Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information:

CuO nanowires growthon Cu_2O by in-situ thermal oxidation in air

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SI-1. Derivation of the Eq.(6)

The relationship between the size of a embryo(or the number of molecules in a embryo) and the radius of the embryo is[1]

$$n = \frac{4\pi}{3} r^3 \overline{\rho} \qquad \text{(S1)}$$

Here $\overline{\rho} = \rho N_A/M$, ρ is the density of CuO, N_A is Avagadro's number and M is molecular weight. Then the free energy of forming a nucleus can be expressed as

$$\Delta G = -n\Delta\mu + 4\pi r^2 \gamma = -n\Delta\mu + 4\pi\gamma \left(\frac{3n}{4\pi\overline{\rho}}\right)^{2/3} \qquad \text{(S2)}$$

Second oreder partial derivative of ΔG at n=n* is

$$\left.\frac{\partial^2 \Delta G}{\partial n^2}\right|_{n=n^*} = -\frac{8}{9}\pi\gamma \left.\left(\frac{3}{4\pi\overline{\rho} n^2}\right)^{2/3}\right|_{n=n^*} = -\frac{\overline{\rho}^2 \Delta\mu^4}{32\pi\gamma^3} \qquad \text{(S3)}$$

Substituting eq S2 and eq S3 into eq 3, one obtains

$$J = Z\beta^* N \exp(\frac{-\Delta G^* - E_a^{CuO}}{kT})$$
$$= \left[\frac{\bar{\rho}^2}{64\pi^2 k}\frac{\Delta\mu^4}{T\gamma^3}\right]^{1/2} \beta^* N \exp\left[\left(-\frac{16\pi\gamma^3}{3\bar{\rho}^2\Delta\mu^2} - E_a^{CuO}\right)/kT\right] \quad \text{(S4)}$$

Under the condition of experimental temperature, the free energy change, Δμ, can be expressed as[2]

$$\Delta\mu \approx \frac{L_V}{T_C}(T_C - T) \equiv a(T_C - T) \quad \text{(S5)}$$

Where L_V is the latent heat, T_C is the critical transformation temperature. Also in the temperature window of the growth of CuO nanowires, the interfacial tension, γ, is in proportion to (T_C-T) approximately[3], in order to simplify the derivation process, a proportional constant b is setted

$$\gamma = b(T_C - T) \quad \text{(S6)}$$

As the density of nanowires is proportional to the nucleation rate, i.e. $P_{NW} \propto J$, we substitute eq S5 and eq S6 into eq S4

$$P_{NW} \propto \left(\frac{T_C - T}{T}\right)^{1/2} \exp\left[\left(-\frac{\eta b^3(T_C - T)}{3a^2} - E_a^{CuO}\right)/kT\right] \quad \text{(S7)}$$

After setting the fitting parameter $\xi = \frac{\eta b^3}{3a^2}$, the final result is obtained

$$P_{NW} \propto \left(\frac{T_C - T}{T}\right)^{1/2} \exp\left[\left(-\xi(T_C - T) - E_a^{CuO}\right)/kT\right] \quad \text{(6)}$$

SI-2. The determination of E_a^{CuO}

The phase transition rate is determined by Gibbs free energy, nucleation rate, nucleation site number, diffusion field and so on. As a phenome-nological treatment, the relationship between phase transition rate V and annealing temperature is given by[2]

$$V = \frac{d\omega}{dt} = K \exp\left(-\frac{\Delta G^{*} + E_a^{CuO}}{RT}\right) \qquad \text{(S8)}$$

Where ω is the mass variation, t is the reaction time, K is a constant, R is the molar gas constant with a value of 8.3145 $Jmol^{-1}K^{-1}$. The eq S8 also can be rewritten as

$$\ln V = \ln\left(\frac{d\omega}{dt}\right) = \ln K - \frac{\Delta G^{*}}{RT} - \frac{E_a^{CuO}}{RT} \qquad \text{(S9)}$$

At the experimental temperature, the critical free energy ΔG* approaches to zero. Then the slope of curve ln(dω/dt)-(1/T) can be represented as

$$\tan\theta = \frac{\partial \ln(d\omega/dt)}{\partial(1/T)} = -\frac{\Delta G^{*}}{RT} - \frac{1}{RT} \times \frac{\partial \Delta G^{*}}{\partial(1/T)} - \frac{E_a^{CuO}}{RT} \approx -\frac{E_a^{CuO}}{RT} \qquad \text{(S10)}$$

The data between the yellow dash in Figure S1a are chosen to fit the eq S10. So the the value of E_a^{CuO} is determined to be 46.652kJ/mol.

Figure S1. (a)Thermo-gravimetric analysis(TGA) curves(red boxes) of Cu_2O slices and the derivative curves of TGA(green line). (b)Arrenius plot of ln(dω/dt) versus the inverse annealing temperature(1/T).

