

Fabrication of asymmetrically coated colloid particles by microcontact printing techniques

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We developed a novel method for preparation of asymmetrically coated colloid particles by using a microcontact printing technique. Films of water-insoluble ionic surfactants deposited on PDMS stamps were printed onto latex particle monolayers of opposite surface charge in order to produce spherical latex particles of dipolar surface charge distribution. We studied the effects of salt on the aggregation of such dipolar particles in aqueous suspensions. Upon addition of salt, dipolar colloid particles were found to give “linear” aggregates. We then extended this microcontact printing technique to the directed assembly of colloidal particles. Microcontact printing of one colloidal monolayer over a latex particle monolayer of opposite charge was used to fabricate particles of complex internal structure. We demonstrated that if the two colloid monolayers consist of particles of comparable sizes, this method allows fabrication of particle doublets. When the particle monolayer was stamped with another colloid monolayer of much smaller particle size complex structures as half-coated “raspberry”-like particles were obtained. Possible applications of these asymmetrically coated colloids include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and water-based electrorheological fluids.

1. Introduction

Colloid particles in aqueous suspensions usually have ionic charges that are uniformly distributed over their surfaces. Design and preparation of asymmetrically coated colloid particles has been a long standing challenge in surface and colloid science. Colloid particles of asymmetric or dipolar charge distribution would have special properties based on additional orientational interactions in aqueous suspensions and may find a number of applications, including preparation of photonic crystals¹ with novel symmetries, colloidal liquid crystals^{2,3} and water-based electrorheological fluids. Over the past 15 years or so there have been only a few reports of preparation of unsymmetrically coated colloids, including Janus particles,⁴ non-spherical shaped “acorn” particles^{5,6} and unsymmetrical 3D macromolecules of large dipolar moment.^{7,8} Recently, two additional techniques have been proposed, based on evaporation of gold on colloid monolayers,⁹ and deposition of polymers on colloids using the Langmuir–Blodgett technique.^{10,11}

Microcontact printing (μ CP) is an easy and efficient way of producing patterns of self-assembled monolayers (SAM) even of sub-micrometer lateral dimensions.^{12–14} An elastomer stamp, usually made from polydimethylsiloxane (PDMS), is used to transfer the ‘ink’ to the surface of the substrate by contact printing. When the stamp is lifted from the surface, a patterned deposit of ink defined by the stamp structure is produced on the surface of the substrate. The quality of the pattern and the resolution of the printed features are dictated by the ink concentration, the procedure of inking of the stamp and the printing conditions, including the surface chemistry of the solid substrate.^{12–14}

Very recently, we communicated a novel method for preparation of dipolar colloid particles which is based on *microcontact printing of water-insoluble ionic surfactants onto*

*colloid monolayers of opposite surface charge.*¹⁴ The idea is presented schematically in Fig. 1. Our method involves the following three steps:

(i) A monolayer of monodisperse polystyrene (PS) latex microparticles is prepared by evaporating a latex particle suspension onto a glass substrate.

(ii) A film of water-insoluble surfactant of opposite charge to

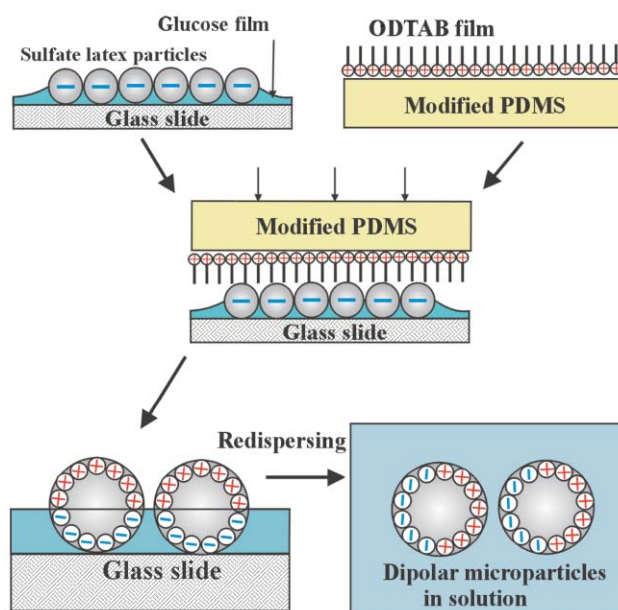


Fig. 1 Scheme of the preparation of dipolar colloid particles by microcontact printing of water-insoluble cationic surfactant (ODTAB) on a monolayer of sulfate latex particles.

that of the particles is deposited on the surface of a flat sheet of elastomer (PDMS).

