ACS NANO
Cite This: *ACS Nano* 2018, 12, 3095−3102
www.acsnano.org

Additive Mixing and Conformal Coating of Noniridescent Structural Colors with Robust Mechanical Properties Fabricated by Atomization Deposition

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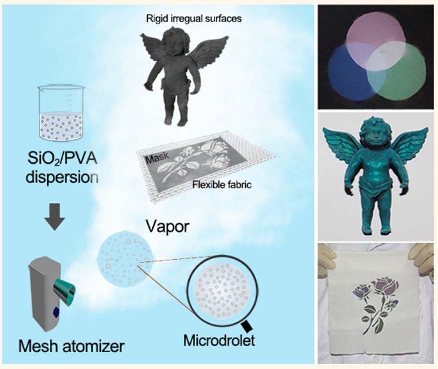
Supporting Information



ABSTRACT: Artificial structural colors based on short-range-ordered amorphous photonic structures (APSs) have attracted great scientific and industrial interest in recent years. However, the previously reported methods of self-assembling colloidal nanoparticles lack fine control of the APS coating and fixation on substrates and poorly realize three-dimensional (3D) conformal coatings for objects with irregular or highly curved surfaces. In this paper, atomization deposition of silica colloidal nanoparticles with poly(vinyl alcohol) as the additive is proposed to solve the above problems. By finely controlling the thicknesses of APS coatings, additive mixing of noniridescent structural colors is easily realized. Based on the intrinsic omnidirectional feature of atomization, a one-step 3D homogeneous conformal coating is also readily realized on various irregular or highly curved surfaces, including papers, resins, metal plates, ceramics, and flexible silk fabrics. The vivid coatings on silk fabrics by atomization deposition possess robust mechanical properties, which are confirmed by rubbing and laundering tests, showing great potential in developing an environmentally friendly coloring technique in the textile industry.

KEYWORDS: *additive color mixing, conformal coating, noniridescent structural colors, atomization deposition, silk fabric*

Chemical pigments and dyes usually lead to serious environmental pollution in the textile dyeing industry, and the dyed colors easily fade over time.[1−3] In recent years, structural colors originating from the interaction of visible light with photonic nanostructures have attracted great attention worldwide owing to their highly bright, fadeless, and pollution-free characteristics.[4−11] Among these photonic structures, the short-range-ordered amorphous photonic structures (APSs) have attracted increasing attention because they can produce angle-independent noniridescent structural colors when the structural characteristic sizes are comparable to the visible wavelengths.[12−15] Such noniridescent structural colors show great potential applications in color-related fields such as paints, cosmetics, textiles, displays, and colorimetric sensors.[16−22]

Noniridescent structural colors produced by APSs were first discovered in living organisms in nature such as birds and longhorn beetles.[23−26] These natural APSs give researchers great inspiration to design and fabricate optical materials and devices.[27,28] To mimic natural noniridescent structural colors, both top-down and bottom-up strategies have been used to fabricate artificial APSs, and self-assembling colloidal nanoparticles (NPs) is the most commonly used bottom-up strategy

Received: November 21, 2017
Accepted: February 13, 2018
Published: February 13, 2018

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DOI: 10.1021/acsnano.7b08259
ACS Nano 2018, 12, 3095−3102

owing to its simplicity and mass production features. A variety of simplified or modified self-assembling methods have been proposed, such as drop casting,[14,15] spin coating,[27] spray coating,[16,29−32] electrophoretic deposition,[22,33,34] microfluidic fabrication,[35] charged gel particle assembly,[36,37] and assembly in ionic liquid.[38] These methods can effectively control the interaction among the NPs and break down their long-range order arrangement, while most of them lack fine control of the APS coatings on substrates. Especially for objects with irregular or highly curved surfaces, such as 3D objects and textiles, their conformal coating in one step was hard to realize until now, greatly hindering the promotion of structural color based artificial pigments in practical industrial applications. Thus, strategies that can tackle the above problems are highly desirable.

In this paper, atomization deposition of colloidal silica NPs with poly(vinyl alcohol) (PVA) as the additive is proposed to fabricate large-area homogeneous APSs with vivid non-iridescent structural colors. The fabrication process of the APS coatings can be finely controlled, and subtle changes in coating thickness could be readily adjusted. Based on this feature, additive mixing of the noniridescent structural colors by stacking APS coatings is realized. Also 3D conformal coating on objects with irregular or curved surfaces can be realized in one step because of the omnidirectional feature of atomization. This approach is available on various substrates such as papers, resins, metal plates, ceramics, or even flexible fabrics. Due to the strongly cohesive PVA, noniridescent structural color patterns on silk fabrics are obtained with substantial mechnical properties.

