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Scalable fabrication of superhydrophobic hierarchical colloidal arrays

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ABSTRACT

Here we report a scalable bottom-up technology for assembling hierarchical colloidal arrays with superhydrophobic surface. Non-close-packed (NCP) colloidal multilayers, which facilitate the formation of more hydrophobic surface than close-packed arrays due to a higher fraction of entrapped air in between colloidal particles, are first fabricated by a simple spin-coating technology. Uniform silica nanoparticles are then assembled on the NCP microsphere arrays by a second spin-coating process. After surface functionalization of silica particles with fluorosilane, the resulting hierarchical colloidal arrays exhibit superhydrophobic surface with high apparent water contact angle (159°) and low contact angle hysteresis (4.7°). The experimental results on both the wettability and contact angle hysteresis can be qualitatively explained by adapting the Cassie's model. This spin-coating-based colloidal self-assembly technology is compatible with standard microfabrication and enables large-scale production of superhydrophobic coatings that could find important technological applications ranging from self-cleaning diffractive optics to microfluidic devices.

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1. Introduction

Inspired by the self-cleaning surface of lotus leaves, superhydrophobic coatings with large water contact angles (>150°) and small sliding angles (<10°) have attracted tremendous recent interests [1–5]. These biomimetic coatings are of great technological importance in developing self-cleaning surfaces [2], antifouling substrates [6], antifogging coatings [7,8], efficient microfluidic devices [9,10], anticorrosive coatings [11,12], and more. A large variety of technologies, such as standard lithography [13-16], layer-by-layer (LBL) assembly [7,17-19], phase separation [20,21], sol-gel processing [22,23], electrospinning [24-26], plasma etching [9,27], and electrochemical treatment [28,29], have been developed. Through the extensive studies, it is well-known that both the chemical composition and the geometric structure are crucial in determining the surface wettability [30–32]. The combination of hierarchical micro- and nano-scale structures with low surface energy materials, which is the origin of the waterrepelling properties of lotus leaves, has been demonstrated as an efficient approach to create superhydrophobic coatings with low contact angle hysteresis [31,33-37].

Among the various methodologies in creating superhydrophobic coatings with hierarchical structures, bottom-up colloidal self-assembly is a simple, fast, and inexpensive technique [36–43]. The micro- and nano-scale structures can be precisely controlled by choosing monodispersed particles with well-defined size. Air, which is the most hydrophobic material, is trapped in the interstitials of the assembled micro/nano-particles to significantly increase contact angles [31]. The hydrophobicitiy can be further improved by functionalizing the surface of colloidal particles using low surface energy chemicals (e.g., fluorosilanes) [40,41]. However, several drawbacks of current colloidal self-assemblies have impeded the development and implementation of superhydrophobic coatings in practical applications. First, most of the available colloidal self-assembly technologies are only favorable for low volume, laboratory-scale production. Second, technical incompatibility with mature microfabrication is a major issue for large-scale production. Third, only close-packed colloidal arrays are available through traditional colloidal self-assembly, whereas non-closepacked (NCP) crystals are favorable for creating more hydrophobic surface as a larger fraction of air can be trapped in between NCP colloidal particles [43].

We have recently developed a scalable and microfabricationcompatible spin-coating technology for assembling large-area colloidal arrays with highly uniform and adjustable thicknesses [44,45]. Wafer-sized colloidal crystals (up to 12-in. or larger), which are nearly three-orders of magnitude larger than currently available through other bottom-up approaches [46–50], can be assembled in minutes. The three-dimensional (3D) ordered colloidal photonic crystals exhibit striking optical diffraction and can be directly used in diffractive optics (e.g., optical filters and lowthreshold lasers) [44,51]. Most importantly, the spin-coated colloidal crystals have unusual non-close-packed structures [44]. Here we show that these NCP colloidal crystals can be used to create

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superhydrophobic coatings with large water contact angles and small sliding angles. Monodispersed silica nanoparticles of 32 nm diameter are uniformly assembled on the NCP microsphere arrays by a second spin-coating process to form hierarchical structures. As only the top two layers of the spin-coated colloidal crystals are used in creating superhydrophobic hierarchical arrays and the silica nanoparticles are too small to scatter visible light, the optical properties of the colloidal photonic crystals are preserved. The combination of the superhydrophobic surface and the unique optical properties of the self-assembled colloidal arrays could find important technological application in self-cleaning diffractive optics.

