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Molecular-like hierarchical self-assembly of monolayers of mixtures of particles

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We present a technique that uses an externally applied electric field to self-assemble monolayers of mixtures of particles into molecular-like hierarchical arrangements on fluid-liquid interfaces. The arrangements consist of composite particles (analogous to molecules) which are arranged in a pattern. The structure of a composite particle depends on factors such as the relative sizes of the particles and their polarizabilities, and the electric field intensity. If the particles sizes differ by a factor of two or more, the composite particle has a larger particle at its core and several smaller particles form a ring around it. The number of particles in the ring and the spacing between the composite particles depend on their polarizabilities and the electric field intensity. Approximately same sized particles form chains (analogous to polymeric molecules) in which positively and negatively polarized particles alternate.

P articles trapped in fluid-liquid interfaces interact with each other via lateral capillary forces that arise because of their weight, and when present also by other forces such as electrostatic forces, to form monolayer arrangements[1–5]. Particles are able to float at the interface because of the vertical capillary forces that arise due to the deformation of the interface. If the interface did not deform, the vertical capillary forces will be zero and the particles will not be able to float on the surface. But, this also results in lateral capillary forces. A common example of capillarity-driven self-assembly is the clustering of breakfast-cereal flakes floating on the surface of milk. The deformation of the interface by the flakes gives rise to lateral capillary forces which cause them to cluster. In recent years, many studies have been conducted to understand this behavior of trapped particles because of their importance in a range of physical applications and biological processes, e.g., formation of pollen and insect egg rafts, self-assembly of particles at fluid-fluid interfaces resulting in novel nano-structured materials, stabilization of emulsions, and the formation of anti-reflection coatings for high-efficiency solar cells, photonic crystals and biosensor arrays[6–12]. Capillarity-driven self-assembly, however, produces monolayers which have defects and lack long-range order, and for monolayers containing two or more different types of particles, which is the focus of this paper, the technique does not allow for any control of the particle-scale structure as capillary forces simply cause particles to cluster.

We show here that monolayers containing two or more types of particles, with different dielectric properties, can be self-assembled by applying an electric field in the direction normal to the interface. We exploit the fact that the lateral dipole-dipole force between two particles can be repulsive or attractive depending on their polarizabilities and that the intensity of the force can be varied by selecting suitable upper and lower fluids. The force is repulsive when both particles are positively or negatively polarized, but attractive when one particle is positively polarized and the other is negatively polarized. The force also depends on their sizes and the electric field intensity.

The differences in the particles' polarizabilities and sizes drive a hierarchical self-assembly process analogous to that occurs at atomic scales. Groups of particles first combined to form composite particles (analogous to molecules) and then these composite particles self-assembled in a pattern (like molecules arrange in a material). The force between similar particles was repulsive (because they have the same polarizabilities), and so they moved apart which allowed particles that attracted to come together relatively unhindered to form composite particles. The net force among the particles forming a composite particle was attractive, and so after a composite particle was formed it remained intact while the electric field was kept on.

It is noteworthy that the energy needed for a particle to desorb from a fluid-liquid interface is several orders of magnitude larger than thermal energy. Therefore, once nano-to-micron sized particles are adsorbed, they remain adsorbed while moving laterally in the interface in response to lateral capillary and dipole-dipole forces. Furthermore, since particles trapped in a fluid-liquid interface are *free* to move laterally, they self-assemble even when lateral forces driving the assembly are small. The only resistance to their lateral motion is hydrodynamic drag which can slow the motion but *cannot* stop it. This is obviously not the case for a monolayer assembled on a

solid substrate since particles are not free to move laterally because of the presence of adhesion and friction forces. In fact, very-small particles do not self-assemble even on a fluid-liquid interface when lateral capillary forces become smaller than Brownian forces. For example, on an air-water interface, lateral capillary forces in the *absence* of an electric field become smaller than Brownian forces for particles smaller than about 10 µm, and so particles smaller than this limiting size undergo Brownian motion on the interface and do not cluster[13–17]. However, as discussed below, when a sufficiently strong electric field is applied, the electrically-induced lateral forces remain stronger than Brownian forces making self-assembly of nanoparticles possible.

