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Defined Transfer of Colloidal Particles by Electrochemical Microcontact Printing

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Soft lithography, in particular microcontact printing (µCP), represents a well-established and widespread class of lithographic patterning techniques. It is based on a directed deposition of molecules or colloidal particles by a transfer process with a micro-structured stamp. A critical aspect of µCP is the adhesion cascade that enables the directed transfer of the objects. Here, the interfacial properties of a µCP-stamp are tuned electrochemically to modify the adhesion cascade. During the printing process, the µCP-stamp is submerged in an electrolyte solution and acted as a working electrode whose surface properties depended on the externally applied potential, thus enabling in situ rapid switching of its adhesion properties. As a proof of principle, defined particle patterns are selectively removed from a monolayer of colloidal particles. The adhesion at the particle/solid interface and the transfer mechanisms are determined by using the colloidal probe technique based on atomic force microscopy (AFM). In this case, a single particle is brought into contact with an electrode with the same surface chemistry as the µCP-stamp. Hence, it became possible to determine the electrochemical potential ranges suitable to establish an adhesion cascade.

1. Introduction

Various techniques for patterning on the micro- and nanometer scale have been introduced in the last quarter-century.[1,2] Among these, microcontact printing (µCP), or generally soft lithography, is the most versatile approach to laterally pattern the surface of a sample.[3–5] Soft lithography requires only modest instrumentation and has found widespread applications in many different fields, such as microelectronics or optical components.[6] A further advantage of µCP is that it can be easily scaled up to produce surface structures on the centimeter scale.[3–5]

The basic principle of µCP relies on the contact-transfer of molecules or colloidal material between two surfaces. This transfer is enabled using an elastic stamp, which is structured in such a way that the deposition can be carried out in a laterally defined pattern. The µCP-technique has been first presented for the deposition of thiols on gold surfaces in well-defined patterns.[7] However, the contact transfer approach is not limited to low molecular weight molecules that form self-assembled monolayers (SAMs), such as thiols and silanes. Besides macromolecules, such as proteins[8] or polyelectrolytes,[9] also colloids have been transferred by elastomeric stamps.[10–12] The lateral resolution of µCP can be significantly improved by replacing commercial poly(dimethylsiloxane) (PDMS) as elastomeric material for the stamp with harder, less deformable materials. This approach enabled the preparation of lateral structures smaller than 100 nm by µCP.[13] However, to obtain such high resolution by the µCP-process, various conditions have to be kept under control, such as preventing the gas phase transfer of molecules or mechanical instabilities of the stamp.[14,15] The former effect can be overcome, for example, by selectively "inking" the stamp with an "inkpad".[16,17]

Soft-lithography with colloidal particles has been reported previously by various groups.[18,19] The preparation of defined colloidal assemblies on flat substrates has received increased interest due to the advent of plasmonic structures.[20–24] In this respect, µCP has proven to be a versatile technique that allows for preparing suitable structures.[25] In 2005, Kraus et al. demonstrated that an adhesion cascade could be used to transfer particles from an original template via a soft stamp to a target substrate.[11] Later, Rogers and coworkers have presented a landmark approach: By tuning the contact time and the velocity with which the elastomeric stamp is removed from the sample, one can achieve precise control of the transferred particles between

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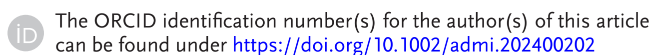
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substrate and stamp and thus on the overall μCP-process.[26] Common to all these methods is the adhesion cascade with increasing "critical" forces required to remove a particle from a given surface for each transfer step until this force reaches its maximum on the final target surface. This approach of controlling the adhesion with the stamp has been extended by various groups.[27,28] In particular switchable adhesives provide an elegant route to control the transfer process in μCP.[29] Applications of tunable transfer in μCP included flexible electronics, photovoltaics, sensors, displays and patterns of nanoparticles.[27,30–33] A table summarizing techniques used for the selective transfer of colloidal particles has been compiled in the supporting information (Table S1, Supporting Information.)

We present a novel approach based on electrochemical techniques that allows for a defined control over the interaction forces at the stamp's interface, enabling manipulation of the "critical" forces in the adhesion cascade. This approach represents a novel alternative to the aforementioned dynamic approach[26,34] or irreversible changes of the stamp's surface chemistry.[35,36] Remarkably, the idea of tuning the interaction forces for μCP-printing in situ by electrochemical techniques has not received much or any attention so far. This omission can probably be attributed to the fact that the surface chemistry of PDMS can be altered more easily in a permanent manner, e.g., by plasma exposure or treatment with solvents.[36] However, the defined, and reversible, tuning of surface forces for colloidal particles has been reported for electrodes under potentiostatic control.[37–40] The influence of surface roughness, interfacial energy, and electrowetting on the total adhesion force have been previously examined in detail for surface-modified gold electrodes.[39]

Here, we used PDMS stamps that have been modified in such a way that they can act as an electrode. Colloidal particles were assembled as a hexagonally-ordered layer on glass slides.[41] These electrodes were coated in the same way as the PDMS stamps, namely by a gold (Au) layer and an hydroxyl-terminated (OH-terminated) SAM from thiols. An OH-terminated SAM was present on both the substrate and the stamp in order to ensure identical chemical adhesion properties. Thereby electrostatic contributions were the only contribution varied for particle transfer by the stamp.[39] However, a recent study based solely on direct force measurements by AFM demonstrates that particles can also be transferred for asymmetric surface compositions.[42] The electrostatic component of the surface forces can be tuned in a defined manner by applying an external potential, as demonstrated by direct force measurements with colloidal probes from silica particles.[39] While the application of external potentials to Au-modified PDMS-stamps has been reported before, such conductive stamps have been primarily used for contact charging of oxides in air.[43] In comparison, the potentials applied in the here-presented series of experiments are much smaller. Furthermore, the experiments were not conducted under ambient conditions but in a 3-electrode electrochemical cell filled with electrolyte solution.

