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Hydrogen-Bonding-Driven Wettability Change of Colloidal Crystal Films: From Superhydrophobicity to Superhydrophilicity

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Recently, superhydrophobic or superhydrophilic surfaces have been extensively investigated as a result of their importance in applications.[1−8] Conventionally, the wettability of a solid surface is governed by the chemical composition and the geometric microstructure. Rough surface can effectively amplify both the hydrophobicity of the hydrophobic surface and the hydrophilicity of the hydrophilic surface.[1] Therefore, many methods have been developed to improve roughness on solid surfaces, such as plasma polymerization/etching,[1g,4a] chemical deposition,[1h] and phase separation.[3c] Distinguished from special creation/enhancement of rough surfaces, Gu et al. developed superhydrophobic or superhydrophilic surfaces by virtue of opal with intrinsic roughness.[7] However, these cases are subject to certain limitations in practical applications, such as expensive low-energy materials (e.g., fluorides, silanes)[8a] and poor durability;[3a] that is, the special wettability diminishes if the surface structure is abased as a result of repeated use.

Hydrogen bonding with a three-dimensional network is usually used to construct stable biomolecular/supramolecular structure;[4b,9] herein, colloidal crystal films with stable superhydrophobicity or superhydrophilicity are achieved in the presence of hydrogen bonding or not. The colloidal crystal films are fabricated from an amphiphilic material of poly(styrene−methyl methacrylate−acrylic acid) (poly(St-MMA-AA)). The stable superhydrophobicity arises from hydrogen bonding association between $SO_3^-Na^+$ of sodium dodecylbenzenesulfonate (SDBS) and hydrophilic COOH around the latex surface, and the association locks hydrophilic groups of the latex sphere surface into a preferable configuration. The approach provides a simple method to control the wettability of materials by hydrogen bonding under ambient temperature without a special coating process. Such special wettability will greatly extend the application of colloidal crystals to many other important fields, such as microfluidic devices.[10]

Monodispersed core−shell latex spheres of poly(St-MMA-AA) were prepared via batch emulsion polymerization by a modified reported procedure[11a,b] except for the charging of the emulsifier of SDBS (0.014 mmol) into the system. The pH of the resulting latex system is 6.0. The core−shell[12a] morphology of latex spheres was characterized by H800 transmission electron microscopy (TEM; JEM2010, Japan) as shown in the inset in Figure 1a. It could be clearly observed that monodisperse latex spheres (with diameter of 160 nm) with a hydrophobic core of polystyrene and a hydrophilic shell of poly(methyle methacrylate)/poly(acrylic acid) are obtained.[11a,12a] The emulsifier SDBS would distribute around the surface of the latex spheres to ensure the formation of a stable emulsion system, which also plays a significant role in the resulting film properties such as

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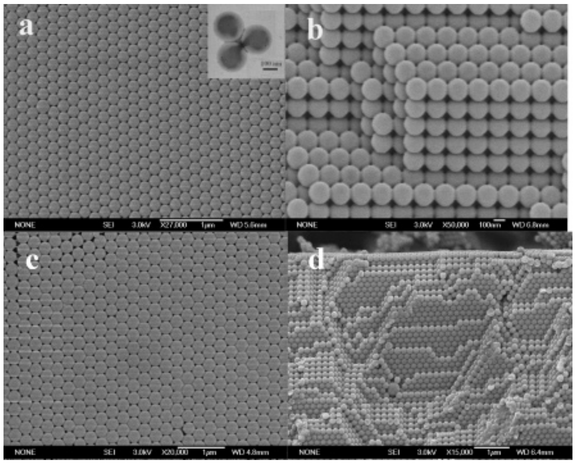

Figure 1. Typical comparison of SEM images of the colloidal crystal film assembly at different pH values. (a, b) Top view and side view of the films assembled at pH = 6.0. (c, d) Top view and side view of the film assembled at pH = 12.0. (Inset: typical TEM image of core−shell spheres of poly(St-MMA-AA); the bar is 100 nm.)