2. Experimental

2.1. Materials and substrates

The reagents used for silica particle synthesis, including tetraethyl orthosilicate (TEOS) (98%), ammonium hydroxide (NH₄OH) (28%), cyclohexane (99%), n-hexanol (99%), and Triton N-101, are all purchased from Sigma-Aldrich. Ethanol (200-proof) is obtained from Pharmaco Products. Ethoxylated trimethylolpropane triacrylate monomer (ETPTA, SR 454) and photoinitiator, Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone) are obtained from Sartomer and Ciba-Geigy, respectively. (Tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane (97%) used for surface modification is purchased from Alfa Aesar. All solvents and chemicals are of reagent quality and are used without further purification except for TEOS which is freshly distilled before use. Silicon wafers (4-in., test grade, n type, (100), Wafernet) and glass microslides (Fisher) are cleaned in a "Piranha" solution (a 3:1 mixture of concentrated sulfuric acid with 30% hydrogen peroxide) for half an hour, rinsed with Milli-Q water (18.2 M Ω cm), and dried in a stream of nitrogen.

2.2. Instrumentation

A standard spin coater (WS-400B-6NPP-Lite spin processor, Laurell) is used to spin-coat colloidal suspensions. The polymerization of ETPTA monomer is carried out on a pulsed UV curing system (RC 742, Xenon). The oxygen reactive-ion etching (RIE) is performed on a Unaxis Shuttlelock RIE/ICP reactive-ion etcher. Scanning electron microscopy (SEM) is carried out on a JEOL 6335F FEG-SEM. The specimens are sputter-coated with a thin layer of gold prior to imaging. A Dimension 3100 atomic force microscope (AFM) is used to measure the surface roughness. Transmission electron microscopy (TEM) is performed on a JEOL 2010F TEM.

2.3. Synthesis of silica particles

The synthesis of uniform silica nanoparticles with \sim 30 nm diameter is performed according to the established microemulsion method [52,53]. In a typical synthesis, a microemulsion is prepared by rapidly stirring 150 mL of cyclohexane, 6 mL of *n*-hexanol, 19 mL of Triton N-101 surfactant, 7 mL of deionized water, and 1.7 mL of 28% ammonium hydroxide. Freshly distilled TEOS (10 mL) is rapidly added to the above microemulsion, and the final solution is stirred at ambient temperature for 2 days. The as-made silica nanoparticles are purified in 200-proof ethanol by five centrifugation-ultrasonication cycles. The synthesis of monodispersed 300 nm silica microspheres with less than 5% diameter variation is performed by following the well-established Stöber method [54,55]. Freshly distilled TEOS (50 mL) is rapidly added to a mixture of 650 mL of 200-proof ethanol, 55.7 mL of deionized water, and 23.1 mL of 28% ammonium hydroxide. The solution is stirred at ambient temperature for 8 h. The synthesized silica microspheres are purified in 200-proof ethanol by five centrifugationultrasonication cycles to remove impurities, such as ammonia, water, and unreacted TEOS.

2.4. Preparation of multilayer colloidal crystals by spin coating

After complete centrifugation of the calculated amount of purified 300 nm silica dispersion and discarding of the supernatant solvent, the silica microspheres are re-dispersed in ETPTA monomer to make a final particle volume fraction of 20% by using a Thermdyne Maxi solution mixer. Darocur 1173 (1 wt.%) is then added as the photoinitiator. After filtration through a 5 μ m syringe filter (Whatman) to remove any large particle aggregates, the transparent colloidal suspension is stored in an open vial for overnight to allow residual ethanol to evaporate. Six hundred microliter of the



