Title	High Heat Resistance of the Structural Coloration of Colloidal Arrays with Inorganic Black Additives
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Relation	

High Heat-resistance of Structural Coloration of Colloidal Arrays with Inorganic Black Additives

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KEYWORDS: structural color, environmentally-friendly colorants, thermal stability, black metal oxides, electrophoretic deposition

ABSTRACT: Structurally colored materials consisting of arrays of submicrometer-sized particles have drawn great deal of attentions because of their advantages, including low-cost, low impact~~s~~ on the human health as well as the environment, and resistance to fading. However, their low thermal stability is considered a critical issue for their practical uses as colorants. Black colored substances that can absorb the white color are added to colloidal array-type structural colored materials to enhance their chromaticity. The poor thermal stability of commonly used black coloring additives, carbon black and Fe_3O_4 nanoparticles, is a main factor that reduces the heat resistance of structural coloration. Here, we demonstrate preparation of structurally colored materials with extraordinary high heat resistance of coloration, up to 900 °C. Several metal oxides, i.e., calcium manganese-based oxide, Cr-Fe-Co-Ni oxide, and lanthanum manganite are synthesized and employed as black additives for structurally colored coatings prepared by electrophoretic deposition of spherical silica particles. When calcium manganese-based oxide is used as a black additive, the coloration heat-resistance of the film is stable up to 700 °C. On the other hand, the films maintain vivid structural colors after exposure to 900- °C temperatures when Cr-Fe-Co-Ni oxide and lanthanum manganite are employed as black additives. On the basis of this finding, high heat resistance of structural colors requires both heat resistance of the black additives and non-reactivity with the components of the spherical particles used for colloidal arrays.

INTRODUCTION

Our world contains a variety of colors. Color has psychological and aesthetic importance in our daily life.[1,2] Organic dyes and inorganic pigments have been used for a wide range of applications such as inks, glasses, ceramics, plastics and others.[3] Inorganic pigments, which are superior in terms of high stabilities and resistance to climate conditions, have advantages over organic dyes because prolonged exposure to light causes color fading of organic dyes. However, there is growing concern that the toxic elements (Cr, Cd, Pb, and Se) contained in inorganic pigments critically affect human health as well as the environment.[4–7] Recently, the Institute for Health Metrics and Evaluation (IHME) estimated that in 2019, Pb exposure accounted for 0.90 million deaths and 21.7 million years lost of healthy life (disability-adjusted life years) world-wide owing to long-term health effects.[8] This situation has led to governmental authorities strictly limiting the use of inorganic pigments that involve toxic elements. Therefore, the development of alternative materials that are applicable as safe and environmentally-benign colorants is strongly desired, and efforts have been devoted to develop such alternatives.[9–11]

Structurally colored materials are expected as alternatives to conventional colorants, i.e., organic dyes and inorganic pigments, that can be fade-resistant and free of hazardous materials.[12–14] Structural color results from interactions between nanoscale structures and light, such as scattering, reflection, diffraction, and interference. Arrays of spherical particles with uniform sizes are typical materials that can exhibit structural color.[15–18] Colloidal arrays with both short- and long-range ordering (colloidal crystals) generate structural color with iridescence and an angle dependence.[15] On the other hand, colloidal arrays with only short-range ordering (colloidal amorphous arrays) are non-iridescent with angle-independent color,[16] which is used in state-of-the-art technology, such as anticounterfeiting labels.[19,20] Therefore, nanoscale design is a critical strategy to control structurally colored materials. The color contrast generated from colloidal amorphous arrays is usually very low because of strong incoherent light scattering across the entire visible wavelength range. To overcome this, black additives that absorb white light are essential to obtain brilliant structural colors.[21−30] Carbon black (CB) nanoparticles,[21−23] graphene,[24] polydopamine particles,[25] melanin,[26] cuttlefish inks[27] and Fe_3O_4 nanoparticles[28−30] are commonly used as black additives for structurally colored colloidal arrays. However, these additives have poor thermal stabilities, making it difficult to use structurally colored colloidal arrays in place of inorganic pigments. Carbon-based materials, such as CB and melanin, are oxidized at high temperatures in air and decompose into CO_2. There have been few reports on the heat-resistance of colloidal-array-type structurally colored materials using carbon-based black additives; only heat-resistances up to 350 °C and 450 °C have been reported.[31,32] Fe_3O_4 is oxidized to Fe_2O_3 and its color is converted from black to red in air at 300 °C.[33] The low heat-resistances of these black additives thus prevent a wide variety of applications for structurally colored materials, such as ceramic glazes.