(iii) The surfactant film is printed onto the colloid monolayer and then the colloid particles are redispersed in an aqueous solution.

We use the natural flexibility of the PDMS to deposit the surfactant film over the exposed surface of the microparticles in a supported monolayer. The PDMS deforms locally when pressed against the particles in the monolayer and the surfactant film is transferred by direct microcontact due to adhesion to the exposed hydrophobic surface of the PS particle. Different fractions of the particle surface can be exposed to the surfactant film by partial embedding of the particle monolayer into a protective film of glucose on a solid substrate. Using water-insoluble surfactants guarantees that the produced surfactant deposit on the particle surface would not desorb and dissolve upon redispersion in water.

In this paper we present more details and additional results obtained by this method. We use different types of fluorescent water-insoluble cationic and anionic dyes, which allows direct observation of the outcome of the microcontact printing on the surface of the microspheres. In addition, we have extended the method to *print with one colloid monolayer onto another colloid monolayer*. This allowed us to produce a number of anisotropic colloidal structures as a result of directed assembly aided by microcontact printing. The scheme illustrating this technique is shown in Fig. 2.

The paper is organized as follows. Section 2 describes the materials and methods used. In section 3 we discuss the preparation of a range of asymmetrically coated particles, including dipolar particles, and comment on some results related to their properties. Here we also describe the results of a novel method for directed assembly of colloid particles into doublets and more complex structures. The main conclusions are summarised in section 4.

2. Experimental

Here we describe the materials and the methods used in our procedure of preparation of the PDMS stamps, the particle monolayers and the surfactant films, the printing procedure and the redispersion of the prepared asymmetric colloids.

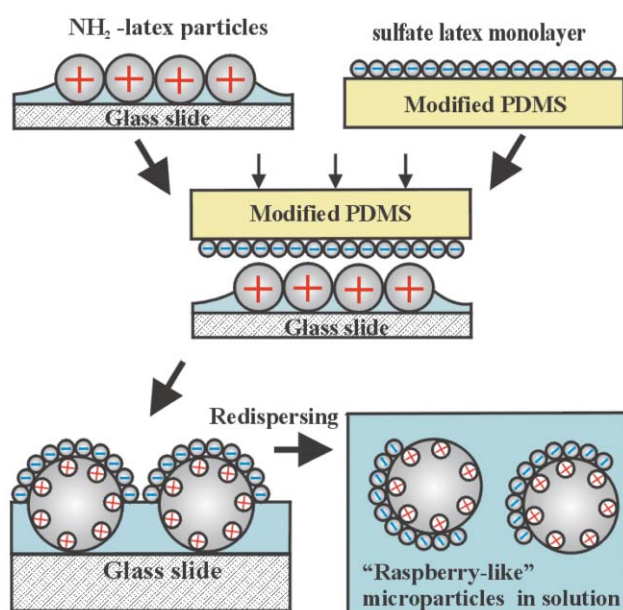


Fig. 2 Scheme of the preparation of “raspberry-like” microparticles by microcontact printing of a monolayer of small colloid particles onto a monolayer of much larger microparticles.

Table 1 Properties of the PS latex particle samples from IDC

Diameter/ μm	Surface groups	Area per surface group/ nm^2
1.5 ± 0.09	Sulfate	N/A
2.5 ± 0.13	Carboxyl	1.24
3.9 ± 0.31	Sulfate	2.14
9.6 ± 0.71	Sulfate	N/A ^a
9.8 ± 0.65	Aliphatic amine	0.20

^aAccording to IDC the latex surface area is not large enough for precise surface charge determination by conductometric titration but the area per surface sulfate group is expected to be between 2.5 and 5.0 nm^2 .

2.1. Materials

The following surfactants, fluorescent dyes and solvents were used: octadecyltrimethylammonium bromide (ODTAB) from Fluka, dipalmitoyl-*sn*-glycero-3-phosphoethanolamine-*N*-(lissamine rhodamine B sulfonyl) from Avanti Polar-Lipids, Neuro-DiO (fluorescent membrane dye, cationic surfactant) from Biotium, isopropanol (98%), sodium chloride (99.5%) from BDH; D-(+)-glucose (from corn sugar, 99.5%) from Sigma, hydrogen peroxide (27.5%) from FSA laboratory supplies. CdSe-ZnS core-shell Q-dot nanoparticles (4.8 nm diameter, catskill green) were purchased as a 0.5 mg ml^{-1} suspension in toluene from Evident Technologies (USA). Monodisperse latex particles of different sizes and surface groups were purchased from Interfacial Dynamics Corporation (USA). Table 1 summarizes the specifications of the latex samples.

