

Fabrication of Large-Area Two-Dimensional Microgel Colloidal Crystals via Interfacial Thiol–Ene Click Reaction

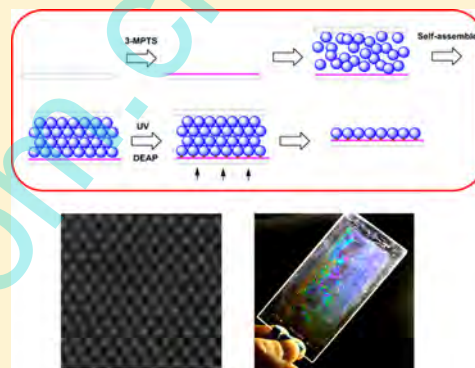
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S Supporting Information

ABSTRACT: A method for the fabrication of high quality, large area 2D colloidal crystals (CCs) using poly(*N*-isopropylacrylamide) (PNIPAM) microgel sphere, an extremely soft colloid, as building block was proposed. First the microgel spheres were assembled into 3D colloidal crystals. The first 111 plane of the 3D crystal close to the substrate was then fixed *in situ* onto the substrate. Highly efficient photoinitiated thiol–ene coupling was chosen for the fixing purpose. Thanks to the high quality of 3D microgel CCs, the resulting 2D CCs exhibit a high degree of ordering. Large area 2D CCs were fabricated because large area 3D microgel CCs can be facilely fabricated. Besides planar substrates, the method allows the fabrication of 2D CCs on curved surface, too. In addition, the interpartical distance in the 2D CCs can be tuned by the concentration of the microgel dispersion.



INTRODUCTION

Two-dimensional colloidal crystals (2D CCs), like their 3D analogues, have numerous applications,¹ including photonic crystals, surface patterns,² sensors,^{3,4} and nanolithography.⁵ Fabrication of high quality, large scale 2D CC is the first step toward these applications. Typically 2D CCs were assembled from hard colloids, such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and SiO₂. Various methods, including spin-coating,^{6–8} interfacial assembly,^{3,4} and convective assembly,^{1,9,10} were developed to assemble these CCs. In spin coating, the normal pressure produced by spin coating squeezes shear-ordered hexagonal layers of the colloid spheres against the substrates to form 2D non-close-packed crystals.⁶ In interfacial assembly, an ordered array of colloidal spheres is first assembled at an air–liquid interface, followed by transferring to a solid substrate.^{3,4} In convective assembly, the colloidal spheres are transported from a reservoir into a meniscus that forms on a wetting substrate and are confined at the contact line. When withdrawing the substrate, the meniscus moves and the spheres are deposited and packed into a crystalline coating.^{1,9,10} A problem with these methods is that the size of the resulting array is usually small. To address this limitation, Asher et al.³ developed a method which allows the assembly of large area 2D arrays.

Besides the widely used hard colloids, soft hydrogel colloids, especially poly(*N*-isopropylacrylamide) (PNIPAM) microgel spheres, could also be assembled into ordered 2D arrays. Unlike hard spheres, microgel spheres could respond to external stimuli,¹¹ making the resulting 2D CCs promising for many potential applications. Previously 2D microgel CCs were fabricated via dip coating,^{12,13} solvent evaporation,^{14–18} or

interfacial assembly.^{19–21} Unfortunately, these methods could only produce 2D CCs with a relatively small size. For example, the 2D microgel array synthesized by Tsuji and Kawaguchi¹⁵ has a small size of 0.36 cm².

Here we propose a facile method to fabricate high quality, large area 2D CC of microgel spheres (Scheme 1). It is well-known that microgel spheres are extremely soft and easy to be deformed. This may present a problem when assembling them in a dynamic mode as in dip coating^{12,13} and solvent evaporation^{14–18} or transferring a preformed ordered array onto a solid substrate.^{19–21} In contrast, the soft nature of microgel spheres makes them ideal building blocks for 3D CCs. Previous studies demonstrated that 3D microgel CCs are intrinsically defect-tolerant.^{22,23} Large area, high quality 3D microgel CCs can be facilely fabricated.^{24–30} Taking advantage of the 3D microgel CCs, here we propose that large area, high quality 2D microgel CCs could be fabricated by first assembly of 3D CC followed by *in situ* fixation of the spheres on substrate (Scheme 1A). Because of its high efficiency, the well-known UV-induced thiol–ene reaction^{31–33} was chosen for the fixing purpose (Scheme 1B). The method not only allows the fabrication of large area, high quality 2D CCs but also using nonplanar substrate and tuning the interparticle distance.

