Supplementary Information

Spray coating of superhydrophobic and angle-independent colored films

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Experimental section

Materials. Tetraethyl orthosilicate (TEOS, 98%), aqueous ammonia (28-30%), toluene (anhydrous), triethylamine (TEA) were all purchased from Sigma-Aldrich. Ethanol (200 proof) was provided from Decom Laboratories, and isopropanol (IPA, 99.8 %) was from Fisher Scientific. (Heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) dimethylchlorosilane (HDFTHD) was purchased from Gelest, Inc. Glass resin (GR-653L), which was polysiloxane resins containing methyl and hydroxyl groups, was provided by Techneglas, Inc. All chemicals were used as received.

Synthesis of monodispersed silica nanoparticles. Monodispersed silica nanoparticles (NPs) were synthesized by the modified Stöber method.¹ In a typical procedure to synthesize 250 nm silica nanoparticles, 50 mL ethanol-based solution consisting of aqueous ammonia (5 mL) and DI water (7.5 mL) was slowly added to 50 mL ethanol solution containing 2 mL TEOS. The reaction at room temperature lasted at least 6 h with stirring. The resulting silica NP suspension was pelletized by centrifugation at 6000 rpm (Centrifuge 5804R, Eppendorf AG, Germany) for 20 min, followed by drying under vacuum for 3 h.

For the synthesis of 200 nm silica NPs, the volume of ammonia and TEOS used in the reaction was changed to 3 mL and 1 mL, respectively. When 5 mL ammonia and 3 mL TEOS were used, monodispersed silica NPs with diameter of 300 nm were obtained. **Hydrophobilization of silica nanoparticles**. Silica NPs were hydrophobilized by treating them with fluorosilane, HDFTHD, according to the literature procedure.² In a typical experiment, 1.0 g silica NPs were then dispersed in 10 mL toluene, and 0.2 mL triethylamine was added under nitrogen atmosphere. Then 1 mL toluene solution of HDFTHD (0.01 M) was added into the reaction solution and stirred for 24 h. The fluorinated silica nanoparticles were collected and purified by centrifugation at 6000 rpm for 30 min, follow by washing with ethanol three times and vacuum dried at room temperature.

Spray coating of colored superhydrophobic films on glass slides. Fluorinated silica NPs mixed with glass resin, GR-653L (0.05 wt%) were dispersed into IPA with a concentration of 10 wt%, followed by ultra-sonication (Branson Ultrasonic cleaner, 2210) for 1 h. GR-653L was used to lower the surface tension of substrates, glass slides, since fluorinated silica NPs were hydrophobic. Glass slides were cleaned by sonication in acetone, isopropanol and DI water for 20 min, respectively, followed by drying at 100 °C for 2 h before spray coating. The silica NP/IPA suspension was loaded into an airbrush with nozzle size of 0.2 mm (Master airbrush model G44, United States). The operating gas was nitrogen under a pressure of 50 kPa, and the distance between the airbrush and the substrate was kept at 5 cm. The needle valve of the airbrush was adjusted to spray a spot of 0.5 cm ~ 1 cm in diameter. The airbrush or the substrate was moved back and forth at a speed of ~ 5 cm/s with each stroke

overlapping with the previous one to ensure a continuous coverage. Overall, the area was coated at a speed of $\sim 1.5 \text{ cm}^2/\text{min}$.

Characterization. The morphologies of the spray-coated films were imaged using a field emission scanning electron microscope (FESEM, JEOL 7500F) operated at 15 kV. The polydispersity index (PDI) of silica nanoparticles was measured by dynamic light scattering (Zetasizer Nano S, Malvern Instruments). The reflectance and scattering spectra were collected from USB4000 fiber optical spectrometer (Ocean Optics). Transmittance of the spray-coated film on a glass slide was measured from the Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies). The chemical structure of the coating was confirmed by the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet 8700, Thermo Scientific). The surface topography of the coatings was imaged by Dimension 3000 Atomic Force Microscopy (AFM, Digital Instruments) with a Si₃N₄ cantilever in the tapping mode. The average roughness (R_a) and root-mean-square (rms) roughness values were calculated from 5 µm×5 µm images using Gwyddion software on the AFM. The static contact angles, advancing contact angles, roll-off angles were measured using the Ramé-Hart standard automated goniometer (Model 290). 5-µL and $10-\mu$ L liquid droplets were used for measurement of static contact angles (SCA) and roll-off angles (RA), respectively.



Fig. S1. Optical image of an angle-independent colored surface (green) spray coated from monodispersed SiO₂ nanoparticles in dry and wet conditions.



Fig. S2. Size distribution of 200 nm (a), 250 nm (b) and 300 nm (c) silica nanoparticles from dynamic light scattering measurement.

As seen in Fig. S2, the average size of synthesized silica nanoparticles was 196.1 nm, 250.9 nm and 299.3 nm, respectively, according to dynamic light scattering. The PDI was 4.5%, 1.1% and 4.3%, respectively.

Optical properties of angle-independent colored surfaces

As shown in the reflectance spectra (Fig. S3a-b), angle-independent colored films exhibited clear reflectance peaks except the film sprayed from 200 nm NPs limited by the spectrometer resolution below 400 nm. By comparing Fig. S3a and Fig. S3b, we could see that the reflectance peaks were nearly the same from different angles of detection (the angle between the detector and the normal plane). Correspondingly, the transmission spectra (Fig. S3c) showed the identical valley positions as the peak positions in the reflectance spectra from samples prepared by 250 nm and 300 nm NPs, respectively.

