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Phase composition controllable preparation of zirconia nanocrystals via solvothermal method

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ABSTRACT

Zirconia nanopowders are synthesized via solvothermal method at a temperature as low as 180 °C without any additives. The pure tetragonal zirconia transforms into nearly pure monoclinic zirconia gradually with the progressing of solvothermal reaction, and the morphology of as-prepared nanoparticles grows up from spherical to short rodlike. The results of crystallite size estimated from XRD patterns using Scherrer equation show that the size of monoclinic zirconia ranges from 10 nm to 50 nm, while the size of tetragonal zirconia is below 5 nm.

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1. Introduction

ZrO₂ has three crystal forms as follows: monolithic zirconia (m-ZrO₂), tetragonal zirconia (t-ZrO₂) and cubic zirconia (c-ZrO₂). The m-ZrO₂ is stable below 1170 $^\circ\text{C}$ and the c-ZrO₂ exists stable above 2370 °C. The pure t-ZrO₂ is considered to be stable in the range of 1170-2370 °C. Due to the martensitic phase transformation originated from volumetric change effect when tetragonal-tomonoclinic phase takes place [1,2], the partial stabilized t-ZrO₂ has been used extensively in ceramic because of its transformation toughening performance. In general, pure t-ZrO₂ is well known as a metastable phase at room temperature, and some oxides like Y₂O₃, Sc₂O₃ and MgO are usually used as additives to prepare t-ZrO₂ [3,4]. Nevertheless, previous study has revealed that the pure t-ZrO₂ can keep its stability at room temperature when prepared through sol-gel method without additives [5]. Furthermore, recent investigations show that the nanocrystalline m-ZrO₂ exhibited much more excellent behaviors than t-ZrO₂ in some aspects such as mechanic and catalytic properties due to its special crystal structure and surface features [6-8]. However, m-ZrO₂ is considered to be even more difficult to synthesis at low temperature especially in a pure state [9,10].

Hence, it is important to synthesis ZrO_2 particles with ideal phase composition, morphology and well dispersibility. Till now, there are many different physical, mechanical, chemical and other methods to obtain ZrO_2 nanoparticles [11–13]. Among the wet chemical synthesis routes, the hydrothermal methods have great potential to fabricate nanocrystals materials at a relatively low temperature. The main advantages of this method is related to the homogeneous nucleation and grow processes and very low grain size due to the elimination of the calcinations step.

In present study, pure t-ZrO₂ and m-ZrO₂ nanopowders were manufactured via solvothermal process of the gel precursors which were prepared by adding KOH ethanol solution dropwise into ZrOCl₂·8H₂O ethanol solution. Furthermore, the phase composition and morphology of the nanoparticles obtained via solvothermal method were determined, and phase transformation of t-ZrO₂ to m-ZrO₂ was observed with increasing solvothermal reaction time.

2. Experiment procedures

A feedstock Zr⁴⁺ solution with fixed concentration of 0.2 M was prepared by dissolving ZrOCl₂·8H₂O (analytical reagent) into ethyl alcohol. The gel precursor was then prepared by adding 1.25 M KOH ethanol solution dropwise into this solution. Zirconia nonapowders were then prepared in Teflon autoclave by the choice of the reaction time range from 0 to 600 min at 180 °C. The precipitates, named as Z1, Z2, Z3, Z4, Z5, Z6 and Z7 respectively, were washed with deionized water to remove the soluble chlorides and ethanol to depress agglomeration and dried in vacuum drying chamber at 85 °C for 5 h. Phase composition of particles was determined by XRD measurement using Cu K\alpha as radiation source. The amount of tetragonal zirconia has been calculated from the ratios of the diffraction intensity of characteristic (011), (111)_m and ($\overline{1}$ 11)_m peaks. The crystallite size were calculated according to the

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Fig. 1. XRD patterns of ZrO_2 nanoparticles obtained from solvothermal methods with different heat treating time at 180 °C.

Sherrer formula from the $(0\,1\,1)_t$ and $(1\,1\,1)_m$ characteristic peaks of the nanopowders. The morphology of the particles was analyzed by TEM (JEM-1230, JEOL, Japan).

3. Results and discussion

Fig. 1 shows the phase composition of nanopowders prepared via solvothermal method. As is shown, the t-ZrO₂ formed at the early stage of solvothermal reaction, and along with the progressing of solvothermal procedure, t-ZrO₂ transformed into a nearly pure phase m-ZrO₂ gradually. Muñoz-Tabares et al. [14] applied several techniques such as TEM, XRD, Raman spectroscopy, nanoindentation and atomic force microscopy to investigate the evaluation of hydrothermal degradation of tetragonal zirconia. Their results indicated that monoclinic phase propagation during degradation was assisted by stress-induced martensitic transformation mechanisms (autocatalytic propagation and self-accommodation variants), where destabilization of tetragonal phase by water attack was necessary to activate these mechanisms. Similarly, as a result of lack of water, the products in our samples are mainly tetragonal zirconia crystals in early stage of the solvothermal reaction. And then, owing to the increasing of the water (as a product of the reaction) in the reaction system, the monoclinic phase was increased with extending reaction time.

