Colloidal Crystals Hot Paper

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Photonic Crystals with a Reversibly Inducible and Erasable Defect State Using External Stimuli**

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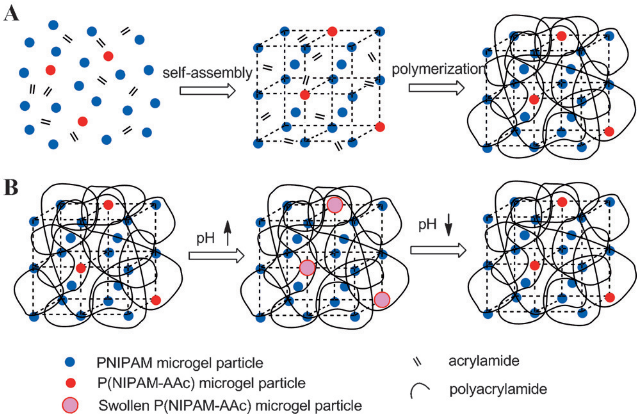
***Abstract:** The controlled introduction of artificial extrinsic defects is critical to achieve the functions of photonic crystals. Smart defects capable of responding to external stimuli lead to more advanced applications. Here we report a microgel colloidal crystal with a defect state which could be induced and erased reversibly by external stimuli. The crystal was assembled from PNIPAM microgel and P(NIPAM-AAc) microgel of the same size. The resulting doped crystal does not exhibit a defect state in its stop band because of the similar optical properties of the dopant and the host. By increasing the pH value, however, the dopant P(NIPAM-AAc) spheres swell to a larger size and turn into real defects in the crystal, resulting in the appearance of defect state. Adjusting the pH value back restores the size of the dopant spheres, and thus erases the defect state. Temperature, a second external stimulus, could also be used to induce and erase defect states of the crystal.*

Photonic crystals (PC), for example, colloidal crystals (CCs), are periodic dielectric structures with a photonic band gap or stop band, in which electromagnetic waves of an energy within this bandgap are prohibited to propagate.[1] They have found potential applications ranging from telecommunication to sensing, displaying, lasing, and optical computing. Similar to the doping of semiconductors, many of the functions of PCs can only be achieved by the controlled introduction of artificially engineered extrinsic defects, including point, line, and planar defects.[2,3] For example, point defect in a PC with a complete photonic band gap can trap or localize photons, and thus act as a microcavity with a high-quality factor.[3–5] However, introduction of artificial defects into PC still remains a big challenge.[2,3] Although various methods have been developed, including lithography,[6] multi-photon photopolymerization,[7] and electron-beam writing,[8] they are often time-consuming, limited to small areas, and possibly not applicable to mass production. On the other hand, it is highly desirable if the defect state of a PC can be tuned using an external stimulus, which will lead to new applications of the PCs. In this regard, Ozin and co-workers[9–13] designed CCs with smart planar defects, however, only a small shift in defect-state wavelength could be induced by an external stimulus.[10] Here we demonstrate that doped microgel CCs could be facilely assembled. More importantly, the defect states in the CCs could be induced and erased reversibly using an external stimulus.



Scheme 1. A) Self-assembly of colloidal crystals from a mixed solution of PNIPAM microgel and P(NIPAM-AAc) microgel with the same size. The ordered structure is then stabilized by embedding within a polyacrylamide hydrogel matrix. B) pH change reversibly induces and erases artificial point defects in PNIPAM microgel colloidal crystal doped with P(NIPAM-AAc) microgel spheres. The microgel CCs are close packed. For the sake of clarity, a non-close packed structure was depicted here.