EXPERIMENTAL DETAILS

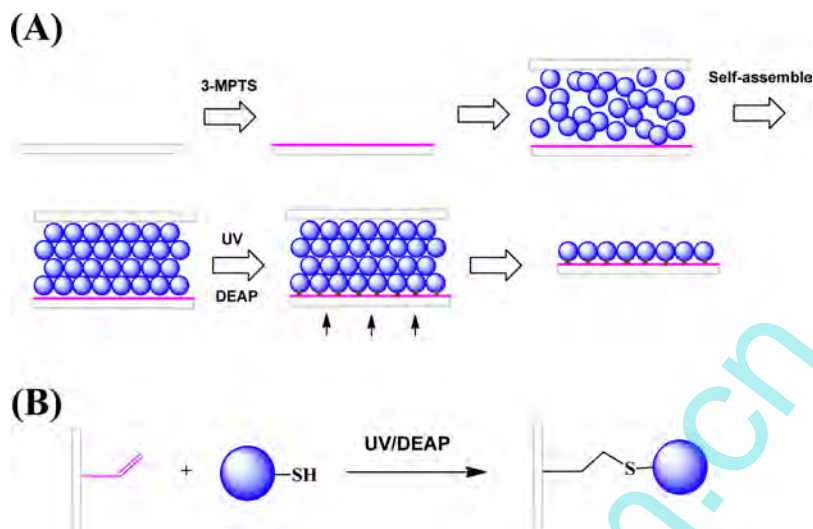
Materials. *N*-Isopropylacrylamide (NIPAM) was purchased from Tokyo Chemical Industry Co. *N,N'*-Methylenebis(acrylamide) (BIS)

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Scheme 1. (A) Fabrication of 2D Microgel CC by First Assembly of 3D Microgel CC Followed by *in Situ* Fixation of the First 111 Plane onto the Substrate; (B) Photo-Initiated Thiol–Ene Reaction between the Vinyl-Modified Substrate and SH-Modified Microgel Sphere



and 2,2-diethoxyacetophenone (DEAP) were purchased from Alfa Aesar. Cysteamine hydrochloride and 3-methacryloxypropyltrimethoxysilane were purchased from Aladdin. Acrylic acid (AAc), potassium persulfate (KPS), and *N*-(3-(dimethylamino)propyl)-*N*'-ethylcarbodiimide hydrochloride (EDC) were purchased from local providers. NIPAM was purified by recrystallization from hexane/acetone mixture and dried in a vacuum. AAc was distilled under reduced pressure. Other reagents were used as received.

Synthesis of P(NIPAM-AAc) Microgels. Poly(*N*-isopropylacrylamide-*co*-acrylic acid) (P(NIPAM-AAc)) microgels were synthesized by free radical precipitation polymerization. The recipes for the 900, 1200, and 1600 nm microgels are listed in Table 1. First NIPAM,

Table 1. Recipes for the Synthesis of P(NIPAM-AAc) Microgels with Different Size

sample name	NIPAM (g)	AAc (g)	BIS (g)
900 nm microgel	1.400	0.100	0.033
1200 nm microgel	1.410	0.100	0.022
1600 nm microgel	1.410	0.100	0.017

AAc, and BIS were dissolved in 95 mL of water. The solution was then transferred to a three-necked round-bottom flask equipped with a condenser and a nitrogen line. It was purged with nitrogen and heated to 70 °C. After 1 h, 5 mL of 0.06 mol/L KPS was added to initiate the reaction. The reaction was allowed to process at 70 °C for 4 h. The resultant microgel dispersion was purified by dialysis against water with frequent water change for at least 1 week.

