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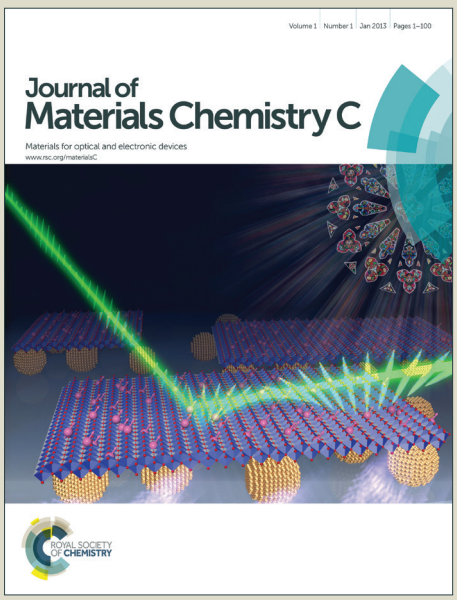

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Biomimetic non-iridescent structural color materials from polydopamine black particles that mimic melanin granules†

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Michinari Kohri,* Yuri Nannichi, Tatsuo Taniguchi and Keiki Kishikawa

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A novel approach for creating non-iridescent bright structural color materials from polydopamine (PDA) black particles was presented. Two biomimetic features, melanin granules and the amorphous structures found in nature, were incorporated into these materials consisting of PDA black particles to develop bright and non-iridescent structural color without using any additives.

Nature produces beautiful structural colors, which are thought to depend on the size and arrangement of nanostructural elements.[1,2] For example, the iridescent structural colors of male peacock feathers are created by arrays of rod-like black melanin granules that are produced by several enzymatic reactions of 3,4-dihydroxyphenylalanine (DOPA).[3] Small changes in the size of these elements can cause substantial variations in the reflected color.[4] Recent studies have also shown that blue bird feathers contain a basal layer of melanin granules that prevents light scattering and is necessary to produce bright structural colors.[5] These reports show that black melanin granules can serve as components of a structural color material and as scattering absorbers. Nature also produces non-iridescent colors from quasi-amorphous structures. Well-known examples of non-iridescent colors include colors produced by *Cotinga maymama* bird feathers,[4] *Cotinga cotinga* bird feathers,[6] mandrill,[7] odonate,[8] and longhorn beetle.[9] Living creatures acquired the ability to produce a variety of non-iridescent colors through nanostructures with short-range order: amorphous structures.[10]

In recent years, there has been enhanced interest in structural color materials based on the self-assembly of colloidal particles, which have unique optical and material properties. Colloidal crystals that are formed via the self-assembly of close-packed monodisperse particles are a promising class of such materials.[11,12] Considerable attention has been focused on preparing structural color materials with biomimetic amorphous structures to produce non-iridescent structural colors.[10,13] For instance, Dufresne et al.[14] and Takeoka et al.[15] prepared amorphous colloidal arrays by mixing two different sizes of particles. Takeoka et al. developed a simple spraying procedure for uniform fine submicrometer-sized spherical silica particles.[16] Kang et al. have reported electrically tunable full-color photonic display pixels that exhibit angle-independent photonic colors.[17] However, most of the aforementioned research has focused on monodisperse silica particles or polymer particles, such as polystyrene particles. These particles exhibit faint structural colors because of light scattering, which produces milky white colors. To overcome these problems, several researchers have investigated carbon black doping because carbon black absorbs the white colors light scattering.[14,16,18] However, these methods require two materials: colloidal particles and carbon black. A method for creating non-iridescent bright structural colors using a single component has not yet been reported.

Herein, we describe a novel and simple method to create non-iridescent bright structural color using polydopamine (PDA)[19] black particles that mimic black melanin granules (Fig. 1). Relatively monodisperse PDA black particles were prepared by dopamine (DA) oxidative polymerization in a water/methanol (4/1) solution. The structural colors and their textures were controlled by changing the particle diameters, the latex concentrations, and the arrangement of the particles. This is the first paper to prepare amorphous colloidal structures using solely black particles, which act as components of the structural color material and scattering absorbers. This novel technique of using

PDA black particles is a promising tool to pioneer a new generation of colloidal particles and can produce non-iridescent bright structural color without the use of additives.

