ACCOUNTS
of chemical research

Bioinspired Colloidal Photonic Crystals with Controllable Wettability

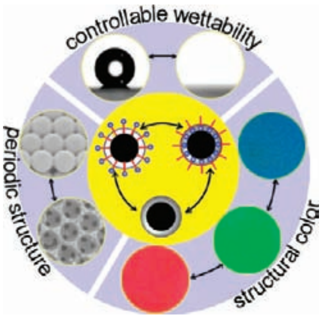
JINGXIA WANG, YOUZHUAN ZHANG, SHUTAO WANG,
YANLIN SONG,* AND LEI JIANG
Beijing National Laboratory for Molecular Sciences (BNLMS), Laboratory of New Materials, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

RECEIVED ON SEPTEMBER 14, 2010

CONSPECTUS

Because of the combinatorial advantage of their unique light manipulation properties and potential applications in novel optical devices, colloidal photonic crystals (PCs), the periodic arrangement of monodispersed latex spheres, have attracted interest from researchers. In particular, colloidal PCs exhibit structural colors based on interference effects within their periodic structures. The wavelength of these colors lies in the visible range, making them particularly attractive for a variety of applications. Colloidal PCs are extensively used in templating, catalysis, and chromatographic separations. Inspired by biological PCs with both structural color and specific wettability, researchers have fabricated colloidal PCs with controllable wettability as described in this Account. The wettability can be adjusted by the intrinsic roughness of colloidal crystals in combination with the tunable chemical composition of latex surfaces. Changes in the chemical composition of the latex surface under external stimuli, such as light, electricity, and heat, can reversibly control the wettability of PCs. Furthermore, the hierarchical structure of latex particles can effectively alter the water adhesive force of superhydrophobic colloidal PCs. Patterned PCs with a variety of wettabilities can be assembled using inkjet printing from well-designed latex suspensions.

By combining their structural color and specific wettability, we also exemplify some of the promising applications of colloidal PCs as templates for the construction of hierarchical structures, as indicators for controllable transport of liquid droplets, and as color-based sensors for the monitoring changes in their environment. These findings offer innovative insights into the design of novel colloidal PCs and will be of great importance for further applications of these materials.



1. Introduction

Colloidal photonic crystals (PCs), the periodic arrangement of monodispersed latex spheres, have attracted much interest from researchers due to their unique light manipulation properties and potential applications in novel optical devices.[1−3] In particular, the structural color of colloidal PCs with a periodic structure corresponding to the wavelength range of the visible light is paramount to fundamental research and potential applications.[4] With their combination of a specific periodic structure and a large ratio of the surface area, colloidal PCs are extensively used in templates,[5] catalysis, and chromatography separation.[6] They are also used to simulate the movement of atoms and molecules.

The special wettability of colloidal PCs can endow materials with novel functions such as self-cleaning properties for optical devices,[7] the fully wetting and spreading of the precursor to infiltrate into the opal template,[8] the full diffusion of a catalyst into a reaction system,[9] or the quick detection of liquid in microfluidic systems.[10] In general, the wettability of a solid surface can be controlled mainly by its surface chemical composition and surface topographic structure. Surface chemical composition determines surface free energy (i.e., hydrophilicity/hydrophobicity), while the surface topographic structure can amplify hydrophilicity or hydrophobicity, based on the Wenzel[11] and modified Cassie equation.[12] For colloidal PCs, their periodic latex arrangement provides an intrinsic and well-ordered surface topographic structure. These structures can manipulate the surface wettability from superhydrophobicity to superhydrophilicity when the chemical composition of latex surfaces is further tuned or subsequent surface modifications are introduced. In fact, wettability is an important property

10.1021/ar1001236

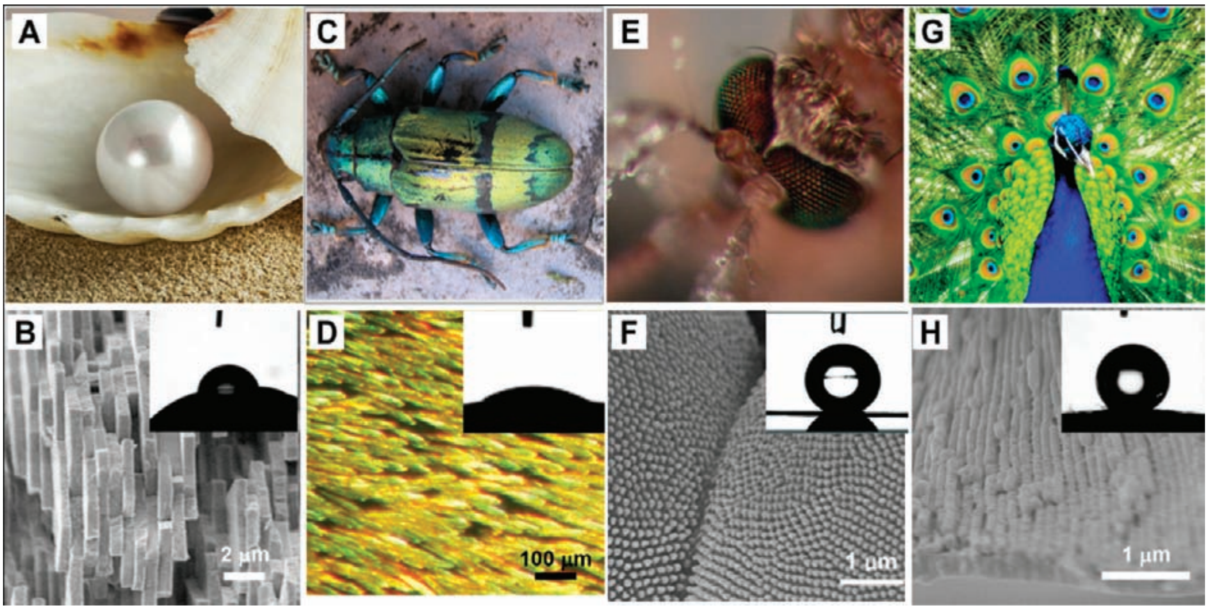


FIGURE 1. Photos and relative SEM images of typical biologic PC periodic structures with special wettability in nature: (A, B) hydrophilic pearl (with water contact angle (CA) of 45°); (C, D) hydrophilic longhorn beetles *Tmesisternus isabellae*[21] (with water CA of 25°); (E, F) superhydrophobic mosquito eye (with water CA of 149.8°);[20] (G, H) superhydrophobic peacock (with water CA of 150°). Insets in panels B, D, F, and H are the water droplet profile on the relative sample.

of a solid surface,[13] which plays an important role in daily life, industry, and agriculture. Functional surfaces with special wettability have aroused much interest because of their great advantages in applications. For example, a superhydrophilic surface with a water contact angle (CA) of almost 0° has been successfully used as a transparent coating with antifogging and self-cleaning properties, while a superhydrophobic surface can avoid contamination, the sticking of snow, and erosion. The combination of the special wettability and light manipulation properties will bring many novel properties and promising applications for colloidal PCs.

