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Bright structural color films independent of background prepared by the dip-coating of biomimetic melanin-like particles having polydopamine shell layers

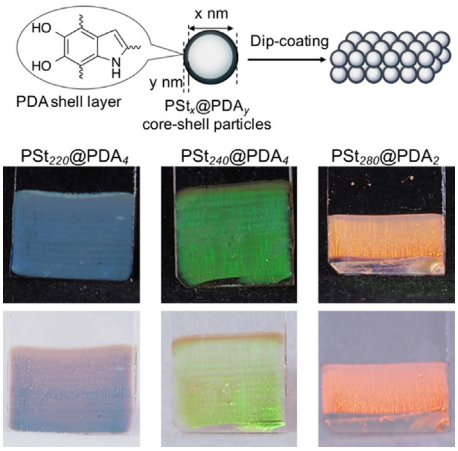
Michinari Kohri*, Shigeaki Yamazaki, Ayaka Kawamura, Tatsuo Taniguchi, Keiki Kishikawa

Division of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

HIGHLIGHTS

- Structural color films were prepared from polydopamine-containing particles by a dip-coating method.
- Film thickness and arrangement of particles in films were controlled by the particle concentration and dipping speed.
- Films obtained showed bright structural colors independent of background color.

GRAPHICAL ABSTRACT



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ABSTRACT

Some beautiful structural colorations found in nature are produced by microstructures of melanin. Polydopamine (PDA), produced by the self-oxidative polymerization of dopamine, is known as a mimetic material of melanin. Previous experiments by our group have shown that PDA-based structural color materials produced bright structural colors upon enhancing the color saturation through the absorption of light scattering. Herein, we describe the preparation of structural color films by a dip-coating of biomimetic melanin-like particles with PDA shell layers. Various parameters of the dip-coating method influencing the structural coloration were investigated in detail. Experimental results revealed that the obtained films exhibited bright and angle-dependent structural colors independent of a background color, i.e., black or white background. These findings provide new insights for the development of dye-free ink technologies.

1. Introduction

In recent years, structural color materials produced by assemblies of colloidal particles have been of interest in many fields, including photonic materials, dye-free inks, reflection-type

* Corresponding author.
E-mail address: kohri@faculty.chiba-u.jp (M. Kohri).

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devices, and anti-counterfeit detection systems [1–3]. Usually, monodisperse silica particles or polymer particles have been used as a component of structural color materials. These particles, however, exhibit faint structural colors because of light scattering, producing milky white colors. To overcome this drawback, several methods have been proposed to prevent light scattering. One approach to produce bright structural colors is an addition of black materials that absorb the white color produced by light scattering. For instance, carbon blacks [4–6] and cuttlefish inks [7] have been used as black materials. Another method is the use of a black background. Bright structural colors are usually obtained on black backgrounds because structural colors are affected by the light scattered from the colloidal particles and the transmitted light, which diffuse through the sample and are then reflected by the background [8]. However, the use of other background colors such as white will be required for some practical applications, e.g., the development of structural color inks. Thus, it remains a challenge to develop an effective strategy to produce bright structural colors independent of the background.

Polydopamine (PDA), which is inspired by mussel adhesive proteins, is prepared by the self-oxidative polymerization of dopamine (2-(3,4-dihydroxyphenyl)ethylamine) under basic conditions on a variety of materials surface [9]. While a number of studies have focused on the use of PDA layers as a universal surface modifier [10–16], there have been few reports on the use of PDA as a mimetic material of melanin. In nature, melanin, which is produced from 3,4-dihydroxyphenylalanine (DOPA), is known to be one of the components of nanostructural elements that produce beautiful structural colors [17–19]. We previously reported the preparation of structural color materials by a self-assembly of relatively monodisperse PDA particles that mimic melanin granules [20,21]. We have also demonstrated the fabrication of high-visibility structural color materials using core-shell type particles having PDA shell layers [22]. By selecting the diameters of the core particles and the PDA shell thicknesses, we were able to produce a full range of structural colors [22]. Furthermore, it has been proposed that structural colors can be produced by constructing hierarchically structured materials composed of PDA thin films and amorphous PDA particles [23,24]. Another study reported the construction of bright structural color films from PDA particle assemblies, with the colors controlled by the thickness of the assembled PDA particles [25,26]. PDA-based particles will act both as components of structural color materials and as scattering absorbers, creating bright structural colors.