To synthesize the 2500 nm P(NIPAM-AAc) microgel, 1.410 g of NIPAM, 0.100 g of AAc, and 0.017 g of BIS were dissolved in 95 mL of water. The solution was then transferred to a three-necked round-bottom flask equipped with a condenser and a nitrogen line. It was purged with nitrogen and heated to 70 °C. After 1 h, 5 mL of 0.06 mol/L KPS was added to initiate the reaction. When the reaction has processed at 70 °C for 4 h, 45 mL of preheated solution containing 0.705 g of NIPAM, 0.050 g of AAc, and 0.009 g of BIS and 5 mL of 0.06 mol/L KPS were added. The reaction was allowed to process at the same temperature for another 4 h. The resultant microgel dispersion was purified also by dialysis.

Synthesis of SH-Modified Microgels. To 50 mL of purified P(NIPAM-AAc) microgel dispersion, 0.142 g of cysteamine hydrochloride and 0.238 g of EDC were added. The reaction mixture was constantly stirred at room temperature for 4 h. The resultant products

were purified by dialysis against water with frequent water change for 1 day.

Preparation of Two-Dimensional Colloidal Crystals. Quartz slides were cleaned in boiling piranha solution (3:7 v/v H₂O₂–H₂SO₄ mixture) (*caution: this solution is extremely corrosive!*) for 4 h, rinsed thoroughly with deionized water, and dried. To introduce vinyl groups, they were immersed in a 1 wt % ethanol solution of 3-methacryloxypropyltrimethoxysilane for 12 h, washed with 95% ethanol, and stored in ethanol.

To assemble 2D CC, the purified solution of the SH-modified microgels was concentrated via centrifugation usually at 14 000 rpm and 15 °C for 1 h. To 1.0 g of the concentrated dispersion 5 μL of 10% DEAP (v/v) in DMSO was added. The mixture was then injected into the space between two quartz slides (one of them was vinyl-modified) separated by two layers of Parafilm. The samples were allowed to equilibrate at room temperature for at least 1 day to allow the microgel particles to self-assemble into 3D colloidal crystals. After the formation of the highly ordered structure, the samples were irradiated with UV light (365 nm) for 120 s using an Intelli-Ray 400 W curing system. The reaction cell was then opened. The quartz slide was rinsed thoroughly with water and dried in the air.

Characterization. The size and size distribution of microgel particles were measured by dynamic light scattering with a Brookhaven 90Plus laser particle size analyzer. All the measurements were carried out at a scattering angle of 90°. The sample temperature was controlled with a build-in Peltier temperature controller. Optical micrographs were obtained on a Leica TCS SP8 confocal microscope in bright field mode. Atomic force microscopy (AFM) images were acquired using a Benyuan CSPM5000s scanning probe microscope in tapping mode.

RESULTS AND DISCUSSION

As shown in Scheme 1A, the substrate, quartz slides, was first treated with 3-methacryloxypropyltrimethoxysilane (3-MPTS) to introduce vinyl groups onto the substrate surface. Monodisperse poly(*N*-isopropylacrylamide-*co*-acrylic acid) (P(NIPAM-AAc)) microgels were synthesized via free-radical precipitation polymerization. They were then treated with cysteamine and *N*-(3-(dimethylamino)propyl)-*N*'-ethylcarbodiimide hydrochloride (EDC) to introduce thiol groups. Successful modification of the microgels was confirmed by the appearance of new peaks at 2.98 and 3.36 ppm in ¹H NMR spectra of the microgel (–N–CH₂–CH₂–SH) (Figure S1).

Meanwhile, a decrease in the intensity of the peak at 1720 cm^{-1} in FTIR spectra of the microgel, which is assigned to the stretching of carboxylic acid groups, was observed, suggesting the consuming of the carboxylic acid groups because of the coupling reaction. (Figure S2). In this way a series of SH-modified microgels were synthesized. They were named according to their hydrodynamic diameter (D_h) at $20\text{ }^\circ\text{C}$ (Figure S3).

