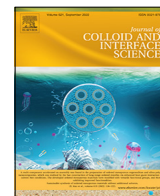




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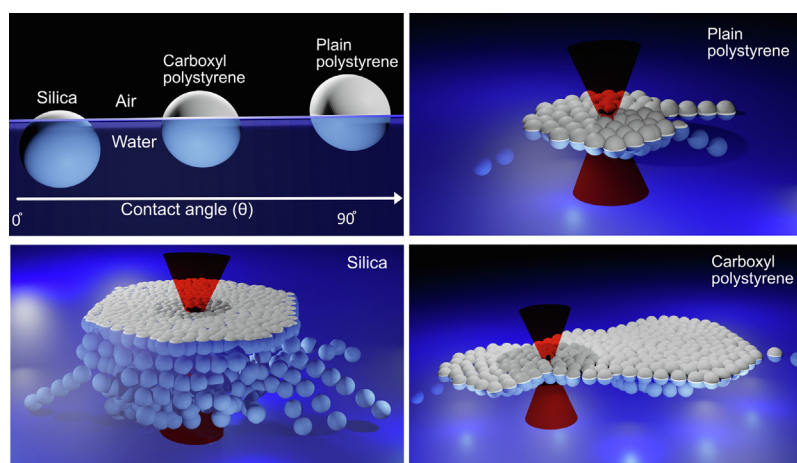
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## Interfacial colloidal assembly guided by optical tweezers and tuned via surface charge

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## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypothesis:** The size, shape and dynamics of assemblies of colloidal particles optically-trapped at an air–water interface can be tuned by controlling the optical potential, particle concentration, surface charge density and wettability of the particles and the surface tension of the solution.

**Experiments:** The assembly dynamics of different colloidal particle types (silica, polystyrene and carboxyl coated polystyrene particles) at an air–water interface in an optical potential were systematically explored allowing the effect of surface charge on assembly dynamics to be investigated. Additionally, the pH of the solutions were varied in order to modulate surface charge in a controllable fashion. The effect of surface tension on these assemblies was also explored by reducing the surface tension of the supporting solution by mixing ethanol with water.

**Findings:** Silica, polystyrene and carboxyl coated polystyrene particles showed distinct assembly behaviours at the air–water interface that could be rationalised taking into account changes in surface charge

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(which in addition to being different between the particles could be modified systematically by changing the solution pH). Additionally, this is the first report showing that wettability of the colloidal particles and the surface tension of the solution are critical in determining the resulting assembly at the solution surface.

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## 1. Introduction

Probing colloidal particles at the microscale with tightly focused laser beams has revolutionised the field of noncontact manipulation of particles in solution [1–4]. This technique is generally referred to as optical trapping or the use of optical tweezers (OT). These capabilities have found applications in various research fields such as studying the biophysical properties of single cells, bacteria, and of single molecules [5–9]. OT have also been utilized in the study of nanoscale entities such as amino acids, lipid membranes, polymers, glycine, and nano-colloidal assemblies [10–13]. Over the years, OT has been expanded to meet the needs of different experimental requirements. Multiple traps can now be formed and manipulated with holographic tweezers, while acoustic optical deflectors (AOD) can be used to oscillate the laser beam at multiple frequencies [14,15].

Recently, there has been increased attention paid to trapping objects not only in the bulk solution but also at different interfaces, namely air/liquid, liquid/liquid, and solid/liquid interfaces [16–18,11,19–21]. Most of these studies show that the assembly of interfacially pinned microscopic particles is induced when a laser is focused at these interfaces. Ordered assemblies can also be generated by introducing a laser through a photonic crystal slab or a plasmonic structure leading to the patterning of particles on the substrate [22–25]. The structure and dynamics of these assemblies have been reported to be dependent on the applied optical potential, the electrostatic repulsion, the local surface tension, and the drive to achieve thermodynamic equilibrium at the interface [11,17,26]. These exciting observations of assemblies at the interface opens up new avenues for colloid scientists working on particles at interfaces. There has been significant research focused on how the mechanism of assembly is related to the applied optical potential, however the effects of particle wettability and surface charge have not been examined.

In this article, the focus is on understanding the assemblies formed at an air–water interface and how this can be tuned by modifying the surface properties of the probe particles. Polystyrene, silica, and carboxyl-coated polystyrene beads were used as probe particles. Crucially, the surface charges of each type of particle are different and each particle type showed unique assembly behaviour at the air water interface. The effect of solution pH is also studied, and the results support the contention that the surface charge is indeed a crucial parameter in controlling optically triggered assembly at the interface. The role of surface tension and the contact angle of the particles (hydrophilicity/phobicity) at the air–liquid interface in directing the formation of the assemblies is also investigated. The understanding developed herein will allow for greater control when exploiting light to manipulate the assembly of particles at fluid interfaces for the fabrication of reconfigurable materials. Along with these interesting fundamental findings, we anticipate that this method for assembling microparticles can have applications in optical crystallization [27], and the binding and optical sorting of microparticles [28,29]. As these microparticle assemblies at the interface also show light scattering and reflectance properties that are dependent on the assembled structure, these assemblies can potentially find uses in light scattering applications. Silica and polystyrene nanoparticles assembled

at the interface can reflect the wavelengths in the visible light spectrum depending on the distance between the particles [30–32].

