



# Size-dependent surface thermodynamic properties of silver oxide nanoparticles studied by electrochemical method

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## ABSTRACT

The unique chemical properties of nanostructured materials are dependent on the surface thermodynamic properties which depend on the size of nanoparticles. But the quantitative influences of particle size on the surface thermodynamic properties of nanoparticles are not clear completely. In this paper, the relations between surface thermodynamics properties and particle size of nanoparticles have been deduced, and the method of obtaining the surface thermodynamic properties by electrochemistry has also been proposed. Experimentally, the electrode potentials and the electrode temperature coefficients of nano-Ag<sub>2</sub>O electrodes with different particle sizes were determined at different temperatures. The results indicate that with the size of Ag<sub>2</sub>O nanoparticles decreasing, the molar surface Gibbs energy, the molar surface entropy and the molar surface enthalpy correspondingly increase. Moreover, when the particle radius exceeds 10 nm, these physical quantities are all linearly related with the reciprocal of average particle radius, and the experimental results are consistent with the theoretical formulas.

## Introduction

Nanothermodynamics have been developed by Hill in the early 1960s, and he nicely deduced the basic thermodynamic equations for nanoscale materials [1–4]. Currently, the thermodynamic properties of nanoparticles made of both the bulk phase and the surface phase are well known [5–7]. Almost all of the particular properties of nanostructured materials are derived from the effect of surface thermodynamics [8]. Understanding and predicting the thermodynamic properties

of nanoparticles are essential for the practical applications of nanostructured materials [9–11]. What is more, a few studies of surface thermodynamic properties of nanoparticles have been reported. Navrotsky et al. [12–14] obtained the surface enthalpies of nano-Akaganeite, nanophase titanium dioxide and nanophase zinc oxide for the first time, using a series of calorimetric measurements. Furthermore, the surface Gibbs energy, surface enthalpy and surface entropy of nano-ferrihydrite and nano-calcium molybdate were also successfully acquired by some researchers [15, 16].

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All of the works mentioned above show that the effect of particle size on the surface thermodynamic properties remains unclear, which is due to the difficulties in determining the parameters of surface thermodynamic properties [6, 17]. To date, how to acquire surface thermodynamic properties of nanoparticles is still an intractable problem. So, it is essential to establish a new method of determining the surface thermodynamic properties of nanoparticles.

In this paper, the relations between surface thermodynamic properties and nanoparticle sizes were deduced. The method of obtaining the surface thermodynamic properties by electrochemistry was proposed and the surface thermodynamic properties of nano-Ag<sub>2</sub>O with different particle sizes were obtained using the electrochemical method. Meanwhile, the influences of particle sizes on surface thermodynamic properties were also discussed.

### Theoretical relations of surface thermodynamic properties with nanoparticle size

Under constant temperature and pressure, the surface Gibbs energy of spherical nanoparticles can be expressed as

$$G^s = \sigma A = \sigma 4\pi r^2 N, \quad (1)$$

where the superscript *s* denotes the surface quantities;  $\sigma$ ,  $A$ ,  $r$ ,  $N$  are the surface tension, interfacial area, particle radius and the numbers of nanoparticles, respectively.

The amount of substance of nanoparticle is

$$n = (4\pi r^3 N \rho) / (3M), \quad (2)$$

where  $M$  and  $\rho$  are the molar mass and the density of the particle, respectively.

Then, molar surface Gibbs energy can be obtained by combining Eqs. (1) with (2),

$$G_m^s = \frac{G^s}{n} = \frac{3\sigma M}{\rho r}. \quad (3)$$

It can be seen from the above formula that the surface tension  $\sigma$  is related to particle radius  $r$ , but the effect of particle size on surface tension will be neglected when the radius of the nanoparticles exceeds 10 nm [18, 19]. So, the surface Gibbs energy increases with the decreasing particle radius.

Surface enthalpy  $H_m^s$  of nanoparticles can be derived by Gibbs–Helmholtz equation,

$$H_m^s = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{G_m^s}{T} \right) \right]_p = \frac{3\sigma M}{\rho r} - \frac{3MT}{\rho r} \left[ \left( \frac{\partial \sigma}{\partial T} \right)_p + \frac{2\sigma\alpha}{3} \right], \quad (4)$$

where subscript  $p$  denotes the pressure,  $\alpha$  is the volume expansion coefficient, namely  $\alpha = 1/V_m(\partial V_m/\partial T)_p$  and  $V_m$  denotes the molar volume of nanoparticles.