Fig. 1. Schematic illustration of the fabrication process for creating superhydrophobic binary colloidal arrays.

silica/ETPTA suspension is then dispensed on a silicon wafer or a glass microslide. The substrate is spin-coated to remove excess silica/ETPTA suspension and align silica microspheres. The coating recipe for obtaining a double-layer colloidal array is 1000 rpm for 1 min, 3000 rpm for 20 s, 6000 rpm for 2 min, and 8000 rpm for 1.5 min. After spin-coating, the sample is transferred to a pulsed UV curing system to rapidly photopolymerize ETPTA monomer in 4 s. The as-made double-layer silica/ETPTA nanocomposite is placed in a reactive-ion etcher, and etched by oxygen RIE operating at 40 mTorr oxygen pressure, 40 SCCM oxygen flow rate and 100 W for 100 s to release the embedded silica microspheres.

2.5. Preparation of binary colloidal arrays by spin coating

The purified 30 nm silica nanoparticles are dispersed in ETPTA monomer to make a final particle volume fraction of 20%. The silica nanoparticles/ETPTA suspensions are then diluted by 200-proof ethanol to adjust the resulting silica nanoparticle volume fractions range from 1% to 10%. We then spin-coat the diluted suspensions on the double-layer silica colloidal crystal as prepared above at 9000 rpm for 2 min. After spin-coating, the sample is transferred to a pulsed UV curing system to rapidly polymerize ETPTA monomer in 4 s. The polymer matrix is then etched at the above RIE conditions for 30 s to release the embedded 30 nm silica nanoparticles.



Fig. 2. Non-close-packed colloidal crystal prepared by spin-coating. (A) Photograph of a 4-in. sample illuminated with white light. (B) Top-view SEM image of a double-layer crystal. Inset shows a magnified SEM image.

2.6. Surface modification of binary colloidal arrays

The hydrophobicity of the assembled binary colloidal arrays can be further improved by functionalizing the surface of silica particles with fluorosilane through the silane coupling reaction [56]. The sample is placed in a sealed vessel with a beaker containing a small amount of (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane. The sealed vessel is then put in an oven at 120 °C to enable the silane groups of fluorosilane vapor to react with the hydroxyl groups on the assembled silica particles. After 1 h, the substrate is moved to another clean vessel and heated at 150 °C for 1 h to vaporize the unreacted fluorosilane molecules adsorbed on the substrate.

2.7. Measurements of apparent water contact angle

The apparent water contact angle is measured using a goniometer (NRL C.A. Goniometer, Ramé-Hart Inc.) with autopipetting and imaging systems. 18.2 M Ω cm water purified with a Millipore Ultrapure Water System is used for the contact angle measurement. A micropipette tip attached to the autopipetting system is



Fig. 3. Uniform silica nanoparticles synthesized by the microemulsion method. (A) TEM image of the as-synthesized nanoparticles. (B) Histogram of the particle size distribution.

lowered to approximately 1 mm above the sample surface. Using the autopipetting system and DROPimage advanced software, a 13 μ L drop is dispensed onto the sample surface. The drop is in contact with both the surface of the sample and the pipette tip. Apparent water contact angle is determined from the image using ImageJ v1.37 with the drop_analysis plugin. Images are opened in ImageJ and then analyzed using DropSnake. Some manual adjustment of the 7-knot snake is required before the curve can be snaked accurately. The gravitational effect on the contact angle measurement has been corrected in these procedures.

3. Results and discussion

The schematic illustration of the fabrication process for creating superhydrophobic binary colloidal arrays is shown in Fig. 1. We start to assemble double-layer silica colloidal crystal/polymer nanocomposites by using the well-established spin-coating technology [44]. This methodology is based on shear-aligning concentrated colloidal suspensions with 20% particle volume fraction. Monodispersed silica particles with diameters ranging from \sim 70 to ~1300 nm are dispersed in nonvolatile ethoxylated trimethylolpropane triacrylate (ETPTA) monomers. The suspensions are spincoated using standard spin-coating equipment. This simple technology enables large-scale production of colloidal crystals with remarkably large domain sizes and unusual non-close-packed structures. Fig. 2A shows a photograph of a 4-in. sample illuminated with white light. The sample exhibits distinctive six-arm Bragg diffraction patterns, indicating long-range hexagonal ordering of silica microspheres. Compared to hours or even days needed to produce a centimeter-sized colloidal crystal using other self-assembly techniques [46–50], the entire crystals can be assembled in minutes by spin-coating.

