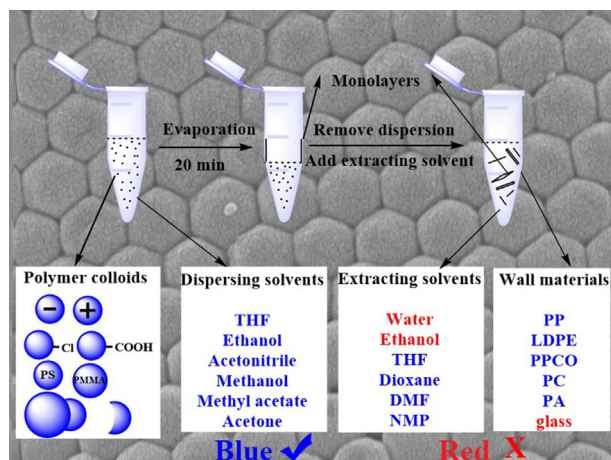


Regular Article

Fabrication of floating colloidal crystal monolayers by convective deposition

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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Well-defined two-dimensional colloidal crystal monolayers (CCM) have numerous applications, such as photonic crystal, sensors, and masks for colloidal lithography. Therefore, significant effort was devoted to the preparation of preparing CCM. However, the fabrication of CCM that can float in the continuous phase and readily transfer to other substrate remains an elusive challenge.

Experiments: In this article a facile approach to prepare floating CCM from polymeric colloids as building blocks is reported. The key to obtain floating CCM is the selection of an appropriate solvent to release the formed CCM from the substrate. There are two steps involved in the preparation of floating CCM: formation and peeling off.

Findings: First, colloids are dispersed in a solvent. Evaporation of this solvent results in the formation of a meniscus structure of the air–liquid interface between the colloids that are on the substrate. The deformation of the meniscus gives rise to capillary attraction, driving the colloids together in a dense monolayer. Once a crystallization nucleus is formed, a convective flow containing additional colloids sets in, resulting in the formation of CCM on the substrate. Second, the remaining bulk dispersion is replaced by an extracting solvent that wets the substrate and peels the formed CCM off. The influence of the

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several solvents, the substrate materials, and the types of colloids on the CCM formation are investigated systematically. The robustness of the approach facilitates the preparation of CCM. Furthermore, the floating feature of the CCM in principle makes transfer of the CCM to other substrates possible, which broadens its applications.

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1. Introduction

Colloidal lithography is a powerful tool to prepare two-dimensional ordered nanostructures, which have potential applications in the areas of photonics, plasmonics, sensing, and solar cells [1–4]. Colloidal crystal monolayers (CCM) are the templates for colloidal lithography [5–9]. Therefore, numerous effort has been devoted to assembling colloids into CCM. The methods developed up to now include convective deposition [10], drop casting [11], spin coating [12], and electrophoretic deposition [13]. However, the major drawbacks of the aforementioned methods are the requirement of (super-)hydrophilic substrates onto which colloids assemble, and the difficulty to transfer the formed colloidal crystals to other substrates. Therefore, a variety of approaches have been attempted to prepare floating CCM [14–18]. As the term suggests, floating CCM are not attached to a substrate but can freely float in the continuous phase. The most commonly employed approach to prepare floating CCM are the liquid interface mediated methods. Instead of using solid substrates like glass and mica, a liquid interface is used in these methods, such as gas–liquid interface and liquid–liquid interface [14–16]. For example, Kondo et al. [16] obtained floating CCM by first spreading monodisperse hydrophobic alkoxy chains coated silica particles at the air–benzene interface and subsequent picking the formed monolayer up with a mica substrate. However, to increase the ordering and packing density in monolayer by the liquid interface mediated methods, the control of the hydrophobicity of colloids [16], the utility of Langmuir–Blodgett trough [19] or the addition of various polymers [20] or surfactants [21] are usually required. Besides the commonly employed liquid interface mediated methods, other methods have been reported. Ramos et al. uses a surfactant-mediated method to prepare floating CCM [17]. By mixing aqueous charge-stabilized polystyrene latex particles with a mixture of an oppositely charged and a neutral surfactant which self-assembled into vesicles, 2D colloidal crystal monolayers were formed on the vesicles. In that system, besides 2D colloidal crystal monolayers, there also were many free particles and random clusters present. Furthermore, the requirement of two types of surfactants as well as the formation of vesicles makes the system complicated and difficult to improve. Tang et al. reported the spontaneous formation of floating CCM of CdTe nanoparticles with tetrahedral shape. The authors ascribed the formation of floating CCM to a combination of electrostatic repulsion and anisotropic hydrophobic attraction [18]. However, the requirement of anisotropic shape limits the potential applications of this method. In addition, optical binding can be another tool to prepare floating CCM which required complicated optical experimental setup and was limited to very small numbers of colloids [22,23].

As mentioned before, convective deposition is a widely employed method to prepare CCM. In a classical convective deposition, (super-)hydrophilic substrate is inserted into an aqueous colloidal dispersion and subsequent slowly withdrawn out of the dispersion. The colloids nucleate at the drying front *via* attractive capillary interactions. Once a crystallization nucleus is formed, a convective flow sets in that contains additional colloids, resulting in the formation of CCM [10]. In this article, a modified convective deposition method to prepare floating CCM is presented. As

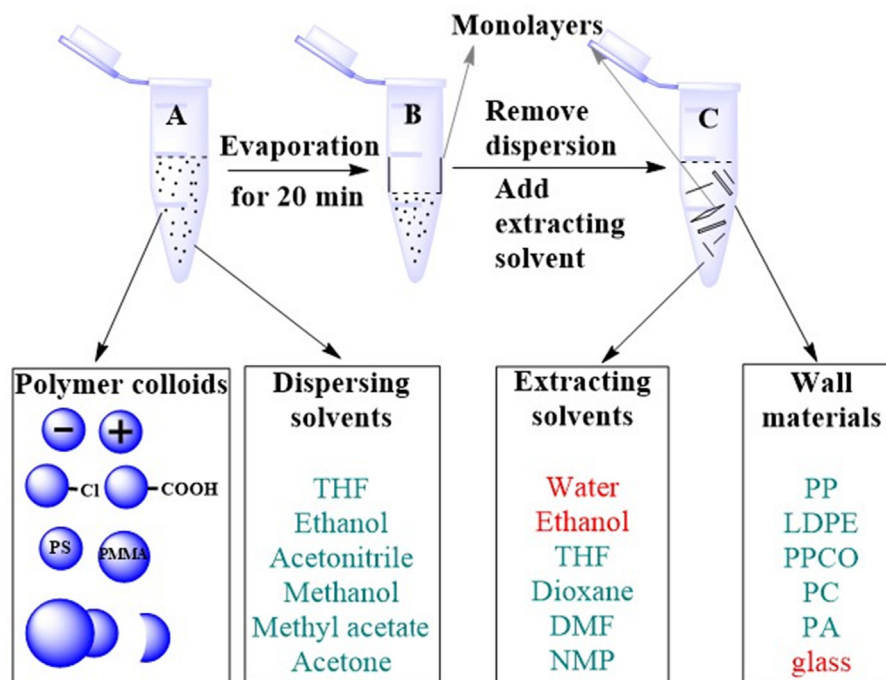
illustrated in Scheme 1, cross-linked polymeric colloids are first dispersed in a volatile dispersing solvent. Instead of withdrawing the substrate out of dispersion, we let the solvent evaporate for approximately 20 min in a fume hood. During evaporation, monolayers are formed onto the inner wall of the centrifugal tube. After removal of the remaining bulk dispersion, an extracting solvent is added. Subsequently, the formed monolayers are peeled off by manual shaking, and eventually dispersed in the extracting solvent. There are three crucial differences between the method reported here and earlier reported procedures that make use of convective deposition. The first difference is the dispersing solvent. While water is generally the solvent of choice, here volatile organic solvents are used which apparently accelerates the formation of CCM. Second, the hydrophobic inner wall of the centrifugal tube instead of (super-)hydrophilic glass is used as a substrate, hence the tedious pretreatment of the substrate is avoided. The last and most important difference is that by using the method present here, CCM can be easily peeled off, and freely float in the dispersion, which is ascribed to the use of appropriate extracting solvents.

