Vol 18 No 10, October 2009
1674-1056/2009/18(10)/4552–06

Chinese Physics B

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

Effect of polyacrylamide on morphology and electromagnetic 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), Yun Jiang-Ni(贠江妮), and Zhang Fu-Chun(张富春)

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

(Received 3 April 2009; revised manuscript received 26 April 2009)

Through hydrothermal process, the chrysanthemum-like ZnO particles are prepared with zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and sodium hydroxide (NaOH) used as main resources under the different concentrations of surfactant polyacrylamide (PAM). The microstructure, morphology and the electromagnetic properties of the as-prepared products are characterized by high-resolution transmission electron microscopy (HRTEM), field emission environment scanning electron microscope (FEESEM) and microwave vector network analyzer, respectively. The experimental results indicate that the as-prepared products are ZnO single crystalline with hexagona wurtzite structure, that the values of slenderness ratio L_d are different in different PAM concentrations, and that the good magnetic loss property is found in the ZnO products, and the average magnetic loss tangent $\tan\delta_u$ increases with PAM concentration increasing, while the dielectric loss tangent $\tan\delta_e$ decreases.

Keywords: chrysanthemum-like ZnO particles, electromagnetic properties, hydrothermal method, PAM

PACC: 8110D, 8116D, 7740

1. Introduction

The electromagnetic interference is one of the most dangerous environmental pollutions and does serious harm to the health of human being , which attracts more attention recently.[1] Therefore, it is urgent for researchers to investigate and develop new typical electromagnetic wave absorbing materials.[2]

It is well known that the morphology of nanoparticle determines its properties to a large extent. Zinc oxide (ZnO), a new typical electromagnetic wave absorbing material, has attracted considerable attention due to its peculiar morphology and good absorbing property for electromagnetic wave.[3–8] Growth of nanostructured ZnO with novel morphology, in particular tetraleg structure, can be achieved through various techniques, such as chemical vapour deposition (CVD),[9,10] metal-organic chemical vapour deposition (MOCVD),[11,12] physical vapour deposition (PVD),[13,14] etc. It is evident that almost all preparation methods need high temperatures ranging about from 800 °C to 1100 °C with a low growth rate and precise instruments to control additionally. However, chrysanthemum-like ZnO particles, prepared through hydrothermal process with the advantage of simple and cheap synthetical procedure, have good electromagnetic wave absorbing property,[15] which indicates that it is worth while investigating hydrothermal synthesis of chrysanthemum-like ZnO particles further.

In the present paper, we report on the effect of surfactant PAM on the morphology and the electromagnetic properties of nanostructured chrysanthemum-like ZnO particles. Importantly, the ZnO product with good magnetic loss property is obtained.

2. Experiment

On the basis of our previous work,[15] a group of experiments were carried out through a hydrothermal process with PAM ($[CH_2CH(CONH_2)]_n$, average

*Project supported by the National High Technology Research and Development Program of China (Grant No 2005A000200), the Xi'an Applied Materials Innovation Fund, China (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

molecular weight: ≥3000000) used as surfactant. The weighing standards for $Zn(CH_3COO)_2{\cdot}2H_2O$, NaOH and surfactant PAM are listed in Table 1, in which the reactants of the Zn^{2+} concentration ($[Zn^{2+}]$) and OH^- concentration ($[OH^-]$) are 0.1 mol/L and 1.2 mol/L respectively and the PAM concentrations ([PAM]) are presented according to the ratio of [PAM] to $[Zn^{2+}]$. In an experiment, deionized water was used as dissolvent, and an appropriate amount of NaOH solution was added into the mixed solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ and PAM together with cold water bath and stirring, which formed transparent and stable precursor. Then the precursor was transferred into a Teflon-lined 50-mL-capacity autoclave, of which the degree of fill was about 70%. After that, those autoclaves were put into a bake oven, with the temperature maintained at 180 °C for 12 h. Finally, the ZnO products were kept scoured and filtered until the PH value of filtrate reached 7, and then dried at 60 °C in air for further characterisation.