In nature, many biological PCs[14−16] have special wettability (shown in Figure 1), apart from the well-known iridescence resulting from their periodic structure. Iridescence, the change in hue of a surface with varying observation angles, is used for species recognition and mate selection by insects, birds, fishes, and reptiles,[17] while the special wettability of creatures in nature is necessary for their environmental adaptability. For example, the microstructure of butterfly wings[18] and peacock feathers[19] (Figure 1G,H) brings about beautiful structural color and special superhydrophobicity shielding them from rainfall. Thus, rain droplets cannot stay stably on those surfaces and can swiftly roll off at the slightest tremble. Simultaneously, dust particles on the surface are easily removed. Likewise, the superhydrophobicity of a mosquito's complex eyes (Figure 1E,F) favors it with good vision in a humid environment because fog droplets easily roll off the surface.[20] This self-cleaning property is not only useful in biology but also very instructive for the design of new materials with antifrost properties. Also, longhorn beetles show us an ingenious example of the harmony of PCs and special wettability (Figure 1C,D). An amazing camouflage behavior has been observed as the color pattern on their hydrophilic elytra changes from yellow to red when environmental humidity increases; vice versa, the color could reversibly return to red when environmental humidity lowers.[21] This is mainly due to water adsorption/desorption of the hydrophilic pattern region under different levels of humidity. Such color changes can remain consistent with the color of the soil on rainy or sunny days in order to protect the beetle from its natural enemies. Understanding these functions of biological PCs will open new opportunities for the design and synthesis of new functional materials.

In this Account, we will present two approaches to fabricating bioinspired colloidal PCs with controllable wettability: simply coating special materials onto the surface of colloidal crystals or using latex particles, which function as well-designed amphiphilic building blocks. Additionally, some applications for colloidal PCs with controllable wettability are demonstrated in liquid droplet transportation and visibly sensing the changes of stimuli. The section 2 is related to the construction of colloidal PCs with controllable wettability based on the topographical structure of colloidal crystals and the modulation of the chemical composition of a latex surface. The

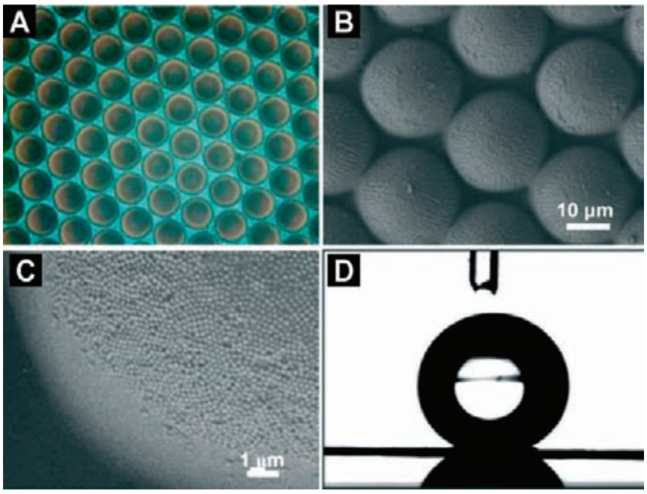


FIGURE 2. (A) An optical microscope image of artificial compound-eye analogues. (B, C) SEM images of hexagonal close-packed poly(dimethyl siloxane) microhemispheres and silica nanospheres mimicking the microstructures of mosquito compound eyes. (D) A spherical water droplet on the artificial compound-eye surface.[20].

section 3 demonstrates some visible sensing of colloidal PCs with controllable wettability. The section 4 lays out the possible development trend of the colloidal PCs with controllable wettability, which may provide promising materials for optical devices.

2. Construction of Colloidal PCs with Controllable Wettability

Various approaches have been used to construct colloidal PCs with controllable wettability. These have mainly been based on either surface topographic structures derived from periodic arrangement or modulation of surface chemical composition. Superhydrophobic/superhydrophilic films can be fabricated by coating the surface of colloidal crystals with hydrophobic/hydrophilic materials. The wettability of colloidal PCs can be further tuned by modifying the roughness of a surface based on different latex arrays or can be reversibly changed by introducing responsive molecules. Herein, we can clarify the construction of the colloidal PCs with controllable wettability mainly based on the intrinsic topography of colloidal crystals and their amphiphilic building blocks.

2.1. Superhydrophobic/Superhydrophilic Colloidal PCs from Topography. Generally, colloidal PCs with special wettability are fabricated by direct application of the intrinsic roughness of the periodic latex arrangement or inverse structure, since surface roughness has been considered as an effective approach to amplifying the intrinsic hydrophilicity/hydrophobicity of materials. Accordingly, the wettability of a film can be tuned by coating the surface of colloidal crystal with a hydrophilic or hydrophobic material or by varying the array or topography of the colloidal crystals.

Ge et al. fabricated a highly hydrophobic colloidal PC simply by the self-assembly of hydrophobic polystyrene (PS) latex spheres. The rough structure of latex assembly enhances the hydrophobicity of the hydrophobic PS.[22] Based on a similar idea, Gao et al. mimicked the superhydrophobicity of a mosquito's eye by the periodic arrangement of the monolayer colloidal crystals upon poly(dimethyl siloxane) hemispheres (Figure 2A−C) and the subsequent chemical modification of the film via a fluoroalkyl silane (FAS) molecule.[20] The film as such, with a water CA of 150°, showed extra-antifogging properties (Figure 2D). The rough structure from a binary colloidal assembly has also been utilized for the fabrication of colloidal PCs with special wettability.[23]

Simultaneously, the wettability of the colloidal PCs can be effectively tuned by adjusting the rough structure of colloidal crystals based on a change of the array or topography of the colloidal crystals. Typically, Shiu et al. fabricated PCs with tunable wettability based on the modification of the fraction of the liquid−solid contact area by varying monodispersed PS nanostructures from a close-packed to a non-close-packed array.[24] After modification of the colloidal crystals with octadecanethiol, the water CA of the PS colloidal crystals varied from 132° for PS arrays with a diameter of 440 nm to 168° for size-reduced PS arrays with a diameter of 190 nm. Subsequently, Han et al. changed the wettability of colloidal crystals by varying their topography while applying a temperature gradient field.[25,26]

It should be mentioned that an inverse opal structure provides an effective approach for the construction of novel, functional colloidal PCs with controllable wettability as well. These multifunctional PCs demonstrate extra properties besides their stopband and wettability, which will greatly expand the range of promising applications. Gu et al. developed the first fabrication of an iridescent superhydrophobic film based on uniform inverse opal structure over a large area.[27] The inverse opal structure was obtained, first, by the self-assembly of the mixing suspension of PS (several hundred nanometers) and silica nanoparticles (6 nm) and, subsequently, by calcinations to remove the polymer. The structure demonstrates hydrophobicity when being modified with FAS by thermal chemical vapor deposition. Following Gu's work, a series of functional PCs with special wettability were fabricated,[28−35] such as superhydrophilic photocatalytic TiO_2,[9] tough SiC PCs,[34] and thermostable polyimide PCs.[35] This artful strategy for fabricating functional PCs has shown its potential applications in various optical devices.

2.2. Colloidal PCs with Controllable Wettability from Amphiphilic Building Blocks. Although the above studies

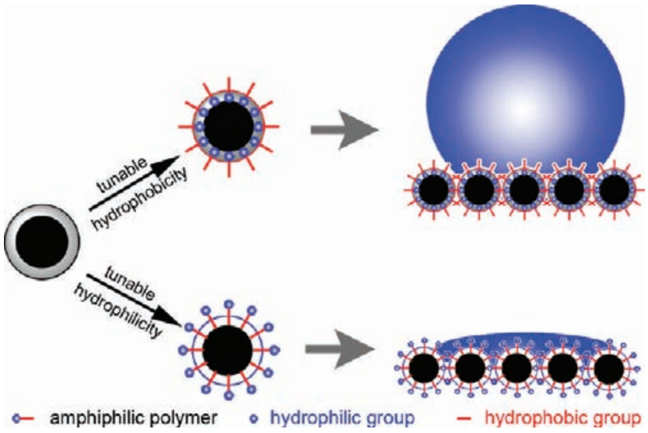


FIGURE 3. Schematic illustration of colloidal PCs with controllable wettability obtained from well-designed amphiphilic latex particles.

have provided several feasible approaches for fabricating colloidal PCs with special wettability, we propose an alternative way to control the wettability of colloidal PCs by utilizing amphiphilic latex particles instead of traditional building blocks. Figure 3 shows an overview of our preparative strategy for fabricating colloidal PCs with controllable wettability, which mainly depends on the fine design of the building blocks of colloidal PCs: amphiphilic latex particles. The core−shell latex spheres are designed and synthesized based on amphiphilic polymers; the chemical composition of the latex surface can be effectively adjusted via phase separation induced by exterior stimuli, which results in an enrichment of the hydrophilic/hydrophobic group on the latex surface and the hydrophilicity/hydrophobicity of PCs. Finally, superhydrophobic/superhydrophilic colloidal PCs are obtained based on the amplification effect of the periodic structure of colloidal crystals.

