

Assembly of Highly Ordered 2D Arrays of Silver-PNIPAM Hybrid Microgels*

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Abstract A strategy was developed for the synthesis of highly ordered 2D arrays of Ag-PNIPAM hybrid microgel. The highly ordered 2D arrays of PNIPAM microgel were prepared by dispersing PNIPAM microgel on a charge-reversible substrate. The microgel spheres self-assembled into a 3D colloidal crystal, and the first 111 plane was fixed *in situ* onto the substrate as a result of spontaneous charge reversal of the substrate, leaving a high-quality 2D array of PNIPAM microgel. Ag nanoparticles were then synthesized *in situ* inside the microgel spheres by introduction of Ag⁺ ions into the microgel spheres and reduction with sodium borohydride. The resulting 2D arrays are highly ordered. The inter-particle distance in the array can be tuned. In addition, the method allows the synthesis of large size arrays and the use of nonplanar substrate.

Keywords 2D colloidal crystal; Microgel; Charge reversal; Self-assembly

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INTRODUCTION

2D colloidal crystals (CCs), or ordered 2D arrays of colloidal microspheres, have important applications in various areas, including 2D photonic crystals^[1], sensors^[2], and surface patterning^[3–6]. Therefore, their fabrication attracted intensive attention in the last three decades. However, the reliable assembly of large area, high quality 2D CCs is still far from being trivial^[6].

Compared to 2D CCs of hard colloids, for example polystyrene (PS)^[2, 7–13], poly(methyl methacrylate) (PMMA)^[14, 15], and SiO₂^[13, 16, 17], the fabrication of large area, high quality 2D CCs from soft hydrogel colloids, such as poly(*N*-isopropylacrylamide) (PNIPAM) microgel spheres, is even harder. Similar with the preparation of 2D CC of hard colloids, presently 2D microgel CCs were also fabricated *via* dip coating^[18, 19], solvent evaporation^[20–24], and interfacial assembly^[25–28]. These methods were originally developed for the fabrication of 2D CCs from hard colloids^[3–6], which exhibited the drawbacks of small size of the resulting arrays^[7, 20, 22], limitation to planar substrates^[26], and/or requirement of specific equipment^[27]. In addition, the 2D ordering is

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easy to be lost in the drying or transferring step involved in these methods^[29] because of the soft nature of microgel spheres.

We recently develop a new method to fabricate 2D CC of microgel spheres. This method includes the assembly of monodisperse microgel spheres into 3D CCs, *in situ* fixing the first 111 plane of the 3D assembly onto the substrate^[30–32]. The *in situ* fixation of microgel spheres can be achieved by a photochemical reaction^[30, 31], or spontaneous surface charge reversal of the substrate^[32]. Since large area, high quality 3D microgel CCs can be facilely assembled^[33–41], and the 111 plane is fixed *in situ*, the new method allows the fabrication of large area, high quality 2D microgel CCs. Beside, planar substrate, 2D microgel CCs can also be fabricated on non-planar substrates. In addition, the inter-particle distance can be facilely tuned^[30–32].

Besides pure PNIPAM microgels, hybrid microgels, in which inorganic nanoparticles are embedded inside the gel spheres, have also been used as building blocks to fabricate 3D^[42, 43] and 2D CCs^[28, 44]. Hybrid microgels are highly attractive functional materials because they combine the unique properties of both microgels and inorganic nanoparticles^[45]. On one hand, the introduction of nanoparticles endows the microgels with novel optical, electronic, and magnetic properties^[43]. On the other hand, the microgel matrix not only provides a suitable support for the nanoparticles and prevents them from aggregating, but also provides the possibility to modulate their catalytic activity^[46, 47] and optical properties^[48–50].