Table 1. Correlative parameters of reactants, surfactant PAM and as-prepared ZnO products.

sample	$[Zn^{2+}]$ (mol/L)	$[OH^-]$ (mol/L)	Ratio of [PAM] to $[Zn^{2+}]$	L_d	ρ/(g/cm^3)
1	0.1	1.2	0	5.32	4.243
2	0.1	1.2	0.0005%	10.90	3.763
3	0.1	1.2	0.0001%	12.18	3.114
4	0.1	1.2	0.00005%	13.89	2.652

The microstructure and morphology of the as-prepared ZnO particles were examined by using HRTEM (JEM-3010, JEOL, Japan) and FEESEM (Quanta 400 FEG, FEI, Holand), respectively. The ZnO particles/paraffin composites were prepared by dispering the ZnO product with a weight ratio of 25% into paraffin, and the electromagnetic properties of the composites in the X band (8.2–12.4 GHz) were measured by microwave vector network analyzer (Agilent technologies E8362B, Agilent, America).

3. Results and discussion

3.1. HRTEM analysis of as-prepared ZnO product

HRTEM images of the nanorod taken from the chrysanthemum-like ZnO particle are given in Fig.1. Figure 1(a) shows a typical ZnO nanorod at 180 °C. The selected-area electron diffraction (SAED) pattern in Fig.1(b) and the HRTEM image in Fig.1(c) confirm that the ZnO nanorod is single crystalline with hexagonal wurtzite structure and space group $p6_3mc$ and the growth direction is along [0001].

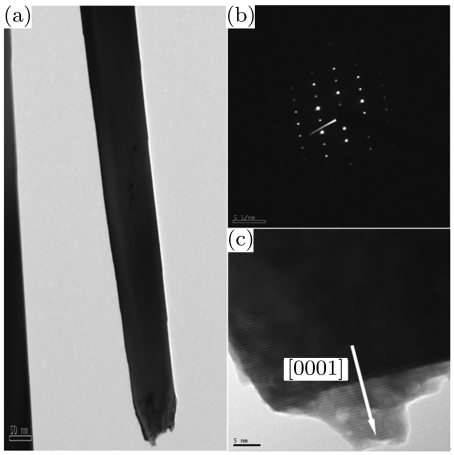


Fig.1. (a) HRTEM image of a nanorod taken from the chrysanthemum-like ZnO particle. (b) SAED image of the nanorod showing a [0001] growth direction. (c) HRTEM image taken from the tip of the nanorod in (a).

3.2. Effect of PAM on the morphology of chrysanthemum-like ZnO particles

A group of SEM images of the as-prepared ZnO particles, i.e. samples 1, 2, 3 and 4, are shown in Figs.2(a)–2(d), in which the inset is the corresponding higher magnification SEM image. By analysing Fig.2, it is clear that all the as-prepared ZnO particles under the different concentrations of PAM have a uniform three-dimensional chrysanthemum-like structure with different values of slenderness ratio L_d, which is defined as the ratio between the radius of the chrysanthemum-like structure and the diameter of a petal-like nanorod, and almost all the nanorods have a tapered front tip except sample 1. In particular, the slenderness ratio of sample 1 is obviously different from those of the other three samples.

By further analysing the technological parameters, the characteristic parameters of the products, i.e. slenderness ratio L_d and density ρ (see Table 1) and the morphologies of the as-prepared ZnO particles, it is noticeable that the surfactant PAM significantly influences the growth process of the chrysanthemum-like ZnO particles.