RESULTS AND DISCUSSION

The fabrication process of APS coatings by atomization deposition is schematically illustrated in Figure 1. An aqueous silica NP dispersion with an appropriate amount of PVA as the additive was filled into a commercial mesh nebulizer. The nebulizer uses high-frequency mesh vibration, which is produced by a piezoelectric actuator, to push liquids out through the filter mesh to generate an aerosol.[39] The pore size of the filter mesh could be varied, and was 3 μm in this study. Thus, a mass of foggy vapor composed of microdroplets was flown out from the nebulizer in a standing cloud at very low velocity. Various substrates, including 3D rigid objects with irregular surfaces and 2D flexible fabrics, were placed in the vapor to be coated. After the coating process, the substrates were taken out and dried under ambient conditions. Owing to the mild deposition of atomizing microdroplets, the coating on the substrates can be realized at a very low deposition rate (Figure S1, Supporting Information), similar to atomic layer deposition (ALD) widely used in physics and material science. As the solvent in the microdroplets can evaporate very quickly during the deposition and there is not sufficient time for silica NPs to normally assemble, close-packed APS films can be easily formed on the substrates. The APS films are homogeneous and can produce uniform noniridescent structural colors. Also, the colors are tunable by using different sized silica NPs. Color patterns can be "dyed" on various substrates by the aid of masks.

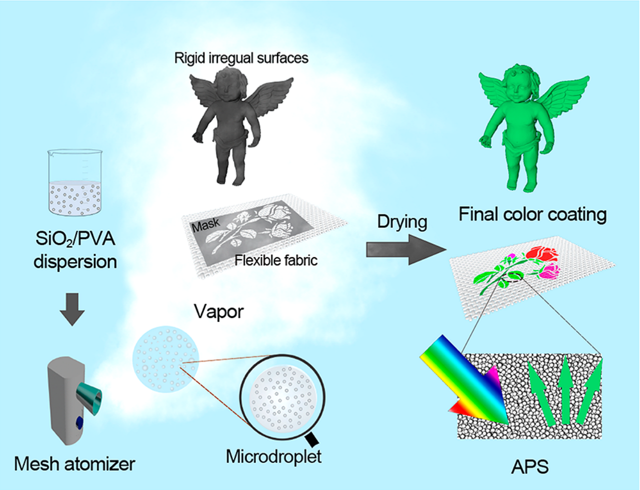

Figure 1. Schematic illustration for the fabricating process of large-area APSs with noniridescent colors on various rigid and flexible substrates by atomization deposition.

Color coatings on black papers were prepared by atomization deposition of silica NPs of various diameters (167, 187, 212, 236, 262, 279, 285, and 308 nm) with 4 wt % PVA as additive in the dispersion. The obtained colors were structural colors and noniridescent, spanning the whole visible light regime (Figure 2a). The coatings were very uniform even at the microscopic scale, as demonstrated by the optical microscope image of the cyan sample prepared by 212 nm silica NPs (Figure 2b). Scanning electron microscopy (SEM) showed that the silica NPs have self-assembled into homogeneous and close-packed structure (Figure 2c and inset). A histogram of the two-dimensional (2D) radial distribution function (RDF) and 2D Fourier transform of the SEM image (Figure 2d) indicated that the coatings were isotropic short-range-ordered APSs with a characteristic size comparable to the visible light wavelengths (242 nm for the cyan sample). The measured normal reflection spectra (Figure 2e) of the eight colored sampes (Figure 2a) possess characteristic peaks that arise from coherent scattering due to structural short-range order and resonant Mie backscattering of individual particles in the visible short-wavelength range.[22,26] It is worth mentioning here that the thicknesses of the above colored APS coatings were about 3−4 μm (Figure S2, Supporting Information). Too thin (<1 μm) or too thick (>8 μm) APSs will reduce the contrasts in the reflection spectra, producing blackish or whitish colors.[27,40] The oblique observation (Figure S3, Supporting Information), small peak shifts in angle-resolved reflection, and scattering spectra for the cyan sample (Figure S4, Supporting Information) indicated that the colors of the fabricated APSs are nearly angle-independent.