The SH-modified microgel dispersions were then concentrated via centrifugation and loaded into a cell consisting of two quartz slides separated by two layers of Parafilm. As reported previously, the microgel particles gradually self-assemble into a highly ordered crystalline structure.^{24–30} As a result, the sample displays colors when illuminated with white light from behind (Figure 1A).³⁴ Examining with an optical microscope reveals

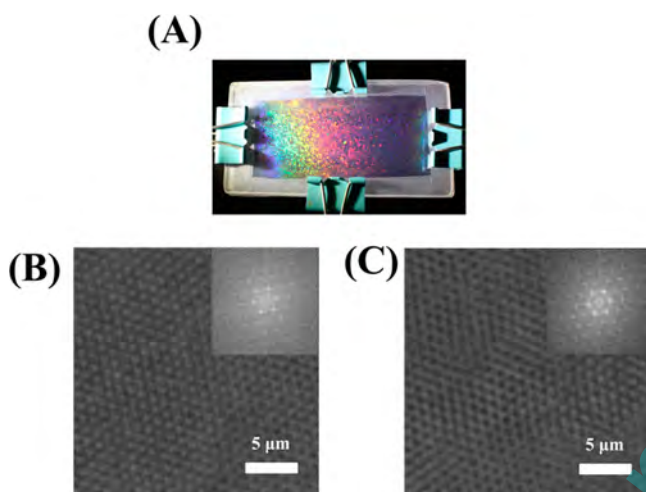


Figure 1. 3D CC assembled from 900 nm SH-modified PNIPAM microgel. (A) Photograph of a sample illuminated with white light from behind. (B) Optical micrograph of the interior region of the 3D CC. The inset is the FFT of the image. (C) Optical micrograph of the layer close to the substrate. The inset is the FFT of the image.

that the particles are arranged into a hexagonally close-packed crystalline array. As an example, Figure 1B shows an image taken from the interior region of a 3D CC assembled from the 900 nm microgel. The average center-to-center distance between two adjacent particles was determined to be ~ 800 nm. The value is slightly smaller than the hydrodynamic diameter (D_h) of the microgel measured at the same temperature (827 nm at $27\text{ }^\circ\text{C}$), revealing a slight compression of the particles in the crystal.

More importantly, the particles close to the substrate were also arranged into a highly ordered structure (Figure 1C). Fast Fourier transformation (FFT) of the image confirms a structure with long-range order and hexagonal symmetry, just like the one taken from the interior (Figure 1B).³⁵ Similar results were previously reported by Lyon et al.³⁶ As they pointed out, the particles close to the substrate actually form the first 111 plane of the face-centered cubic (fcc) lattice of the 3D CC. In fact, the 111 planes in the 3D crystal are all parallel to the substrate.^{35,36} It seems the substrate does not reduce the degree of order of the first 111 plane. In a previous study on 3D CC of PNIPAM microgel, it was even found that compared to the interior region, the region close to the wall of the container has fewer defects.³⁷

The samples were then irradiated through the quartz slide with UV light (Scheme 1A). In the presence of photoinitiator 2,2-diethoxyacetophenone (DEAP), thiol–ene reaction^{31–33} occurs between the vinyl groups on the substrate and the thiol groups on the microgel particles (Scheme 1B). As a result, the microgel particles close to the substrate were bonded covalently with the substrate. In this way, the first 111 plane of the 3D crystal would be fixed on the substrate. Since the particles were bonded *in situ* with the substrate, it is expected that the ordered crystalline structure will remain intact.