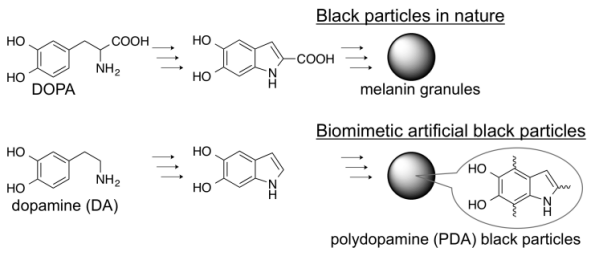

Fig. 1. Melanin granules and polydopamine (PDA) black particles.

PDA is typically prepared by polymerizing DA in water, and most studies in which a PDA layer has been used have involved modifying the material's surface.[20–22] We have also demonstrated the preparation of a colorless PDA layer containing functional groups to produce functional polymeric materials.[23,24] There have been a few reports on the preparation of PDA particles; however, in these studies, the polymerization rate of the DA in water was too fast to control the particle size and size distribution, resulting in PDA particles with a wide size distribution.[25,26] We prepared PDA particles in a water/methanol solution because previous studies in our laboratory have demonstrated that DA polymerization can be controlled in the presence of methanol.[27] A typical procedure consisted of adding tris(hydroxymethyl)aminomethane to a water/methanol (4/1) solution of DA and stirring the resulting mixture 20 h at 30 °C. The mixture was then purified by centrifugation, producing PDA black particles. The DA concentration significantly affected the PDA particle size (Fig. 2a (solid squares)). Increasing the DA concentration from 0.9 to 2.2 mg/mL increased the particle sizes, as measured by dynamic light scattering (DLS), from approximately 92 to 441 nm. Further increasing the DA concentration (to 3.0 mg/mL) induced aggregation of the obtained PDA particles. Scanning electron microscope (SEM) micrographs showed that relatively monodisperse particles with smooth spherical surfaces were obtained, which is consistent with the results obtained using DLS (Fig. 2b). The SEM images also show the diameter distribution of the particle diameters in terms of the coefficient of variation (CV), which ranged from approximately 4.4 to 7.8% (Fig. 2a (open squares), Fig. S1†). Fig. 2c shows images of the PDA black particle dispersion (0.5 wt% in water). The obtained latex particles were very stable in water, and no marked change was observed after 3 months of storage. Although the suspension of PDA_{92} and PDA_{441} latex particles exhibited the black color that is the typical absorption color of PDA, the $PDA_{130\text{-}256}$ latex particles exhibited structural colors with a black tone (Fig. 2c). Recently, Deng et al.[28] and Lu et al.[29] prepared monodisperse PDA particles in a mixture of water and ethanol in parallel with our research study. However, these authors did not identify the potential for creating structural colors using PDA particles.

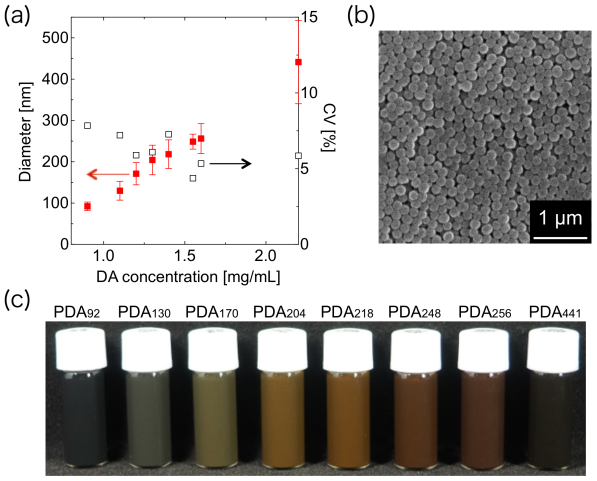

Fig. 2 (a) Diameters and coefficient of variation (CV) of PDA black particles as a function of DA concentration: particle diameters were measured using DLS; in each sample, the sizes of 100 particles were measured using SEM to calculate the CV of the particles. (b) Typical SEM image of PDA black particles (PDA_{204}). (c) Photographs of a dispersed solution of PDA black particles (0.5 wt% in water).