The additive PVA is found to spread between silica particles (inset of Figure 2c). To evaluate the influence of PVA additives on APSs, coatings consisting of 212 nm silica NPs with different amounts of PVA were prepared (Figure S5, Supporting Information). When the PVA contents in the dispersions are low (*i.e.*, 2 wt % or lower), some various sized spherical close-packed photonic polycrystal aggregates were embedded in the APS coatings. When the PVA contents were higher than 4 wt %, the aggregation could be significantly hindered, and homogeneous APSs were obtained. Excessive PVA introduction (10 wt % or higher), unfortunately, could lead to some structural cracks. In addition, the addition of PVA in a proper amount did not cause macroscopic color changes except a slight decrease in color brightness (Figure S6, Supporting Information), which could be attributed to the reduced refractive index

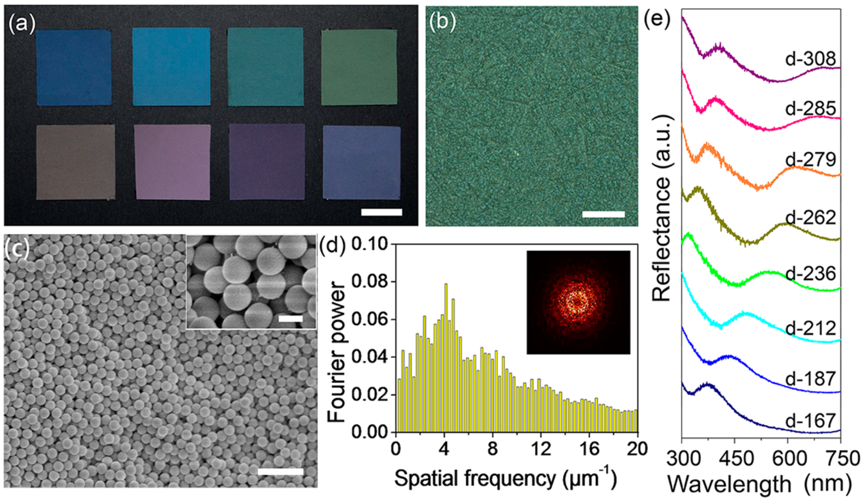

Figure 2. Microstructures and optical properties of the APS coatings. (a) Images of the fabricated noniridescent structural colors using eight different sized silica NPs with 4 wt % PVA. (b) Microscopic optical image of the cyan-colored sample in (a). (c) SEM image of the cyan-colored sample. Inset is the close-up view showing the interstitial PVA between the silica spheres. (d) Histogram of two-dimensional RDF of the structures in (c), and inset is the 2D Fourier transform. (e) Reflection spectra corresponding to the samples in (a). Scale bars: (a) 1 cm; (b) 500 μm; (c) 1 μm (inset: 200 nm).

