Vol 18 No 9, September 2009
1674-1056/2009/18(09)/4019-06

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Hydrothermal synthesis and dielectric properties of chrysanthemum-like ZnO particles*

Yan Jun-Feng(闫军锋), Zhang Zhi-Yong(张志勇)†, You Tian-Gui(游天桂), Zhao Wu(赵 武), and Yun Jiang-Ni(员江妮)

School of Information Science and Technology, Northwest University, Xi'an 710069, *China*

(Received 5 December 2008; revised manuscript received 10 March 2009)

By orthogonal design theory, technological parameters of chrysanthemum-like ZnO particles prepared in a hydrothermal process are optimized. This paper reports a set of technological parameters for growing chrysanthemum-like ZnO particles on a large scale. It investigates the morphologies and crystalline structures of the as-synthesized three-dimensional ZnO particles with a scanning electron microscope, x-ray diffractometer and transmission electron microscope, and the possible growth mechanism on the three-dimensional ZnO particles. The experimental results indicate that the values of ε', ε'' and $\tan\delta_e$ gradually increase in the X band with the improvement of the developmental level of chrysanthemum-like ZnO particles, implying that the electromagnetic wave absorbing property depends on the morphologies of three-dimensional ZnO particles.

Keywords: ZnO, orthogonal design, hydrothermal process, chrysanthemum-like particles
PACC: 8110D, 8116D, 7740

1. Introduction

As a specific environmental pollutant, electromagnetic interference has been attracting more attention recently, due to the increasing uses of large-power electromagnetic equipment in industrial, commercial and military fields.[1] Therefore, electromagnetic wave absorbing materials play an important role in green living space and advanced military concealment technology.[2]

Zinc oxide (ZnO), a new typical electromagnetic wave absorbing material, has attracted considerable attention since Zhou, Zhang and Cao *et al*[3−7] reported that ZnO particles with peculiar morphology have good absorbing properties for electromagnetic waves. However, domestic and overseas research mainly focuses on the electromagnetic wave absorbing property of tetraleg ZnO at present. In particular, almost all kinds of preparing methods[8−13] of tetraleg ZnO need high temperature (about from 800 to 1100 °C) with a low rate of finished products; this makes them unsuitable to prepare on large scales. Nevertheless, as another special morphology, chrysanthemum-like ZnO particles, prepared by a hydrothermal process at low temperature, have not only uniform morphology but also good electromagnetic wave absorbing properties, which has scarcely been reported.

In this paper, we report the hydrothermal process technological parameters in fabricating chrysanthemum-like ZnO particles and the dependent relation between the dielectric properties and the developmental level of chrysanthemum-like structures, and propose a possible growth mechanism on chrysanthemum-like ZnO particles.

2. Experiment

We considered four factors (Zn^{2+} concentration ($[Zn^{2+}]$), ratio of OH^- concentration ($[OH^-]$) to $[Zn^{2+}]$, reacting temperature and time) and four levels for every chosen factor, and there were sixteen experiments (samples 1–16) to be performed according to the Taguchi L_{16} (4^4) orthogonal array. The technologic parameters for samples 1–16 are listed in Table 1.

In the experiment, deionized water was used as a solvent, and an appropriate sodium hydroxide

*Project supported by the National High Technology Research and Development Program of China (Grant No 2005A000200), the Xi'an Applied Materials Innovation Fund (Grant No XA-AM-200712), and the Innovative Experiment Program for Chinese students (Grant No State 200721).

†Corresponding author. E-mail: zhangzy@nwu.edu.cn

(NaOH) solution was added to zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) solution accompanied with a cold water bath and stirring, which formed a transparent and stable precursor. The precursor was then put in an autoclave with a Teflon lining, the compactedness of which was about 70% of the effective capacity. After that, the autoclaves were put into a bake oven and kept at a temperature of 140–200 °C for 6–12 h. Finally, the products were not stopped scouring and filtering until the pH value of the filtrate reached 7, and the ZnO particles were dried at 60 °C for further characterization.