2. Results and Discussion

In this study, we combined microcontact printing (μCP) with electrochemistry to achieve a well-defined, in situ tuning of the adhesion between colloidal particles and the μCP-stamp. The latter acted as a working electrode immersed in an electrolyte solution. As first proof of principle, we demonstrated the selective removal of silica nanoparticles from a substrate. In contrast to previously reported approaches,[26,34] the removal is controlled externally by a potential applied to the μCP-stamp. Hydrophilic silica particles with a diameter of 180 nm were deposited onto glass or silicon surfaces in highly ordered structures by means of capillary forces.[19,41] **Figure 1** illustrates the basic components of electrochemically-enhanced microcontact printing as developed in this study: A PDMS stamp is rendered conductive by evaporating a thin gold layer onto the stamp as shown schematically in Figure 1a (cf. Figure 1b for a corresponding SEM image). Using an external potentiostat, the surface potential of the stamp, which is immersed in an electrolyte solution, can be controlled. This approach allowed for the selective removal of silica particles, that have been beforehand deposited as monolayer on a solid substrate. Figure 1c,d shows a schematic representation and a typical SEM image, respectively, of such an initial particle layer that completely covered the sample surface. The local structure observed is comparable to the one obtained on other surfaces such as silicon or glass.[19,41]

A quantitative assessment of the silica's adhesive behavior on the OH-terminated SAMs is an important prerequisite for selective removal of the colloidal silica particles by the stamp. In order to determine the potentials at which the adhesion on an OH-modified electrode is switching from strongly adhesive to non-sticking behavior, we performed direct force measurements by the colloidal probe technique. By attaching colloidal silica particles with a diameter of several μm to the end of an AFM cantilever, quantitative measurements in a defined interaction geometry could be performed. This approach allows electrochemical (EC) μCP to be directly related to previous studies on the adhesion of colloidal silica particles by direct force measurements.[39,40]

2.1. Tuning the Adhesion of Colloidal Particles by External Potentials

Stöber-type silica particles comparable to the ones in the particle layers on the substrate (cf. Figure 1c,d) have been used to prepare colloidal probes, albeit with a much larger diameter of 6.8 μm. The determination of the adhesion forces under potentiostatic control has been carried out in a purposely constructed electrochemical cell, which has been incorporated into a dedicated AFM setup.[44] Here, the OH-terminated SAM acted as the working electrode in a 3-electrode electrochemical cell filled with an electrolyte solution, and its potential could be varied by means of a potentiostat. A schematic representation is given in **Figure 2a**.

Figure 2b,c shows exemplary interaction force profiles for three different external potentials ϕ that have been applied to the SAM-modified electrode. For the lowest potential $\phi_0 = -226$ mV (vs a saturated calomel electrode, SCE), the interaction was completely repulsive over the full interaction range. No adhesion between the colloidal particle and the substrate could be observed (cf. Figure 2b). By contrast, the interaction was fully attractive at larger applied potentials, i.e., $\phi_1 = -26$ mV and $\phi_2 = +474$ mV, respectively (cf. Figure 2c). Hence, an adhesive force was observed that always became more attractive with increasing potential (Figure 2c). Here, the forces have been