The strategy for the fabrication of doped microgel CCs is shown in Scheme 1. Doping is a simple way to obtain CCs with artificial point defects. For semiconductors, doping is often carried out by the diffusion of acceptor or donor atoms into the host lattice that has already been formed in advance. For CCs, however, the dopant colloids have to be added into a dispersion of the host colloids before the 3D crystalline lattice is assembled. Unfortunately the introduction of colloids with a different size (dopant) often leads to disordering and phase segregation in the resulting structure.[14,15] Consequently the doped crystals usually do not exhibit a defect state but severely decreased Bragg peak intensity.[14,15] To circumvent this problem, here we used poly(*N*-isopropylacrylamide-co-acrylic acid) (P(NIPAM-AAc))

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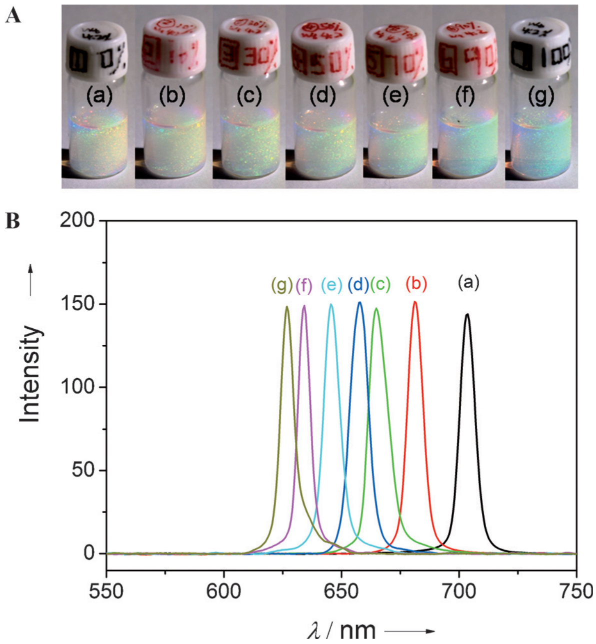

Figure 1. A) Photographs of colloid crystals assembled from PNIPAM microgel dispersions containing 0% (a), 10% (b), 30% (c), 50% (d), 70% (e), 90% (f), and 100% (g) P(NIPAM-AAc) microgel. B) Reflection spectra of the microgel colloidal crystals. The pH value of the dispersions is about 3.5. The hydrodynamic radius at 20°C and pH 3.5 is 160 nm for PNIPAM and 158 nm for P(NIPAM-AAc), respectively.

microgel with the same size as the host poly(*N*-isopropylacrylamide) (PNIPAM) microgel as dopant. As shown in Figure 1 A it is easy for the pure dispersions (a: PNIPAM; g: P(NIPAM-AAc)) to self-assemble into highly ordered crystalline structure, as indicated by their iridescent color, because both microgels are monodispersed.[16–19] For the mixed dispersions (b to f in Figure 1 A), highly ordered colloidal crystals were also successfully obtained. The fraction of P(NIPAM-AAc) microgel in the dispersions varies from 0 in sample a to 100% in sample g. The results suggest colloidal crystals could be assembled from a mixed microgel dispersion with any composition. Figure 1 B shows the reflection spectra of the samples. A sharp diffraction peak was observed from all the samples, including both the pure CCs (a and g) and the doped ones (b–f). The appearance of a diffraction peak confirms again the formation of periodical ordered structure in all these samples. The successful assembly of crystalline structures from the mixed dispersions may be mainly attributed to the same size of the two microgels. Therefore the addition of P(NIPAM-AAc) microgel into PNIPAM microgel does not affect its monodispersity. The soft nature of the microgel spheres which makes microgel CCs intrinsically defect-tolerant may also play an important role in the assembly of the doped CCs.[20,21]

Although doped CCs were successfully fabricated from two kinds of microgel spheres with same size, optical characterization indicates that the doped samples do not exhibit a defect state.(Figure 1 B) Indeed, the doped CCs (i.e., b–f) behave similar to the undoped ones (i.e., a and g). The results indicate that the two kinds of microgel spheres in the crystals are indistinguishable for light, because both their size and refractive index are similar under the experimental conditions.