Previously, 2D^[28, 44] and 3D CCs^[42, 43] of hybrid microgels were fabricated by the synthesis of hybrid spheres, and then by assembling them into ordered structures. The resulting 3D arrays are highly ordered; however, the ordering of 2D CCs is not satisfying. Herein, we report the use of a new developed method to fabricate 2D arrays of hybrid microgels by taking Ag-PNIPAM microgel as a representative hybrid microgel. Our new method includes the procedure of first assembly of PNIPAM microgels into ordered 2D arrays, and then *in situ* synthesis of Ag nanoparticles by using the microgel spheres as nanoreactor^[51–53], which is different from the previous approach by synthesis of hybrid microgels at first. The advantages of such a method are that the large area, high quality 2D CCs of Ag-PNIPAM hybrid microgels can be fabricated; and the fabrication of a large size array, the use of non-planar substrates and the tuning of inter-particle distance^[30–32] can be achieved.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAM), acrylic acid (AAc), and *N,N'*-methylenebis(acrylamide) (BIS) were purchased from Alfa Aesar. 3-Aminopropyltriethoxysilane (APTES) was purchased from Acros. Sodium dodecyl sulfate (SDS) was purchased from Sigma-Aldrich. Potassium persulfate (KPS), 1,6-diaminohexane, 2,2-dimethylsuccinic anhydride, tetraethyl orthosilicate (TEOS), sodium borohydride (NaBH₄), silver nitrate (AgNO₃), potassium hydroxide (KOH) and ethylenediamine were purchased from local providers. The monomer NIPAM was purified by recrystallization from hexane/acetone. AAc was distilled under reduced pressure. Toluene was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone before use.

Microgel Synthesis

The microgels were synthesized by free-radical precipitation polymerization. For the 850 nm microgel, NIPAM, AAc, SDS and BIS were dissolved in 95 mL of distilled water. The total amount of the monomers was 0.015 mol and the molar ratio of the monomers NIPAM:AAc:BIS was 88.45:10:1.55. The solution was purged with nitrogen and heated to 70 °C. After 1 h, 5 mL of 0.06 mol/L KPS solution was added to initiate the polymerization. The reaction was allowed to process for 4 h. The resulting microgel was purified by successive centrifugation, decantation and redispersion. 1200 nm microgel and 1430 nm microgel were synthesized by adding a shell to a core microgel as described previously^[54]. For the synthesis of the core microgels, the total amount of the monomers was still 0.015 mol, and the molar ratio of the monomers NIPAM:AAc:BIS was 88.8:10:1.2 for 1200 nm and 88.6:10:1.4 for 1430 nm microgel, respectively. The solution was purged with nitrogen and heated to 70 °C. After 1 h, 5 mL of 0.06 mol/L KPS solution was added to initiate the polymerization. When the reaction proceeded for 4 h, a 100 mL preheated shell solution with the same

composition was added. After purging with nitrogen for another 30 min, 5 mL of 0.06 mol/L APS solution was added. The reaction was allowed to process for additional 4 h. The resulting microgels were purified again by successive centrifugation, decantation and redispersion. The microgels were named according to their hydrodynamic diameter (D_h) at 20 °C and pH 3.5.

Fabrication of 2D Ordered Microgel Arrays

The 2D microgel arrays were fabricated on the charge-reversible substrates. The substrates (glass slides, silicon wafers and quartz slides) were cleaned by using freshly prepared piranha solution (1/3 V/V H₂O₂-H₂SO₄ mixture) (Caution: This solution is extremely corrosive!). They were then modified with amino groups by soaking in 1 wt% anhydrous toluene solution of APTES for 4 h, followed by washing with toluene. The substrates were incubated in anhydrous THF containing 10 mg/mL 2,2-dimethylsuccinic anhydride and 5% triethylamine for 10 h. After rinsing with methanol and DI water, they were blow-dried with nitrogen.

To assemble the microgel arrays, concentrated microgel dispersions (pH ~3.5) were loaded into cells composed of a glass slide and a surface-modified substrate separated by 2 layers of Parafilm. After standing at room temperature for 5 days, the cells were opened and the substrates were rinsed thoroughly in flowing DI water. They were then blow-dried with nitrogen.

Introduction and Reduction of Ag⁺ Ions

To introduce Ag⁺ ions into the microgel particles, a 0.1 mol/L solution of AgNO₃ was prepared and the pH was adjusted to 8 by 1.0 mol/L KOH. The film was then immersed in the solution for 3 h. After a brief washing in DI water, the film was immersed in 0.1 mol/L NaBH₄ at 0 °C for 3 h^[52]. The film was then washed thoroughly and blow-dried.

