Facile Synthesis of Monodispersed SiO$_2$@Fe$_3$O$_4$ Core–Shell Colloids for Printing and Three-Dimensional Coating with Noniridescent Structural Colors

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ABSTRACT: Amorphous photonic structures (APSs) with short-range ordered arrangement have attracted great interest because of their wide view angles. However, the presented methods for the APSs color printing and 3D coating on different substrates and curvatures are lack of control. Here, APSs with angle-independent structural colors were fabricated by the self-assembly of SiO$_2$@Fe$_3$O$_4$ core–shell nanostructures, which were prepared by the hydrolysis of Fe(acac)$_3$ on the silica surfaces. The size of SiO$_2$@Fe$_3$O$_4$ core–shell colloids can be controlled well through the tuning of SiO$_2$ particle size, whereas the coverage of Fe$_3$O$_4$ on silica surfaces can be precisely tailored through altering the mass ratio between Fe$_3$O$_4$ precursor and SiO$_2$. APSs with only short-range ordered structures, uniform noniridescent structural colors, and high color visibility can be obtained through the self-assembly of SiO$_2$@Fe$_3$O$_4$ colloids of different particle sizes in a few minutes. They are mainly attributed to the weak electrostatic repulsion interactions between SiO$_2$@Fe$_3$O$_4$ colloids because of the partial coverage of Fe$_3$O$_4$ on silica surfaces and absorption of the incoherent multiple scattering of visible light from Fe$_3$O$_4$. Moreover, SiO$_2$@Fe$_3$O$_4$ colloids show good adhesion to various substrates, such as paper, glass, plastics, resins, ceramics, and wood, which facilitates the formation of uniform APSs on different substrates. Multicolor prints and 3D coating of APSs on substrates with different curves and roughness can be realized on the basis of the fast assembly of SiO$_2$@Fe$_3$O$_4$ colloids.

INTRODUCTION

Dyes and pigments have wide applications in paints, inks, and fabrics, but they cause environmental pollution, are unstable under UV light, and will fade over time because of their absorption of light.$^{1,2}$ Structural colors, originating from selective reflection of the light because of the interactions between the ordered structures and light, have intrinsic advantages of environmental friendly mass production and fadeless features compared with pigments.$^{3−11}$ Artificial building blocks, such as SiO$_2$ and polystyrene, can be produced in a large batch, which is well investigated for their applications especially for color printing.$^{12}$ However, the traditional long-range ordered photonic structures usually produce iridescent color, which means their structural color would alter depending on the view angle and orientation of the sample. This feature cannot satisfy the requirement for color display, in which the structural color should not change when observed from different view angles. In contrast to the long-range ordered structures, amorphous photonic structures (APSs) have attracted considerable interest because they show noniridescent structural color due to their short-range ordered arrangement.$^{13−15}$ These noniridescent structural colors obtained from the APSs have important potential applications in paints, cosmetics, textile, and displays.$^{16−23}$

To produce noniridescent structural color, both top-down and bottom-up strategies have been developed to fabricate APSs. The former is usually subjected to the time-consuming process, complex fabrication technologies, and expensive instruments, whereas the latter has received wide attention because of their remarkable merit of low cost, large batch production, and simplicity. Until now, various strategies have been used to create APSs, such as assembling two different sized colloids,$^{24−28}$ assembling particles in ionic liquid$^{29,30}$ or electric field,$^{31}$ spray coating,$^{16,19,31−33}$ drop casting,$^{34−38}$ electrophoretic deposition,$^{39,40}$ infiltration-assisted colloidal assembling,$^{41}$ layer-by-layer assembling,$^{41}$ and microfluidic fabrication.$^{42}$ These approaches can effectively restrain the long-distance electrostatic interactions between colloids, thus resulting in short-range ordered arrangement, but long-range amorphous. However, most of the reported approaches fail in precise control for color printing and coating of APSs on 3D substrates with different roughness and curvatures. Furthermore, a proportion of additional black substances are always required to reduce the incoherent multiple scattering of light.
but their distributions to the whole APSs may not be uniform owing to the physical mixing process.\textsuperscript{43,44} Therefore, it is highly desirable to develop new methods to deal with the above problems.

