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Photonic Hydrogels

Polymerized Microgel Colloidal Crystals: Photonic Hydrogels with Tunable Band Gaps and Fast Response Rates**

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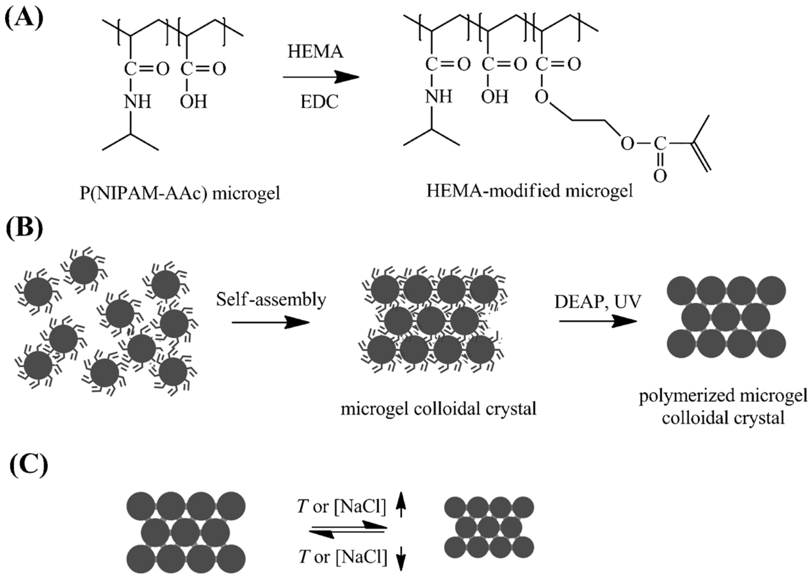
Colloidal crystals, three-dimensional periodic arrays of submicron particles, have attracted considerable attention because of their novel applications in a wide range of disciplines, especially as photonic band-gap materials.[1,2] Usually monodisperse hard microspheres, such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and SiO_2 spheres, are used to assemble colloidal crystals. However, soft hydrogel microspheres, especially poly(N-isopropylacrylamide) (PNIPAM) microgels, can also self-assemble into highly ordered colloidal crystals.[3–5] In contrast to the hard spheres, PNIPAM microgels are stimuli-responsive.[6–8] In addition, microgel colloidal crystals are intrinsically defect-tolerant, thanks to the soft nature of the particles.[9] Therefore it is believed that PNIPAM microgels are promising candidates for the fabrication of large arrays of colloidal crystals.[10] Unfortunately the ordered structure of microgel colloidal crystals is fragile.[11] It remains an unresolved problem for their use in the large-scale production of photonic crystals.[10]

Some efforts have been made to solve this problem. One way is to embed the colloidal crystals in a hydrogel matrix.[12,13] Unfortunately the matrix may significantly reduce the extent of the volume phase transition of the microgel particles.[14] Alternatively the microgel particles in colloidal crystals can be cross-linked directly, using a suitable cross-linker.[15,16] However addition of the cross-linker solution may disturb the preformed ordered structure. Cross-linker diffusion is also time-consuming and always results in a heterogeneous distribution of the cross-linker. The cross-linking reactions are not efficient enough and may require harsh conditions. A new method was developed later in which P(NIPAM-NMA) microgels (NMA: N-hydroxymethylacrylamide) cross-link simultaneously when the microgels assemble into ordered structures at the air–water surface, taking advantage of the self-cross-linking property of NMA.[17] This method is also time-consuming and difficult to control. Herein we propose a facile method to cross-link microgel colloidal crystals. The PNIPAM microgel particles, with polymerizable vinyl groups on their surface, first self-assemble into highly ordered colloidal crystals. Then the ordered structure is locked by light-initiated free-radical polymerization of the surface-bonded vinyl groups (see Scheme 1). The resulting polymerized microgel colloidal crystals (PMCC) can respond to both temperature and salt, and the band gap can be tuned in a wide range. In contrast to colloidal crystals embedded in a hydrogel matrix, the swelling of the microgel particles is almost unaltered. In addition the response of PMCC is quite fast.



Scheme 1. A) Synthesis of HEMA-modified microgels by coupling of P(NIPAM-AAc) microgels with HEMA under catalysis by EDC. B) Synthesis of polymerized microgel colloidal crystals (PMCC). C) Response of PMCC to temperature or salt.

