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Nucleation and Growth of $\text{BaF}_x\text{Cl}_{2-x}$ Nanorods

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The tentative mechanism of the nucleation and growth of BaF_xCl_{2-x} nanorods

Fundamental equation of surface chemical thermodynamics (SCT) (eq 1) may not be accurate enough for a quantitative description of a crystallization process in the nanometer regime, but it should provide us with a starting point.

$$dG = -SdT + Vdp + gds + \sum_{i=1}^n m_{Bi} dn_{Bi} \dots\dots\dots (1)$$

Where **S** is the surface area of nanocrystals; **g** is the specific surface energy, also called the surface tension; **m_b** is the chemical potential of each component; T is the absolute temperature; p is pressure; V is the volume of the materials, and S is the entropy of the system. A series of solvothermal syntheses in the work were fixed at an immobile temperature, such as 160° for Ba₂F₃Cl nanorods and nanowires. Thus, T is consistent, that is, dT = 0. Moreover, the total volume of each autoclave is considered approximately to be the same, so is the solvent volume. Therefore, the pressure (p) is nearly unchanged, thus, dp = 0. After the discussion, eq 1 converts to eq 2.

$$dG = gds + \sum_{i=1}^n m_{Bi} dn_{Bi} \dots\dots\dots (2)$$

Under conditions of high adsorbate coverage (ligands/surfactant), it has been shown that **g** is dominated by the chemical potential of the adsorbate (**m_{ads}**).¹

$$g \approx g_0 - (m_{ads} - m'_{ads}) \Gamma_{max} \dots\dots\dots (3)$$

Where **g₀** refers to the specific surface energy of pristine interface; **m'_{ads}** is defined as the value of **m_{ads}** when **g = g₀**; and **Γ_{max}** is the saturated surface adsorbate density. A basic assumption is that the entire surface of nanocrystals is saturated by ligands/surfactants. The whole system has reached equilibrium in all likelihood after 24 hours aged. The chemical potential of the surface of nanocrystals (**m_{ads(surface)}**) is equal to that of solution (**m_{solution}**). The chemical potential of the adsorbate can be expressed as

$$m_{ads(surface)} = m_{solution} = m_0^p + RT \ln a_{ligands / surfactants} + \int_{p^0}^p V_m^\infty dp \dots\dots\dots (4)$$

Because pressure in this process is constant, that is dp = 0, we can change eq 4 to eq 5

$$m_{ads(surface)} = m_{solution} = m_0^p + RT \ln a_{ligands / surfactants} \dots\dots\dots (5)$$

The solvent activity (**a_{ligands / surfactants}**) is attributed to the concentration of oleic acid, and it's also a constant as a result of the unaltered concentration of oleic acid. The abundance of oleic acid leads to a tremendous absolute value of **a_{ligands / surfactants}**. In principle, when **a_{ligands / surfactants}** is large enough, **g < 0** can be achieved. Because of the invariability of the concentration of oleic acid, **m_{solution}**, **m_{ads(surface)}** and **g** are all constants. In other word, the force of oleic acid combined with the nanocrystals surface is so vigorous as to expand the specific surface area of nanocrystals. The increasing of surface area is likely to stabilize the system. The impetus of this progress accounts for **g < 0**, which arises from the high enough concentration of oleic acid on the surface of nanocrystals. To integrate eq 2

$$\Delta G = g\Delta S + \int_i^f \sum_{i=1}^n m_{Bi} dn_{Bi} \dots\dots\dots (6)$$

Here, we assume that the process of subjoining raw materials is reversible, thereby contemplating **ΔG = 0**. Therefore,

$$-g\Delta S = \int_i^f \sum_{i=1}^n m_{Bi} dn_{Bi} \dots\dots\dots (7)$$

$$m_B = m_{B0}^{\ominus} + RT \ln a_B + \int_{p^{\ominus}}^p V_{Bm}^{\infty} dp \dots\dots\dots (8)$$

p is constant as discussed above. Since $g < 0$, $-g > 0$ is deserved; m is dependent on the activity of ions in solution.

$$m_B = m_{B0}^{\ominus} + RT \ln a_B + \int_{p^{\ominus}}^p V_{Bm}^{\infty} dp = m_{B0}^{\ominus} + RT \ln a_B \dots\dots\dots (9)$$

