

Fabrication of dipolar colloid particles by microcontact printing

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A novel technique for preparation of dipolar colloid particles has been developed which is based on microcontact printing of films of water-insoluble ionic surfactants onto monolayers of colloid particles of opposite surface charge.

Colloid particles usually have surface charges that are uniformly distributed over their surfaces. Design and preparation of unsymmetrically coated colloid particles has been a long standing challenge in surface and colloid science. Colloid particles of asymmetric or dipolar charge distribution would have a number of 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. There have been only a few reports of preparation of unsymmetrically coated colloids, including Janus particles,⁴ acorn particles^{5,6} and unsymmetrical 3D macromolecules of large dipolar moment.⁷ Recently, two additional methods were proposed, based on evaporation of gold on colloid monolayers,⁸ and deposition of polymers on colloids using Langmuir–Blodgett technique.^{9,10}

Here we report a novel preparation method for dipolar colloid particles which is based on microcontact printing of a film of water-insoluble ionic surfactant onto colloid monolayers of opposite surface charge as shown schematically in Fig. 1. The method includes the following 3 stages: (i) A monolayer of polystyrene (PS) latex microparticles is prepared by evaporation of latex suspension spread on a glass substrate. (ii) A film of insoluble surfactant is deposited on hydrophilised elastomer

stamp. (iii) The colloid monolayer is “stamped” with the surfactant film and then the colloid particles are redispersed in water. A part of the deposited surfactant is transferred due to adhesion to the exposed part of the hydrophobic polystyrene surface. Using of water-insoluble surfactants guarantees that the produced surfactant deposit on the particle surface would not desorb upon redispersion in water. Details of the method are given below.

PDMS (polydimethylsiloxane) slides were prepared on solid support from Sylgard 184 elastomer (Dow Corning) with PDMS-to-cross linker ratio 10 : 1. The PDMS surface was made hydrophilic by surface oxidation with piranha solution (conc. H₂SO₄ and 30% H₂O₂ 3 : 1 (v/v)) for 30 s at 40 °C, rinsing several times with deionised water and treatment with 10% APTES (3-aminopropyltriethoxysilane) in water for 2 h at 50 °C. The hydrophilic stamps were stored in milliQ water prior to the deposition of the surfactant. Latex particles monolayers were prepared by spreading of fixed amount of latex suspension (9.6 µm sulfate latex from IDC) on a microscope slide (25 × 25 × 1 mm, 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 up with 1% glucose solution in water and dried up again to produce a film of glucose with a monolayer of latex particles protruding from its surface. The glucose film sticks the particles to the glass interface and protects the bottom part of the particle surface from exposure to the surfactant during the stamping. 50 µL of 5 mM octadecyltrimethylammonium bromide (ODTAB) in ethanol was spread on the surface-modified PDMS slide. When the OTDAB film was nearly dry, the PDMS slide was stamped against the particle monolayer on a glass slide and kept in contact for 10 s with a typical pressing force of 500 g/cm². The latex particles on the glass slide were then redispersed in water and treated with ultrasonic probe at 5 W for 30 s to break up the aggregates.

To prove that the microcontact printing method described above can “address” only the exposed part of the particle surface, we performed the same experiment by using 100 µL 10 µM solution of a fluorescent lipid, lissamine rhodamine (Avanti Polar Lipids, Inc) in ethanol instead of OTDAB. A sample of the redispersed 9.6 µm PS latex particles (“half-coated” with lissamine-rhodamine) was observed by fluorescent microscope, with a filter set for rhodamine. As seen in the typical images presented in Fig. 2 the particles are only partially coated with a fluorescent layer. Particle samples taken from different areas of the slide showed similar coating positions.

Using the same technique, we produced PS latex particles “half-coated” with OTDAB. Upon redispersion in water, the particle surface treated with OTDAB is expected to be positively charged due to dissociation of OTDAB while the untreated particle surface is negatively charged due to dissociation of the sulfate groups. Such particles are expected to have electric dipolar moment in aqueous suspensions which can strongly modify 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. 3A) and the treated (Fig. 3C)

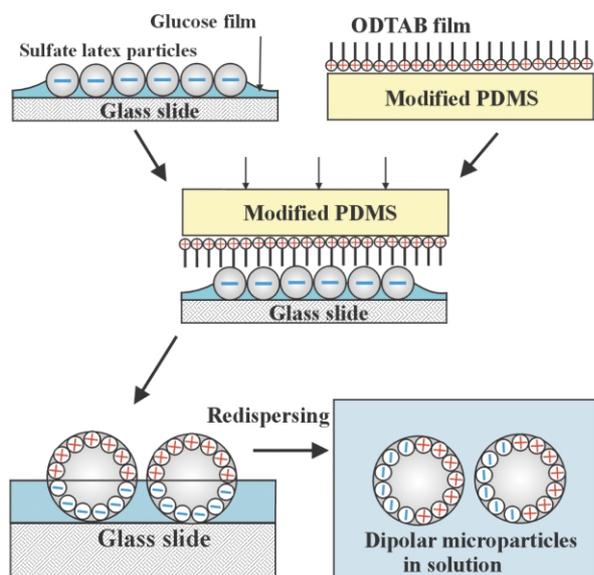


Fig. 1 Schematics of the preparation of dipolar colloid particles by microcontact printing of water-insoluble cationic surfactant (ODTAB) on a monolayer of sulfate latex particles.