Thanks to their stimuli-responsivity, it is possible to make the two kinds of spheres distinguishable by applying an external stimulus. As a result the doped CCs will exhibit a defect state. One way to achieve this goal is by pH change because the P(NIPAM-AAc) microgel is pH-sensitive while the PNIPAM microgel is not.(Scheme 1 B) Since the crystalline structure of microgel CCs is fragile and can be easily destroyed by heating or shearing,[22] it was first stabilized by forming a hydrogel matrix surrounding the microgel spheres, as shown in Scheme 1 A.[23–25] As an example we synthesized a PNIPAM microgel CC doped with 10% P(NIPAM-AAc) microgel. The ordered structure was stabilized using a polyacrylamide hydrogel matrix. As shown in Figure 2 A, the sample displays a sharp Bragg peak centered at about 818 nm when measured at 34°C and at pH value of 3.5. At this pH the sizes of the two microgels are comparable (Figure 2 C). They are indistinguishable by light, therefore no defect state was found. When the pH is adjusted to 4.0, however, a narrow dip (transmission window) appears within the CC's stop band frequency (Figure 2 A).[10–12,26] Apparently the appearance of the defect state (or impurity mode, pass band as called in some literatures[27]) should be attributed to the pH-induced swelling of the P(NIPAM-AAc) microgel spheres. As shown in Figure 2 C, when the pH increases to 4.0, the P(NIPAM-AAc) microgel swells to a larger size, while the size of PNIPAM microgel remains unchanged. In this way, the P(NIPAM-AAc) spheres become distinguishable from the PNIPAM host spheres. The defect state becomes more pronounced when further increasing the pH to 5.0 and 6.0, (Figure 2 A) because the size differences between the dopant and the host becomes even larger (Figure 2 C). Simultaneously, the stop band is significantly widened and becomes asymmetric. A similar phenomenon has been observed previously from other CCs with point[26] or planar artificial defects.[10–12] The widening of the stop band is much more pronounced than that previously observed, possibly because of a high defect density in the present sample.[10–12,26] According to Pradhan et al.[26] the introduced impurities can be an "acceptor" or a "donor", depending on their size and refractive index.[27–29] Here although the size of the dopants (swollen P(NIPAM-AAc) spheres) is larger than that of the hosts (PNIPAM spheres), their refractive index is lower than that of the hosts. For microgel spheres, the refractive index factor dominates over the size factor in determining their scattering efficiency,[23] therefore the swollen P(NIPAM-AAc) dopants could be regarded as "acceptor" impurities. The dopant P(NIPAM-AAc) spheres are randomly distributed throughout the structure, so are the resulting point defects. Upon increasing the pH, the stop band also moves to a longer wavelength, which may be explained by the swelling of the hydrogel matrix because of the mutual interaction between the hydrogel matrix and the embedded microgel particles.[25]

The defect state cannot only be introduced by increasing the pH value, but also be erased by decreasing the pH value. As shown in Figure 2 B, when the pH is adjusted back to 3.5, the defect state disappears totally. In addition, the stop band is

