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SUPPORTING INFORMATION

The Role of Polarity and Surface Energy in the Growth Mechanism of ZnO from Nanorods to Nanotubes

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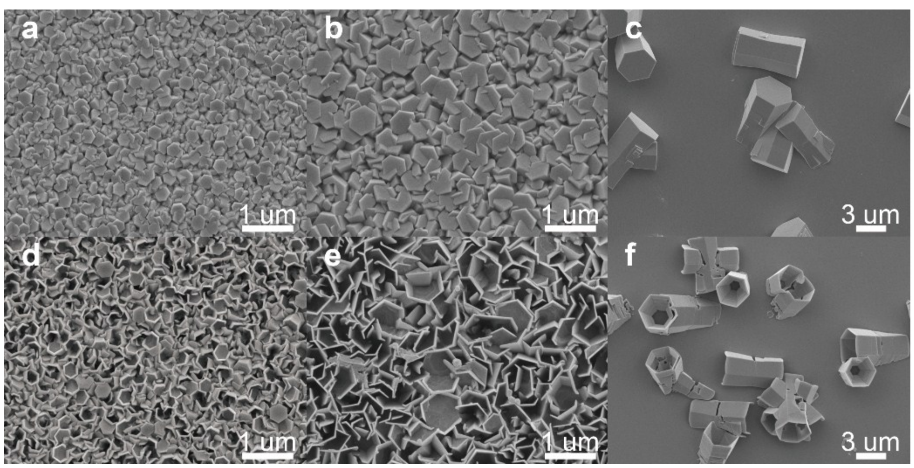

Figure S1. The SEM images of nanorods fabricated in acidic bath by adding HCl at (a)pH 6.2, (b) pH 5.9, (c) pH 5.0. After KOH etching, the etched morphologies of nanorods of (d) pH 6.2 (f) pH 5.9, (c) pH 5.1.

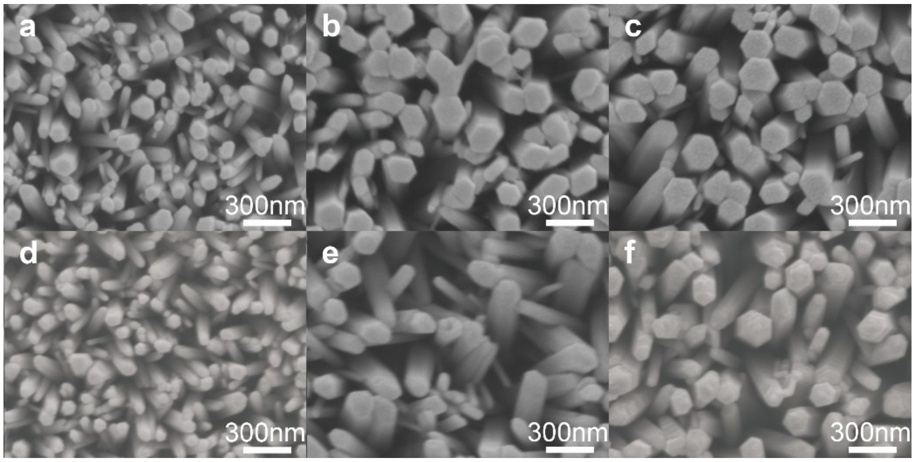

Figure S2. The SEM images of nanorods fabricated in acidic bath by adding NH_3 at (a) pH 9.8, (b) pH 10.1, (c) pH 10.2. After KOH etching, the etched morphologies of nanorods of (d) pH 9.8 (f) pH 10.1, (c) pH 10.2