In this paper, we demonstrated the fabrication of bright structural color films from PDA-coated biomimetic melanin-like particles having light absorption capability. Monodisperse polystyrene (PSt) particles were used as a core particle. Structural color films composed of PSt@PDA core-shell particles were fabricated onto a glass substrate using the dip-coating method, and the film thickness and arrangement of particles in the films were controlled by the particle concentration and lifting speed. The effect of the background colors on the structural coloration was also investigated. The findings from this study will provide a step toward the development of dye-free coloration strategies for inks or other practical applications.

2. Experimental

2.1. Materials

Dopamine hydrochloride (DA) was obtained from Sigma-Aldrich. Tris(hydroxymethyl)aminomethane (Tris) was obtained from Kanto Chemical. Deionized water with a resistance of 18.2 MΩ was obtained using a Millipore Simplicity UV system. Highly monodisperse PSt@PDA core-shell particles with different diameters were prepared according to a method reported in the literature [22]. All other chemicals and solvents were of reagent grade and used as received.

2.2. Measurements

The hydrodynamic diameter (D_h) of the particles were measured by dynamic light scattering (DLS) (ELSZ; Otsuka Electronics). Scanning electron microscopy (SEM) micrographs of the samples were obtained using a scanning electron microscope (JSM-6510A; JEOL). Reflection spectroscopy was performed using a spectrophotometer (V-650; JASCO) equipped with a reflection spectroscopy unit (ARSV-732; JASCO) and a microscopic spectrophotometer (MSV-370; JASCO). Photographs of the samples were taken with a digital camera (OM-D; Olympus). The structural color films were prepared using a dip-coater (ND-0407-S4; SDI)

2.3. Preparation of structural color films

After immersion in the prepared water dispersions of PSt@PDA core-shell particles (solid contents: 0.3, 0.5, 1.0, and 3.0 wt%), the glass substrate, treated with a plasma processing technique, was withdrawn and dip-coated at various lifting speeds (100, 10, 1.0, and 0.1 μm/s).

3. Results and discussion

PSt@PDA core-shell particles were chosen as the component of the structural color films. PSt core particles with different diameters (220, 240, and 280 nm) were prepared by emulsifier-free emulsion polymerization. According to our previous paper, the PDA shell thicknesses were set at ca. 2–4 nm to produce high-visibility structural colors [22]. The synthesized products are designated $PSt_x@PDA_y$ core-shell particles (x: diameter of PSt core particles, y: thickness of PDA shell layer). As shown in Fig. 1a, the obtained core PSt particles (PSt_{220}, PSt_{240}, and PSt_{280}) and core-shell particles ($PSt_{220}@PDA_4$, $PSt_{240}@PDA_4$, and $PSt_{280}@PDA_2$) were highly monodisperse and display smooth spherical shapes. To investigate the structural colors from the obtained particles, pellet samples were fabricated by pouring core or core-shell particle suspensions (solid contents: 10 wt%) onto a silicone rubber plate and allowing them to dry at room temperature for 12 h. While the pellets from the PSt core particles showed milky-white colors, high-visibility structural color pellets were obtained from PSt@PDA core-shell particle dispersion (Fig. 1b). The PDA shell layers effectively absorbed the light scattering, enhancing the structural coloration. By tuning the core-shell particle diameters, the colors of the pellets changed from blue to green to red. The Fig. 1b insets show the maximum values of the reflection spectra (λ_{max}) of three pellets obtained from $PSt_x@PDA_y$ core-shell particles together with those obtained from bare PSt particles. The reflection peaks underwent a red shift upon increasing the particle diameter, in agreement with a previously reported result [22].

