Thermodynamic functions and growth constants of web-like ZnO nanostructures

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Web-like ZnO nanostructures have been successfully synthesized using the potassium nitrate route at various temperatures to simplify conventional preparation methods. The structures and morphologies of the as-prepared products were characterized by X-ray powder diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The results showed that the reaction temperature was an important parameter, and that there was a feedback effect between nano-structure and growth parameters, combined with *in situ* micro-calorimetry, the reaction rate constants of the three systems were found to have been: 2.43×10^{-6} , 2.70×10^{-8} and $3.12 \times 10^{-7} \text{ s}^{-1}$ respectively. Furthermore, based on the relationship governing the potential differences between nano- and bulk ZnO, thermodynamic functions of nano-ZnO such as standard molar entropy ($S_{\text{m,ZnO(nano)}}^{\ominus}$), standard molar Gibbs free energy of formation ($\Delta_f G_{\text{m,ZnO(nano)}}^{\ominus}$), and standard molar enthalpy of formation ($\Delta_f H_{\text{m,ZnO(nano)}}^{\ominus}$) have been calculated by the electrochemical method.

nano-thermodynamics, nano-ZnO, thermal properties, microcalorimetry, thermodynamic functions

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Semiconductor nanomaterials have attracted considerable attention in recent years: ZnO, an important functional semiconductor with a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, is widely used in optoelectronic devices, ultraviolet lasers, sensors, etc. To date, various properties of ZnO nanostructures have been reported in the literatures [1–6], but there is little information on their thermodynamic properties.

Researches into the growth process of nanomaterial has mainly focused on the following categories: classical crystallization kinetic theory [7], *in situ* electron microscopy [8–10], scanning tunneling microscopy [11,12], *in situ* ellipsometry [13], and *in situ* synchrotron X-ray absorption [14]. However, these techniques are unable to provide a complete description of the entire nanomaterial growth

process: this justified the need to develop simple practical methods of obtaining thermodynamic functions.

In the present study, the one-step synthesis and characterization of ZnO nanomaterials without a catalyst is described at three different temperatures; micro-calorimetric techniques were used to obtain their reaction rate constant (k) and order of reaction (n). In addition, thermodynamic functions of nano-ZnO were calculated by an electrochemical method, which was found to have been more accurate and reliable.

1 Experimental

1.1 Chemicals

Analytical grade potassium nitrate (KNO_3) and ethanol were purchased from Xilong Chemical Reagent Factory and used without further purification. Deionized water was used

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to prepare all the aqueous solutions.

1.2 Preparation of the initial synthesis solutions

The equipment used for ZnO synthesis is shown in Figure 1. For system A, 5 mL of 0.1 mol L⁻¹ KNO₃ was placed in a small glass tube above the zinc electrode, which was in a larger glass tube. After establishing equilibrium at 283.15 K, the thermogram was recorded. The samples were thoroughly washed with absolute ethanol and deionizer water to remove all impurities. The open circuit potential was measured by an electrochemical workstation (Gaoss Union EC550, Wuhan Gao Shi Rui Lian Technology Co., Ltd, China) at 288.15, 293.15, 298.15, 303.15 and 308.15 K, respectively. Nano-ZnO, bulk ZnO and saturated calomel electrode were used as working, auxiliary and reference electrode, respectively. The conditions for systems B and C were similar to those for system A except for the equilibrium temperatures which were 288.15 K and 298.15 K, respectively.

The energy evolution was measured using a micro-calorimeter (RD496-CK2000, MianYang CP Thermal Analysis Instrument Co., Ltd, China). The structure and technical parameters of this calorimeter have been described previously [15]. The as-prepared products were characterized by X-ray powder diffraction (XRD, Philips PW 1710 with Cu K α radiation, $\lambda=1.5406$ Å) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F).

2 Results and discussion

2.1 Methodology

In essence, a chemical reaction is a process with old chemical bonds breaking and new chemical bonds forming: the final state of a reaction is not related to the size and shape of reactants. Nano-ZnO and bulk ZnO can be considered to be different materials albeit ones with the same chemical composition. Therefore, according to the thermodynamic potential function method [16], the thermochemical cycle is described in Figure 2.

This leads to the following equations:

$$S_{m,ZnO(bulk)}^{\ominus} - S_{m,ZnO(nano)}^{\ominus} = \Delta_r S_m^{\ominus} = zF \left(\frac{\partial E^{\ominus}}{\partial T} \right)_P, \quad (1)$$

Figure 1 Reaction equipment used in this study.