Characterization

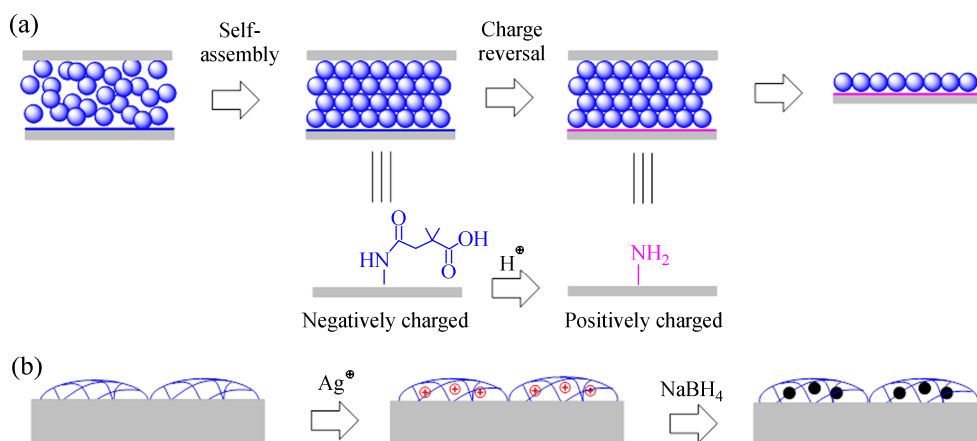
The size and size distribution of microgel particles were determined by dynamic light scattering with a Brookhaven 90 Plus laser particle size analyzer. The sample temperature was controlled with a build-in Peltier temperature controller. Atomic force microscopy (AFM) of 2D arrays was measured on a CSPM5500 scanning probe microscope in tapping mode (Benyuan, China). The optical images were acquired on a Leica TCS SP8 Confocal Microscope in bright field mode. UV-Vis absorption spectra were measured on a TU 1810PC UV-Vis spectrophotometer (Purkinje General, China). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin Elmer PHI 1600 spectrometer.

RESULTS AND DISCUSSION

Assembly of 2D Microgel Arrays

The 2D CCs of Ag-PNIPAM hybrid microgel were fabricated by firstly fabricating a 2D array of PNIPAM microgel, followed by *in situ* synthesis of Ag nanoparticles in the microgel spheres (Scheme 1), instead of assembling the arrays directly from Ag-PNIPAM hybrid microgel. The 2D CCs of PNIPAM microgel were fabricated by using our new method. The microgel spheres were assembled into 3D CCs at first, then *in situ* fixing of the first 111 plane of 3D assembly. For the method to fix the microgel spheres, the charge reversal approach was chosen^[32] (Scheme 1a).

The building blocks, PNIPAM microgel spheres, were synthesized by free-radical precipitation polymerization. AAc units were incorporated to make them bear negative charges. The incorporation of AAc units also allowed the loading of Ag⁺ ions in the second step (Table S1 in supporting information, SI). The particles with temperature-dependent sizes are shown in Fig. S1 (in SI). To make a charge-reversible substrate, the substrates were modified with APTES to introduce amino groups on the surface, and then treated with 2,2-dimethylsuccinic anhydride for converting amino groups to carboxylic acid groups. The modified substrates are charge-reversible because amides with neighboring carboxylic acid groups exhibit pH-dependent hydrolysis^[55]. With the hydrolysis of amides, the amino groups were regenerated. Therefore, the surface charge can be reversed from negative to positive (Scheme 1a).



Scheme 1 (a) Fabrication of 2D microgel CC on charge-reversible substrate (A 3D microgel CC was first assembled on the substrate. With the spontaneous charge reversal of the substrate during aging, the first 111 plane was fixed *in situ* onto the substrate *via* electrostatic interaction. Removal of the unbound spheres gave a 2D microgel CC.); (b) *In situ* synthesis of Ag nanoparticles using the surface-bound microgel spheres as nanoreactors

3D microgel CCs were then assembled on the substrates. The originally negatively-charged surface allowed the microgel spheres close to the substrate, which were also negatively charged, to self-assemble into a highly ordered structure. With the gradual hydrolysis of the amides and the regeneration of the amino groups, the negatively charged microgel spheres were close to the substrate and formed the 111 plane of the 3D CC. They were fixed *in situ* on the substrate because of the electrostatic interaction between the microgel spheres and the substrate^[32]. After the unbound microgel spheres were washed away, a 2D microgel array attached on the substrate was obtained.

The structure of the resulting 2D arrays was studied by AFM and optical microscopy. As shown in Fig. 1, all of these arrays exhibit a highly ordered structure. The highly ordered structure of 2D arrays apparently inherited from the highly ordered structure of 3D microgel CC. More importantly, because the microgel spheres