The remainder of the paper is organized as follows. We next describe the forces that act on particles trapped at fluid-liquid interfaces when an electric field is applied normal to the interface. This is followed by a description of the hierarchical arrangements of binary mixtures obtained using our approach and a description of the experimental method.

Results

The lateral force F_l between two particles, i and j, adsorbed at a fluid-liquid interface in the presence of an electric field in the direction normal to the interface is given by:

$$F_l = -\frac{w_i \, w_j}{2\pi\gamma}\frac{1}{r} + \frac{3p_i p_j}{4\pi\varepsilon_o\varepsilon_L}\frac{1}{r^4}. \tag{1}$$

Here w_j is the vertical force acting on the jth particle, p_j is the induced dipole moment of jth particle, ε_0 is the permittivity of free space, ε_L is the permittivity of the lower liquid, γ is the interfacial tension, and r is the distance between the particles (see SI for the details). The first term represents the lateral capillary force that arises because of the total vertical force acting on the particles which includes their buoyant weights and the vertical electric forces, and the second term represents the dipole-dipole force between them. The force depends on the inter-particle distance, but it is *independent* of their positions on the interface.

For the cases considered in this paper, the first term was negative which means that it caused the particles to come together. The second term is repulsive when both particles are positively or negatively polarized, and so the force between two particles of the same type is always repulsive. If one particle is positively polarized and the other is negatively, the dipole-dipole force is attractive. In this case, since both terms on the right side of equation (1) are attractive, the particles come together to touch each other.

From equation (1) we note that the capillary force varies as $1/r$ and the dipole-dipole electric force varies as $1/r^4$. Therefore, the former dominates when the distance is large and the latter dominates for smaller distances. Both of these contributions vary with the electric field intensity. A *stable* equilibrium in which particles are not in contact is possible only when the dipole-dipole force is repulsive and the capillary force is attractive. The dimensionless equilibrium spacing (r_{eq}) between the particles can be obtained by setting the total lateral force equal to zero and solving the resulting equation to obtain

$$\frac{r_{eq}}{a_i} = \left(\frac{3\,\gamma\,p_i p_j}{2\varepsilon_0\varepsilon_L w_i\,w_j\,a_i^3}\right)^{\frac{1}{3}}. \tag{2}$$

Here a_i is taken to be the larger of the two radii. The spacing (r_{eq}) depends on the electric field intensity and other parameters appearing in the equation. The particles touch each other in equilibrium if r_{eq} is less than the sum of their radii. If $p_i p_j$ is negative, both terms on the right side of equation (1) are negative. Thus, the particles come together to touch each other. In the presence of a strong electric field, the capillary and dipole-dipole forces are stronger than Brownian forces making self-assembly of micron- to nano-sized particles possible (see SI for details).

Monolayers in our experiments were formed by sprinkling mixtures of particles onto the surface of a liquid contained in a chamber or were suspended in the liquids in which they sedimented or rose to the liquid-liquid interface (see "Methods" below). The chamber was then covered with a transparent upper electrode and the electric field was applied. The focus of this paper is on binary mixtures for which the dipole-dipole forces between the particles of different types were attractive. Therefore, for most of the cases considered in this paper, the liquids and the particle mixtures were selected so that one type of particles were positively polarized and the second type were negatively polarized. For example, copolymer particles were negatively polarized on corn oil and on a mixture of castor and corn oils (see SI for details). Glass particles and cubical salt crystals were polarized positively on both of these liquid surfaces. Therefore, the dipole-dipole forces among glass and copolymer particles were attractive, as the former were positively polarized and the latter negatively. The dipole-dipole forces among copolymer particles and salt crystals were also attractive.

The dielectric mismatch is another important parameter. Glass particles, and also salt crystals, adsorbed on corn oil surface repelled each other strongly because they were intensely polarized. Copolymer particles repelled relatively weakly on these liquids as they were weakly polarized. Furthermore, their repulsion on the surface of corn oil was weaker than on the surface of the oil mixture as the dielectric mismatch on the corn oil surface was smaller, making their intensity of negative polarization weaker. The strengths of dipole-dipole and capillary forces also depended on the particles sizes and the electric field intensity.

