Near-zero surface pressure assembly of rectangular lattices of microgels at fluid interfaces for colloidal lithography

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Understanding and engineering the self-assembly of soft colloidal particles (microgels) at liquid-liquid interfaces is broadening their use in colloidal lithography. Here, we present a new route to assemble rectangular lattices of microgels at near zero surface pressure relying on the balance between attractive quadrupolar capillary interactions and steric repulsion among the particles at water-oil interfaces. These self-assembled rectangular lattices are obtained for a broad range of particle sizes and, after deposition, can be used as lithography masks to obtain regular arrays of vertically aligned nanowires via wet and dry etching processes.

Microgels are versatile soft colloids that self-assemble at water/air and water/oil interfaces enabling their controlled deposition on a solid substrate and their use for soft colloidal lithography. Although microgels made of Poly(N-isopropylacrylamide) (PNIPAM) are hydrophilic and easily dispersed in water, they can be readily adsorbed at liquid-liquid interfaces using a spreading agent. Upon adsorption at the interface, each microgel spreads to reduce the area of the bare fluid-fluid interface until the deformation is counterbalanced by the microgel internal elasticity. The spreading can be tuned by adjusting the particle crosslinking density, leading to effective diameters at the interface greater than twice the diameter in bulk dispersions. Once at the interface, structural and dynamical behaviour of assemblies of microgels is mainly dictated by capillary and steric interactions. Upon compression, microgel monolayers can reach a point at which all microgels enter into contact to form hexagonal lattices whose lattice spacing can be reduced by further compression. In order to expand the applications of soft colloidal lithography, new routes need to be developed to produce patterns with symmetries beyond the hexagonal one. A broad range of Bravais lattices can be obtained for particles interacting via soft electrostatic repulsion during drying. Additional structures, including binary colloidal alloys and Moiré and complex tessellations, can also be obtained by sequential depositions of microgels, respectively of different sizes or of the same size. Nevertheless, they require multiple steps and a careful control of the surface pressure Π to achieve the target structure. In order to circumvent sensitive processes, it would be desirable to obtain directly non-hexagonal structures via robust self-assembly at the fluid interface. The existence of complex two-dimensional structures beyond the triangular symmetry was numerically predicted by Jagla twenty years ago for colloids with a repulsion potential exhibiting two distinct length scales (e.g. a hard core and a soft shell) and recently experimentally realised by Rey et al. for polystyrene colloids with a microgel soft shell confined at a water-oil interface. Non-triangular assemblies, including strings and rectangular lattices, occur at high values of Π, beyond compact hexagonal monolayers, where the microgel shells are under compression. However, the parameter space in the phase diagram where such structures are obtained is fairly small, and their kinetic access is delicate, making their experimental realization a complex task with limited tuneability.

We report here a novel, robust route to obtain self-assembled rectangular microgels at fluid interfaces for a broad range of different particles. In contrast to the lattices predicted by Jagla, we find rectangular lattices at Π ∼ 0, arising from the combination of steric repulsion and leading-order quadrupolar capillary attraction between microgels at the interface, which are the result of the nanometre-scale roughness induced by the microgels adsorbed at the interface.

The microgels used here were synthesized via precipitation polymerization in water. The monomer and crosslinker were added in one or two steps to grow larger shells as reported in a previous work. Their labeling is CXY, where X = 3, 5, 7 % is the mass ratio between crosslinker and monomer, whereas the total amount of monomer is constant, and Y = 0, 1 is the number of steps for additional shell growth (protocol reported in ESI). In Fig. 1, we show examples of rectangular lattices obtained for values of Π ∼ 0 mN/m for each type of microgel. In order to understand in which region of a 2D phase diagram the structures are obtained, in Fig. 2 we show the compression curve of the C7S1 microgels. In these experiments, we deposit the particles on a substrate, which crosses the water/hexane interface at the same time as the monolayer is compressed (protocol reported in ESI). From the reading of Π using a Wilhemy plate and the direct measurement of the area per particle A_p (extracted by image analysis after deposition), we observe that lattices with a four-fold coordination (e.g. rectangular and rhomboidal) are found for values of Π ∼ 0 mN/m in the compression curve. As Π grows, the structures transition to the well-known hexagonally packed monolayers. The transition between the two types of coordination is clearly displayed in the inset to Fig. 2 which shows the...
order parameters $\Psi_4$ and $\Psi_6$ calculated as in Equation 1, where $j = 4, 6$ represents the symmetry of the order parameter $\Psi_j$, $N$ is the total number of particles, the index $k$ refers to a given particle with $N_j$ neighbours and $\theta_{lk}$ is the angle formed between the particle $k$ and its neighbour $l$ respect to a fixed axis.

$$\Psi_j = \frac{1}{N} \sum_k N_j \sum_l e^{ij\theta_{lk}}$$

The $\Psi_4$ and $\Psi_6$ parameters are closer to 1 when there is a mainly rectangular or hexagonal lattice, respectively. Therefore, from the data it is clear that for $\Pi \sim 0 \text{mN/m}$, $\Psi_4 > \Psi_6$, while the point at which $\Pi$ starts rising corresponds to a transition to an hexagonal layer, where $\Psi_4 < \Psi_6$. Above 10 mN/m an isostructural phase transition occurs, which results in a decrease of $\Psi_6$, as reported in previous works.