## 2. Materials and methods

### 2.1. Experimental setup

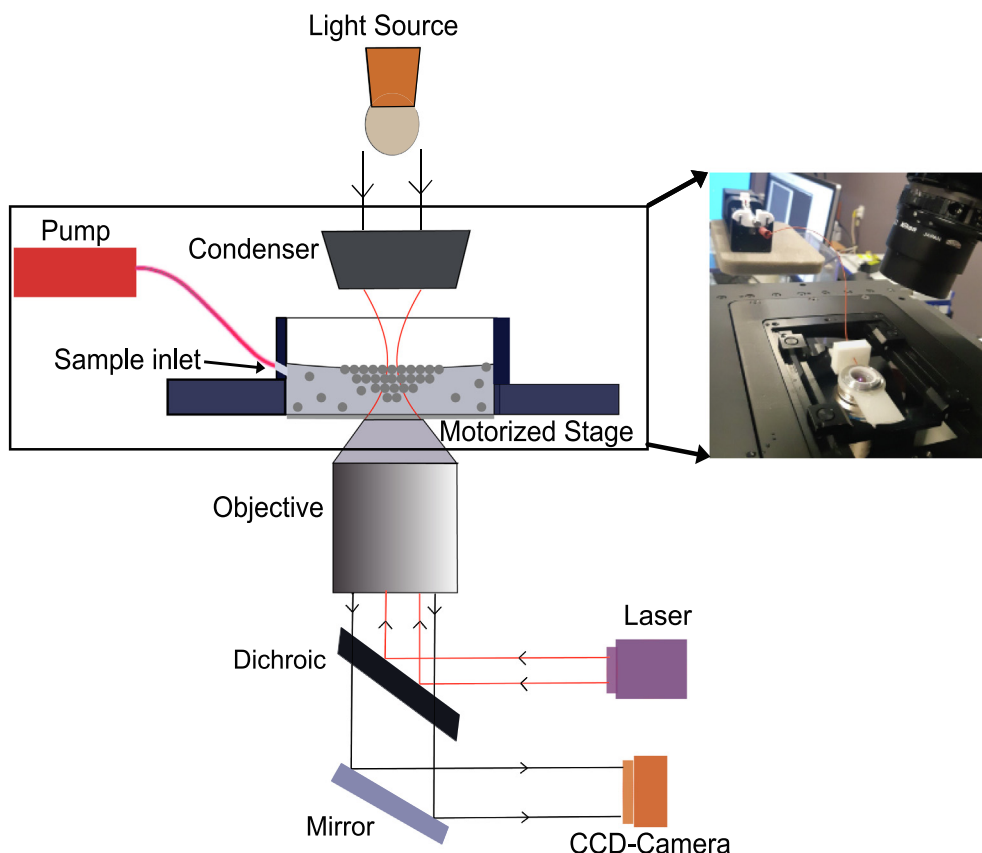
The OT setup was built on an inverted microscope (Nikon Eclipse TE2000-U) with a 60x 1.2NA (Nikon, Plan Apo VC 60x WI) water immersion objective lens, a high precision motorized driven stage (Prior Stage, HLD117) and a CCD camera (Andor Neo). A Nd:Yag Laser (Spectra Physics) of power 1 W at the laser head and a wavelength of 1064 nm was used to optically trap beads. Trap stiffness was calibrated *in situ* by recording the power spectrum of the diffusion of a bead within the trap. The stiffness constant for 1 W laser power at the source was found to be  $(48 \pm 0.9)$  pN/μm on the X-axis and  $(54 \pm 0.7)$  pN/μm along the Y-axis (error represents standard error (SE)). The sample holder used was made from a rectangular aluminium plate with 18 mm diameter holes over which square cover slips were attached at the top and bottom to form a chamber and prevent evaporation. The chamber has a 1 mm inlet hole connected to a tube which was attached to a syringe pump (whiterabbitscientific.com) for introducing samples. This chamber was mounted on a motorized microscope stage. A schematic of the setup is shown in Fig. 1.

### 2.2. Sample preparation

Three probe particles of diameter 1 μm were used, namely polystyrene (Poly Sciences Polystyrene 2.6% solids latex, aqueous suspension), silica (Bang Labs, 10% solids (w/w), aqueous suspension) and carboxyl coated polystyrene particles (Poly Sciences Carboxylate Polystyrene 2.6% solids latex, aqueous suspension). These particles were chosen as they have different contact angles and surface charge properties at air–water interface. The properties of the particles are known from literature and summarised in [supplementary table S1](#). A colloidal suspension was formed by mixing the particles with filtered Milli-Q water (resistivity: 18 MΩ.cm) at 0.040 vol% and sonication (Elmasonic S 10H Ultrasonic Cleaner) at room temperature for 30 min to avoid aggregation of particles. Potassium bisulphate (KHSO<sub>4</sub>) (Sigma, 7646–93–7), an acidic salt, at a concentration of 0.07 M was used to lower the pH of the solution, while sodium hydroxide (NaOH) (Sigma, 1310–73–2) at a concentration of 0.1 M was used to increase the pH of the solution. The pH of the solution was measured using a pH meter (Mettler Toledo).