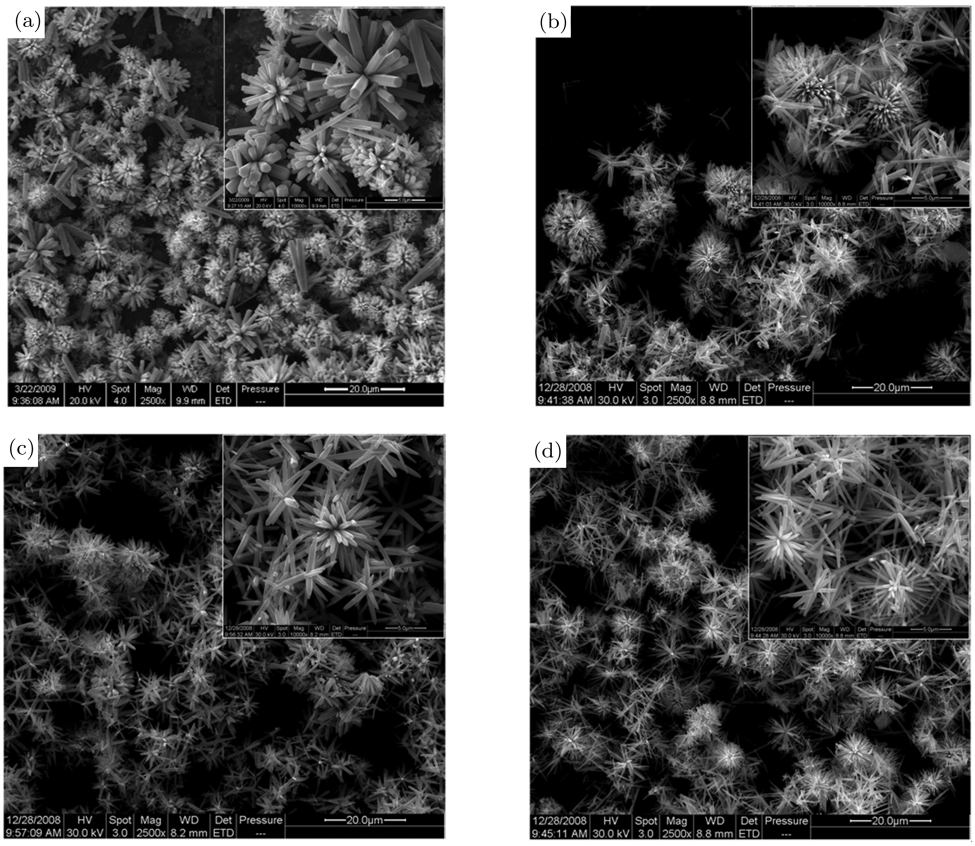


Fig.2. FEESEM images of the as-prepared ZnO particles under the different concentrations of PAM: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4.

On the one hand, due to the fact that the surfactant PAM reduces the surface tension of water, the colloidal particles can evenly distribute in the disperse system so as to form the uniform multi-twin central nucleus[15] at an appropriate temperature in the formation period of precursor. Simultaneously, the PAM in a certain concentration range effectively reduces the gradient of supersaturation. Thus, at the ratios of [PAM] to $[Zn^{2+}]$: 0.0005%, 0.0001% and 0.00005% respectively, for ZnO products of such a kind, such as samples 2, 3 or 4, the morphologies of the chrysanthemum-like ZnO particles are uniform and so are the petal-like naorods', but the morphologies of samples 2, 3 and 4 are different from each other.