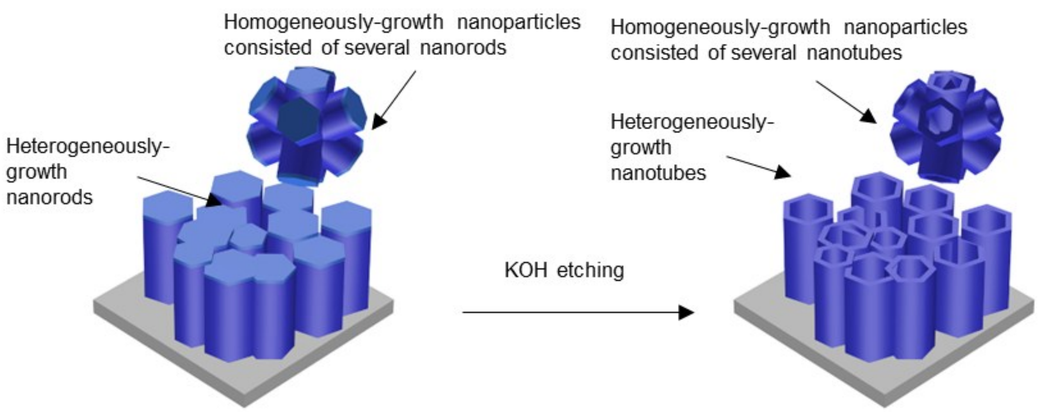

Figure S3. The schematic diagram of homogenously-grown nanoparticles and heterogeneously-growth of ZnO nanorods. The homogenously-grown nanoparticles consist of several nanorods before etching and nanotubes after etching.

In thermodynamic model of predominance, the stability constants are adopted from Hubert et al.[1] and Goux et al.[2] The detailed calculation method has been mentioned in the book written by Benjamin.[3]

Temperature (°C)	Log K_1	Log K_2	Log K_3	Log K_4	Log K_5	Log K_6	Log K_7	Log K_8
25	6.17	10.08	14.26	15.49	2.43	4.92	7.48	9.26
50	6.47	10.13	13.83	14.90	2.30	4.59	6.91	8.42
60	6.59	10.17	13.73	14.74	2.26	4.47	6.69	8.10
70	6.71	10.23	13.64	14.61	2.23	4.36	6.48	7.78
80	6.83	10.29	13.59	14.50	2.21	4.25	6.27	7.46
90	6.95	10.36	13.55	14.43	2.20	4.15	6.06	7.15

List of equilibrium in the chemical bath stability constant

$$Zn^{2+} + OH^{-} \rightleftharpoons Zn(OH)^{+} \qquad K_1 \qquad (S1)$$

$$Zn^{2+} + 2\,OH^{-} \rightleftharpoons Zn(OH)_2 \qquad K_2 \qquad (S2)$$

$$Zn^{2+} + 3\,OH^{-} \rightleftharpoons Zn(OH)_3^{-} \qquad K_3 \qquad (S3)$$

$$Zn^{2+} + 4\,OH^{-} \rightleftharpoons Zn(OH)_4^{-} \qquad K_4 \qquad (S4)$$

$$Zn^{2+} + NH_3 \rightleftharpoons Zn(NH_3)^{2+} \qquad K_5 \qquad (S5)$$

$$Zn^{2+} + 2\,NH_3 \rightleftharpoons Zn(NH_3)_2^{2+} \qquad K_6 \qquad (S6)$$

$$Zn^{2+} + 3\,NH_3 \rightleftharpoons Zn(NH_3)_3^{2+} \qquad K_7 \qquad (S7)$$

$$Zn^{2+} + 4\,NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} \qquad K_8 \qquad (S8)$$

By the conservation principle to this chemical bath system, the total concentration of Zinc ions is equal to the sum of the concentrations of all Zinc ions species, below:

$$[Zn] = [Zn^{2+}] + [Zn(OH)^{+}] + [Zn(OH)_2] + [Zn(OH)_3^{-}] + [Zn(OH)_4^{2-}] + [Zn(NH_3)^{2+}] + [Zn(NH_3)_2^{2+}] + [Zn(NH_3)_3^{2+}] + [Zn(NH_3)_4^{2+}]$$

By using the eq. S1-9, we can calculate the distribution of each Zinc complex ions species.

