` Supporting Information

1. Strain and Biaxial Modulus of CdSe Cores in Nanocrystal Films

For a system with no shear stresses, strain is related to stress as

$$\varepsilon_{xx} = \frac{\sigma_{xx} - v(\sigma_{yy} + \sigma_{zz})}{E} \tag{1}$$

$$\varepsilon_{yy} = \frac{\sigma_{yy} - v(\sigma_{xx} + \sigma_{zz})}{E} \tag{2}$$

$$\varepsilon_{zz} = \frac{\sigma_{zz} - v(\sigma_{xx} + \sigma_{yy})}{E} \tag{3}$$

The in-plane tensile strain for the unrelaxed film is $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon$ and the isotropic in-plane stress is $\sigma_{xx} = \sigma_{yy} = \sigma$. With the normal stress $\sigma_{zz} = 0$, it follows that $\varepsilon_{zz} = -\left[\frac{2v}{1-v}\right]\varepsilon$,

where ν is Poisson's ratio and *E* is Young's modulus.

For {100} planes the Raman shift is[1]

$$\omega = \omega_0 + \frac{p\varepsilon_{zz} + q(\varepsilon_{xx} + \varepsilon_{yy})}{2\omega_0} \tag{4}$$

Therefore, $\omega = \omega_0 + \left[\frac{q - \frac{pv}{1-v}}{\omega_0}\right]\varepsilon$ in the fully strained region, $\omega = \omega_0 + \left[\frac{q - \frac{pv}{1-v}}{2\omega_0}\right]\varepsilon$ in the partially relaxed delaminated regions near a channel crack, and ω_0 for the completely delaminated region.

We use[2] $p = -\omega_{LO}^2 = -0.454\text{x}10^5$ cm^{-2}, $q = -1.8\omega_{LO}^2 = -0.817\text{x}10^5$ cm^{-2}, and $\omega_0 =$ 213 cm^{-1}. Consequently, Equation 4 can be written as

$$\omega - \omega_0 = \left[\frac{\omega_0 v}{1-v} - 1.8\omega_0\right]\varepsilon \tag{5}$$

Using the angle averaged value of $v = 0.37$ for CdSe, as reported previously,[3]

$\omega - \omega_0 = -258\varepsilon$ (in cm^{-1}), and for $\varepsilon = +1\%$, $\omega - \omega_0 = -2.58\ cm^{-1}$ in the completely strained region. For our film we measure a 6.4 cm^{-1} Raman shift ($\delta_2 = 6.4 \pm 1.5\ cm^{-1}$), which corresponds to a total core strain of ~2.5%. The strain in the entire film as derived from optical microscopy is 11.7%.

The biaxial modulus for the CdSe core: $E_{CdSe}/(1-v_{CdSe}) = 41.5/(1-0.37) = 65.9$ GPa, using values of 41.5 GPa and 0.37 for E and v, respectively, for hexagonal CdSe.[3] The in-plane stress is $\sigma = \varepsilon E/(1-v)$ = 1.6 GPa for 2.5% strain. Thus the biaxial modulus for the film, $E_{film}/(1-v_{film}) = 0.025/0.117 E_{CdSe}/(1-v_{CdSe}) = 0.21 E_{CdSe}/(1-v_{CdSe}) \sim$ 13.8 GPa. For $v_{film} = 0.1\text{-}0.5$, we obtain $E_{film} = 6.8\text{-}12.4$ GPa

From the micromechanics models discussed in the next section it is reasonable to take $E_{film}/(1-v_{film}) = 2.75 E_{TOPO}/(1-v_{TOPO})$. From this, $E_{TOPO}/(1-v_{TOPO}) =$ $(0.21/2.75) E_{CdSe}/(1-v_{CdSe}) = 0.077 E_{CdSe}/(1-v_{CdSe}) = 0.077 \times 65.9$ GPa = 5.1 GPa. For $v_{TOPO} = 0.1\text{-}0.5$, we see that $E_{TOPO} = 2.45\text{-}4.41$ GPa.

2. Micromechanics Models

Assuming a close-packed arrangement of spheres, the volume density of the CdSe cores in the film is assumed to be $\rho = 0.43$. We use this and assume $E_{CdSe} >> E_{TOPO}$ in each of the below micromechanics models, and find this assumption is consistent with the results.

2.1. Halpin-Tsai Model

This model predicts[4]

$$\frac{E_{film}}{E_{TOPO}} = \frac{1+\xi\eta\rho}{1-\eta\rho} \tag{6}$$

with $\xi = 2 + 40\rho^{10}$ for spherical particles, where ρ is the fraction of the particulate material in the matrix and

$$\eta = \frac{\frac{E_{film}}{E_{TOPO}} - 1}{\frac{E_{film}}{E_{TOPO}} + \xi} \tag{7}$$

E and K scale in the same way, $E_{\mathrm{film}}/E_{\mathrm{TOPO}} = K_{\mathrm{film}}/K_{\mathrm{TOPO}} = 3.26$. Therefore, $E_{\mathrm{film}}/(1-\nu_{\mathrm{film}}) = 3.26E_{\mathrm{TOPO}}/(1-\nu_{\mathrm{TOPO}})$.