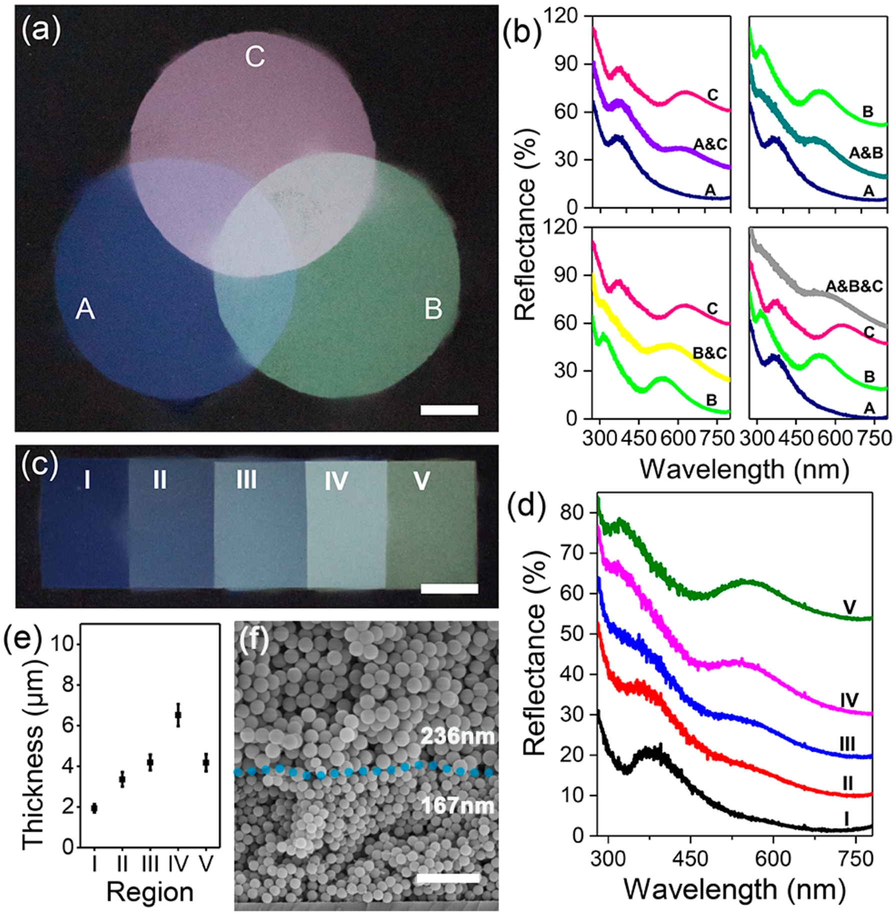

Figure 3. Additive mixing of noniridescent structural colors by APS coatings. (a) Image of additive mixing by the fabricated noniridescent structural colors using 167, 236, and 279 nm sized silica NPs. (b) Corresponding reflection spectra of the primary colors and additive-mixed colors in (a). (c) Finer mixed colors by varying the thicknesses of green coatings (236 nm NPs) over the blue one (167 nm NPs). (d) Corresponding reflection spectra of the colors in (c). (e) Coating thicknesses of different regions in (c). (f) Cross-sectional view of the heterostructure for region III in (c), and the dotted line indicates a heterogeneous interface. Scale bars: (a, c) 1 cm and (f) 1 μm. Each spectrum is equal-offset shifted (20% in (b) and 10% in (d)) for comparison.