### 2.3. Optical Tweezers experiments

In all the experiments, 200 μl of colloidal suspension at concentration of 0.040 vol% (volumetric concentration) was injected into a small amount of the same pre-loaded colloidal suspension containing particles in the sample chamber using a syringe pump. As the system is restricted to a very small amount of colloidal suspension due to the focusing limit of the microscope objective used for trapping, for the practicality of the experiment, this small amount



**Fig. 1.** Schematic and experimental optical tweezers setup. Particles assemble at the interface around the optical trap focal point.

of pre-loaded colloidal suspension was added to the chamber using the syringe pump to wet the surface and the edges homogeneously to avoid the solution getting clumped to one side of the chamber. With the addition of the colloidal solution, a thin film with a thickness of approximately  $150\ \mu\text{m}$  was formed (this thickness was known from the  $60\times 1.2\text{NA}$  objective which has a focal length of approximately  $155\ \mu\text{m}$  from the bottom of the coverslip to the air–water interface). The laser power is fixed to  $1\ \text{W}$  at the laser head, corresponding to a  $\approx 100\ \text{mW}$  in the focal plane. In this work, due to laser heating, we estimate that a maximum temperature increase of around  $5\ \text{K}$  may have been induced [33]. The local temperature increases could influence the dynamic of the assembly formation mediated through surface tension changes driving assembly in a Marangoni-type mechanism.

### 3. Results and discussions

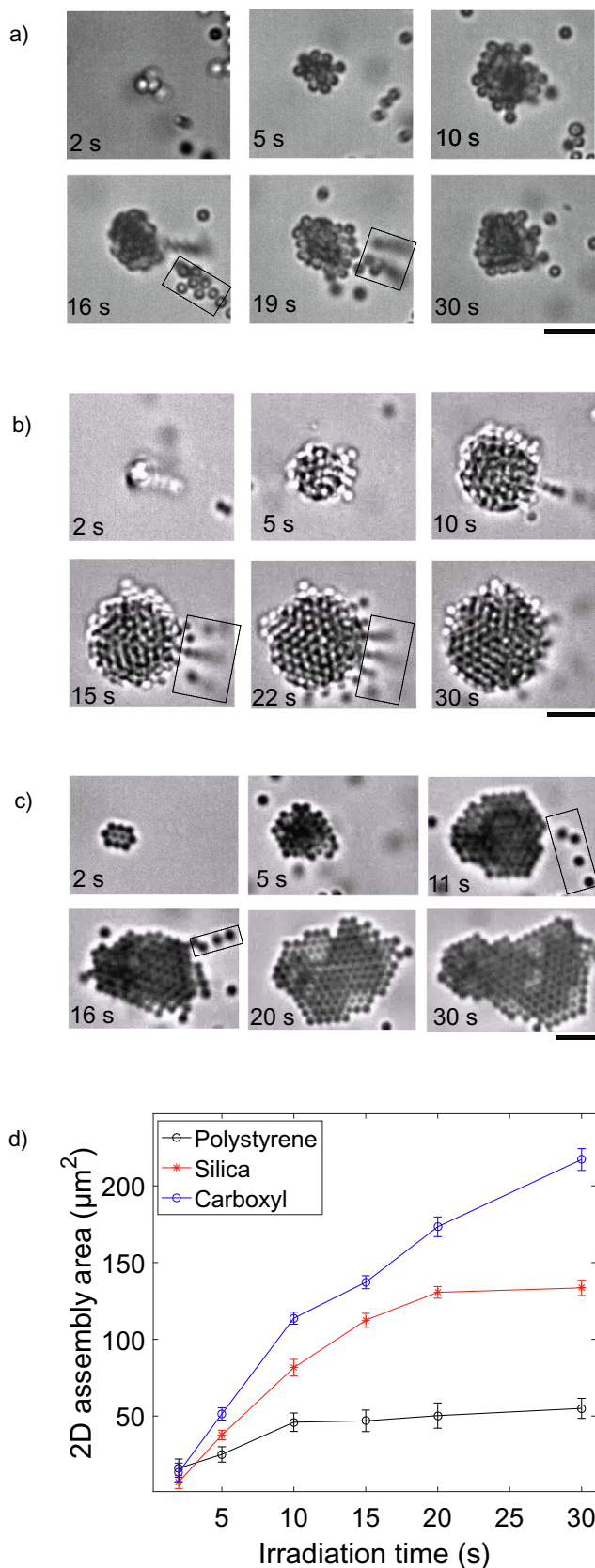
#### 3.1. Assembly of differently charged particles at the air–water interface

Here, the laser trapping behaviour of three different particle types, namely, polystyrene, silica, and carboxyl coated polystyrene particles each  $1\ \mu\text{m}$  in diameter and at a concentration of  $0.040\ \text{vol}\%$  (volumetric concentration) are investigated. In water at the pH of these initial experiments the surfaces of the silica particles are more negatively charged and hydrophilic [34–36], than the polystyrene and carboxyl coated polystyrene beads (carboxyl charge-stabilized hydrophobic polystyrene microspheres). Using a controlled syringe pump, particle solutions were introduced slowly into the chamber at a speed of  $20\ \mu\text{m/s}$ . Once equilibrated with the pump turned off, an intense  $1064\ \text{nm}$  laser beam of laser power  $1\ \text{W}$  ( $\approx 100\ \text{mW}$  at the surface) was subsequently focused at the air–water interface as shown in Fig. 1. Upon irradiation at the