In this work, we first demonstrate that using our new method, the formed assemblies are indeed monolayers and these monolayers can freely float in the dispersion. Subsequently, we systematically investigate the experimental parameters in terms of the dispersing solvent, the extracting solvent, the wall materials, and the colloid on the formation of the floating CCM. Eventually, a possible mechanism is proposed which includes CCM formation and peeling off: the CCM formation step involves the capillary attractions that originated from the deformation of a meniscus structure of the air–liquid interface between the colloids, while the CCM peeling off is caused by the penetration of the extracting solvent into the gap between the CCM and the substrate.

2. Experimental section

2.1. Materials

Styrene (St, 99%), divinylbenzene (DVB, 55% mixture of isomers, tech. grade), 1-(chloromethyl)-4-ethenylbenzene (VBC, $\geq 90\%$, tech. grade), acrylic acid (AA, 99%), methanol (anhydrous, 99.8%), *N,N*-dimethylformamide (DMF, $\geq 99\%$), acetone (AR, $\geq 99.5\%$), methyl acetate (anhydrous, 99.5%), acetonitrile (GC, $\geq 99.5\%$), 1,4-dioxane (DOX, ACS reagent, $\geq 99.0\%$), 1-methylpyrrolidin-2-one (NMP, anhydrous, 99.5%), 1-ethenylpyrrolidin-2-one (PVP, K30, $M_w = 40$ kg/mol), polyvinyl alcohol (PVA, $M_w = 85$ – 124 kg/mol, 87–89% hydrolyzed), poly(acrylic acid) (PAA, $M_v \approx 450$ kg/mol) were obtained from Sigma-Aldrich. Sodium dodecylsulfate (SDS) was purchased from BDH. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%), oxolane (THF, for analysis, ACS reagent), sodium hydrogen sulfite (NaHSO₃, ACS reagent) and potassium persulfate (KPS, >99% for analysis) were purchased from Acros Organics. Ethanol (p.a., ACS reagent) was purchased from Merck. 2,2'-Azobis(2,4-dimethylvaleronitrile) (V65) was purchased from Wako chemicals GmbH. All of the chemicals were used as received. The water used throughout all of the experiments was purified using a Milli-Q water purification system.



Scheme 1. Schematic illustration of the proposed method to prepare two-dimensional floating colloidal crystal monolayer (CCM). (A) Colloids disperse in a dispersing solvent. (B) CCM are formed onto the wall of the centrifugal tube after evaporation of the dispersing solvent. (C) CCM are peeled off and freely float after the remaining bulk dispersion is replaced by the extracting solvent. Red color indicates that no CCM are observed in those samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Synthesis of negatively charged chlorinated polystyrene nanospheres (CPS-Cl) [24]

CPS-Cl were synthesized by seeded emulsion polymerization. A 500 mL round-bottom flask equipped with a magnetic stir bar was placed in an oil bath of 80 °C. Water (200 mL) was charged into the reactor and allowed to reach the bath temperature. Styrene (23 mL, 0.2 mol), DVB (0.7 mL, 5 mmol), and SDS (0.125 g, 0.45 mmol) dissolved in water (50 mL) were added. The complete mixture was allowed to heat up to the temperature of the bath. Polymerization was initiated by the addition of KPS (0.780 g, 2.8 mmol dissolved in 37.5 mL water). The reaction was allowed to continue for 24 h. The obtained particles were used as seeds for the preparation of CPS-Cl. The above crude emulsion (25 mL) and water (10 mL) were introduced into a 50 mL three-neck round-bottom flask equipped with a magnetic stir bar. The dispersion was bubbled with nitrogen for 30 min at room temperature. Subsequently, VBC (1 mL, 7 mmol) mixed with DVB (20 μ L, 0.14 mmol) was injected in the flask under an inert atmosphere. The seeds were swollen for 1 h, after which the temperature was raised to 60 °C. Subsequently, the initiator solution containing KPS (0.040 g, 0.15 mmol), sodium hydrogen sulfite (0.03 g, 0.3 mmol) and water (2.5 mL) was injected. The reaction was stopped after 4 h. The final product was washed with ethanol and water twice, respectively. Finally, the particles were stored in water.

2.3. Preparation of floating colloidal crystal monolayers

Scheme 1 illustrates the formation process of the floating colloidal crystal monolayers. Typically, an aqueous colloids dispersion (10 μ L, solid content = 5 wt%) and water (190 μ L) were added into a 1.5 mL centrifugal tube (Eppendorf Safe-Lock Tubes, colorless) and

centrifuged, the supernatant was removed and 200 μ L of the appropriate solvent was added to re-disperse the particles. Subsequently, the centrifugal tube with colloidal dispersion was put in a fume hood with the centrifugal cap open for approximately 20 min. Afterwards, the remaining bulk dispersion was removed and THF (200 μ L) was refilled. After manual shaking, the dispersion was transferred to a capillary (0.20 mm \times 2.00 mm internal dimensions, Vitrotubes). The filled capillary was placed on a microscope slide (Menzel-Gläser), sealed with high vacuum grease (DOW Corning, Sigma-Aldrich) and fixated using tape. Finally, the sample was examined with an optical microscope.

2.4. Characterization

Transmission electron microscopy pictures were taken with a Philips Tecnai 10 electron microscope typically operating at 100 kV. The samples were prepared by drying a drop of diluted aqueous dispersion on top of polymer-coated copper grids. In order to freeze-dry TEM samples, 1 μ L dispersion was placed on top of a polymer coated copper grid. The grid was vitrified in liquid nitrogen and mounted onto a cryo-transfer unit which was brought under vacuum (10^{-4} Pa). The temperature was increased to -90 °C at 5 °C/min and kept constant for roughly 6 h under vacuum to allow the water to sublime.

Scanning electron microscopy (SEM) images were taken with a Philips SEM XL FEG 30 typically operating at 5–10 kV. The dried samples of particles were sputter-coated with platinum (thickness = 6 nm) prior to imaging.

Optical microscopy (OM) images were taken with a Nikon Ti-E inverted microscope. The microscope was equipped with a Nikon Plan Fluor ELWD 10 \times , 40 \times air immersion objectives, and a Nikon TIRF NA 1.49 100 \times oil immersion objective, intermediate magnification of 1.5 \times , and a Hamamatsu ORCA Flash camera.

3. Results and discussion

3.1. Experimental proof of floating CCM

Chlorinated cross-linked colloids, further abbreviated as CPS-Cl, with a diameter of 418 ± 8 nm and a zeta potential of -38 ± 4 mV were first used as the building blocks. The colloids were synthesized by seeded emulsion polymerization and fluorescent labeling in combination with confocal microscopy indicates that the particles are chemically isotropic (S2, Supporting Information). THF was introduced as both the dispersing solvent and the extracting solvent for CPS-Cl, which were kept in a centrifugal tube made of polypropylene (PP). The colloidal dispersions were extensively (ultra) sonicated to avoid aggregation, as random colloidal aggregates may cause disorder, which eventually results in the formation of cracks and multiple layers [10]. After evaporating THF for approximately 20 min in a fume hood, we directly shook the centrifugal tube manually to re-disperse the formed assemblies. Fig. 1a and 1b show the optical microscopy images of a colloidal dispersion at different times. Clearly, the colloidal assembly is two-dimensional which can freely move and rotate in the continuous medium. In a closer view, the individual particles can clearly be distinguished in Fig. 1b, revealing the monolayer feature of the formed colloidal assembly. The monolayer feature was further confirmed by scanning electron microscopy (SEM). The SEM sample of the assemblies was prepared by first transferring the assemblies into water, followed by drying under atmospheric condition. As shown in Fig. 1c, from the curved edge of the colloidal assembly we can clearly see the colloidal assembly is a monolayer. In

Fig. 1c, locally, bilayers seem to have formed. However, this has hardly been seen in optical microscope images. We hypothesized that the bilayer parts shown in Fig. 1c were formed during the drying stage in the sample preparation for electron microscopy. Furthermore, Fig. 1d shows that a number of CCM can be prepared in one batch. Roughly, there are 200–500 CCM per mm^2 , which varies among different samples. The formed CCM are quite polydisperse in size, with typical dimensions in between roughly $25 \mu\text{m}^2$ and $10,000 \mu\text{m}^2$ (S3, Supporting Information). The shape of these CCM is irregular, and sometimes curved monolayers are observed. Both the size polydispersity and the shape irregularity can be ascribed to the mechanical force generated during the re-dispersion process. Additionally, Fig. 1 also shows that the colloids in the CCM are mostly hexagonally close-packed. The formation of close-packed colloidal crystals rules out that pinning of the particles onto the substrate plays a role, since pinning would lead to random aggregates and certainly not (close-packed) crystalline sheets. These results show that close-packed floating CCM are prepared.