The reaction cell was subsequently opened and the substrate was washed with water to remove the unbonded microgel particles. Finally, a 2D array of microgel particles was obtained (Scheme 1A). Figures 2A and 2B show the optical microscopy and AFM images of the 2D arrays fabricated from microgels with four different particle sizes. Representative large area microscopy images are given in the Supporting Information

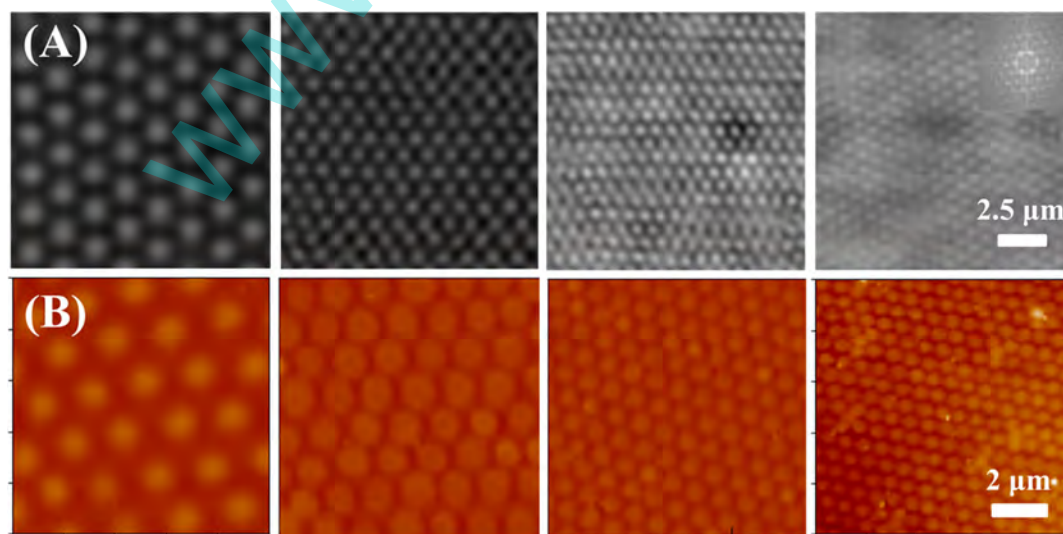


Figure 2. Optical microscopy (A) and AFM (B) images of the 2D CCs fabricated from four different microgels (2500, 1600, 1200, and 900 nm microgel, from left to right). The inset is the FFT of the image.

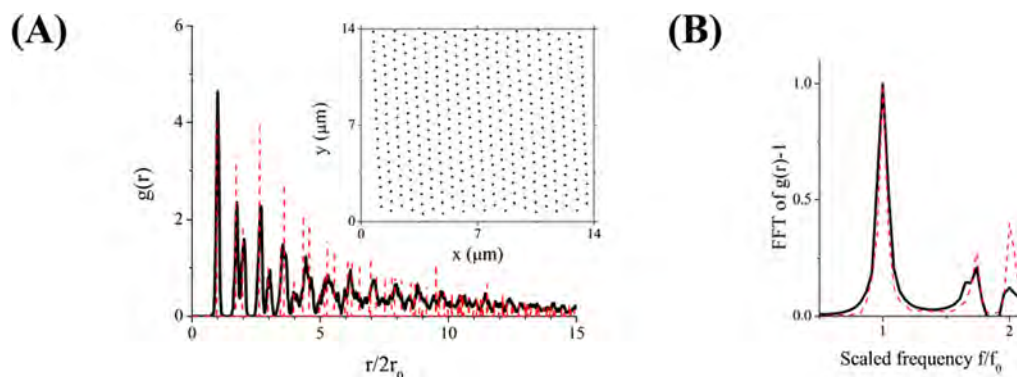


Figure 3. (A) Pair correlation function, $g(r)$, of the 2D CC from 900 nm microgel. Dashed vertical lines indicate the peaks of $g(r)$ of an ideal hexagonally packed monolayer generated numerically. The inset highlights the centers of the particles as found from the automated particle location procedure.²⁰ (B) Single-sided power spectra Fourier transforms (FT) of $g(r)$ of 900 nm microgel 2D CC compared to FT of the corresponding perfectly ordered arrays. The power spectra were scaled to have identical maxima at $f/f_0 = 1$.³

(Figures S4 and S5). These images show that all four particles can be arranged into a hexagonally crystalline array. FFT of the images demonstrated that the 2D arrays also have a long-range order. These results confirm that the ordered structure of the microgel array close to the substrate was successfully fixed via the *in situ* interfacial thiol–ene reaction. In addition, the following washing in water and drying in the air do not destroy the preformed ordered structure.