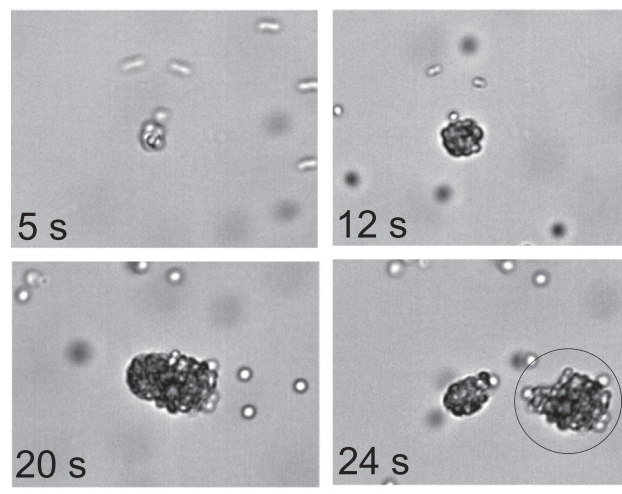
interface, the particles assemble around the laser focal point into aggregates that grow uniformly or non-uniformly depending on the surface charge of the particles. Interestingly, particles do not assemble in the bulk solution but rather on the solution surface, likely due to the high surface tension at the air–water interface [37,38] pinning the particles around the focal point of the trap as shown in [Supplementary material \(Movie - S1\)](#). Aggregates of both polystyrene and silica particles uniformly expand around the focal point going from an approximately circular to a hexagonal arrangement as shown in Fig. 2a and Fig. 2b, respectively. Formed assemblies of polystyrene particles were relatively smaller in 2D area as compared to silica and carboxyl coated polystyrene particles after  $20\ \text{s}$ . The evolution of the 2D area of assemblies as a function of irradiation time is shown in Fig. 2d. Polystyrene and silica particles appear to have a circular or hexagonal assembly, however, in contrast, the carboxyl coated particles (Fig. 2c) show the formation of an ordered structure which expands laterally. The movies of the image sequence shown in Fig. 2 are available in [supplementary information \(Movie - S2, S3, and S4\)](#).

Along with the surface charge of the particles, the three-phase air–water–particle contact angles [39] of these particles are also different at the air–water interface, giving an indication of their different wettabilities. Silica particles are the most hydrophilic giving contact angles much less than  $90^\circ$  compared to plain polystyrene ( $\approx 90^\circ$ ) and carboxyl polystyrene particles ( $\approx 60^\circ$ ) [40–49]. In summary the contact angles are in the following order: silica < carboxyl polystyrene < plain polystyrene particles (shown in the graphical abstract figure). Polystyrene particles have the largest contact angles, of  $90^\circ$ . This means that when they reside at the interface, they are half immersed in water and half immersed in the air. Assemblies of polystyrene particles at the interface appear slightly out of focus compared to the other particles (Fig. 2a),





**Fig. 2.** Image sequence of assembly formation upon laser irradiation at the solution surface for a) polystyrene particles ( $n = 10$ ), b) silica particles ( $n = 11$ ), c) carboxyl coated polystyrene particles ( $n = 8$ ). d) Approximate 2D assembly area for polystyrene, silica, and carboxyl coated polystyrene particles as a function of irradiation laser time. Rectangular insets shows the ejection of particles. Scale bars:  $6\mu\text{m}$ . Error bars represents standard error in mean. 'n' indicates the total number of repeated experiments.



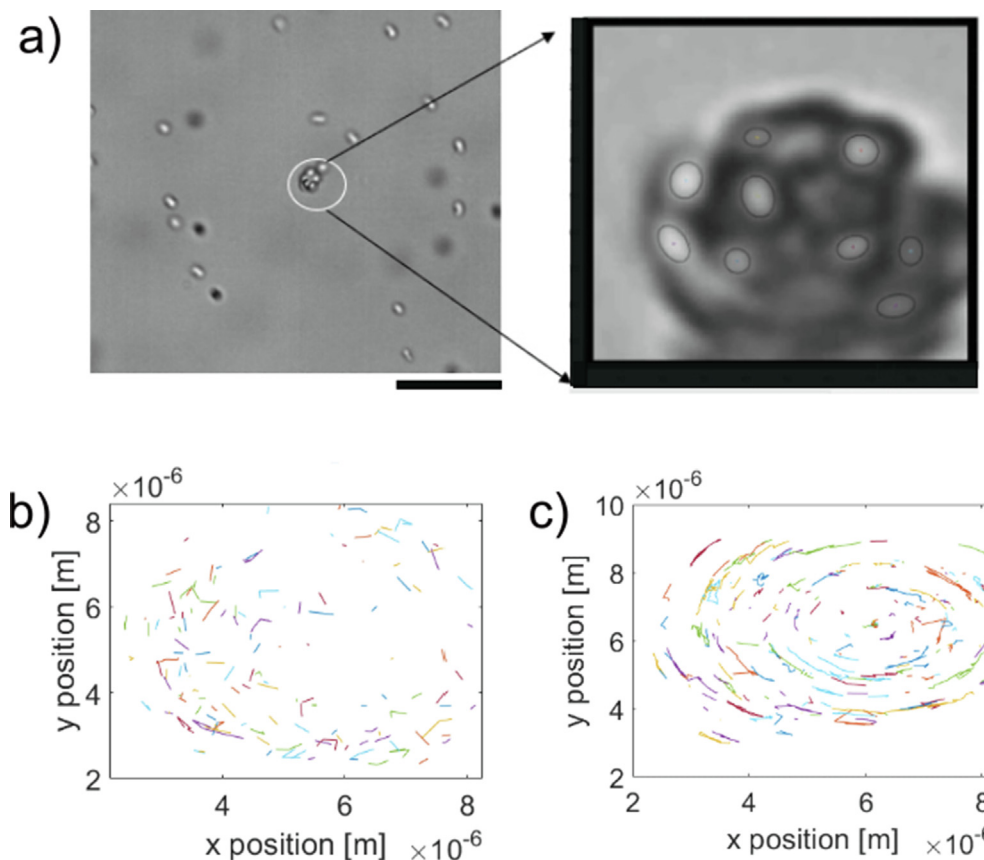
**Fig. 3.** Image sequence of polystyrene particle assembly as  $\text{KHSO}_4$  solution was flown into the chamber (Flow is from left to right of the image). Black circle shows that the particles eject as an assembly of particles.