To study the roles of these parameters in the hierarchical self-assembly process, we considered mixtures of glass particles of three different sizes and copolymer particles whose size was held fixed. A mixture of ~71 µm copolymer and ~150 µm glass particles on the surface of corn oil self-assembled when an electric field was applied (see Fig. 1). Glass particles moved several diameters apart to arrange on a triangular lattice, as the repulsive dipole-dipole forces amongst them were the strongest because of their larger size and also because they were intensely polarized (see equation (2)). The spacing among copolymer particles increased only marginally and some remained agglomerated because the dipole-dipole forces for them were relatively weaker. The dipole-dipole force between copolymer and glass particles was attractive, and so several copolymer particles became attached to each of the glass particles to form composite particles (see Fig. 1). A composite particle consisting of a glass particle at the center and surrounded by a ring of copolymer particles was stable in the sense that it remained intact while the electric field was kept on. The number of particles in the ring of a glass particle depended on the number of copolymer particles that were present near it. (There was an area of influence for the glass particle from which it attracted copolymer particles. When there were more copolymer particles present in the area of influence of a glass particle its ring contained more copolymer particles, and *vice versa*. Therefore, for ensuring that the composition of the assembled composite particles is uniform, the mixtures must be mixed uniformly.) Also, since the repulsion among copolymer particles was relatively weaker than their attraction towards more intensely polarized glass particles, the copolymer particles of a ring touched each other and some copolymer particles joined in later to make the ring of particles two layers thick. The spacing between the composite particles increased with increasing electric field intensity, while the spacing between the copolymer particles of a ring remained unchanged since they were tightly held by the glass particle (see Figs. 1b and 1c). There is good agreement between these experimental results and the numerical simulation results shown in Fig. 1d for which the parameter values and the particles sizes were selected to match the experimental values (see SI for details).
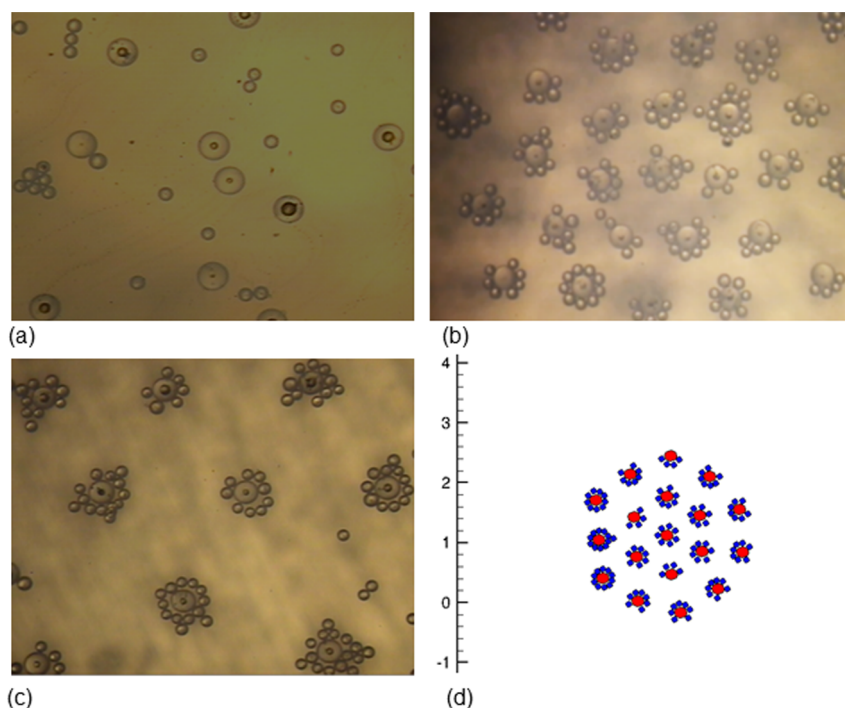
Figure 1 | Monolayers of mixtures of 71 µm copolymer and 150 µm glass particles on the surface of corn oil. The magnification is 50X. (a) Initial distribution. (b) After a voltage of 5000 V was applied, the mixture self-assembled to form composite particles which were arranged on a triangular lattice. The gap between the electrodes was 10 mm, and so the applied electric field intensity was 500 kV/m. A composite particle consisted of a glass particle at the center which was surrounded by a ring of copolymer particles. The distance between the composite particles was 6.6*a*, where *a* is the diameter of glass particles. (c) The distance between the composite particles increased when the voltage was increased to 10000 V, but this did not alter the structure of composite particles. (d) Numerical simulation of self-assembly of mixtures of particles on liquid surfaces. The parameters were selected to match 71 µm copolymer and 150 µm glass particles on corn oil. The electric field intensity was 500 kV/m. The ratio of the number of smaller to larger particles was 7:1. The distance between the composite particles was 7.4*a* which was approximately 12% larger than the experimental distance in (b) for the same electric field intensity. Also notice that since the concentration of smaller particles was initially larger near the left and lower sides, the particle rings in these regions contain more particles.