2.2.1. Control of the Wettability of Colloidal PCs. The wettability of colloidal PCs can be effectively controlled by appropriately modifying the surface chemical composition or surface free energy of a latex particle. Thus, superhydrophilic colloidal PCs could be assembled from latex spheres presenting a hydrophilic group, such as a hydroxyl group[36] or carboxyl group,[37] while a hydrophobic carbon chain, fluorine, or silicon group on a latex surface will contribute to superhydrophobic colloidal PCs.

Phase separation of a hydrophilic or hydrophobic polymer segment has become one of the important strategies for the modulation of the surface chemical composition of the latex particles and the wettability of the colloidal PCs. Colloidal PCs with controllable wettability are fabricated based on the use of amphiphilic latex spheres with a hydrophobic PS core and a hydrophilic poly(acrylic acid) (PAA) shell.[38−40] The hydrophilicity or hydrophobicity of colloidal PCs mainly depends on whether the carboxyl group is on the latex surface, originating from the reorientation of the hydrophilic polymer segment under various assembly conditions. In this case, the assembly temperature plays a key role in the reorientation of the hydrophilic polymer segment of a latex surface in Figure 4.[39,40] When the assembly temperature is higher than the temperature of the glass transition (T_g) of the polymer segment on a latex surface,[41] the polymer segment will reconstruct when driven from the lowest surface free energy. The reorientation process of a polymer segment will result in changes of the surface chemical composition and the wettability of the colloidal PCs. In contrast, the wettability of the latex surface will remain unchanged when the assembly temperature is far lower than the surface T_g of the latex polymer. For latex particles with a PS core−PMMA/PAA shell, superhydrophobic PCs are obtained at higher assembly temperature (>80 °C), while superhydrophilic PCs need a lower assembly temperature (<20 °C). Films with increased water CA can be obtained by increasing the assembly temperature. In fact, thermodynamics is a primary driving force in the phase separation of a polymer segment toward minimum interfacial energy,[42,43] which mainly depends on the assembly temperature or surface T_g of the polymer segment (Figure 4).[40] The latter could be easily adjusted by finely modifying the ratios of the soft/hard polymer segment, or the ratio of comonomers of poly(*N*-isopropylacrylamideso-*co*-*N*-isopropylmethylacrylamide) based on the lower critical solution temperature of poly(*N*-isopropylacrylamide).[44] Furthermore, the introduction of roughness will greatly enlarge the change in the wettability of colloidal PCs. The exterior atmosphere also affects the resultant wettability of the film.[25]

Meanwhile, the wettability of the films can be effectively controlled by the chemical bonding interaction of a latex surface. For instance, the hydrogen-bonding interaction can effectively lock the hydrophilic or hydrophobic group into a suitable configuration and fix the wettability of the films.[45,46] Oppositely, the breakage of the hydrogen bonding can destroy the configuration and vary the wettability of the colloidal PCs. For the colloidal PCs assembled from the latex of a PS core−PAA shell, the hydrogen bonding association among hydrophilic COOH and SO_3^- of emulsifier SDBS (when the pH of the latex system is 6.0) locks the hydrophilic COOH group of the latex surface into a preferable configuration (Figure 5), with its hydrophobic carbon chain spreading outward toward air[47−49] and the hydrophilic group extending inward toward the latex interior in Figure 5. This morphology contributes to a stable hydrophobicity of PCs.[50] In contrast, hydrogen bonding is

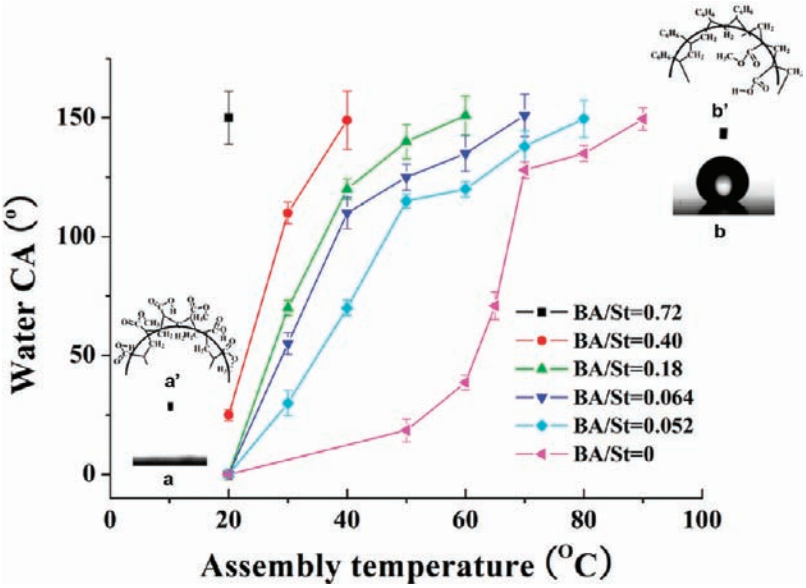


FIGURE 4. The relationship of assembly temperature and water CA of the as-prepared PCs from latex spheres with varying ratios of *n*BA/St. Inset is the possible chemical composition of the latex surface and the relative water droplet profile: (a, a′) low assembly temperature; (b, b′) high assembly temperature.[40]

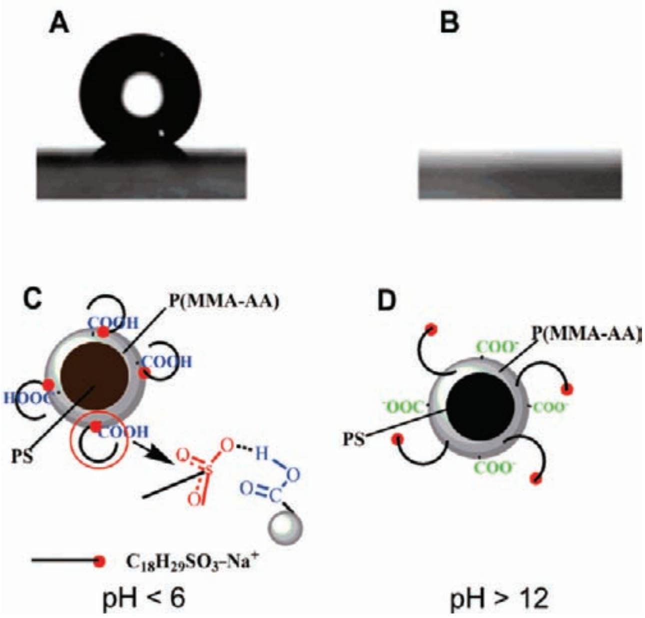
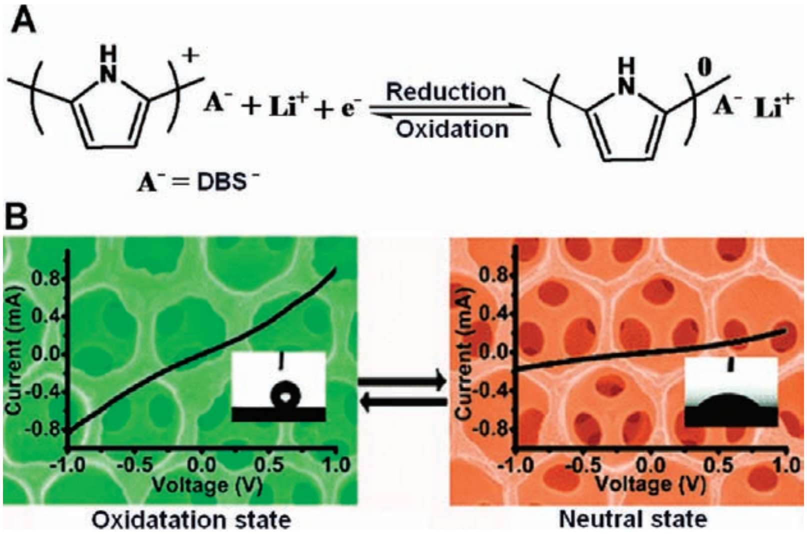