which is consistent with them protruding out into the air. On the other hand, the silica particles have contact angles much lower than  $90^\circ$ . This means a large fraction of the particle surface will reside in the water (rather than the air). Therefore, the particles sit lower with respect to the interface and the aggregates remain in focus (Fig. 2b). Carboxyl coated polystyrene particles have intermediate contact angles of around  $60^\circ$ . This is close to the contact angle required to maximise froth stability when attaching fine particles to air bubbles in froth flotation [42]. In this case, fine particles are known to form close-packed arrays on bubble surfaces. This is consistent with the observed organised planar arrays formed by the carboxyl coated polystyrene particles when they assemble in the optical potential.

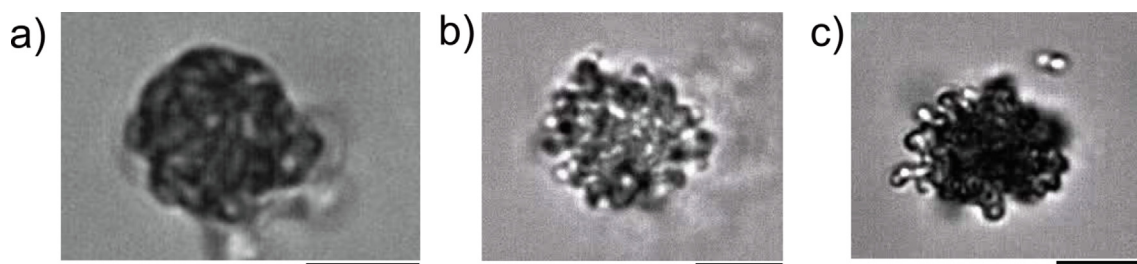
### 3.2. Ejection of particles

As polystyrene and silica particle assemblies move from a circular to hexagonal type of packing, some particles are ejected in a linear manner that has been termed 'pistol-like ejection' [17]. Lu et al. ([17]) describes this phenomenon as a result of new particles colliding with the assembly which in return transfers their momentum resulting in local destabilization and ejection of particles [50] and the acquisition of the thermodynamically favoured hexagonal-like packing assembly. The rectangular boxes shown in Fig. 2a and b highlight the particles being ejected from the aggregates. Polystyrene assemblies eject particles both below the surface (particles ejected below the solution surface are out of focus - Fig. 2a (19 s-frame)) and along the air-water interface (particles ejected are in the focal plane - Fig. 2a (16 s-frame)). Silica particles are more hydrophilic and are wetted to a greater extent by aqueous solutions than polystyrene particles and carboxyl polystyrene particles [51,52], which could be a possible explanation for silica particles preferring to eject into the bulk of the solution rather than along the surface.

Both polystyrene and silica particles are ejected at a similar velocity (Polystyrene -  $43 \pm 8 \mu\text{m/s}$  ( $n = 23$ ); silica -  $40 \pm 9 \mu\text{m/s}$  ( $n = 36$ )) at the same laser power and particle concentration which is consistent with recent literature values ([17]). With an increase in laser irradiation time, silica particles show a compact assembly which maintains a compact hexagonal/cubic shape while polystyrene particle assemblies keep oscillating between circular to hexagonal shapes. In the first 30 s of the laser irradiation time, silica particle assemblies ejected more particles compared to polystyr-



**Fig. 4.** Multiple particle tracking (MPT) of polystyrene particle assemblies at the focal point. a) The inset shows the region where the particles (multiple black circles) are tracked. Scale bar:  $20\mu\text{m}$ . b) MPT for control polystyrene particle assemblies. c) MPT for polystyrene particles assembly in  $\text{KHSO}_4$  solution. Multiple colours indicate multiple particles tracked in a span of time and x-y coordinates shows the position of the particles.