As is observed from Eq. (4),  $(\partial \sigma / \partial T)_p$  is usually a negative value, and the order of magnitude of volume expansion coefficient  $\alpha$  for nanocrystals is usually  $10^{-5}$  [20, 21], and therefore,  $\{(\partial \sigma / \partial T)_p + 2\sigma\alpha/3\}$  is a negative value. So, the molar surface enthalpy increases with the decreasing nanoparticle radius.

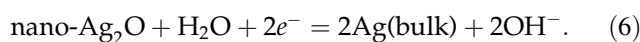
Similarly, the molar surface entropy  $S_m^s$  can be expressed as

$$S_m^s = - \left( \frac{\partial G_m^s}{\partial T} \right)_p = - \frac{3M}{\rho r} \left[ \left( \frac{\partial \sigma}{\partial T} \right)_p + \frac{2\sigma\alpha}{3} \right]. \quad (5)$$

So, in conclusion, it is obvious that there is a linear relationship between the surface thermodynamic properties (the molar surface Gibbs energy, the molar surface enthalpy and the molar surface entropy) and the reciprocal of particle radius when the radius exceeds 10 nm.

### A determination method of surface thermodynamic properties of nanoparticles by electrochemistry

The electrode reaction of nano-Ag<sub>2</sub>O is expressed as follows:



For chemical reaction in nanosystem, the change in molar Gibbs energy function can be expressed as Eq. (7) if both the bulk ( $\Delta_r G_m^b$ ) and the surface ( $\Delta_r G_m^s$ ) were taken into account [5]:

$$\Delta_r G_m = \Delta_r G_m^b + \Delta_r G_m^s. \quad (7)$$

Under constant temperature and pressure, Eq. (7) can be expressed as follows:

$$\Delta_r G_m = \sum_B \nu_B \mu_B^b + \sum_B \nu_B \mu_B^s, \quad (8)$$

where  $\nu_B$  denotes the stoichiometric number of component  $B$ ;  $\mu_B^b$  and  $\mu_B^s$  denote the chemical potential of

component *B* in bulk phase and surface phase, respectively.

Since there is only one dispersed phase (nano-Ag<sub>2</sub>O) in the electrode reaction, we can drive the change in molar surface Gibbs energy:

$$\Delta_r G_m^s = \sum_B \nu_B G_B^s = -G_{Ag_2O}^s = -(\partial G^s / \partial n_{Ag_2O})_{T,p}. \quad (9)$$

In the above-mentioned electrode reaction, the number of nanoparticles is invariable, but the particle radius has changed. So, the partial derivative of *G<sup>s</sup>* against *n* can be obtained by simultaneous Eqs. (1) and (2), and the partial molar surface Gibbs energy *G<sub>Ag<sub>2</sub>O</sub><sup>s</sup>* is given by

$$G_{Ag_2O}^s = (\partial G^s / \partial n_{Ag_2O})_{T,p} = (2\sigma M) / (\rho r). \quad (10)$$

Similarly, the partial molar surface enthalpy and the partial molar surface entropy of nanoparticles can be deduced as follows:

$$H_{Ag_2O}^s = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{G_{Ag_2O}^s}{T} \right) \right]_p = \frac{2\sigma M}{\rho r} - \frac{2MT}{\rho r} \left[ \left( \frac{\partial \sigma}{\partial T} \right)_p + \frac{2\sigma\alpha}{3} \right], \quad (11)$$

$$S_{Ag_2O}^s = - \left( \frac{\partial G_{Ag_2O}^s}{\partial T} \right)_p = - \frac{2M}{\rho r} \left[ \left( \frac{\partial \sigma}{\partial T} \right)_p + \frac{2\sigma\alpha}{3} \right]. \quad (12)$$

So, comparing Eqs. (3), (4), (5) to Eqs. (10), (11), (12), respectively, we can draw a conclusion that the molar surface quantities to partial molar surface quantities ratio is 3:2.

When the electrode reaction occurs reversibly, the change in molar Gibbs energy is equal to the reversible electric work, as follows:

$$\Delta_r G_m = -zFE, \quad (13)$$

where *z* is charge transfer number, *E* is the electrode potential in the electrode reaction and *F* is the Faraday constant.