3.2. Influence of dispersing solvent

In the first set of experiments, THF was used as the dispersing solvent but under different temperatures. Centrifugal tubes with particles dispersed in THF were placed in water baths with temperatures of 30°C , 40°C , 50°C , and 60°C , respectively. As shown in Fig. 2, CCM were obtained in all of the four samples after the same evaporation time of 20 min. Moreover, no significant differences in terms of shape and size of the formed CCM were observed among

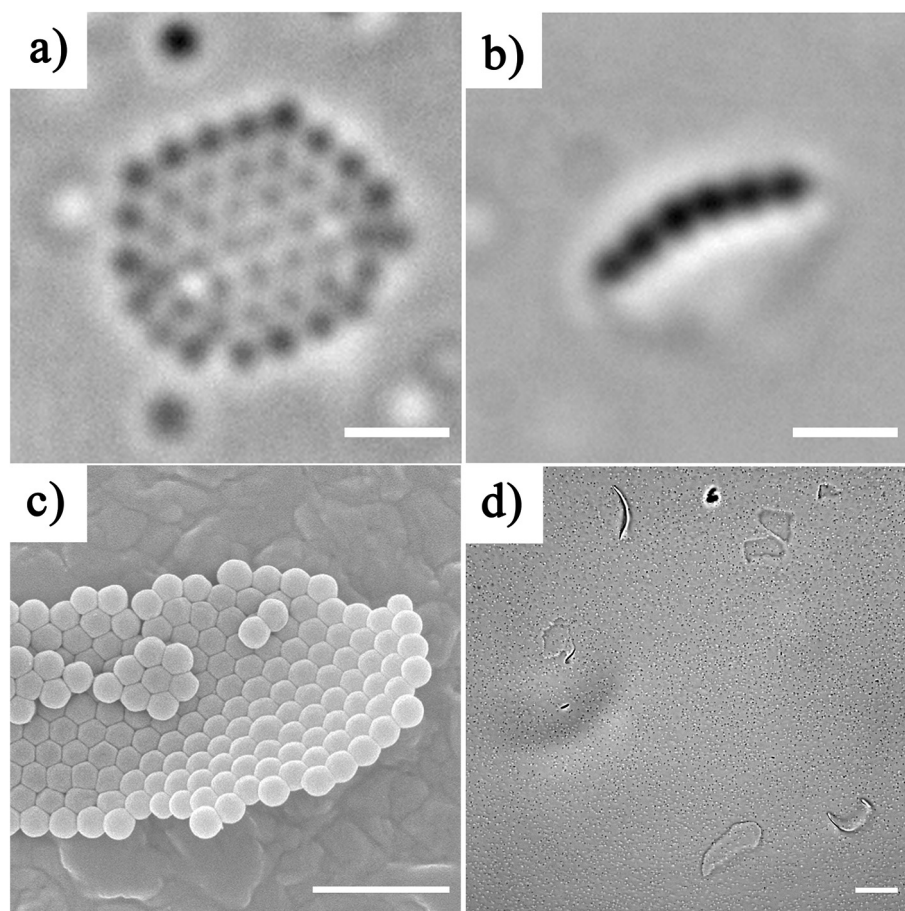


Fig. 1. (a, b) Optical microscopy images of the same colloidal crystal monolayer (CCM) captured at different times. (c) SEM image of the CCM, the sample was dried under atmospheric conditions. (d) Low magnification of optical microscopy image of the CCM. Scale bars: $2 \mu\text{m}$ for a, b and c, and $20 \mu\text{m}$ for d.

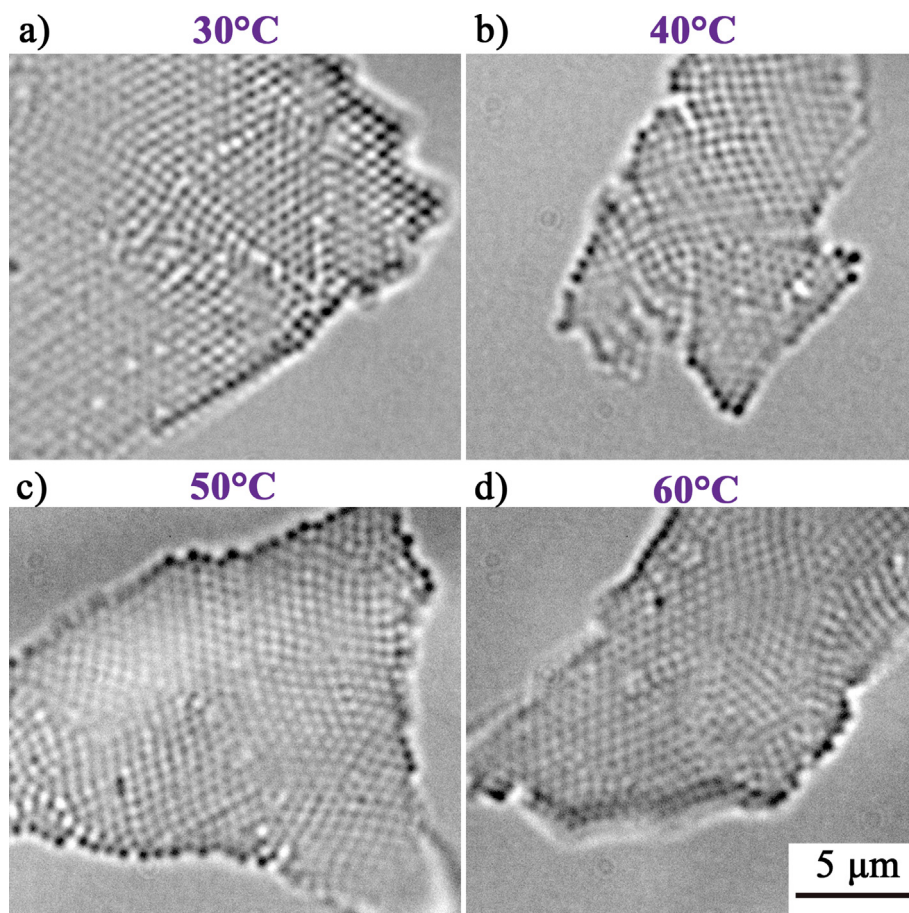


Fig. 2. Optical microscopy images of the colloidal crystal monolayer prepared in THF with evaporation temperatures of (a) 30 °C, (b) 40 °C, (c) 50 °C and (d) 60 °C. Conditions: CPS-Cl and THF were used as the building blocks and the extracting solvent, respectively. The centrifugal tube was made of polypropylene. Scale bars: 5 μm for all images.

these samples. The weak variation in crispiness and intensity of the image in Fig. 2c and d is likely caused by the slight tilt of the CCM in the samples and sometimes due to intrinsic curvature. The temperature influences the vapor pressure of a solvent. The vapor pressure of THF at 60 °C is 1.3 times higher than that at 30 °C [25]. This low vapor pressure difference might explain that no significant differences of the formed CCM were observed in these samples.

In the second set of experiments, various dispersing solvents including ethanol, acetonitrile, methanol, acetone, THF and methyl acetate were tested. The above dispersing solvents were selected

for two reasons. On the one hand, all of them disperse CPS-Cl well. On the other hand, they all have relatively high vapor pressure (Table 1). The high vapor pressure under atmospheric conditions allows for performing the experiments in a relatively short time. The other conditions were kept constant, in all of these samples CCM were observed (Fig. 3). Considering the selected dispersing solvents have significantly different dielectric constant and dipole moment (Table 1), while CCM were found in all the selected dispersing solvents, hence we concluded that the variation of the Van der Waals interaction, the electrostatic interaction and the dipolar-dipolar interaction is not large enough to lead to significant differences in this system. Furthermore, the vapor pressure difference of the selected dispersing solvents are as large as 4 times (Table 1), while CCM were observed in all the samples, we concluded that the vapor pressure within that range has negligible influence on the CCM formation.