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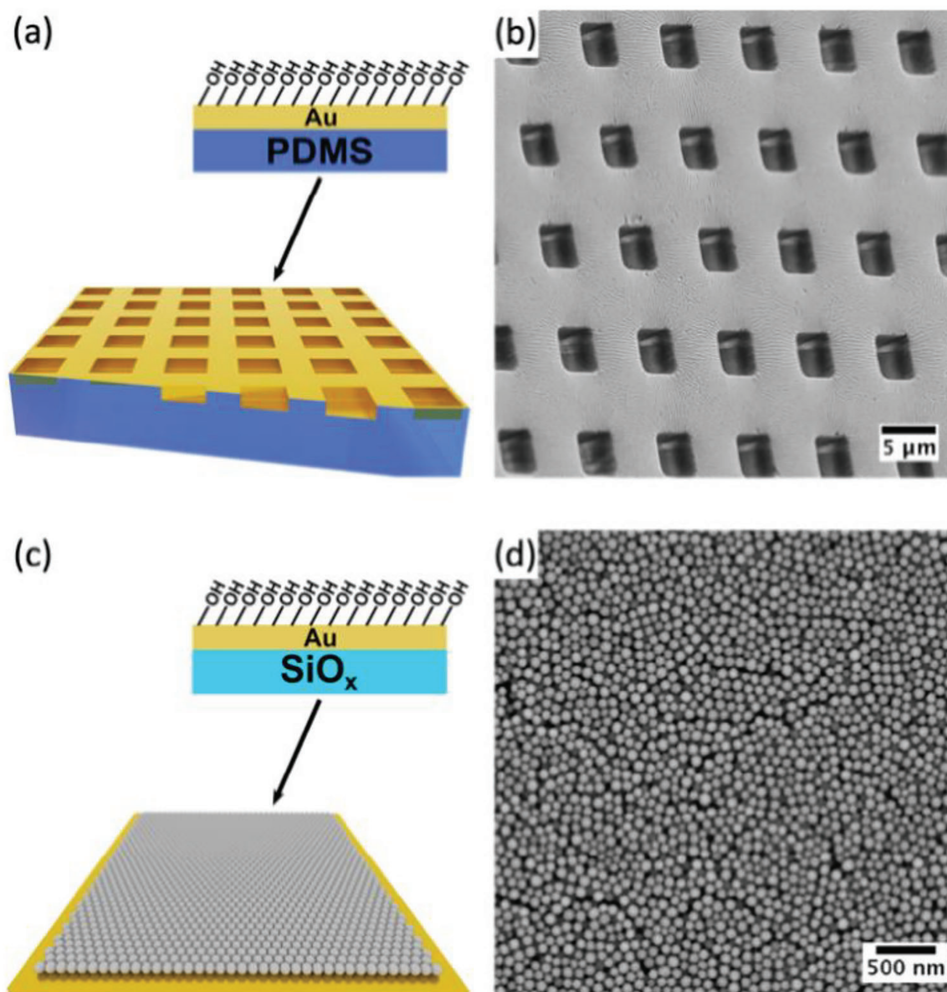

Figure 1. a) Schematic representation of a PDMS stamp rendered conductive by evaporating a 60 nm thick layer of gold onto its surface. This Au-coated stamp has been modified by an OH-terminated thiol SAM as shown in the inset. b) SEM-image of OH-modified Au-PDMS stamp. c) Schematic representation of the substrate from which 180 nm-sized silica particles have been taken up with the potentiostatically-controlled µCP-stamp. A glass slide has been coated with a 20 nm-thick gold layer modified by an OH-terminated SAM followed by the deposition of densely packed layers of silica particles via convective assembly. d) SEM image of a layer of colloidal silica particles on an Au-coated glass substrate modified by OH-terminated SAM.

normalized to the effective radius in agreement with the Derjaguin approximation for the sphere/plane interaction upon approach[40,45] and Johnson-Kendall-Roberts (JKR) as well as Derjaguin-Muller-Toporov (DMT) theory for the adhesion upon retraction.[39,45] In the case the of sphere/plane interaction the effective radius corresponds to the particle radius of the colloidal probe particle, which has been determined independently by the SEM. In addition to the forces measured at externally applied potentials, open-circuit conditions were investigated, too. Figure 2d shows the corresponding interaction force profile. The results indicate the "inherent" adhesion of the silica particles on the semi-transparent substrate that has not been connected to a potentiostat. In Figure 2e, the corresponding distributions for the normalized pull-off forces $F_{adh}(\phi)$ have been summarized for a series of ≈100 force curves for various potentials, namely $\phi_1 = -26$ mV, $\phi_2 = +474$ mV, and open circuit conditions (OCP). The applied potentials ϕ_1 and ϕ_2 lead to adhesion forces $F_{adh}(\phi_1)$ and $F_{adh}(\phi_2)$ that are significantly smaller and larger, respectively, than the ones for open circuit conditions (i.e., $F_{adh}(\phi_0) < F_{adh}(\phi_1) < F_{adh}(\mathrm{OCP}) < F_{adh}(\phi_2)$). The adhesion forces could be tuned almost linearly with the applied potential as previously observed (Figure 2f).[39] Hence, an adhesion cascade could be established where external potentials allow to tune the interaction forces between the silica particles and a substrate larger and smaller. This difference in adhesion is utilized in the following for tuning the transfer of colloidal silica particles during µCP. A similar approach has been followed in order to implement electrochemical grippers.[42]

2.2. The Basic Principle of Electrochemical µCP

"Conventional" µCP comprises two central steps:[3–5] First, the stamp is moistened or "inked" with a solution containing the colloidal objects (i.e., particles, molecules, or proteins) that are going to be transferred and that remain at the surface or diffuse into the