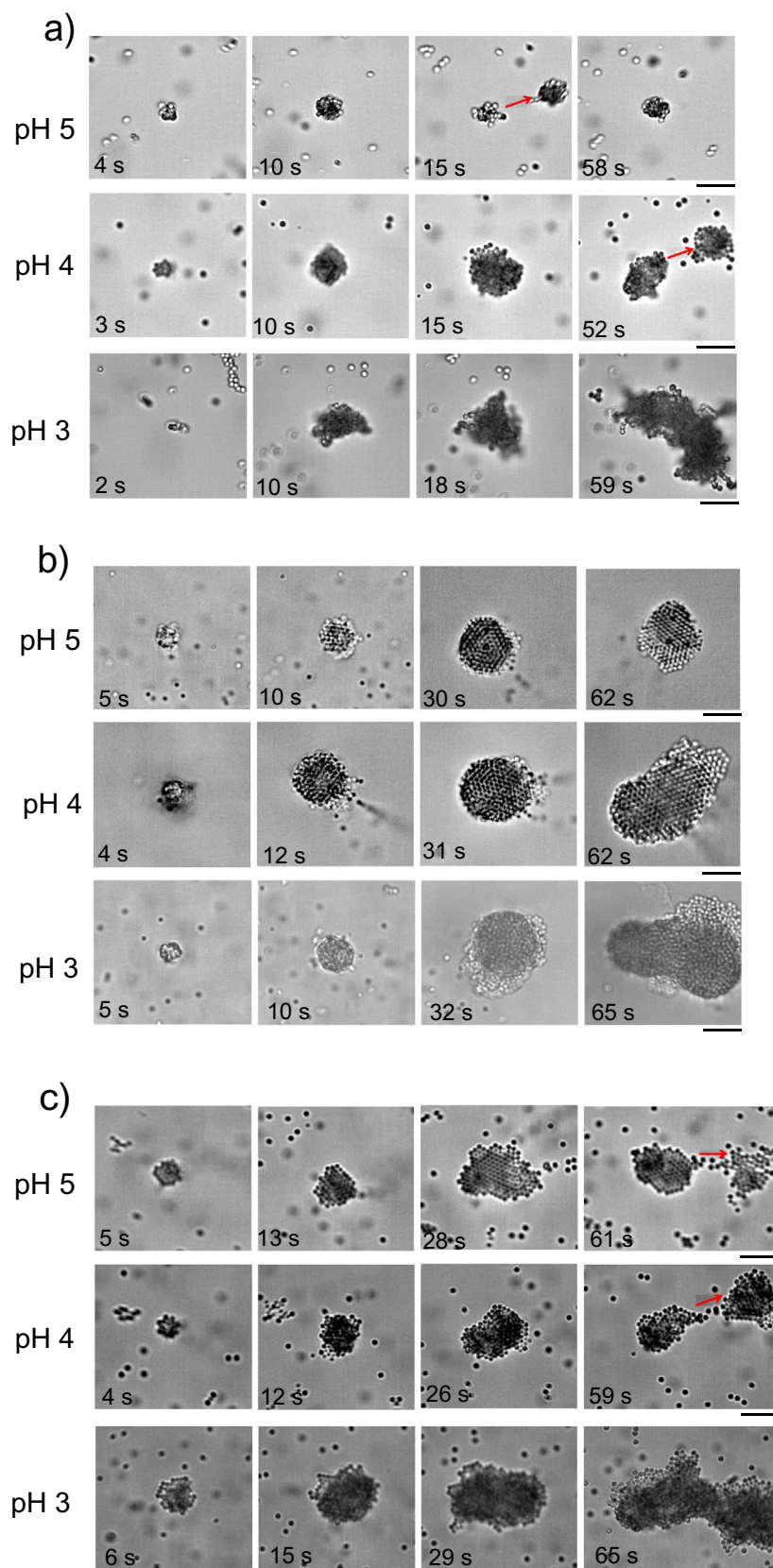
**Fig. 5.** Particle assembly in  $\text{KHSO}_4$  solution for a) Polystyrene, b) Silica and c) Carboxyl polystyrene particles. Scale bars:  $10\mu\text{m}$ .

ene particles (Movie - S2, S3), consistent with the fact that the assembly size of the silica particles is larger. Contrastingly, carboxyl coated beads did not have pistol-like ejections compared to polystyrene and silica particles. As reported by Lu et al., particles are ejected when the assembly moves from an unstable shape to a more ordered shape. The carboxyl coated particles assemble into a structure within a few seconds of irradiation. The arrangement of the particles in the structure changes from a single hexagonal layer to multiple, layered hexagonal shape similar to opal-like structures (Fig. 2c - 2s frame). Hence, ejections of particles are not observed as in comparison to silica and polystyrene particle assemblies. However, particles do detach from the assembly, albeit at a relatively slow rate as shown in the rectangular box in Fig. 2c.

### 3.3. Particle assemblies in different physical environments

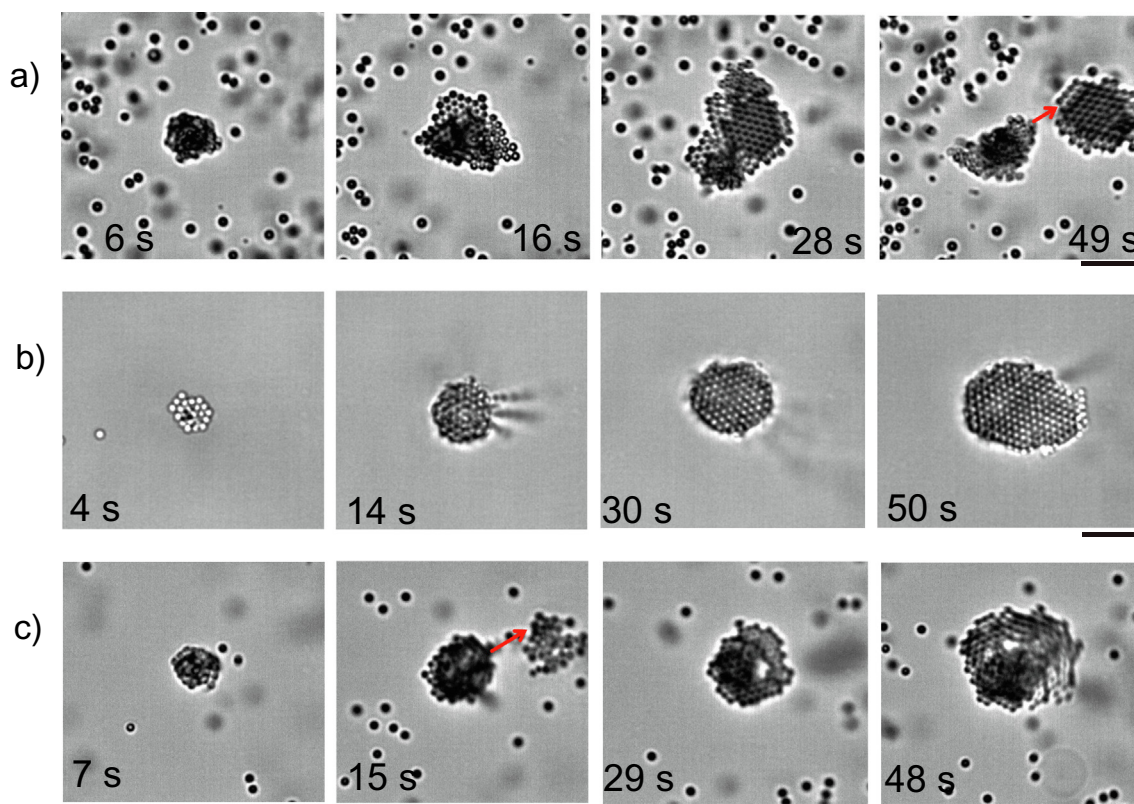
The particle assembly depends on parameters such as optical potential (created by the optical trap around the focal point), elec-

