Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Size- and Shape-Dependent Phase Transformations in Wurtzite ZnS Nanostructures

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Electronic Supplementary Information

As described in the main text, owing to the multiple special orientations we consider, it is convenient to introduce a simple naming convention. With reference to Figure 1 in the main text, we define each WZ shape completely through the use of four parameters: (i) average particle diameter $\langle D \rangle$ ranging from 3.0 nm $\leq \langle D \rangle \leq$ 33.0 nm (in the present study); (ii) the prism aspect ratio x (not to be confused with the total aspect ratio referred to in other works, which includes the pyramidal "caps"), where $0 < x$ for prisms capped with $\{0002\}$ basal planes and $0 \leq x$ for shapes with pyramidal "caps"; (iii) the degree of $\{10\bar{1}0\}$ prism truncation in the $\langle 11\bar{2}0 \rangle$ direction x', where $0 \leq x' \leq 1$; and (iv) the degree of truncation of the pyramidal caps x'' in the $\langle 0001 \rangle$ directions, where $0 \leq x'' \leq 1$. In the case of the x' geometric parameter, x' = 0 and 1 corresponds to prism walls consisting entirely of $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes, respectively (as seen in Figures 4a and 4f in the main text). For the purposes of this study, truncation of the pyramidal cap is at a maximum ($x'' = 1$) at the point where the $\{0002\}/\{000\bar{2}\}$ and $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$ planes intersect. This definition slightly reduces the generality but significantly reduces the geometric complexity of the model.

Based on these geometric parameters, we will refer to specific shapes in the following manner: $[x, x', x'']_l$; where x, x' and x'' refer to the prism aspect ratio, degree of truncation of the $\{10\bar{1}0\}$ planes in the $\langle 11\bar{2}0 \rangle$ direction, and pyramidal cap truncation, respectively, as indicated in Figure 1 in the main text. For pyramidal caps $\{10\bar{1}1\}$, $\{10\bar{1}2\}$ and $\{10\bar{1}3\}$, the value of l is 1 to 3, respectively, in reference to the l index in the standard $\{hkil\}$ notation. In the case of flat $\{0002\}$ basal planes with no pyramidal capping, l will have a value of 0. For example, $[2.0, 0.50, 0.2]_3$ indicates a prism with an aspect ratio of x = 2.0, $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes in comparable proportions making up the prism walls, and $\{10\bar{1}3\}$ planes forming the pyramidal cap which is truncated to 20% of the maximum degree (as defined above). Note that in the case of l = 0, x'' exists as a redundant variable and will be omitted.

Using this notation, the expressions for q and f_{hkil}, required for the nanomorphology model presented in Equation 1 of the main text, are presented below. Readers should note that there are undoubtedly a number of different ways of defining these variables, and that the following expressions are by no means intended to be the only representations; although they do have the advantage of being based on simple geometric expressions.

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Simple Prismatic Shapes

In the case of the simple prismatic shape enclosed by the open $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ form and terminated by a pinacoid of $\{0002\}$ basal planes ($l = 0$), the surface to volume ratio, q can be described by:

$$q = \frac{1}{a} \frac{\frac{4}{\sqrt{3}}x(1-x') + 2(1-x'^2) + 2xx' + \frac{3}{2}x'^2}{x(1-x'^2) + \frac{3}{4}xx'^2}, \quad (1)$$

where x and x' are defined above, and a is defined in terms of the total volume V, such that:

$$a = \left[\frac{2V}{3\sqrt{3}x(1-x'^2) + \frac{9}{4}\sqrt{3}xx'^2} \right]^{1/3} \quad (2)$$

In this case the fractional surface areas f can be described by:

$$f_{10\bar{1}0} = \frac{6x(1-x')}{3\sqrt{3}(1-\frac{x'^2}{4} + \frac{2}{\sqrt{3}}(1-x') + xx')}, \quad (3)$$

$$f_{11\bar{2}0} = \frac{3\sqrt{3}xx'}{3\sqrt{3}(1-\frac{x'^2}{4} + \frac{2}{\sqrt{3}}(1-x') + xx')}, \quad (4)$$

and

$$f_{0002} = \frac{3\sqrt{3}(1-\frac{x'^2}{4})}{3\sqrt{3}(1-\frac{x'^2}{4} + \frac{2}{\sqrt{3}}(1-x') + xx')}. \quad (5)$$