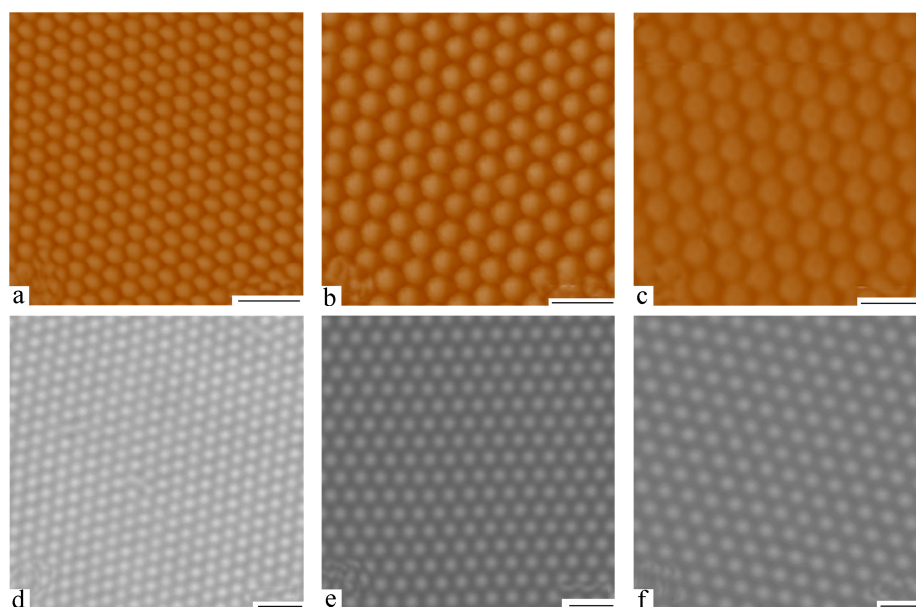


Fig. 1 (a–c) AFM and (d–f) optical microscopy images of 2D microgel CCs from (a, d) 850 nm, (b, e) 1200 nm and (c, f) 1430 nm microgel. The concentration of the microgel dispersions is 3.20 wt%, 3.42 wt% and 3.10 wt%, respectively. Scale bar: 2 μ m.

were fixed onto the substrate *in situ* via the spontaneous charge reversal of the substrate, the ordered structure was maintained.

Introduction and Reduction of Ag^+ Ions

The 2D arrays of PNIPAM microgel were then converted to 2D arrays of Ag-PNIPAM composite microgel *via in situ* synthesis of nanoparticles in the interior of the microspheres^[42, 52] (Scheme 1b). For this purpose, the films were soaked in AgNO_3 solution. Ag^+ ions were loaded into the microgel spheres through an ion-exchange mechanism and bound with the carboxylate groups of AAc repeat units^[42, 52, 56–58]. The loaded Ag^+ ions were then reduced by NaBH_4 to generate Ag nanoparticles^[52].

Figure 2(a) compares the UV-Vis spectra of 2D microgel CC, the same array loaded with Ag^+ ions and the same array after Ag^+ ions were reduced. The characteristic surface plasmon resonance band of Ag nanoparticles centered at ~ 400 nm, confirming the successful synthesis of Ag nanoparticles^[42, 52, 53]. Figure 2(b) shows the Ag 3d region of the XPS spectra of array. The Ag $3d_{5/2}$ and Ag $3d_{3/2}$ core level binding energies appear at 368.8 and 374.8 eV, respectively. The values are in good agreement with bulk metallic silver values (368.4 and 374.4 eV, for Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively)^[59], evidencing again the formation of metallic silver in microgel array.

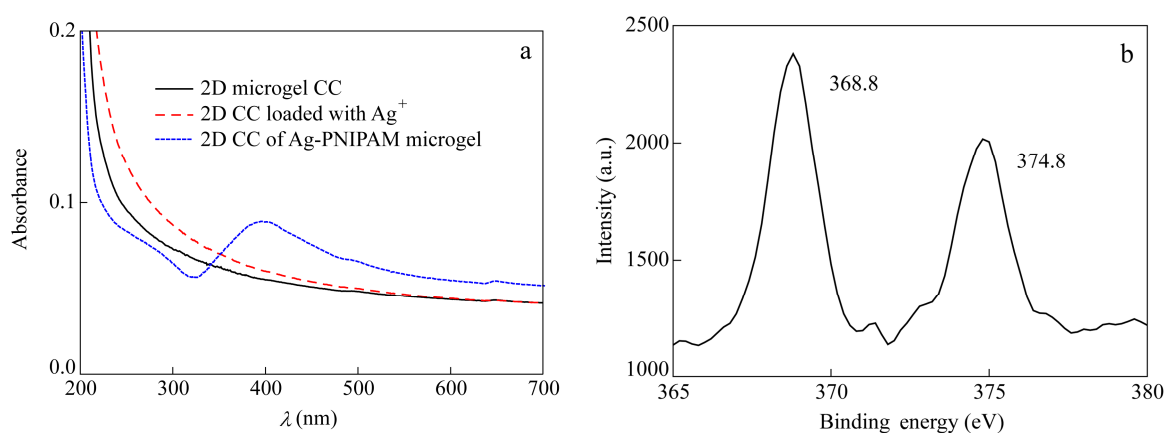


Fig. 2 (a) UV-Vis absorption spectra of a 2D microgel CC (line), the same array loaded with Ag^+ ions (dash) and the array after Ag^+ ions were reduced (dot); (b) Ag 3d region of XPS spectrum of a 2D array of Ag-PNIPAM hybrid microgel