In this study, various inorganic metal oxides were examined as black additives to improve the coloration heat resistance of structurally colored materials composed of arrays of monodispersed spherical silica (SiO_2) particles. Here, it should be required to accurately evaluate heat-induced changes in the structural coloration of colloidal arrays. In other words, it is important to eliminate changes in coloration due to changes in the particle arrangements that are unrelated to the presence or absence of the black additives. In the case of colloidal crystals, there is a possibility that the structural coloration may be affected by the disturbance of the particle arrangements during heating process. Therefore, colloidal amorphous arrays were employed for evaluation in this study, though their coloration saturation is low. To evaluate uniform colloidal amorphous arrays of SiO_2 particles, coating films prepared via electrophoretic deposition method (EPD)[17,22,30] were examined. Calcium manganese-based oxide (CCMO), Cr-Fe-Co-Ni oxide (CFCNO), and lanthanum manganite (LMO) were synthesized and investigated as metal-oxide black additives. Calcium manganese oxides have recently been investigated as near-infrared reflective black pigment, one of the environmentally benign black pigments.[34,35] CFCNO is typically used as a black pigment for pottery and porcelain,[36] and lanthanum manganite-based oxides are also known to have black color.[37] Though CCMO and LMO contain the rare earth elements, Ce and La, respectively, these elements are currently in an oversupply. This is because, the rare earth mining amount increased year by year to meet the increasing huge demand of minerals including Nd towards NdFeB magnets for developing the motor market of electric vehicles (EV), while Ce and La which have limited applications, are more abundant than Nd in the rare earth minerals.[38] Therefore, the use of Ce- and La-containing compounds as black additives is reasonable in terms of cost and environmental compatibility. CB and Fe_3O_4 were also used for comparison to evaluate chromaticity and heat-resistance of coloration of the coating films.

RESULTS AND DISCUSSION

First, we synthesized CCMO, CFCNO, and LMO and evaluated their blackness. Figure 1 displays photographs of the synthesized CCMO, CFCNO, and LMO. All the synthesized metal oxides were obtained as fine powders that could be judged to be sufficiently black in appearance. For a more quantitative consideration, the Commission International de l'Eclairage (CIE) 1976 $L^*a^*b^*Ch^\circ$ color parameters for the synthesized CCMO, CFCNO, and LMO were compared to those for the commercially available CB and Fe_3O_4 as summarized in Table 1. The a^* (the red-green axis) and *b** (the yellow-blue axis) parameters that express chromaticity coordinates were close to 0 for the synthesized oxides, and these values were sufficiently similar to those of CB and Fe_3O_4. The lightness (*L**) parameters of the synthesized oxides were slightly higher than that of CB and Fe_3O_4, but comparable to metal oxide black pigments reported in the literatures.[34,35,39] Consequently, we conclude that the synthesized CCMO, CFCNO, and LMO are desirable black powders used as additives for colloidal arrays for enhancement of their structural coloration by the reduction of strong incoherent light scattering.

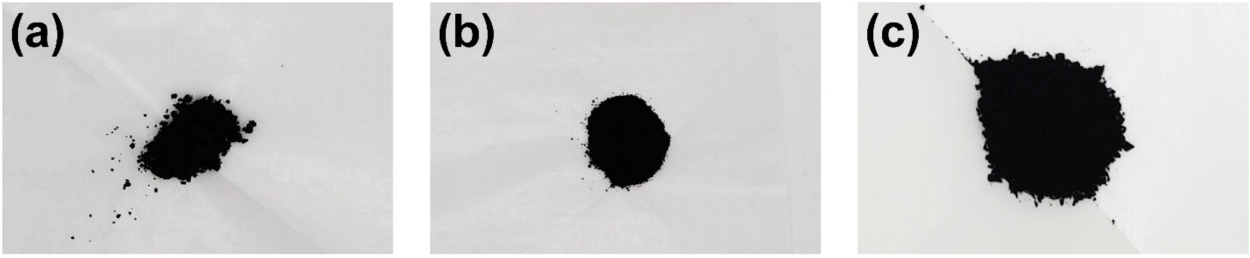

Figure 1. Photographs of the synthesized metal oxides: (a) CCMO, (b) CFCNO, and (c) LMO.