trostatic repulsion among the particles, the properties of the solution surface, and the drive for thermodynamic equilibrium [11]. We have shown in Fig. 2 that depending on the surface charge of the particles and hence the strength of their electrostatic interactions with each other, these particles form different types of assemblies around the focal point of the optical trap. To investigate whether surface charge was indeed playing a role in the assembly, the pH of the solution was systematically changed. This was used to modulate the surface charge of the particles by going above or below the  $\text{pK}_a$  of the charged groups on the particle surfaces. Firstly, an acidic salt solution ( $\text{KHSO}_4$ ) as described in Section 2.2 was used to lower the pH of the solution. In neutral Milli-Q water solution, the particles disperse as soon as the laser is turned off. However, when the pH is lowered (pH 1–3), the electrostatic repulsion between the particles decreases and the surface charge of all particles (Silica, polystyrene, and carboxyl) should have a minimum effect in these assemblies.



**Fig. 6.** Particle assembly at fixed pH 3, 4 and 5 using KHSO<sub>4</sub> solution for a) Polystyrene, b) Silica and c) Carboxyl polystyrene particles. The red arrows indicate detachment of particles from the assembly. Scale bars: 10 μm.





**Fig. 7.** Assembly dynamics on using surface tension using ethanol - water mixture for a) Polystyrene, b) Silica and c) Carboxyl coated polystyrene particles. The red arrows indicate detachment of particles from the assembly.

Using a syringe pump as described in Section 2.3, 50  $\mu\text{l}$  of  $\text{KHSO}_4$  (0.07 M) solution was added into a chamber containing 100  $\mu\text{l}$  of Milli-Q water-particle solution. The pH of this mixture was measured before the OT experiments were done. The pH reduced from 7 to 1.5 in approximately 20 s. This was an important observation as the  $\text{KHSO}_4$  solution was slowly introduced into the sample chamber. The flow was stopped and the optical trap laser was turned on after approximately 30 s, giving time for the solution to become stable and for focusing at the air-water interface. Fig. 3 (Movie - S5) shows the image sequence of assembly formation in the presence of  $\text{KHSO}_4$  solution (at low pH). It shows that the particles tend to cluster and stick to each other ejecting compact assemblies instead of dispersing into the medium as shown in Fig. 2a. Similarly on switching the trap off, the particles do not disperse but remains clustered. To examine how the particles in the assembly are interacting with each other, assembled particles were tracked at the trap focal point for both control (Milli-Q solution) and  $\text{KHSO}_4$  solution using the polyparticle tracker algorithm [53].

Fig. 4a shows how the technique of Multiple Particle Tracking (MPT) is used to track particles that have assembled around the trap focal point. MPT of the control polystyrene particle in Fig. 4b shows that the particles are quickly exchanged. This suggests that the particles are replaced by new particles, which is also evident by observing movie S2. However, MPT for the polystyrene particles in  $\text{KHSO}_4$  solution shows longer periods of tracking in comparison to control particles which shows that the particles are not replaced. Interestingly, the MPT of these assemblies (Fig. 4c) shows that the whole assembly rotates (resembling a vortex). Silica and carboxyl coated particles show a similar behaviour as compared to polystyrene particles (Fig. 5a) where the assemblies tend to cluster and rotate at the trap focal point as shown in Fig. 5 (b and c).

All the above experiments in  $\text{KHSO}_4$  solution were carried out within a few minutes of the addition of  $\text{KHSO}_4$ . However, if we wait for longer times, the particles assemble into long chain-like structures (Movie - S6). Detailed pH measurements were carried out by making solutions with a fixed pH (pH - 3, 4, 5) using a  $\text{KHSO}_4$  solution as shown in Fig. 6. To check that the pH of the solution did not alter over time, the pH of  $\text{KHSO}_4$  solution was monitored for two days using a pH meter, before experiments were carried out. At pH 5 and 4, polystyrene and carboxyl coated polystyrene particles tend to detach from the assembly with time (leaving the assembly as a cluster) as shown by the red arrows in the figure, whereas the assembly of silica particles increases with time and maintains this assembly area by ejecting particles (similar to control experiments). Moreover it is evident that on lowering the pH, the assembly of polystyrene and carboxyl coated polystyrene particles increases, consistent with the pH-induced reduction of electrostatic repulsion between particles showing an increased propensity for aggregation. Similar pH-dependent aggregation behaviour of carboxyl particles in colloidal suspensions has been reported by Behrens et al. [54]. On further lowering the pH to 3, the assembly of all three different particle types grows into chain like structures with increasing laser irradiation time ( $> 50$  s). Interestingly, at an irradiation time greater than 60 s, all three different particles show distinct chain-like structures.

