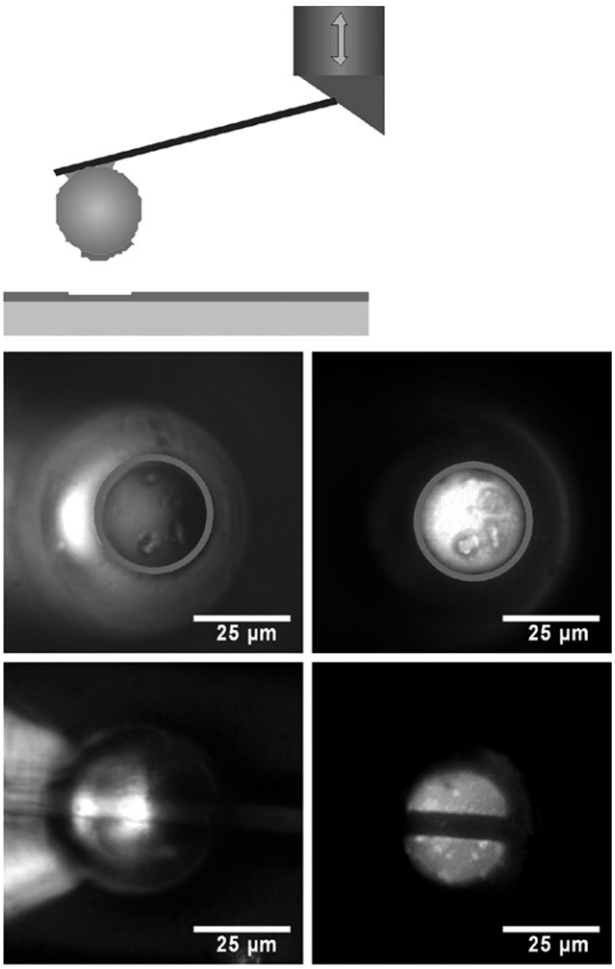

Fig. 2 Top scheme: after retraction from the surface; left: images of the colloids in reflection mode; right: fluorescence images show the contact to the substrate and the transfer of the ink to the colloid at the adhesion area, which is related to the applied load; bottom: micrograph of a colloidal probe having contact to a structured PDMS surface. A fluorescence micrograph shows the transfer of substrate's structure to the colloidal probe.

Fig. 2 (top), where the coating on the colloid is visualized using fluorescence microscopy. Comparison between the contact area and the fluorescent area on the colloid (*i.e.* the coated area) shows that both are of the same size. When applying larger loads, the coated area is increased as a result of increasing the contact area (data not shown). The coated polyectrolyte area is stable in water and can therefore be used also in liquid environment.

If a structured PDMS layer is used as an inking pad, the structure is reproduced on the colloid, as would be the case for a flat surface. This way not only homogeneous coatings of defined size can be transferred to a single colloid, also more complex structures can be imprinted on the colloid, which is to the best of our knowledge the first presentation of such colloids. For the sake of using microinterferometry for monitoring contact areas during loading, we prepared imprints on relatively large colloids (20–30 μm size). However, microinterferometry is not strictly necessary if only patterning of the colloidal particle is desired. This can be carried out without monitoring the contact areas, provided a more detailed understanding of the underlying forces is achieved. Thus the fundamental limit for the size of colloidal particles that can be imprinted, is much lower. For homogeneous spherical-cap printed areas, this limit is given by the capillary forces which cause an "offset" in the contact area, thus limiting the smallest size printable for a given particle. For patterned contact areas, the pattern of the PDMS structure used as stamp pad is limiting. PDMS structures can however be produced with submicron dimensions,[40] such that micron-sized colloids should be possible to pattern. To measure the forces acting between the colloidal probe and the PDMS the deflection of the cantilever was measured and converted in the applied load, while the contact radius of the colloid was measured using RICM. This was done for different samples: untreated PDMS, plasma cleaned PDMS. All experiments were performed in air and water. The adhesion area and the respective force were plotted and compared with the Johnson–Kendall–Roberts (JKR) theory[36] (see Fig. 1). The experiments performed in water fit the JKR predictions and result in adhesion energies of $(1.6 \pm 0.1)^{-15}$ J. However, the experiments performed in air, which are more relevant as a model of microcontact printing, did not fit the JKR predictions. This is due to the fact that capillary forces play an important role in this case, whereas capillarity is switched off for data collected in water. The result is an additional capillary contribution to the applied load in air. Hence, over the whole range of applied loads, the adhesion area in air is larger than in water (see Fig. 3). Capillary forces are not included in the JKR model as they depend on the indentation depth of the particle into the PDMS substrate.[37,38] The capillary force (F_{Orr}) between a colloid and flat substrates was described theoretically by Orr.[39] It depends on the contact angles of PDMS (θ_{PDMS}) and the colloid (θ_{coll})