Even though CCM were found in all of the samples, however, the CCM obtained in different dispersing solvents display slightly different structures. In ethanol (Fig. 3a) and acetonitrile (Fig. 3b), CCM with many cracks were formed; in methanol (Fig. 3c) and acetone (Fig. 3d), relatively small CCM were observed; while in THF (Fig. 3e) and methyl acetate (Fig. 3f), larger CCM with less cracks were obtained. The average size and standard deviation of CCM obtained in ethanol, acetonitrile, methanol, acetone, THF and methyl acetate are 280 ± 180 , 180 ± 60 , 40 ± 20 , 100 ± 60 , 1500 ± 2400 and $650 \pm 750 \mu\text{m}^2$ respectively by measuring at least 20 CCM in each sample. It is well known that the last two solvents are good solvent for polystyrene while the first mentioned solvents are not. Therefore, we speculated that the solubility of polystyrene

Table 1

The dielectric constant, vapor pressure and dipole moment of solvents.

Solvent	Dielectric Constant ¹	Vapor Pressure 21 °C/mmHg ²	Polystyrene solubility ³
Acetone	21.01	194.0	bad
Acetonitrile	36.64	71.0	bad
<i>N,N</i> -Dimethylformamide (DMF)	38.253	8.0	good
Dimethyl sulfoxide (DMSO)	47.240	7.0	good
1,4-Dioxane	2.223	2.0	good
Ethanol	25.304	5.7	bad
Methanol	33.001	10.3	0
Methyl acetate	7.071	71.0	good
1-Methylpyrrolidin-2-one (NMP)	32.550	3.0	good
Oxolane (THF)	7.521	33.0	good
Water	80.101	9.0	bad

¹ Obtained from 'W. M. Haynes, CRC Handbook of Chemistry and Physics, 97th Edition, CRC Press, 2016'.

² Obtained from 'Ian M. Smallwood, Handbook of organic solvent properties, Arnold, 1996'.

³ Obtained from 'Mark, J.E., Polymer Data Handbook, 2nd Edition. Oxford University Press, 1999.'

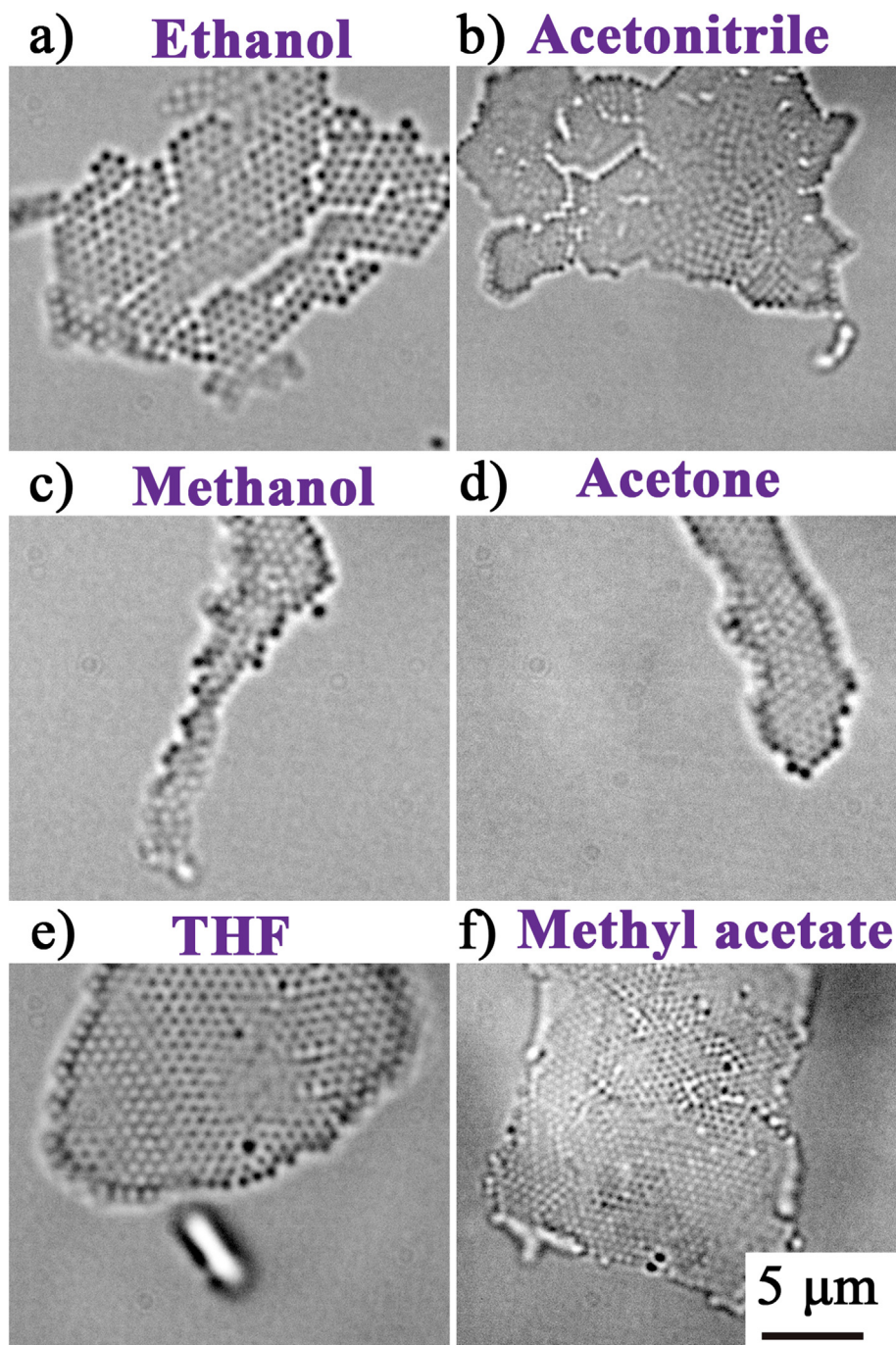


Fig. 3. Optical microscopy images of the colloidal crystal monolayers obtained in the dispersing solvents of (a) Ethanol, (b) Acetonitrile, (c) Methanol, (d) Acetone, (e) THF and (f) Methyl acetate. Conditions: CPS-Cl colloids were used, THF was used as the extracting solvent. The centrifugal tubes were made of polypropylene. Scale bars: 5 μm for all images.

in the dispersing solvent might contribute to the slightly different CCM structures obtained in different dispersing solvents. Before investigating the influence of the solubility of polystyrene in the dispersing solvent on the formed CCM structures, we first look into the morphologies of the colloids CPS-Cl after treatment with different types of dispersing solvents. Ethanol and THF are chosen as representatives for bad solvent and good solvent for polystyrene, respectively. The colloids are first dispersed in either ethanol or THF, and subsequently in water after washing three times. Afterwards, both samples are placed on the TEM grids and dried by a freeze-drying process so that shrinkage of the CPS-Cl is prevented

[26]. Fig. 4a and b are the TEM images of CPS-Cl after treatment with ethanol and THF, respectively. Evidently, CPS-Cl remains intact after treatment with ethanol, while a yolk-shell structure is formed when CPS-Cl is treated with THF. The formation of the yolk-shell structure in THF is ascribed to the etching of the linear polystyrene in CPS-Cl by THF [27]. Based on these results, we further speculated that the yolk-shell structure formed in THF allows the colloids to pack closer and even interpenetrate upon evaporation. Fig. 4c shows a TEM image of CCM obtained by using THF as the dispersing solvent. This TEM sample is also prepared by using the freeze-drying method. Compared to the free yolk-shell colloids