The arrangement for a mixture of ~71 µm copolymer and ~20 µm glass particles on the surface of corn oil was qualitatively similar. It consisted of composite particles in which the larger sized copolymer particles were at the center, and a ring of glass particles surrounded them. However, although glass particles were smaller in size, they arranged on a triangular lattice as they were more intensely polarized than copolymer particles. The positions of copolymer particles which became embedded in the lattice of glass particles depended on their initial positions. Since they were negatively polarized and of larger size, they attracted the nearby glass particles to form composite particles locally distorting the lattice of glass particles. The glass particles of a ring did not touch each other because of the strong dipole-dipole repulsion between them which limited their number in a ring to six or less (see Fig. 2a). Furthermore, although the distance between the glass particles forming the lattice increased with increasing electric field intensity, there was a range of intensity for which the number of glass particles in the ring of a composite particle did not change. But, when the intensity was increased beyond this range, one of the glass particles was pushed out of the ring because of the increased repulsive forces between them, and then this number was maintained for a range of electric field intensity. The glass particle pushed out of the ring occupied a position in the lattice of glass particles which reorganized to accommodate the additional particle. This shows that the intra-composite particle forces here were relatively weaker. These results are in agreement with our numerical simulation results reported in Fig. S.9 for the same parameter values.

For the case described in Fig. 1, on the other hand, the intra-composite particle forces were stronger, i.e., the copolymer particles of a ring were tightly held by the glass particle at the center, and so

when the electric field intensity was increased although the distance between composite particles increased, the microstructures of composite particles did not change. The attractive forces between the glass and copolymer particles were much stronger than the repulsive forces between the copolymer particles. It is noteworthy that for a given mixture of particles the intra-composite particle forces and the number of particles in the rings (analogous to the number of atoms in a molecule), as well as the spacing between the composite particles can be varied by selecting suitable upper and lower fluids and the electric field intensity. For example, the microstructure in Fig. S4b of Supplementary Information (for ~71 µm copolymer and ~150 µm glass particles) was similar to that in Fig. 2 (~71 µm copolymer and ~20 µm glass particles) as the dielectric constant of Silicone oil was closer to that of glass particles and so the glass particles were weakly polarized and the copolymer particles were strongly polarized. This shows that in addition to the particles' sizes, their polarizabilities, which can be modified by selecting suitable upper and lower fluids, are important in determining the structure of composite particles.

The monolayer arrangement for a mixture of ~71 µm copolymer and ~63 µm glass particles was qualitatively different because of their comparable sizes. The repulsive force between glass particles was stronger than between copolymer particles, and the attractive force between glass and copolymer particles was moderately strong. The preferred arrangement for them was to form chains. Short particle chains formed immediately after the electric field was applied and then some of these chains merged to form longer chains. The simplest chains contained two particles, one glass particle and one copolymer particle (see Fig. 3). The next simplest chains contained a copolymer (or glass) particle in the middle and two glass (or copoly-