To obtain clear structural colors, $PDA_{130\text{-}256}$ latex particles (10 wt% in water) in quartz cells were centrifuged at approximately 1,500 rpm for 12 h. The upper row of Fig. 3a shows bright and deep blue, blue, green, yellowish green, orange, and red structural colors were obtained after centrifugation of samples using $PDA_{130\text{-}256}$ latex particles (approximately 50 wt% in water). Fig. 3b shows the normalized reflection spectra of the materials obtained using $PDA_{130\text{-}256}$ particles. The spectrum of the deep blue material that was prepared using PDA_{130} particles had a clear reflection peak at 339 nm. The reflection peaks increased with the particle size, in accordance with previously reported experimental results.[16,18] Blue (λ_{max} = 439 nm), green (λ_{max} = 522 nm), yellowish green (λ_{max} = 559 nm), orange (λ_{max} = 648 nm), and red (λ_{max} = 671 nm) colors were obtained using $PDA_{170\text{-}256}$ particles, clearly indicating that the structural colors could be easily controlled by altering the size of the PDA black particles (Fig. 3c). As shown in Fig. S2a†, the highest reflectance was approximately 9% since black particles uniformly absorb light scattering, which is agreement with the carbon black doping reported in Takeoka et al.[16] While reflectance was relatively low, saturated structural colors were observed in naked eye.[16] We checked the differences in different parts of the quartz cells. Five points were randomly selected, and reflection spectra were measured. As seen in Fig. S2b†, the intensities of reflectance spectra and λ_{max} were not changed, clearly indicating the uniformity of the samples. Note that the structural color did not depend on the angle (see Fig. 3a, lower row). The reflection spectra were measured at a different angle by fixing the source and the

sample and rotating the detector. Fig. S2c† shows that the λ_{max} values for the reflection spectra of the samples were virtually angle-independent. Fig. 3d is a plot of λ_{max} versus the corresponding detection angles. The spectral shifts of the reflection spectra that were taken at several different angles for each sample were less than 10 nm, clearly indicating that the structural colors were non-iridescent.