This observation was also very similar when pH was increased (pH 11) using NaOH solution as shown in Supplementary information (Movies - S7, S8 and S9). These structures can extend up-to hundreds of micrometers. This demonstrates that surface charge does play an important role in the assembly behaviour. Dasgupta et al. [55] emphasizes how surface tension also plays a major role in assembly formation. Laser induced heating also changes the local surface tension around the optical trap which could also be a contributing factor to assembly formation [56].

### 3.4. Assembly of particles by tuning surface tension

As Dasgupta et al. [55] showed that surface tension is also an important parameter in assembly formation, we tuned the surface tension by mixing ethanol and water. A mixture (5% ethanol in water by weight) was preprepared which decreases the surface tension from 72.75 mN/m to 56.41 mN/m (at 20°C) as reported by Vazquez et al. [57]. On decreasing surface tension the assembly dynamics of these particles are altered as shown in Fig. 7. The polystyrene particles exhibit an ordered structure as shown in Fig. 7a, which on detachment (49 s, Fig. 7a) from the main assembly retains this order. Silica particles showed similar features as compared to control experiments (Fig. 2b) at similar irradiation time, however at times greater than 45 s the assembly changes to a more egg-shaped structure (Fig. 7b, 50 s). Carboxyl coated polystyrene particles lose their extremely ordered structure to a more hexagonal shape as observed in Fig. 2c.

The addition of ethanol to water effectively reduces the contact angles of the particles. In the case of the silica particles, which are almost fully wetted, this has a negligible effect on the aggregate structure. It seems that the contact angle of the plain polystyrene particles approaches the optimum value for attachment to the liquid surface, as they assemble into highly ordered aggregate structures. On the other hand, assemblies of the carboxyl latex particles are less ordered than those formed in the absence of ethanol. This suggests that the contact angle of the carboxyl latex particles is significantly lower than 60°.

## 4. Conclusion

Building on previous studies of colloid assembly by optical trapping [11,16–21], this article reveals the central role of the particle surface properties. This is the first report to show different assembly behaviour for the same environmental conditions, but with systematic variations in surface charge and wettability. By comparing the behaviour of polystyrene, silica and carboxyl-coated polystyrene particles, the surface properties for assembling highly ordered structures were identified. Polystyrene and silica particles show pistol-like ejection (similar to that reported by Lu et al. [17]) when moving to an ordered structure, however, the carboxyl coated particles remain highly ordered showing minimal ejections. By moving away from the pH value of 7 (neutral), the electrostatic interaction between particles decreases, causing the particles to aggregate around the optical trap similar to amino acid crystallization upon irradiation with a laser [13,10,58]. Reducing the surface tension by mixing the aqueous solution with ethanol [57] also affects the assembly dynamics of these particles by modifying their contact angles. A substantial amount of modelling based on the DLVO theory and using SEI (Surface Element Integration) has been applied in order to understand the interaction forces between pairs of particles in a bulk solution. It is worth noting that even standard DLVO theory is not effective in describing ordering processes involving multiple particles such as the evolution of colloidal crystals and cannot explain the dependence on salt concentration [59].

Interaction forces between particles at an air–water or liquid–liquid interface are not considered in the basic DLVO theory [60–65]. Pieranski [37] proposed an additional electrostatic repulsion of the particles due to the formation of dipole moments directed perpendicular to the air–water interface while Danov et al. [66] and Stamou et al. [67] proposed that immersion capillary forces and flotation forces appear between particles due to the formation of an irregular meniscus at the air–water interface, resulting in attractive forces which extend to several hundreds of nanometers. They suggest that these forces are jointly responsible for the two-dimensional crystallization of particles leading into highly ordered

hexagonal colloidal aggregates. Martinez-Hidalgo et al. have modelled the total energy between two colloidal particles at an interface by considering the impact of capillary, dipolar, hydrophobic and DLVO interactions [68]. However, these models do not consider multiple particles or the impact of an optical trap on the behaviour of particles at interfaces. To quantitatively model the behaviour of particles optically trapped at an air–water interface all the previously mentioned variables should be included together with those characterising the optical trap, and their spatial dependencies. In the future, our intention is to extend the model developed by Martinez-Hidalgo et al. [68] to predicting the interactions between multiple particles that are optically trapped at an interface.

Further work aims to look at the dynamics of assembly formation in three dimensions and use backscattered light to gain insights on the homogeneity of the different packing structures.

### CRediT authorship contribution statement

**Susav Pradhan:** Conceptualization, Methodology, Formal Analysis, Investigation, Writing – Original Draft. **Catherine P. Whitby:** Conceptualization, Methodology, Writing – Review & Editing, Supervision. **Martin A.K. Williams:** Conceptualization, Writing – Review & Editing, Supervision. **Jack L. Y. Chen:** Conceptualization, Writing – Review & Editing. **Ebubekir Avci:** Conceptualization, Funding acquisition, Writing – Review & Editing, Supervision, Project administration.

### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Ebubekir Avci reports financial support was provided by The MacDiarmid Institute for Advanced Materials and Nanotechnology.]

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcis.2022.04.044>.

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