In this work, SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} core–shell nanostructures with tunable sizes were synthesized to fabricate APSs for multicolor printing and coating of APSs on 3D substrates. The SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids were prepared through the in situ deposition of Fe\textsubscript{3}O\textsubscript{4} uniformly on the silica surfaces, forming a thin shell of black Fe\textsubscript{3}O\textsubscript{4} nanoparticles on the silica surfaces. The morphology and coverage of Fe\textsubscript{3}O\textsubscript{4} nanoparticles on silica can be finely controlled by altering the Fe\textsubscript{3}O\textsubscript{4} precursor concentration. Through the evaporation-induced self-assembly (EISA) of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloid solution, APSs can be produced in short time, in which the color can be controlled by colloids of different sizes. The APSs show noniridescent structural colors with wide view angles (10–80°), which can be attributed to the reduced electrostatic repulsion between SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids. Because of the fast assembly process of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids and good adhesion of the colloids to various substrates, the prepared SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloid solutions are versatile in multicolor printing and APS coating on 3D substrates with different curvatures and roughness.

\section*{EXPERIMENTAL}

\textbf{Materials.} Tetraethyl orthosilicate (98%), ethanol (EtOH, 99%), aqueous ammonia (28%), and Fe(acac)\textsubscript{3} were purchased from Sinopharm Chemical Reagent Co. Ltd. Triethylene glycol (TEG) was obtained from Sigma-Aldrich. All chemicals were used directly as received without further purification.

\textbf{Synthesis of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} Core–Shell Nanostructures.} Monodispersed SiO\textsubscript{2} colloids with tunable sizes were synthesized according to the well-established Stöber method. The SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} nanostructures were obtained through the decomposition of Fe(acac)\textsubscript{3} on the silica surfaces. Briefly, SiO\textsubscript{2} colloid solution (500 mg dispersed in EtOH) was first mixed with TEG (20 mL) with the help of sonication (10 min), and then, Fe(acac)\textsubscript{3} (350 mg, 1 mmol) was added to the above solution. The mixture was stirred and heated to 120 °C for 1 h to remove EtOH and subsequently heated to 210 °C for 1 h. After the reaction was cooled down to RT, the SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids were collected by centrifugation and washed with EtOH at least three times. The products were finally dispersed in EtOH for further use.

\textbf{Fabrication of APS Film.} A very fast evaporation-induced colloidal assembly strategy was used to fabricate APS films. Prior to use, all glass slides and silicon wafers were cleaned by ultrasonication in EtOH for 5 min and dried in an oven. Typically, the SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloid solution (0.1 mL) was casted on the silicon wafer (2 × 2 cm), which was then transferred to the oven preheated to 70 °C. After heating for 3 min, the substrate with APS film was obtained.

\textbf{Characterization.} The size and morphology of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} were determined at 200 kV using a JEOL JEM-2100 HRTEM. The optical microscope images were taken on an Olympus BXFM reflection-type microscope operated in dark-field mode. The reflectance and backscattering spectra at different angles were measured by a NOVA spectrometer (Hamamatsu, S7031).

\section*{RESULTS AND DISCUSSION}

The fabrication of APSs assembled from monodispersed SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} core–shell nanostructures can be divided into three stages: (1) synthesis of monodispersed SiO\textsubscript{2} cores, (2) overgrowth of Fe\textsubscript{3}O\textsubscript{4} shell on the silica surfaces, (3) and self-assembly of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids, as shown in Figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.pdf}
\caption{Schematic illustration of the synthesis of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids for the fabrication of APSs.}
\end{figure}

Monodispersed SiO\textsubscript{2} colloids with an average size of 230 nm were prepared through the well-established Stöber method. Afterward, SiO\textsubscript{2} colloids were coated with Fe\textsubscript{3}O\textsubscript{4} shell through decomposition of Fe(acac)\textsubscript{3} in the presence of TEG and silica seeds at high temperature. Finally, the SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids assembled into APSs through the EISA process.