The ordering of a 2D array can be characterized quantitatively by calculating the dimensionless pair correlation function, $g(r)$, defined by the equation

$$g(r) = \frac{1}{\langle \rho \rangle} \frac{dn(r, r + dr)}{da(r, r + dr)}$$

where a is the shell area and $n(r, r + dr)$ the number of particles that lie within the shell considered.^{3,38} This function describes the probability of finding a particle at a distance r from a given particle in the 2D space. The peaks in the distribution indicate the preferred distances and are considered as a signature of order of the 2D array. As an example, Figure 3A shows $g(r)$ calculated from a 2D CC of 900 nm microgel. A series of peaks were found, suggesting the extension of structural order over a long distance. In addition, the positions of the peaks coincide with those calculated for a perfectly packed hexagonal array, confirming hexagonal packing of the particles.

A quantitative measure of ordering, i.e., the ratio of the full width at half-maximum, k , of the first peak in the Fourier transform of the function $g(r) - 1$ to that of a perfectly packed array, k_0 , was further extracted from $g(r)$.^{3,38} For an array with a perfectly packed structure, the ratio will be 1. Increasing disorder in the structure results in an increased value of k/k_0 . The k/k_0 values for the 2D CCs from 2500, 1600, 1200, and 900 nm microgels were calculated to be 1.19, 1.15, 1.16, and 1.06, respectively (see Figure 3B for an example). The results confirm again that all the samples are highly ordered. In addition, the ordering of the 2D CC is independent of the size of the microgel particles.

The structure of the 2D microgel CCs was also studied by laser diffraction in transmitted mode (see Figure S6 for the experimental setup). When illuminated with monochromatic laser light, 2D CCs show strong forward light diffraction.^{34,39} For normal incidence, the diffraction pattern of a perfect hexagonal crystal should be a set of distinct spots with 6-fold symmetry.³⁹ As shown in Figure 4, the 2D microgel CC

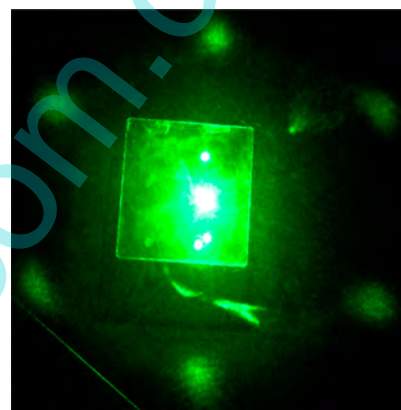


Figure 4. Diffraction of normally incident laser beam transmitted through the 2D CC of 900 nm microgel.³⁴

displays a diffraction pattern with six symmetrical spots, confirming again its highly ordered structure. In addition, the diffraction pattern demonstrates that the microgel particles in the illuminated area (~ 2 mm in diameter) are arranged perfectly into a hexagonal crystalline array. In contrast, many 2D CCs reported previously display a diffraction pattern of a sharp circle (Debye ring), instead of distinct spots, because the illuminated area contains crystallites with a size significantly smaller than the beam diameter which randomly oriented in the area.^{34,39}

2D microgel CCs fabricated using the new method cannot only be of high quality but also be of large size. Previous studies revealed that the only prerequisite for a PNIPAM microgel dispersion to crystallize is that its concentration should fall into a narrow range.²⁹ In principle, 3D microgel CC of any size can be assembled, provided the concentration of the microgel dispersion is suitable.²³ Taking this advantage of 3D microgel CC, it is possible to assemble an ordered 2D array of microgel particles on a substrate of any size. Subsequent fixation of the 2D array will give a 2D microgel CC of the same size. As an example, Figure 5A shows a photograph of a 2D microgel CC with a size of 7.7 cm \times 3.5 cm. When illuminated with white light from behind, the monolayer displays vivid diffraction color, revealing a highly ordered structure. Different parts of the array show different colors, which can be explained by the different angle at which the individual part is illuminated. Other 2D colloidal crystals were also reported to display different