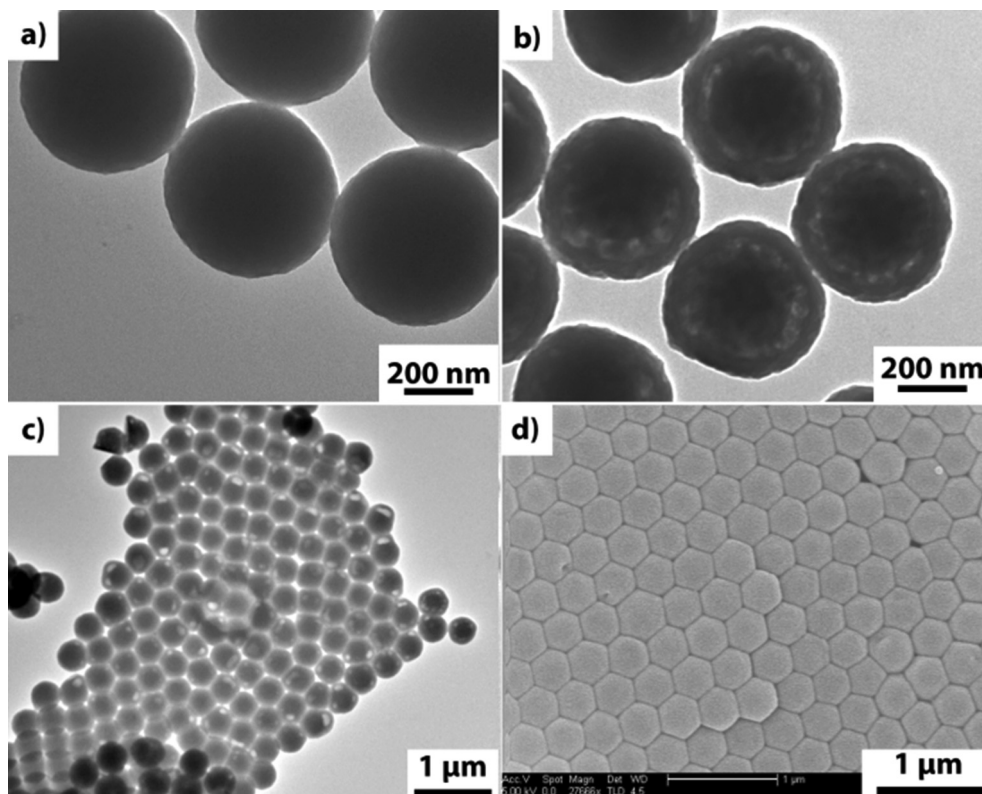


Fig. 4. TEM images of CPS-Cl after treated with (a) ethanol and (b) THF, the samples are dried by the freeze-drying process. (c) TEM image of the freeze-drying colloidal crystal monolayers (CCM) sample. The CCM are prepared by using THF as both the dispersing solvent and the extracting solvent. (d) SEM image of the CCM sample dried under atmospheric conditions. The CCM are prepared by using THF as both the dispersing solvent and the extracting solvent. Scale bar: (a, b) 200 nm, (c, d) 1 μ m.

in Fig. 4b, the yolk-shell colloids in CCM have hexagonal shapes. The colloids are deformed and compressed by the neighboring colloids, resulting in compression and flattening of the shell at the contact regions. Furthermore, the colloids center-to-center separation in CCM is approximately 343 nm, significantly smaller than the diameter of the free yolk-shell colloids (394 nm), further indicating that the colloids are compressed by the neighboring colloids. Fig. 4d shows a SEM image of CCM dried under atmospheric conditions, as can be seen, the spherical colloids are also deformed into hexagonally shaped colloids, further indicating that the shell of the colloids is deformable. These results show that in a good solvent, the colloids are etched into a yolk-shell structure and the shell is deformable, which allows the colloids to pack closer. Furthermore, on the yolk-shell colloids, there will be some “dangling ends” or outer layers with low polymer density that can extend into neighboring particles, the interpenetration of the “dangling ends” eventually resulting in the formation of relatively larger CCM with fewer defects [28]. On the other hand, even though CCM can form on the wall when ethanol is used as the dispersing solvent, however, a good solvent such as THF is required to peel off the CCM. The use of THF during the peel off procedure may interfere the structure of the formed CCM. Therefore, we do not have TEM or SEM images of CCM in ethanol.

3.3. Influence of extracting solvent

The essential difference between the method shown here and the classical convective deposition reported before [9,10] is that the formed CCM can readily peel off and freely float in the solvent by using the method described here. Since THF was used as the extracting solvent in our method instead of water being commonly used in classical convective deposition, we speculated that the

properties of the extracting solvent have a significant influence on the detachment of the CCM. To study the influence of the extracting solvent, water was employed as the extracting solvent at first. In the experiments conducted here, THF and CPS-Cl were used as the dispersing solvent and the colloids, respectively, and the centrifugal tubes were made of polypropylene. After evaporating colloidal THF dispersion for approximately 20 min in the fume hood and removing the remaining bulk dispersion carefully, water as the extracting solvent was refilled and the sample was manually shaken. Fig. 5a and g shows that no CCM were found when water was used as the extracting solvent. There are two possibilities for the absence of CCM in this sample. The first possibility is that the CCM disintegrated into their separate colloidal building blocks. The dielectric constants of THF and water are 7.52 and 80.1 respectively (Table 1), in the experimental conditions here, the electrostatic repulsion between particles in water is much higher than that in THF. The increased repulsion between particles in water may result in the disintegration of CCM. The other possibility is that water is too polar to significantly swell CCM which mainly consists of polystyrene. CCM remains stuck to the wall and hence no CCM were found in water. To find out, further experiments were conducted. In the first experiment, the water in the above sample was removed and THF was added, followed by manual shaking. Clearly, CCM were observed as shown in Fig. 5b and h, excluding the possibility that water disintegrates the CCM. In the second experiment, ethanol and 1-Methylpyrrolidin-2-one (NMP) were selected as the extracting solvent which have similar dielectric constant (Table 1), but the latter is a good solvent for polystyrene while the former is not [29]. Clearly, no CCM were found in ethanol (Fig. 5c and i) while many CCM were present in NMP (Fig. 5d and j). In the last experiment, 1, 4-dioxane and *N,N*-dimethylformamide (DMF) were selected as the extracting solvent which are both good