FIGURE 5. (A, B) Photographs of water droplet shape on PCs assembled from latex suspensions with pH of 6.0 and 12, respectively; (C, D) illustrations of the structure of the latex sphere in the PCs of parts A and B, respectively. The conformation of hydrogen bonding is noted by the arrow.[46]

suppressed when gradually introducing $NH_3 \cdot H_2O$ into the latex suspension and the deprotonation of COOH to COO^-, with hydrophilic groups of both COO^- and SO_3^- spreading outward toward air. The resultant film is hydrophilic. As a result, superhydrophobic or superhydrophilic PCs can be obtained at pH = 6 or 12, respectively. More importantly, a hydrophilic surface can be switched back to a hydrophobic one by treatment with an acidic vapor, such as HCl.

2.2.2. Colloidal PCs with Reversible Wettability. PCs with reversible wettability can be obtained when a responsive group is introduced onto the latex surface or into its inverse structure. The wettability of PCs can be reversibly controlled by stimuli such as light,[28] electricity,[51] or heat[52] when the corresponding responsive groups are introduced onto the latex surface. Typically, inverse opal PCs with electroresponsive wettability are obtained after electrically tunable polypyrrole (Ppy)[51] is infiltrated into the interstice of the opal template and the template is removed. The wettability of the PCs can be reversibly changed when being altered between an oxidized (left) and a neutral (right) state (Figure 6). This could be mainly attributed to the insertion or desertion of Li^+ during the oxidation–reduction process. For the neutral state, the introduction of hydrophilic Li^+ arouses enhanced hydrophilicity, while desertion of hydrophilic Li^+ leads to hydrophobicity of the resultant PCs. Furthermore, the wettability of the PC film can be finely tailored based on the gradual increase of the inserted amount of Li^+ by varying the oxidation/reduction time. The process of gradual oxidation/reduction accompanies the change of the conductivity and stopband of the PCs as well.

Similarly, inverse opal PCs with photoresponsive wettability are obtained by electrostatic layer-by-layer self-assembly of an azobenzene monolayer upon the silica inverse opal. An Azo molecule[28] can experience isomerization



Oxidatation state

Neutral state

FIGURE 6. (A) Schematic illustration for electroresponse change of chemical structure of Ppy. (B) Multiresponsive change (*I*/*V* curve, SEM, water CA change (from 139.4° to 48.7°), and structural color) of film when being altered between oxidized (green) and neutral (orange) state.[51].

between the *cis* and *trans* states, which results in a distinguished dipole moment and a wettability difference of 2°. The roughness that arises from an inverse opal structure will amplify this wettability difference. The wettability of the resultant film can be reversibly switched from 140.8° ± 3.0° to 121.8° ± 4.3° under alternated UV/vis irradiation. This reversible wettability change of colloidal PCs will have a potential application as a visible monitor of a microfluidic system. Recently, colloidal PCs with thermoresponsive wettability were built from core–shell poly(styrene/α-*tert*-buoxy-ω-vinylbenzylpolyglycidol) microspheres; the wettability of the PC's was also shown to reversibly switch from hydrophilic to hydrophobic as a function of the assembly temperature.[52] The current work on these responsive colloidal PCs suggests exciting possibilities for the creation of novel colloidal crystal arrays from smart colloidal spheres.

2.2.3. Superhydrophobic Colloidal PCs with Tunable Adhesion Properties. Interestingly, the hierarchical morphology of a latex surface plays a critical role in the wettability[53] and the water adhesive force of colloidal PCs as well.[54] Colloidal PCs assembled from latex spheres with an uneven latex surface show distinct water adhesion properties, which are similar to that of rose petals aroused from their special hierarchical structure.[55,56] This high water adhesion force of colloidal crystals has mainly arisen from the multiscale roughness produced from a hydrophilic polymer segment. The colloidal crystal shows primary roughness from a latex arrangement and secondary roughness from an uneven latex surface. Recently, we fabricated one kind of anisotropic colloidal PC from mushroom-capped latex particles.[57] The homogeneous orientation of a latex cavity showed special optic properties. This anisotropic assembly morphology can produce outstanding oil adhesion properties.

2.3. Patterned Wettability of Colloidal PCs by Inkjet Printing. Based on the above construction strategy, the colloidal PCs with controllable wettability are generally obtained from the self-assembly of the latex particles with responsive wettability. In fact, self-assembly has become a simple and common approach for the fabrication of colloidal PCs with a stopband at UV and visible ranges, and it could be easily modified for widespread manufacturing purposes. A series of approaches to improve assembly procedures have been carried out since the first publication of details about the interparticle forces governing the packing of two-dimensional latex aggregates by Nagayama's group.[55] These improvements mainly refer to a facile apparatus,[58] increased quality,[59] and a larger latex diameter. Recently, Song et al. succeeded in the rapid fabrication of large-scale colloidal PCs by spray coating.[59] The latex spheres could be effectively self-assembled during a rapid spray process. In this process, the hydrogen-bonding association among a hydrophilic COOH group around a latex surface could effectively enhance the assembly force among latex spheres, which contributes to the rapid assembly of the latex spheres during the spray process. Subsequently, Song et al. fabricated the pattern PCs by inkjet printing[60] (Figure 7) based on the effective modulation of the substrate wettability and latex composition. As-prepared colloidal PCs showed distinct structural color at different pattern regions. And the wettability of the pattern region could be modified when

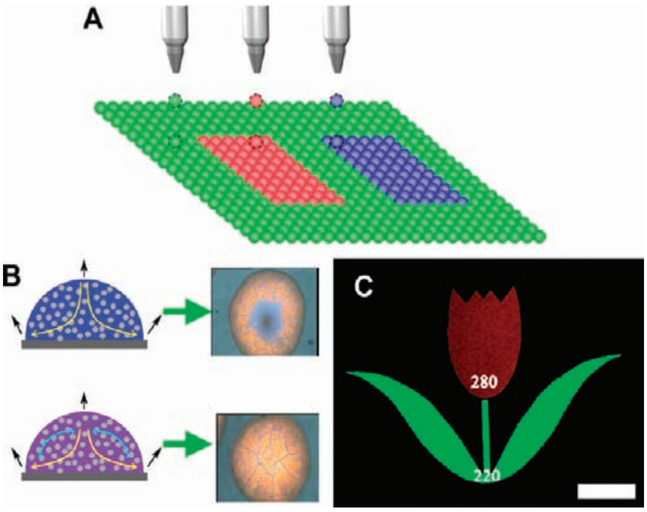


FIGURE 7. (A) Schematic illustration of patterned colloidal PCs fabricated from inkjet printing; (B) the influence of the dewetting process on spreading of latex droplets; (C) photograph of the PCs with flower-leaf pattern,[60] scale bar = 1 cm.

using latex spheres with different latex surfaces. This assembly opened a facile approach for the rapid fabrication of colloidal PCs with controllable wettability.