Figure 2 presents the SEM (Figure 2a) and TEM (Figure 2b,c) images of SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} core–shell nanostructures.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.pdf}
\caption{(a) SEM, (b,c) TEM, and (d) HRTEM images of synthesized SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} colloids. The silica core size is 230 nm. The scale bar in (a–c) and (d) is 100 and 5 nm, respectively.}
\end{figure}

Clearly, plenty of Fe\textsubscript{3}O\textsubscript{4} nanoparticles with an average size of 1–3 nm were homogeneously deposited on the silica surfaces and formed a layer of Fe\textsubscript{3}O\textsubscript{4} shell. A small proportion of free Fe\textsubscript{3}O\textsubscript{4} nanoparticles were also observed from the TEM images (Figure 2b), which is dispersed in solution. These free Fe\textsubscript{3}O\textsubscript{4} nanoparticles not bound to the silica surfaces can be easily removed through centrifugation because of their large mass difference. Measuring the distance between two adjacent planes in a specific direction gives a value of 0.255 nm, which corresponds to the lattice spacing of (311) planes of magnetite (Figure 2d). The crystallinity and phase purity of the produced products were also examined by XRD. As can be seen from Figure S1, the corresponding diffraction peaks of the products can all be indexed to pure Fe\textsubscript{3}O\textsubscript{4} (JCPDS No. 19-0629). No diffraction peaks from impurities and/or other phases can be detected. The broad peak of the XRD pattern indicated the small size of Fe\textsubscript{3}O\textsubscript{4} nanocrystals. Calculations with the Debye–Scherrer formula for the strongest peak (311) gave grain sizes of 1.5 nm, which is comparable to the TEM observations.

The size of the SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} core–shell nanostructures can be precisely tailored from 200 to about 285 nm by simply
tuning the silica size while keeping all other parameters fixed (Figure 3). Almost all the Fe₃O₄ nanoparticles were uniformly attached on each silica colloid, suggesting the versatile tunability of the presented strategy.

The loading amount of Fe₃O₄ on silica surfaces can be controlled by altering the silica and Fe(acac)₃ ratio. As the mass ratio of Fe(acac)₃ to silica increased from 0.035 to 0.175 and 3.5, the amount of Fe₃O₄ nanoparticles on each SiO₂ surface was significantly increased (Figure S2a−c), and their corresponding Fe₃O₄ loading concentrations were 1.3, 5.6, and 12.0%, respectively. As shown in Figure S2d−f, the products turned from black, green, to pale green as the Fe₃O₄ concentration increased. Therefore, the optimized concentration of Fe₃O₄ was determined to be 5.6% to enhance the color contrast and favor the colloidal assembly.

We then choose the SiO₂@Fe₃O₄ colloids (230 nm) as the building blocks and developed the EISA strategy to yield APSs. SEM images of self-assembled SiO₂@Fe₃O₄ APS film at various magnifications are presented in Figure 4a−c. It is apparent that the SiO₂@Fe₃O₄ colloids are closely packed to each other and their structures lack long-range ordering in the (111) plane. Two-dimensional FFT was also utilized to investigate the APSs. As can be seen from Figure 4d, a ring-like feature of the Fourier components suggests that the structure has a well-defined short-range order, consistent with the SEM observations.