The crystallite size was calculated according to the Sherrer formula from the $(011)_t$ and $(111)_m$ characteristic peaks, and the volume fraction of each phase of the as-prepared ZrO_2 nanoparticles was calculated with the empirical Eqs. (1) and (2) respectively [15] as follow:

$$x_{\rm m} = \frac{I_{\rm m}(1\,1\,1) + I_{\rm m}(\bar{1}\,1\,1)}{I_{\rm m}(1\,1\,1) + I_{\rm m}(\bar{1}\,1\,1) + I_{\rm t}(0\,1\,1)}$$
(1)
$$x_{\rm t} = 1 - x_{\rm m}$$
(2)

where x_m and x_t represent the volume fraction of monoclinic and tetragonal ZrO_2 nanopowders, respectively, and the intensity of characteristic peaks are expressed as I_m and I_t .

Table 1
Phase composition and crystallite size of as prepared nanoparticles.

	Time of solvothermal/min	Tetragonal phase		Monoclinic phase	
		Xt%	<i>D</i> ₀₁₁ (nm)	X _m %	<i>D</i> ₁₁₁ (nm)
Z1	0	100	3.82	0	-
Z2	30	58.49	4.46	41.51	13.73
Z3	60	48.26	3.97	51.74	22.32
Z4	180	28.43	4.36	71.57	32.13
Z5	300	11.12	4.96	88.88	34.13
Z6	420	4.43	4.86	95.57	34.41
Z7	600	1.75	4.98	98.25	44.64

The phase composition and the crystallite size of as-prepared nanopowders as a function of solvothermal time are presented in Table 1. As is shown, there are no marked differences on crystallite size of t-ZrO₂ among five samples, while the content and crystallite size of m-ZrO₂ increase with the progressing of solvothermal reaction.

The formation mechanism of $m-ZrO_2$ was investigated with Avrami equation [Eq. (3)]:

$$\ln(-\ln(1-x)) = n\ln t + \ln m \tag{3}$$

where x is the fraction crystallized at time t, m a rate constant dependent on the frequency of the nucleation and growth rate, and n a constant dependent on the geometry of the system.

Plots of the left side of Eq. (3) versus $\ln t$ yield roughly linear fits with slopes *n*, these slopes may fall within any of three distinct ranges that are characteristic of specific reaction mechanisms [16]. For n = 0.54-0.62, a diffusion-controlled dependence is implied. A zero-order, first-order, or phase-boundary-controlled mechanism is implied for n = 1.0-1.24. Control by nucleation and growth is connoted for n = 2.0-3.0.

Fig. 2 shows the relationship between $\ln(-\ln(1-x))$ and $\ln t$. As is shown, the growth process of zirconia nanopowders is composed of two stages. Many authors limited their data to 0.15 < x < 0.5 primarily to ensure linear behavior when Avrami equation was applied to investigate the crystal growth. However, linear regression of our complete range of data (Table 1) shows good linear relationship over both of the resultant segments (Fig. 2), and regression yields *n* values of 0.48 and 0.98 for the early and late regimes, respectively. Also, a similar phenomenon can be seen in hydrothermal synthesising of barium titanate [17]. As shown in Table 2, the *n* value for the first regime does not fall into any of the three ranges listed above, which implies a mechanism other than those 3 reaction mechanisms discussed above. On the contrary, the value of *n*



Fig. 2. Relationship between $\ln(-\ln(1-x))$ and $\ln t$.



Fig. 3. TEM images of as-prepared zirconia nanoparticles. a, b, c, d and e are corresponding to Z1, Z2, Z3, Z4 and Z7 sample, respectively.

Table	2
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The values of *n* calculated from Eq. (3).

	Solvothermal reaction time/min	п
Stage 1	0-180	0.48
Stage 2	180-600	0.98

for the second stage is 0.98, very close to 1, which suggests rate control of the late regime of the reaction by a zero-order, first-order, or phase-boundary-controlled mechanism. Additionally, Eq. (3) has been derived for spheres, discs, and rods, representing three-, two-, , and one-dimensional forms of growth, and the constants were summarized according to different crystallization mechanism and different mode of crystal growth. So it can be deduced that the m-ZrO₂ grows in one dimension in this period, and it is in accordance with the result of TEM analysis in Fig. 3. The morphology of as-prepared samples is shown in Fig. 3. It can be seen the spherical particles with several nanometers grew up to short rodlike ones with around 50 nm in diameter and 200 nm in length, along with the progressing of solvothermal reaction. At the same time, Fig. 3 shows lots of small spherical particles attached on the surface of rodlike particles, which indicates that the growth of larger rodlike particles are based on the dissolving of tiny particles in this reaction system. In addition, both pure t-ZrO₂ and pure m-ZrO₂ show perfect dispersibility.

4. Conclusion

In this study, tetragonal ZrO_2 nanopowders transform progressively into monoclinic phase during the solvothermal procedure at 180 °C, and the transformation process can be divided into two

regimes based on reaction progress. Kinetic analysis, according to the Avrami equation, was inconclusive in the analysis of the early reaction-rate regime. While a zero-order, first-order, or phaseboundary-controlled mechanism implied in the late reaction-rate regime. The TEM images show the particles grow up from spherical to short rodlike, which indicates the particles grow along one-dimension during the late regime of the reaction. It agrees well with the mode of crystal growth which is derived from the Avrami exponent. Crystallite size estimated from XRD patterns using Scherrer equation shows that the t-ZrO₂ is below 5 nm, and has no marked changes during the whole solvothermal procedure, while the size of the m-ZrO₂ varies from 10 nm to 50 nm.

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