The slenderness ratio L_d of petal-like nanorods in chrysanthemum-like ZnO particles was calculated and analyzed according to field emission environment scanning electron microscope (SEM, type Quanta 400 FEG, FEI, Holand) images. The microstructure and morphology of the ZnO particles were examined using an x-ray diffractometer (XRD, type D/Max2550VB+/PC, Rigaku, Japan), SEM and a high-resolution transmission electron microscope (TEM, type JEM-3010, JEOL, Japan). The dielectric properties of ZnO particles versus frequency in the X band (8.2–12.4 GHz) were measured by a microwave vector network analyzer (type Agilent technologies E8362B, Agilent, America).

Table 1. Experimental parameters using the Taguchi L_{16} (4^4) orthogonal array design.

sample	parameters				L_d	absoluted $[OH^-]$/mol·L^{-1}
	$[Zn^{2+}]$ /mol·L^{-1}	ratio of $[OH^-]$ to $[Zn^{2+}]$	reacting temperature/°C	reacting time/h		
1	0.1	8	140	6	1.46	0.4
2	0.1	10	160	8	1.70	0.6
3	0.1	12	180	10	5.32	0.8
4	0.1	14	200	12	11.25	1.0
5	0.3	8	160	10	1.70	1.2
6	0.3	10	140	12	2.20	1.8
7	0.3	12	200	6	7.20	2.4
8	0.3	14	180	8	5.58	3.0
9	0.5	8	180	12	1.00	2.0
10	0.5	10	200	10	6.67	3.0
11	0.5	12	140	8	–	4.0
12	0.5	14	160	6	–	5.0
13	0.7	8	200	8	3.92	2.8
14	0.7	10	180	6	2.70	4.2
15	0.7	12	160	12	–	5.6
16	0.7	14	140	10	–	7.0

3. Results and discussion

3.1. X-ray diffraction

Figure 1 shows the typical XRD spectrum of the as-synthesized products. From the characteristics of diffraction peaks, it is easily seen that the as-synthesized product is crystalline ZnO (space group $p6_3mc(186)$; JCPDS card No. 36–1451) with a hexagonal wurtzite structure.

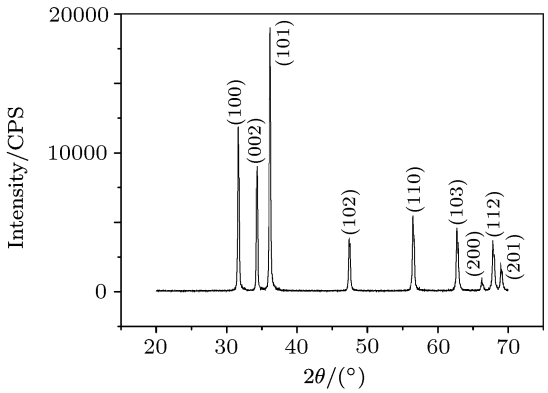


Fig.1. Typical XRD spectrum of the synthesized products.

3.2. Orthogonal-design analysis and morphology

Figures 2(a)–2(d) exhibit four typical SEM images of as-synthesized ZnO particles, i.e. samples 1, 4, 7 and 10, respectively. From Fig.2, we can see that there are three-dimensional structures of as-synthesized ZnO particles. Every sample obviously has a chrysanthemum-like structure except sample 1, and sample 4 in particular has the best morphology. The inset of Fig.2(b) is a selected-area electron diffraction (SAED) pattern taken from an individual ZnO nanorod in a chrysanthemum-like structure. The electron beam is along the $(01\bar{1}0)$ zone axis and the diffraction spots demonstrate that the ZnO nanorod is single crystalline with its long axis along the (0001) direction and presents an obvious hexagonal phase, which is consistent with the result of XRD.

