Supporting Information

Ammonia-induced Seed Layer Transformations in A Hydrothermal Growth Process of Zinc Oxide Nanowires

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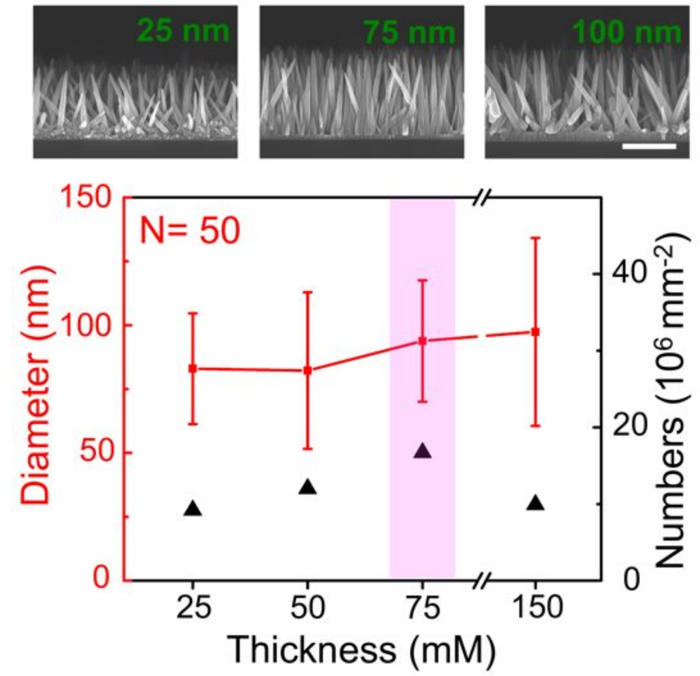

Figure S1 SEM images, diameter and areal density of ZnO nanowires grown with various seed layer thickness. The data was taken with growth time for 3 h and without NH_3. (scale bar = 1 μm).

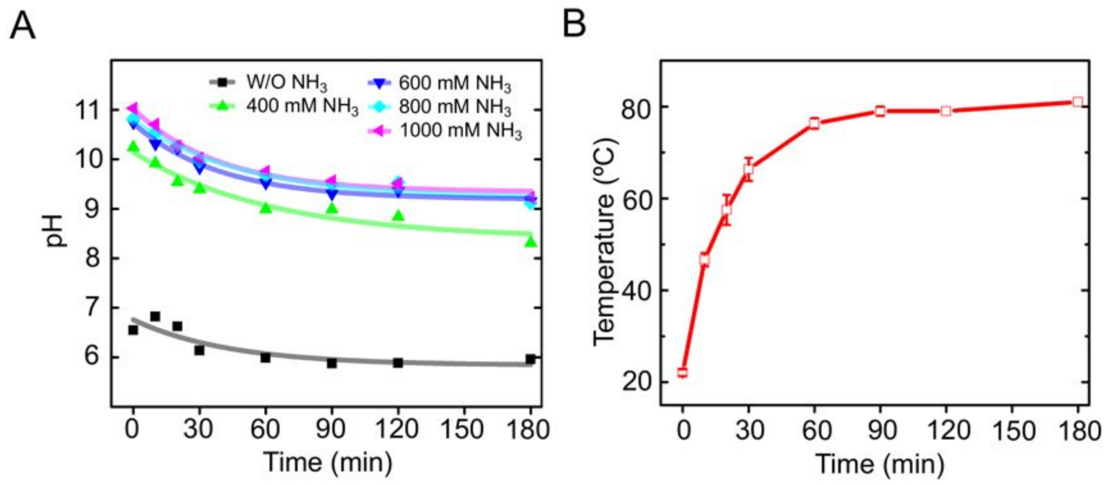

Figure S2 pH value and temperature of growth solution over time.