In order to eliminate the possibility that the rectangular lattices are an artifact induced by the deposition process, as reported for drying droplets, we imaged these microgels directly at the water/hexadecane interface in conditions of $\Pi \sim 0$ using several complementary approaches. The first approach is optical microscopy at the fluid interface. To avoid the large convection flows present in the system, we fabricated a ring of microgels at the water/air interface ensuring that we are close to $\Pi \sim 0$. Then, the Teflon beaker was enclosed in a methacrylate box next to a droplet of cyanoacrylate. The evaporating cyanoacrylate reacts at the water/air interface, and after an overnight wait, it is able to create a film that immobilizes the particles. Next, the substrate was extracted from water, collecting the particles immobilized within a cyanoacrylate film. The cured film was characterized by AFM and SEM, highlighting the presence of rectangular lattices (Fig. 2 and ESI). Similar rectangular lattices were also observed in freeze-fractured shadow-casted cryo-SEM images at the water/decane interface (see Fig. 3 and ESI), a technique that allows us to characterize the microgels in-situ at the water/oil interface.

The formation of the four-fold coordinated structures can be rationalized by assessing the magnitude of capillary interactions induced assembly and disassembly of the structures can be seen (see Fig. 3 and Movies S2 and S3). As a complementary set of measurements, we employed two different ways of immobilizing and imaging the particle at the interface. In a first set of measurements, we placed a silicon wafer in a Teflon beaker filled with water, forming a ~30° angle with the interface and partially crossing it. We then deposited C7S1 microgels at the water/air interface ensuring that we are close to $\Pi \sim 0$. Then, the Teflon beaker was enclosed in a methacrylate box next to a droplet of cyanoacrylate. The evaporating cyanoacrylate reacts at the water/air interface, and after an overnight wait, it is able to create a film that immobilizes the particles. The absence of confinement effects is rationalized by assessing the magnitude of capillary interactions.
among the microgels. Although the particles are in close proximity, where near-field capillary interactions play an important role\textsuperscript{19}, the clear presence of rectangular symmetries brings us to hypothesize that the quadrupolar term in the multipole expansion of capillary forces is the dominating one.

The steric repulsion between microgels at interfaces has been described as via Hertzian or generalized Hertzian potentials\textsuperscript{11,20}. As we are in the regime where the microgels are not compressed, the specific form of the steric potential is not relevant and the contribution is effectively 0 until the particles overlap. However, we can consider the steric repulsion, once the particles enter into contact, to be much steeper than the quadrupolar attractive interaction. This implies that, essentially, capillary forces bring the particles at a center-to-center distance approximately equal to their single-particle diameter at the interface, and not closer. In order to reduce this separation further, external compression, i.e. with the barriers of a Langmuir-Blodgett trough, is required and leads to the formation of 2D hexagonal crystals with lattice parameters smaller than the single-particle diameter. The fact that the microgels can rearrange at the interface, furthermore indicates that the attractive capillary potential at contact is comparable to $K_b T$.

With these assumptions, we can estimate the capillary quadrupolar potential between two microgels as a function of their center-to-center distance $d$ as

$$V(d) \sim -12 \pi \gamma_{\text{cap}} H_1 H_2 \cos(2 \varphi_1 - 2 \varphi_2) \frac{R^4}{d^7},$$

where $j = 1, 2$ denote the two considered particles, $\gamma_{\text{cap}} \sim 55 mN/m$ for a water/hexadecane interface, $H_j$ represent the amplitude of the interface deformation and $\varphi_j$ their phase, and $R$ is the radius of the particles at the interface\textsuperscript{11}. This expression is valid for $d >> 2 R$, but it is still in the same order of magnitude even in the limit $d \sim 2 R$\textsuperscript{21}.

Taking the example of 7CS1 microgels, we measure an experimental value of $d \sim 1.8 \mu m$ between particles in rectangular configurations, while $2 R = 1.2 \mu m$ (see ESI). Assuming $T = 25^\circ C$, and the orientation of the phases that gives the maximum attraction, we find that $H_{1,2} = [1.3, 4.0] mN$ for $V(1.8 \mu m) \approx [10, 100] K_b T$. These interface roughness values are in the same range as the ones we measure from the outer part of the microgels via AFM, after deposition on a substrate, as reported here (see ESI) and in previous work\textsuperscript{22}. These considerations indicate that the formation of four-fold coordinated structures can emerge as a consequence of attractive capillary interactions with a quadrupolar leading order balanced by steric repulsion upon contact in the absence of external compression, i.e. for $\Pi \sim 0$.