It has been suggested that the angle-independent colors seen in quasi-amorphous photonic structures arises from constructive interference of scattered light.³⁻⁵ For a period colloidal crystal, the wavelength of constructive interference λ can be expressed by Bragg's law

$$m\lambda = 2d\sin\theta \tag{1}$$

Where *d* is the distance between two diffracting planes, θ is the incidence angle, *m* is an integer. The reflectance peaks for the (111) plane of an face-centered cubic (fcc) lattice is {Kim, 2011 #34}

$$\lambda = 2dn_{eff} = \left(\frac{\pi}{3\sqrt{2}\phi}\right)^{1/3} \left(\frac{8}{3}\right)^{1/2} D\left(n_p^2\phi + n_m^2(1-\phi)\right)^{1/2} = aD$$
(2)

where n_{eff} is the effective refractive index, D is the diameter of particles, and a is the structure factor, which is the function of volume filling fraction ϕ , and the refractive index of nanoparticles (n_p) and medium (n_m) , respectively. Here, a should be the same for films sprayed from different particle sizes due to similarity in structures. Therefore,

the position of reflectance peak should have a linear relationship with the particle size,



which was in agreement with experimental observation shown in Fig. S3d.

Fig. S3. (a-b) Reflectance spectra of colored films composed of silica NPs with diameter of 200 nm, 250 nm and 300 nm, respectively. The incident angle is 15° and the angle of detection is (a) 15° and (b) 45°. (c) Transmission spectra of the colored films which were placed vertically in the optical path. (d) Correlation between the reflectance peak position and the particle size.

different sized i SiO ₂ nanoparticles						
Particle size	$\theta_{\rm st}(^{\rm o})$	$ heta_{ m adv}(^{ m o})$	Roll-off angle (°)			
200 nm	156.2±1	162.5±1	1.5±0.5			
250 nm	155.5±1	160.8±1	1.5±0.5			
300 nm	153.8±1	159.2±1	2.0±0.5			

Table S1. V	Water contact angles of angle-independent colored films sprayed from
	different sized F-SiO ₂ nanoparticles

 θ_{st} : apparent static water contact angle; θ_{adv} : advancing water contact angle



Fig. S4. ATR-FTIR spectra of the green NP film.



Fig. S5. (a) 2D and (b) 3D AFM images of the moccasin superhydrophobic film from 300 nm-diameter F-SiO₂ NPs. (c) Line scan of (b).

Prediction of water wetting state on particle surfaces

There are two distinct models predicting wettability on rough surfaces. In the Wenzel model,⁶ roughness effectively increases the actual surface area and the apparent Wenzel contact angle, θ_w is

$$\cos\theta_w = r\cos\theta_0 \tag{3}$$

where *r* is the roughness factor and defined as the ratio of actual surface area over the apparent surface area, and θ_0 is Young's contact angle on a homogeneous smooth surface. Here, θ_0 =110.6°, which was obtained from perfluorosilane, (heptadecafluoro-1,1,2,2- tetrahydrodecyl) trichlorosilane treated glass slide. The roughness factor *r* was estimated from the AFM images to calculate θ_w . As seen in Table 2, the measured static water contact angle, θ_{st} , on the colored films was much larger than the predicted θ_w , indicating water droplets were not in the Wenzel wetting state.

In the Cassie-Baxter model,⁷ it is considered that liquid contacts a composite surface of solid and air. The apparent contact angle, θ_c , can be described as

$$\cos\theta_c = f(\cos\theta_0 + 1) - 1 \tag{4}$$

where *f* is the fraction of liquid-solid contact. Due to the hierarchical and random NP assembly, we cannot calculate the *f* value to predict θ_c . Instead, we estimated *f* value according to the static water contact angle θ_{st} . As seen in Table S2, *f* was very small for all films, < 0.2, confirming the air-solid composite nature of the sprayed films.

Table S2. Apparent static water contact angle, θ_{st} , roughness factor *r*, and the theoretical Wenzel contact angle θ_w and filling fraction *f* of samples.

Particle size	$\theta_{st}(^{o})$	r	$\theta_w(\overset{\mathrm{o}}{})$	f
Fluorinated glass slide	110.6	1	110.6	1
200 nm	156.2	1.82	129.8	0.13
250 nm	155.5	1.75	128.0	0.14
300 nm	153.8	1.73	127.5	0.16

Preparation of superhydrophobic colored patterns for anti-counterfeiting

The preparation of the superhydrophobic colored pattern for anti-counterfeiting was shown in Fig. 3b. First, the glass substrate was covered by the pattern "N" (mask 1). IPA solution containing pristine monodispersed silica NPs (250 nm in diameter, 10 wt%) and GR-653L (0.05 wt%) were sprayed onto the substrates. Then mask 2 with pattern hollow "N" was placed on top of the colored area. IPA solution containing monodispersed fluorinated silica NPs (250 nm in diameter, 10 wt%) and GR-653L (0.05 wt%) were sprayed onto the substrates. Then mask 2 with pattern hollow "N" was placed on top of the colored area. IPA solution containing monodispersed fluorinated silica NPs (250 nm in diameter, 10 wt%) and GR-653L (0.05 wt%) were sprayed onto the "N" pattern area. Since the size of silica NPs sprayed in both steps was the same, homogeneous green colored coating was achieved on the entire substrate.

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