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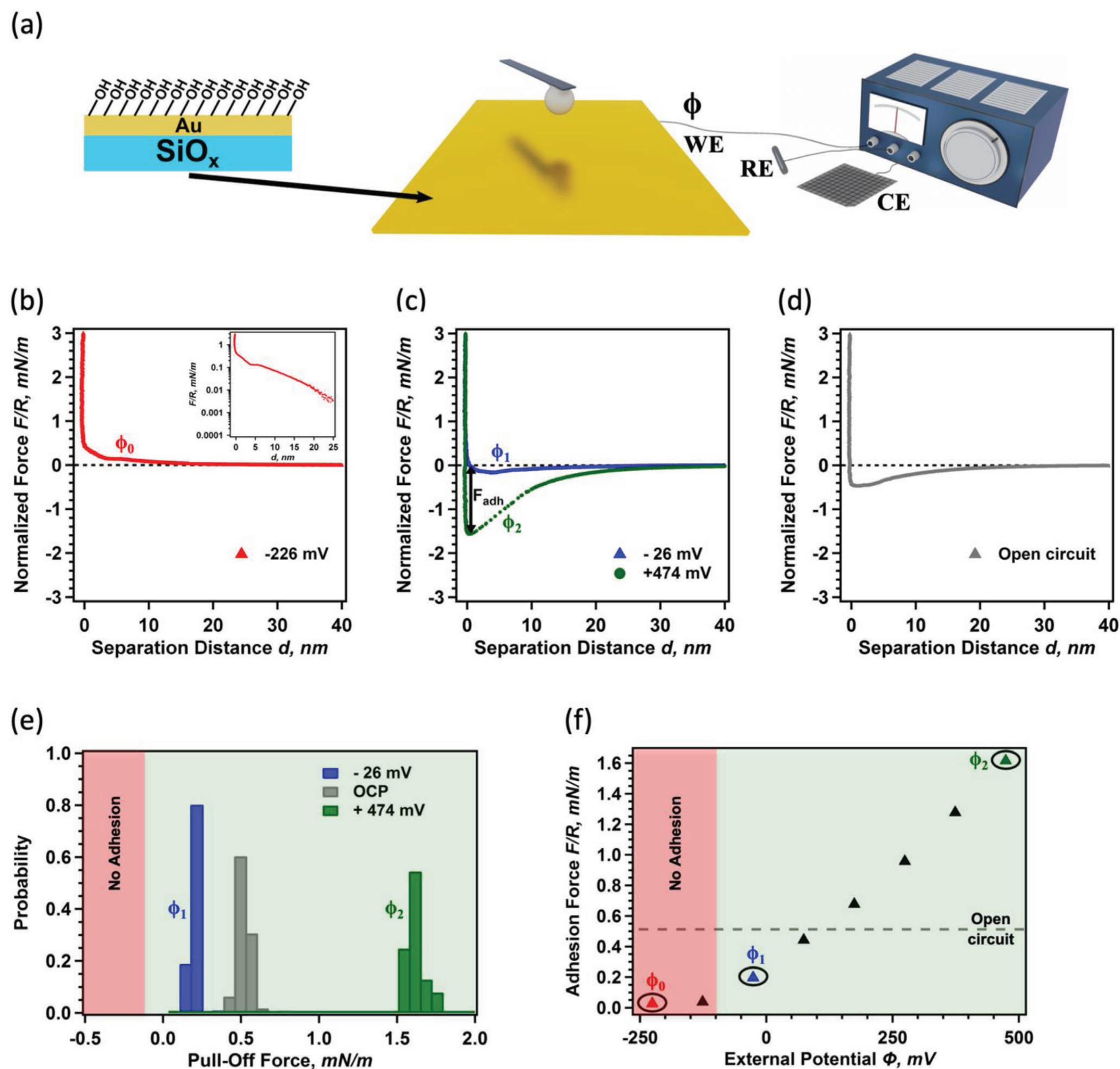

Figure 2. a) Schematic representation of the setup. The Au-substrate modified by an OH-terminated SAM is the working electrode in a 3-electrode electrochemical cell, and its potential can be varied using a potentiostat. b) Exemplary averaged interaction force profiles upon retraction for an applied potential of -226 mV and c) for applied potentials of -26 mV and +474 mV (vs SCE). d) Exemplary averaged interaction force profile upon retraction under open circuit conditions. e) Distributions of the pull-off forces for a series of ≈100 force curves for each potential. f) Pull-off force versus externally applied potential ϕ and the pull-off force under open-circuit conditions (dashed line).

PDMS of the stamp.[16,17] Second, the actual transfer takes place by pressing the moistened stamp onto the target surface and releasing it after a defined time. Here, we will focus on how the "*taking-up*" and "*lifting-off*" of colloidal objects can be rendered more selective by electrochemically controlling the stamp's interfacial properties. Similar approaches have been presented in the past, albeit not under electrochemical control.[26,34,46]

Figure 3 illustrates how the principle of selective "*lifting-off*" by an electrochemical control of the μCP-stamp can be implemented: Instead of moistening the stamp, pre-adsorbed particles are removed from an ordered layer as shown in Figure 1c. The μCP-stamp acts as an electrode with an externally controlled potential during this process, which takes place in an electrolyte solution (cf. Figure 1a). Depending on the applied potential, two different cases can be distinguished. If the potential leads to stronger particle adhesion on the stamp than to the substrate, it results in the "*lifting-off*" of particles from the substrate. In the following this potential is denoted as ϕ_1. If the applied

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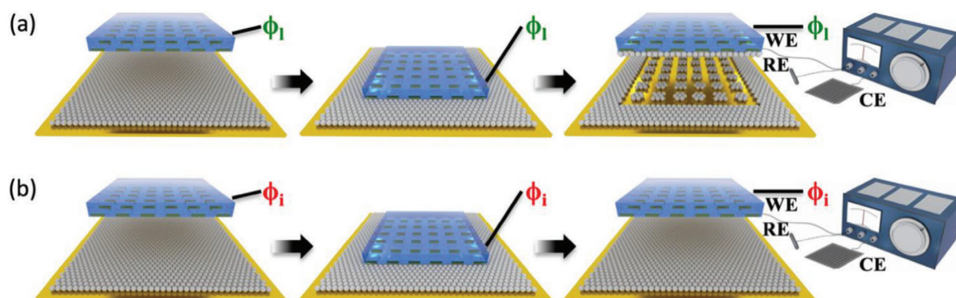