Elastomer (flat) stamps for microcontact printing were made from PDMS elastomer Sylgard 184 and curing agent (Dow Corning). All water used in the experiments was from a Milli-Q Reagent Water System. All experiments were done at room temperature.

2.2. PDMS stamp preparation

Flat sheets of PDMS were prepared by spreading a layer of Sylgard 184, PDMS-to-cross linker ratio 10 : 1, of a thickness of 4 mm on a solid support and curing at 60 °C for 2 hours. To improve the spreading of the ethanol based surfactant solutions (the “ink”) on the PDMS surface, the PDMS sheets were hydrophilised by surface oxidation with piranha solution (conc. H_2SO_4 and 30% H_2O_2 3 : 1 (v/v)) for 30 s at 40 °C, rinsing several times with milliQ water and treatment with 10% APTES (3-aminopropyltriethoxysilane) in water for 2 hours at 50 °C.

Caution: the piranha solution is an extremely strong oxidant and should be handled very carefully!

After this treatment the surface layer of oxidized PDMS is grafted with more hydrophilic APTES residues. The hydrophilised PDMS sheets (stamps) were stored in milliQ water prior to the deposition of surfactant film and the microcontact printing.

2.3. Preparation of colloid particle monolayers

Latex particle monolayers were prepared by spreading a fixed amount of latex suspension (e.g. 9.6 μm sulfate latex from IDC) on microscope slides (25 × 25 × 1 mm), which had been pre-cleaned with acetone and dried under nitrogen. The amount of suspension was calculated to contain enough particles to cover the whole surface of the glass slide with a densely-packed monolayer. After drying, the particle monolayer was lifted with 0.1% glucose solution in water and dried up again on the slide to produce a film of glucose with a monolayer of latex particles protruding from its surface. The function of the glucose was (i) to “glue” the particles to the glass interface and (ii) to protect the lower part of the latex particle surface from exposure to the

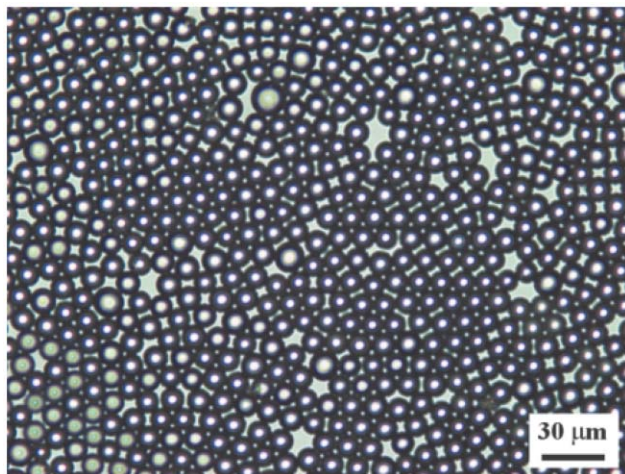


Fig. 3 An optical micrograph of a monolayer of 9.6 μm sulfate PS latex particles deposited on a microscope glass slide. The particles are partially immersed in a protective film of glucose (see text).

surfactant film during the stamping procedure. Fig. 3 presents a typical image of the monolayer of 9.6 μm sulfate latex particles prepared by this technique.

2.4. Printing with surfactant films on particle monolayers

Two different procedures for preparation of surfactant films were explored. (i) A sample of 50 μL 5 mM ODTAB in ethanol was spread on the hydrophilised PDMS slide. When the ethanol was almost fully evaporated, the PDMS slide was stamped against the latex particle monolayer on a glass slide and kept in contact for 10 seconds. The latex particles on the glass slide were redispersed in milliQ water and the suspension was treated with an ultrasonic probe at 5 W for 30 seconds (in an ice bath) to break up the particle aggregates. The latter procedure was used with the 9.6 μm latex particles with a typical pressing force of 500 g cm^{-2} . (ii) In the case of 2.5 μm carboxyl PS latex particles the surfactant film was prepared by spreading 0.1 mM ODTAB solution in amyl acetate on water, and subsequent collection of the film by gradually submerging of the PDMS sheet in the water. Then the glass slide with the particle monolayer was pressed against the PDMS sheet with the ODTAB film and the treated particles were redispersed in aqueous solution of pH 10, followed by ultrasonic treatment.