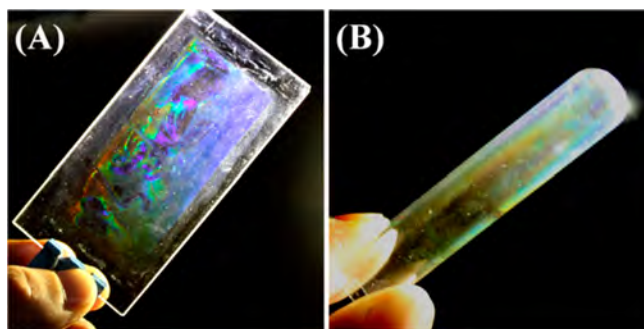


Figure 5. (A) Photograph of a 2D microgel CC deposited on a glass slide. The size of the array is 7.7 cm \times 3.5 cm. (B) A 2D microgel CC coated inside a test tube. Length and inner diameter of the tube are 5 and 0.8 cm, respectively. In both cases, the crystalline order of the microgel array leads to bright diffraction and vivid color when illuminated with white light from behind.

colors when illuminated with white light.^{3,34} The polycrystalline nature of the array²⁵ may be a second reason for the observed different colors.

The method proposed here also allows for the fabrication of 2D microgel CCs on curved surfaces. As an example, the inner surface of a test tube was modified with vinyl groups. SH-modified PNIPAM microgel dispersion was then added and allowed to self-assemble into a 3D colloidal crystal. The microgel particles close to the tube wall were then fixed by UV irradiation. As shown in Figure 5B, the tube also displays vivid diffraction color when illuminated with white light from behind. The result suggests that a crystalline array of microgel particles was successfully fabricated on the inner surface of the tube.

The method also allows for adjusting the distance among the particles in the 2D CCs. To this end, dispersions of 2500 nm microgel with different concentrations were prepared by centrifuging at different temperatures.²⁵ They self-assemble into 3D CCs, and then the first 111 plane close to the substrate was fixed. As shown in Figure 6, highly ordered 2D CCs were all successfully obtained; however, the interparticle distance in the 2D arrays decreases with increasing concentration of the microgel dispersion. As previous studies demonstrated, higher concentration dispersion self-assembles into a 3D CC with a shorter interparticle distance and shorter lattice constant.^{25,27,29} Therefore, the corresponding 2D CC will have a shorter interparticle distance.

CONCLUSIONS

In conclusion, we developed a method to assemble 2D colloidal crystals using soft microgel spheres as building blocks. This method combines the strength of 3D microgel CCs (large area,

high quality 3D CCs can be facily fabricated) and photoinitiated thiol–ene reaction (high efficiency, mild conditions). The resulting 2D microgel CCs are of highly ordered crystalline structure. Large area 2D microgel CC can be facily synthesized. The method can even allow the fabrication of 2D microgel CCs on curved surface. In addition, the interparticle distance in the 2D CCs can be tuned by the concentration of the microgel dispersion. We hope the method developed here will pave the way for the applications of 2D microgel CCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b00835.

Characterization of the microgels, large area optical microscopy and AFM images of 2D CC, and experimental setup for laser diffraction (PDF)

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Notes

The authors declare no competing financial interest.

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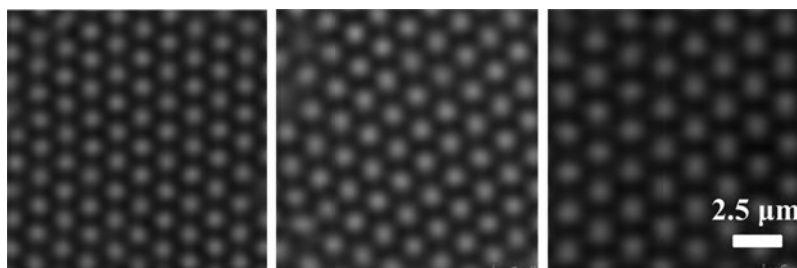


Figure 6. Optical microscopy images of 2D CCs fabricated using 2500 nm microgel dispersions with different concentrations (\sim 4.1, \sim 3.0, and \sim 1.9 wt %, from left to right).

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