The morphology of resulting 2D arrays was studied by AFM. As shown in Fig. 3, all the 2D microgel arrays remain highly ordered. The result suggests that the loading of Ag^+ ions and the following reduction reaction do not disturb the pre-formed ordered structure, attributing to the strong interaction between the microgel spheres and the substrate. Figure 4 compares the morphology of a microgel array before and after introducing Ag nanoparticles. For this purpose, AFM images with a higher magnification are acquired. It can be seen that the microgel spheres present a smooth morphology before the introduction of Ag nanoparticles; however, their surface becomes rough after the introduction of nanoparticles. The change in morphology can be observed more clearly from the line profile of the AFM images (Figs. 4b and 4d).

The ordering of 2D arrays was also characterized quantitatively by pair correlation function $g(r)$, which is defined as the Eq. (1):

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

where $\langle \rho \rangle$ is the average particle number density, a is the shell area and $n(r, r+dr)$ is the number of particles that lie within the shell considered^[7, 60]. The function describes the probability to find a particle at a distance r from a given particle in the 2D space. The peaks in the distribution indicate the preferred distances as shown in Fig. 5. They all display a series of peaks, suggesting the extension of structural order over a long distance. Comparison of $g(r)$ of the 2D arrays to that of a perfectly packed hexagonal array reveals that the peaks appear at

the same positions, confirming that the hybrid microgel spheres are arranged hexagonally.

Another quantitative measurement of ordering, *i.e.*, the ratio of full width at half maximum of the first peak in the Fourier transform of the function $g(r) - 1$, k , to that of a perfectly packed array, k_0 , was also calculated for the 2D arrays^[7, 60] (Fig. 6). The k/k_0 value was determined to be 1.09, 1.07, and 1.16, for the arrays from 850, 1200 and 1430 nm microgel, respectively. It is known that k/k_0 value is 1 for a perfectly packed array, and it

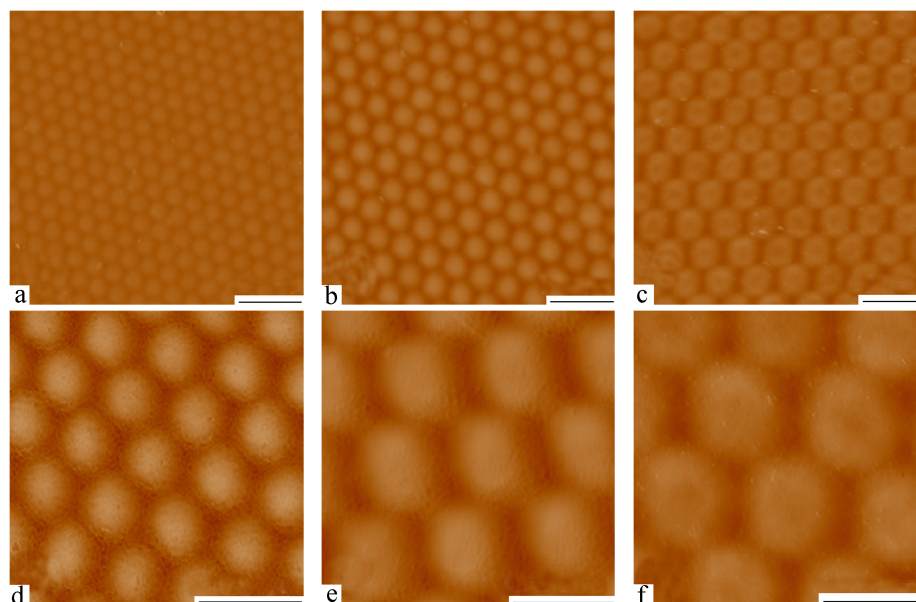


Fig. 3 AFM images of 2D arrays of Ag-PNIPAM hybrid microgel

The parent 2D microgel arrays were fabricated using microgels with different sizes: (a, d) 850 nm microgel; (b, e) 1200 nm microgel; (c, f) 1430 nm microgel. The scale bar is 2 μm for (a–c) and 1 μm for (d–f).