(a)
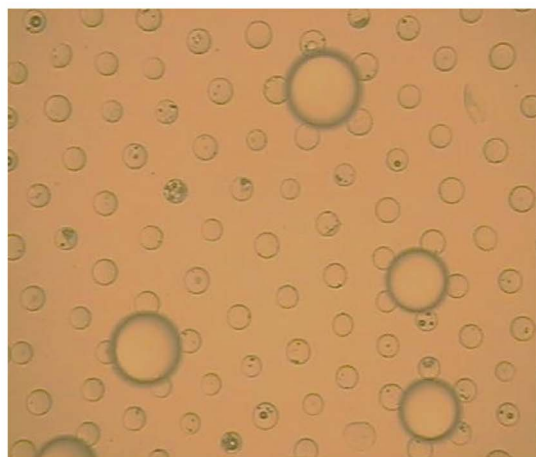
(b)
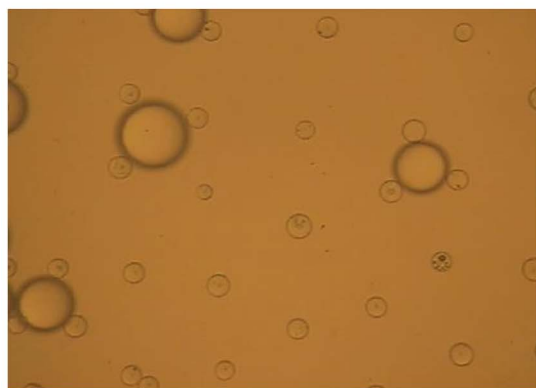
(c)

Figure 2 | **Monolayers of mixtures of 20 μm glass and 71 μm copolymer particles on the surface of corn oil.** The magnification for the first photograph is 50X and for the later photographs 200X. The applied voltage in (b) was 5300 V and in (c) was 7100 V. Glass particles were arranged on a triangular lattice and copolymer particles were embedded in this lattice. The latter attracted nearby glass particles to form composite particles. The lattice spacing increased with increasing electric field intensity, but the number of particles in the ring of a composite particle remained constant only for a range of intensity. When the intensity was increased above this range the number decreased by one as a particle was expelled from the ring. The expelled particle became a part of the lattice of glass particles.

mer) particles on the diagonally opposite sides. The repulsion between the glass (or copolymer) particles made three-particle chains approximately linear. Longer chains with 10–15 particles in which glass and copolymer particles alternated formed because of the merger of shorter chains. Some of the chains were not linear and contained branches. The orientation of chains varied. This result is similar to that for the orientation of ellipsoidal and rod-like particles in a monolayer which was also found to be random[16]. The net dipole-dipole force amongst the chains was repulsive which kept them apart and thus stable while the electric field was kept on. These experimental results are in good agreement with our numerical simulation results shown in Fig. S.10.

The structure of chains depended on the intensities of polarization of the particles which in turn depended on the dielectric properties of the upper and lower fluids. The average chain length was longer when both positively and negatively polarized particles were intensely polarized. For example, the average chain length on corn oil was shorter than on the oil mixture (see Fig. S7a of Supplementary Information) because the intensity of negative polarization of copolymer particles was weaker on the former. The dielectric constant of the oil mixture was larger which increased the dipole-dipole force between copolymer particles and increased the attractive force between a copolymer and a glass particle, making the attractive and repulsive forces more comparable and thus the formation of chains more likely.

We also studied monolayer arrangements of the mixtures of cubical and spherical particles on the surface of corn oil. The cubical particles were salt crystals with sides ∼250 μm which were positively polarized. The spherical particles considered were 71 μm copolymer particles and 63 μm glass particles. Fig. 4a shows a monolayer of salt crystals and copolymer particles. Salt crystals clustered quickly under the action of lateral capillary forces before the electric field was applied because of their relatively larger size. After the field was applied, the dipole-dipole forces caused salt crystals to move apart (see Fig. 4a). The hierarchical arrangement in this case was qualitatively similar to that for a mixture of spherical particles described in Fig. 1. A composite particle consisted of a salt crystal at the center and several copolymer particles formed a ring around it. The repulsion among the copolymer particles of a ring was weaker compared to their attraction with the salt crystal, and so they touched each other.

The microstructure of a monolayer of salt crystals and glass particles, as Fig. 4b shows, was qualitatively different. Since salt crystals and glass particles were both positively polarized, the dipole-dipole forces among them were also repulsive. Thus, in this case, the force between all three particle pairs was repulsive. However, the repulsive force between glass particles was different from that between salt crystals because their sizes were different and also because their intensities of polarizations were different, and so the corresponding inter-particle distances were also different.