After spin-coating, the ETPTA monomer is rapidly polymerized by exposure to ultraviolet radiation. A brief oxygen reactive-ion etching (RIE) process is then applied to partially etch the ETPTA polymer matrix. The residual polymer matrix maintains the mechanical robustness of the released colloidal crystals. Fig. 2B shows a top-view SEM image of a double-layer colloidal crystal prepared by spin-coating. The long-range hexagonal ordering of silica microspheres is clearly evident. The magnified SEM image (inset of Fig. 2B) illustrates another major merit of the spin-coating process - the resulting colloidal crystals are non-close-packed as compared to close-packed crystals produced by traditional selfassemblies [46-50]. The silica particles of the top layer (bright spheres in the magnified SEM image) are not touching each other. while they fill in the triangularly arranged crevices made by the non-touching spheres of the bottom laver (grev spheres). Although only a double-layer colloidal crystal is schematically illustrated in Fig. 1, multilayer crystals can also be utilized to create superhydrophobic binary arrays by using the same approach. As demonstrated in our previous work, the thickness of the spin-coated crystals can be precisely controlled from a monolayer to hundreds of layers by adjusting the spin speed and time [44,45]. Flexible multilayer silica colloidal crystal/polymer nanocomposites can be peeled off from the substrates [44]. As only the top two layers of a multilayer nanocomposite are used in creating superhydrophobic binary arrays, we can easily laminate the self-standing multilayer films onto a large variety of substrates with both planar and curved surfaces.

Compared to close-packed crystals created by traditional selfassemblies, the unusual NCP structure of spin-coated crystals facilitates the formation of more hydrophobic surface as a higher frac-



Fig. 4. Typical top-view SEM images of binary colloidal arrays prepared by spin-coating silica nanoparticles/ETPTA/ethanol dispersions with different particle volume fractions on NCP colloidal arrays. (A) 2.0 vol.%. (B) 4.0 vol.%. (C) 5.0 vol.%. (D) 7.0 vol.%.



Fig. 5. Tapping mode AFM images and height profiles of (A and B) smooth NCP colloidal crystal and (C and D) rough binary colloidal array after spin-coating 5 vol.% silica nanoparticles.



Fig. 6. Apparent water contact angles of binary colloidal arrays prepared by spincoating dispersions of 32 nm silica nanoparticles with different concentrations on NCP colloidal crystals. Insets show water droplet profiles on samples with maximum and minimum contact angles as indicated by arrows.

tion of air can be trapped in between silica microspheres [13,35]. However, as demonstrated later, the NCP colloidal arrays consisting of smooth silica microspheres are insufficient to create superhydrophobic surface even after surface modification with fluorosilane. We therefore try to create raspberry-like binary colloidal arrays by assembling silica nanoparticles on NCP microspheres to further increase the surface roughness and the trapped air fraction. Fig. 3A shows a TEM image of silica nanoparticles synthesized by the microemulsion method using Triton N-101 as surfactant [52,53]. The as-synthesized nanoparticles are uniform as confirmed by the TEM image and the histogram of the particle size distribution shown in Fig. 3B. The average diameter of silica nanoparticles is determined to be 32.1 ± 1.8 nm by averaging over 200 particles.