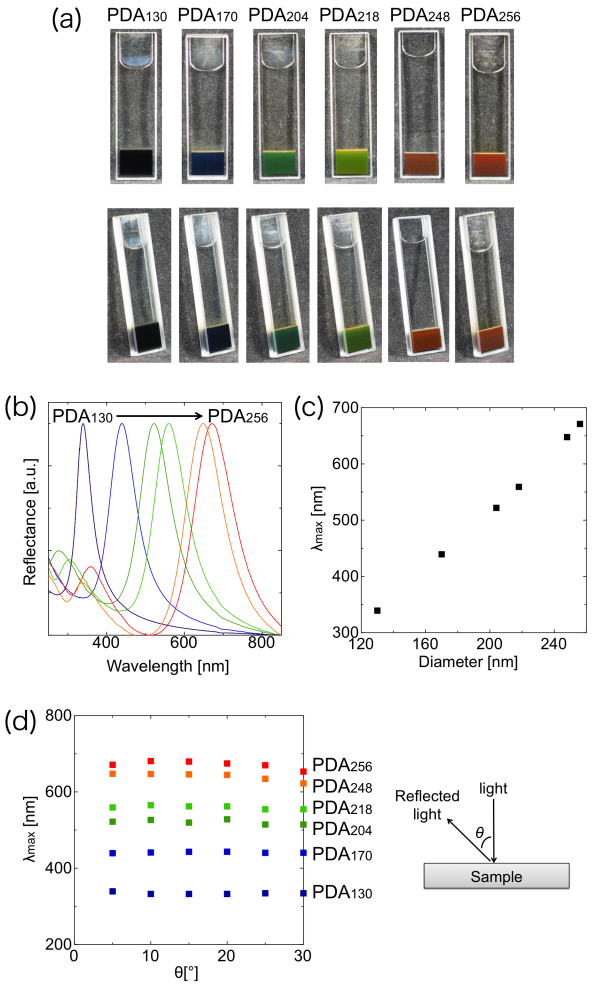

Fig. 3 (a) Digital camera images of concentrated dispersions of PDA black particle (approximately 50 wt% in water). (b) Reflection spectra of samples shown in (a). (c) λ_{max} for reflection spectra in (b) versus diameters of PDA black particles. (d) Plots of λ_{max} for reflection spectra of the samples as a function of incident angle (θ).

The $PDA_{170,204,256}$ powders also showed bright structural blue, green, and red colors when viewed with the naked eye (Fig. 4a). To investigate the arrangement of the PDA black particles, we performed a 2D fast Fourier transform (FFT) of the SEM images of the $PDA_{170,204,256}$ powders to obtain their spatial information.[15] Fig. S3† shows that the spectra of the SEM images contained clusters of white pixels that were concentrated in symmetrical, circular patterns around the origin, indicating that the particles were amorphous.[10] This unique structure displayed a non-iridescent structural color because of wavelength-selective light scattering by the amorphous colloidal structure.[10,15] Usually, the CVs of colloid particles that are used for structural color materials are below 3%. The use of these highly monodisperse particles is advantageous for fabricating colloidal crystals but impedes the formation of amorphous colloidal structures. Thus, amorphous colloidal structures are usually prepared by mixing particles with two different sizes[14,15] or by rapid assembly of equally sized particles.[16] In the present method, however, the CVs of the PDA black particles obtained were approximately 4.4 to 7.8%, as previously mentioned (Fig. 2a). Relatively monodisperse PDA black particles were used to prevent the formation of colloidal crystals and create amorphous colloidal structures.

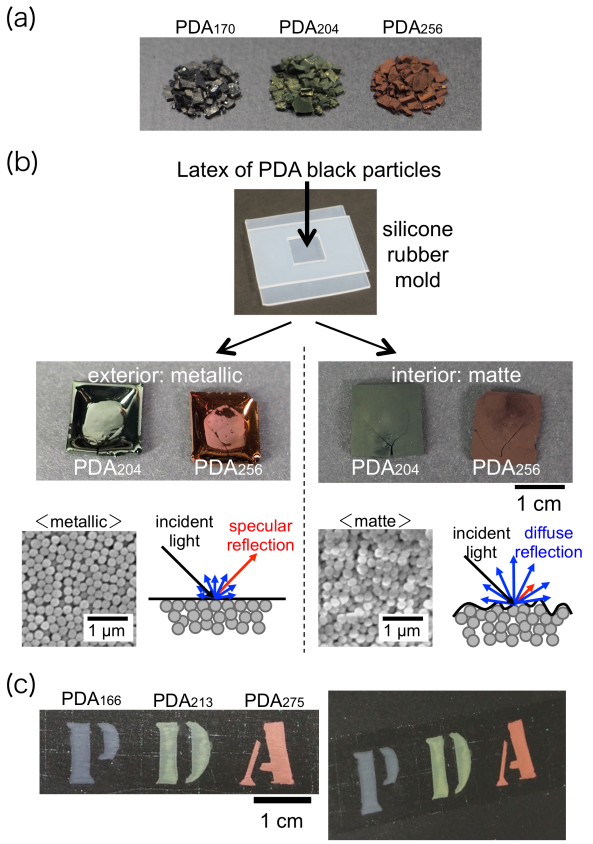

Fig. 4 (a) Photograph of $PDA_{170,204,256}$ powders. (b) Preparation of structural color plates using PDA black particles; plates were fabricated by pouring 10 wt% PDA suspensions into a silicone rubber mold and allowing the suspensions to dry at room temperature for 24 h. SEM images show structural color plates prepared using PDA_{256} black particles. (c) Photographs of structural color films from PDA black particles (0.5 wt% in water, 1 mL). Patterns 'P', 'D', and 'A' were fabricated from PDA_{166}, PDA_{213}, and PDA_{275} black particles, respectively.