Shapes with Pyramidal Caps

In the case of the prismatic shape enclosed by the open $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ form and terminated by a pyramidal cap and/or a pinacoid of $\{0002\}$ basal planes ($l \neq 0$), the surface to volume ratio, q can be described by:

$$q = \frac{S}{V} \quad (6)$$

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$$S = a^2\Big[6x + 3\sqrt{3+4\alpha^2} - 4\sqrt{3}x(x'\tfrac{\sqrt{3}}{2}) - 24A + 6x(x'\tfrac{\sqrt{3}}{2}) + \sqrt{3}\alpha(x'\tfrac{\sqrt{3}}{2})^2 - 3\sqrt{3+4\alpha^2}\big[x''(1-\tfrac{x'}{4})\big]^2 + 3\sqrt{3}\big[x''(1-\tfrac{x'}{4})\big]^2\Big], \quad (7)$$

where $\alpha = c_0/(a_0 l)$ with a_0 and c_0 being the lattice constants and l being the Miller index in $\{hkil\}$ format. In this expression, for simplicity,

$$A = \sqrt{u(u-d_1)(u-d_2)(u-d_3)}, \quad (8)$$

with,

$$u = \frac{1}{2}(d_1 + d_2 + d_3), \quad (9)$$

and,

$$\begin{aligned} d_1 &= \tfrac{1}{\sqrt{3}}x'\tfrac{\sqrt{3}}{2} \\ d_2 &= \tfrac{1}{2}\sqrt{1-\tfrac{\alpha^2}{3}}x'\tfrac{\sqrt{3}}{2} \\ d_3 &= \tfrac{1}{2\sqrt{3}}\sqrt{1+\alpha^2}x'\tfrac{\sqrt{3}}{2}. \end{aligned} \quad (10)$$

In this case,

$$V = a^3\Big[\tfrac{3}{2}\sqrt{3}x + \sqrt{3}\alpha - \tfrac{\sqrt{3}}{2}(x'\tfrac{\sqrt{3}}{2})^2 - \tfrac{\alpha}{6}(x'\tfrac{\sqrt{3}}{2})^3 - \sqrt{3}\alpha\big[x''(1-\tfrac{x'}{4})\big]^3\Big], \quad (11)$$

so that,

$$a = \left[\frac{V}{\tfrac{3}{2}\sqrt{3}x + \sqrt{3}\alpha - \tfrac{\sqrt{3}}{2}x(x'\tfrac{\sqrt{3}}{2})^2 - \tfrac{\alpha}{6}(x'\tfrac{\sqrt{3}}{2})^3 - \sqrt{3}\alpha\big[x''(1-\tfrac{x'}{4})\big]^3}\right]^{1/3}.$$

The fractional surface areas f can be described by:

$$f_{10\bar{1}0} = \frac{a^2\Big[6x - \tfrac{\sqrt{3}}{2}x(x'\tfrac{\sqrt{3}}{2})\Big]}{S}, \quad (12)$$

$$f_{11\bar{2}0} = \frac{a^2\Big[6x(x'\sqrt{3}2) + \sqrt{3}\alpha x^2(x'\tfrac{\sqrt{3}}{2})^2\Big]}{S}, \quad (13)$$

and,

$$f_{10\bar{1}l} = \frac{a^2\Big[3x^2\sqrt{3+4\alpha^2} - 24A - 3\sqrt{3+4\alpha^2}[x''(1-\tfrac{x'}{4})]^2\Big]}{S}.$$

Note that this set of equations is not a general case that can be used for the simple prismatic shape, as $l = 0$ will result in a singularity, and one should use the set for the simple case (above).