To assemble silica nanoparticles on NCP microsphere arrays, we test spin-coating of dispersions of silica nanoparticles in ethanol. Unfortunately, most of silica nanoparticles are repelled from the substrate during spin-coating. We then disperse silica nanoparticles in nonvolatile ETPTA monomer to make a final particle volume fraction of 20%. The resulting nanoparticle dispersions are transparent and viscous. The electrostatic repulsion between silica nanoparticles (zeta potential ca. -40 mV in ETPTA monomer) stabilizes the refractive index-matched colloidal dispersions [57]. The nanoparticle volume fraction is adjusted from 1% to 10% by adding the calculated amount of ethanol. The final silica nanoparticles/ETPTA/ethanol dispersions are spin-coated at 9000 rpm for 2 min to form a uniform nanoparticle/ETPTA composite coating over the NCP microsphere arrays. After photopolymerization, the ETPTA matrix is removed by brief oxygen RIE to release the silica nanoparticles. As the small silica nanoparticles are too small to scatter visible light, the striking optical diffraction enabled by the highly ordered NCP microsphere arrays is well preserved after nanoparticle assembly.

Fig. 4A–D show typical SEM images of binary colloidal arrays prepared by spin-coating silica nanoparticle dispersions with different particle volume fractions (2, 4, 5, and 7 vol.%, respectively).



Fig. 7. Water droplet profiles used to determine the advancing and receding contact angles for (A and B) fluorinated smooth microsphere array and (C and D) fluorinated binary colloidal array prepared by using 5 vol.% silica nanoparticles.

The formation of raspberry-like binary colloidal arrays is apparent for the samples prepared with relatively dilute dispersions (Fig. 4A-C). The surface coverage of nanoparticles increases when the dispersion becomes more concentrated. However, when the dispersion concentration is above ~7 vol.%, a continuous nanoparticle film covers the whole surface of the NCP microsphere arrays (Fig. 4D). Although the underneath silica microspheres are indistinguishable in Fig. 4D, a lower-magnification SEM image (not shown here) confirms that the long-range ordering of large microspheres is retained during the spin-coating of nanoparticle dispersions. From the SEM images in Fig. 4, it is also clear that the silica nanoparticles are disordered. We have demonstrated that a nearly 1 order of magnitude higher shear rate is required to align silica nanoparticles compared to submicrometer-scale particles by spin-coating [57]. In addition, the non-planar surface rendered by the non-close-packed microspheres hinders the formation of periodic nanoparticle arrays during spin-coating.

As the surface roughness is crucial in determining the wetting properties of a substrate [31,32], we further evaluate this important parameter of binary colloidal arrays by AFM. Fig. 5A and C compare the AFM images of a NCP microsphere array and a binary colloidal array. It is evident that the latter is much rougher than the former. The root mean square surface roughness (R_{rms}) of the two samples determined by AFM is 2.26 and 3.74, respectively. The depth profiles in panels B and D of Fig. 5 show that the protrusion height of the rough binary array is ~30 nm higher than that of the smooth crystal, which is comparable to the diameter of silica nanoparticles. This indicates that the spin-coated nanoparticles form a monolayer on the large microspheres. The SEM images in Fig. 4 also confirm this observation.

The hydrophobicity of the binary colloidal arrays is further improved by functionalizing the surface of silica particles with (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane through the well-known silane coupling reaction [56]. The apparent water contact angles (CA) of the final samples are measured by a dynamic contact angle analyzer (Ramé-Hart Goniometer) and the results as shown in Fig. 6 are obtained by averaging over 20 random measurements on any individual sample. The fluorinated NCP



Fig. 8. Comparison of (A) advancing and receding contact angles and (B) sliding angles for samples prepared by spin-coating dispersions of 32 nm silica nanoparticles with different concentrations on NCP colloidal crystals.

microsphere array with smooth surface is hydrophobic, exhibiting a water CA of $124 \pm 3^{\circ}$. When silica nanoparticles are assembled on NCP microsphere arrays by spin-coating nanoparticle dispersions with different concentrations, the water CA increases until a maximum CA of $159 \pm 3^{\circ}$ is achieved at a nanoparticle concentration of 5.0 vol.%. For more concentrated dispersions, the formation of continuous nanoparticle films on NCP arrays (see Fig. 4D) reduces the water CA.