Structural color films were prepared using the dip-coating method. First, the effect of lifting speeds on the formation of films was investigated. The glass substrate, treated with a plasma processing technique, was dipped into a water solution containing $PSt_{280}@PDA_2$ core-shell particles (solid content: 3.0 wt%) and withdrawn at a constant speed between 100 and 0.1 μm/s. A thin layer of the solution was pulled out from the reservoir, and evaporation transformed it into a dry solid particle film. At high lifting speeds (100, 10, and 1.0 μm/s), although partially structural colors were observed, clear films were not obtained (Fig. 2a). In contrast, uniform and bright structural color films were obtained at a lifting speed of 0.1 μm/s (Fig. 2a). To investigate the arrangement

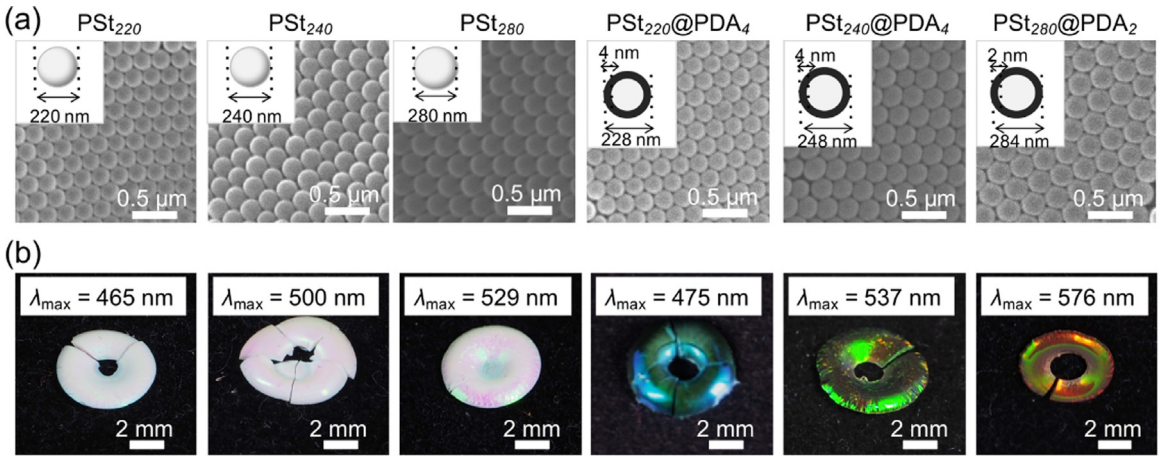

Fig. 1. (a) SEM images of core PSt particles (PSt_{220}, PSt_{240}, and PSt_{280}) and core-shell particles (PSt_{220}@PDA_4, PSt_{240}@PDA_4, and PSt_{280}@PDA_2). (b) Structural color pellets from core PSt and core-shell particles shown in Fig. 1a. Insets show the λ_{max} of reflection peaks.

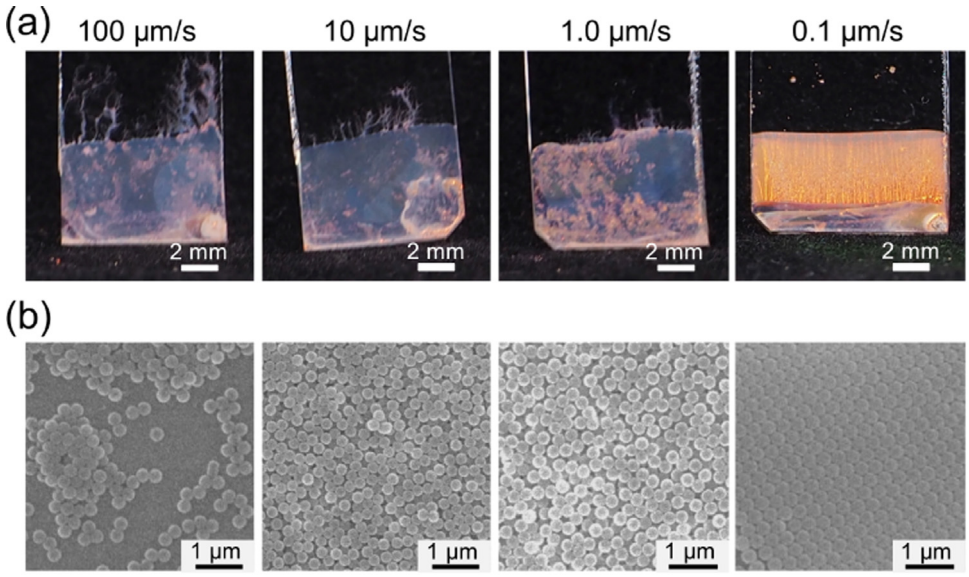

Fig. 2. (a) Photographs and (b) SEM images of structural color films from PSt_{280}@PDA_2 core-shell particles (solid content of dispersion: 3.0 wt%) with different lifting speeds.