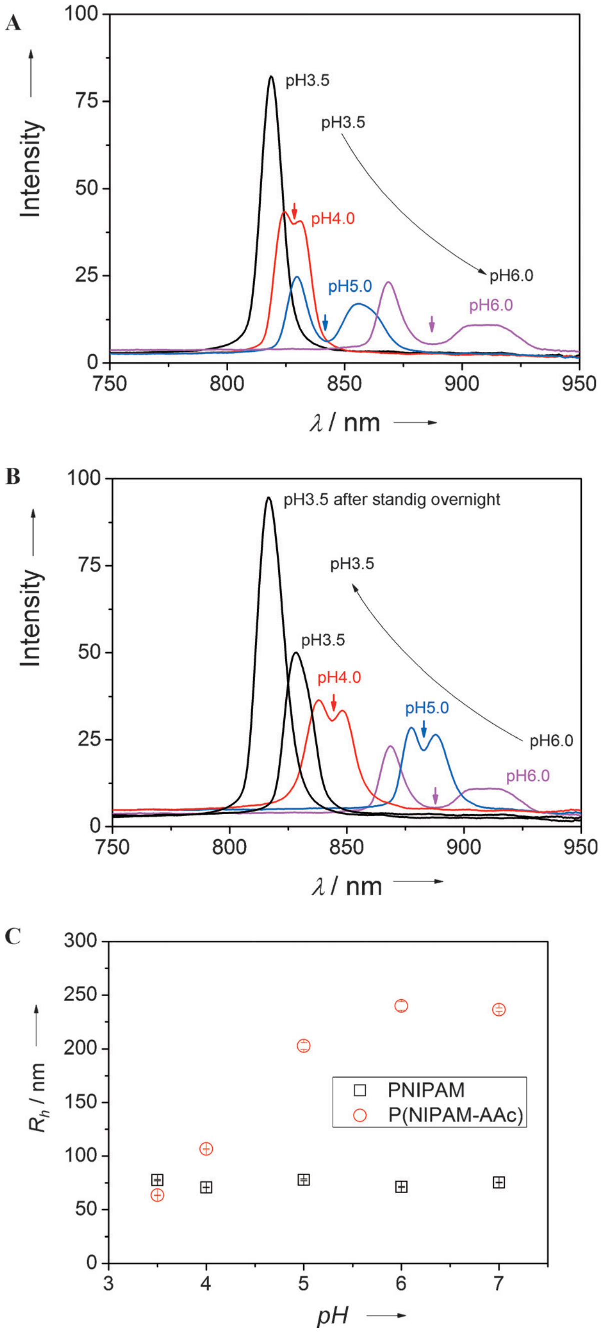

Figure 2. A) Inducing defect state in a stabilized microgel colloidal crystal film by increasing the pH value from 3.5 to 6.0. B) Erasing the defect state via decreasing the pH from 6.0 to 3.5. C) Hydrodynamic radii (R_h) of the free microgel spheres as a function of pH. The deflection spectra and R_h values were measured at $T = 34$ °C. The arrows in (a) and (b) indicate defect states.

restored to be sharp and symmetric. The disappearance of the defect state could be explained by the fact that the size of the P(NIPAM-AAc) microgel spheres is restored when pH is adjusted back. Therefore the two kinds of microgel spheres become again indistinguishable by light (Figure 2C). The position of the stop band also shifts back to a shorter wavelength. Compared to the process of increasing the pH value, a hysteresis was observed in the process of decreasing the pH, which should be attributed to the slow kinetics of the hydrogel matrix.[25] Indeed, the stop band shifts back to its original position after standing overnight (Figure 2B). The defect state could be induced and erased quickly because the small size of the microgel spheres allows the spheres to respond to external stimuli instantly.[30–33] As shown in Figure S3 (see the Supporting Information), the defect state disappears in about 60 s after changing the pH. As shown in Figure S4, the defect state could be induced and erased repeated by pH cycling.

Besides the pH value, the P(NIPAM-AAc) microgel is also thermosensitive, therefore temperature could be used as another external stimulus to induce and erase defect states in P(NIPAM-AAc) microgel-doped PNIPAM microgel colloidal crystals. A similar stabilized colloidal crystal film doped with 10% P(NIPAM-AAc) microgel was used for this test. The film was first immersed in a pH 5.0 buffer at 34 °C. Under these conditions, there is a significant difference in size between the two microgels,(Figure 2C) therefore a defect state was observed within the stop band of the film, as shown in Figure 3A. The film was then heated to erase the defect state. Figure 3A shows the reflection spectra of the film measured at different temperatures. Upon heating the stop band of the film shifts gradually to shorter wavelengths as a result of the shrinkage of the hydrogel matrix (Figure 3C). At 37 and 40 °C a clear defect state can still be observed, however, when further heated to 45 and 51 °C, the defect state disappears completely. Meanwhile the Bragg peak is restored to be sharp and symmetric. As shown in Figure 3C, when heated from 34 to 51 °C, the size of PNIPAM microgel spheres remains unchanged, however, the P(NIPAM-AAc) microgel spheres shrink significantly. At 37 and 40 °C there is still a difference in their size, therefore P(NIPAM-AAc) microgel spheres could act as artificial defects. When heated to 45 and 51 °C, however, both PNIPAM and P(NIPAM-AAc) spheres are fully collapsed and their size becomes comparable. Therefore the P(NIPAM-AAc) spheres could no longer act as defects and the defect state disappears from the stop band.