DOI: 10.1021/acsnano.7b08259
ACS Nano 2018, 12, 3095−3102

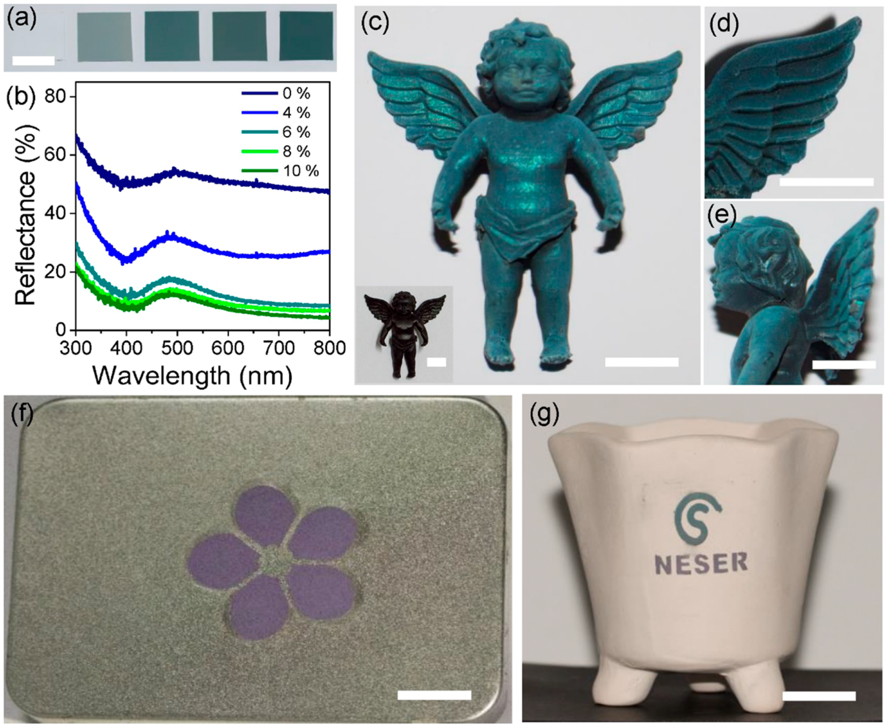

Figure 4. Demonstration of APS coatings on various substrates. (a) Images of cyan coatings on white paper using 212 nm sized silica NPs with different contents of CB and their corresponding reflection spectra (b). (c) Cyan-color dyed angel toy by using 212 nm sized silica NPs with 4 wt % PVA (inset, pristine angel toy) and enlarged rear view (d) and side view (e) of the wing in (c). (f) Purple flower coated on a steel plate by using 285 nm sized silica NPs with 6 wt % CB and 4 wt % PVA. (g) Colored laboratory logo (http://neser.suda.edu.cn) coated on ceramic by using 285 and 212 nm sized silica NPs with 6 wt % CB and 4 wt % PVA for different regions. Scale bar: (a, f, g) 2 cm and (c, c (inset), d, e) 1 cm. The toy model was used with permission from the Web site 3D CAD Browser (https://www.3dcadbrowser.com). The laboratory logo was used with permission from National Engineering Laboratory for Modern Silk, Soochow University.

contrast between silica NPs ($n_{\text{silica}} \approx 1.52$) and air ($n_{\text{air}} \approx 1$) after PVA ($n_{\text{PVA}} \approx 1.48$) filled in the gaps.

Nevertheless, the addition of PVA can significantly improve the mechnical properties of the APS coating on substrates and facilitate the formation of homogeneous APSs mentioned above, which is crucial for structural colors in practical applications. Sandpaper abrading with the loading force applied on the cyan samples shows that APSs with 4 wt % or higher PVA content not only can maintain the integrity of the structures and the colors but also possess good fixation stability on the substrates (Figure S7, Supporting Information).

Additive color mixing by photonic structures can broaden the color gamut with limited coloring materials. It has been realized by stacked opaline heterostructures using various layer-by-layer deposition methods[41−45] or mixing of photonic crystal particles,[46] while the additive mixing of noniridescent structural colors by APS heterostructures is rarely reported. The main difficulties are the lack of layered stacking and fine thickness-controlled abilities of APS coatings for most of the previously reported methods. Utilizing the fine control ability of atomization deposition at several NP levels, heterogeneous APSs can be readily fabricated layer by layer; thus additive mixing of large-area noniridescent structural colors was easily realized. The sequentially prepared blue, green, and pink colors, by atomization deposition of 167, 236, and 279 nm silica NPs with 4 wt % PVA, respectively, were used as three primary colors for mixing (Figure 3a, marked as "A", "B", and "C", respectively). The thicknesses of the color films were fixed at about 2 μm here. Incidentally, a pure red color cannot be produced based on close-packed NPs due to the strong backscattering resonances of individual NPs in the visible short-wavelength range (Figure 2e).[14,22,47] The additive mixed colors along with the three primary colors and their measured normal reflection spectra are shown in Figure 3a and b. The overlapping mixing of blue and green colors produces the intervening cyan color (A&B). The mixing of blue and pink colors produces a purple-red color (A&C). The mixing of green and pink colors produces a yellow color (B&C). Additive mixing of the three primary colors produces a gray-white (A&B&C). The typical characteristic reflection peaks of each individual color component and new reflection peaks due to their additive superposition obtained from the spectra measurements (Figure 3b) further confirm the validity of the APS-based color mixing. The spectral intensities and color appearances of the APS coatings here are sensitive to the structure thickness.[27,40]

Finer thickness control of the deposited APSs and thus finer color mixing can also be realized by atomization deposition. The above blue and green colors were used as an example demonstration. A blue-colored coating with a mean thickness of 2 μm was first deposited, followed by green-colored coatings with three gradient thicknesses. The intervening indigo, cyan, and turquoise colors were subsequently obtained (Figure 3c), and their reflection spectra (Figure 3d) record the spectral changes during the color mixing. The thicknesses of each colored layer are shown in Figure 3e. A cross-sectional view of the heterostructure (Figure 3f) shows that the silica NPs of two sizes have a clear boundary without permeation, and in each part the APSs are as homogeneous as previously individual coatings.