Discussion

In conclusion, we have shown that it is possible to perform hierarchical self-assembly of mixtures of particles with different dielectric properties on fluid-liquid interfaces by applying an electric field in the direction normal to the interface. We exploit the fact that the lateral dipole-dipole force between two particles is repulsive when both particles are positively or negatively polarized, but attractive when one particle is positively polarized and the other is negatively. The particles also experience an attractive capillary force that arises because of the net vertical forces acting on the particles which include their buoyant weights and vertical electric forces. The dipole-dipole force varies inversely with the fourth power of the inter-particle distance and the lateral capillary force varies inversely with the distance.
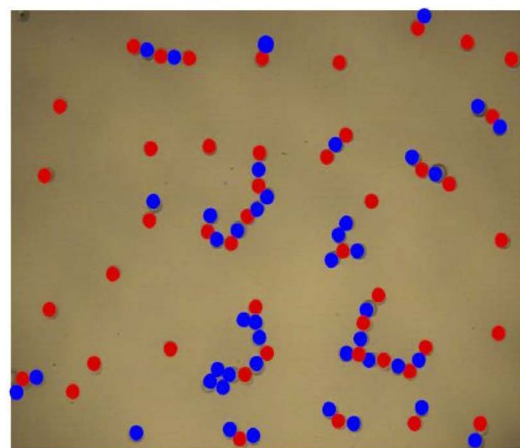
The differences in the polarizabilities and sizes of the particles allow us to vary the relative magnitudes of the inter-particle forces
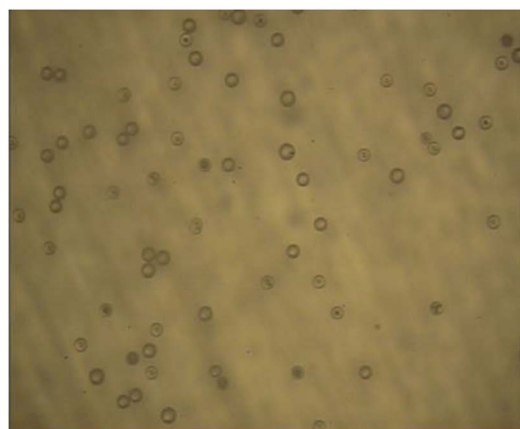
Initial

Final

graphical representation
- 🔴 63 μm glass particles
- 🔵 71 μm copolymer particles

Figure 3 | Monolayers of mixtures of 63 μm glass and 71 μm copolymer particles on the surface of a 30% castor oil and 70% corn oil mixture. The applied voltage was 5000 V. The magnification is 50X. For clarity, a graphical representation of the final monolayer, showing glass and copolymer particles in different colors, is also included. Particle mixtures self-assembled under the action of electric field induced lateral forces into an arrangement consisting of chains in which copolymer and glass particles alternated. The number of particles in the chains varied. Notice that some copolymer particles remained agglomerated.
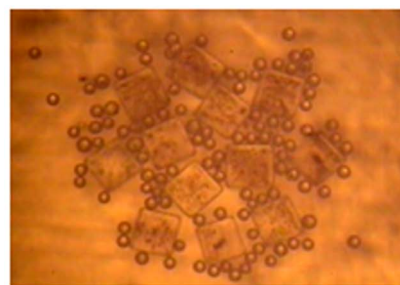
(a)
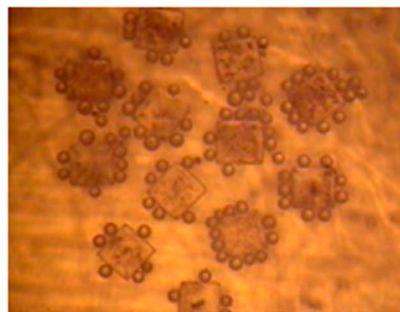
(b)