Figure 3. a) Schematic representation of the controlled lifting of colloidal particles from a monolayer by electrochemical control. The potential ϕ_l applied to the stamp leads to adhesion forces of the particles that are larger for the particle/stamp combination than for the particle/substrate combination. b) By contrast, the potential ϕ_i applied to the stamp leads to larger particle adhesion to the substrate. Thus, no particles can be lifted by the stamp.

potential makes the stamp inert toward particle adhesion, no or only a negligible number of particles are removed from the substrate. Analogously, we refer to a corresponding potential as ϕ_i. The choice of these potentials is motivated by the direct force measurements described in the previous paragraph. Both cases are schematically depicted in Figure 3. Due to the linear dependence of the adhesion on particle radius according to DMT and JKR theory, the results obtained by the chemically analog particles are comparable for µm- and nm-sized silica particles.

Here, we consider only the case of potential-induced *particle removal* by the stamp acting as electrode. The adhesion force depends on the applied potential ϕ and can be tuned from repulsive interaction, i.e., no adhesion, to a strong normalized adhesion force of 1.6 mN m^{-1}. The adhesion force $F_{adh}(\phi)/R$ dependence on the potential is approximately linear (Figure 2e,f).[39] When an external potential $\phi \geq 100$ mV (vs SCE), which corresponds to the potential at which the same adhesion as for OCP has been observed, is applied to the stamp, the adhesion between the silica particles and the stamp will be larger than between silica particles and substrate (cf. Figure 2e,f). Therefore, the particles stick to the stamp and are removed from the substrates, leading to a pattern depicted in Figure 3a. By contrast, for potentials $\phi < 100$ mV, the adhesion between silica particle and stamp is strongly reduced by the repulsive diffuse layer repulsion, and the particles remain on the substrates (cf. Figure 2b). Hence, no particle transfer occurs, as depicted schematically in Figure 3b.

2.3. Potentiostatic Control of a µCP-Stamp

The basic idea of a selective µCP-process based on tuning adhesion forces by electrochemical control has been presented in the previous paragraph. In the following experiments, we used a gold-coated, patterned PDMS-stamp as the working electrode connected to the potentiostat. Figure 1a schematically depicts the stamps used in this study: Conventional PDMS stamps were formed from a master, with a pattern of quadratic 5 µm-sized squares with a spacing of 5 µm. The resulting PDMS-stamps were rendered conductive by evaporating a 60 nm Au-layer that was subsequently modified by a SAM of OH-terminated thiols. A thin, PTFE-insulated Ag-wire connects the Au-coated stamp and the potentiostat. Figure 1b shows an SEM image of a typical stamp used in our experiments.

The substrates from which the colloidal particles were later removed had been prepared beforehand by convective particle assembly on the surface of semi-transparent, SAM-modified gold-coated coverslips.[41] Figure 1d shows a SEM-image of a typical layer of silica particles on such a substrate. The colloidal silica particles used here had a diameter of 180 nm and could be clearly resolved by SEM. The resulting particle film shows only partly hexagonal order (cf. in Figure S2, Supporting Information). The stamps were mounted on a holder that sits on an inverted optical microscope and allowed for tilt correction between stamp and substrate. Upon immersion in the electrolyte solution, the stamps were carefully approached via a micrometer screw to a semi-transparent substrate (cf. in Figure S1, Supporting Information). The contact between the stamp and a semi-transparent surface could be observed by optical microscopy through the semi-transparent substrate in order to align both surfaces for symmetric contact. This process was carried out in the electrochemical cell under electrochemical control, where a preselected potential ϕ remained constant during the process.

2.4. Selective Removal of Colloidal Particles by Electrochemical µCP

Figure 4 summarizes how particles can be removed from selected areas as a function of the externally applied potential. Figure 4a shows a substrate after a stamp has been brought into contact under an external potential $\phi_l = -35$ mV and has been subsequently removed. The time of contact was ≈10 s. It should be pointed out that this potential is significantly smaller than the + 100 mV at the intersection with the adhesion under OCP. At this potential only a small adhesion has been observed (cf. Figure 2c, $\phi_1 = -26$ mV), which was smaller than the one observed for the OCP (cf. Figure 2d). However, we assume that the difference in the elastic behavior between the Au-electrodes on a soft PDMS stamp and the hard glass surface plays an important role. It has been reported that tuning of the elastic properties of the stamp provides also an approach to tune the adhesion cascade for particle transfer.[47,48]

The selective removal of silica nanoparticles can be visualized using optical dark-field microscopy and SEM. Prior to image acquisition, the substrates were dried by a gentle stream of nitrogen. These imaging techniques demonstrate particle removal on the level of several hundreds of µm (Figure 4a). Additionally, AFM