Table 1. CIE *L*a*b*Ch*° color coordinates of the synthesized metal oxides (CB, Fe_3O_4, CCMO, CFCNO and LMO)

Black additives	*L**	*a**	*b**	*C*	*h*°
CB	12.30	+1.16	+0.40	1.23	19.03
Fe_3O_4	10.31	+3.01	+3.05	4.29	45.38
CCMO	26.34	+0.38	−0.55	0.67	304.64
CFCNO	26.71	+2.52	+4.57	5.22	61.13
LMO	19.23	+0.66	+0.72	0.98	47.49

Next, coating films consisting of colloidal amorphous arrays of spherical SiO_2 particles were prepared by EPD with the addition of the synthesized black oxides (CCMO, CFCNO, and LMO), as well as CB and Fe_3O_4 for comparison. Initially, 200-nm-diameter SiO_2 particles were used for the EPD coating. Uniform coating films composed of SiO_2 particle were obtained via cathodic EPD using Mg^{2+} for 5 min under a 30-V applied voltage. All the coatings exhibited high robustness attributed to the co-deposition of the $Mg(OH)_2$ binder.[30] Figure 2 depicts photographs and scanning electron microscopy (SEM) images of coatings prepared from SiO_2 particles and various black additives. As shown in Figure 2a, films containing black additives exhibited a vivid blue color, which is a typical hue of structurally colored materials composed of 200-nm-diameter SiO_2 particles.[21] The CIE $L^*a^*b^*Ch^\circ$ color coordinates of each film were almost equal by optimizing the amounts of black additives (Table S1 in the Supporting Information). All the coatings were composed of colloidal amorphous arrays of SiO_2 as shown in Figure 2b-f, where the sizes of the black additives were ~50 nm (CB), ~100 nm (Fe_3O_4), 0.5−1 μm (CCMO), 500 nm (CFCNO), and 500 nm (LMO). Both CB and Fe_3O_4 were difficult to find in the SEM images because of their small sizes and small amounts.[17,22] All the films remained colloidal amorphous, regardless of the type and size of the black additives. As reported previously, amorphous arrangement was induced by cathodic EPD using Mg^{2+},[30] and comparable colored coatings containing various black additives had no fine structure differences.

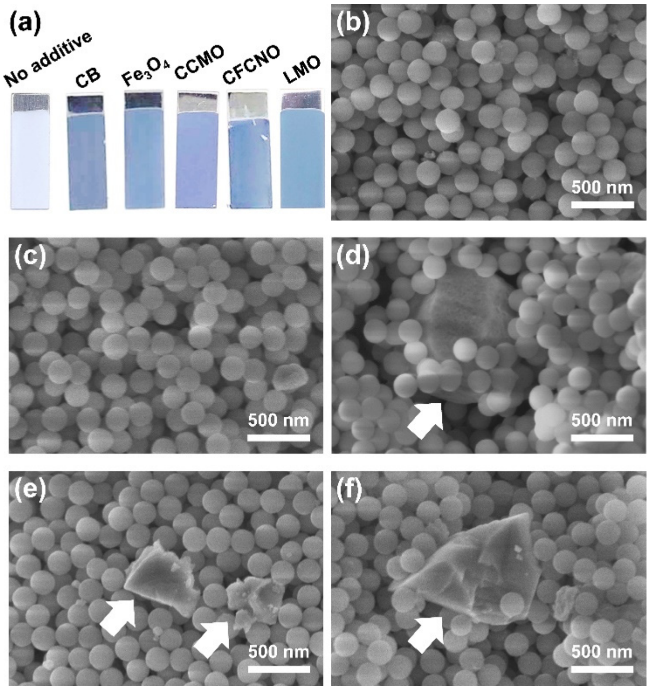

Figure 2. (a) Photographs of EPD films composed of 200-nm-diameter SiO_2 particles with various black additives. SEM images of EPD films containing: (b) CB, (c) Fe_3O_4, (d) CCMO, (e) CFCNO, and (f) LMO. The arrows in (d−f) indicate the black additives.

