Electronic Supplementary Material (ESI) for Soft Matter.

ESI: Structural color from pigment-loaded nanostructures

Tianqi Sai,[1] Luis S. Froufe-Pérez,[2] Frank Scheffold,[2] Bodo D. Wilts,[3] and Eric R. Dufresne[1,4,*]

[1]Department of Materials, ETH Zürich, 8093 Zürich, Switzerland.
[2]Department of Physics, University of Fribourg, 1700 Fribourg, Switzerland
[3]Department of Chemistry and Physics of Materials University of Salzburg, 5020 Salzburg, Austria
[4]Department of Materials Science and Engineering,
Department of Physics, Cornell University, Ithaca, NY, 14850, USA.
(Dated: September 8, 2023)

I. DESIGN RULE FOR A PIGMENT-LOADED MULTILAYER REFLECTOR

According to the classical design rule for a quarter-wave mirror, the phase changes after passing through a double layer, a high index layer, and a low index layer are $4\pi n_d d/\lambda = 2\pi$, $4\pi n_h t_h/\lambda = \pi$ and $4\pi n_l t_l/\lambda = \pi$, respectively. d, t_h, t_l are the thickness, and n_d, n_h, n_l are the (average) refractive index, of a double layer, a high index layer, and a low index layer, respectively. To check whether the classical design rule is still valid in the presence of absorption and strong dispersion, we calculate the phase changes, ϕ for multilayers with calculated optimal thickness combinations (which gives the highest reflectance), and plot them in Figure S1 a-c. They are $4\pi n_d d/\lambda$ and $4\pi n_h t_h/\lambda$ and $4\pi n_l t_l/\lambda$ for a doublelayer, a high index layer and a low index layer, respectively. It is shown that when outside the absorption band, after 552 nm, 560 nm, 570 nm for 33w/w% BC/PS, 50w/w% BC/PS and 67w/w% BC/PS, the optimization agrees with the classical design rule.

The optimal peak reflectances are plotted in Figure S1 a. It is shown that for all three BC concentrations, the optimal reflectances are the highest in the range around 550 nm, where the high refractive index and low absorption window as expected. The reflectance can be as high as 0.89 at the wavelength of 573 nm for 67w/w% BC/PS. From 400 nm to 500 nm, the reflectance is around 50% because of the large absorption, which is the imaginary part of the complex refractive index. For all three concentrations, the optimal reflectance drops slowly towards higher wavelengths because the refractive index enhancement gets weaker.

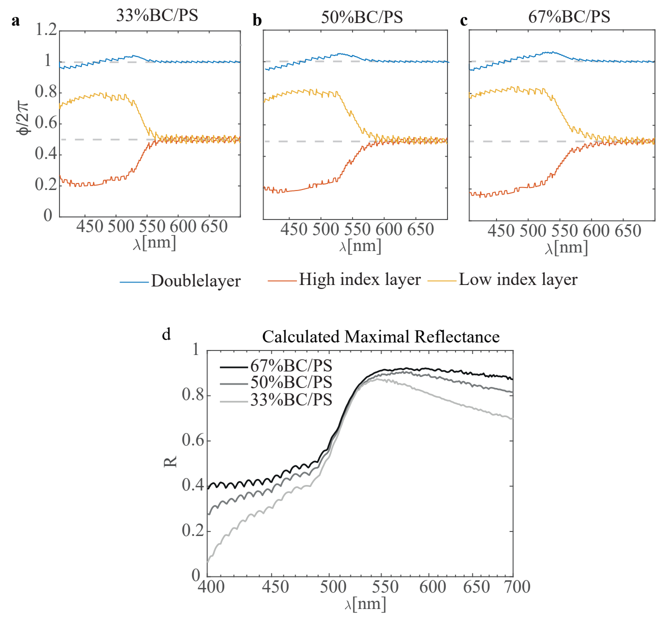


FIG. S1. *Design rule for a pigment-loaded multilayer reflector.* (a)-(c) Calculated phase difference after passing through a doublelayer, a high index layer (33w/w% BC/PS, 50w/w% BC/PS and 67w/w% BC/PS respectively) and a low index layer (PVA) with optimal thicknesses. $\phi = \pi$ and $\phi = 2\pi$ are marked in dashed grey lines in the plots as guidance. (c) Calculated maximal reflectances, consisting of 10 doublelayers of alternating low refractive index (PVA) and high refractive index films (33w/w% BC/PS, 50w/w% BC/PS and 67w/w% BC/PS respectively) with optimal thicknesses. The substrates are infinite slabs of glass.

II. ROLE OF INITIAL REFRACTIVE INDEX CONTRAST

We have discussed how the BC concentration and the number of repeating layers influence the reflectance of a Bragg reflector, assuming it consists of alternating PVA and BC/PS films. The refractive index of PVA is about 0.1 lower than that of PS, and the initial refractive index contrast when the BC concentration is zero, is 0.1.