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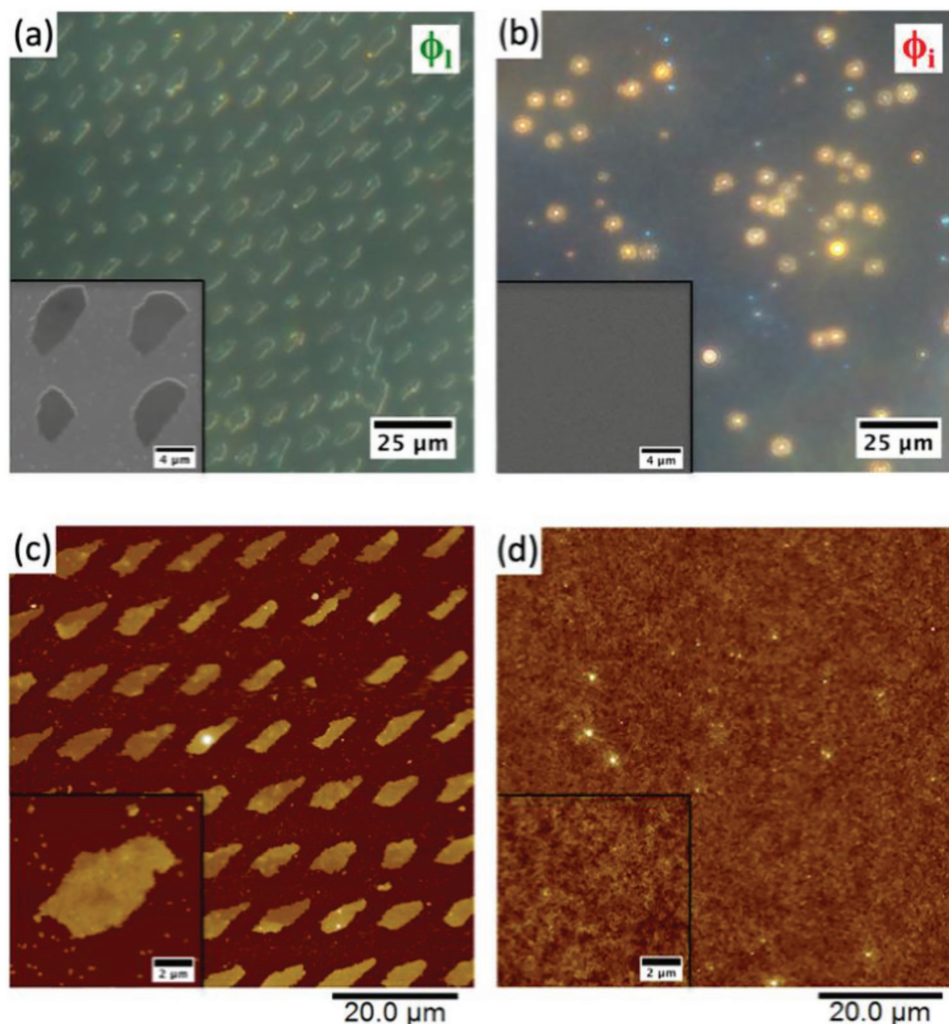

Figure 4. a) Dark-field microscopy image with SEM-inset of the substrate after removing particles by electrochemical µCP applying a stamp potential $\phi_l = -35$ mV. b) Dark-field microscopy image with SEM-inset of the substrate showing the particle layer remaining on the surface after stamp contact with a stamp potential $\phi_i = -535$ mV. c) AFM image of the substrate shown in (a). d) AFM image of the substrate shown in (b).

images confirm the successful patterning down to the level of single particles. They show that the substrate is practically particle-free in the area where the stamp has been in contact with the particle layer (Figure 4c). These findings obtained by imaging techniques are in line with the direct force measurements summarized in Figure 2. At these potentials, the adhesion between the silica particles and an OH-modified gold electrode has been clearly detectable (cf. Figure 2c). However, it should be pointed out that due to the different elastic behavior of the PDMS, and the increased pressure when bringing the stamp into contact with the particle layer, the direct force measurements cannot be directly compared to the µCP experiments. Nevertheless, the former provide a good base to determine the influence of the potential on the overall adhesion forces and thus the likelihood of a transfer. The film structure of the particles remaining on the substrate after removal of the stamp is not significantly altered (cf. in Figure S2, Supporting Information).

Increasing the stamp potential to $\phi_h = +465$ mV also led to the removal of colloids from the particle layer (cf. in Figure S1c,d, Supporting Information). However, at such high external potential, the specificity of the process was significantly reduced. We attribute this behavior to the stronger electrostatic forces acting at higher electrode potentials. Hence, applying the higher potential ϕ_h led to the removal of much more particles from the substrate, and discontinuities in the particle pattern were apparent (cf. Figure S1c,d, Supporting Information).

By contrast, applying very negative potentials to the stamp, such as $\phi_i = -535$ mV, prevented any particle transfer due to highly repulsive interaction forces, which have already been observed in the direct force measurements (cf. Figure 2b). Figure 4b shows the substrate after applying the potential ϕ_i to the stamp. Dark-field microscopy and SEM confirm that no removal of the particles by the stamp has taken place and that the particle monolayer remains unchanged. Hence, no structures on the µm-scale could be observed. AFM images of the same substrate corroborate this result also for smaller length scales (cf. Figure 4d).