Since these results are reproducible across different microgels, exploiting the spontaneous formation of non-hexagonal structures opens up new opportunities for soft colloidal lithography. As a demonstration, Fig. 3\textsuperscript{a} shows a square array of C7S0 microgels, which are subsequently used as a mask for the metal-assisted chemical "wet" etching, of vertically aligned silicon nanowires (VA-NWs) in a square lattice configuration (Fig. 4\textsuperscript{b}). To achieve this, a silicon substrate similar to the ones in Fig. 1\textsuperscript{a} was prepared. Next, it was exposed to AZ1518 photoresist for 30 min, baked at 100°C, and rinsed with acetone and subjected to O\textsubscript{2} plasma for 40 s to remove the excess of photoresist. Next, 10 nm-thick gold layer was sputter-coated and the substrate was immersed in the etching solution containing HF and H\textsubscript{2}O\textsubscript{2} (see ESI) for 4 min. Finally, the substrate was exposed to I\textsubscript{2} : KI to remove the gold layer and imaged via SEM, tilting the substrate by 30°. The VA-NWs are $\sim 2.6 \mu m$-long and the partially removed microgels in the washing process are visible, which can be removed via further O\textsubscript{2} plasma treatment\textsuperscript{23}. Furthermore, we tested the capability of such soft colloidal masks to be used in conventional deep reactive ion etching, "dry" etching. To this end, we deposited C3S0 microgels in a square lattice configuration and swelled them in photoresist as described above. Next, we performed the dry etching for 60 s, obtaining the VA-NWs in the SEM image in Fig. 4\textsuperscript{c}, where the substrate is tilted by 30°. The pillars were $\sim 640 nm$-long and the microgels were etched away in the process. Although the dry etching could not produce VA-NWs as long as in the equivalent wet etching process, in the former the etching occurs in a very homogeneous way all over the substrate, while in wet etching there is typically a wider distribution of VA-NWs lengths as the etching happens in a less homogeneous way. Ideally, we could improve the performance of such soft colloidal masks for dry etching by improving the photoresist swelling process and combining it with a Bosch etching process where etching steps are alternated with the deposition of protective passivating layers\textsuperscript{24}. 

Fig. 3 Spontaneous assembly of square lattices of C7S1 microgels at the interface. (a) Frame of Movie S1 at the water/hexadecane interface at the center of a 800 nm-diameter ring (scale bar: 10 nm). Four-fold coordinated clusters highlighted in false colour. The inset shows the FFT, which presents a diffuse ring characteristic of 2D disordered liquids. (b) Two frames of Movie S2 of a water/hexadecane interface showing the spontaneous detachment of a microgel from a cluster, marked for clarity (scale bar: 5 nm). (c) AFM height image of a cured microgel-laden water/air interface after exposure to cyanoacrylate (scale bar: 1 nm). (d) Cryo-SEM image of a water/decane interface where the interface has been fractured and the oil phase removed, showing the microgels protruding from the vitrified water phase (scale bar: 1 μm).
There are no conflicts to declare.

Finally, Fig. 4d, shows the possibility to do sequential deposition where the first layer is a square lattice instead of a hexagonal one, as previously shown. First, a square lattice of C750 is produced at $\Pi \sim 0\text{mN/m}$ (Fig. 4a). Next, the same substrate is immersed in water and a second deposition of smaller P(NIPAM-co-MAA) microgels at $\Pi \sim 25\text{mN/m}$ is performed to produce 2D binary colloidal alloys (see ESI for further details). The combination of different symmetries for sequentially deposited microgel layers offers exciting opportunities for the future realization of complex structures.

Concluding, we show that interesting possibilities emerge from the interfacial self-assembly of soft colloids at close to zero surface pressures. This region of the compression curves is seemingly overlooked, as usually one finds 2D random gas and liquid phases for repulsion-dominated systems, or isolated aggregates if there are strong attractive forces. Here, by carefully exploring this region for soft microgels, we find that, at the right values of surface coverage, large-scale assemblies with four-fold symmetry emerge, which we hypothesize are caused by weak capillary attraction counterbalanced by stiff steric repulsion. We expect that these new lattices can not only be added to the extensive library of self-assembled 2D structures for colloidal lithography, but also that they can inspire further engineering of the particle pair potentials, e.g. through targeted roughness of the particles at the interface. Detailed numerical studies of the interplay between particle architecture and interactions at the interface, paying close attention to near-field capillary forces, may direct the design of tailored soft colloids for the fabrication of new functional materials.

Conflicts of interest
There are no conflicts to declare.

Author contributions
Author contributions are defined based on the CRediT (Contributor Roles Taxonomy) and listed alphabetically. Conceptualization: MNA, MAFR, LI. Formal analysis: MNA, MAFR. Funding acquisition: LI. Investigation: MNA, MAFR. Methodology: MNA, MAFR, LI. Project administration: LI. Software: MAFR. Supervision: MAFR, LI. Validation: MNA, MAFR. Visualization: MNA, MAFR, LI. Writing original draft: MAFR, LI. Writing review and editing: MNA, MAFR, LI.

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