To further study the chrysanthemum-like ZnO structure quantitatively, the slenderness ratio L_{d}, defined as the ratio between the radius of a chrysanthemum-like structure and the diameter of a petal-like nanorod, which reveals the developmental level of the chrysanthemum-like structure, is calculated and the results are listed in Table 1. It is clear that sample 4 with a value of $L_{\mathrm{d}} = 11.25$ has developed quite well. Simultaneously, in order to further detect the fact that the samples 11, 12, 15 and 16 have no corresponding products, the absolute $[\mathrm{OH}^-]$ is calculated as listed in Table 1 on basis of the following chemical equation:

$$\mathrm{Zn}^{2+} + 4\mathrm{OH}^- \leftrightarrow [\mathrm{Zn(OH)_4}]^{2-}. \tag{1}$$

It is easily found that their absolute $[\mathrm{OH}^-]$ values are all equal to or larger than 4 mol/L in the experiments. It is possible that the excessive $[\mathrm{OH}^-]$ restrains the basic cells of crystalline growth $[\mathrm{Zn(OH)_4}]^{2-}$ from folding together to form a ZnO crystal nucleus, so the corresponding products can not appear. But sample 14 is exceptional, which is probably caused by the reacting temperature.

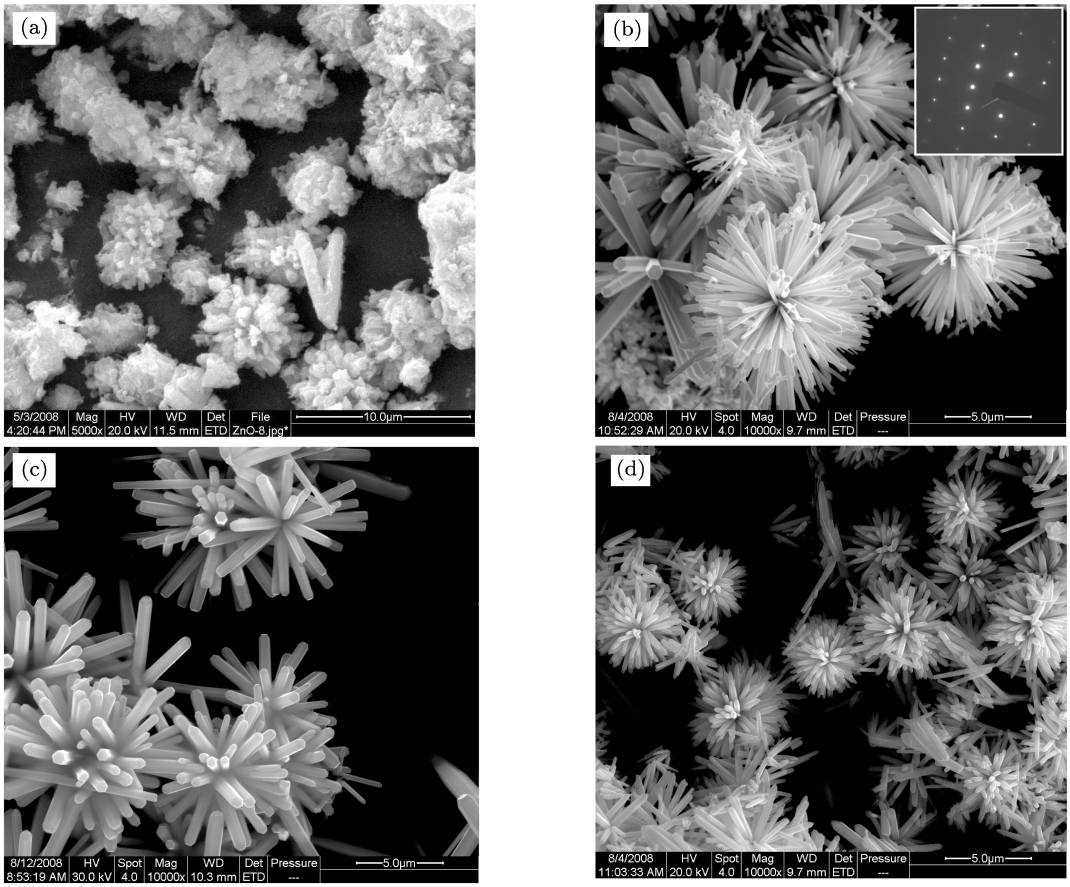


Fig.2. SEM images of three-dimensional ZnO particles: (a) sample 1; (b) sample 4; (c) sample 7; (d) sample 10.