The films were heat-treated in air at 200−900 °C for 1 h to evaluate heat-dependent color changes. Figure 3 shows photographs and ultraviolet−visible (UV−vis) reflectance spectra of the films before and after heat-treatment at 400 °C, 700 °C, and 900 °C. More details are shown in Figure S1 in the Supporting Information. The CIE $L^*a^*b^*Ch^\circ$ color coordinates of the EPD films before and after the heat-treatments are summarized in Table S2 in the Supporting Information. UV−vis reflectance spectra for the EPD films before heat-treatment had peaks at 420 nm that corresponded to coherent light scattering from the colloidal amorphous array of 200-nm-diameter SiO_2 particles, and the blue coloration was observed regardless of the type of the black additives. For films containing CB, the color became whitish with increasing heat- treatment temperature, especially above 400 °C (Figure 3a). Reflectance values also increased for the entire wavelength range, indicating increased incoherent light scattering because of CB decomposition. The color of the films containing Fe_3O_4 became pink-purple above 300 °C (Figure 3b). The UV−vis reflectance spectra over the range 550−800 nm increased with temperature, which indicated oxidation of Fe_3O_4 (black) to Fe_2O_3 (red).[33] Hence, the films containing Fe_3O_4 after heat-treatment had a blended color derived from the colloidal arrays (blue) and the Fe_2O_3 (red). In contrast, the color of the film containing CCMO remained essentially unchanged up to 700 °C (Figure 3c). However, after heat-treatment at 900°C, the blue structural coloration faded slightly. For the films containing CFCNO and LMO, negligible color changes were confirmed after heating at 900 °C (Figure 3d,e). The color difference, ΔE, is one of the criteria of color change, where $\Delta E > 5$ indicates a different color.[40] According to this criterion, the maximum temperatures of the heat-resistant structural colorations were 300 °C for CB, 200 °C for Fe_3O_4, 700 °C for CCMO, and 900 °C for both CFCNO and LMO. These results thus revealed that the use of CCMO, CFCNO, and LMO metal oxides as black additives enabled high heat-resistant coloration for the structurally colored colloidal arrays.

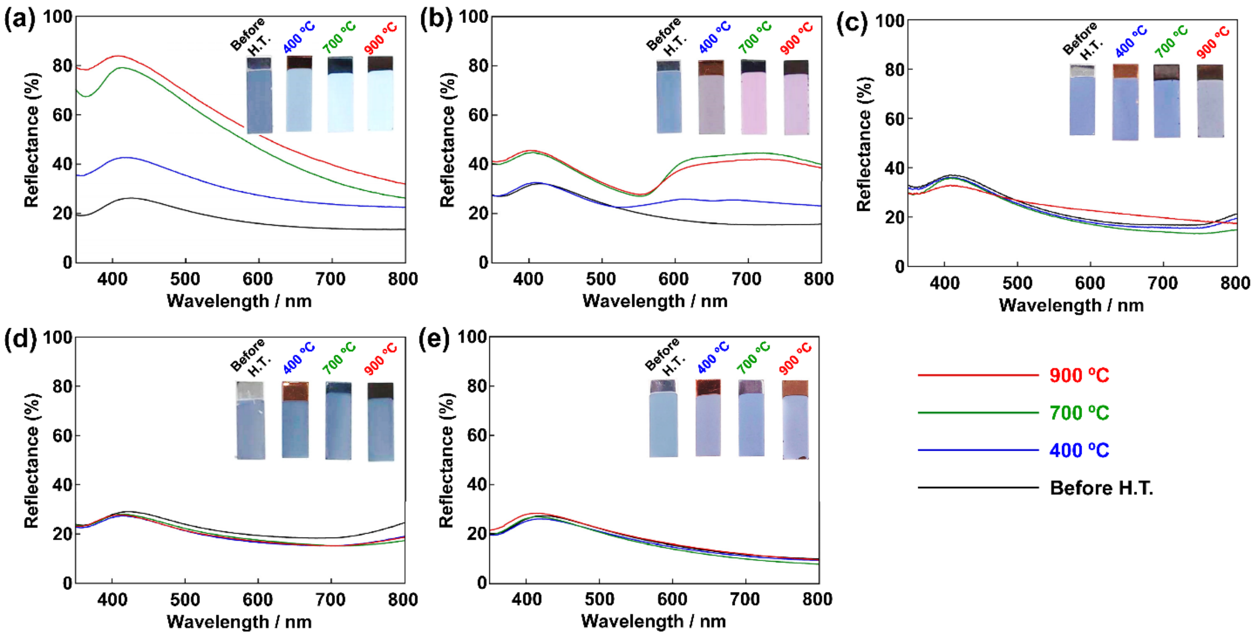

Figure 3. Photographs and UV−vis reflectance spectra of EPD films composed of 200-nm-diameter SiO_2 particles with black additives: (a) CB, (b) Fe_3O_4, (c) CCMO, (d) CFCNO, and (e) LMO, before and after heat-treatment at 400 °C, 700 °C, and 900 °C for 1 h.