According to Eq. (7), the electrode potential of a nanoelectrode can be expressed as follows:

$$E = -[\Delta_r G_m / (zF)] = E^b + E^s, \quad (14)$$

where *E<sup>b</sup>* is the electrode potential of ordinary electrode and *E<sup>s</sup>* is the surface electrode potential.

The change in molar surface Gibbs energy can be expressed as follows:

$$\Delta_r G_m^s = -zFE^s. \quad (15)$$

Applying Eqs. (10) and (15), the molar surface Gibbs energy of nano-Ag<sub>2</sub>O can be obtained as follows:

$$G_m^s = \left[ 3 / \left( 2G_{Ag_2O}^s \right) \right] = [3 / (2zFE^s)]. \quad (16)$$

Similarly, the molar surface entropy and the molar surface enthalpy of nano-Ag<sub>2</sub>O can be derived as follows:

$$S_m^s = 3 / 2S_{Ag_2O}^s = -3/2 \left[ zF(\partial E^s / \partial T)_p \right], \quad (17)$$

$$H_m^s = 3/2H_{Ag_2O}^s = 3/2 \left( zFE^s - zFT \left( \frac{\partial E^s}{\partial T} \right)_p \right). \quad (18)$$

The relation between electrode potential of nano-Ag<sub>2</sub>O electrode and particle radius can be expressed according to the theory of electrochemical thermodynamics for nanoelectrodes deduced by our research group [22, 23]:

$$E = E^b + E^s = E^b - \frac{2\nu_{Ag_2O} \sigma_{Ag_2O} M_{Ag_2O}}{zF \rho_{Ag_2O} r_{Ag_2O}}, \quad (19)$$

where the *ν<sub>Ag<sub>2</sub>O</sub>* denotes the stoichiometric number in the electrode reaction, *M<sub>Ag<sub>2</sub>O</sub>*, *ρ<sub>Ag<sub>2</sub>O</sub>*, *σ<sub>Ag<sub>2</sub>O</sub>* and *r<sub>Ag<sub>2</sub>O</sub>* are the molar mass, density, surface tension and particle radius of nano-Ag<sub>2</sub>O, respectively.

It is well known that the surface tension *σ* is related to particle radius *r*, but when the particle size of dispersed phase becomes larger (*r* > 10 nm), the effect is not significant, and the *σ* can be regarded as a constant approximately [17, 18]. Then, it can be seen from Eq. (19) that there is a linear relation between the electrode potential and the reciprocal of radius of nano-Ag<sub>2</sub>O.

When the particle radius tends to infinity, the electrode potential of ordinary electrode *E<sup>b</sup>* can be obtained. Furthermore, the surface electrode potential *E<sup>s</sup>* can also be obtained. Meanwhile, the surface temperature coefficient is obtained by linear fitting the surface electrode potentials at different temperatures, and the molar surface Gibbs energy, molar surface entropy and molar surface enthalpy of nano-Ag<sub>2</sub>O with different particle radii can be calculated using Eqs. (16), (17), (18), respectively.

## Experimental procedure

### Preparation method and process

Complex precipitation method was used to synthesize nano-Ag<sub>2</sub>O, using silver nitrate as raw materials and sodium hydroxide as precipitating agent. After

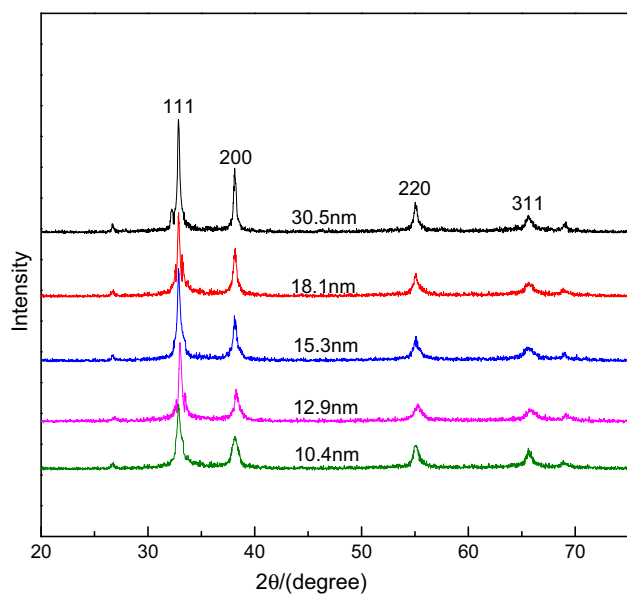
**Table 1** Particle radius of the nano-Ag<sub>2</sub>O synthesized in different conditions