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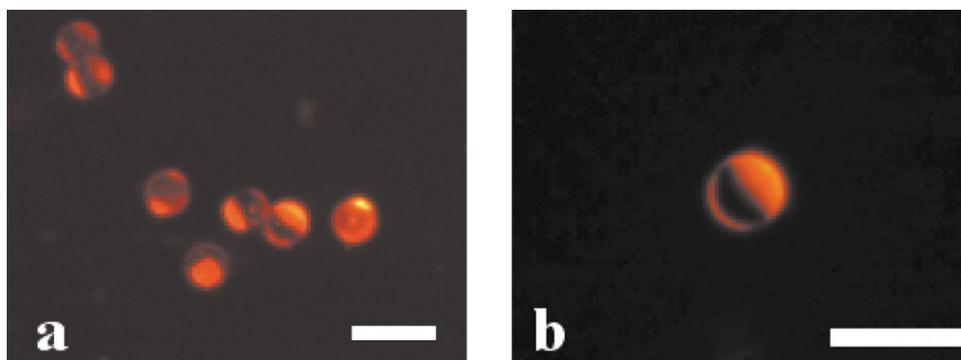


Fig. 2 Fluorescent microscopy images of 9.6 μm sulfate PS latex particles stamped with lissamine-rhodamine deposited on an elastomer stamp. (a) Partially coated particles in milliQ water. (b) An individual partially coated PS particle in water at high magnification (bars are 20 μm).

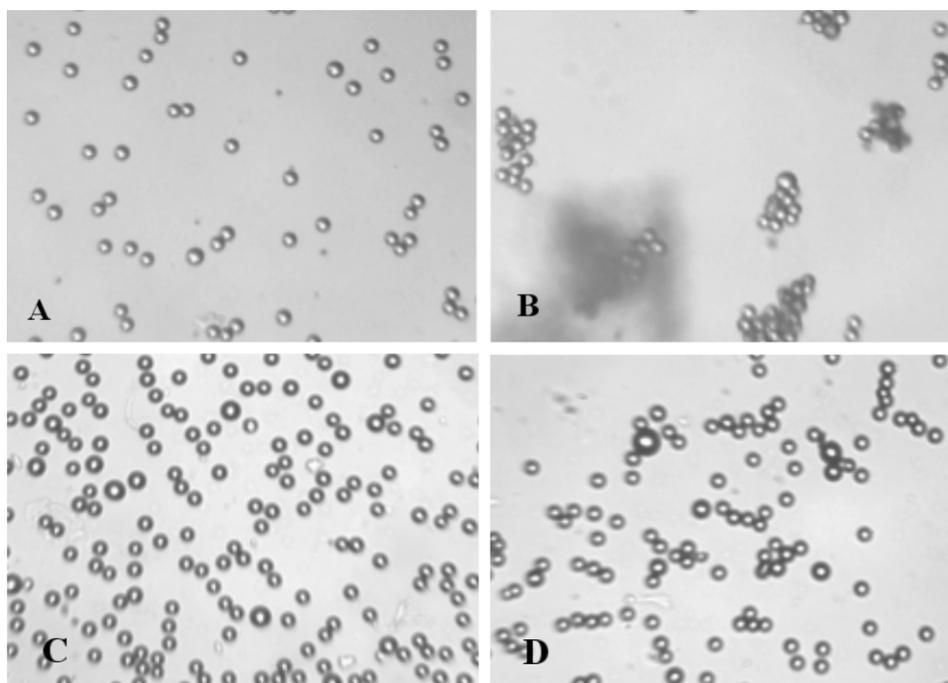


Fig. 3 (A) Non-treated 9.6 μm sulfate latex particles after being spread as a monolayer with glucose solution, dried up and re-dispersed in milliQ water as a control experiment. (B) The same particles as (A) in 0.25 M NaCl after ultrasonic treatment. (C) 9.6 μm sulfate latex particles stamped with ODTAB (see text) and redispersed in milliQ water. (D) The same particles as (C) in 0.25 M NaCl after ultrasonic treatment.

particles did not aggregate in pure milliQ, however, at high salt concentration, particles stamped with ODTAB (Fig. 3D) formed primarily linear aggregates while the non-treated particles (Fig. 3B) produced bulky aggregates. We suggest a possible explanation for this behaviour. If the particles in Figs. 3C and 3D are similarly coated with ODTAB as the fluorescent particles in Fig. 2 with lissamine rhodamine, they would have a net charge and in milliQ water would experience strong electrostatic repulsion which dominates the dipole–dipole interaction. This is why, in milliQ water no substantial chaining of particles has been observed. At high salt concentration, the repulsion due to the net surface charge is suppressed and then orientation effects due to dipole–dipole interactions take place.

In summary, we have designed 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 half-coated 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.

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