2.5. Details of the microcontact printing procedure

In a series of experiments with both procedures (i) and (ii) we encountered problems with the uniformity of the stamping, which were resolved by sticking the PDMS sheet (stamp) to a solid support and applying the force in the centre of the stamped slide. Our observations showed that there is an optimal force which should be applied in order to achieve transfer of the surfactant film to the particle surface. Much smaller applied force resulted in incomplete transfer of the deposited surfactant film on the particle monolayer while much larger applied force produced non-selective coating (on both sides) and did not result in better quality of the transfer. Samples of particles taken from different areas of the slide showed similar coating fractions of the stamped areas. A bigger problem is the polydispersity of the latex particles, which may produce coated areas of different size on the particle surface for particles of different size within the monolayer.

2.6. Printing with colloids on colloid monolayers

A colloid monolayer of small particles on a hydrophilised PDMS sheet was prepared by spreading a fixed volume of particle suspension on the surface. The amount of particles was

calculated to form a dense monolayer on the PDMS surface. Stamping of this latex monolayer against a monolayer of bigger latexes was done in a way similar to the one with the surfactant film. After pressing of the two colloid monolayers against each other, the stamped particles on the glass slide were redispersed in milliQ water.

Printing with Q-dots (CdSe–ZnS core–shell nanoparticles) on latex monolayers was done as follows. A solution of 4.8 nm CdSe–ZnS nanoparticles diluted 100 times in toluene was spread over a sheet of PDMS stuck on a solid support and left for the solvent to evaporate. Then the microscope slide with the latex monolayer was pressed on this film for 10 s. After that, the latex particles on the glass slide were redispersed in milliQ water and the suspension was treated with ultrasound to break up the particle aggregates.

The particles produced by all stamping procedures were imaged by using fluorescence microscope (Olympus BX-51) equipped with a filter set for TRITC (ex 520–550/em 570–580) and FITC (ex 470–490/em 510–540), CCD camera (Pixera DP50) and Image Pro Plus image analysis software.

3. Results and discussion

3.1. Printing with surfactant films on colloid monolayers

To prove that the microcontact printing method described above can “address” only the exposed part of the particle surface, we repeated the experiment by spreading 100 μL 10 μM solution of lissamine-rhodamine B in ethanol on the PDMS slide. This fluorescent lipid is negatively charged at high-to-moderate pH and has properties similar to water-insoluble surfactants. A sample of the redispersed 9.6 μm PS latex particles (“half-coated” by stamping with lissamine-rhodamine film) was observed by fluorescent microscopy, with a filter set for TRITC. As seen in the typical images presented in Figs. 4A and B the particles are Janus-like, *i.e.* they have two faces, only one of which is coated with a film of fluorescent material. To understand the interactions and the transfer mechanism of the surfactant film to the particle surface we conducted the same experiment with the cationic fluorescent dye Neuro-Dio, which is practically insoluble in water (similarly to ODTAB). The fluorescent images with a filter set for FITC, presented in Figs. 4C and D indicate that these particles are also Janus-like. From these results one can conclude that the surfactant film remains on the surface of the stamped particles due to hydrophobic interaction (adhesion) with the polystyrene surface, *i.e.* both anionic and cationic surfactant films can be printed on the surface of sulfate latex particles.

Using the same technique we produced PS latex particles which are half-coated with ODTAB film. Upon redispersion in water, the particle surface treated with ODTAB is expected to have a net positive surface charge due to dissociation of the ODTAB film while the untreated part of the particle surface is negatively charged due to dissociation of the original sulfate groups. Such particles are expected to have large electric dipolar moment in aqueous suspensions, which can strongly influence their interaction due to additional “charge–dipole” and “dipole–dipole” forces. We examined the aggregation behaviour of these dipolar colloid particles upon addition of salt. Both the untreated (Fig. 5A) and the treated (Fig. 5C) particles did not aggregate in pure milliQ water. Their behaviour, however, was very different after the addition of electrolyte. The particles stamped with ODTAB (Fig. 5D) formed primarily “linear” aggregates at high salt concentration, while the non-treated particles (Fig. 5B) produced bulky three-dimensional aggregates under the same conditions. Our current understanding of these results is the following. Assuming that the particles in Figs. 5C and D are similarly coated with ODTAB as the fluorescent particles in Fig. 4, they