Figure 4 | Monolayers of mixtures of cubical salt crystals and spherical particles on the surface of corn oil. (Top image) Before the electric field was applied. (Bottom image) After the electric field was applied, the dipole-dipole force caused salt crystals to move apart. (a) Spheres were 71 μm copolymer particles. The dipole-dipole force among salt crystals and copolymer particles was attractive and so the latter formed rings around the salt crystals. (b) Spheres were 63 μm glass particles. The dipole-dipole forces between glass particles were repulsive. Thus, glass particles moved away from salt crystals and also from each other, except those that were agglomerated.

to drive a hierarchical self-assembly process that is analogous to the formation of molecules and their self-assembly in materials. Many different arrangements can be obtained by changing the fluids and particles properties. The technique is applicable to a broad range of particles of various shapes and is suitable for non-magnetic and uncharged particles since it manipulates particles based on their
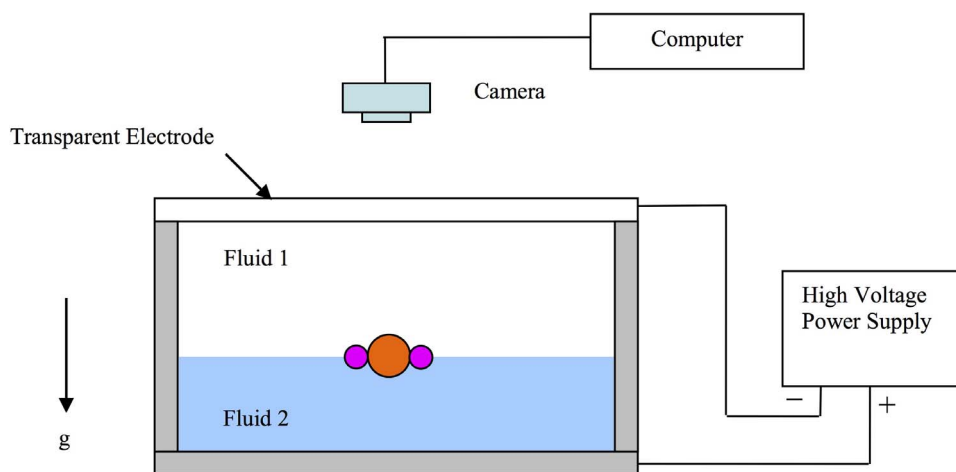
Figure 5 | Schematic diagram of the experimental setup.

dielectric properties. It works for particles trapped in both liquid-liquid and air-liquid interfaces. When the electric field was turned off, the particles used in this study clustered, but clustered slowly and the speed with which they clustered decreased with decreasing particle size. The speed was negligibly small for 20 μm and smaller particles. This was however not the case in the presence of an electric field which induced stronger capillary and dipole-dipole forces. Also, although the self-assembled monolayers do not remain intact after the electric field is switched off, they can be frozen if one of the fluids is solidifiable in which case the monolayer is embedded on the surface of the solidified film[18].

The fluid-liquid interface based platform used here for self-assembling monolayers of mixtures of particles has two advantages. First, it allows us to vary the inter-particle forces and thus the monolayer arrangement for a given mixture, by changing the fluids properties which can be done by selecting suitable upper and lower fluids, and also by changing the electric field intensity. Second, the technique exploits the fact that particles adsorbed in a fluid-liquid interface are free to move laterally, and therefore the equilibrium distance between two particles is independent of their initial positions in the interface. The latter is a consequence of the fact that the attractive force varies inversely with the inter-particle distance and the repulsive force varies inversely with the fourth power of the distance. On a solid substrate, on the other hand, particles cannot move freely because of the presence of frictional and adhesive forces.

Three distinct size dependent regimes were identified for the mixtures of glass and copolymer particles on corn oil. These regimes were also numerically simulated by keeping the particles and fluids properties fixed and only changing the sizes of the particles. When glass particles were about two times larger than copolymer particles, the former attracted copolymer particles to form composite particles. A composite particle consisted of a glass particle at the center which was surrounded by a ring of copolymer particles. The spacing between the composite particles increased with increasing electric field intensity, while the spacing between the copolymer particles of the rings remained unchanged. A second regime was obtained when the size of glass particles was about three times smaller. Although smaller in size, glass particles formed a triangular lattice in which copolymer particles were embedded, as the former were more intensely polarized and repelled each other more strongly. Copolymer particles attracted nearby glass particles to form composite particles. In this regime the intra-composite particle forces were weaker than for the first regime. The particles forming the rings did not touch each other and interacted strongly with the lattice of glass particles. The latter is the reason why some of the glass particles escaped from the rings to occupy positions in the lattice when the field strength was increased above a critical value. A third regime was obtained when

the sizes of glass and copolymer particles were comparable. Here instead of forming ring-like arrangements, particles arranged in chains in which the positively and negatively polarized particles alternated. In some instances, the chains contained sub-branches. This formation of chains is analogous to the formation of long chained polymeric molecules, except that the former were formed by particles in two dimensions on the surface of a liquid.