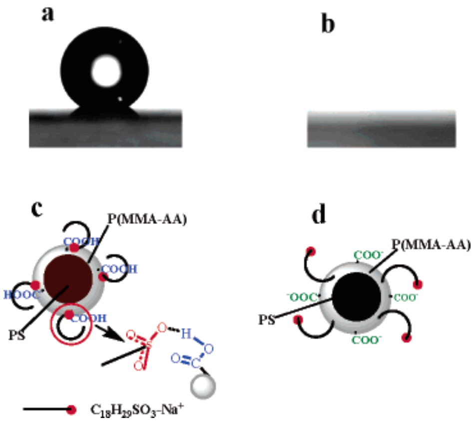

Figure 2. (a and b) Photographs of water droplet shape on the films assembled from suspensions with pH of 6.0 and 12, respectively; (c and d) illustrations of the structure of the latex sphere in the films of parts a and b, respectively. The conformation of hydrogen bonding is noted by the arrow.

adhesion and wettability and other physical properties. Subsequently, colloidal crystal films are fabricated from latex suspension by the vertical deposition method[12b] at 25 °C with relative humidity of 70%. The pH of the latex suspension was varied from 6.0 to 12 by introducing $NH_3{\cdot}H_2O$ into the latex suspension. The typical scanning electron microscopy (SEM) images of the films assembled under different pH values are presented in Figure 1a−d. Clearly, the perfectly packed hexagonally ordered structure has been formed, which can greatly affect the wettability of the films by the Cassie−Baxter law.[1c,d]

Interestingly, the wettability of the films shows dramatic change when assembled from latex suspensions with different pH values. As shown in Figure 2a,b, the superhydrophobic films with a water contact angle (CA) of approximately 150.4 ± 0.8° (with advancing and receding angles of 152.5 ± 0.2° and 130.0 ± 0.05°, respectively; the large hysteresis can be attributed to the well-ordered nature of periodic strucutre)[1a,5c] are fabricated from a latex suspension with pH of 6.0, while the superhydrophilic films with a water CA of 0° are fabricated from a suspension with a pH of 12. The results indicate that the wettability of the films can be easily controlled between superhydrophobic and superhydrophilic by pH value of the latex suspensions at constant temperature. Generally, the wettability lies on the effects of both surface chemical composition and roughness deriving from intrinsic topology of the colloidal crystal films.[1] Because a little roughness change is observed when comparing SEM images (in Figure 1a,c) of films assembled fromlatex suspensions with different pH values, surface chemical composition change of the latex spheres is responsible for the distinguished wettability of the resulting films.

A possible illustration of surface chemical composition change during the assembly procedure is shown in Figure 2c,d. The change mainly arises from the presence or absence of hydrogen bonding between $SO_3^-Na^+$ and COOH (as noted by the arrow) under different assembly pH values. Figure 2c,d presents respectively the two distinct absorbed conformations for the emulsifier SDBS due to different pH environments. When pH = 6.0, the hydrogen bonding (noted by the arrow) immobilizes the head groups of SDBS on the surface of the latex sphere in Figure 2c, which would lead to a nearly inverted absorbate morphology of SDBS ultimately.[13a] Its hydrophobic tails spread toward air in Figure 2c,[13a,b,d] which prevents the hydrophilic group from being exposed to air and contributes to stable hydrophobicity of the film.[13c] Accordingly, the cooperation of the roughness surface derived from the colloidal crystals and its hydrophobicity would result in the formation of a stable superhydrophobic film in Figure 2a. Additionally, the observation pH value when forming hydrogen bonds (with pH = 6) is more closely related to the apparent pK_a (6.8) of the polymer species rather than the intrinsic pK_a of acrylic acid (4.3),[14] which could be attributed to the low content of COOH groups in the whole assembly system.

Compared with Figure 2c, when introducing $NH_3{\cdot}H_2O$ into the latex suspension (pH = 12), hydrogen bonding is suppressed due to deprotonation of COOH to COO^- in Figure 2d.[13a] Additionally, the strong static repulsion force between COO^- and SO_3^- favors the conformation that hydrophilic groups of both COO^- and $SO_3^-Na^+$ are exposed upon air, which gives rise to the hydrophilicity of the resulting films. The combination of the hydrophilic surface and rough structure promotes the formation of the superhydrophilic film, and the water CA approaches 0° as shown in Figure 2b.