No.	Stirring method	Reaction temperature/°C	Dispersing agent	AgNO <sub>3</sub> /mol L <sup>-1</sup>	Adding order	r/nm
1	Ultrasonic stirring	25	PVP	0.5	a	10.4
2	Ultrasonic stirring	20	PVP	0.5	a	12.9
3	Ultrasonic stirring	30	PEG	1.0	a	15.3
4	Ultrasonic stirring	20	PVP	0.5	b	18.1
5	Magnetic stirring	40	PVP	2.0	b	30.5

PVP polyvinyl pyrrolidone; PEG polyethylene glycol

<sup>a</sup> Drop the silver nitrate into the sodium hydroxide solution

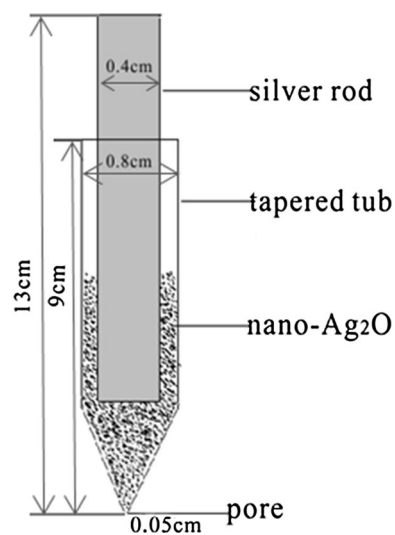
<sup>b</sup> Drop the sodium hydroxide solution into the silver nitrate

**Figure 1** XRD patterns of nano-Ag<sub>2</sub>O in experiment.

the reaction was completed, the nano-Ag<sub>2</sub>O particles were washed with distilled water and anhydrous ethanol, and then dried in the vacuum drying box for 30 h at 333 K. Nano-Ag<sub>2</sub>O particles with different sizes were obtained by changing the reaction concentration, adding order, stirring method, dispersing agent and the reaction temperature, which are shown in Table 1.

### Characterization of nano-Ag<sub>2</sub>O

The nano-Ag<sub>2</sub>O structure was characterized using a Germany Bluker D8 Advance Powder diffractometer (Cu K $\alpha$ ,  $\lambda = 0.154178$  nm), and the XRD spectrum is shown in Fig. 1. The average crystallite radius  $r^-$  of nano-Ag<sub>2</sub>O is the average value of different diffraction directions of the crystallite. The crystallite size was calculated by Scherrer formula based on the half

**Figure 2** Schematic of tapered glass tube electrode.

peak width of a characteristic diffraction peak. The crystallite sizes used in this experiment are 10.4, 12.9, 15.3, 18.1 and 30.5 nm, respectively.

### Preparation of nano-Ag<sub>2</sub>O electrode

The tapered glass tube was made by blowtorch and a piece of silver rod was inserted into the tube. The blocky nanoelectrode was fabricated by pouring the nanoparticles into the tube, and the schematic of nano-Ag<sub>2</sub>O electrode is shown in Fig. 2.

### Measurement of electrode potential

A 1.00 mol/L sodium hydroxide solution was prepared as electrolyte solution, and primary cell was composed of the saturated calomel electrode and nano-Ag<sub>2</sub>O electrode. Finally, the electromotive force of the cell was determined by compensation method using potentiometer. Then, nano-Ag<sub>2</sub>O electrode

**Table 2** Electrode potentials of nano-Ag<sub>2</sub>O electrodes at different temperatures

T/K	288.15	298.15	308.15	318.15	328.15
$\bar{r}/\text{nm}$					
Electromotive force of the primary cell/V					
30.5	0.107	0.111	0.119	0.125	0.130
18.1	0.150	0.156	0.162	0.167	0.173
15.3	0.172	0.177	0.183	0.188	0.192
12.9	0.211	0.215	0.219	0.223	0.225
10.4	0.241	0.243	0.246	0.249	0.252
SCE/V [24]	0.251	0.245	0.238	0.231	0.225
Electrode potential of nano-Ag <sub>2</sub> O/V					
30.5	0.358	0.356	0.357	0.356	0.355
18.1	0.401	0.401	0.400	0.398	0.398
15.3	0.423	0.422	0.421	0.419	0.417
12.9	0.462	0.460	0.457	0.454	0.450
10.4	0.492	0.488	0.484	0.480	0.477

SCE is the saturated calomel electrode

potential is equal to the electromotive force plus the saturated calomel electrode potential.