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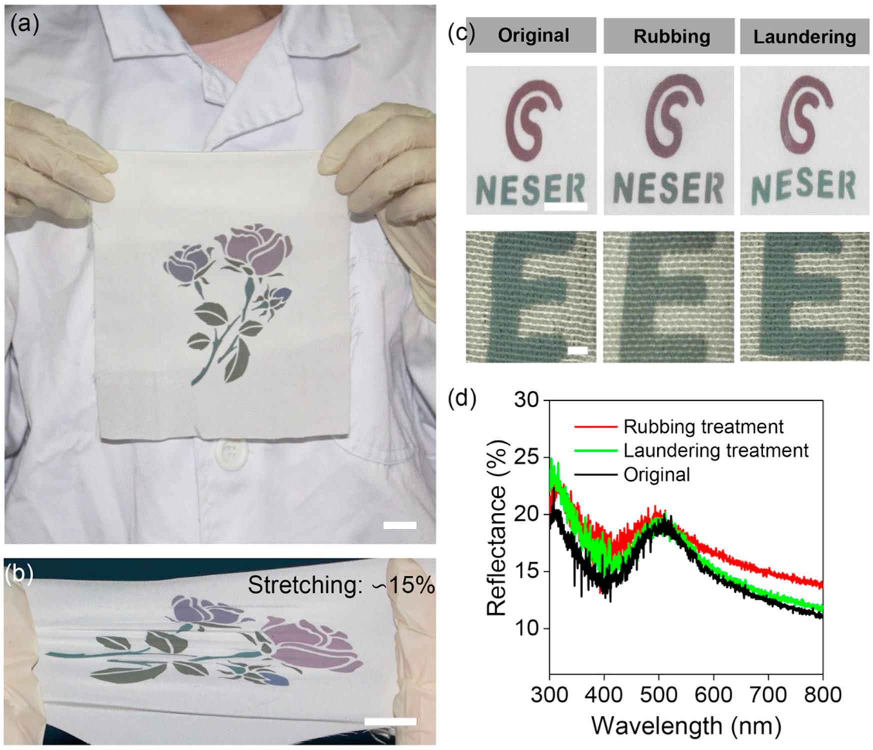

Figure 5. Patterned APS coatings on silk fabric and their mechanical stability. (a) Colored rose pattern coated on silk fabric using five kinds of fabricated noniridescent colors. (b) Image showing the stretching of silk fabric in (a) with ~15% elongation. (c) Images of the two-colored laboratory logo (http://neser.suda.edu.cn) coated on silk fabric in macroscopic (top) and microscopic (bottom) observations before (original) and after rubbing and laundering treatments and their corresponding reflection spectra for the cyan part (d). Scale bars: (a, b) 2 cm, (c) 1 cm (top), 1 mm (bottom). The rose pattern was reproduced with permission from The Stencil Library (Northumberland, UK). The laboratory logo was used with permission from National Engineering Laboratory for Modern Silk, Soochow University.

Usually to enhance the saturation of the noniridescent colors produced by APSs, either a black absorbing background or short-wavelength absorbing additives are required.[14,16,27,31,40,48] The method of atomization deposition here can also be applied onto white substrates to obtain vivid structural colors by adding carbon black (CB) particles. The color brightness and saturation depend on the content of CB particles and weakly on the thicknesses of APSs. A series of cyan-colored coatings using 212 nm silica NPs and 4 wt % PVA with varying contents of CB on white photopaper were fabricated (Figure 4a). As shown in the measured reflection spectra (Figure 4b), the spectral saturation of the coatings increases with the CB content, while the spectral brightness decreases with the CB content. Thus, the intervening CB content at 6 wt % approaches the optimal saturation and brightness to obtain vivid structural cyan colors. Furthermore, the method has versatile applicability for other various substrates such as 3D-printed black angel toys made of resin, steel plates, ceramics, flexible silk fabric, *etc.* The cyan-colored resin toy was prepared by atomization deposition of 212 nm silica NPs and 4 wt % PVA dispersions (Figure 4c). Compared with previously reported large-area coating methods, which suffer from a coffee-ring effect[14,15,49,50] or are limited on flat rigid substrates,[27] this method realizes homogeneous APS coatings on all surfaces of the 3D substrates in only one step. The back (Figure 4d) and even the indirectly exposed regions (inside of the wing, Figure 4e) as well as the front side of the toy were coated simultaneously. Meanwhile, the APS coatings maintain the original morphology and details of the coated substrates, which is called "conformal". To further evaluate the conformal ability of this method, we deposited APS coatings on human hair. SEM images (Figure S8, Supporting Information) show that silica NPs uniformly spread on the surface of a ~140 μm thick hair, and the typical scale patterns on human hair are well maintained, which means the conformality can even be controlled at the micrometer scale. Structural color patterns on the steel plate and ceramic vessel were also fabricated with the assistance of masks using this method. As shown in Figure 4f and g, a purple flower was dyed on a steel plate and the laboratory logo was dyed on a ceramic vessel, respectively.