Polymerizable vinyl groups were introduced onto the surface of the microgel particles by modification of a P(NIPAM-AAc) microgel (AAc: acrylic acid) with 2-hydroxyethyl methacrylate (HEMA) using *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) as catalyst (Scheme 1 A, Supporting Information, Figure S1 and S2). An approximately 4.3 wt% solution of the HEMA-

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modified microgels, containing photo-initiator DEAP, were then prepared and allowed to self-assemble into highly ordered colloidal crystals (Scheme 1B).[3–5] With the formation of crystalline structure, the dispersion becomes iridescent, however, the ordered structure can be easily destroyed by heating or shearing.[18] To stabilize it, the dispersion was exposed to UV irradiation. With the polymerization of the surface vinyl groups, a cross-linked hydrogel film was obtained. Direct visual inspection reveals that the crystalline structure is intact after polymerization. The sample is still iridescent (Figure 1A), with crystallites ranging from hundreds of micrometers to millimeters in diameter. More importantly, a sharp diffraction peak was observed from the reflection spectra of the polymerized sample, confirming again its periodical ordered structure (Figure 1B).

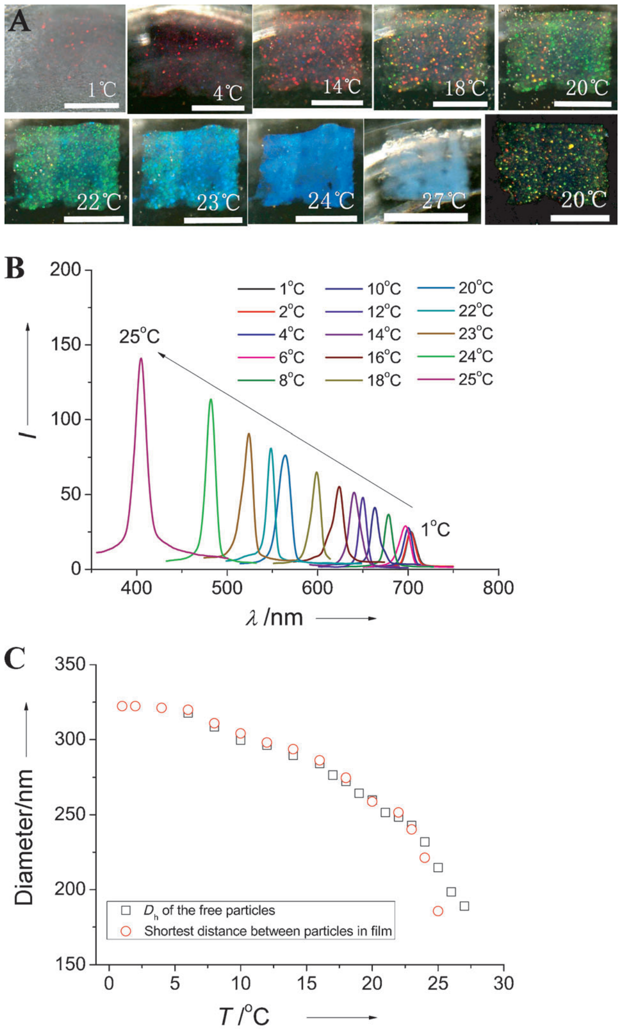

Figure 1. A) Photographs of a freestanding PMCC film taken when temperature rising from 1 to 27 °C. The last one (bottom right) was taken when the film was cooled back to 20 °C. The film was immersed in 0.5 M NaCl solution. pH 3.0. Scale bar: 0.5 cm. B) Reflection spectra of the PMCC film measured at various temperatures. C) Hydrodynamic diameter (D_h) of microgel particles in diluted microgel dispersion measured by dynamic light scattering and the shortest distance between two microgel particles in PMCC films, or the diameter of the particles (D_f), calculated from light diffraction, as a function of temperature.

The PMCC films remain thermosensitive. As shown in Figure 1A, the film is highly swollen and red in color at 1 °C. Upon heating, it shrinks gradually. Simultaneously, its color turns gradually to green (22 °C), blue (24 °C), and finally white (27 °C). Figure 1B shows that the diffraction peak of the film gradually shifts to a shorter wavelength with increasing temperature. At 1 °C, the peak centers at 703 nm. It moves to 549, 482, and 405 nm when heated to 22, 24, and 25 °C, respectively. Note that the diffraction peak of the PMCC film, or the band gap, can be finely tuned in the whole visible spectrum, simply by changing temperature. The color change observed in Figure 1A is in excellent agreement with the shift of the diffraction peak. When heated to 27 °C, the peak shifts into the UV range, therefore the film becomes white (Figure 1A).