## Experimental results and discussion

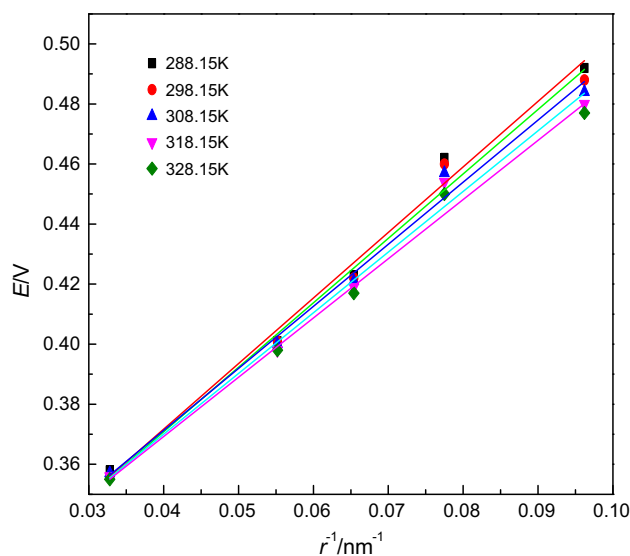
### Electrode potential and surface electrode potential

The electromotive forces of the primary cell and the electrode potentials of nanoelectrodes with different particle radii of Ag<sub>2</sub>O particles at different temperatures are shown in Table 2.

The relation between the electrode potentials of nano-Ag<sub>2</sub>O and particle sizes is shown in Fig. 3. It can be seen clearly that the electrode potentials of different temperatures were affected by particle sizes, which increase with the decreasing particle radius, and there are better linear relationships.

According to Eq. (19), the value of the electrode potential of ordinary electrode  $E^b$  was deduced from Fig. 3 when the particle radius tended to infinity. The surface electrode potential with different average particle radii of nano-Ag<sub>2</sub>O particles were calculated at different temperatures by combining the values of  $E^b$  and Eq. (19). The results are shown in Table 3.

The relations between the surface electrode potential of nano-Ag<sub>2</sub>O and temperature are shown in Fig. 4. It can be seen that the surface electrode potentials with different particle sizes were affected by temperature. The surface electrode potentials



**Figure 3** Electrode potential as a function of the reciprocal of average radius for nano-Ag<sub>2</sub>O at different temperatures.

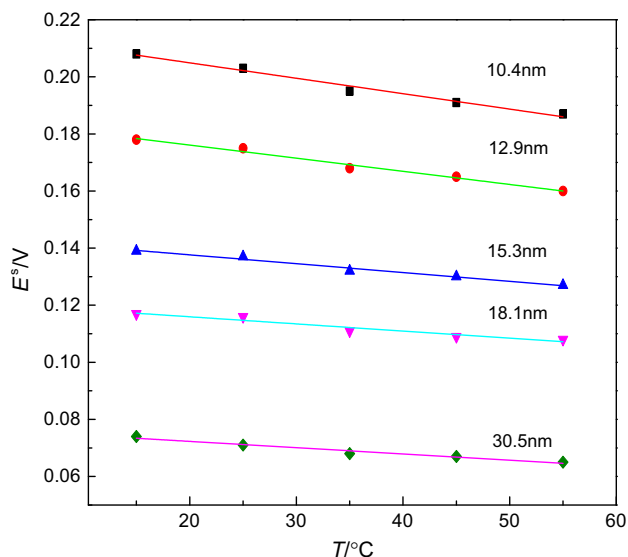
decrease with the increasing temperature, and there are better linear relationships. Therefore, the surface electrode potential and temperature coefficients of nano-Ag<sub>2</sub>O particles were evaluated from the slopes provided in Fig. 4 and are listed in Table 4.

### Molar surface Gibbs energy of nano-Ag<sub>2</sub>O

The molar surface Gibbs energy of nano-Ag<sub>2</sub>O can be directly determined from Eq. (16), and the values are given in Table 5.