The technique allows us to modify the hierarchical structure of a monolayer of a given mixture, e.g., the structure of its composite particles and the distance between them, by changing the dielectric properties of the upper and lower fluids which determine the inter-particle forces. In this sense, this study can be considered a preliminary investigation of the possible hierarchical arrangements as many more could be obtained by varying the dielectric properties of the fluids and the particles sizes. Also, for ~20–200 μm sized particles considered in this work, Brownian forces were negligible and so after their adsorption at the interface the particles did not mix. Consequently, the structure of the assembled monolayers depended strongly on the initial distribution of particles. Therefore, for obtaining composite particles with uniform composition, the particles mixture must be uniformly mixed at particle scales. This may not be an issue for nano-particles for which Brownian forces can cause mixing. A study of such smaller sized particles is beyond the scope of the present work.

Methods

A schematic diagram of the setup used to carry out the experiments is shown in Fig. 5. It consists of a circular chamber partially filled with a liquid or two liquids, one atop the other, forming a fluid-liquid interface. The top surface of the chamber was covered with a glass electrode coated with indium-tin-oxide (ITO). The coating made it electrically conducting while remaining transparent which allowed us to visualize the inside of chamber from the top. The bottom surface of the chamber had a copper electrode. A variable frequency ac signal generator (BK Precision Model 4010 A) was used along with a high voltage amplifier (Trek Model 610E) to apply a voltage to the electrodes at a frequency of 100 Hz. In our experiments, the maximum applied voltage was 10 kV, peak-to-peak. The diameter of the chamber was 52 mm and the height was 10 mm. A relatively large diameter of the device ensured that the electric field in the middle of the device where monolayers were formed was approximately uniform and in the direction normal to the liquid surface. The fluid-liquid interface was approximately at one half of the device height. Particles were sprinkled onto the surface of the liquid or placed in the liquids, through which they sedimented (or rose) to the liquid-liquid interface, and then the chamber was covered with the top electrode and the field was applied. The particle positions were recorded using a camera connected to a Nikon Eclipse ME600 microscope.

In the experiments reported in this paper, we used 150, 63 and 20 μm diameter glass particles (MO-SCI Corporation), and 71 μm copolymer particles (Duke Scientific Corporation). In addition to these spherical particles, we used salt crystals which were cubical with sides around 250 μm. The liquids used were corn oil (Mazola, ACH Food Companies), castor oil (Acros Organics) and Silicone oil (Dow Corning, FS1265). We also did experiments on a 30–70% mixture of corn and castor oils. The density and viscosity of corn oil were 0.922 g/cm³ and 65.0 cP, of castor oil were 0.957 g/cm³ and 985.0 cP, and of Silicone oil were 1.27 g/cm³ and 381 cP. The dielectric constant of corn oil was 2.87 and the conductivity was 32.0 pSm⁻¹, for castor oil they were 4.7 and

32.0 pSm^{-1}, and for Silicone oil they were 6.7 and 370 pSm^{-1}. The dielectric constant of glass particles was 6.5 and the density was 2.5 g/cm^3. The dielectric constants of copolymer spheres and salt crystals were 2.5 and 5.8, respectively. The density of salt crystals and copolymer particles were 2.5 g/cm^3 and 1.05 g/cm^3, respectively.

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Acknowledgments

Author contributions

P.S. and I.F. designed experiments. H.M., S.K.G., K.S., E.A., D.J., M.J. and S.N. performed experiments; P.S. and H.M. analyzed data. All authors contributed in the discussion and presentation of the results. P.S. wrote the paper.

Additional information

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