Supporting information for

Self-Assembled ZnS Nanostructured Spheres: Controllable Crystal Phase and Morphology

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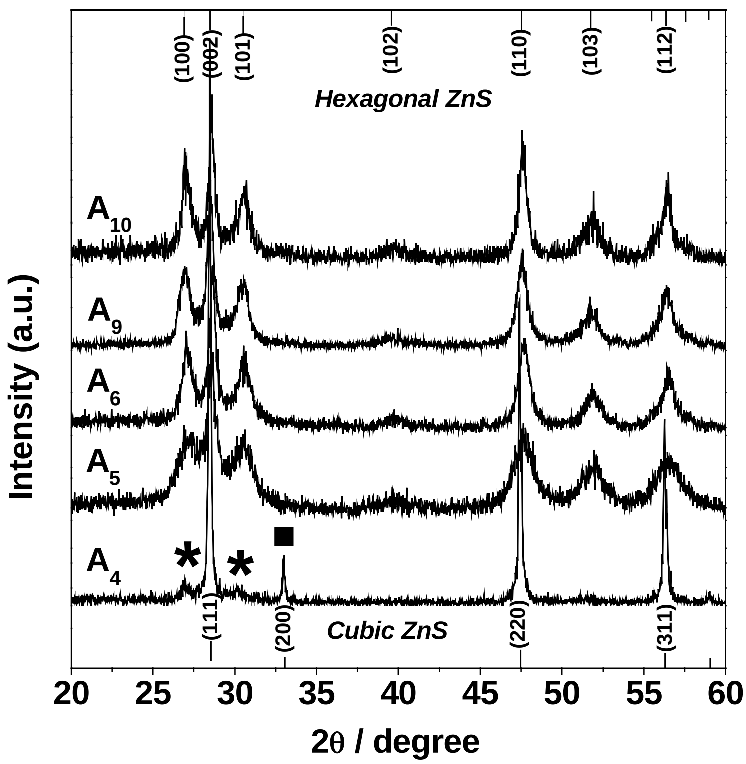

Figure S1 XRD patterns of ZnS samples (A_4-A_6, A_9 and A_{10}). (■) (200) diffraction peak of the cubic ZnS; (∗) (100) and (101) diffraction peaks of the hexagonal ZnS.

The eduction of the formula

Gibbs-Thompson equation (eq.1) indicates that the solubility of a small crystal is dependent on its size and surface energy.

$$S_r = S_b \exp(2\sigma V_m / rRT) \qquad (1)$$

Where r is the radius of the crystal, σ is the surface energy, V_m is the molar volume of the material, R is the gas constant, T is the absolute temperature, S_b and S_r are the solubility of bulk crystal and crystal with a radius *r*, respectively. Herein, the crystal is viewed as a sphere with a small radius r and a homogeneous surface. Replacing *r* with the crystal surface area $A = 4\pi r^2$ in eq. 1, then

$$S_A = S_b \exp(4\pi^{1/2} V_m \sigma / RTA^{1/2}) \qquad (2)$$

Where, S_A and S_b are the solubility of a crystal with a small surface area A and bulk crystal, respectively. Equation 2 indicates that the solubility of a small crystal is also dependent on its surface area and surface energy.

Dissolution is a process occurring on the surface of a crystal and is +related to surface features of a crystal. Therefore, it is reasonable to consider the solubility of a crystal as the solubility of the surface. For a small anisotropic crystal with the surface made up of a series of planes, the solubility of the crystal is the summation of those from a series of planes. The solubility of a specific plane in a small crystal can be described by Equation 3 educed from Equation 2.

$$S_A = S_b \exp(4\pi^{1/2} V_m \sigma_A / RTA^{1/2}) \qquad (3)$$

Where, σ_A is the surface energy of a specific plane, S_A and S_b are the solubility of a specific plane with a small surface area A and the same plane on bulk crystal, respectively. Suppose $C = S_b\, exp(4\pi^{1/2}V_m/RT)$, C may be regarded as a constant at a specific temperature due to neglectable difference in S_b for different planes on a bulk crystal. Replacing C into eq.2, then

$$S_A = C \exp(\sigma_A / A^{1/2}) \qquad (4)$$