**Table 3** Surface electrode potential of nano-Ag<sub>2</sub>O at different temperatures

$\bar{r}/\text{nm}$	$r^{-1}/\text{nm}^{-1}$	$E^s/\text{V}$				
		288.15 K	298.15 K	308.15 K	318.15 K	328.15 K
10.4	0.0962	0.208	0.203	0.195	0.191	0.187
12.9	0.0775	0.178	0.175	0.168	0.165	0.160
15.3	0.0654	0.139	0.137	0.132	0.130	0.127
18.1	0.0552	0.117	0.116	0.111	0.109	0.108
30.5	0.0328	0.074	0.071	0.068	0.067	0.065

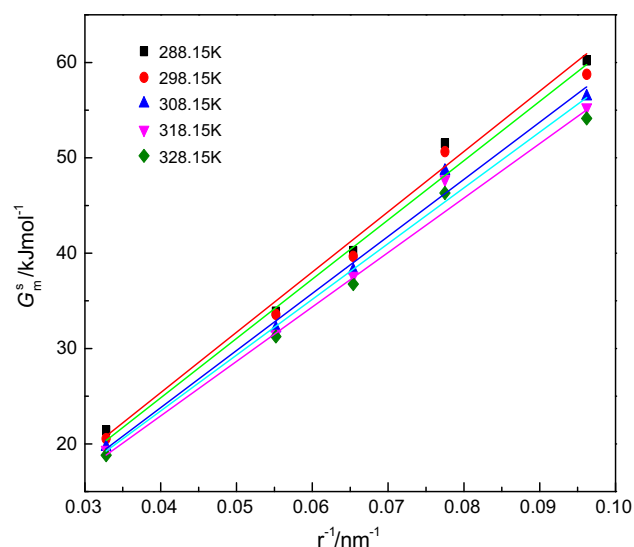
**Figure 4** Correlation between surface electrode potential and temperature of nano-Ag<sub>2</sub>O.**Table 4** Surface temperature coefficients of nanoelectrode

$\bar{r}/\text{nm}$	10.4	12.9	15.3	18.1	30.5
$(\partial E^s/\partial T)_p/10^{-4} \text{ V K}^{-1}$	-5.4	-4.6	-3.1	-2.5	-2.2

It is estimated that for the general metal nanoparticles, the order of magnitudes of  $\sigma$ ,  $M$  and  $\rho$  are  $10^0$ ,  $10^{-2}$ – $10^{-1}$  and  $10^3$ – $10^4$ , respectively. So, the Gibbs energy of metal spherical nanoparticles with different particle sizes can be calculated using Eq. (3).

**Table 5** Molar surface Gibbs energy with different particle sizes at different temperatures

$\bar{r}/\text{nm}$	$r^{-1}/\text{nm}^{-1}$	$G_m^s/(\text{kJ mol}^{-1})$				
		288.15 K	298.15 K	308.15 K	318.15 K	328.15 K
10.4	0.0962	60.21	58.76	56.44	55.29	54.13
12.9	0.0775	51.52	50.65	48.63	47.76	46.31
15.3	0.0654	40.23	39.66	38.21	37.63	36.76
18.1	0.0552	33.87	33.58	32.13	31.55	31.26
30.5	0.0328	21.42	20.55	19.68	19.39	18.81

**Figure 5** Molar surface Gibbs energy as a function of the reciprocal of average radius of nano-Ag<sub>2</sub>O at different temperatures.

Therefore,  $r = 10^{-6}$  m, the order of magnitude of  $G_m^s$  is  $10^{-3}$ – $10^{-1}$  kJ/mol.  $r = 10^{-9}$  m, and the order of magnitude of  $G_m^s$  is  $10^0$ – $10^2$  kJ/mol. The order of magnitude is in good accordance with the electrochemical experimental value of Table 5.

The plot of  $G_m^s$  versus  $r^{-1}$  is shown in Fig. 5.

It can be seen from Fig. 5 that the molar surface Gibbs energy increases with the decreasing particle size, which is in agreement with the theoretical

analysis of Eq. (3). The results indicate clearly that under constant pressure and temperature conditions, the smaller the particle sizes are, the higher the chemical activity and more unstable the nanoparticles will be.