Despite a thermal stability above 1200 °C for CCMO itself, the film containing CCMO additive had a lower coloration heat-resistance relative to those containing CFCNO and LMO. SEM observation and X-ray diffraction (XRD) measurements were performed to investigate the origin of these differences. Figure 4 shows SEM images the EPD films composed of 200-nm-diameter SiO_2 particles with black additives (CCMO, CFCNO, and LMO) after heat-treatment at 900 °C for 1 h. XRD patterns of the EPD films composed of 200-nm-diameter SiO_2 particles with various black additives before and after heat-treatment are displayed in Figure 5. For the film containing CCMO, deformations of SiO_2 particles were observed near the CCMO grains (Figure 4a). For SiO_2 particle arrays without any additives, deformation should not occur unless the temperature is above the SiO_2 melting or softening temperatures, which are well above

900 °C. As shown in the XRD pattern, generation of $CaSiO_3$ occurred when CCMO was used as the additive (Figure 5), which indicated that the SiO_2 reacted with Ca in CCMO.[41,42] In contrast, deformation of SiO_2 particles was not observed in the cases of CFCNO and LMO additives (Figure 4b,c). Although SiO_2 particles assumed to shrink considering blue shift of reflectance peak (λ_{max} shifted from 424 to 415 nm) as shown in Figure S2, this gave minor effect on the color of coating films (ΔE = 1.27 as given in Table S2). XRD patterns also indicated that reactions of SiO_2 with these additives to form any silicate compounds had not occurred (Figure 5). These results revealed that the chemical stabilities of the black additives, i.e., their reactivities with the components of the spherical particles, were important as well as the thermal stabilities for improvement of the high-temperature structural coloration stabilities of colloidal array. Further heat-treatment was performed at 1000 °C for 1 h. Resulting EPD films includes fused and deformed SiO_2 particles due to melting or softening (Figure S3). Conclusively, it was found that CFCNO and LMO can maintain their black color up to the limit of the temperature at which SiO_2 particles are thermally deformed, and high heat-resistant structurally colorant will be obtained using CFCNO and LMO as black additives.

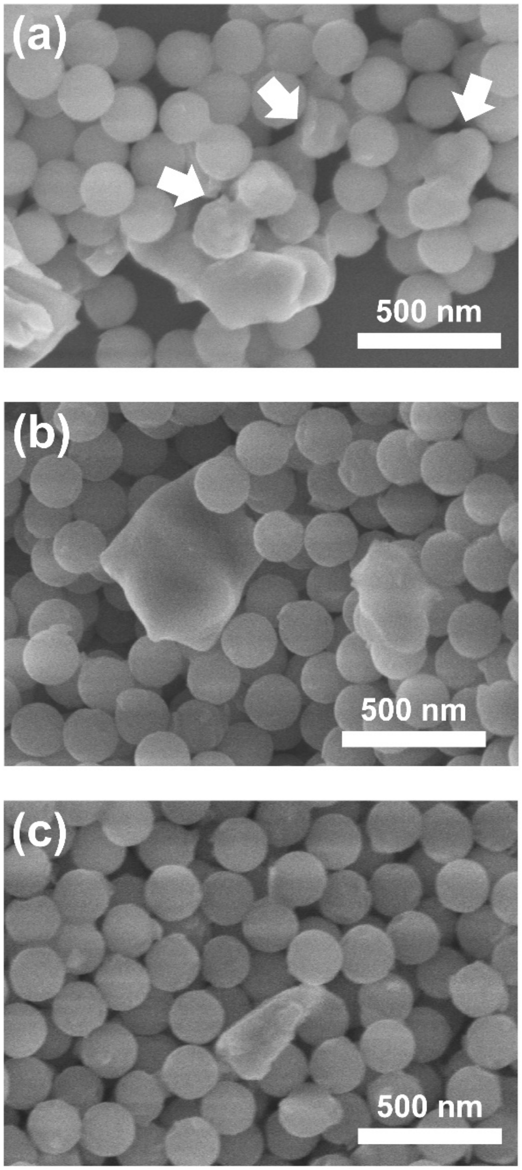

Figure 4. SEM images of EPD films composed of 200-nm-diameter SiO_2 particles with black additives: (a) CCMO, (b) CFCNO, and (c) LMO after heat-treatment at 900 °C for 1 h The arrows in (a) point to deformed spherical SiO_2 particles.