More orthogonal experimental analysis can help us to further optimize the technique parameters.[14] For one factor, $L_{\mathrm{d\ average}}$ of particles with the same level can properly reflect the contribution of the level for the developmental level of the chrysanthemum-like structure, and thus a better estimation is made by $L_{\mathrm{d\ average}}$ for different levels of each factor. Especially for the orthogonal experimental results partly without product, $L_{\mathrm{d\ average}}$ represents the average of L_{d} values for one level and for one factor. The values of $L_{\mathrm{d\ average}}$ of the particles are listed in Table 2, in which the ranges R, differences between the maximum and the minimum, of the particles are also displayed. Generally, when R is large, the change of the process parameter has a significant effect on the developmental level of the chrysanthemum-like structure. Table 2 clearly shows an influence sequence, that is, the most important factor, i.e. ratio of $[OH^-]$ to $[Zn^{2+}]$, then reacting temperature, the third $[Zn^{2+}]$, and finally reacting time. Table 2 also exhibits a set of optimized technological parameters. It is evident that appropriate control of the ratio of $[OH^-]$ to $[Zn^{2+}]$ and reacting temperature are essential for the developmental level of the chrysanthemum-like structure.

A detailed analysis of the influence sequence factors on the developmental level of chrysanthemum-like structure can help us to further clarify the growth mechanism of chrysanthemum-like ZnO particles. By analyzing the technological parameters of Table 1 and the morphologies of samples, a possible growth mechanism is supposed to be that the as-synthesized ZnO particles with three-dimensional structure derive from multi-twin central nuclei, i.e. multi-twin central nuclei further develop to form three-dimensional ZnO particles. The multi-twin central nucleus is a spherical aggregate with multiple nuclei which can adjust their states under certain hydrothermal conditions. However, different technological parameters determine the different morphologies of three-dimensional ZnO particles. Under the technological conditions of sample 1, although the reacting temperature and the ratio of $[OH^-]$ to $[Zn^{2+}]$ are low, the formation conditions of multi-twin central nuclei can nearly be achieved. At this time, due to the inadequate environmental driving force which is a result of the interaction with several factors, such as supersaturation, the reacting temperature, the ratio of $[OH^-]$ to $[Zn^{2+}]$ and systematical pressure, the individual nuclei randomly collocate in a multi-twin central nucleus. Therefore, in this situation, the density of the multi-twin central nuclei is high, and the irregular morphology of sample 1 is formed. With the change of technological parameters, the environmental driving force changes correspondingly. When the ratio of $[OH^-]$ to $[Zn^{2+}]$ varies from 10 to 14 and the reacting temperature stays at 200 °C, the environmental driving force causes a concentric spherical multi-twin central nucleus with c axes along the radial direction of the sphere to form. Thus, multi-twin central nuclei with special internal structures form and further develop to form chrysanthemum-like ZnO particles. Under certain technological conditions, the polar surfaces' axial growth is found to have a different relative growth rate from that of non-polar surface lateral growth.[15] When the ratio of $[OH^-]$ to $[Zn^{2+}]$ and the reacting temperature are equal to 14 and 200 °C respectively, the growth rate of a positive polar surface (0001) is obviously larger than that of non-polar lateral surfaces. Thus, the morphology of sample 4 with $L_{\mathrm{d}} = 11.25$ is formed. However, with the distinct increase of absolute $[OH^-]$, the excessive $[OH^-]$ results in s small decrease of the relative growth rate between the positive polar surface (0001) and the non-polar lateral surfaces. Therefore, the L_{d} of sample 7 is a little larger than that of sample 10.