On the other hand, the ionized surfactant PAM contains the positive hydrophilic group ($-CONH_2$) and negative hydrophobic group ($-CH_2\overset{|}{C}H-$). In the developmental stage of the multi-twin central nucleus, the positive hydrophilic groups can bond with the basic cells of crystalline growth $[Zn(OH)_4]^{2-}$ easily by Coulomb force, which means that the positive hydrophilic groups become the carriers of $[Zn(OH)_4]^{2-}$; while the negative hydrophobic groups are absorbed on the non-polar lateral surfaces of ZnO nanorods by van der Waals force, implying that the hydrophobic films formed by the negative hydrophobic groups appear on the non-polar lateral surfaces. Thus, the aeolotropic growth pattern forms, i.e. the basic cells of growing $[Zn(OH)_4]^{2-}$ carried by the positive hydrophilic groups can reach the polar axial surface (0001) easily to hold together and reside at the proper lattice sites but difficultly reach the non-polar lateral surfaces because of the existence of the hydrophobic films. This means that the growth rate of positive polar surface (0001) is larger than that of non-polar lateral surfaces in a certain [PAM] range, suggesting that the [PAM] is an important factor in maintaining a large slenderness ratio of the petal-like nanorods in chrysanthemum-like ZnO particles. So obviously the sample 1 has the smallest value of L_d in all of the samples. Also, 0.00005% is found to be the optimum ratio of [PAM] to $[Zn^{2+}]$ for obtaining a large slenderness ratio (Fig.2(d)). When the ratio of [PAM] to $[Zn^{2+}]$ increases, for example, to 0.0001% (Fig.2(c)), the slenderness ratio becomes smaller than that at 0.00005%. This is due to the fact that the excessive negative hydrophobic groups and non-ionized PAM molecules restrain the basic cells

of growth carried by the positive hydrophilic groups to reach the positive polar surface (0001) at high [PAM] so as to reduce the relative growth rate of polar surface to non-polar surface to a certain extent. When the [PAM] increases to 0.0005% (Fig.2(b)), this restraining action becomes more obvious. Therefore, the morphology and value $L_d = 10.90$ of sample 2 are easily understood. At the same time, the relation between the density ρ and the L_d value is obvious, i.e. the larger the slenderness ratio L_d is, the smaller the density of the chrysanthemum-like ZnO particles will be.

3.3. Effect of PAM on the electromagnetic properties of chrysanthemum-like ZnO particles

3.3.1. Dielectric properties in *X* band

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, 2, 3 and 4 in X band respectively. As shown in Fig.3, the real parts of permittivity ε' of samples 1, 2, 3 and 4 have almost constant behaviour in the 8.2–12.4 GHz frequency range, and the values of ε'' and $\tan\delta_e$ gradually increase in X band with the improvement of the developmental level of chrysanthemum-like structure, i.e. the value of L_d. Obviously, not only the permittivity (ε', ε'') but also the dielectric loss tangent $\tan\delta_e$ of sample 1 are all the smallest and greatly different from ones of samples 2, 3 and 4 in X band. Contrasting the values of $\tan\delta_e$ in Fig.3(c) with the L_d values in Table 1 clearly shows that the value of L_d, associated closely with the [PAM], determines the dielectric properties of the chrysanthemum-like ZnO particles. The larger the value of L_d is, the better the dielectric properties will be.