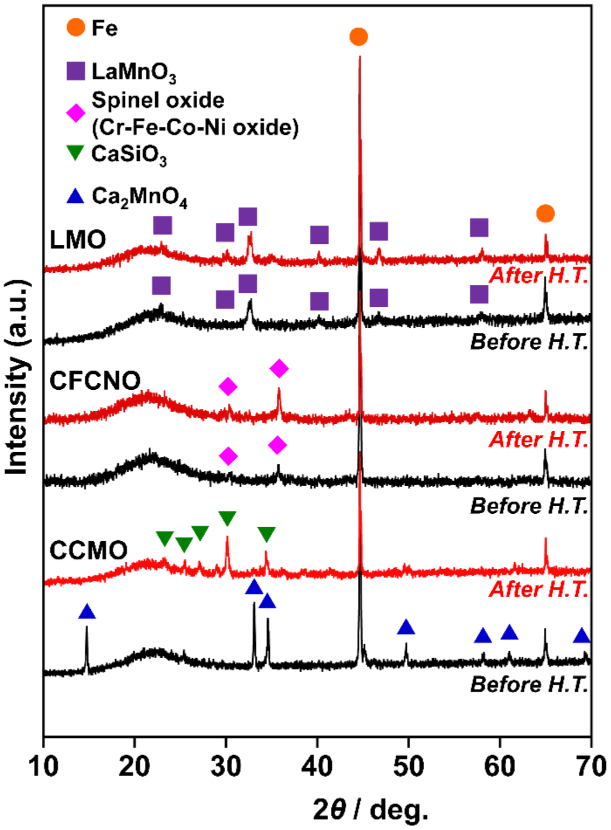

Figure 5. XRD patterns of EPD films composed of 200-nm-diameter SiO_2 particles with black additives before and after heat-treatment at 900 °C for 1 h.

Next, SiO_2 particles with different diameters were examined to confirm heat resistance of structural coloration for various colors. CFCNO was used as a black additive. Photographs and UV−vis reflectance spectra of films prepared with 260-nm and 300-nm-diameter SiO_2 particles before and after treatment at 900 °C for 1 h are displayed in Figure 6. The CIE $L^*a^*b^*Ch^{\circ}$ color coordinates of the films before and after the heat-treatments are summarized in Table S3 in the Supporting Information. Films that exhibited green and red structural colors were obtained from the 260-nm and 300-nm-diameter SiO_2 particles, respectively. The difference in their colors was attributed to the different periodic lengths of the colloidal arrays.[22] Almost no changes were detected in the apparent colors and reflectance spectra of the films before and after heat-treatment. Figure 7 depicts SEM images of films prepared with 260-nm and 300-nm-diameter SiO_2 particles before and after treatment at 900 °C for 1 h. Neither deformation of the SiO_2 particles nor formation of silicate compounds with components of CFCNO was observed, consistent with the 200-nm-diameter SiO_2 particles (Figure 2e). Color differences, ΔE, of the films before and after heat-treatment were 1.68 (260-nm-diameter) and 2.05 (300-nm-diameter), indicating that the structural colors were unchanged after treatment at 900 °C. Various structurally colored colloidal arrays with high heat-resistance were thus prepared by using inorganic black additives that maintained high thermal and chemical stabilities.

