Structural Color via Layer-by-Layer Deposition: Layered Nanoparticle Arrays with Near-UV and Visible Reflectivity Bands

SUPPLEMENTARY INFORMATION

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PART I

The fundamental difference between the colors from 1D and 3D photonic structures: Previous work on tenability of structural color and context to this approach.

Previously Colvin and Xia attacked the problem of tunability of structural color.[1,2] Colvin’s work[1] presented a self-assembly approach of colloid crystals to generate 3D structures. Similarly Xia presented[2] tunability of such nanoparticle assemblies to generate structural colors. In each case, mono-dispersed polystyrene particles are assembled into a 3D structure which has been investigated by many researchers in the past. Controlling nanoparticle 3D structure through a self-assembly approach is motivated by the morph butterfly structure, where light reflects from 3D periodic sites to cause interference. In general it is difficult to maintain periodicity over a large scale. Control of color is achieved by swelling of the 3D structure causing change in the optical path length. This approach is however limited by the flexibility of nanoparticles to size changing and the triggering mechanism.

Our case is fundamentally different since we are targeting 1D photonic crystals where light reflects from a 1D periodic structure. In this case structural control is simpler and since we used periodic multilayer stacks of nanoparticle assemblies consisting of two alternate materials, light is reflected from multilayer interfaces causing interference. The resultant light interference wavelength is controlled by the thickness of the layers which makes it suitable for application in many areas. Since vacuum deposited processes are in general expensive, introduction of a cheap, water based layer-by-layer process makes it attractive for practical application in future.
\[ m\lambda = 2d_{hkl}(n_a^2 - \sin^2 \theta) \]

**Periodic Nanoparticle (100s of nanometer) Assembly**

**Colvin or Xia’s work: Diffraction 3D photonic crystal**

\[ m\lambda = n_H d_H \cos \theta_H + n_L d_L \cos \theta_L \]

**Nanoparticle (5-30nm) Assembly of periodic stacks**

**Our work: Interference From reflected light in multiple layers: 1D photonic crystal**

**Fig S1.** Left figure shows the typical 3D photonic structure of previous work by Colvin and Xia. Right hand figure show 1D photonic structure used in this work.

Secondly, a key point of this work is not only the control of color, but control of color while maintaining multiple reflectivity bands.

**PART II.**

**Theoretical design approach to control of multiband reflectance**

**Fig S2.** Figure shows a schematic of a light travelling path in a multilayer stack.
Here we show the design strategy and numerical relation between the multiband reflection and the \( p \) and \( q \) numbers.

A general relation between the multiple stop-bands and the \( p \) and \( q \) should be as follows,

\[
2n_Ld_{\lambda}p \cos(\theta) + 2n_Hd_{\mu}q \cos(\theta) = M\lambda, \quad M=1, 2, 3 \quad \text{--------(1)}
\]

Here \( p \) and \( q \) are adjustable parameters to the quarter-wave optical thickness and \( M \) is an integer. Adjustable parameters are varied based on the design need and control of the location of the multiband reflector peak. For a normal incidence, Eq.1 turns out to be,

\[
2n_Ld_{\lambda}p + 2n_Hd_{\mu}q = M\lambda \quad \text{----------------(2)}
\]

And,

\[
d_{\lambda} = \frac{\lambda_0}{4n_L}, \quad d_{\mu} = \frac{\lambda_0}{4n_H} \quad \text{--------------(3)}
\]

In the case of a quarter-wave design when \( p=q=1 \), the multilayer stack will have fixed multiband peaks at \( \lambda_0/M \) (\( \lambda_0, \lambda_0/2, \lambda_0/3 \ldots \)). In our non-quarter wave case we used \( p = 0.37 \) and \( q = 3.46 \) for the color blue (\( \lambda_0=450 \) nm), \( p = 0.29 \) and \( q = 1.79 \) for the color green (\( \lambda_0=580 \) nm) and \( p = 0.243 \) and \( q = 1.73 \) for the color red (\( \lambda_0=690 \) nm) as multipliers to the quarter-wave thickness. So location of the peak for blue, green and red can be obtained from Eq. 2 given by, \( \lambda = (1/M)1.914\lambda_0, (1/M)1.04\lambda_0 \) and \( (1/M)0.986\lambda_0 \). For the case of blue we see the peaks at \( \lambda=861 \) nm (\( M=1 \)), 430 nm (\( M=2 \)), 287 nm (\( M=3 \)). Similarly, we see the green and red peaks are at 603 nm, 301 nm, 201 nm and 680 nm, 340 nm, 226 nm respectively. Changing \( p \) and \( q \) it is possible to change the location of the peaks as needed for any other wavelength range, where as in a quarter-wave design locations of the peaks are fixed.

REFERENCES