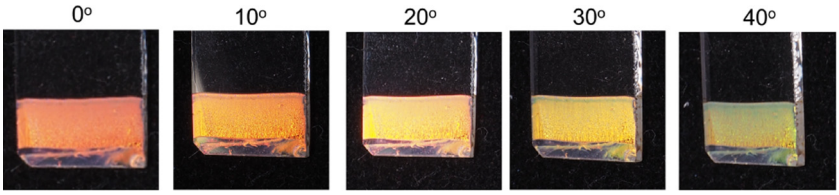

Fig. 3. Digital camera images of structural color films from PSt_{280}@PDA_2 core-shell particles (solid content of dispersion: 3.0 wt%) at various angles.

of the core-shell particles, SEM measurements were performed on the obtained films. As shown in Fig. 2b, the particle density gradually increased with decreasing lifting speed. At 0.1 μm/s, closed-packed structures were observed, indicating the formation of a colloidal crystal structure. Usually, angle-dependent structural colors are obtained from colloidal crystal structures. Thus, we examined the film obtained (solid content: 3.0 wt%) at various angles. The digital camera images in Fig. 3 clearly showed structural color changes, indicating that the structural colors from films were angle-dependent.

Next, the effect of solid contents on the film formation was investigated. Films of assembled PSt_{240}@PDA_4 core-shell particles were prepared at different suspension solid contents, ranging from 0.3 to 3.0 wt% (Fig. 4a). As shown in Fig. 4b, under all experimental conditions, the assembled core-shell particles showed colloidal crystal structures. Fig. 4c shows the cross-section of the films obtained. Close-packed structures were also observed in the films, indicating their uniformity. The film thickness and number of particles were measured by SEM images. The average film thickness, based on measurements at 10 different places on the film, gradually increased from 1.3 to 12.2 μm with the increasing solid contents (Fig. 4d). The number of particles also increased with the solid contents. These results clearly indicated that the film thickness as well as the number of particles were easily controlled by the concen-

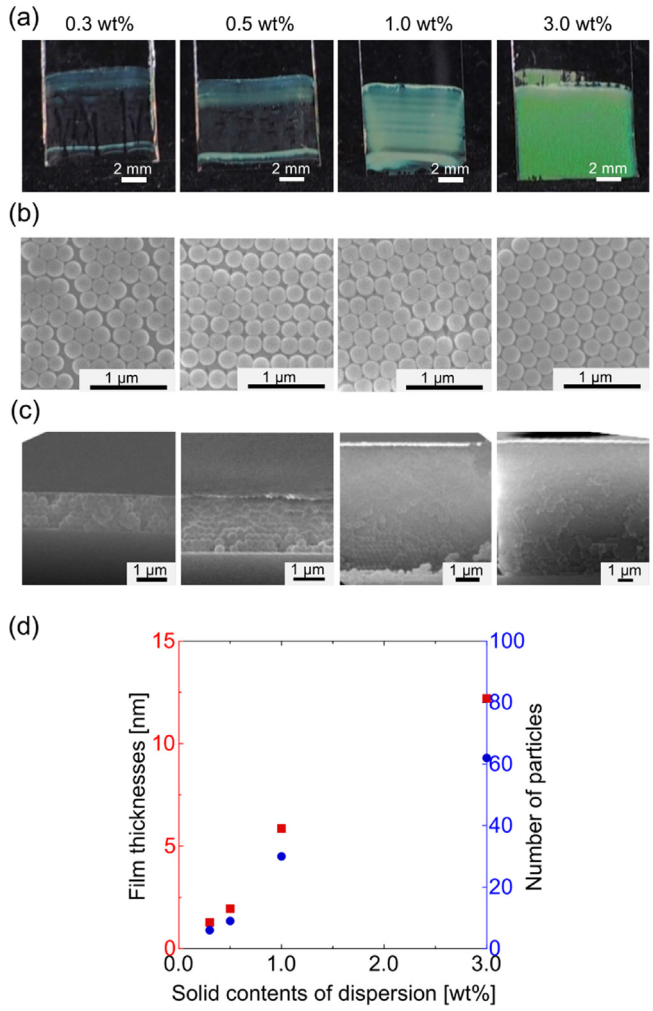

Fig. 4. (a) Photographs, (b) SEM images, and (c) cross-section SEM images of structural color films from PSt_{240}@PDA_4 core-shell particles (lifting speed: 0.1 μm/s) with different solid contents. (d) Average film thickness and number of particles.