After changed the concentration of ions in the solution, $\sum \Delta m_B$ can be calculated by:

$$\sum \Delta m_B = \sum \Delta \ln a_B = \sum \Delta \ln x_B + \sum \Delta \ln g_B \dots\dots\dots (10)$$

$$I = \frac{1}{2} \sum m_i Z_i^2 \dots\dots\dots (11)$$

$$\ln g_B = -A |Z_+ Z_-| \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I \right] \dots\dots\dots (12)$$

Combine eq 10, eq 11 (ionic strength definition) and eq 12 (Davies equation):

$$\sum \Delta m_B = \sum \left(\ln \frac{x_{B2}}{x_{B1}} - A |Z_+ Z_-| \left(\left[\frac{\sqrt{I_2}}{1 + \sqrt{I_2}} - 0.30I_2 \right] - \left[\frac{\sqrt{I_1}}{1 + \sqrt{I_1}} - 0.30I_1 \right] \right) \right) \approx \sum \ln \frac{x_{B2}}{x_{B1}} > 0 \dots\dots\dots (13)$$

Apparently, $dn_B > 0$ So,

$$-g \Delta S = \int_i^f \sum_{i=1}^n m_{Bi} dn_{Bi} > 0 \dots\dots\dots (14)$$

Moreover, m_B is linear with $\ln c_{Bi}$, assuming

$$m_B = k \ln c_B + b \dots\dots\dots (15)$$

Replace m_{Bi} and n_{Bi} with c_{Bi} , after integrating:

$$-g \Delta S = \sum k \Delta [c_B (\ln c_B - 1)] \dots\dots\dots (16)$$

We can conclude from eq 16 that the raise of the concentration of raw materials conducts the expanding of nanocrystals surface area.

The deduction of Eq 10

The number of the surface atoms and the total atoms should be proportional to the surface area and the volume, respectively. If we define the surface atom ratio as d . Since the number of the surface atoms and the total atoms has proportional relationship with the surface area and the volume respectively, we tempted to calculate d for these BaF_xCl_{2-x} nanorods via surface area divided by the volume with several constants.

$$d = \frac{k_1(\text{total_area_of_nanorod})}{k_2(\text{volume_of_nanorod})} = \frac{k_1(2pr^2 + 2prl)}{k_2pr^2l} = \frac{k_1(2p(\frac{d}{2})^2 + 2p(\frac{d}{2})l)}{k_2p(\frac{d}{2})^2l} = 2k_3(\frac{1}{l} + \frac{2}{d})$$

k_1 , k_2 and k_3 are all proportional constants; r is the average radius of nanorods, that is half of the diameter.

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Figure S1. TEM image of LSS results depending on initiate concentrations of Ba^{2+} 0.1000mol/L. This is the origin TEM photo of Figure 2a. The vertically stacked and horizontal nanorods were highlighted by dashed ring.

Figure S2. Another raw TEM image of LSS results depending on initiate concentrations of Ba^{2+} 0.1000mol/L. The vertically stacked and horizontal nanorods were highlighted by dashed ring once more.