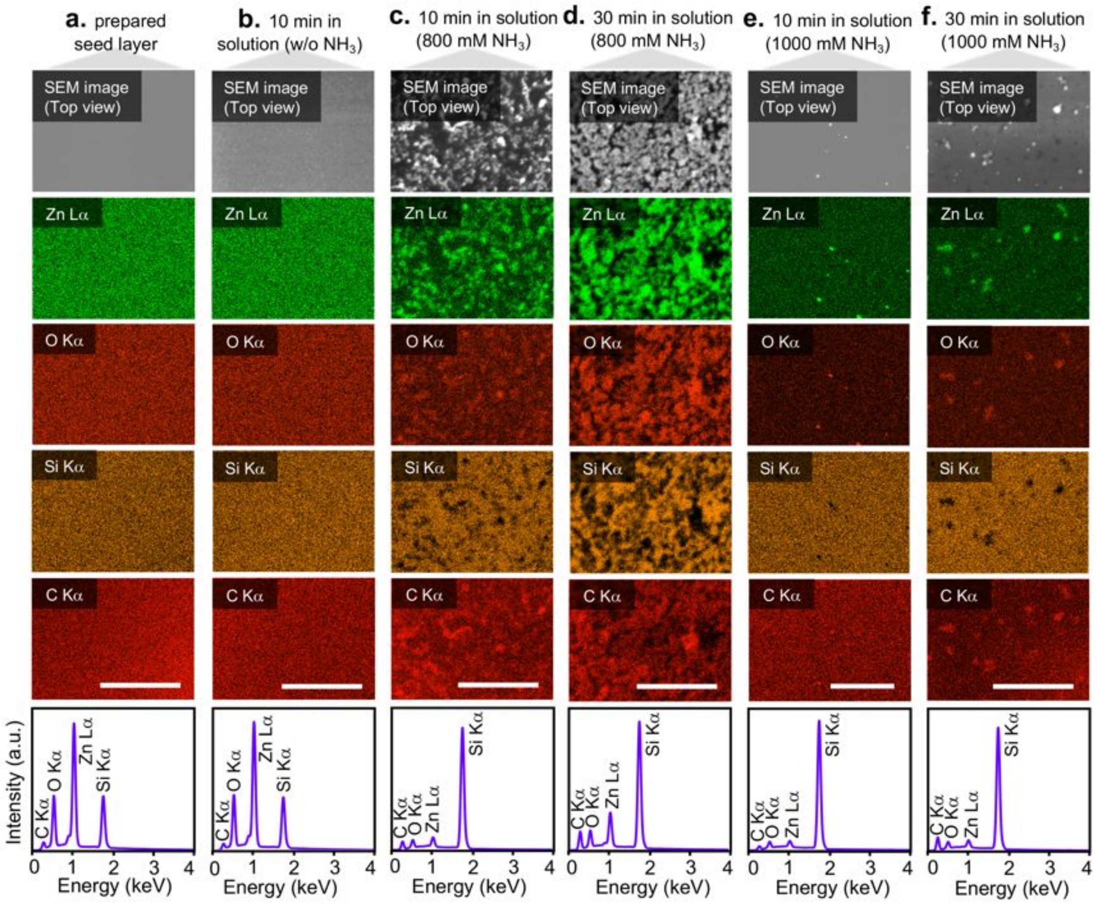

Figure S3 EDS mapping analysis of seed layer on silicon substrate after immersing into growth solution with varied ammonia concentration for 10 and 30 min, respectively (a, b, c, d, f scale bar = 1 μm; e scale bar = 5 μm).

S4 Thermodynamic calculation of Zn(II) solubility in aqueous solutions.

The solubility of Zn(II) (y axes) calculate from relevant chemical equilibria is the maximum concentration of zinc ions without precipitating ZnO in solution, that is, the total concentration of zinc ions in all soluble zinc-containing compounds at equilibrium.

Consider the relevant reaction

$$aA + bB \rightleftharpoons cC + dD, \tag{1.1}$$

for which

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}. \tag{1.2}$$

This relationship is known as the law of mass action, where K_{eq} is the equilibrium constant for the reaction 1.1. In 1.2, [A], [B], [C] and [D] are activities of each species (in dilute solution, the activity is assumed to be equal to equilibrium concentration approximatively); a, b, c and d are stoichiometric numbers. Known the equilibrium constant K_{eq} at 298.15 K (25 ºC) refer to [1] and [2], all the concentrations of zinc-containing compounds as a function of temperature, pH, and total ammonia concentration can be solved. The solubility of ZnO is then calculated as the sum of the concentration of zinc ions in all soluble zinc-containing compounds at equilibrium.

For the solubility of ZnO at other temperatures (e.g., 333.15 K in this work), we calculate the K_{eq} from

$$ln\frac{K_{eq(T_2)}}{K_{eq(T_1)}} = -\frac{\Delta_r H_m^{\ominus}}{R}(\frac{1}{T_2} - \frac{1}{T_1}), \tag{1.3}$$

where $K_{eq(T_1)}$ is defined as equilibrium constant at temperature T_1, $K_{eq(T_2)}$ is defined as equilibrium constant at temperature T_2; $\Delta_r H_m^{\ominus}$ is standard molar reaction enthalpy change. According to Hess's Law

$$\Delta_r H_m^{\ominus} = \sum_B \left[\mu_B \Delta_f H_m^{\ominus}(B)\right], \tag{1.4}$$

where $\Delta_f H_m^{\ominus}$ is enthalpy of formation, μ_B is stoichiometric number. We assume that $\Delta_r H_m^{\ominus}$ is independent of temperature, which is often a very reasonable approximation. In current work, we obtain the K_{eq} at 333.15 K (60 ºC) base on known K_{eq} at 298.15 K (25 ºC.) and calculated $\Delta_r H_m^{\ominus}$, and then calculate the sum of zinc ions concentration at 333.15 K.

[1] Richardson, J. J.; Lange, F. F. Controlling low temperature aqueous synthesis of ZnO. 1. Thermodynamic analysis. *Cryst. Growth Des.* **2009**, *9*, 2570-2575.