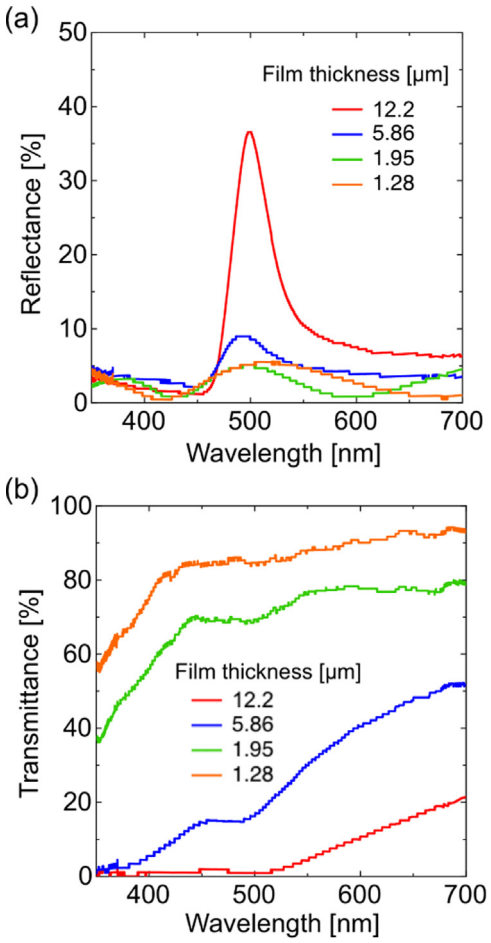

Fig. 5. (a) Reflection and (b) transmission spectra of structural color films shown in Fig. 4a.

tration of the core-shell particles in the dispersion. The reflectance spectrum for each structural color film was measured by a reflection spectrophotometer (Fig. 5a). The spectrum of the green film that was prepared from PSt_{240}@PDA_4 core-shell particles had a clear reflection peak at approximately 500 nm. The reflection values gradually increased with increasing particle concentrations (=film thicknesses), indicating the decrease in the transmitted light. Fig. 5b shows the transmittance spectra of structural color films with different thicknesses. As expected, films having thin thicknesses (<2 μm) had a high transmittance value. Further increasing the film thicknesses caused a decrease in the transmittance value, suggesting that PDA-coated core-shell particles effectively absorbed both transmitted light and multiple scattering light.

Finally, the effect of background colors on the structural coloration was investigated. As mentioned before, a decrease in the scattering light is required to obtain clear structural colors, and many researchers have prepared structural color materials using the black background. Thus, we first investigated the structural coloration using the black background. Although the colors became clouded, weakly blue, green, and red structural colored films were obtained from PSt_{220}, PSt_{240}, and PSt_{280} core particles (Fig. 6a). In contrast, high-visibility structural color films were obtained from PSt@PDA core-shell particles on the black background, indicating the usability of the PDA-coated particles (Fig. 6b). Fig. 7 shows the reflection spectra of the films on the black background. The reflection spectra from films composed of core PSt particles showed a high reflectance due to light scattering over the entire area (Fig. 7 dotted lines). On the other hand, the reflectance due to light scattering was effectively decreased by the PDA coating (Fig. 7 solid lines). Although the highest reflectance of the films from the core-shell particles was decreased compared with that of the films from the core particles, saturated structural colors were observed by the naked eye. The λ_{max} values of the reflection spectra of films from PSt_{220}@PDA_4, PSt_{240}@PDA_4, and PSt_{280}@PDA_2 were 466, 500, and 565 nm, respectively. In colloidal crystal structures, the peak value can be estimated from the Bragg-Snell's law (1), where m is the order of diffraction, λ is the wavelength of light, n is the refractive index of the particles, d is the center-to-center distance between the nearest particles, and θ is the angle between the incident light and the diffraction crystal planes [27].