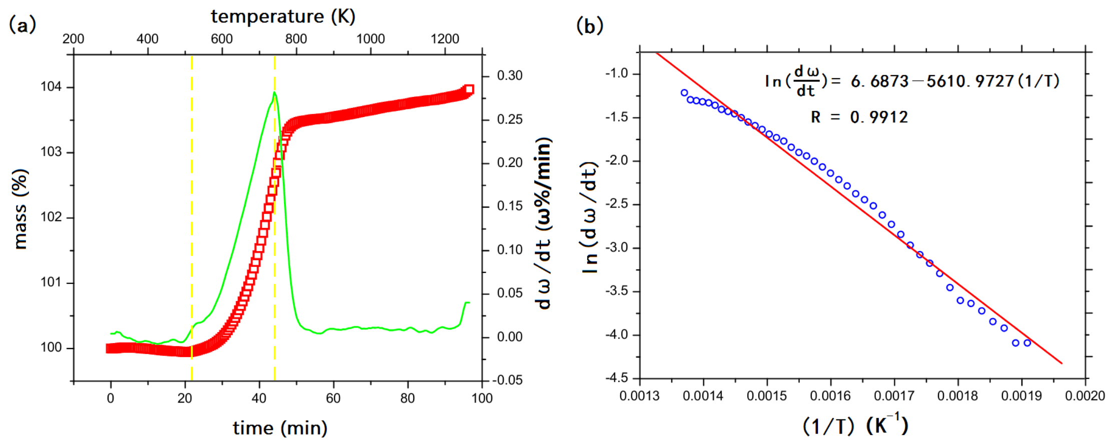


Figure S2. The inhomogeneous crystallines on the surface of CuO nanowire(in yellow dash boxes)

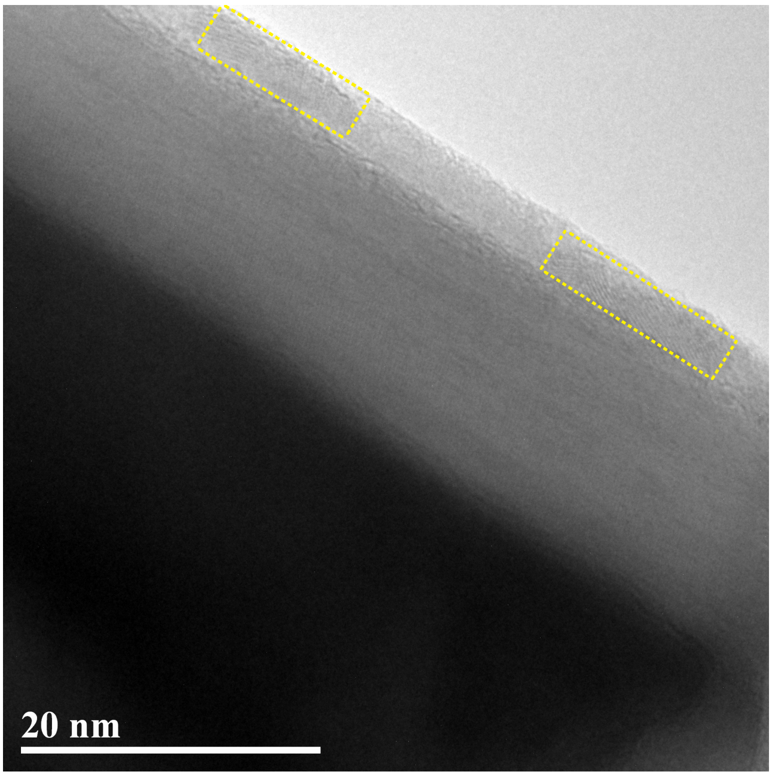
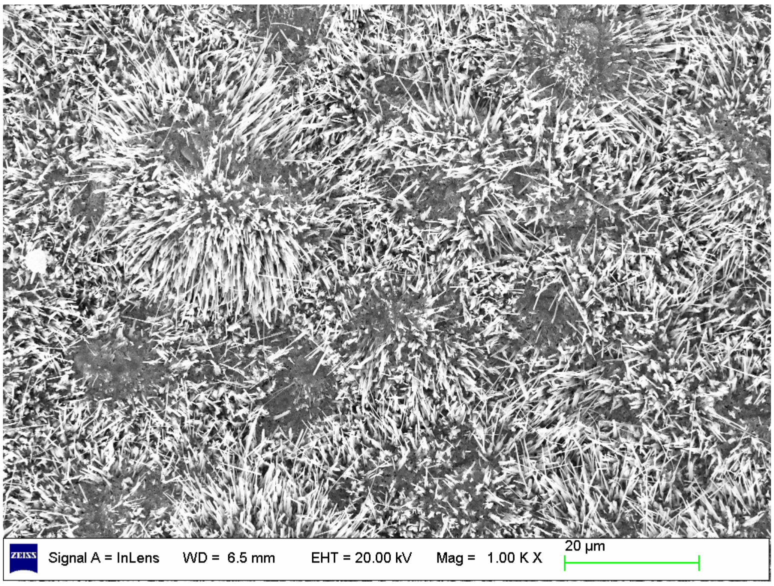


Figure S3. Morphology of the annealed compressed copper powder slices at 600℃ in air for 6h



References

(1) Adamson, A. W. *Physical Chemistry of Surfaces 6th Ed*; Wiley: New York, U.S., 1997.

(2)Cheng, X. N.;Dai, Q. X.; Shao, H. H. *Solid-state transformation and diffusion in materials;* Chemical industry press: Beijing, China, 2006.

(3) Luo, J. X. *Controllable synthesis and optical properties of some semiconductor nanomaterials*; Xiamen University: Xiamen, China, 2010.