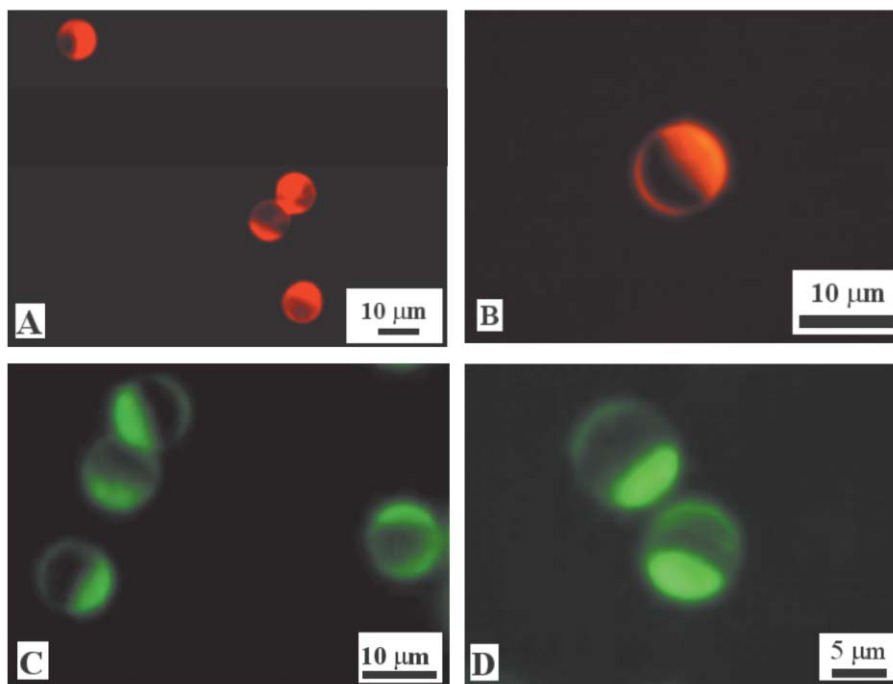


Fig. 4 (A) A fluorescent microscopy image of 9.6 μm sulfate PS latex particles stamped with a film of lissamine-rhodamine (fluorescently-tagged lipid, negatively charged at high pH) deposited on an elastomer stamp, and redispersed in milliQ water. (B) An individual particle partially coated with lissamine-rhodamine at high magnification. (C) and (D) High magnification fluorescent microscopy images of 9.6 μm sulfate PS latex particles stamped with a film of Neuro Dio (hydrophobic fluorescent cationic dye) deposited on an elastomer stamp, and redispersed in milliQ water. The anionic and cationic amphiphilic molecules stick equally well on the PS latex particles predominantly due to hydrophobic interactions with the PS surface.

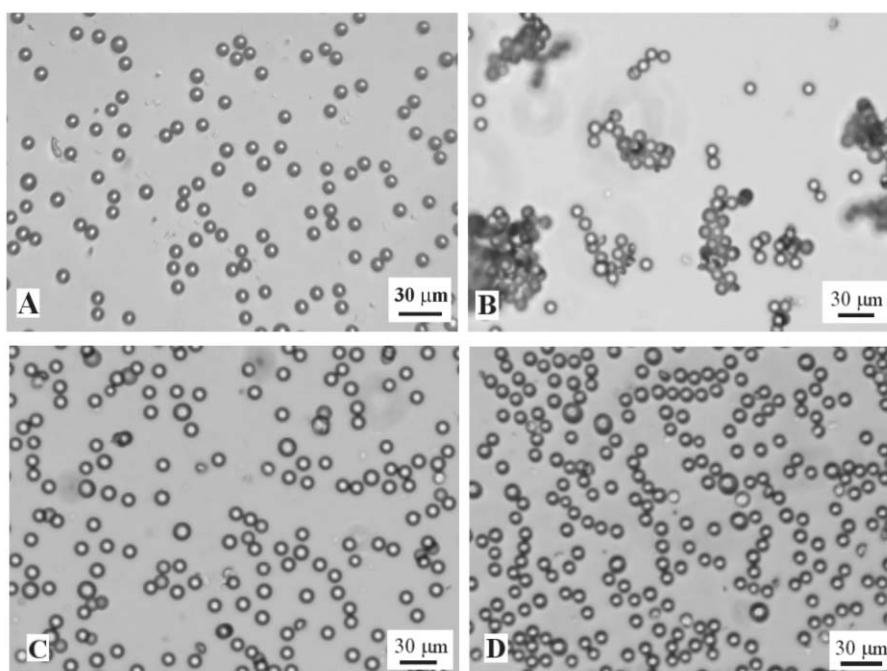


Fig. 5 (A) Non-treated 9.6 μm sulfate latex particles after being spread as a monolayer with glucose solution, dried up and re-dispersed in milliQ water as a control experiment. (B) the same particles as (A) in 0.25 M NaCl after ultrasonic treatment. (C) 9.6 μm sulfate latex particles stamped with ODTAB (see text) and redispersed in milliQ water. (D) the same particles as (C) in 0.25 M NaCl after ultrasonic treatment.

should have a net charge and then in milliQ water they would experience long-range electrostatic repulsion which dominates the closer range dipole-dipole interaction. For this reason no substantial particle chaining has been observed in milliQ water. At high salt concentration, the electrostatic repulsion due to the net surface charge is screened and closer range orientation effects due to interaction between the electric dipoles of the particles operate. Note that the sample of 9.6 μm sulfate latex,

available from IDC, has significant polydispersity. In spite of that, we have used this sample in the experiments in Figs. 4 and 5 since we can visualize the particle coating position with fluorescent microscopy (Fig. 4) only with large (albeit not perfectly monodisperse) latex particles.