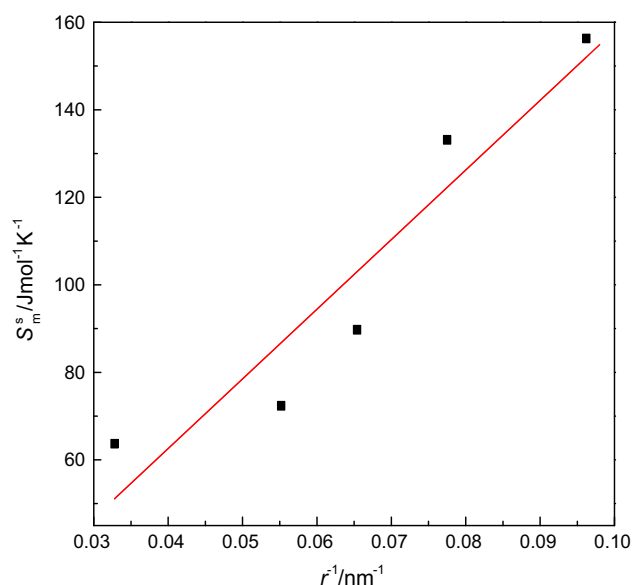
### Molar surface entropy and enthalpy of nano-Ag<sub>2</sub>O

According to the surface electrode potentials and the surface temperature coefficients, the molar surface entropy and enthalpy of nano-Ag<sub>2</sub>O are calculated using Eqs. (17) and (18); the results are shown in Table 6.

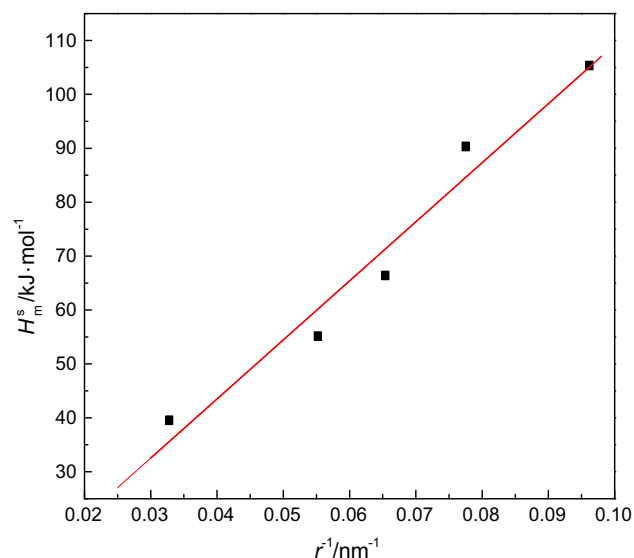
The relations between the molar surface entropy, the molar surface enthalpy, respectively, and the reciprocal of average particle radius can be obtained from the data of Table 6 and are shown in Figs. 6 and 7.

**Table 6** Surface thermodynamic properties of nanoelectrode reaction at 298.15 K

$\bar{r}/\text{nm}$	$r^{-1}/\text{nm}^{-1}$	$S_m^s/\text{J mol}^{-1} \text{K}^{-1}$	$H_m^s/\text{kJ mol}^{-1}$
10.4	0.0962	156.31	105.36
12.9	0.0775	133.15	90.35
15.3	0.0654	89.73	66.41
18.1	0.0552	72.36	55.15
30.5	0.0328	63.68	39.54



**Figure 6** Molar surface entropy of nano-Ag<sub>2</sub>O versus the reciprocal of average radius.



**Figure 7** Molar surface enthalpy of nano-Ag<sub>2</sub>O versus the reciprocal of average radius.

As illustrated in Figs. 6 and 7, it is obvious that when the radius of nanoparticles decreases, the molar surface entropy and the molar surface enthalpy increase, respectively, which are in agreement with the above-mentioned theoretical analysis of Eqs. (17) and (18). It also can be seen that when the particle radius tends to infinity, the molar surface entropy and the molar surface enthalpy can be viewed as zero.

### Conclusions

The above results show that the surface thermodynamic properties of nanoparticles are strongly affected by their size. With the decreasing particle radius of nano-Ag<sub>2</sub>O, the molar surface Gibbs energy, the molar surface entropy and the molar surface enthalpy increase, and there are better linear relations between them and the reciprocal of particle size. The experimental results are also in good agreement with the theoretical equations.

The theoretical equations and the influence regularities of particle size on the surface thermodynamic properties can provide both tools to guide experiments and a basis for testing the foundations. In this paper, the electrochemical determination of the surface thermodynamic properties of nanoparticles is reliable and accurate. Although the method is applied to the study on the surface thermodynamic

properties of nano-Ag<sub>2</sub>O, there is no reason to believe that its success is restricted to this nanomaterial.

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