Photonic Crystals with Thermally Switchable Stop Bands
Fabricated from Se@Ag₂Se Spherical Colloids**

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Estimation of Shell thickness and Dimensional Change

Once the atomic fraction of silver ($f_{Ag}$) of a sample has been determined by EDX, both the shell thickness and the dimensional change involved in this template-engaged reaction can be estimated. First, we can express $f_{Ag}$ as the following:

$$\frac{w_{core,Se} + w_{shell,Se}}{M_{Se}} : \frac{w_{shell,Ag}}{M_{Ag}} = (1 - f_{Ag}) : f_{Ag}$$

(1)

where $M_{Se}$ and $M_{Ag}$ represent the atomic masses of Se and Ag; and $w$ is the weight of Se or Ag in the core or shell. The volumes of core and shell are related to the known densities ($\rho$) of $\alpha$-Se (4.4 g/cm$^3$) and $\beta$-Ag$_2$Se (8.2 g/cm$^3$) through the following relationship:

$$\frac{w_{core}}{V_{core}} : \frac{w_{shell}}{V_{shell}} = \rho_{core} : \rho_{shell}$$

(2)
Since the stoichiometry of the shell is Ag\(_2\)Se, the volume ratio between the shell and the core can be calculated as:

\[
\frac{V_{\text{shell}}}{V_{\text{core}}} = \left(1 + 2\frac{M_{\text{Ag}}}{M_{\text{Se}}}, \frac{\rho_{\text{Se}}}{\rho_{\text{Ag},\text{Se}}} \left(\frac{f_{\text{Ag}}}{2 - 3f_{\text{Ag}}}\right) = \frac{2f_{\text{Ag}}}{2 - 3f_{\text{Ag}}} \right)
\]  

(3)

Because the fraction of \(a\)-Se that has been converted to Ag\(_2\)Se is equal to \(f_{\text{Ag}}/(2-2f_{\text{Ag}})\), the volume \((V_o)\) of as-synthesized \(a\)-Se colloids should become \(V_{\text{core}}/[1-f_{\text{Ag}}/(2-2f_{\text{Ag}})]\). As a result, Eq. (3) can be rearranged to express the change in volume due to the reaction, from which the change in diameter \((D/D_o)\) can be easily derived:

\[
\frac{V_{\text{core}} + V_{\text{shell}}}{V_o} = (1 - f_{\text{Ag}}) \left(1 + \frac{V_{\text{shell}}}{V_{\text{core}}}\right)
\]

(4)

\[
\frac{D}{D_o} = \left[1 - \frac{f_{\text{Ag}}}{2 - 2f_{\text{Ag}}} \left(1 + \frac{V_{\text{shell}}}{V_{\text{core}}}\right)\right]^{1/3} = \left(\frac{2 - f_{\text{Ag}}}{2 - 2f_{\text{Ag}}}\right)^{1/3}
\]

(5)

From Eq. (3), shell thickness \((t)\) relative to the radius \((R)\) can also be obtained:

\[
\frac{t}{R} = 1 - \frac{1}{\left(1 + \frac{V_{\text{shell}}}{V_{\text{core}}}\right)^{1/3}} = 1 - \frac{1}{\left(\frac{2 - f_{\text{Ag}}}{2 - 3f_{\text{Ag}}}\right)^{1/3}}
\]

(6)

Figure S1A compares the results from experimental measurements (dots) and calculations (line) showing how the sizes of the core-shell colloids vary as \(f_{\text{Ag}}\) is increased. The diameters
were directly measured from SEM images. For each sample, the average diameter was obtained from more than 100 particles by calculating the cross-sectional area of each particle with the aid of commercial software (Scion images, Scion, Frederick, MD). The standard deviation of the particle size was below 5% for all core-shell colloids reported here. Figure S1B displays the calculated change in shell thickness as $f_{Ag}$ is increased. From these two plots, we can easily estimate the diameter and shell thickness from $f_{Ag}$ as long as we know the diameter ($D_o$) of initial $\alpha$-Se colloids. The value of $f_{Ag}$ can be, in turn, obtained from the EDX measurements. For instance, the diameter and shell thickness of the colloids displayed in Figure 1C was 310 and 22 nm, respectively, as calculated with $f_{Ag}$=0.32 and $D_o$=289 nm. These values were in reasonable agreement with TEM studies.
Figure S1. (A) Dependence of the diameter of core-shell colloids (normalized against the size of the starting Se colloids) on the value of $f_{Ag}$. Solid circles are experimental data obtained from SEM images and the solid line is based upon Eq.(4). (B) Dependence of the shell thickness (normalized against the radius of the core-shell colloids) on the value of $f_{Ag}$. 