To check how smaller particles behave after being half-coated by the microcontact printing technique and to explore other ways of deposition of surfactant film on the surface of

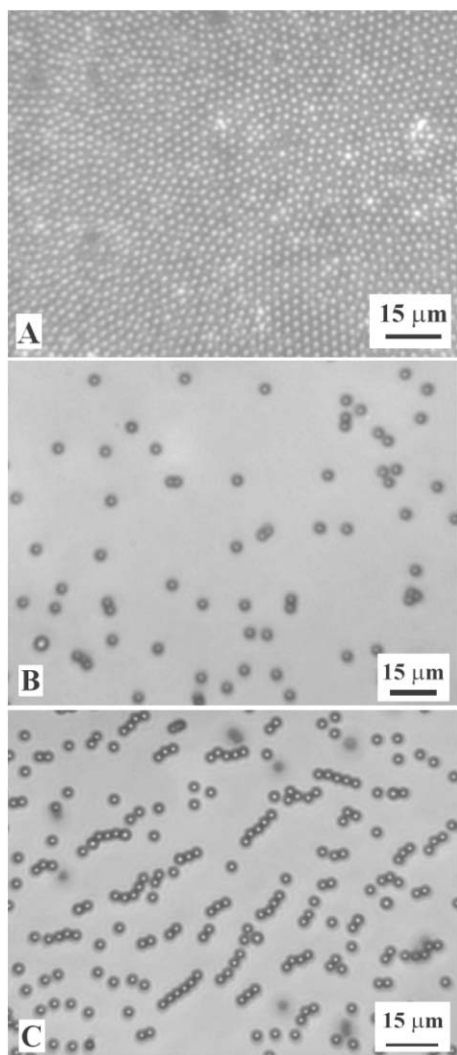


Fig. 6 2.5 μm carboxyl PS latex particles stamped with ODTAB film. (A) The particle monolayer on a glass support before stamping. (B) The control experiment where the particle monolayer was redispersed in a water solution of pH 10 without stamping with the ODTAB film. (C) Particles sample redispersed in solution at pH 10 after being stamped with the ODTAB film.

PDMS we treated a monolayer of 2.5 μm carboxyl PS latex particles with the procedure (ii) described in section 2.4. The results are presented in Fig. 6. Surprisingly, we observed significant chaining of the treated particles in water at pH 10 (ionic strength $I = 10^{-4}$ M). This might be an indication that at this pH the bipolar particles produced by our stamping procedure are close to their point of zero charge (PZC), which depends on the degree of particle immersion in the protective film of glucose. The depth of immersion depends on the wetting of the particles surface by the glucose solution when they are adsorbed at the liquid interface (prior to the monolayer formation). Thus the particle dipole could be controlled by the following means during the stamping techniques: (a) by the particles three-phase contact angle (*e.g.* by addition of a suitable non-ionic surfactant to the glucose solution) or (b) by pH, which charges or neutralises selectively one of the particle halves. Hence, it could be possible to adjust the number of the negative surface charges on the bottom side of the particle to be exactly equal to the number of positive charges on the top size (the exposed side) of the particle surface. In this particular case, it would be possible to have zero overall particle charge and maximal dipolar moment. Further research is needed to estimate the role of these factors in determination of the PZC of these colloids.

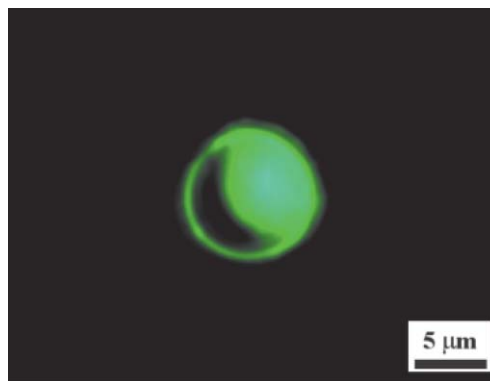


Fig. 7 9.8 μm amine PS latex particle printed with a photoluminescing film of Q-dot nanoparticles (CdSe–ZnS, core–shell particles grafted with TOPO coating), deposited on a PDMS slide (see text for details).