The heat-induced shift of diffraction peak is attributed to the shrinkage of the microgel particles.[6–8] The size of the free particles dispersed in the same aqueous solution was measured by dynamic light scattering. As shown in Figure 1C, the particles shrink gradually with increasing temperature. Fast shrinkage was observed at 23 °C, which can be identified as the onset of phase transition. The particles in PMCC films should experience a similar heat-induced shrinkage. As a result the lattice constant of the crystal decreases (Scheme 1C) and the diffraction peak shifts to a shorter wavelength. The shrinkage of the microgel particles also results in an increased refractive index.[19] As the dielectric constant modulation increases, light is diffracted more efficiently, therefore the intensity of the diffraction peak increases with increasing temperature. (Figure 1B)

Immobilization of a PNIPAM microgel usually results in a reduced thermo-responsivity. When adsorbed onto a solid substrate, the swelling capacity can be reduced by one order of magnitude.[20] When embedded in hydrogel matrixes, the swelling of the particles can also be reduced to a large degree.[14,21] To study the effect of immobilization, the size of the microgel particles in the PMCC films was determined from the diffraction wavelength, λ, which is described by Bragg's law [Eq. (1)]:

$$\lambda_{h,k,l} = \frac{2na\sin\theta}{\sqrt{h^2+k^2+l^2}} \tag{1}$$

where h, k, and l are the Miller indices, θ the diffraction angle (90° for normal incidence), a the lattice constant, and n the refractive index of the film. PNIPAM microgel colloidal crystals are reported to have a bcc[19] or fcc structure.[12,22,23] Assuming a bcc lattice and identifying the observed diffraction peak as the (1,1,0) reflection, or assuming an fcc lattice and identifying the diffraction peak as the (1,1,1) reflection, the shortest distance between two microgel particles in the film, or the diameter of the particles in the film, D_f, can be calculated from the diffraction wavelength λ_m, using the same equation [Eq. (2)]:[14]

$$D_f = \frac{\sqrt{6}}{4n}\lambda_m \tag{2}$$

Using Equation (2), and taking n of the film as that of water (ca. 1.335) because of the high water content of the film,[23] D_f values at various temperatures were determined from the corresponding λ_m. As expected, D_f decreases with increasing temperature, following a same trend as D_h.(Figure 1C) In addition, D_f is comparable to D_h measured at the same temperature. In other words, immobilization of the microgel particles does not affect their swelling. Although cross-linked with neighboring particles in the film, they can still swell freely as those free particles. This behavior is very different from other immobilized microgel particles.[14,20,21]

PNIPAM microgels are not only sensitive to temperature, but also ionic strength.[24–26] Therefore ionic strength can also be used as an external stimulus to tune the color and band gap of PMCC films. Figure 2A shows a PMCC film is almost transparent and colorless at [NaCl] = 10 mM. It turns to red, green, and blue, when [NaCl] increases to 40, 256, and 562 mM, respectively. The corresponding reflection spectra of the film are shown in Figure 2B. With increasing [NaCl], the diffraction peak shifts gradually towards short wavelength, from 760 nm at [NaCl] = 10 mM, to 403 nm at [NaCl] = 667 mM. The λ_m is 760, 663, 561 and 452 nm, when [NaCl] is 10, 40, 256, and 562 mM, respectively, which corresponds well with the color. In addition the intensity of the diffraction peak increases with increasing [NaCl]. All these phenomena can be explained by the salt-induced deswelling of the microgel particles in the film, which results in a smaller lattice constant of the film and an increased refractive index of the microgel particles. Diameter of free particles, D_h, and diameter of particles in the film, D_f, were also determined. As shown in Figure 2C, both D_h and D_f decrease with increasing [NaCl]. At the same [NaCl], D_f is comparable to D_h, suggesting again that the swelling of the microgel particles is not affected by immobilization. Relatively large deviation between D_h and D_f at high [NaCl] may be explained by the partial aggregation of PNIPAM particles at high [NaCl]. As a result, D_h of the free particles measured by light scattering may be larger than their real size.