The amorphous structure of the SiO₂@Fe₃O₄ photonic crystals (PCs) is probably due to their reduced surface charge that interrupts their self-assembly process. For comparison, we employed EISA strategy to obtain the long-range ordered SiO₂ PC films. Because of the highly charged surfaces of the silica particles, they could be self-assembled into highly ordered 3D lattice (Figure S3) by balancing the repulsive and attractive interactions between silica colloids during the solvent evaporation process. The obtained SiO₂ PC films always show bright structural colors (Figure 6a) and angle-dependent structural colors. In comparison, when a layer of Fe₃O₄ nanoparticles was coated on the silica surfaces, the ζ-potential of the silica colloids was reduced from −57 to −16 mV, far below the critical value of −30 mV for electrostatic-stabilized colloidal suspensions. This, to some extent, also suggests that the SiO₂@Fe₃O₄ core−shell colloids were not sufficiently stable and may partially aggregate during the self-assembly process. In the initial stage of the colloid assembly process, the SiO₂@Fe₃O₄ core−shell colloids can be dispersed in solvent in a low particle concentration, where the distances between the particles are relatively large and particles randomly move in the solution, in which the particles are mainly balanced by the attractive and repulsive forces. As the solvent was gradually evaporated, the neighboring particles become closer to each other, which results in the enhanced repulsion and van der Waals forces between colloidal particles. However, as the charge separation of SiO₂ (Si−OH → Si−O−H⁺) was partially inhibited by the coating of Fe₃O₄ nanoparticles, the attractive interactions will become stronger than the repulsion between colloids. Therefore, the SiO₂@Fe₃O₄ colloids tend to aggregate in a short distance in the solution. This means the SiO₂@Fe₃O₄ colloids can be balanced by attractive and repulsive interactions only in a short distance that contributed to the short-range ordered structures of APSs. To verify this hypothesis, we employed a digital camera to record the EISA process at different times. As shown in Figure 5, the SiO₂@Fe₃O₄ core−shell colloids were firstly dispersed in EtOH, which was then casted on the glass before evaporation. As the EtOH evaporated from the solution, plenty of brown aggregations with an average size of 200−500 μm appeared and could be easily observed and recorded. These results...
strongly demonstrated our assumption that the SiO₂@Fe₃O₄ core–shell colloids tended to aggregate during solvent evaporation, because of their weak repulsion interactions between building blocks. Besides, the bumpy surfaces of the SiO₂@Fe₃O₄ core–shell colloids may also contribute to the formation of short-range ordered structures, rather than long-range ordered structures.

To investigate the optical properties of the as-prepared SiO₂@Fe₃O₄ APSs, the reflection spectra and the corresponding digital photos of the PC films fabricated by SiO₂ and SiO₂@Fe₃O₄ colloids were recorded (Figure 6). The SiO₂ PC films exhibited iridescence and strong reflection intensity with a narrow stop band owing to their highly ordered nanostructures (Figure 6a,c). In comparison, the reflection intensity of the SiO₂@Fe₃O₄ colloids PC films was greatly diminished and their stop band was greatly broadened. These can be attributed to the amorphous structures of the SiO₂@Fe₃O₄ colloids PC films. Furthermore, the peak position of the SiO₂@Fe₃O₄ colloids PC films was slightly red-shifted to 515 nm compared to that of SiO₂ PC film because of the high refractive index of Fe₃O₄ nanoparticles. The reflection intensity of PC film is usually determined by the degree of order of PC film and the refractive index contrast between the building blocks and the air. Highly ordered structures and large refractive index contrast will lead to a higher reflection intensity of PC film. In our work, the weight percentage of the Fe₃O₄ on the surfaces of silica is only 5%, which makes negligible contribution to the refractive index contrast. With respect to the periodic structures, the traditional long-range ordered structures diffract light strongly according to Bragg’s law, which results in the strong reflection intensity. However, the APSs only have short-range ordered structures, which decrease the diffraction intensity of visible light, observing a weak and broad peak. The reflection intensity of APSs may be greatly enhanced by carefully selecting a building block with high reflective index, such as CeO₂.