When there is no initial refractive index contrast, and all the refractive index contrast comes from the incorporation of BC, the BC concentration shows a much stronger effect on the reflectance, as shown in Figure S2 a. We observe that with low BC pigment loadings (below 5%), the refractive index contrast is too low to give a fair reflectance even when there are hundreds of double layers. By adding more BC (20%-30%), the reflectance would increase significantly. The contour lines in Figure S2 a are much steeper than in Figure S2 b when BC concentration is below 30%.

If we make the initial refractive index contrast even larger (for example, $\delta n_0 = 0.6$, which is the refractive

* eric.r.dufresne@cornell.edu

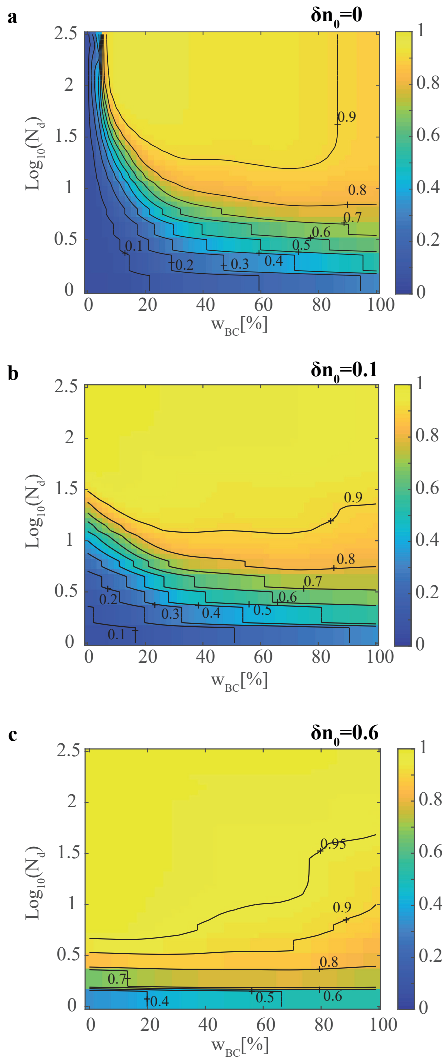


FIG. S2. *Effect of initial refractive index contrast.* a)-c) Colormap of calculated maximal reflectance at the wavelength of 550 nm for multilayers with different numbers of repeating doublelayers and different BC concentrations as high refractive index layers, with δn_0 equals to 0, 0.1 and 0.6 respectively.

index contrast between PS and air), high BC concentration would always make the reflectance lower, as shown in Figure S2 c.

In conclusion, absorption is beneficial in enhancing the multilayer reflectance when the initial refractive index contrast is low. It has a negative effect when there is sufficient initial contrast.

III. COMPETITION OF ABSORPTION AND SCATTERING IN A BRAGG REFELECTOR

To obtain a complete understanding of the competition between absorption and scattering, we conduct the same optimization and find the highest reflectivities for varying BC concentrations and numbers of doublelayers at 500 nm and 600 nm as well, plotted in Figure S3 a-c. We also compare the absorption length, ℓ_{abs} and the scattering length, ℓ_{sca} in Figure S3 d-f. Here, the scattering length is taken as the number of doublelayers needed to reflect back most of light (R is larger than 0.63) without absorption, but with the change of refractive index caused by absorption. This means that we input the true real refractive index of BC/PS composites and set the imaginary part to zero. This can not be true in reality because real and imaginary part of the refractive index come as a "package". However, separating the real and imaginary parts here helps us to disentangle the complex problem and understand the underlying physics.

The comparison of absorption length and scattering length helps us understand the reflectance colormaps. At 500 nm, the refractive index contrast between the high-index and the low-index layer can be up to 0.4, but the absorption length is below 10μm even for 10%BC/PS, which corresponds to tens of doublelayers. At this wavelength, the absorption length is almost always lower than the scattering length and absorption is dominating. Therefore, no reflectance higher than 0.65 can be achieved, even though the refractive index contrast is not small. At 550 nm, the absorption length and scattering length is comparable. So, the final reflectance is limited slightly by the absorption and 100% reflectance can not be achieved. While at 600 nm, the scattering length is much lower than the absorption length and the scattering dominates. When the thickness of the multilayer is higher than the scattering length, but lower than the absorption length, high or even 100% reflectance is possible.

IV. FULL EXTENDED GAMUT

To explore the full gamut, we varied the ratio of BC and PS in the spheres, the average center-to-center spacing, s, sphere diameter, d, as well as the sample thickness, t. We did not systematically sample this high-dimensionality space, but explored some interesting limiting cases.