Because the volume phase transition of PNIPAM microgels is reversible,[6,7] the response of PMCC films to external stimuli, in terms of both temperature and ionic strength, is also reversible. As an example, Figure 1A shows that, after a heating/cooling cycle, the color of the film is largely recovered when temperature is restored to be 20 °C. Similar recovery of the film color was found when [NaCl] is adjusted back to be 250 mM (Figure 2A). Figure S3 further shows that when temperature cycles between 19.0 and 23.8 °C, the diffraction peak shifts from approximately 587 to approximately 489 nm and then moves back. Only a small variation was observed in 5 heating/cooling cycles.

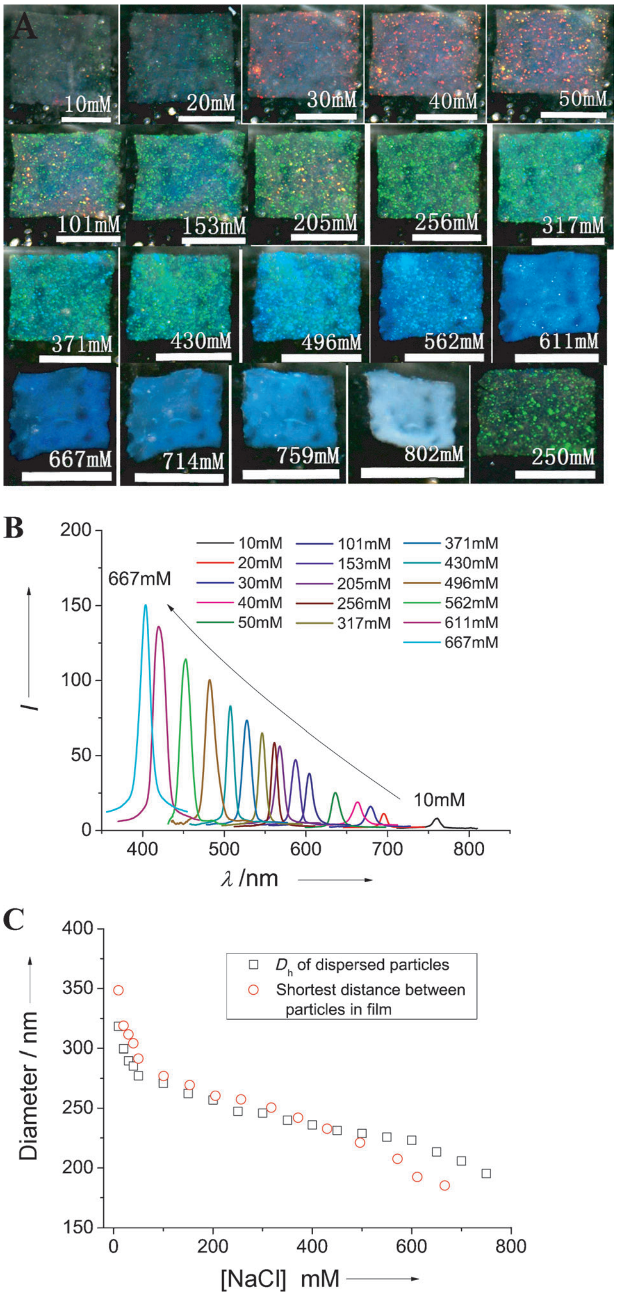

Figure 2. A) Photographs of a freestanding PMCC film taken with [NaCl] increasing from 0 to 750 mM. The last one (bottom right) was taken when [NaCl] was decreased back to 250 mM. Scale bar: 0.5 cm. pH 3.0. $T = 23$ °C. B) Reflection spectra of the PMCC film measured at various [NaCl] values. C) Hydrodynamic diameter (D_h) of microgel particles in diluted microgel dispersion measured by dynamic light scattering and the shortest distance between two microgel particles in the PMCC film, or the diameter of the particles (D_f), calculated from light diffraction, as a function of [NaCl] in the media.