3. Visible Sensing of the Colloidal PCs with Controllable Wettability

Colloidal PCs with controllable wettability show promising applications in many fields, such as the controllable manipulation of small volumes of liquids in microfluidics,[36] identifiable sensing by optical signal[30] or color[29] for some systems, the fabrication of pattern PCs, etc. These applications are mainly based on the change of their optic signal/structural color responding to exterior stimuli, that is, exterior stimuli induce a change of the interplanar spacing, crystal structure, or refractive index of the composite PC systems, which leads to a change of optical signal (stopband) or structural color based on Bragg law.[61] For example, the film can identify the presence or movement of the small volumes of liquids in microfluidics[36] by optical signal[30] or color.[29] In these aqueous or solution systems, the proper wettability of colloidal PCs is especially important, which favors the full wetting or spreading of the solution upon PCs, and the extensive change in the periodic structure or refractive index. In the following part, we demonstrate a typical application of the colloidal PCs with controllable wettability in the visible sensing of exterior stimuli in reaction monitoring, humidity/oil sensing, and self-oscillation systems.

Sailor et al.[36] demonstrated a vivid example of the visible manipulation of a liquid droplet using amphiphilic magnetic one-dimensional PC chaperones. The amphiphilic PC microparticles will accumulate and spontaneously align at the interface of a two-phase liquid such as dichloromethane/water, which makes it easy to incorporate superparamagnetic nanoparticles of Fe_3O_4 into the porous nanostructure. This allows the material to chaperone microliter-scale liquid droplets when an external magnetic field is applied. The reflection spectrum of the PCs displays a peak that can identify the droplet. Meanwhile, PC nanoparticle can effectively monitor the following reaction procedure by its reflection spectra, which includes filling or draining a chaperoned droplet and combining two different droplets to perform a chemical reaction. In this work, the amphiphilic property of PCs makes it feasible for the films to accurately align around the liquid droplet.

Colloidal PCs with controllable wettability can also be employed to monitor humidity or kinds of oil. Inspired by the humidity sensing behavior of the elytra of longhorn beetles, an artificial humidity-sensitive colloidal PC was fabricated by infiltration of a hydrophilic polyacrylamide (PAAm) solution into the interstice of the opal template and subsequent photopolymerization.[62] When the humidity increases or decreases, the PAAm swells or shrinks, which results in a color change of the hydrogel responding to the humidity change[62] (Figure 8). The hydrophilicity of PCs is useful for the quick contact and spreading of the water vapor inside the film, which contributes to the swift sensing of the humidity change. The above-mentioned strategy of structural color change may not only help us get insight into the biological functionality of structural coloration but also may inspire the design of novel artificial optical devices.

By infiltration of an oleophilic phenolic resin into the opal template, oil-sensitive PCs (see Figure 9B,C) can be obtained.[30] The macroporous structure of the inverse opal benefits the oil adsorption, while the PC structure provides an optical signal upon oil adsorption. The as-prepared phenolic resin inverse opal showed distinct optic detection signals when adsorbing different kinds of oil, while carbon inverse opal[29] with a higher refractive index demonstrated an obvious color change after adsorbing different oils (Figure 9D). In this system, the superoleophilicity (Figure 9A) favors oil infiltration into the macroporous structure of the PC film, while the superhydrophobicity can effectively avoid the confusion of water/humidity to oil detection.

The optic properties of PCs and their distinct color could be effectively applied to monitor dynamic processes, such as self-oscillation systems,[63] which are always used to mimic biosystem actions.[64] To meet this special application, several details have to be satisfied. First, the hydrophilicity of

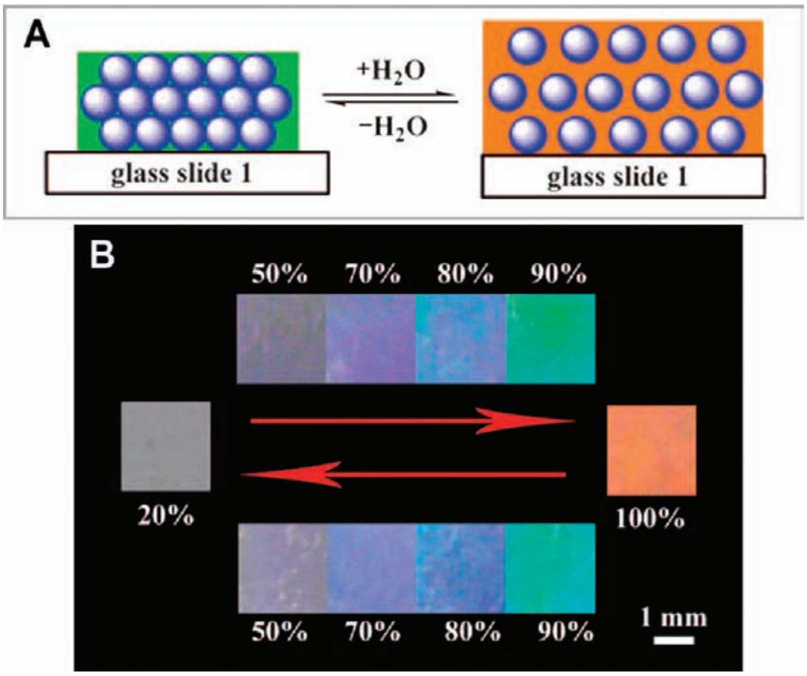


FIGURE 8. (A) The schematic illustration of the periodic structure change of a PC hydrogel before and after being fully wetted in water. (B) Photographs of the as-prepared PC hydrogel corresponding to different humidity.[61]

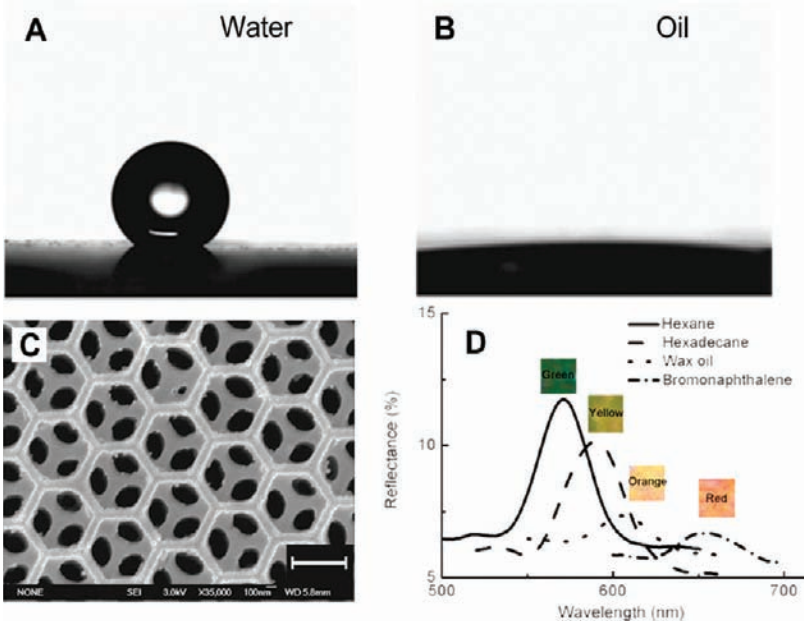


FIGURE 9. (A) Water or (B) oil droplet profile when dropped on the PCs. (C) SEM images of the PCs.[30] (D) Reflection spectra of the carbon inverse opal adsorbing four different oils. The insets show the colors of the carbon inverse opal with different oils absorbed.[29]

PCs matching the aqueous oscillation system benefits the full diffusions of the oscillation solution into the film and swift response of oscillation stimuli. At the same time, a tough film[65] is necessary for enduring changes in the periodic oscillation. Finally, a special response from the PC is required for special exterior stimuli.[66] As a result, we could synchronously and visibly monitor a pH-oscillation system by an iridescent color change in Figure 10. The controllable wettability of the colloidal PCs facilitates the quick and accurate response of the optical signal to exterior stimuli.