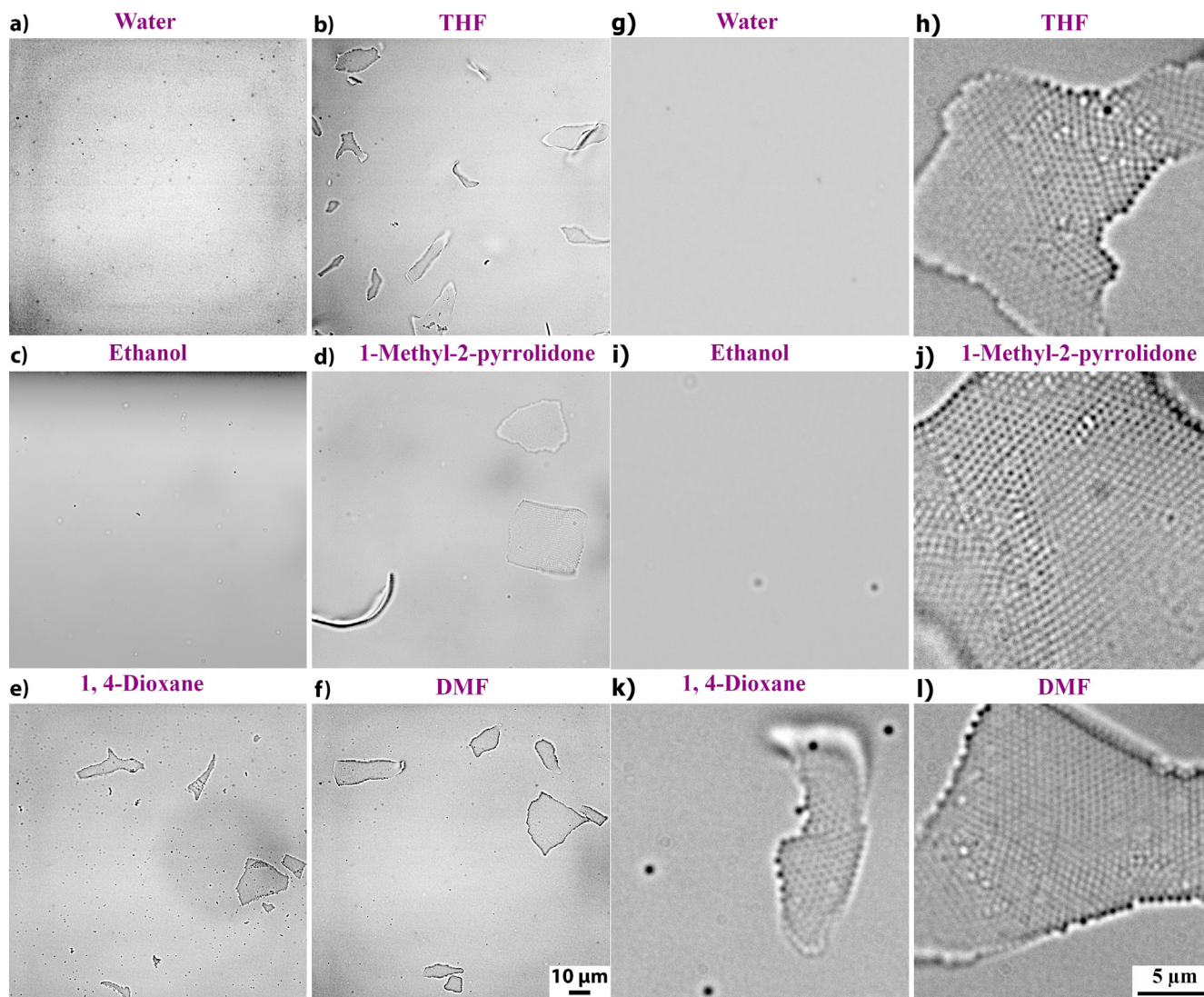


Fig. 5. Optical microscopy images of samples obtained by using extracting solvent of (a) Water, (c) Ethanol, (d) 1-Methylpyrrolidin-2-one (NMP), (e) 1, 4-dioxane and (f) DMF. (b) Removed water in (a), then THF was added. (g–l) are the high magnification images of (a–f), respectively. Conditions: CPS-Cl and THF were used as the building blocks and the dispersing solvent, respectively. The centrifugal tube was made of polypropylene. Scale bars: 10 μm for a–f and 5 μm for g–l.

solvents for polystyrene but with significantly different dielectric constant (Table 1) [29]. As shown in Fig. 5e as well as 5k (1, 4-dioxane), and 5f as well as 5l (DMF), CCM were observed in both solvents. Therefore, we can conclude that the solubility of polystyrene in the extracting solvent is more important than the dielectric constant to peel the CCM off.

3.4. Influence of substrate

Centrifugal tubes made of different materials, including polypropylene (PP), low-density polyethylene (LDPE), polypropylene-copolymer (PPCO), polycarbonate (PC), polyallomer (PA, ethylene propylene copolymer) and glass were tested. Since THF is a good solvent for most of the above materials while ethanol is not, ethanol was employed as the dispersing solvent to study the influence of the substrate materials [30]. As shown in Fig. 6, CCM were observed in all materials except for glass. Considering that the glass is hydrophilic while most of the polymer materials used here are hydrophobic, the fact that CCM only formed on the organic polymer-based substrates while not on the glass implies the importance of the hydrophobicity of wall materials on the

CCM formation. The hydrophobicity of a material can be quantified by the contact angle of the material with water. The contact angle of a liquid drop on a solid surface is the angle measured through the liquid, where a liquid–vapor interface meets a solid surface. If the water contact angle of the materials is smaller than 90° , the solid surface is considered hydrophilic while it is hydrophobic if the water contact angle is larger than 90° . The water contact angle of the glass is approximately 10° indicating that glass is quite hydrophilic [31], while the organic polymer-based materials have contact angles in the range from 82° (PC) to 102° (PP) [32]. Therefore, a slightly hydrophilic or hydrophobic substrate is required for the formation of CCM.

3.5. Influence of colloids

Various types of colloids were tested to investigate the versatility of the procedure. Regardless of the materials, the morphologies, the size and the surface chemical functionalities of the colloids, CCM were found in all cases, indicating the versatility of the present method (Table 2 and Fig. 7).

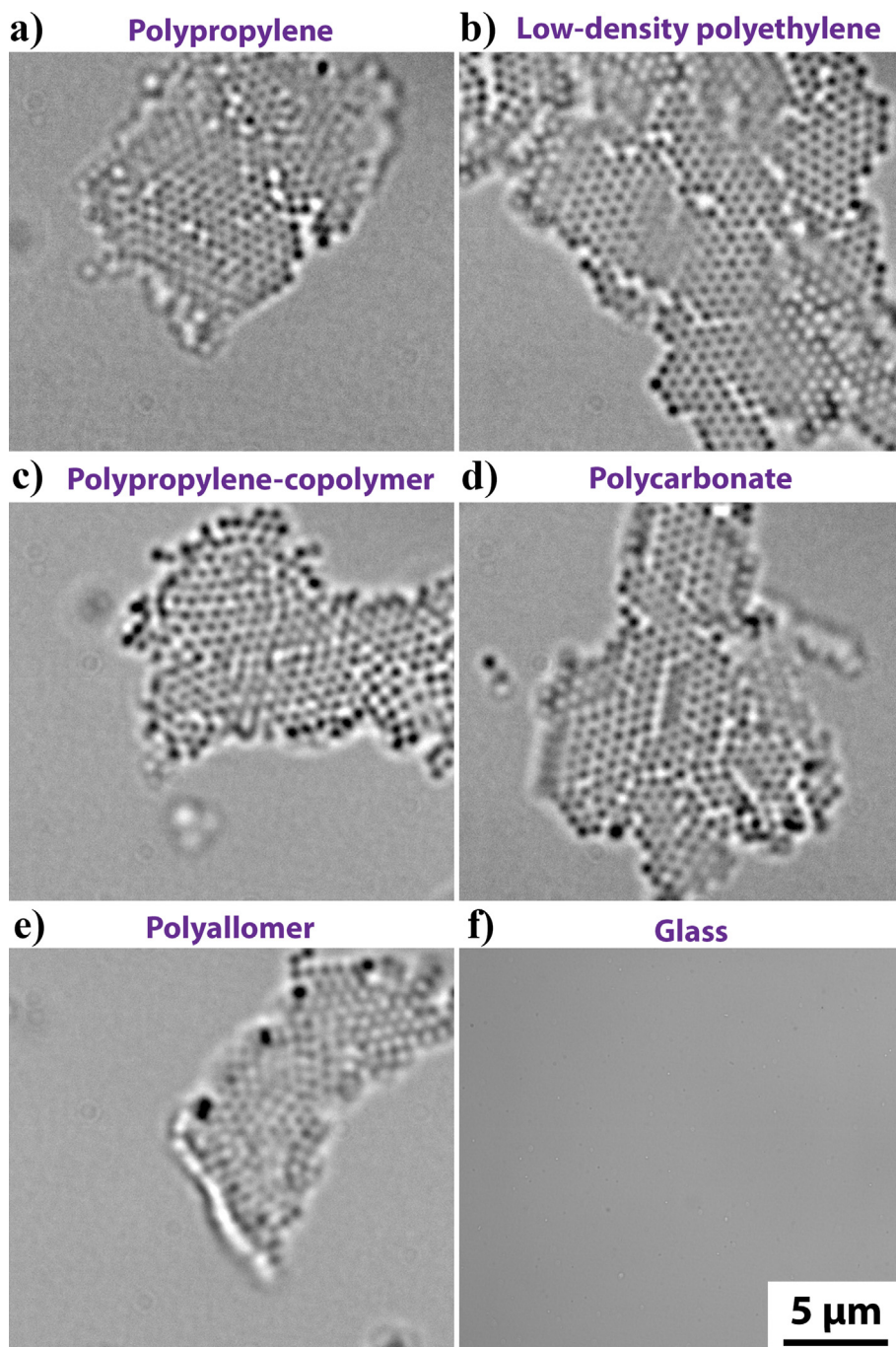


Fig. 6. Optical microscopy images of samples prepared in the centrifugal tubes made of (a) Polypropylene (PP), (b) Low-density polyethylene (LDPE), (c) Polypropylene-copolymer (PPCO), (d) Polycarbonate (PC), (e) Polyallomer (PA, ethylene propylene copolymer) and (f) Glass. Conditions: CPS-Cl colloids were used, ethanol and THF were used as the dispersing solvent and the extracting solvent, respectively. Scale bars: 5 μm for all images.