Colored fabrics in daily life have always been dyed by chemical pigments or dyes, which are usually environmentally unfriendly and may fade over time. A green dyeing technique based on artifical structural colors is a promising alternative, and there is still a lack of a mass-productive method to prepare noniridescent structural colors on fabrics with good conformality, improved mechanical property, and stability. The atomization deposition method in this work can successfully tackle these issues. Silk, a specialty of China, was chosen as an example for illustration. Silk fabric has been widely used in textiles for thousands of years owing to its elegant shiny appearance and skin-friendliness. However, traditional dyeing techniques on silk fabric need many complicated chemical processes for color fastness due to its highly smooth surface and susceptibility to environmental stimuli such as temperature, sunlight, and solvents. Here, large-area silk fabrics were quickly dyed by atomization deposition of APSs composed of silica NPs with some carbon black and PVA (Figure 5a). Four vivid colors, prepared using four sized silica NPs, were patterned as a rose with a multistep mask process. Clear boundaries and no color crossing between the dyed and undyed areas were found, and colored warp and weft yarns and even single fibers were still well seen without being submerged (Figure S9, Supporting Information), which are hard to achieve by other reported methods such as gravitational sedimentation and the vertical deposition method.[51,52] As a comparison, the colored silk fabric prepared by drop coating is also shown in Figure S10 in the Supporting Information. The coating suffered from a serious coffee-ring effect and nonuniformity in both the macro- and microscale. The silk fabric with colored patterns can stand vigorous stretching and bending and can maintain its original exceptional flexibility (Figure 5b), and there was almost no color loss after ~15% stretching more than 10 times (Figure S11, Supporting Information). To further evaluate the mechanical stability of the color coatings considering potential practical applications, color fastness through rubbing and laundering was tested, respectively. Almost no obvious color fading was observed after the rubbing test by about 11196 Pa load pressure 15 times and the rotating laundering test for 15 min, which can be observed in both the macroscopic and microscopic images shown in Figure 5c. The corresponding reflection spectra in Figure 5d show that only the rubbing treatment leads to a small increase in peak width, while the spectrum for the laundering treatment stayed the same as the original. These results confirm that the APS coatings on silk fabrics by atomization deposition have good mechanical properties and stability. Although the mechanical stability can be further increased by adding a higher content of PVA into the coatings, severe color degradation happens (Figure S12, Supporting Information) due to the reduced refractive index contrast between silica nanoparticles and air, as mentioned above. Considering the good color visibility and stability of APS coatings, the addition amount of PVA should also be controlled in the range of 4−10 wt % in this case.

The excellent color fastness here is attributed to the additive PVA, a widely used agent in the textile sizing process.[53] PVA contains large amounts of hydroxyl groups; thus hydrogen bonds are easily formed intramolecularly or with some other hydroxyl-group-rich molecules. It is noted that silk fabrics and silica NPs also have many hydroxyl groups.[54−56] Thus, a strong link between silk fabrics and silica NPs is formed by PVA, which significantly enhances the mechanical property and stability of the APS coatings. We believe that by using some additives with special functions, more functional APS dyeing with noniridescent vivid structural colors can also be realized.

CONCLUSIONS

In summary, the fabrication of large-area homogeneous APS coatings and uniform noniridescent structural colors is demonstrated by atomization deposition of colloidal silica NPs with some PVA as the additive. The addition of PVA facilitates the formation of homogeneous APS coatings and improves the mechnical properties as well. The whole coating process is simple, mild, environmentally friendly, and well-controlled. Based on the fine thickness-controlled capability, heterogeneous APSs and additive mixing of noniridescent structural colors were realized easily. Due to the omnidirectional coating feature, 3D conformal coating on substrates with irregular or curved surfaces in one step is readily obtained. The strategy can be applied on various substrates such as black/white paper, resins, metal plates, ceramics, or flexible silk fabrics. The vivid structural colors coated on silk fabrics by the atomization depostion possess robust mechanical properties, which can withstand rubbing and laundering tests, showing great potential in developing a green coloring technique in the textile industry.