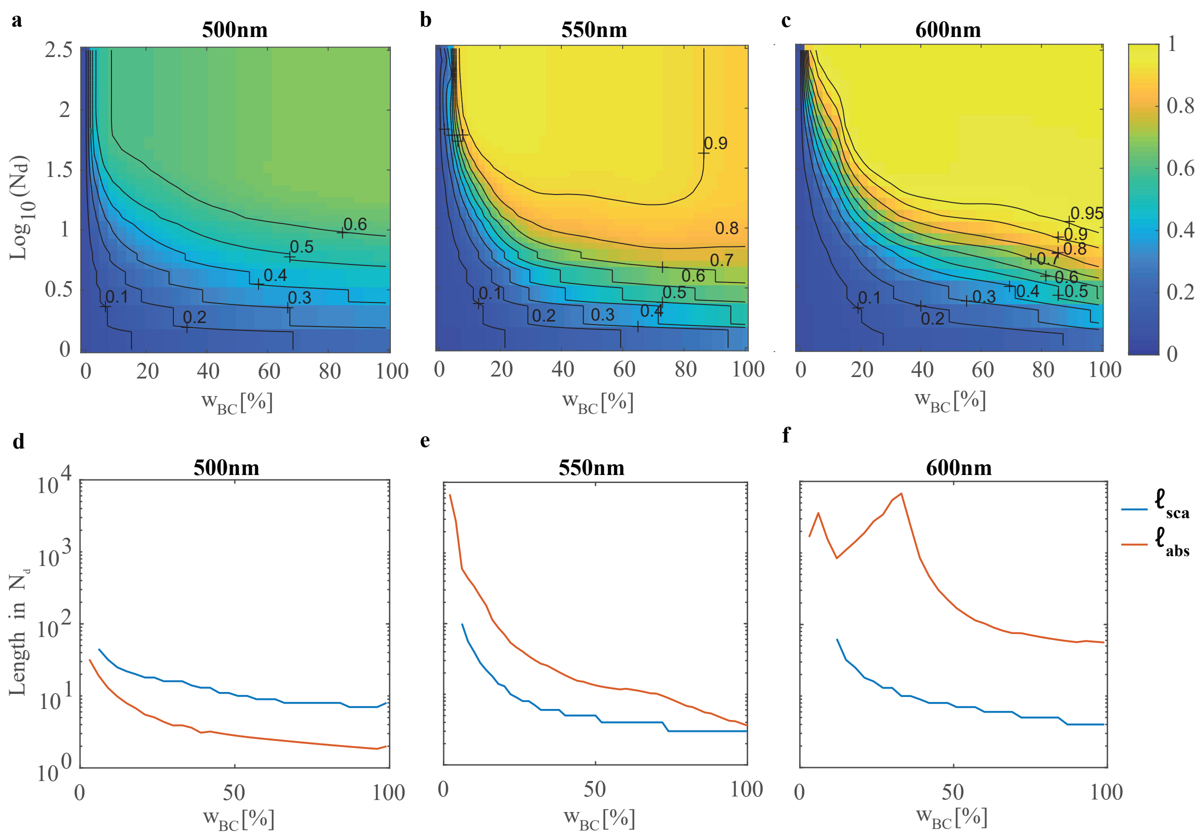
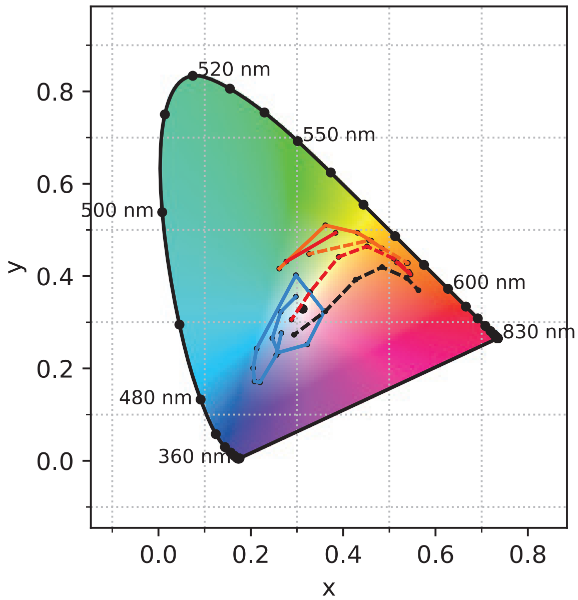


FIG. S3. *Competition between two length scales.* (a)-(c) Colormaps of calculated maximal reflectance for multilayers with different numbers of repeating doublelayers and different BC concentrations as high refractive index layers with $\delta n_0 = 0$, at the wavelength of 500 nm, 550 nm and 600 nm, respectively. (d)-(f) Corresponding absorption lengths and scattering lengths in number of repeating doublelayers at the wavelength of 500 nm, 550 nm and 600 nm, respectively.



Line style	% BC	s/d	s [nm]	t [μm]
solid blue	0	1	140-390	3
solid orange	33	1	300-370	3
dashed orange	33	2	300-440	10
solid red	67	2	300-370	3
dashed red	67	2	240-480	10
dashed black	100	2	240-390	10

FIG. S4. The CIE chromaticity diagram with all the simulated colors from photonic glasses assemblies with different scatterer properties, pigment loadings, and thicknesses. Dots on each line represent colors from photonic glasses with varying sphere diameter, d, and spacing, s, but with the same pigment loading, thickness, t, and diameter/spacing ratio.