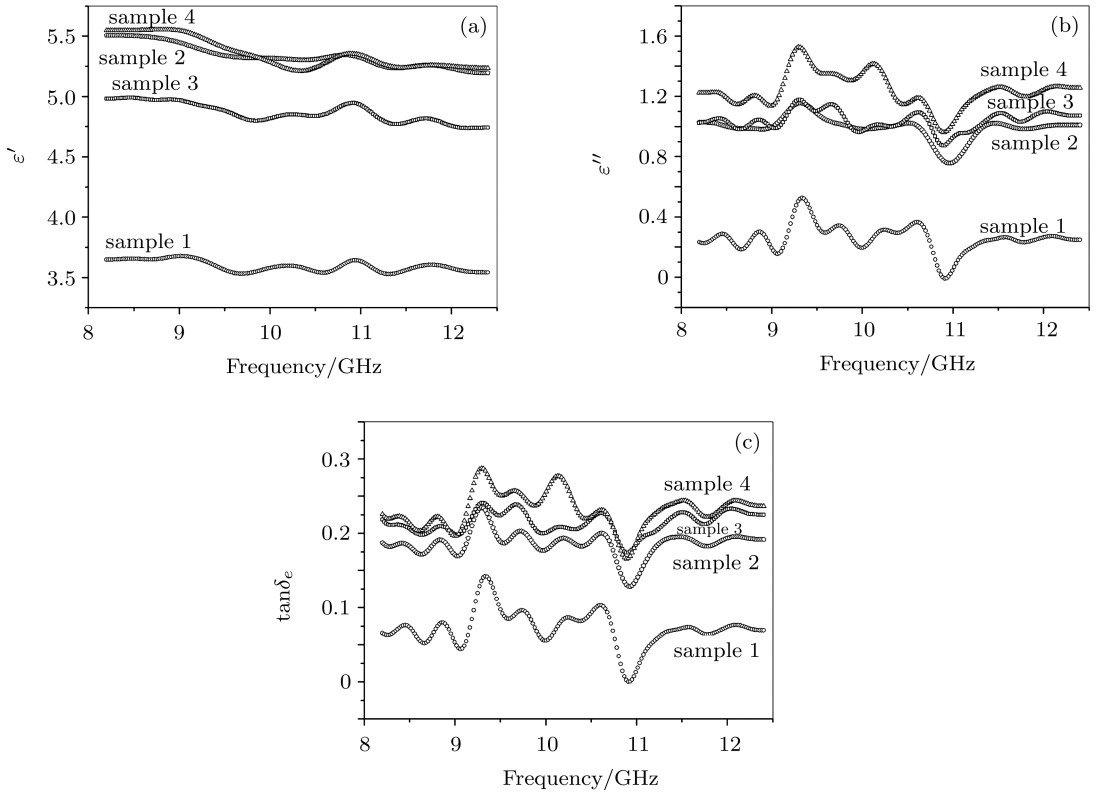


Fig.3. (a) Real part of permittivity ε', (b) imaginary part of permittivity ε'' and (c) dielectric loss tangent $\tan\delta_e$.

The real part of permittivity ε', contributed by displacement polarization, depends on the crystalline quality of the ZnO product to a large extent. Although the L_d value of sample 2 is smaller than that of sample 3, due to high ratio of [PAM] to [Zn^{2+}], i.e. 0.0005%, some O and Zn vacancy defects appear in ZnO crystalline to induce

the formation of space charges so as to give rise to additional displacement polarization under the imposed electric field. While, the dielectric loss tangent $\tan\delta_e$, defined as the ratio of ε'' to ε', represents the phase lag of the dipole oscillation with respect to the applied electric field and the contribution from the finite conductivity of the ZnO product, and it reflects the electromagnetic wave absorbing property of absorber. The turning-direction polarisation of electric dipole, the associated relaxation phenomena and the conducting network formed easily in the chrysanthemum-like ZnO particles with the large value of L_d, constitute the dielectric loss mechanism of the ZnO product[15] due to the fact that the basic cell of ZnO crystalline growth with tetrahedron structure determines the features of electric dipole, and thus it is easy to understand that a large $\tan\delta_e$ is accompanied with a large L_d.

3.3.2. Magnetic properties in *X* band

Figures 4(a)–4(c) show the real and imaginary parts of permeability (μ', μ'') and the magnetic loss tangent $\tan\delta_u$ of samples 1, 2, 3 and 4 in X band. The real parts of permeability for all samples show a decreasing trend with the increase of frequency. Although the imaginary parts of permeability greatly undulate and mutually intervein, the average values of μ'' increase in sequence of samples 1, 4, 3 and 2, that is to say, of them, the average of μ'' of sample 2 is the largest, and that of sample 1 is the smallest. The features of the curves in Figs.4(a) and 4(b) determine that the average values of $\tan\delta_u$, defined as the ratio of μ'' to μ', necessarily increase in the same sequence, i.e. 0.0626 for sample 1, 0.0691 for sample 4, 0.1203 for sample 3 and 0.1334 for sample 2. Further comparing the magnetic properties of all samples with the ratios of [PAM] to [Zn^{2+}] evidently shows that the [PAM] plays a vital role in forming the microstructure related to magnetic properties to a large extent.