Figure 2 Schematic diagram of thermochemical cycle between the nano-ZnO and bulk ZnO reaction systems.

$$\Delta_f G_{m,ZnO(bulk)}^{\ominus} - \Delta_f G_{m,ZnO(nano)}^{\ominus} = \Delta_r G_m^{\ominus} = \Delta_r G_{m,ZnO(nano)}^{\ominus} - \Delta_r G_{m,ZnO(bulk)}^{\ominus} = (\Delta_r G)_{T,P} = -W_{r,max} = -zE^{\ominus}F, \quad (2)$$

$$\Delta_r H_m^{\ominus} = \Delta_f H_{m,ZnO(bulk)}^{\ominus} - \Delta_f H_{m,ZnO(nano)}^{\ominus} = \Delta_r H_{m,ZnO(nano)}^{\ominus} - \Delta_r H_{m,ZnO(bulk)}^{\ominus}, \quad (3)$$

$$(\Delta_r G)_{T,P} = -W_{r,max} = -zE^{\ominus}F = \Delta_r H_m^{\ominus} - T\Delta S^{\ominus}, \quad (4)$$

where $S_{m,ZnO(nano)}^{\ominus}$, $\Delta_r G_{m,ZnO(nano)}^{\ominus}$ and $\Delta_r H_{m,ZnO(nano)}^{\ominus}$ represent the standard molar entropy, standard molar Gibbs free energy and standard molar enthalpy of reaction of nano ZnO, respectively. $S_{m,ZnO(bulk)}^{\ominus}$, $\Delta_r G_{m,ZnO(bulk)}^{\ominus}$ and $\Delta_r H_{m,ZnO(bulk)}^{\ominus}$ represent the standard molar entropy, standard molar Gibbs free energy, and standard molar enthalpy of reaction of bulk ZnO, respectively. The related reactions are as follows:

Accordingly, the overall reaction between Zn and KNO₃ is given by

2.2 Characterizations

All of the powder XRD diffraction peaks in Figure 3(a) can be indexed to hexagonal wurtzite ZnO with cell parameters of $a=3.249$ Å and $c=5.206$ Å (JCPDS card No. 36-1451). No impurity peaks were detected, indicating the formation of pure products. The FE-SEM images in Figure 3(b)–(d) indicated that the products had web-like structures.

2.3 Calculation of k and n

Generally, the energy change of A reaction system is strongly dependent on the reaction's progression. An RD496-III type micro-calorimeter, based on thermokinetic theory, provided simultaneous thermodynamic and kinetic information. The thermokinetic equation for irreversible

Figure 3 (a) XRD pattern of the as-prepared ZnO. FE-SEM images of the web-like ZnO nano for systems A (b), B (c) and C (d), respectively.

reactions at constant temperature and pressure is [17]:

$$\ln\left(\frac{1}{H_0} \frac{dH_i}{dt}\right) = \ln k + n \ln\left(1 - \frac{H_i}{H_0}\right), \quad (5)$$

where H_0 is the total enthalpy of the reaction the ZnO nano-crystal growth process, k is the rate constant in s^{-1} , n is the reaction order and dH_i/dt is the enthalpy change rate. Thus, the rate constant can be obtained through regression analysis of the thermokinetic data (Figure 4).

After nucleation, it was necessary to maintain a slower growth rate to ensure directional arrangement of particles, and then to form an exquisite web-like structure. Too fast a growth rate resulted in the particles around the mesh growing quickly, with the result that the meshes decreased and eventually disappeared. The reaction rate constants lay in the sequence $k_{283.15} > k_{288.15} < k_{298.15}$, thus if a lower growth rate was required for the formation of the web-like structure (Table 1), this suggested a feedback-style regulation of growth rate.

As shown in Table 1, the lower growth temperature of system A resulted in a greater growth rate ($2.43 \times 10^{-6} s^{-1}$). Therefore, the particles could accumulate quickly in the growth process of ZnO. According to the aforementioned feedback regulation, the randomness of system A increased, which led to the increase of the standard molar entropy. The tiny branches of nano-zinc of system B could grow along different directions, due to the original induction of zinc-based material. With the tiny branches' growth, they would become inter-related and formed a web-like body. In the following process of morphological evolution, the particles of zinc gradually filled the vacancies and formed stable structures. Consequently, the standard molar entropy was smaller. The stability of intermediate decreased with the increased growth temperature, and led to the reaction being quicker. The growth rate of system C was smaller than those of system A. Therefore, a more-refined process of regulation could proceed. The surface effect of nanomaterials was fully embodied and the standard molar entropy increased.

Figure 4 Microcalorimetric heat curve of nano ZnO at the crystal growth stage for systems A (a), B (b) and C (c), respectively.