An opposite process was observed when cooling the film back to 34 °C. As shown in Figure 3B, the stop band remains sharp and symmetric when cooled to 45 °C, a temperature at which the size of the two microgel spheres are comparable. When further cooled to 40 °C, a well-defined defect state appears within the stop band. The appearance of the defect state indicates that the two microgels become different in terms of optical properties. As shown in Figure 3C, the P(NIPAM-AAc) spheres swell to a larger size upon cooling. Below ~40 °C, the P(NIPAM-AAc) spheres become larger than the PNIPAM spheres. As a result the scattering efficiency of the P(NIPAM-AAc) spheres will become smaller than PNIPAM spheres,[23] therefore these spheres turn into real defects in the host lattice. Similarly the red-shift of the stop band could be attributed to the swelling of the hydrogel matrix.[25]

In conclusion, we demonstrate that colloidal crystals could be facilely assembled from mixed microgel dispersions in which the two kinds of spheres have the same size. Because of the similar optical properties of the two kinds of spheres, the doped crystals do not exhibit defect state in their stop band.

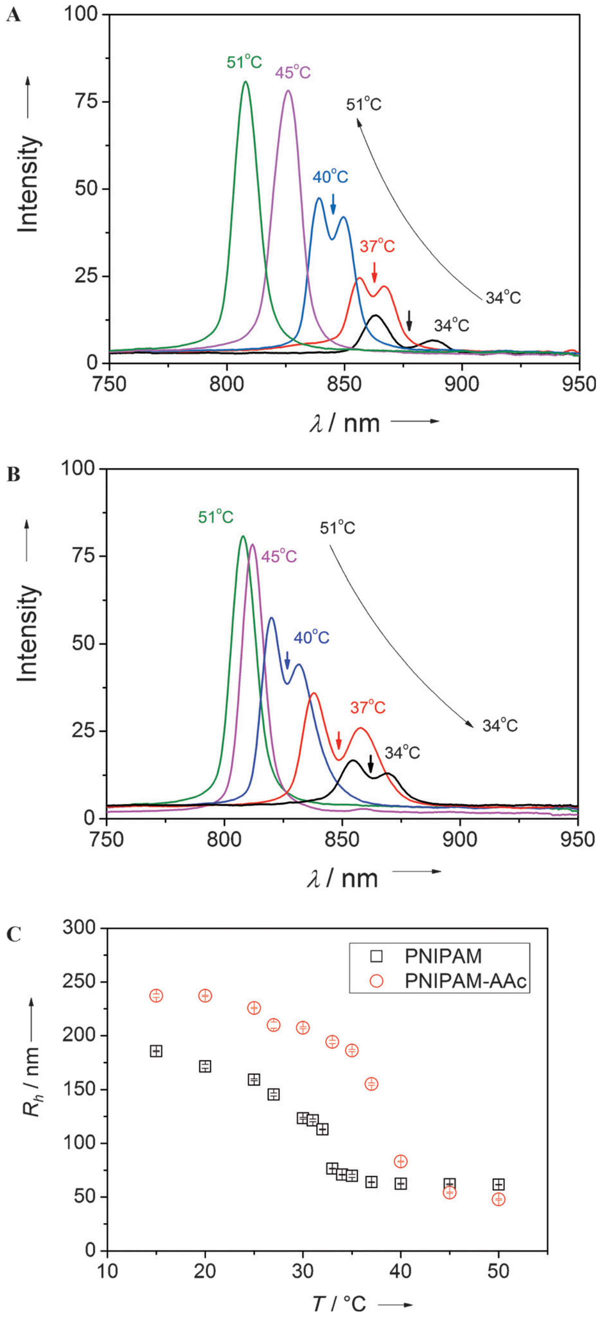

Figure 3. A) Erasing defect state in a stabilized microgel colloidal crystal film by heating from 34 to 51 °C. B) Inducing the defect state by cooling from 51 to 34 °C. C) R_h values of the free microgel spheres as a function of temperature. The deflection spectra and R_h values were measured at a pH value of 5.0. The arrows in (a) and (b) indicate defect states.

However, defect states could be induced by applying an external stimulus, such as pH and temperature, and erased reversibly. The colloidal crystals with the ability to transfer between a state with artificial defects and a state without artificial defects will allow for moulding or controlling the properties of light, and may find applications in light switching, sensing, and optical computing.

Keywords: artificial defects · colloidal crystals · defect states · microgels · stimuli-responsive materials

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