Fig. 4b shows the structural color plates that were prepared using PDA_{204} and PDA_{256} black particles. Surprisingly, the texture of the structural color was different on the two sides of the plates. Although the exterior of the plates had a metallic

texture, the interior of the plates has a matte texture. This phenomenon was most likely caused by the arrangement of the particles on the outermost surface layer. Solvent (water) evaporation from the exterior of the plates caused the PDA particles to condense and pack together roughly, producing relatively flat surfaces that are shown in the SEM image in the left column of Fig. 4b. This process was controlled by thermocapillary forces that were driven by Marangoni convection.[30] Previous studies have shown that flat surfaces made of colloidal materials increase specular reflectance and produce a metallic texture.[31,32] In contrast, the rough surfaces on the interior of the plates were obtained (Fig. 4b, right column). While PDA black particles are easily adsorbed to the hydrophilic substrate such as glass plates, these are hardly adsorbed to silicone rubber, which has water-repellent (hydrophobic) surfaces. During the evaporation of water, PDA black particles were easily peeled off from silicone rubber surfaces and were roughly aggregated, giving rise to plates having rough surfaces. The surface roughness greatly decreased the specular reflectance and increased the diffuse reflection, producing a matte texture.[31,32] The aforementioned results indicate that the textures of the structural color materials were controlled by the balance between the specular and diffuse reflectance from the arrangement of PDA black particles. We measured reflection spectra for both sides of the plate. For an exterior side (metallic) of the plate composed of PDA_{256}, we observed a λ_{max} of 676 nm (Fig. S4a†). Relatively same λ_{max} value of 687 nm was observed for an interior side (matte) (Fig. S4b†). In both sides of the plate, angle-independent colors due to amorphous structures were obtained. The relationship between reflectance intensities and textures, however, remained unclear since reflectance intensities notably depended on the roughness and shape of plate surface.

Finally, structural color films from PDA black particles were fabricated using spray coating.[16,33,34] As seen in Fig. 4c, the films sprayed from PDA_{166}, PDA_{213}, and PDA_{275} black particles (0.5 wt% in water) showed bright blue, green, and red structural color, respectively. Obtained structural color films have also showed angle-independent colors. The PDA black particles were synthesized by a facile single-step synthesis, and the resulting suspensions were used to directly prepare amorphous colloidal structures, resulting in materials with non-iridescent bright structural color. The simplicity of this method facilitates the practical use of these particles.

In conclusion, inspired by the structural color found in nature, we have prepared non-iridescent bright structural color materials from PDA black particles for the first time. We combined two abilities found in nature to creative non-iridescent bright structural color materials: amorphous structures for non-iridescent structural colors, and nanostructural elements (melanin granules) for bright colors. PDA black particles, which act as components of the structural color material and scattering absorbers, were successfully synthesized in a water/methanol solution using a facile single-step synthesis. This procedure was conducted under mild conditions, and the particle size could be controlled via the DA monomer concentration. Relatively monodisperse PDA black particles were used to prevent the formation of colloidal crystals, and to create non-iridescent bright structural color materials, which have poor periodicity of colloidal crystal structures, i.e., amorphous structures. Since black particles absorb light scattering, a bright structural color was produced without using any additives, e.g., carbon black. This simple and novel process of using PDA black particles is useful for understanding biological systems and can be used in basic research on structural color materials and practical applications.

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Notes and references

Division of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. Tel.: +81 43 290 3393; Fax: +81 43 290 3393; E-mail: kohri@faculty.chiba-u.jp

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Table of Contents (TOC)

A novel approach for creating non-iridescent bright structural color materials from polydopamine (PDA) black particles that mimic melanin granules found in nature was presented.