The above results show that superhydrophobic coatings with large CA (>150°) can be achieved by assembling hierarchical colloidal arrays. However, the static CA alone is insufficient for the full evaluation of the dewetting properties of a surface [31]. We therefore measure the advancing and receding contact angles associated with the increase and decrease of droplet volumes using the above dynamic contact angle analyzer. When measuring the advancing contact angle, water is kept adding to the water droplet until the contact angle stops increasing. While for measuring the receding contact angle, water is kept drawing out from the water droplet until the contact angle stops decreasing Fig. 7 compares the water droplet profiles which are used to determine the advancing and receding CAs on a fluorinated NCP microsphere array (panels A and B) and a binary colloidal array with maximum CA (panels C and D). The former has a large contact angle hysteresis of 53°, while the hysteresis for the latter is only 4.7°. The measured advancing and receding CAs and sliding angles for binary colloidal arrays prepared by spin-coating 32 nm silica nanoparticle dispersions with different concentrations are summarized in Fig. 8. By comparing Figs. 8B and 6, it is apparent that the sliding angles and the apparent water CAs are directly correlated - a larger CA is associated with a lower sliding angle.

The above experimental results on both the wettability and contact angle hysteresis can be qualitatively explained by adapting the traditional models [58,59]. In Wenzel's model [59], complete wetting of all surface features leads to:

$$\cos\theta' = r\cos\theta \tag{1}$$

where θ' is the apparent CA on a rough surface, θ is the intrinsic CA on a flat surface, and *r* is the surface roughness factor defined by the ratio of the total area in contact with the liquid to the projected area. As *r* is always larger than 1, for a hydrophobic surface $(\theta > 90^{\circ})$, a higher surface roughness leads to a larger CA. This agrees with the experimental observation as shown in Fig. 6. However, in Wenzel wetting, the contact angle hysteresis is predicted to increase with an increase in surface roughness [60], contradicting with our experimental results (Fig. 8). We therefore adapted Cassie's model to explain our experimental observations. In Cassie wetting [58], the liquid droplet wets a composite surface consisting of both solid and entrapped air. This incomplete wetting can be described by the Cassie equation (2):

$$\cos\theta' = f\cos\theta - (1-f) \tag{2}$$

where f is the fraction of the area of the solid in direct contact with the liquid droplet.

Fig. 9 shows the schematic illustration of the different dewetting behaviors exhibited by NCP microsphere arrays covered with various amounts of silica nanoparticles. For a smooth microsphere array (Fig. 9A), water partially wets the fluorinated silica microspheres and occupies a large fraction of the interstitials between neighboring microspheres. This leads to a larger f and a smaller air fraction (1 - f), thus a small CA. When a dilute silica nanoparticle dispersion is used to form binary colloidal arrays, the silica nanoparticles are sparsely distributed on the large microspheres (Fig. 9B). Although a slightly higher fraction of air can be trapped around and in between silica nanoparticles, the contribution to the overall entrapped air fraction is small, leading to a limited increase of water CA. A significant increase of the air fraction and the apparent water CA occurs at an optimal surface coverage of nanoparticles. In this case, water will be prevented from entering into the large interstitials between silica microspheres by sitting presumably on the arrays of small nanoparticles (Fig. 9C). The small water/nanoparticle contact area also leads to a very small contact angle hysteresis as non-wetting droplets can roll off the



Fig. 9. Schematic illustration of the different dewetting behaviors exhibited by NCP colloidal arrays covered with various amounts of silica nanoparticles.

surface with the application of a low force (e.g., a low tilting angle) [31]. When continuous nanoparticle films form at high nanoparticle concentrations (Fig. 9D), the entrapped air fraction will decrease and thus results in smaller CA and larger contact angle hysteresis.

4. Conclusions

In conclusion, we have developed a scalable and microfabrication-compatible bottom-up technology for assembling silica nanoparticles on NCP microsphere arrays. The resulting hierarchical colloidal arrays exhibit distinctive optical diffraction properties and superhydrophobic surface with high apparent water contact angle and low contact angle hysteresis. These bioinspired multifunctional coatings could find important technological application in self-cleaning diffractive optics.

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