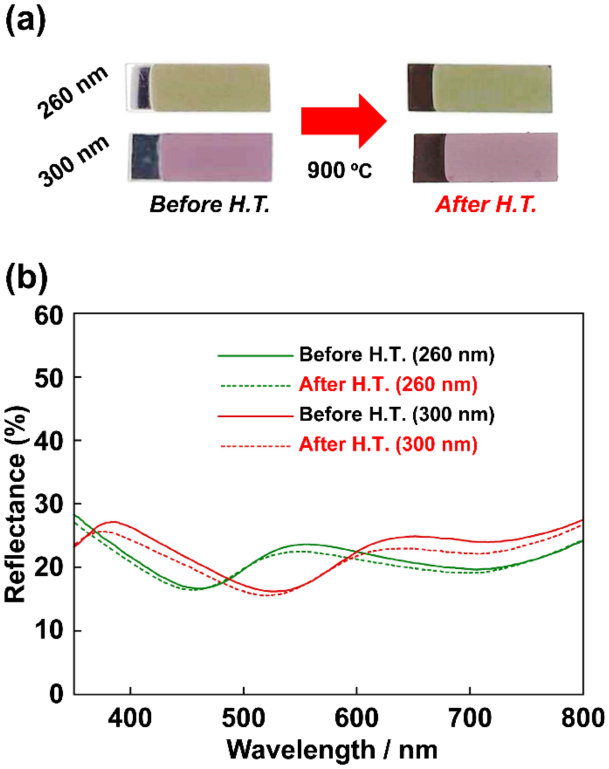

Figure 6. (a) Photographs and (b) UV−vis reflectance spectra of EPD films composed of SiO_2 particles (260-nm or 300-nm diameter) and CFCNO before and after heat treatment at 900 °C for 1 h.

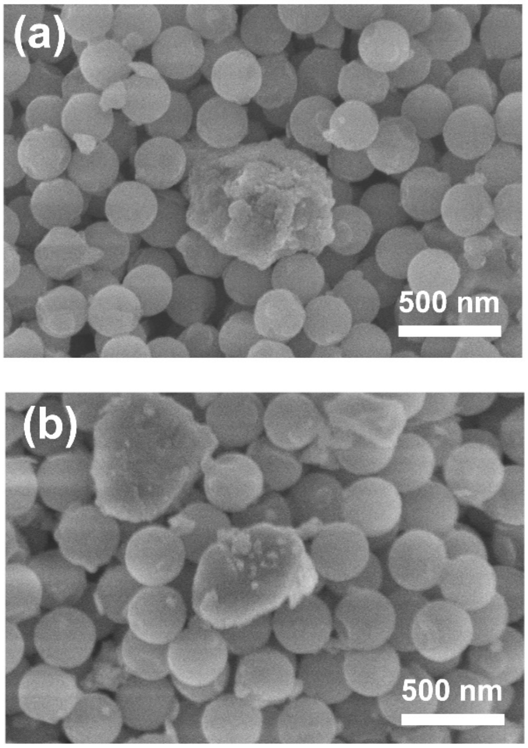

Figure 7. SEM images of EPD films composed of SiO_2 particles: (a) 260 nm diameter and (b) 300 nm diameter, and CFCNO after heat-treatment at 900 °C for 1 h.

CONCLUSIONS

We have successfully achieved high heat-resistance of structural coloration in arrays of monodispersed spherical particles. Several metal-oxide compounds were investigated as black additives to preserve the structural coloration formed by arrays of monodispersed spherical SiO_2 particles. When CCMO was used as a black additive, the coloration heat-resistance of the film was stable up to 700 °C, while heat-resistances up to 900 °C were obtained by using CFCNO and LMO black additives. This indicated that high heat resistance of structural colors required both heat-resistance of the black additives and non-reactivity with the components of the spherical particles used for colloidal arrays. In particular, LMO does not contain toxic heavy metals, such as Cr. Therefore, it indicates that vivid structural colored materials with high coloration heat-resistance can be prepared using only non-toxic materials. The prepared films maintained their coloration after heating to 900 °C, which far exceeded temperatures in previous reports.[16,17] Cr and Co contained in CFCNO are recognized as toxic elements, therefore, it is desired to reduce their amounts used in colorants. Compared with typical inorganic pigments containing Cr and Co, such as chrome yellow ($PbCrO_4$, Cr: 16.7 at%) and cobalt blue ($CoAl_2O_4$, Co: 16.7 at%), structurally colored material containing CFCNO prepared in this study contained only trace amount of toxic elements (Cr: 0.35 at% and Co: 0.71 at%) in overall material. This reveals that a significant reduction in the use of toxic elements is achieved. In addition, because Ce and La in CCMO and LMO are rare earth elements but abundant and non-toxic elements and currently being sought for new applications due to oversupply,[38] therefore their use as black additives in structural colored materials makes sense. Such a high heat-resistance allow structurally colored materials to be applied to various materials, e.g., baking coatings and painting on potteries and porcelains. We believe that the findings in this study can bring new aspects in structurally colored colloidal arrays to be alternatives to inorganic pigments, and expand the range of applications.