To further investigate the change of surface chemical composition, which arose from the presence or absence of hydrogen bonding and plays a crucial role in the wettability change of the as-prepared films, the hydrogen bonding association of SO_3^- and COOH in the films assembled from different pH latex suspensions is followed by monitoring the attenuated total reflectance Fourier transform infrared ATR-FTIR spectra in Figure 3. When introducing $NH_3{\cdot}H_2O$ into the latex suspension and varying the pH from 6 to 12, there

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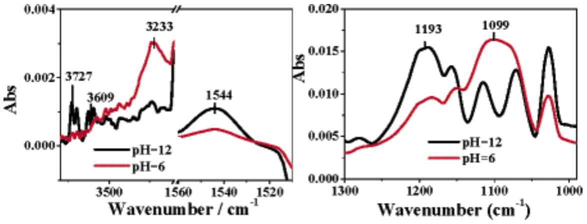

Figure 3. ATR-FTIR spectra of both colloidal crystal films assembled from different pH latex suspensions.

is a dramatic increase of the S−O peak of 1193 cm^{-1} attributed to free SO_3^- of SDBS and an obvious decrease of 1099 cm^{-1} attributed to bonded SO_3^- resulting from hydrogen bonding between SO_3^- and COOH. The obvious pH dependency of the SO_3^- peak is consistent with Sperline's result[13a] that hydrogen bonding (lower pH) would lower the symmetry of the SO_3^- and cause the bathochromic shift of SO_3^-, while absence of the association (higher pH) would cause a hypsochromic shift of the SO_3^-, which indicates $NH_3 \cdot H_2O$ suppresses the formation of bonded SO_3^- and favors intensification of the free SO_3^-. This is also in good agreement with Evanson and Urban's experimental result[13b] that the introduction of a base, such as NaOH or NH_4OH, into the latex system would break apart the association between SO_3^- and COOH.

Additionally, the introduction of $NH_3 \cdot H_2O$ into the system would cause the deprotonation of COOH and formation of COO^-, and the occurrence of the new peak of 1544 cm^{-1} (pH = 12) assigned to COO^- could be clearly observed from Figure 3. There is steady decrease for the C═O peak strength, and although there is little shift of its wavenumber (see Supporting Information, Table S2), the result is consistent with the literature.[13b] Meanwhile, the disappearance of the OH peak at 3233 cm^{-1} and the occurrence of new bands at 3609 and 3727 cm^{-1} attributed to the N−H strentching is resulted from the introduction of $NH_3 \cdot H_2O$. The ATR-FTIR results further confirm the change of the surface chemical composition of the films in Figure 2c,d, that is, the presence or absence of hydrogen bonding when assembled from different pH latex suspensions, as contributing to different wettabilities of the films in Figure 2a,b. On the other hand, the hydrophilic surface can be switched back to the hydrophobic one by a treatment with an acidic vapor, such as HCl, and the resulting hydrophobic film can be further switched back to a hydrophilic one by a basic vapor, such as NH_3. The phenomenon may be attributed to the reverse of the presence or absence of hydrogen bonding between SO_3^- and COOH at different pH conditions, as is consistent with the experimental observation reported in the literature.[13a]

XPS analysis (measured at 30° and 90°) results further clarify the change of the surface chemical component assembled from different pH values. It is found that the ratios of S/C and O/C are 0.0806 and 5.898% (measured at 30°) and 0.372 and 7.44% (measured at 90°), respectively, for the film prepared at pH = 6, which suggests that the hydrophilic SO_3^- groups mainly distribute in the interior of the film. In contrast, the ratios of S/C and O/C become 0.317 and 6.77% (measured at 30°) and 0.407 and 8.402% (measured at 90°), respectively, when the film is prepared at pH = 12, which indicates that more hydrophilic SO_3^- groups are exposed on the surface after introducing $NH_3 \cdot H_2O$ into the system. The results coincide with the ATR results and the wettability change of the films.

As the wettability is controlled by the hydrogen-bonding network throughout the films, the wettability of the films is expected to be consistent. As is proved by the further experimental result, the water CAs reach 153.2 ± 1.2° and 0° for the cross section of films assembled from pH values of 6.0 and 12, respectively. Apparently, the specific wettability of the films could be kept even if their surface is worn during use. In addition, the stable specific wettability could be kept even after being exposed to air for several months, as is of great significance for further applications.

In conclusion, stable superhydrophobic or superhydrophilic colloidal crystal films have been successfully fabricated under ambient conditions from an amphiphilic material of poly(St-MMA-AA) in the presence of hydrogen bonding or not. The consistent hydrogen-bonding network in the films contributes to the stable superhydrophobicity, while the absence of the hydrogen bonding leads to superhydrophilicity. The result provides new insights into controlling the wettability of the colloidal crystal film by appropriate design of the latex surface. The approach would be of great significance for the practical application of colloidal crystal films and could be further extended to control the surface wettability of a wide variety of materials.

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Supporting Information Available: Experimental details of synthesis and characterization of latex spheres and colloidal crystals (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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