The APS films assembled from the SiO₂@Fe₃O₄ colloids showed bright structural color, blue, green, yellow, and red colors, and have wide view angles when directly observed with naked eyes (Figure 7). The optical images of the four different PC films, which are obtained from the SiO₂@Fe₃O₄ colloids with a SiO₂ core size of 200, 230, 260, and 285 nm, respectively, display almost identical structural color at various viewing angles under ambient illumination (Figure 7a–7d). The structural color saturation of APS film (Figure 7e–7d) was measured and is shown in Figure S5. The colorful region in the CIE diagram specifies a theoretical gamut containing all the colors sensed by the human eye, with less saturated colors inside and monochromatic color on the edge, which is also called spectral locus. The CIE diagram shows that each point is close to the center of the spectra, which indicate that the structural colors produced by the current APS film are less saturated. However, the APS film still shows vivid structural color under ambient light, which can be distinguished well by the naked eyes. To test whether our samples do show angle-independent structural color, the reflection spectra of the green SiO₂@Fe₃O₄ PC films at various angles were measured. The reflection spectra were measured from 0 to 80° by fixing the source and the sample and rotating the detector. Figure 7f shows that the wavelength values for the reflection spectra of the green sample were identically angle-independent. Figure 7e is a plot of wavelength values versus the corresponding detection angles. The spectral shifts of the reflection spectra that were taken at several different angles were less than 5 nm, clearly indicating that the structural colors were noniridescent. In general, the short-range ordered structure of the PC film would result in white color to the naked eyes because of their incoherent multiple light scattering. In our presented work, because the black Fe₃O₄ nanoparticles coated on the SiO₂ surfaces absorbed scattering light uniformly, the SiO₂@Fe₃O₄ PC films showed angle-independent structural color with enhanced color contrast. Furthermore, the reflectance spectra in Figure 7e are more broadened than those for the long-range ordered PCs, which may be due to the higher scattering intensity of amorphous structures.

Because of the robust synthetic method and the quick assembly of SiO₂@Fe₃O₄ colloids into APSs, the SiO₂@Fe₃O₄ colloids have various versatile applications for various substrates. such as color inks or printing pigments. Before printing the colorful patterns, we test the APSs assembled on various substrates to confirm whether our methods are applicable in practical application. The APSs still show bright color on the different substrates (Figure S4), including glass, ceramics, resins, plastics, wood and paper. Based on the good adhesion of APSs on various substrates, we printed green PCs on a paper in Chinese using SiO₂@Fe₃O₄ colloids with SiO₂ core size of 230 nm as the color inks (Figure 8a). For the similar reason, a colorful rabbit with blue, green, yellow, and red color was also printed by controlling the particle size of SiO₂@Fe₃O₄ colloids (Figure 8d). These prints showed bright color visibility and angle-independent color for the naked eyes (Figure 8a–8f).

Besides printing APS patterns on 2D substrates, our strategy is also successful in uniformly coating APSs on 3D objects of highly curved and rough surfaces. For example, all the surfaces of the dragon toy were coated with green APSs uniformly through one-step brushing process (Figure 8g). Meanwhile, the APS coatings keep the original morphology and details (Figure 8h,i) of the coated substrates, which is so called “conformal”. These results strongly demonstrate that our strategy is versatile in printing or coating on various substrates with flat/bumpy surfaces.
CONCLUSIONS

In summary, monodispersed SiO$_2$@Fe$_3$O$_4$ core–shell nanostructures with tailored sizes were synthesized for fabrication of APSs with noniridescent color by the fast EISA method. SiO$_2$@Fe$_3$O$_4$ colloids can be obtained through decomposition of Fe(acac)$_3$ on the silica surfaces, and their sizes were controlled by tuning the SiO$_2$ core size. Through the EISA process, SiO$_2$@Fe$_3$O$_4$ APSs with short-range ordered structures were created because of the scattering light absorbing ability of Fe$_3$O$_4$ nanoparticles and the limited repulsion interactions between SiO$_2$@Fe$_3$O$_4$ colloids. The APSs show angle-independent property with high color contrast, and their maximum wavelength value can be tailored by tuning the SiO$_2$@Fe$_3$O$_4$ core size. The presented assembling strategy for APSs exhibits superior advantages such as multicolor inks for printing and coatings on various substrates, including 2D/3D substrates with different curvatures and roughness.

ASSOCIATED CONTENT

S Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02987.

XRD pattern of SiO$_2$@Fe$_3$O$_4$ colloids; TEM images of SiO$_2$@Fe$_3$O$_4$ colloids; SEM images of SiO$_2$ PC film; APSs assembled on various substrates (PDF).

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