A big problem for macroscopic hydrogels is that their response to external stimuli is extremely slow.[27] To study the response rate of the new photonic hydrogel, the shift course of the diffraction peak of a PMCC film, as a result of a jump in ionic strength, was monitored.(Figure 3A) Similar to many hydrogels,[28] the kinetic curves of PMCC can be well-fitted with a single-exponential function (Figure 3B), suggesting its swelling/deswelling can be described by Tanaka–Fillmore theory.[29] According to this theory, the swelling/deswelling kinetics of a hydrogel are governed by the cooperative diffusion of the gel network. It is noteworthy that ordinary hydrogels are networks of linear polymer chains, while PMCCs are networks of spherical microgel particles. From single-exponential fitting, the characteristic response time, τ, was determined to be 150.3, 131.8, and 114.5 s, when [NaCl] increases stepwise from 200 to 250, 300, and 350 mM (Fig-

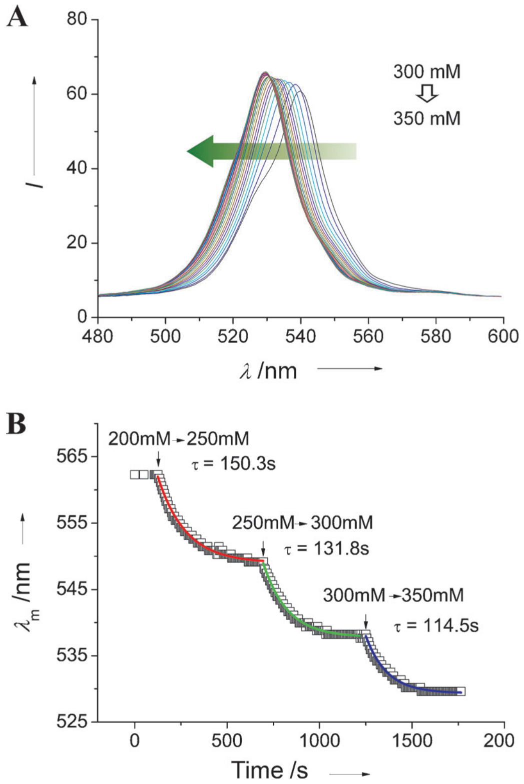

Figure 3. A) Reflection spectra showing the response of a PMCC film with time upon increasing [NaCl] from 300 to 350 mM. The spectra were recorded every 25 s. pH 3.0. T = 23 °C. B) Shift of the diffraction peak position with time in response to stepwise increase in [NaCl] as indicated. The solid line shows the best single exponential fit to the data.

ure 3C). Considering the size of the gel (side length is approximately 0.7 cm at [NaCl] = 350 mM), the response rate is extremely fast. The collective diffusion coefficient of the PMCC film was estimated to be around 4×10^{-4} cm^{2}s^{-1}, which is about three orders of magnitude larger than that of ordinary PNIPAM hydrogels (on the order of 10^{-7} cm^{2}s^{-1}).[30] The fast response of PMCC may be attributed to its structural unit, the small microgel particles. It is well established that microgels respond much fast than macroscopic hydrogels.[12,31,32] The interconnected porous structure of the PMCC film, which allows the solvent to diffuse into and out of the gel smoothly, should also play an important role.[33] Previously it was reported that an inverse opal hydrogel, with a similar mesoporous structure, responds more than 1000 times faster than ordinary homogeneous gels.[34] Usually porous structures were introduced into hydrogels by polymerization in the presence of pore-forming agents followed by removal of these agents.[27] In contrast, the interconnected porous structure in PMCC, which is actually the interstitial space among the microgel particles, is inherent. (Scheme 1C)

In conclusion, we developed a facile method to stabilize the highly ordered structure of a PNIPAM microgel colloidal crystal. The cross-linking reaction is highly efficient and does not require the addition of a cross-linker, therefore will not disturb the highly ordered structure. The resulting polymerized microgel colloidal crystals can respond to external stimuli, including temperature and ionic strength. Using these stimuli the color and the band gap of the hydrogel can be finely tuned in the whole visible range. The response is reversible and fast. The swelling of the immobilized microgel particles is almost unaffected, which is quite different from those stabilized by embedding in a hydrogel matrix. The inherent mesoporous structure not only provides a quick response, but also allows big biomolecules to diffuse into the interior of the gel. As the low refractive index of the PNIPAM microgel can be improved by the incorporation of inorganic particles as shown by Karg et al.,[35] it is expected this new photonic hydrogel will find applications in areas such as sensing and displays.

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