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2.5. Limits and Generalization of Electrochemical μCP

The electrochemical μCP-transfer did not lead to perfect structures on the particle-coated substrate (cf. Figure 4a,c). The particle free-zones on the substrate did not have the aspect ratio 1 of the perfect squares on the μCP-stamp. We attribute this defect to experimental restrictions related primarily to the modified PDMS-stamp: Evaporating gold on a PDMS structure results in material layers with two very different elastic moduli. Upon contact with the substrate, cracks are forming, and buckling at the borders of the square-like structures occurs. The formation of cracks in the rigid gold layer on the highly elastic PDMS stamp is likely to impair the particle transfer. Moreover, the rigid layer prevents homogeneous contact between stamp and substrate and is probably responsible for the observed deviations from square-like structures. These limitations could be overcome by incorporating a gradient in the elastic moduli as proposed previously.[49] Furthermore, a stretchable, conductive layer, as shown by Kotov et al.,[50] or the use of an additive to render the PDMS conductive, would allow to reduce the thickness of the gold layer and enable a better electrical contact for the stamp.

A slight tilt of the stamp during substrate contact might contribute additionally to the asymmetric removal of particles by the resulting lateral deformation of the stamp. Therefore, the pattern of the particles remaining on the substrate was distorted in the direction of the stamp deformation. In order to avoid this deformation it would be required to ensure a parallel alignment of the stamp in respect to the substrate.

It is important to highlight that the presented approach is not limited to silica particles but can be applied to many different types of colloids, such as latex particles or other inorganic particles. Furthermore, our approach would be most likely suitable for the transfer of particles with anisotropic shape.[51,52] However, it should be noted that modifications induced during these processes can make it challenging to remove particles after treatment due to increased adhesion to the substrate.[51] Recently, it has been demonstrated that particle transfer only requires one conductive surface as an electrode.[42] Hence, electrochemical μCP with a conductive stamp alone would allow also for transfer particles from dielectric substrates, such as SiO_x.

Moreover, the principle of electrochemical μCP is not limited to colloidal particles: Just as "conventional" μCP allows for the transfer of macromolecules,[8,9] such a transfer should also be possible by electrochemical μCP. For example, the potential-dependent adhesion of DNA and polymers, respectively, has been demonstrated.[53,54] Hence, the principle is not limited to μm-to nm-sized colloidal particles but could also be used for biosystems, e.g., in the framework of sensors, hybrid-plasmonic or soft electronic systems.[27]

Direct force measurements on modified electrodes under potentiostatic control demonstrated that solvent exclusion and electrostatic Derjaguin-Landau-Verwey-Overbeek (DLVO)-forces are dominating the adhesion, where only the latter depend on the externally applied potential, while electrowetting can be neglected. However, the surface roughness of electrode and particles also plays a crucial role and determines how far the externally applied potential ϕ can tune the overall interaction force.[39,40] Solvent exclusion represents in this respect a kind of offset for adhesion forces and thus allows to "match" the adhesion between substrate and stamp. By tuning surface roughness and chemical modification of both surfaces (i.e., stamp and substrate), the preferential adhesion to both surfaces can be adjusted separately. Hence, a tunable transfer between the surfaces can be achieved depending on the electrostatic force component, which is varied by the applied potential. The interdependence of the parameters can be determined, if necessary, by direct force measurements. Therefore, electrochemical μCP represents a more universal approach than "conventional" μCP.

3. Conclusion

Active adhesion control, as demonstrated here, is a valuable extension to soft lithography with wide-ranging possible applications. By tuning in situ the interfacial properties of the μCP-stamp, a highly selective lifting-off and placement procedure can be developed for various systems. In our opinion, the advantages of this technique are not limited to the lifting-off step of the μCP-process. The technique can also be used to transfer particle layers to different positions or substrates, respectively. Direct technical applications could include, for example, the development of a placement procedure for the contact stamp where a stamp misalignment does not automatically lead to contamination of the stamp. Contamination could be prevented, for example, by switching the stamp to repulsive interaction by applying a suitable potential. This procedure could be especially powerful combined with automatic pressurized systems[55] and roll-to-roll processes based on μCP.[56,57]

The presented extension of the μCP-technique should be specifically suitable for preparing mesostructures on multiple length scales up to the mm-scale. The technique might be particularly well suited for the preparation of plasmonic structures.[23,24] A significant advantage is that the process can be carried out entirely under aqueous conditions. Future applications of electrochemical μCP could cover more elaborate procedures such as in situ cleaning by applying a suitable potential.

4. Experimental Section

All chemicals were obtained in analytical grade quality (VWR, Germany) and used without purification unless explicitly noted.

Preparation of Semi-Transparent Substrates Coated by Self-Assembled Monolayers: Glass coverslips (35 mm diameter) were cleaned using a modified RCA-cleaning procedure.[58] Coverslips were sonicated in a mixture of isopropanol and Milli-Q water (v/v = 3:1) before treatment with a mixture of Milli-Q water, ammonia, and hydrogen peroxide (v/v/v = 5:1:1) for 20 min at 80 °C. Between these steps, the substrates have been rinsed with Milli-Q water. Afterwards, a semi-transparent gold film was deposited on the glass substrates by thermal evaporation of 2 nm of chromium (Oerlikon Balzers, Liechtenstein) and 20 nm of gold (Agosi, Germany). The substrates were immersed in a solution of 2 mM 16-mercaptohexadecan-1-ol (Purity 99%, Frontier Scientific, USA) in ethanol overnight. After rinsing with ethanol and MilliQ water, the substrates were dried in a stream of nitrogen. Subsequently, these substrates were used for the deposition of particle layers.