EXPERIMENTAL PROCEDURE

Synthesis of Calcium Manganese-based Oxide ($Ca_{1.98}Ce_{0.02}MnO_4$; CCMO). Calcium carbonate ($CaCO_3$) (1.99 g), manganese(IV) oxide (MnO_2) (0.87 g), and cerium(IV) oxide (CeO_2) (0.03 g) were mixed well using an agate mortar for 30 min (molar ratio of Ca:Mn:Ce =

1.98:2:0.02). The mixture was calcined using a furnace. The furnace was heated at a rate of 200 °C h^{-1} and maintained at 1200 °C for 6 h.

Synthesis of Cr-Fe-Co-Ni oxide (CFCNO). Chromium(III) oxide (Cr_2O_3), iron(III) oxide (Fe_2O_3), cobalt(II) oxide (CoO), and nickel(II) oxide (NiO) powders (weight ratio of 0.16:0.35:0.32:0.17) were grounded in a mortar. Mixed powder (4.0 g) and deionized water (20 mL) were mixed well using a planetary ball mill (Pulverisette 7, classic line, Fritsch GmbH, Idar-Oberstein, Germany) with a rotation speed of 1200 rpm for 1 h. The ZrO_2 pod (45 mL of inner volume) and ZrO_2 ball (4 mm in diameter, 40 g) were used for milling. After evaporation of water, the obtained powder was calcined using a furnace. The furnace was heated at a rate of 5 °C min^{-1} and maintained at 1250 °C for 6 h. After calcination, the obtained powders (4.0 g) was wet-milled using a planetary ball mill for 3 h with same conditions described above to obtain suspension. Finally, the water was evaporated.

Synthesis of Lanthanum Manganite ($LaMnO_3$; LMO). Lanthanum(III) oxide (La_2O_3) and MnO_2 were mixed in a mortar at a molar ratio of 1:2. The mixture was calcined using a furnace. The furnace was heated at a rate of 5 °C min^{-1} and maintained at 1300 °C for 6 h. After calcination, the obtained powders (4.0 g) was wet-milled using a planetary ball mill for 3 h with a condition same as CFCNO to obtain suspension. Finally, the water was evaporated.

Preparation of Coating Films via the Cathodic Electrophoretic Deposition (EPD). The coating sols of EPD were prepared according to the literature.[30] Briefly, 0.70 g of monodispersed spherical SiO_2 particles (diameters: 200, 260, and 300 nm) were dispersed in 2-propanol (80 mL) by ultrasonic irradiation. Then, aqueous suspensions of black additives and aqueous solution of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) (5 mL, 3.5×10^{-2} mol dm^{-3}) were added to the dispersion. The amounts of black additives in the dispersions were listed in Table S4 in the

Supporting Information. The preparation of the coating films by EPD was also performed according to our previous paper.[30] Stainless-steel plates were used as coating substrates (cathodes). Spiral shaped stainless-steel wires were employed as the counter electrodes (anodes). A specific voltage (30 V) was applied for 5 min using a direct current power supply (PAN110-3A, Kikusui Electronics Corp., Yokohama, Japan). After EPD, the coating substrates were dried in air at room temperature.

Characterizations. Photographs were taken by a digital camera. Scanning electron microscopy (SEM), X-ray diffraction (XRD) measurements, and ultraviolet−visible (UV−vis) spectroscopy were conducted for characterizations of the obtained EPD coating films. The chromatic properties of the obtained samples were analyzed using the Commission International del'Eclairage (CIE) 1976 colorimetric method. Further details on the characterization methods are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.xxxxxxxx.

Details of experimental section (materials and characterizations), color coordinates of EPD films with various black additives, Detailed data of photographs and UV−vis reflectance spectra of EPD films with various black additive before and after heat-treatment, color coordinates and total color coordinate difference of EPD films with black additives before and after heat treatment, Compositions of EPD sols containing various black additives.

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Author Contributions

TY performed the investigation and the writing of the original draft. NT developed the methodology, and edited the writing. KK was responsible for conceptualization, funding, methodology, supervision, and editing. KI supervised the work. YT was responsible for the methodology and resources. TM was responsible for resources. All authors have discussed the results, commented on the paper, and have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

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