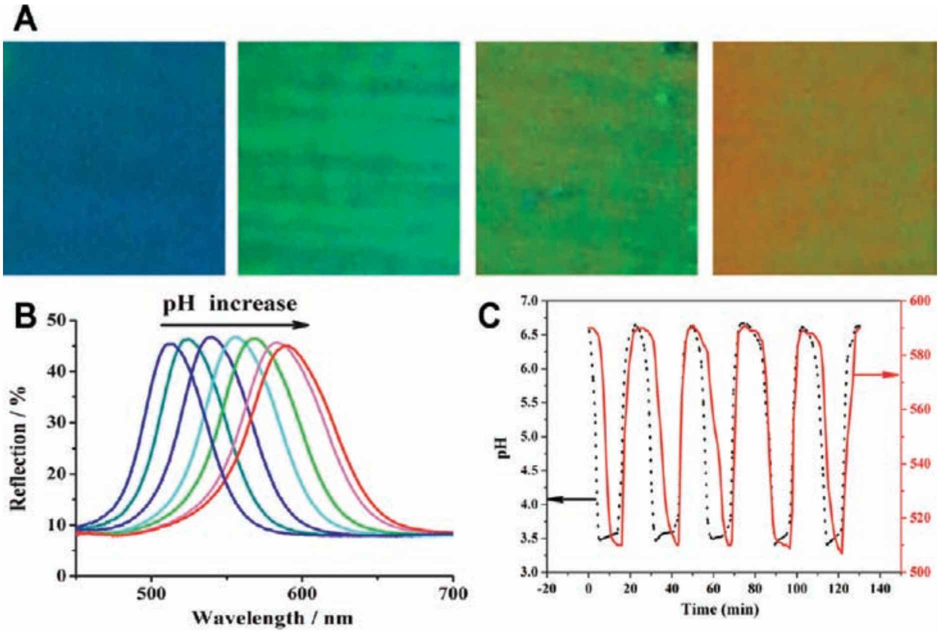


FIGURE 10. (A) Typical photos and (B) reflection spectra of a PC hydrogel during a pH oscillation cycle. (C) Time course of pH (black dot-line) induced by the bromate/sulfite/ferrocyanide oscillating reaction and the corresponding stopband position (solid line) of the PC hydrogel immersed in the pH oscillation system.[62]

4. Conclusion and Outlook

This Account reviews recent progress on the bioinspired construction of colloidal PCs with special wettability and their applications. The fabrication approach mainly refers to taking advantage of the intrinsic rough structure of colloidal crystals by just modifying surface coating or based on amphiphilic latex particles and pattern fabrication from inkjet printing. This fabrication of colloidal PCs with controllable wettability will greatly broaden the applications of PCs in various optical devices.

The research on colloidal PCs with special wettability is still on going, and numerous challenges remain in its development. First, it is necessary to design, synthesize, and apply new materials into PC systems and for the wettability of these materials to be responsive to exterior stimuli. Second, the relationship between the hierarchical structure of building blocks and special wettability needs to be further explored and revealed. For example, the design and fabrication of latex spheres with novel morphology and structure (such as, mushroom-cap shaped, snowman, or other anisotropic latex structure)[67] will greatly influence their wettability behavior. Learning from nature will guide us to optimize the structural design of artificial surfaces. Exploring new natural PCs with special wettability and illustrating the relationship between their structure and function provides new clues for producing brand-new functional materials and for developing promising new applications. This will be an effective route to bioinspired design of colloidal crystals with controllable wettability.

This work was supported by grants of the Major State Basic Research Development Program (Grant 2007CB936403) and the National Nature Science Foundation of China (Grants 21074139, 50973117, U0634004, 50625312).

BIOGRAPHICAL INFORMATION

Jingxia Wang received her Ph.D. from Tsinghua University in 2004. She worked as postdoctoral fellow in the Lei Jiang and Yanlin Song group at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) (2004−2006). She is currently an associate professor at ICCAS. Her research interest is the fabrication and application of polymer colloidal crystals.

Youzhuan Zhang received his Ph.D. degree from ICCAS in 2009. He then joined ICCAS as an assistant professor. His research interest is in the application of the colloidal crystals on solar cells.

Shutao Wang received his Ph.D. degree (2007) from ICCAS (Lei Jiang's group). After that, he worked as a postdoctoral fellow in California NanoSystem Institute and University of California at Los Angeles (Hsian-Rong Tseng's group). In 2010, he returned to ICCAS as a Professor of Chemistry. His research interest focuses on bioinspired interfacial materials and bio/nano interface.

Yanlin Song received his Ph.D. from Peking University in Department of Chemistry in 1996. He then worked as a postdoctoral fellow in Tsinghua University in 1996−1998. He is currently a professor at ICCAS. His research interest is the design and fabrication of organic functional films.

Lei Jiang received his Ph.D. degree (1994) from Jilin University in China (Tiejin Li's group). He then worked as a postdoctoral fellow in Prof. Akira Fujishima's group at Tokyo University. In 1996, he worked as a senior researcher in the Kanagawa Academy of Sciences and Technology under Prof. Kazuhito Hashimoto. In 1999, he joined ICCAS as part of the Hundred Talents Program. In 2009, he was elected academician of the Chinese Academy of Sciences. He is currently a professor at ICCAS and Dean of the School of Chemistry and Environment, Beihang University. His research interest focuses on bioinspired interfacial functional materials.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: ylsong@iccas.ac.cn.

REFERENCES

1 Xia, Y. N.; Gates, B.; Yin, Y. D.; Lu, Y. Monodispersed colloidal spheres: Old materials with new applications. *Adv. Mater.* **2000**, *12* (10), 693–713.

2 Lu, L. H.; Eychmüller, A. Ordered macroporous bimetallic nanostructures: Design, characterization, and applications. *Acc. Chem. Res.* **2008**, *41* (2), 244–253.

3 Ge, J. P.; Goebl, J.; He, L.; Lu, Z. D.; Yin, Y. D. Rewritable photonic paper with hygroscopic salt solution as ink. *Adv. Mater.* **2009**, *21* (42), 4259–4264.

4 Harun-Ur-Rashid, M.; Seki, T.; Takeoka, Y. Structural colored gels for tunable soft photonic crystals. *Chem. Rec.* **2009**, *9* (2), 87–105.

5 Stein, A.; Li, F.; Denny, N. R. Morphological control in colloidal crystal templating of inverse opals, hierarchical structures, and shaped particles. *Chem. Mater.* **2008**, *20* (3), 649–666.

6 Moon, J. H.; Yang, S. Chemical aspects of three-dimensional photonic crystals. *Chem. Rev.* **2010**, *110* (1), 547–574.

7 Sato, O.; Kubo, S.; Gu, Z. Z. Structural color films with lotus effects, superhydrophilicity, and tunable stop-bands. *Acc. Chem. Res.* **2009**, *42* (1), 1–10.