3.2. Printing with colloids on colloid monolayer

Printing with colloids on solid surfaces has already been done with palladium and copper particles.¹⁵ Here we used this technique to print colloids onto colloids. We conducted a series of experiments of stamping of a monolayer of colloid particles of different size deposited on PDMS against a monolayer of large latex particles on a solid (glass) support. Fig. 7 shows the result of stamping a 9.8 μm amine latex particle with a film of nanoparticle Q-dots imaged by fluorescence microscopy. The image was taken with a fluorescence filter set for FITC. In this case, the toluene-based Q-dot suspension was spread and dried on the PDMS sheet and then stamped onto the latex particle monolayer. The photoluminescence of the Q-dots is strongly localised on the stamped part of the particle, although a very low intensity signal is also visible at the bottom part of the particle surface. The latter is possibly an optical effect of reflection of photoluminescence light from the bottom part of the particle surface. Since the Q-dot nanoparticles have a hydrophobic coating (TOPO), we expect that the transfer (and retention) of Q-dots to the latex surface is again a result of hydrophobic interaction, similarly to the case of surfactant films.

We also explored the versatility of the microcontact printing

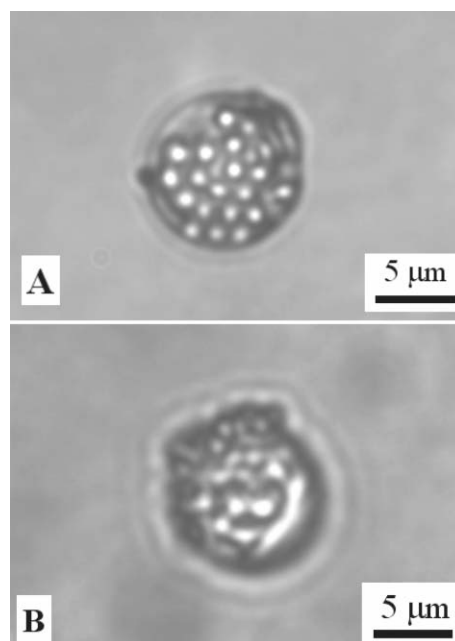


Fig. 8 9.8 μm amine PS latex particles stamped with a monolayer of 1.5 μm sulfate latex particles, followed by redispersion in water and ultrasonication. (A) and (B) present similar “raspberry-like” particles with different orientations with respect to the microscope objective.

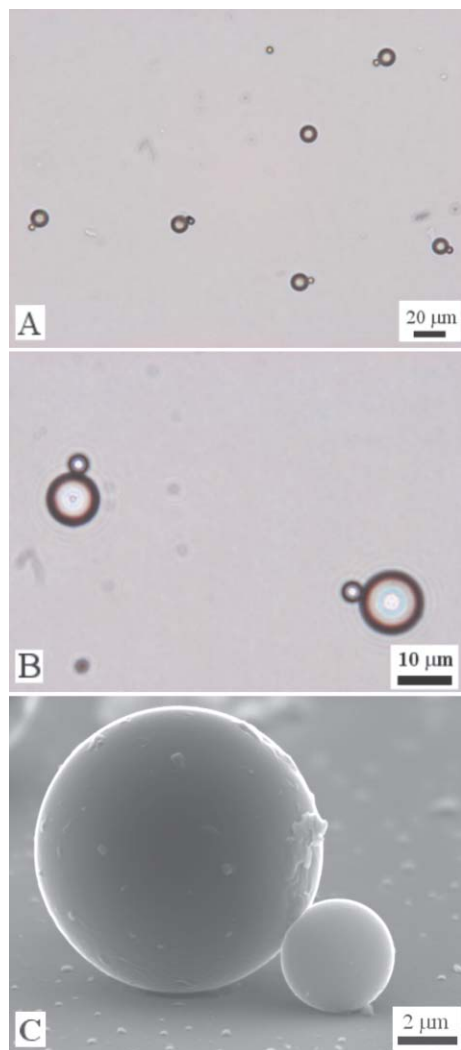


Fig. 9 Particle doublets prepared by microcontact printing of a monolayer of 3.9 μm sulfate PS latex particles over a monolayer of 9.8 μm aliphatic amine PS latex particles, followed by redispersion in milliQ water and ultrasound treatment. (A) and (B): Images of the suspension of particle doublets with an optical microscope at different magnifications. (C) A scanning electron microscopy image of an individual particle doublet deposited on a glass slide by evaporation of the suspension of redispersed particles.