MATERIALS AND METHODS

Materials. Poly(vinyl alcohol) (DP = 1750 ± 50) was purchased from Sigma-Aldrich and used as received without further purification. Carbon black (99.5%, 30 nm) was bought from Aladdin, Co., Shanghai, China. Ultrapure water was used in all the experiments. Monodisperse silica NP aqueous suspensions (CV < 3%, 10% solids by weight) with diameters of 167, 187, 212, 236, 262, 279, 285, and 308 nm were purchased from Nanjing Dongjian Biological Technology Co., Ltd. The black angel toys were produced by a commercial 3D printer. The steel plate, ceramic vessel, and plain silk fabric were brought from a local supplier.

Preparation of APS Coatings. The silica NPs were dispersed into water with adding certain amounts of 10 mg/mL PVA solutions, followed by ultrasonication for 1 h to prepare the atomization solutions. The concentration of NPs in the mixed suspension was kept at 2.5 wt %, and carbon black was optionally added according to the substrates to be coated. A commercial vibrating mesh nebulizer (mini Air 360, Banglijian Co., Ltd., China) with optional filter mesh pores of 3 μm loaded with the prepared suspension was used to produce the aerosol. Plasma-pretreated substrates were placed in the vapor, about 6−20 cm away from the outlet. To speed up the rate of atomization deposition, the coated substrate can be dried in an oven at 50 °C for about 3−5 min. Different amounts of 10 mg/mL PVA solutions were used in the dispersions to find the proper proportion for samples with both good color and considerable mechanical robustness. The weight percent (wt %) of PVA (or carbon black) was determined according to the following equation:

$$W(\text{wt\%}) = \frac{W_1}{W_1 + W_0} \times 100\%$$

where W_1 and W_0 are the weights of the PVA (or carbon black) and silica NPs in mixed solutions, respectively.

Characterization and Spectra Measurement. A Canon EOS 700D digital camera was used to capture the photographs of samples. Enlarged view and microscopic pictures were taken by a VHX-100 digital microscope (Keyence Corporation, Japan). The morphologies of silica NPs were observed by a field emission scanning electron microscope (S-4800, Hitachi Ltd., Japan). All reflection spectra at normal incidence were collected by a PG2000-Pro spectrometer (Idea Optics Co., Ltd., China) equipped with a UV−vis−NIR light source. The angle-resolved reflection and scattering spectra were measured by a home-built angle-resolved optical spectroscopy apparatus equipped with a xenon lamp light source at Fudan University.[57] A standard white board (Spectralon Reflectance Standards) was used as reference.

Mechanical Stability Tests. Rubbing and accelerated laundering tests were performed to assess the mechanical durability of the APS coatings on silk fabrics. The rubbing test is performed by referring to the textile ISO 105-X12:2001 method. Briefly, a 5 × 5 cm standard rough cotton rubbing cloth was loaded on a rubbing finger (16 mm in diameter) under a downward force of 9 N as an abrading surface, facing the tested silk fabric, and moved forward in one direction 15 times. Typically, up to ~11196 Pa pressure was applied on the tested silk fabric. For the laundering test, the silk fabric was put into a rotating closed canister in a 150 mL water bath containing 0.15% detergent at 40 ± 2 rpm/min for 15 min under ambient temperature, similar to the daily washing process for a drum washing machine. After that, the sample was dried in air. Then the samples were collected to observe their surface and carry out spectra measurement. To evaluate the stability of the APS coatings with different amounts of PVA on Kraft paper, an abrasion test was conducted as follows: paper with a size of 1.5 × 1.5 cm was loaded with 200 g of force, facing 3000-grit SiC sandpaper as an abrading surface, and moved forward in one direction at a rate of 5 cm/s for 10 cm. The pressure of the weight can be calculated as 8.7 kPa.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b08259.

> Figures of morphologies of silica NPs on a glass slide after placing in vapor for short time; side view of the APS coatings on a glass slide; angle-resolved optical spectra of APS coatings on paper; structures and optical and mechanical properties of APS coatings with different PVA content; conformal APS coatings on human hair; enlarged view of the colored rose-patterned silk fabric in Figure 4h; colored silk fabric prepared by drop casting as a comparison; optical properties of colored silk fabric after stretching (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (51373110, 11604355, 11774063, and 11727811), the 973 Program (2015CB659400), China National Key Basic Research Program (2016YFA0301100 and 2016YFA0302000), Science and Technology Commission of Shanghai Municipality (17ZR1442300), State Key Laboratory of Surface Physics (ZA2014-01 and KF2015-04), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions, Project for Jiangsu Scientific and Technological Innovation Team (2013), and the Youth Innovation Promotion Association of the Chinese Academy of Sciences (2015256).

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