[2] Joo, J.; Chow, B. Y.; Prakash, M.; Boyden, E. S.; Jacobson, J. M. Face-selective electrostatic control of hydrothermal zinc oxide nanowire synthesis. *Nat. Mate.* **2011**, *8*, 596-601.

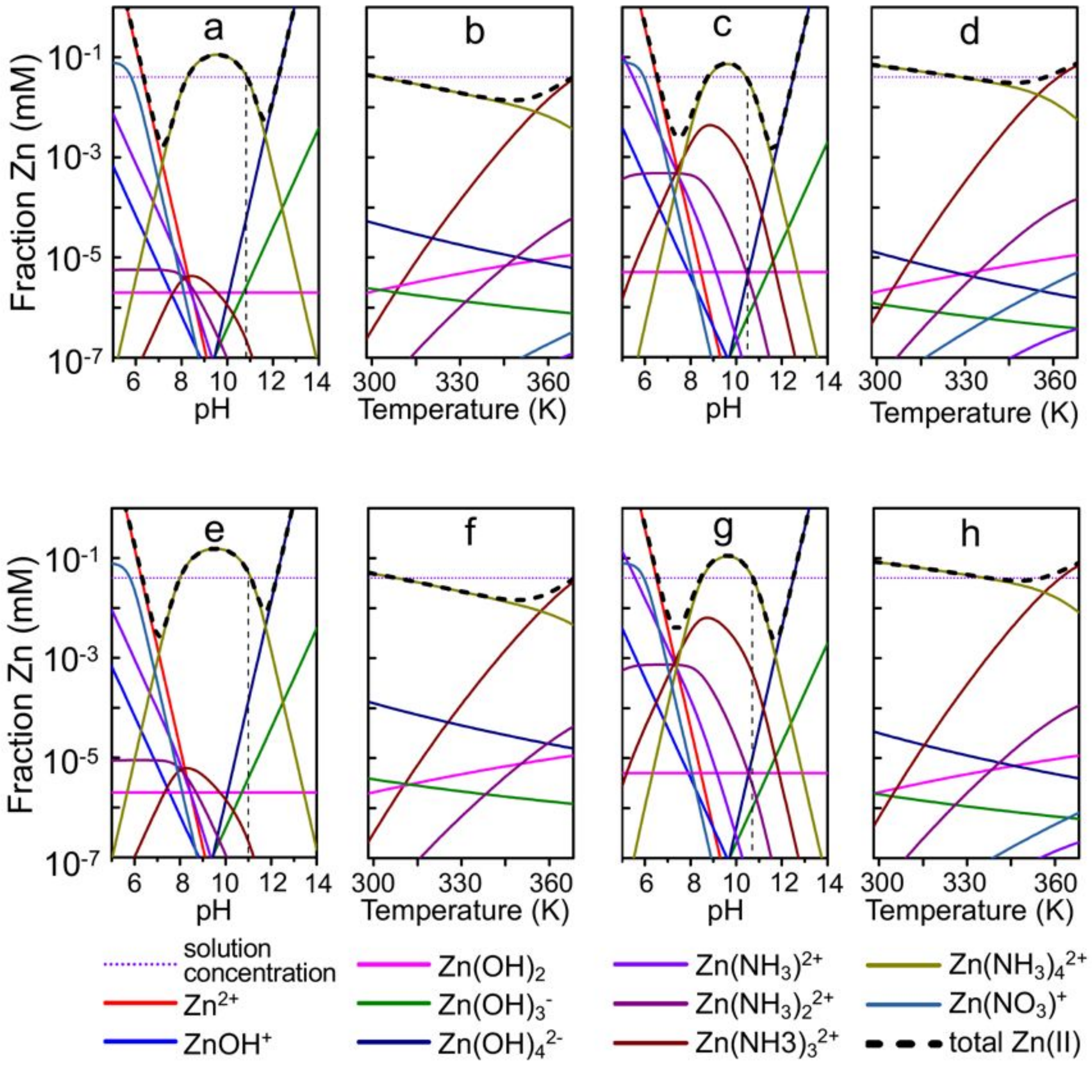

Figure S5 Speciation of dissolved Zn(II) versus pH and temperature in growth solution. **a**. Solution with 800 mM ammonia, 25 ºC (298 K). **b**. Solution with 800 mM ammonia, pH 10.8 (measured value at 25 ºC). **c**. Solution with 800 mM ammonia, 60 ºC (333 K). **d**. Solution with 800 mM ammonia, pH 10.5 (measured value at 60 ºC). **e**. Solution with 1000 mM ammonia, 25 ºC (298 K). **f**. Solution with 1000 mM ammonia, pH 11.0 (measured value at 25 ºC). **g**. Solution with 1000 mM ammonia, 60 ºC (333 K). **h**. Solution with 1000 mM ammonia, pH 10.7 (measured value at 60 ºC). Vertical dash line in a, c, e and g are measureed pH value.