3.6. Stability of CCM

Fig. 8a shows an optical microscopy image of a CCM sample after storing in THF overnight. Clearly, the CCM kept intact, neither aggregation nor disintegration of the CCM was observed. In contrast, CCM completely disintegrated upon sonication of a sample for 1 min. As shown in Fig. 8b, free colloids instead of CCM were found. However, the stability of CCM against sonication can be improved to some extent by centrifuging the sample. Before placing the CCM sample in the sonication bath, it was centrifuged at 10,000g for 2.5 min. As indicated in Fig. 8c, the centrifuged CCM were still present after sonication. We speculated that the colloids

separation in CCM became shorter and the colloids even penetrated into each other to some extent upon centrifugation, which may result in stabilization of the aggregates (against sonication) by Van der Waals attraction. Interestingly, no 3D-aggregation of the CCM was found, even if the monolayer sample was centrifuged, indicating that the CCM are quite stable. Moreover, the CCM can readily be transferred into water. Fig. 8d shows an optical microscopy image of CCM dispersed in water. The appearance of CCM in water is quite different compared to that in THF, we do not fully understand at this point, one possibility is the difference in refractive index between water and THF. However, from the edge of the CCM, we can clearly distinguish the individual particles, indicating

Table 2

The materials, morphologies, size and surface chemical functionalities of the colloids CPS-Cl, CPS2, CPSAA, CPS-N, d-CPS, db-CPS and PMMA.

Entry	Materials	Morphologies	Diameter	Surface chemical functionalities
CPS-Cl	PS	sphere	460 nm ^c	-OSO ₃ ⁻ / Cl
CPS2	PS	sphere	470 nm ^c	-OSO ₃ ⁻
CPSAA	PS	sphere	461 nm ^c	-OSO ₃ ⁻ / -COO ⁻
CPS-N ^a	PS	sphere	460 nm ^c	-OSO ₃ ⁻ / -N(C ₂ H ₅) ₃ ⁺
d-CPS	PS	dimple	871 (400 ^e) nm ^d	PVP
db-CPS	PS	dumbbell	820 (476 ^f) nm ^d	PAA/Cl
PMMA ^b	PMMA	sphere	1080 nm ^d	PHS ^g

Notes:

^a) Prepared based on CPS-C₂ in ref [33].^b) Prepared based on 17P#2 in ref [34].^c) Obtained from DLS.^d) Obtained from TEM.^e) Diameter of the cavity of the dimple particle.^f) Diameter of the small lobe.^g) Poly(12-hydroxystearic acid) graft copolymer.

that they are CCM instead of some other materials such as dust. More importantly, after drying under atmospheric condition, the SEM image of the sample was taken which confirms the monolayer feature of the CCM (Fig. 1c). Considering that water is ubiquitous and environmentally friendly, the fact that the CCM can transfer into water from organic solvents widens the potential applications of the CCM, makes the present method more practical. Furthermore, transferring of the CCM to a desired substrate can also be easily achieved by placing the desired substrate on the bottom of the container with CCM dispersion. After deposition of the CCM, followed by draining out of the solvent, a substrate with CCM can be obtained.

3.7. Formation mechanism hypothesis

A possible mechanism for the CCM formation is proposed, as summarized in Scheme 2. Firstly, a wetting film of the dispersion arises upward along the wall of the centrifugal tube as the wall is wettable by the dispersing solvent. In fact, the contact angle is significantly smaller than 90° as the dispersing solvent can spread over the surface of the centrifugal tube, see Scheme 2a. With the evaporation of the dispersing solvent, the thickness of the upper part of the wetting film decreases which presses the colloids towards the wall. We speculated that the colloidal volume fraction plays a key role in determining the layer numbers of the colloidal arrays. Under low colloids concentration, the colloids move to the substrate to form monolayers. However, under high colloids concentration, due to the steric effect of neighboring colloids, some colloids cannot complete approach the substrate, which results in the formation of multiple layers. As the colloidal volume fraction is relatively low here (0.25%), the colloids can freely approach the wall, resulting in a dense layer of colloids onto the wall (Scheme 2b) [11,35]. Further evaporation of the dispersing solvent results in the formation of a meniscus structure of the air–liquid interface between the colloids on the wall. The deformation of the meniscus structure gives rise to capillary attraction, driving the colloids towards the nucleus, hence a monolayer is formed onto the wall. Simultaneously, more colloids are delivered towards the monolayer growth front by a solvent flux which is built up by the evaporation of the dispersing solvent (Scheme 2c, d) [9–10]. During this process, the capillary attractions are responsible for pushing the colloidal particles through their stabilizing electrical double layer and steric stabilization layer. Once the particles surface separation is sufficiently close, Van der Waals attraction starts dominating and it is probably Van der Waals attraction that ultimately stabilize the CCM. After replacing the dispersing solvent by an extracting solvent, the extracting solvent penetrates the

gap between the colloidal monolayers and the wall surface. Since the attractive forces between the CCM and the wall are weaker in the presence of the extracting solvent, and the CCM prefer to go to the extracting solvent phase due to the good swellibility of the extracting solvent towards the building blocks of CCM, the monolayers peel off from the wall and freely float in the extracting solvent (Scheme 2e).

4. Conclusion

We report a modified convective deposition method to prepare floating colloidal crystal monolayers (CCM) consisting of sub-micron polymeric building blocks. The method involves two major steps. In the first step, we make plausible that evaporation of the dispersing solvent results in the formation of a meniscus structure of the air–liquid interface between the colloids on the substrate. The deformation of the meniscus gives rise to capillary attraction, driving the colloids towards the crystal zone, and monolayers are formed on the substrate. The capillary attractions are responsible for pushing particles together while it is probably the Van der Waals attractions that ultimately stabilize the CCM. Subsequently, the remaining bulk dispersion is replaced by an extracting solvent which is a good solvent for polystyrene. Floating CCM are obtained by peeling off the colloidal monolayers from the substrate and dispersing in the extracting solvent.

The influences of the dispersing solvent, the extracting solvent, the substrate, and the colloid on the formation of the CCM are systematically investigated. We found that the evaporation rate of the dispersing solvent indicated by its vapor pressure has negligible influence on the formation of the CCM, while the swellibility of the dispersing solvent has to some extent influence on the structure of the formed CCM. Larger CCM with less cracks can be prepared provided that the dispersing solvent is a good solvent for polystyrene. The key to peel the CCM off from the substrate is the selection of the appropriate extracting solvent which is also a good solvent for polystyrene. Furthermore, the CCM formation process is robust in terms of the substrate and the colloid.

Notably, compared to the previous reported methods including convective deposition [10], drop casting [11], spin coating [12], and electrophoretic deposition [13], which have a major drawback of the difficulty to transfer the formed CCM to other substrates, the method outlined here allows for preparing floating CCM which makes the transfer of the CCM to other substrates possible. Furthermore, compared to the liquid interface mediated methods and the surfactant mediated method which require various polymers or surfactants as well as complicated procedures to fabricate floating CCM [14–17,21], no additives are employed by the simple