8 Gu, Z. Z.; Fujishima, A.; Sato, O. Biomimetic titanium dioxide film with structural color and extremely stable hydrophilicity. *Appl. Phys. Lett.* **2004**, *85* (21), 5067–5069.

9 Liu, J.; Li, M. Z.; Wang, J. X.; Song, Y. L.; Jiang, L.; Murakami, T.; Fujishima, A. Hierarchically macro-/mesoporous Ti-Si oxides photonic crystal with highly efficient photocatalytic capability. *Environ. Sci. Technol.* **2009**, *43* (24), 9425–9431.

10 Brennan, D.; Justice, J.; Corbett, B.; McCarthy, T.; Galvin, P. Emerging optofluidic technologies for point-of-care genetic analysis systems: A review. *Anal. Bioanal. Chem.* **2009**, *395* (3), 621–636.

11 Wenzel, R. N. Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.* **1936**, *28* (8), 988–994.

12 Cassie, A.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551.

13 Feng, L.; Li, S. H.; Li, Y. S.; Li, H. J.; Zhang, L. J.; Zhai, J.; Song, Y. L.; Liu, B. Q.; Jiang, L.; Zhu, D. B. Super-hydrophobic surfaces: From natural to artificial. *Adv. Mater.* **2002**, *14* (24), 1857–1860.

14 Kinoshita, S.; Yoshioka, S.; Miyazaki, J. Physics of structural colors. *Rep. Prog. Phys.* **2008**, *71* (7), No. 076401.

15 Vukusic, P.; Sambles, J. R. Photonic structures in biology. *Nature* **2003**, *424* (6950), 852–855.

16 Zhang, Y. Z.; Li, Z. R.; Zheng, Y. M.; Wang, J. X.; Song, Y. L.; Jiang, L. Bioinspired fabrication of polymer colloidal crystals. *Acta Polym. Sin.* **2010**, *11*, 1341–1349.

17 Whitney, H. M.; Kolle, M.; Andrew, P.; Chittka, L.; Steiner, U.; Glover, B. J. Floral iridescence, produced by diffractive optics, acts as a cue for animal pollinators. *Science* **2009**, *323* (5910), 130–133.

18 Zheng, Y. M.; Gao, X. F.; Jiang, L. Directional adhesion of superhydrophobic butterfly wings. *Soft Matter* **2007**, *3* (2), 178–182.

19 Zi, J.; Yu, X. D.; Li, Y. Z.; Hu, X. H.; Xu, C.; Wang, X. J.; Liu, X. H.; Fu, R. T. Coloration strategies in peacock feathers. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100* (22), 12576–12578.

20 Gao, X. F.; Yan, X.; Yao, X.; Xu, L.; Zhang, K.; Zhang, J. H.; Yang, B.; Jiang, L. The dry-style antifogging properties of mosquito compound eyes and artificial analogues prepared by soft lithography. *Adv. Mater.* **2007**, *19* (17), 2213–2217.

21 Liu, F.; Dong, B. Q.; Liu, X. H.; Zheng, Y. M.; Zi, J. Structural color change in longhorn beetles Tmesisternus isabellae. *Opt. Express* **2009**, *17* (18), 16183–16191.

22 Ge, H. L.; Song, Y. L.; Jiang, L.; Zhu, D. B. One-step preparation of polystyrene colloidal crystal films with structural colors and high hydrophobicity. *Thin Solid Films* **2006**, *515* (4), 1539–1543.

23 Zhang, G.; Wang, D. Y.; Gu, Z. Z.; Mohwald, H. Fabrication of superhydrophobic surfaces from binary colloidal assembly. *Langmuir* **2005**, *21* (20), 9143–9148.

24 Shiu, J. Y.; Kuo, C. W.; Chen, P.; Mou, C. Y. Fabrication of tunable superhydrophobic surfaces by nanosphere lithography. *Chem. Mater.* **2004**, *16* (4), 561–564.

25 Zhang, J. L.; Xue, L. J.; Han, Y. C. Fabrication gradient surfaces by changing polystyrene microsphere topography. *Langmuir* **2005**, *21* (1), 5–8.

26 Han, J. T.; Xu, X. R.; Cho, K. W. Diverse access to artificial superhydrophobic surfaces using block copolymers. *Langmuir* **2005**, *21* (15), 6662–6665.

27 Gu, Z. Z.; Uetsuka, H.; Takahashi, K.; Nakajima, R.; Onishi, H.; Fujishima, A.; Sato, O. Structural color and the lotus effect. *Angew. Chem., Int. Ed.* **2003**, *8*, 894–897.

28 Ge, H. L.; Wang, G. J.; He, Y. N.; Wang, X. G.; Song, Y. L.; Jiang, L.; Zhua, D. B. Photoswitched wettability on inverse opal modified by a self-assembled azobenzene monolayer. *ChemPhysChem* **2006**, *7* (3), 575–578.

29 Li, H. L.; Chang, L. X.; Wang, J. X.; Yang, L. M.; Song, Y. L. A colorful oil-sensitive carbon inverse opal. *J. Mater. Chem.* **2008**, *18* (42), 5098–5103.

30 Li, H. L.; Wang, J. X.; Yang, L. M.; Song, Y. L. Superoleophilic and superhydrophobic inverse opals for oil sensors. *Adv. Funct. Mater.* **2008**, *18* (20), 3258–3264.

31 Li, Y.; Li, C. C.; Cho, S. O.; Duan, G. T.; Cai, W. P. Silver hierarchical bowl-like array: Synthesis, superhydrophobicity, and optical properties. *Langmuir* **2007**, *23* (19), 9802–9807.

32 Raza, M. A.; Kooij, E. S.; van Silfhout, A.; Poelsema, B. Superhydrophobic surfaces by anomalous fluoroalkylsilane self-assembly on silica nanosphere arrays. *Langmuir* **2010**, *26* (15), 12962–12972.

33 Yang, H. T.; Jiang, P. Self-cleaning diffractive macroporous films by doctor blade coating. *Langmuir* **2010**, *26* (15), 12598–12604.

34 Zhou, J. M.; Li, H. L.; Ye, L.; Liu, J.; Wang, J. X.; Zhao, T.; Song, Y. L. Facile fabrication of tough SiC inverse opal photonic crystals. *J. Phys. Chem. C* **2010**, *114*, 22303–22308.

35 Chen, X.; Wang, L. H.; Wen, Y. Q.; Zhang, Y. Q.; Wang, J. X.; Jiang, L.; Song, Y. L.; Zhu, D. B. Fabrication of closed-cell polyimide inverse opal photonic crystals with excellent mechanical property and thermal stability. *J. Mater. Chem.* **2008**, *18*, 2262–2267.

36 Dorvee, J. R.; Derfus, A. M.; Bhatia, S. N.; Sailor, M. J. Manipulation of liquid droplets using amphiphilic, magnetic one-dimensional photonic crystal chaperones. *Nat. Mater.* **2004**, *3* (12), 896–899.

37 Brozell, A. M.; Muha, M. A.; Abed-Amoli, A.; Bricarello, D.; Parikh, A. N. Patterned when wet: Environment-dependent multifunctional patterns within amphiphilic colloidal crystals. *Nano Lett.* **2007**, *7* (12), 3822–3826.

38 Wang, J. X.; Wen, Y. Q.; Ge, H. L.; Sun, Z. W.; Zheng, Y. M.; Song, Y. L.; Jiang, L. Simple fabrication of full color colloidal crystal films with tough mechanical strength. *Macromol. Chem. Phys.* **2006**, *207* (6), 596–604.

39 Wang, J. X.; Wen, Y. Q.; Feng, X. J.; Song, Y. L.; Jiang, L. Control over the wettability of colloidal crystal films by assembly temperature. *Macromol. Rapid Commun.* **2006**, *27* (3), 188–192.