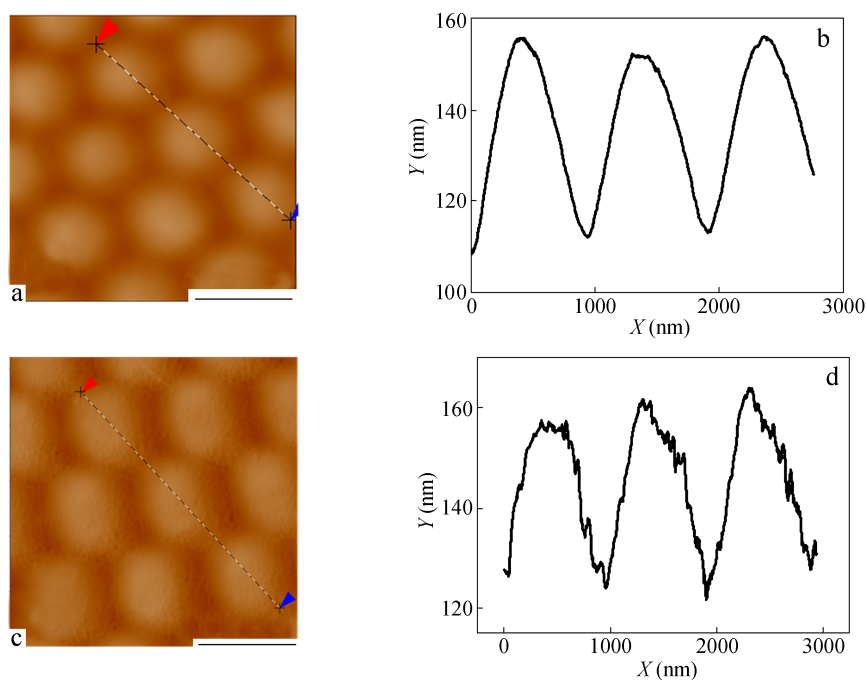


Fig. 4 (a, c) AFM height images and (b, d) line profiles of (a, b) a 2D array of 1200 nm microgel and (c, d) the corresponding 2D array of Ag-PNIPAM hybrid microgel (Scale bar: 1 μm .)

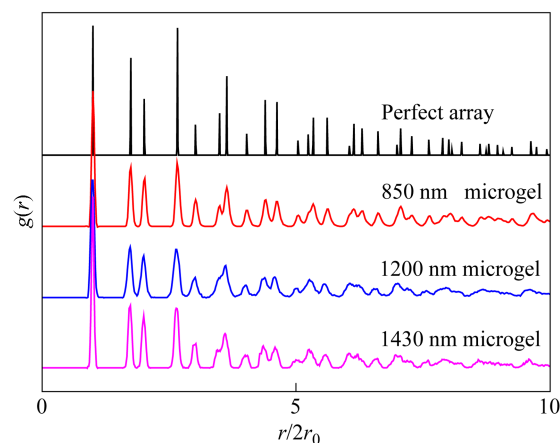


Fig. 5 Pair correlation function, $g(r)$, of the 2D arrays of Ag-PNIPAM hybrid microgel. The parent 2D microgel arrays were fabricated using 850 nm microgel, 1200 nm microgel, and 1430 nm microgel, respectively.