$$m\lambda = \sqrt{\frac{8}{3}d^2\left(n^2 - \sin^2\theta\right)} \quad (1)$$

The reflection wavelength was calculated using equation (1), assuming that the Bragg-Snell's law holds ($m = 1$, $\theta = 90$, and d is the diameter of the PSt_x@PDA_y core-shell particles). Our recent study showed that the refractive index of PSt_x@PDA_y core-shell particles with thin shell layers (>4.5 nm) is nearly the same as the refractive index of the core particles [22]. Therefore, the refractive index (n) of the PSt_x@PDA_y core-shell particles were set at 1.59. The reflection wavelengths of the structural color films obtained by PSt_{220}@PDA_4, PSt_{240}@PDA_4, and PSt_{280}@PDA_2 core-shell particles were calculated to be ca. 464 nm, 505 nm, and 578 nm, which were

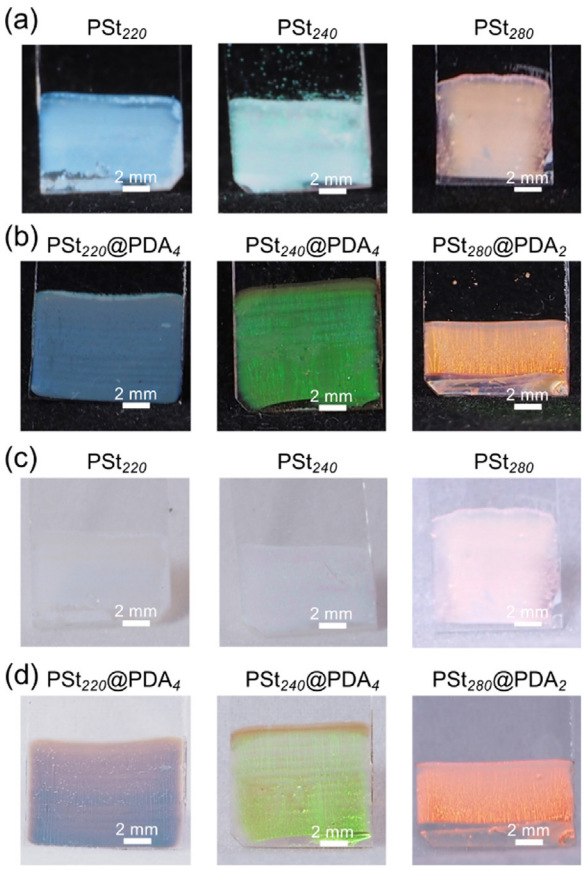

Fig. 6. Photographs of structural color films from (a) core PSt particles (PSt_{220}, PSt_{240}, and PSt_{280}) and (b) core-shell particles (PSt_{220}@PDA_4, PSt_{240}@PDA_4, and PSt_{280}@PDA_2) on a black background. Photographs of films from (c) core PSt particles (PSt_{220}, PSt_{240}, and PSt_{280}) and (d) core-shell particles (PSt_{220}@PDA_4, PSt_{240}@PDA_4, and PSt_{280}@PDA_2) on a white background.

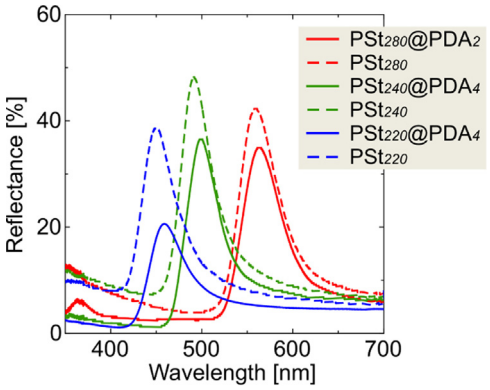

Fig. 7. Reflection spectra of films shown in Fig. 6a,b.

in relatively agreement with the experimental values (*vide supra*). On the white background, pale white films were obtained due to the light scattering from the core particles (Fig. 6c). In contrast, bright structural color films were obtained from core-shell particles on the white background, again indicating the usability of the PDA shell layers that effectively absorb the scattering light (Fig. 6d). These characteristics will be beneficial for practical applications.

4. Conclusion

In summary, we developed a method for the fabrication of bright structural color films from biomimetic core-shell particles with PDA shell layers. The lifting speeds and particle concentrations strongly affected the formation of uniform films containing close-packed particles. The films obtained showed bright structural colors independent of the background due to the PDA layers that act as scattering light absorbers. The results presented here are a promising step in the development of structural color-based ink materials with high visibility. Topics for future studies include the development of applications of this methodology using substrates other than glass, and the results of these investigations will be described in future reports.

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