Table 2. L_{d} of ranges of particles. $L_{\mathrm{d\ average}}$ (x) means $L_{\mathrm{d\ average}}$ derived from all the samples with x level.

process parameters	$[Zn^{2+}]$/mol·L^{-1}	ratio of $[OH^-]$ to $[Zn^{2+}]$	reacting temperature/°C	reacting time /h
$L_{\mathrm{d\ average}}(1)$	4.93	2.02	1.83	3.79
$L_{\mathrm{d\ average}}(2)$	4.17	3.32	1.70	3.73
$L_{\mathrm{d\ average}}(3)$	3.84	6.26	3.65	4.63
$L_{\mathrm{d\ average}}(4)$	3.31	8.42	7.26	4.82
R	1.62	6.40	5.56	1.09

3.3. Dielectric properties

Although all the products have the same components, ZnO particles with different developmental levels have different dielectric properties. In order to investigate the dielectric properties of three-dimensional ZnO particles, ZnO particles/paraffin composites are prepared by dispersing the three-dimensional ZnO particles with a weight ratio of 40% into paraffin. Figures 3(a)–3(c) show the real part of permittivity ε', the imaginary part of permittivity ε'', and the dielectric loss tangent $\tan\delta_e$ of samples 1, 4, 7 and 10 respectively. From Figs.3(a) and 3(b), we can see that the values of ε' and ε'' gradually increase in the X band with the improvement of the developmental level of the chrysanthemum-like structure, i.e. L_{d}. The values of ε' of samples 1, 4, 7 and 10 vary from 4.67 to 8.12; however, the values of ε'' fluctuate in the range between 0.43 and 2.23. The $\tan\delta_{\mathrm{e}}$, defined the ratio of ε'' to ε', represents the phase lag of the dipole oscillations with respect to the applied electric field. The values of $\tan\delta_{\mathrm{e}}$ gradually increase according to the sequence of samples 1, 10, 7 and 4 respectively in Fig.3(c). It is evident that the value of L_{d} determines the dielectric properties of three-dimensional ZnO particles. The larger the value of L_{d} is, the larger the total values of ε', ε'' and $\tan\delta_e$ are. The sample 4 with $L_{\mathrm{d}} = 11.25$ has the best dielectric properties.

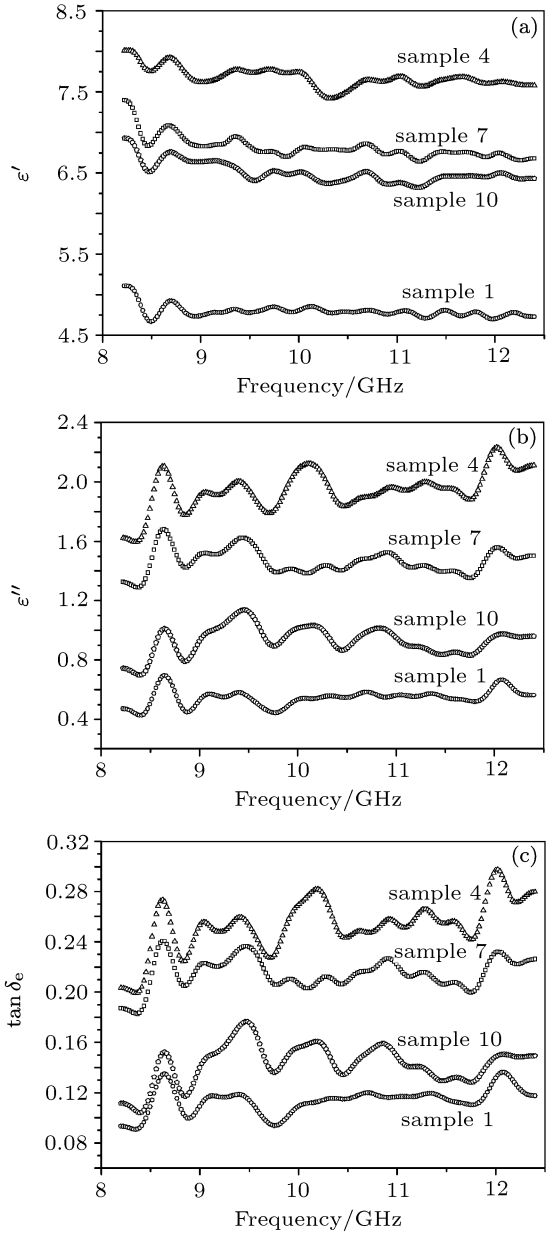


Fig.3. (a) Real part of permittivity ε'; (b) imaginary part of permittivity ε''; (c) the dielectric loss tangent $\tan\delta_{\mathrm{e}}$.