method in assembling of colloidal structures by stamping a monolayer of 1.5 μm sulfate latex particle deposited on PDMS onto a monolayer of 9.8 μm amine PS latex particles deposited on a solid support. The sample was treated as described in section 2.6. The resulting structures after redispersion of the particle monolayer in water were half-coated “raspberry-like” particles. Fig. 8 shows typical optical micrographs of the results of the stamping procedure where one can see the “fine” structure of the coating, consisting of a dense monolayer of smaller particles. The bond between the “satellite” monolayer of small particles and the large particle is enhanced not only by the hydrophobic interaction at the point of local contact but also by the electrostatic interaction between the negatively charged sulfate groups with the positively charged amine groups on their surfaces. This is an example of how the microcontact printing of particle monolayers can be used for directed assembly of complex anisotropic colloidal particles.

The capability of this assembly technique was examined further by stamping particle monolayers of comparable size

against each other. Fig. 9 presents the result of this procedure with 9.8 μm amine PS latex particles and 3.9 μm sulfate latex particles. We found that, in this case, the method gives a high yield of doublets that are apparently stable upon redispersion in water followed by a mild ultrasonic treatment. SEM images of the doublets (see Fig. 9C) reveal that there is a notable local flattening of the two particles at the point of contact which increases the contact area between the particles and enhances the stability of the doublets.

4. Conclusions

We have developed a new method for fabrication of microparticles of bipolar surface charge distribution by microcontact printing of a film of water-insoluble ionic surfactant onto a colloidal monolayer of oppositely charged particles. The method works with both cationic and anionic surfactants. The half-coated “bipolar” particles exhibit orientational interactions resulting in the formation of linear chain aggregates at high salt concentration. The directional, electrolyte-controlled assembly of these particles in linear aggregates could be used for making photonic crystals with novel symmetries, electrolyte sensitive gels and in electrorheological fluids. We have also extended this method to print colloid monolayers onto colloid monolayers. For monolayers of particles of similar size, the printing produced a high yield of particle doublets, while for monolayers of particles of very different size, complex structures such as “raspberry-like” particles have been fabricated. This method may find further applications for directed assembly of other colloidal structures.

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References

- O. D. Velev, T. A. Jede, R. F. Lobo and A. M. Lenhoff, *Nature*, 1997, **389**, 447; O. D. Velev and A. M. Lenhoff, *Curr. Opin. Colloid Interface Sci.*, 2000, **5**, 56; V. L. Colvin, *MRS Bull.*, 2001, **26**, 637.
- A. P. Philipse and D. G. B. M. Maas, *Langmuir*, 2002, **18**, 9977.
- Z. Dogic, A. P. Philipse, S. Fraden and J. K. G. Dhont, *J. Chem. Phys.*, 2000, **113**, 8368.
- C. Casagrande, P. Fabre, E. Rhabphael and M. Veyssié, *Europhys. Lett.*, 1989, **9**, 251; T. Ondarcuhu, P. Fabre, E. Rhabphael and M. Veyssié, *J. Phys. France*, 1990, **51**, 1527.
- A. T. Skjeltrop, J. Ugelstad and T. Ellingsen, *J. Colloid Interface Sci.*, 1986, **113**, 577.
- A. Loxley and B. Vincent, *J. Colloid Interface Sci.*, 1998, **208**, 49.
- K. L. Wooley, C. J. Hawker and J. M. Fréchet, *J. Am. Chem. Soc.*, 1993, **115**, 11505.
- I. M. Saez and J. W. Goodby, *Chem. Commun.*, 2003, 1726.
- H. Takei and N. Shimizu, *Langmuir*, 1997, **13**, 1867.
- K. Fujimoto, K. Nakahama, M. Shidara and H. Kawaguchi, *Langmuir*, 1999, **15**, 4630.
- K. Nakahama, H. Kawaguchi and K. Fujimoto, *Langmuir*, 2000, **16**, 7882.
- J. L. Wibur, A. Kumar, N. L. Abbott, E. Kim and G. M. Whitesides, *Adv. Mater.*, 1994, **6**, 600.
- A. Kumar and G. M. Whitesides, *Appl. Phys. Lett.*, 1993, **63**, 2002; Y. N. Xia, M. Mrksich, E. Kim and G. M. Whitesides, *J. Am. Chem. Soc.*, 1995, **117**, 9576.
- O. Cayre, V. N. Paunov and O. D. Velev, *Chem. Commun.*, 2003, DOI: 10.1039/b307296g, in press.
- P. C. Hidber, W. Helbig, E. Kim and G. M. Whitesides, *Langmuir*, 1996, **12**, 1375.