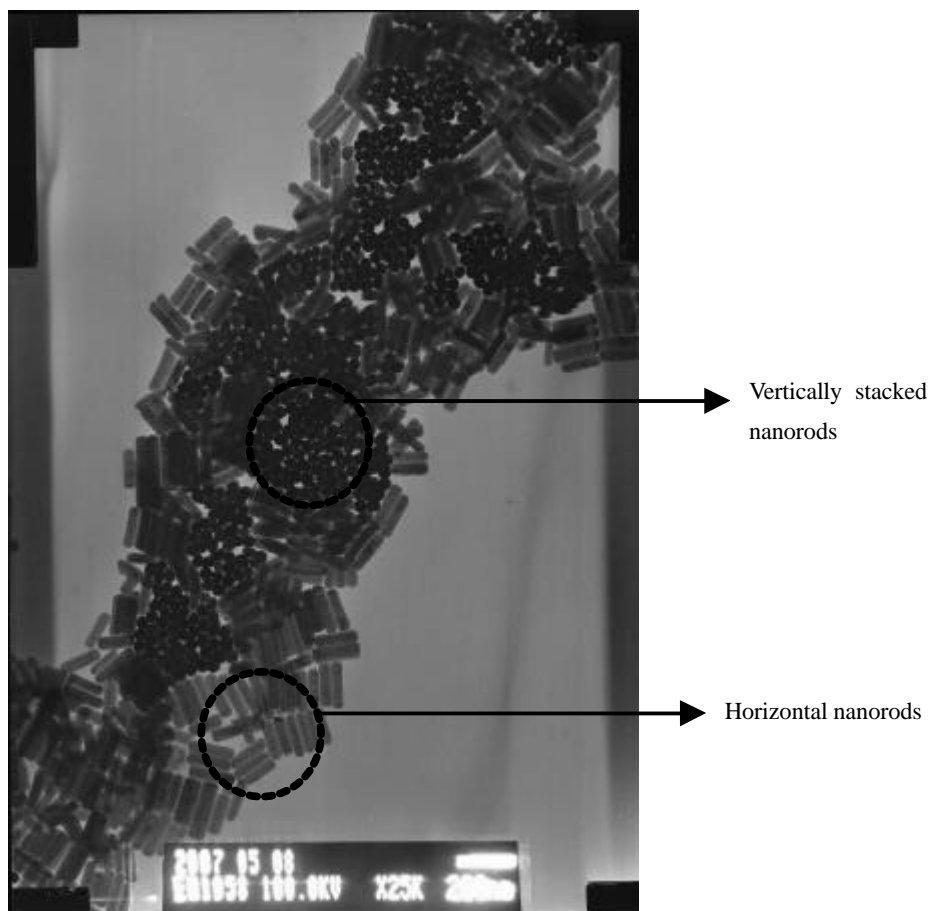


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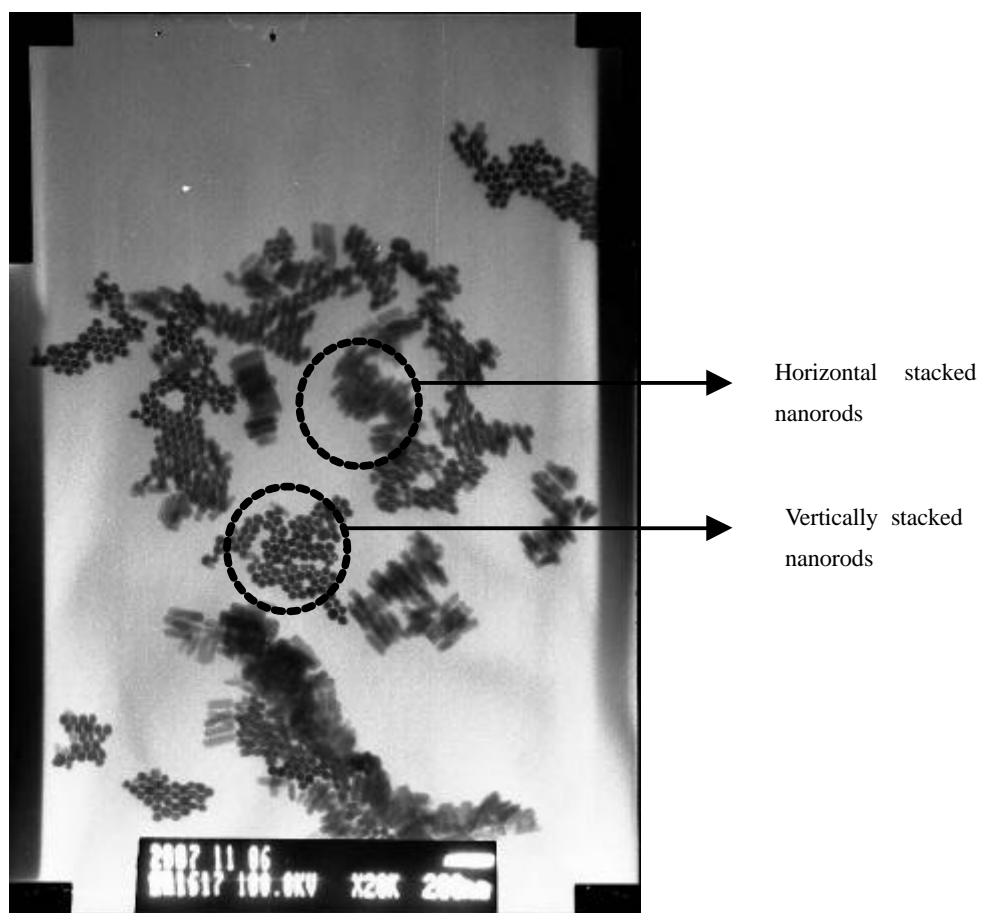


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Reference:

- [1] Z. Lin, B. Gilbert, Q. L. Liu, G. Q. Ren, F. Huang, *J. Am. Chem. Soc.* **2006**, *128*, 6126-6131.
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