$$\frac{[Zn^{2+}]}{[Zn]} = 1/\{1 + K_1[H^+]^{-1}10^{-14} + K_2[H^+]^{-2}10^{-28} + K_3[H^+]^{-3}10^{-42} + K_4[NH_3][H^+]^{-1} + K_5[NH_3][H^+]^{-1} + K_6[NH_3]^2[H^+]^{-2} + K_7[NH_3]^3[H^+]^{-3} + K_8[NH_3]^4[H^+]^{-2}\} \quad (S1)$$

$$\frac{[Zn(OH)^{+}]}{[Zn]} = 1/\{K_1^{-1}[H^+]1 \ldots 10^{-42} + \{K_5K_1^{-1}[\ldots 10^{14} + K_8K_1^{-1}[NH \ldots$$

$$\frac{[Zn(OH)_2]}{[Zn]} = 1 \ / \ \{K_2^{-1}[H^+]^2 10^{28} + K_1K_2^{-1}[H^+]10^{14} + 1 + K_3K_2^{-1}[H^+]^{-1}10^{-14} + K \ldots \quad (S3)$$

$$\frac{\left[Zn(OH)_3^-\right]}{[Zn]}$$

$$= 1 \ \Big/ \ \{K_3^{-1}[H^+]^3 10^{42} + K_1K_3^{-1}[H^+]^2 10^{28} + K_2K_3^{-1}[H^+]10^{14} + 1 + K_4K_3^{-1}[H^+]^{-1} 10^{-14} + \left\{K_5K_3^{-1}[NH_3][H^+]^3 10^{42}\right\} + K_6K_3^{-1}[NH_3]^2[H^+]^3 10^{42} + K_7K_3^{-1}[NH_3]^3[H^+]^3 10^{42} + K_8K_3^{-1}[NH_3]^4[H^+]^3 10^{42}\} \qquad (S4)$$

$$\frac{\left[Zn(OH)_4^{2-}\right]}{[Zn]}$$

$$= 1 \ \Big/ \ \left\{K_4^{-1}[H^+]^4 10^{56} + K_1K_4^{-1}[H^+]^3 10^{42} + K_2K_4^{-1}[H^+]^2 10^{28} + K_3K_4^{-1}[\right. \qquad (S5)$$

$$\frac{\left[Zn(NH_3)^{2+}\right]}{[Zn]}$$

$$= 1 \ \Big/ \ \left\{K_5^{-1}[NH_3]^{-1} + K_1K_5^{-1}[NH_3]^{-1}[H^+]^{-1}10^{-14} + K_2K_5^{-1}[NH_3]^{-1}[H\right. \qquad (S6)$$

$$\frac{\left[Zn(NH_3)_2^{2+}\right]}{[Zn]}$$

$$= 1 \ \Big/ \ \left\{K_6^{-1}[NH_3]^{-2} + K_1K_6^{-1}[NH_3]^{-2}[H^+]^{-1}10^{-14} + K_2K_6^{-1}[NH_3]^{-2}[H\right. \qquad (S7)$$

$$\frac{\left[Zn(NH_3)_3^{2+}\right]}{[Zn]}$$

$$= 1 \ \Big/ \ \left\{K_7^{-1}[NH_3]^{-3} + K_1K_7^{-1}[NH_3]^{-3}[H^+]^{-1}10^{-14} + K_2K_7^{-1}[NH_3]^{-3}[H\right. \qquad (S8)$$

$$\frac{\left[Zn(NH_3)_4^{2+}\right]}{[Zn]} = 1 \ / \ \{K_8^{-1}[NH_3]^{-4} + K_1K_8^{-1}[NH_3]^{-4}[H^+]^{-1}10^{-14} + K_2K_8^{-1}[NH_3]^{-4}[H \quad (S9)$$

References

1. Hubert, C.; Naghavi, N.; Canava, B.; Etcheberry, A.; Lincot, D. Thermodynamic and Experimental Study of Chemical Bath Deposition of Zn(S,O,OH) Buffer Layers in Basic Aqueous Ammonia Solutions. Cell Results with Electrodeposited $CuIn(S,Se)_2$ Absorbers. *Thin Solid Films* **2007**, *515*, 6032-6035.

2. Goux, A.; Pauporté, T.; Chivot, J.; Lincot, D. Temperature Effects on ZnO Electrodeposition. *Electrochim. Acta* **2005**, *50*, 2239-2248.

3. Benjamin, M. M. *Water chemistry;* Waveland Press: 2014; 363-430.