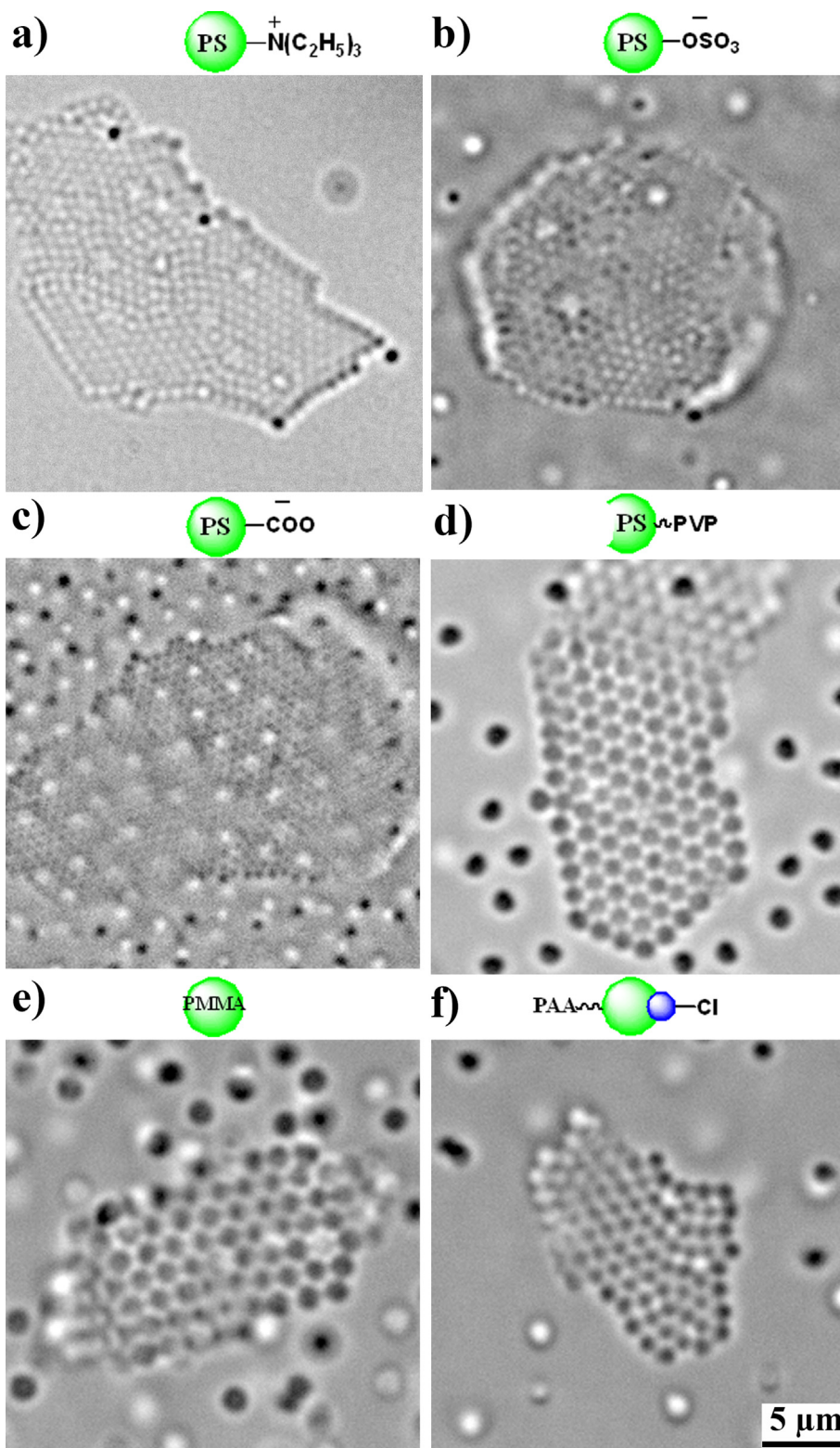


Fig. 7. Optical microscopy images of the colloidal crystal monolayers made from (a) Positively charged PS nanospheres CPS-N; (b, c) Negatively charged PS nanospheres CPS2 and CPSAA; (d) PVP stabilized PS dimple particles d-CPS; (e) Hydrophobic PMMA nanospheres; (f) Dumbbell particles db-CPS. Conditions: THF was used as both the dispersing solvent and the extracting solvent. The centrifugal tubes were made of polypropylene. Scale bars: $5 \mu\text{m}$ for all images.

and robust method reported here. Lastly, various types of colloids in terms of morphology, size and surface chemical functionalities can form floating CCM by our method, while anisotropic nanoparticles were required in previous report [18].

The robustness of the synthetic approach and the floating feature of the CCM broadens its applications in the areas, such as photonic crystal [36], sensors [37], and colloidal lithography [38,39]. For example, the CCM on the substrate can be used as a mask for

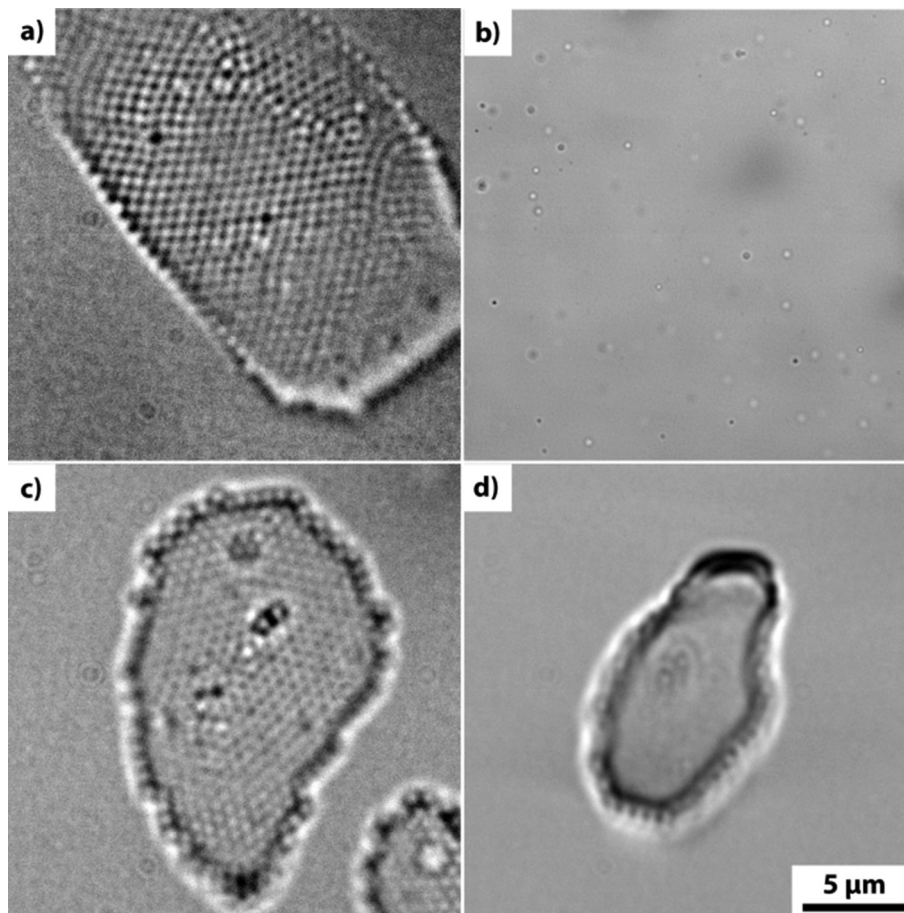
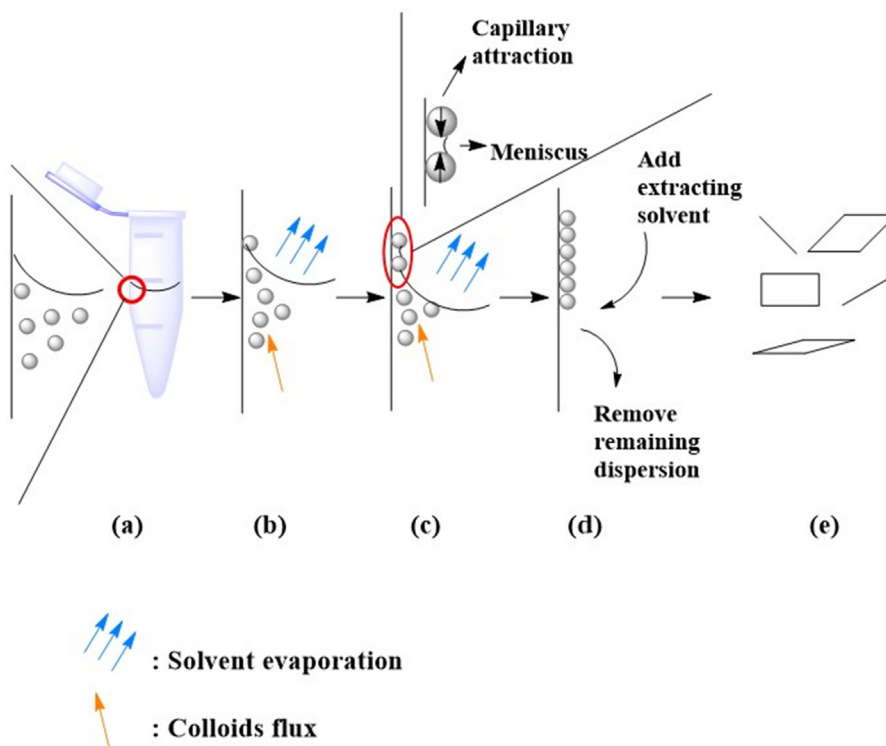


Fig. 8. Optical microscopy images of CCM samples (a) After storing in THF overnight. (b) After sonication for 1 min. (c) After centrifugation at 10,000g for 2.5 min, followed by sonication for 1 min. (d) In water. Scale bars: 5 μm for all images.



Scheme 2. Schematic illustration of a possible mechanism for the colloidal crystal monolayers formation.

lithography. After lithography, it can be easily peeled off by gentle shanking so that scratching will be avoided. Furthermore, the floating feature of the CCM allows for the study of the diffusion behavior, sediment behavior or packing behavior of 2D materials in solvent.

CRedit authorship contribution statement

Yong Guo: Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition. **Willem K. Kegel:** Supervision, Project administration, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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