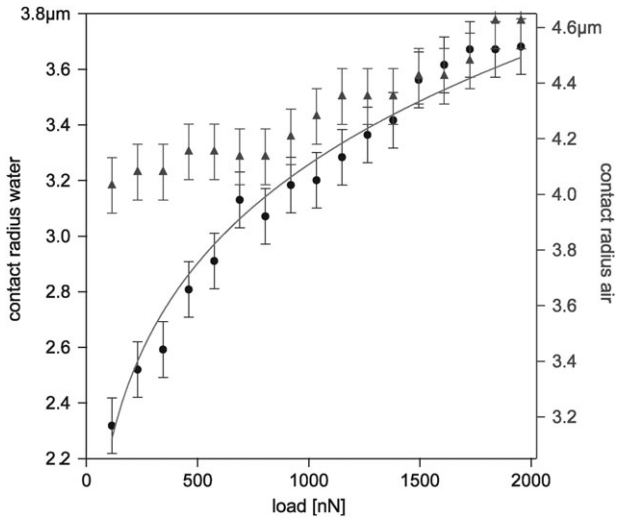

Fig. 3 The load/adhesion behaviour and the JKR fit (line) of the colloidal probe on polyelectrolyte inked PDMS in water (circles) and in air (triangles). The error bars were estimated from the profile pots of the interference pattern (see Fig. 1).

with water and the water surface tension (γ) as well as on the radius of the colloid (R).

$$F_{\mathrm{Orr}} = 2\pi\gamma R(\cos\theta_{\mathrm{coll}} + \cos\theta_{\mathrm{PDMS}})$$

We calculated the resulting force for different contact angles, 5° for the colloid and 30° (plasma cleaned) and 110° (untreated) PDMS, which results in a capillary force of 4.1 µN and 10.2 µN for untreated and plasma cleaned PDMS, respectively. These values are in good agreement with those determined by analyzing the peel-off forces in the AFM experiment [3.4 µN (untreated) and 10 µN (plasma cleaned)]. Due to the dependence of the capillary force on the indentation into the deformable substrate the contact area resulting from these forces could not be calculated as not all parameters of the theory could be determined in the experiment. At large loads the "capillary offset" becomes negligible and the experiment in air approaches the JKR prediction.

In summary, we could show that it is possible to selectively coat single colloidal particles using a microcontact printing approach. This was possible using a colloidal probe AFM on a deformable PDMS substrate with a polyelectrolyte layer as "ink". The combination of the AFM technique with microinterferometry allowed us to simultaneously vary the load and record the contact area between probe and surface. The forces acting in the printing process are driven in the dry state mainly by capillarity, which depends on the contact angle of substrate and colloid, respectively. The JKR theory can describe the contact force/adhesion area behaving only in water, as the capillary forces in the dry state depend on the substrate's deformation, which is not included in the JKR model. The contact area and the imprint could be compared and were of same size. Not only homogeneous coatings of defined sizes can thus be generated, also structures from the substrate can be reproduced on the colloid.

We would like to acknowledge fruitful discussions with Helmuth Möhwald and funding from the European Community STREP project "Active Biomimetic Systems" within the 6th Framework Programme as well as from the Fraunhofer/MPG cooperative project "Bioactive Surfaces".

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