Deposition of Colloidal Particles on Flat Substrates: Ordered layers of silica particles with a mean diameter of 180 nm (Bang's Laboratories, USA) were deposited on the gold-coated coverslips by convective assembly using a home-built setup similar to one reported previously.[19]

Preparation of Modified μCP-Stamps: The poly(dimethylsiloxane) (PDMS) for the modified PDMS-stamps was prepared by mixing 10 parts

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of pre-polymer with 1 part of curing agent (Sylgard 184, Dow Corning, USA). The mixture was filled into a clean and plane polystyrene box, which contained "master structures" with a 5 µm square pattern spaced by 5 µm etched into silicon (GeSiM, Germany). M2 PEEK screws (CHEMIS Nippon Chemical Screw, Japan) with a length of 8 mm were embedded in the PDMS on the reverse side of the stamps to allow for later fixation of the PDMS-stamps on a holder (cf. following paragraph on µCP). After pre-polymerization at room temperature overnight, the PDMS was cured at 80 °C for 5 h. The PDMS was then peeled from the masters and cut into size, leaving one inclined edge for posterior electrical connections. A conductive Au-layer was deposited on the stamps by thermal evaporation of 2 nm chromium and 60 nm gold. Afterward, a 0.125 mm diameter PTFE-insulated Ag-wire (Goodfellow, UK) was attached to the inclined edge with silver paint (G 3692, Plano, Germany). This connection was sealed with Norland Optical Adhesive 63 (Norland Products, USA). The Au-coated stamp was modified with an OH-terminated thiol SAM by immersing the stamp overnight in 2 mm 16-mercaptohexadecan-1-ol (Purity 99%, Frontier Scientific, USA) in ethanol. After rinsing with ethanol and MilliQ water, the stamps were dried in a nitrogen stream and directly mounted on the electrochemical µCP setup.

Direct force measurements by AFM: The direct force measurements under electrochemical control were performed according to procedures previously reported.[39,40] In brief, the colloidal probes were prepared from 6.8 µm diameter silica particles using a sintering procedure where the particles were directly attached to the cantilever without any additional glue.[59] Gold surfaces with a low roughness were prepared by the "template stripping" method.[39,60] Surface modification with 16-mercaptohexadecan-1-ol (Frontier Scientific, USA) was carried out analogously to the substrates for particle deposition (see above).

The direct force measurements in 1 mM KCl, pH 4.7 solution were performed with a dedicated AFM setup (MFP-3D, Asylum Research, USA) combined with a homemade potentiostat. A series of at least 100 approach and retraction cycles at ≈0.8 µm s^{-1} were acquired for each applied potential. No significant differences between the first and last curves could be observed for the force profiles of one series. The curves were analyzed in terms of the adhesion forces by a custom-written set of procedures in IGOR-PRO (Wavemetrics, USA). Further details were given before.[39,40]

Electrochemical µCP: For the electrochemical µCP process, a custom-built setup was used; details are shown in the supporting information (cf. Figure S1a, Supporting Information). The setup consisted of the following parts: i) A carrier arm featuring an x-y-z translation stage with micrometer screws and a two-axis tilt platform. This arm was attached to an inverted light microscope (Axiovert 200 from Zeiss, Germany). The PDMS stamp for electrical µCP was mounted by its embedded M2-8 PEEK screw to a threaded PEEK bar, clamped in a bar-type lens holder connected to the two-axis tilt platform. This setup allowed for defined movements of the stamp in x-, y-, z-direction, and tilt correction with micrometer precision. The semi-transparent gold substrates allowed for in situ observation of the contact between the stamp and the substrate carrying the particle layer by inverted optical microscopy.

The 3-electrode electrochemical cell for the transfer experiments (cf., Figure S1b, Supporting Information) consisted of a silver/silver chloride reference electrode (DRIREF-L 87 947, World Precision Instruments, USA), the SAM-modified µCP stamp as the working electrode, and a platinum-mesh (Goodfellow, UK) acting as the counter electrode. The electrochemical cell was filled with a 1 mm KCl, pH 4.7 solution, analogously to the electrolyte solution used for the direct force measurements. The potential difference (−35 mV) between the silver/silver chloride electrode used for the experiments and a saturated calomel reference electrode (ALS 0 02056 RE-2B, BASi, USA) was measured in 3 m KCl solution with a Keithley 6514 System Electrometer (Keithley Instruments, USA). For µCP under electrochemical control, constant potentials were applied to the µCP-stamp using a potentiostat (ZENNIUM Electrochemical Workstation, ZAHNER-Elektrik, Germany).

Characterization of Particle Layers on Solid Substrates: Prior to image acquisition, the substrates were dried in a gentle stream of nitrogen. Dark-field microscopy images of the structured silica particle layers were acquired using an Eclipse Ti-U microscope (Nikon, Japan). Scanning electron microscopy (SEM) images were obtained with an FEI Quanta 400F scanning electron microscope (FEI, USA). AFM images were acquired by tapping mode in air with a dedicated AFM (Dimension Icon with a Nanoscope V controller, Bruker, USA) and standard tapping cantilevers (AC160TS-R3, Olympus, Germany).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

colloidal adhesion, direct force measurements, electrochemistry, microcontact printing, soft lithography

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