2.2 Cohen-Ishai Model

This model predicts[5]

$$E_{film} = E_{TOPO}\left(1 + \frac{\rho}{\frac{M}{M-1} - \rho^{1/3}}\right) \tag{8}$$

where $M = E_{\mathrm{CdSe}}/E_{\mathrm{TOPO}}$, to give $E_{\mathrm{film}}/E_{\mathrm{TOPO}} = 2.75$. Using the assumptions of cubic filler in a cubic matrix implicit in this model with $\nu = 0.33$, gives $E_{\mathrm{film}}/(1-\nu_{\mathrm{film}}) = 2.75E_{\mathrm{TOPO}}/(1-\nu_{\mathrm{TOPO}})$.

2.3 Mori-Tanaka Model

This model predicts[6]

$$\frac{E_{film}}{E_{TOPO}} = 1 + \frac{\rho}{(1-\rho)}\left[1 + \frac{(9K_{TOPO} + 8E_{TOPO})}{6(K_{TOPO} + 2E_{TOPO})}\right] \tag{9}$$

$$\frac{K_{film}}{K_{TOPO}} = 1 + \frac{\rho}{(1-\rho)}\left[1 + \frac{4E_{TOPO}}{3K_{TOPO}}\right] \tag{10}$$

We examine two reasonable scenarios:

i) For $E_{TOPO} = K_{TOPO}$, we have $E_{\text{film}}/E_{\text{TOPO}} = 2.46$ and $K_{\text{film}}/K_{\text{TOPO}} = 2.76$, and therefore $E_{\text{film}}/(1\text{-}v_{\text{film}}) = 2.33E_{\text{TOPO}}/(1\text{-}v_{\text{TOPO}})$.

ii) For $E_m = 0.5K_m$, we have $E_{\text{film}}/E_{\text{TOPO}} = 2.57$ and $K_{\text{film}}/K_{\text{TOPO}} = 2.25$, and therefore $E_{\text{film}}/(1\text{-}v_{\text{film}}) = 2.65E_{\text{TOPO}}/(1\text{-}v_{\text{TOPO}})$.

2.4. Christensen-Lo Model

This model predicts[6]

$$K_{film} = K_{TOPO} + \frac{\rho(K_{CdSe} - K_{TOPO})}{1 + (1-\rho)\dfrac{(K_{CdSe} - K_{TOPO})}{\left(K_{TOPO} + \frac{4}{3}E_{TOPO}\right)}} \tag{11}$$

i) For $E_m = 0$, we have $K_{\text{film}}/K_{\text{TOPO}} = 1.75$.

ii) For $E_m = K_m$, we have $K_{\text{film}}/K_{\text{TOPO}} = 2.76$.

2.5. New Christensen Model

This model predicts[7]

$$\frac{E_{film}}{E_{TOPO}} = \frac{1 - \dfrac{(1-5v_{TOPO})}{2(4-5v_{TOPO})}\rho}{1-2\rho} \tag{12}$$

$$\frac{K_{film}}{K_{TOPO}} = \frac{1 + \left(\dfrac{1-5v_{TOPO}}{1+v_{TOPO}}\right)\rho}{1-2\rho} \tag{13}$$

i) For $v = 0.1$, $E_{film}/E_{TOPO} = 6.92$ and $K_{film}/K_{TOPO} = 8.5$, which gives $E_{film}/(1-v_{film}) = 3.96 E_{TOPO}/(1-v_{TOPO})$.

ii) For $v = 0.33$, $E_{film}/E_{TOPO} = 7.6$ and $K_{film}/K_{TOPO} = 5.6$, which gives $E_{film}/(1-v_{film}) = 9.1E_{TOPO}/(1-v_{TOPO})$.

iii) For $v = 0.5$, $E_{film}/E_{TOPO} = 8.7$ and $K_{film}/K_{TOPO} = 4.1$, which gives $E_{film}/(1-v_{film}) = 8.7E_{TOPO}/(1-v_{TOPO})$.

2.6. Overall Conclusions

On the basis of the first four models, we use $E_{film}/(1-v_{film}) = 2.75E_{TOPO}/(1-v_{TOPO})$. The last model gives very different predictions because it assumes the capping ligands are randomly distributed—which would suggest direct contact of some cores, and this is important in this model---but the ligands are not distributed in this manner because they are bound to the cores.

References

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