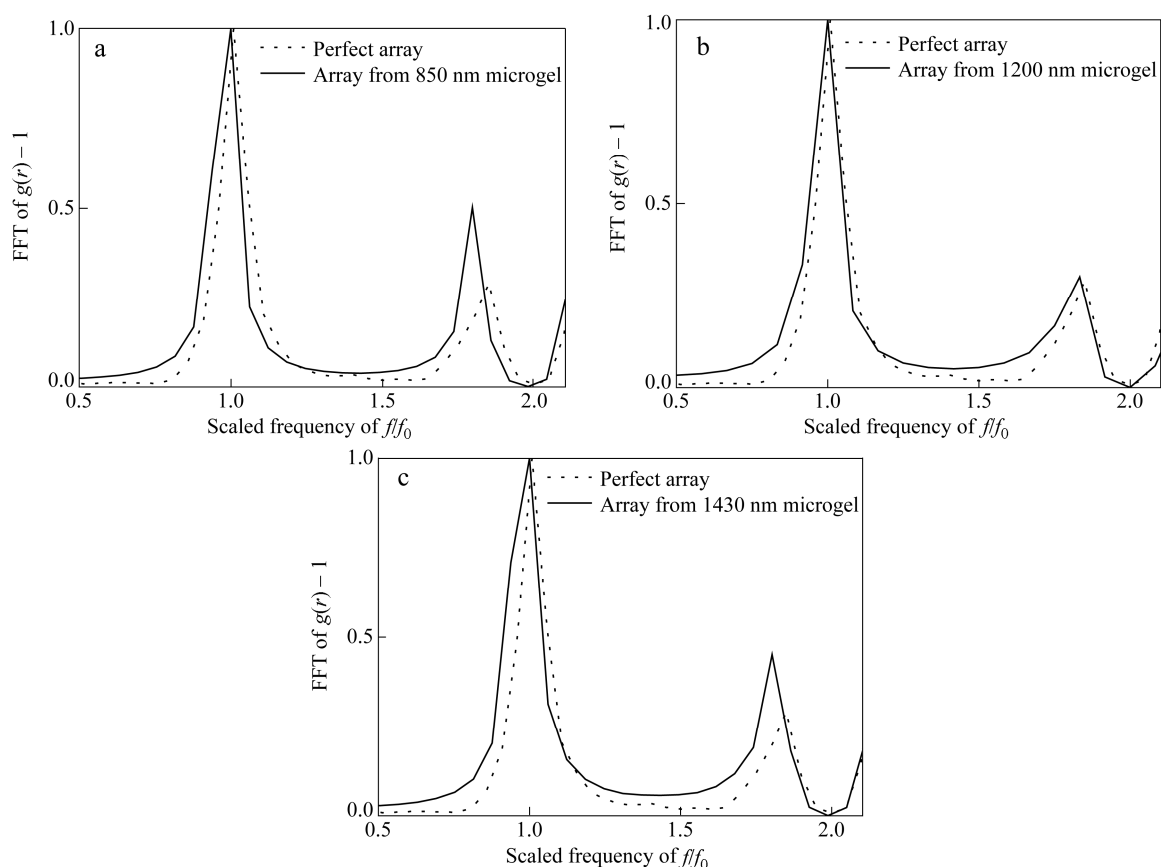


Fig. 6 Single-sided power spectra Fourier transforms (FT) of $g(r)$ of the 2D arrays of Ag-PNIPAM hybrid microgels compared to FT of the corresponding perfectly ordered arrays. The power spectra were scaled to have identical maxima at $f/f_0 = 1$. The parent 2D microgel arrays were fabricated using (a) 850 nm microgel, (b) 1200 nm microgel and (c) 1430 nm microgel, respectively.

becomes larger with increasing disorder. Particularly, a k/k_0 value less than 1.5 indicates a highly ordered structure^[7]. The k/k_0 values close to 1 confirm again that the 2D arrays of Ag-PNIPAM hybrid microgel are highly ordered.

The highly ordered structure of arrays was also confirmed by laser diffraction. When illuminated with monochromatic laser light, the array displays a diffraction pattern with symmetrical distinct spots, suggesting that the hybrid microgel particles in the illuminated area are arranged perfectly into a hexagonal crystalline array^[61, 62] (Fig. 7).

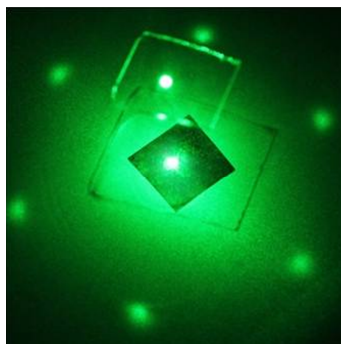


Fig. 7 Diffraction pattern of normally incident laser beam transmitted through a 2D array of Ag-PNIPAM hybrid microgel (The online version is colorful.)

The method developed here allows tuning of the inter-particle distance of 2D CCs. When fabricating the parent 2D arrays of PNIPAM microgel, the inter-particle distance decreases with increasing the concentration of microgel dispersion^[30–32]. The introduction and consequent reduction of Ag^+ ions will not change the inter-particle distance. Therefore, the inter-particle distance of resulting 2D CCs of Ag-PNIPAM microgel also decreases with increasing the concentration of microgel dispersion. As an example, Fig. 8 shows three 2D arrays of Ag-PNIPAM microgel fabricated using 1200 nm PNIPAM microgel. The three PNIPAM microgel dispersions with different concentrations were used to assemble 2D microgel CCs. The hybrid microgel arrays were obtained by the *in situ* synthesis of Ag nanoparticles. The resulting arrays are all highly ordered. In addition, when the concentrations of microgel dispersion decrease from 3.88 wt% to 3.12 wt%, the inter-particle distance of hybrid microgel arrays increases from ~815 nm to ~1100 nm.