Table 1 Linear fitting data of crystal growth process for nano ZnO at different temperature

T (K)	k (s^{-1})	n	R	SD
283.15	2.43×10^{-6}	155.45	0.9996	5.81×10^{-3}
288.15	2.70×10^{-8}	30.89	0.9992	6.55×10^{-3}
298.15	3.12×10^{-7}	355.90	0.9993	6.90×10^{-3}

2.4 Calculation of chemical thermodynamic functions for systems A, B and C

Electrode reaction: (+): $ZnO_{(nano)} + 2e^- + H_2O = Zn_{(s)} + 2OH^-$

(-): $Zn_{(s)} - 2e^- + 2OH^- = ZnO_{(bulk)} + H_2O$

Battery net reaction: $ZnO_{(nano)} \rightarrow ZnO_{(bulk)}$

The equation as $E^\ominus = a + bT$ was obtained by a linear fit of the $E^\ominus - T$ plots (Figure 5):

$$\left(\frac{\partial E^\ominus}{\partial T}\right)_p = b \text{ V} \cdot K^{-1}, \quad E^\ominus = a + 298.15b \rightarrow E^\ominus = |c| \text{ V}. \quad (6)$$

According to eqs. (1)–(4), the thermodynamic functions were obtained thus:

$$S_{m,ZnO(nano)}^\ominus = S_{m,ZnO(nano)}^\ominus - zF\left(\frac{\partial E^\ominus}{\partial T}\right)_p (S_{m,ZnO(bulk)}^\ominus) \\ = 43.65 \text{ J K}^{-1} \text{ mol}^{-1} [18] = (43.65 - 192970b) \text{ J K}^{-1} \text{ mol}^{-1} \quad (7)$$

$$\Delta_f G_{m,ZnO(nano)}^\ominus = \Delta_f G_{m,ZnO(bulk)}^\ominus + zE^\ominus F (\Delta_f G_{m,ZnO(bulk)}^\ominus = \\ -320.52 \text{ kJ mol}^{-1} [18]) (-320.52 + 192.970|c|) \text{ kJ mol}^{-1} \quad (8)$$

$$\Delta_f H_{m,ZnO(nano)}^\ominus = \Delta_f H_{m,ZnO(bulk)}^\ominus - T\Delta S^\ominus + zE^\ominus F \\ (\Delta_f H_{m,ZnO(bulk)}^\ominus = -350.46 \text{ kJ mol}^{-1} [18]) \\ = (-350.46 + 192.970|c| - 57534.0055b) \text{ kJ mol}^{-1} \quad (9)$$

Values of $\Delta_f H_{m,ZnO(nano)}^\ominus$, $\Delta_f G_{m,ZnO(nano)}^\ominus$ and $S_{m,ZnO(nano)}^\ominus$ for nano-ZnO can be calculated from eqs. (7)–(9), respec-

tively. The results are listed in Table 2.

The values of $\Delta_f G_{m,ZnO(nano,283.15)}^\ominus$ at different temperatures were all higher than those of $\Delta_f G_{m,ZnO(bulk)}^\ominus$. In the growth process of nano-ZnO, the atoms of noumenon moved to the surface. As a result, nano-ZnO with a high specific surface area was formed, and the increasing surface energy was attributed to surface Gibbs free energy. The surface structure of systems A, B and C differed from one to another, so the Gibbs free energy of formation of the three systems showed different values.

The fact that $\Delta_f H_{m,ZnO(nano,283.15)}^\ominus$, $\Delta_f H_{m,ZnO(nano,288.15)}^\ominus$ and $\Delta_f H_{m,ZnO(nano,298.15)}^\ominus$ were higher than $\Delta_f H_{m,ZnO(bulk)}^\ominus$ meant that less heat was generated in the production of nano-ZnO than was the case for bulk zinc oxide. In addition, parts of surface and noumenon atoms rearranged in the process of morphological evolution, which would absorb heat. Both the configurations of atoms and structures varied across the systems examined. The endothermic level was different. Therefore, there were differences among the standard molar enthalpy of formation of the three systems.

3 Conclusion

In summary, the reaction rate constants for the formation of web-like ZnO nanostructures were variable as a consequence of non-equilibrium growth of nanomaterials. The results suggested a feed-back effect between the reticular structure and the growth rate. Through building the relationship between standard molar enthalpies of formation of nano-ZnO and bulk ZnO, the reaction rate constants were derived for three different temperatures of formation; $S_{m,ZnO(nano)}^\ominus$, $\Delta_f G_{m,ZnO(nano)}^\ominus$ and $\Delta_f H_{m,ZnO(nano)}^\ominus$ could be obtained by determining the potential difference between nano ZnO and bulk ZnO at different temperatures.

Figure 5 Plots of open circuit potential-temperature for system A (a), B (b) and C (c), respectively.**Table 2** The data of chemical thermodynamic functions

T (K)	a	b (10^{-3})	R	SD (10^{-4})	$S_m^\ominus$ ($J K^{-1} mol^{-1}$)	$\Delta_f G_m^\ominus$ ($kJ mol^{-1}$)	$\Delta_f H_m^\ominus$ ($kJ mol^{-1}$)
283.15	0.453	-2.07	0.9995	5.88	443.10	-288.76	-199.60
288.15	0.391	-1.93	0.9996	4.91	416.08	-285.00	-203.90
298.15	0.516	-2.08	0.9995	6.15	445.03	-300.39	-210.66

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