The dielectric loss tangent $\tan\delta_{\mathrm{e}}$ reflects the electromagnetic wave absorbing properties of a dielectric to a certain extent. The basic cell of ZnO crystalline growth, with a tetrahedron structure, determines the characteristic of the electric dipole. Due to the fact that the turning direction polarization of the electric dipole lags behind the imposed high-frequency electric field in X band, relaxation polarization occurs, and the dielectric loss tangent $\tan\delta_e$ increases. On the other hand, the conducting network forms easily in three-dimensional ZnO particles with the large L_{d} so as to increase the conductivity of the dielectric and further enhance the dielectric loss tangent $\tan\delta_e$. At the same time, under the high-frequency electromagnetic field, the local high electric-field intensity appears at the sharp tip of the petal-like nanorods in chrysanthemum-like ZnO particles with large L_{d}, which causes them to enhance their polarization degree and restrain adjacent electric dipoles from turning direction polarization. That is to say, the large L_{d} of chrysanthemum-like ZnO particles results in dramatic dielectric loss.

4. Summary

The hydrothermal technological parameters for preparing chrysanthemum-like ZnO particles are optimized by an orthogonal-design experiment. Four factors and four levels are investigated. The results show that, in the range of our experimental parameters, the ratio of $[OH^-]$ to $[Zn^{2+}]$ and the reacting temperature significantly affect the developmental level of the chrysanthemum-like structure. The other two factors affect it a little. The value of L_{d} determines the dielectric properties of three-dimensional ZnO particles. The larger the value of L_{d} is, the larger the dielectric loss tangent $\tan\delta_{\mathrm{e}}$ is. It is suggested that chrysanthemum-like ZnO particles with large L_{d} have a predominant electromagnetic wave absorbing property.

References

[1] Xin T and Ke-ao H 2007 *Materials and Engineering* B **139** 119

[2] Ghasemi A, Hossienpour A, Morisako A, Saatchi A and Salehi M 2006 *Journal of Magnetism and Magnetic Materials* **302** 429

[3] Zhou Z W, Peng W M, Ke S Y and Deng H 1999 *J. Mater. Process. Technol.* **89-90** 415

[4] Cao J W, Huang Y H, Zhang Y, Liao Q L and Deng Z Q 2008 *Acta Phys. Sin.* **57** 364 (in Chinese)

[5] Chen Y J, Cao M S, Wang T H and Wan Q 2004 *Appl. Phys. Lett.* **84** 3367

[6] Zhou Z W, Chu L S and Hu S C 2006 *Mater. Sci. Eng.* B **126** 93

[7] Cao M S, Shi X L, Fang X Y, Jin H B, Hou Z L, Zhou W and Chen Y J 2007 *Appl. Phys. Lett.* **91** 203110

[8] Shi X L, Yuan J, Zhou W, Rong J L and Cao M S 2007 *Chin. Phys. Lett.* **24** 2994

[9] Zhou Z W, Deng H, Yi J and Liu S K 1999 *Materials Research Bulletin* **34** 1563

[10] Chen Y F, Tang M T and Yang S H 2005 *The Chinese Journal of Nonferrous Metals* **15** 423

[11] Wu J J and Liu S C 2002 *Adv. Matter.* **14** 215

[12] Park W L, Yi G C, Kim J M and Park S M 2003 *Appl. Phys. Lett.* **82** 4358

[13] Choi J H, Tabata H and Kawai T 2001 *J. Cryst. Growth* **226** 493

[14] Yan J F, Zhao L L and Zhang Z Y 2008 *Chin. Phys. Lett.* **25** 2253

[15] Xu S, Lao C, Weintraub B and Wang Z L 2008 *J. Mater. Res.* **23** 2072