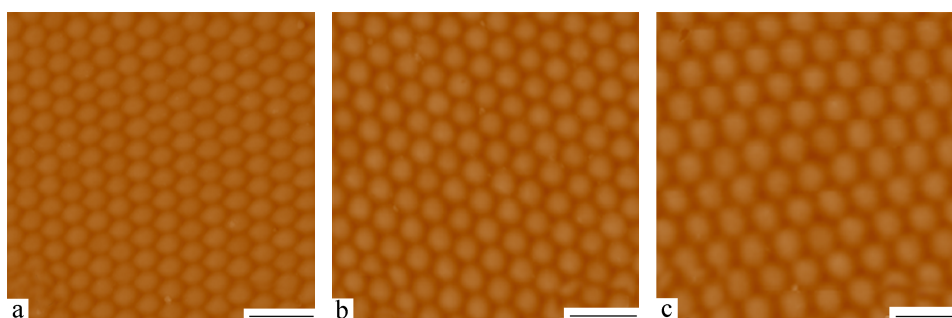


Fig. 8 AFM images of 2D arrays of Ag-PNIPAM microgel from 1200 nm microgel. Concentration of the microgel dispersion is (a) 3.88 wt%, (b) 3.42 wt% and (c) 3.12 wt%, respectively. The inter-particle distance is (a) ~815 nm, (b) ~960 nm and (c) ~1100 nm, respectively. Scale bar: 2 μm .

The method also allows the fabrication of large area 2D CCs from hybrid microgels, because large area 2D microgel CCs can be facily fabricated^[30–32]. Figure 9(a) shows the photo of a 2D array of Ag-PNIPAM hybrid microgel. The array displays vivid diffraction colors, indicating its highly ordered structure. The size of the area is ~8 cm $\times$ ~6 cm. Another advantage of the method is that the 2D arrays of hybrid microgels can be fabricated on nonplanar substrates. To demonstrate this, a 2D CC of PNIPAM microgel was fabricated on the inner wall of a quartz tube. The array was then converted to an array of Ag-PNIPAM hybrid microgel by *in situ* synthesis of Ag nanoparticles. Because of its crystalline structure, the array also displays vivid diffraction color, as shown in

Fig. 9(b). The successful assembly of ordered 2D microgel CCs on the bent surface may be attributed to the soft nature of microgel spheres, which makes microgel colloidal crystals intrinsically defect-tolerant^[40].

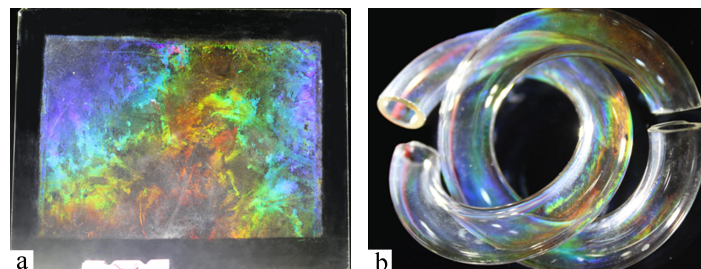


Fig. 9 (a) Optical photograph of a 2D array of Ag-PNIPAM hybrid microgel fabricated using a 10 cm × 8 cm glass slide as substrate; (b) A 2D array of Ag-PNIPAM hybrid microgels fabricated inside the inner wall of quartz tubes (The online version is colorful.)

CONCLUSIONS

In conclusion, the 2D arrays of Ag-PNIPAM hybrid microgels have been fabricated by assembling of 2D CCs of PNIPAM microgel, and then *via in situ* synthesis of Ag nanoparticles inside the PNIPAM microgel spheres as the nanoreactor. Taking advantage of this method, the resulting 2D arrays of Ag-PNIPAM hybrid microgels present highly ordered structure. In addition, such a simple method allows the tuning of inter-particle distance in the arrays, the fabrication of a large area array, and the use of nonplanar substrates. Besides Ag nanoparticles, many other nanoparticles, including semiconductors (e.g. CdS)^[42, 52], metal oxide (e.g. Fe₃O₄)^[52] and other metal nanoparticles (e.g. Au)^[43] can be synthesized *in situ* inside the microgel spheres by a similar way. It is expected that other 2D CCs of hybrid microgels can also be prepared with a similar method.

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