40 Wang, J. X.; Wen, Y. Q.; Hu, J. P.; Song, Y. L.; Jiang, L. Fine control of the wettability transition temperature of colloidal-crystal films: From superhydrophilic to superhydrophobic. *Adv. Funct. Mater.* **2007**, *17* (2), 219–225.

41 Ton-That, C.; Shard, A. G.; Daley, R.; Bradley, R. H. Effects of annealing on the surface composition and morphology of PS/PMMA blend. *Macromolecules* **2000**, *33* (22), 8453–8459.

42 Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos, A. Linear and nonlinear triblock terpolymers. Synthesis, self-assembly in selective solvents and in bulk. *Prog. Polym. Sci.* **2005**, *30* (7), 725–782.

43 Mathur, A. M.; Drescher, B.; Scranton, A. B.; Klier, J. Polymeric emulsifiers based on reversible formation of hydrophobic units. *Nature* **1998**, *392* (6674), 367–370.

44 Zhao, T. Y.; Nie, F. Q.; Jiang, L. Precise control of wettability from LCST tunable surface. *J. Mater. Chem.* **2010**, *20* (11), 2176–2181.

45 Han, J. T.; Lee, D. H.; Ryu, C. Y.; Cho, K. W. Fabrication of superhydrophobic surface from a supramolecular organosilane with quadruple hydrogen bonding. *J. Am. Chem. Soc.* **2004**, *126* (15), 4796–4797.

46 Wang, J. X.; Hu, J. P.; Wen, Y. Q.; Song, Y. L.; Jiang, L. Hydrogen-bonding driven wettability change of colloidal crystal films from superhydrophobicity to superhydrophilicity. *Chem. Mater.* **2006**, *18*, 4984–4986.

47 Sperline, R. P.; Song, Y.; Freiser, H. Fourier-transform infrared attenuated total-reflection linear dichroism study of sodium dodecylbenzenesulfonate adsorption at the Al_2O_3/water interface using Al_2O_3-coated optics. *Langmuir* **1994**, *10* (1), 37–44.

48 Evanson, K. W.; Urban, M. W. Surface and interfacial ftir spectroscopic studies of latexes. 1. Surfactant copolymer interactions. *J. Appl. Polym. Sci.* **1991**, *42* (8), 2287–2296.

49 Zhao, Y. Q.; Urban, M. W. Mobility of SDOSS powered by ionic interactions in Sty/n-BA/MAA core-shell latex films. 21. A spectroscopic study. *Langmuir* **2000**, *16* (24), 9439–9447.

50 Miranda, P. B.; Pflumio, V.; Saijo, H.; Shen, Y. R. Chain—chain interaction between surfactant monolayers and alkanes or alcohols at solid/liquid interfaces. *J. Am. Chem. Soc.* **1998**, *120* (46), 12092–12099.

51 Xu, L.; Wang, J. X.; Song, Y. L.; Jiang, L. Electrically tunable polypyrrole inverse opals with switchable stopband, conductivity, and wettability. *Chem. Mater.* **2008**, *20* (11), 3554–3556.

52 Griffete, N.; Dybkowska, M.; Glebocki, B.; Basinska, T.; Connan, C.; Maitre, A.; Chehimi, M. M.; Slomkowski, S.; Mangeney, C. Thermoresponsive colloidal crystals built from core—shell poly(styrene/α-tert-butoxy-ω-vinylbenzylpolyglycidol) microspheres. *Langmuir* **2010**, *26* (13), 11550–11557.

53 Yao, T. J.; Wang, C. X.; Lin, Q.; Li, X.; Chen, X. L.; Wu, J.; Zhang, J. H.; Yu, K.; Yang, B. Fabrication of flexible superhydrophobic films by lift-up soft-lithography and decoration with Ag nanoparticles. *Nanotechnology* **2009**, *20* (6), No. 065304.

54 Du, C. G.; Cui, L. Y.; Zhang, Y. Z.; Zhao, T. Y.; Wang, J. X.; Song, Y. L.; Jiang, L. Fabrication of colloidal crystals with hierarchical structure and its water adhesion properties. *J. Nanosci. Nanotechnol.* **2010**, *10*, 7766–7769.

55 Feng, L.; Zhang, Y. A.; Xi, J. M.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal effect: A superhydrophobic state with high adhesive force. *Langmuir* **2008**, *24* (8), 4114–4119.

56 Feng, L.; Zhang, Y.; Li, M.; Zheng, Y.; Shen, W.; Jiang, L. The structural color of red rose petals and their duplicates. *Langmuir* **2010**, *26* (18), 14885–14888.

57 Xu, L.; Li, H.; Jiang, X.; Wang, J. X.; Li, L.; Song, Y. L.; Jiang, L. Synthesis of amphiphilic mushroom cap-shaped colloidal particles towards fabrication of anisotropic colloidal crystals. *Macromol. Rapid Commun.* **2010**, *31* (16), 1422–1426.

58 Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. Two-dimensional crystallization. *Nature* **1993**, *361* (6407), 26–26.

59 Cui, L. Y.; Zhang, Y. Z.; Wang, J. X.; Ren, Y. B.; Song, Y. L.; Jiang, L. Ultra-fast fabrication of colloidal photonic crystals by spray coating. *Macromol. Rapid Commun.* **2009**, *30* (8), 598–603.

60 Cui, L. Y.; Li, Y. F.; Wang, J. X.; Tian, E. T.; Zhang, X. Y.; Zhang, Y. Z.; Song, Y. L.; L., J. Fabrication of large-area patterned photonic crystals by ink-jet printing. *J. Mater. Chem.* **2009**, *19*, 5499–5502.

61 Richel, A.; Johnson, N. P; McComb, D. W. Observation of Bragg reflection in photonic crystals synthesized from air spheres in a titania matrix. *Appl. Phys. Lett.* **2000**, *76* (14), 1816–1818.

62 Tian, E. T.; Wang, J. X.; Zheng, Y. M.; Song, Y. L.; Jiang, L.; Zhu, D. B. Colorful humidity sensitive photonic crystal hydrogel. *J. Mater. Chem.* **2008**, *18* (10), 1116–1122.

63 Tian, E. T.; Ma, Y.; Cui, L. Y.; Wang, J. X.; Song, Y. L.; Jiang, L. Color-oscillating photonic crystal hydrogel. *Macromol. Rapid Commun.* **2009**, *30* (20), 1719–1724.

64 Shinohara, S.; Seki, T.; Sakai, T.; Yoshida, R.; Takeoka, Y. Photoregulated wormlike motion of a gel. *Angew. Chem., Int. Ed.* **2008**, *47* (47), 9039–9043.

65 Tian, E. T.; Cui, L. Y.; Wang, J. X.; Song, Y. L.; Jiang, L. Tough photonic crystals fabricated by photo-crosslinkage of latex spheres. *Macromol. Rapid Commun.* **2009**, *30* (7), 509–514.

66 Howse, J. R.; Topham, P.; Crook, C. J.; Gleeson, A. J.; Bras, W.; Jones, R. A. L.; Ryan, A. J. Reciprocating power generation in a chemically driven synthetic muscle. *Nano Lett.* **2006**, *6* (1), 73–77.

67 Wang, T. Q.; Li, X.; Zhang, J. H.; Wang, X. Z.; Zhang, X. M.; Zhang, X.; Zhu, D. F.; Hao, Y. D.; Ren, Z. Y.; Yang, B. Elliptical silicon arrays with anisotropic optical and wetting properties. *Langmuir* **2010**, *26* (16), 13715–13721.