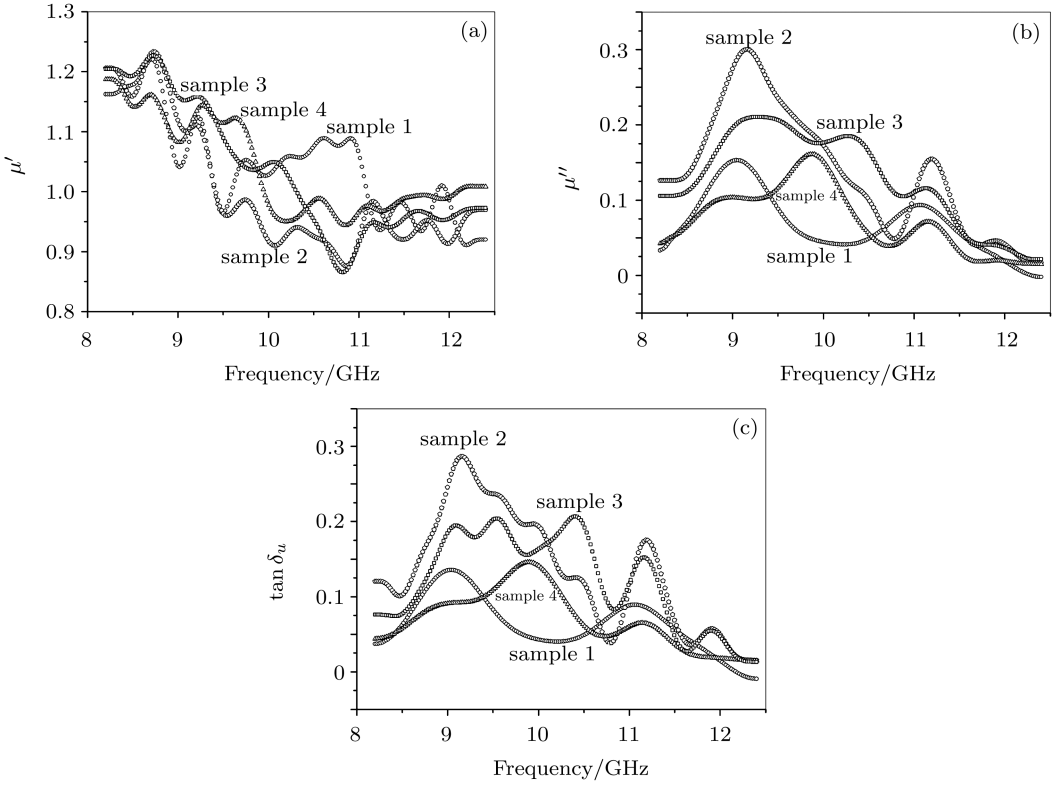


Fig.4. (a) Real part of permeability μ', (b) imaginary of permeability μ'' and (c) magnetic loss tangent $\tan\delta_u$.

The magnetic loss tangent $\tan\delta_u$ represents the phase lag of the magnetic-dipole oscillation and the associated relaxation magnetisation with respect to the applied magnetic field. According to Ref.[16], Zn vacancy defects induce magnetism, derived from the unpaired $2p$ electrons at O sites surrounding the Zn vacancy, in

the undoped nanostructured ZnO, which may be the essential causation to lead to the magnetic loss under high-frequency magnetic field. At the low ratio of [PAM] to [Zn^{2+}], i.e. 0.00005%, the large relative growth rate of polar surface to non-polar surface is propitious to the improvement of the developmental level of the chrysanthemum-like ZnO particles but not to the creation of Zn vacancy defects. However, the weak $\tan\delta_u$ of sample 4 in Fig.4(c) is determined by few Zn vacancy defects caused by the hydrothermal technological conditions like that of sample 1. With the ratio of [PAM] to [Zn^{2+}] increase, for example, to 0.0001%, more Zn vacancy defects are induced so as to form the average value of $\tan\delta_u$ 0.1203. Thus, it is easy to understand that the sample 2 has a large magnetic loss, tangent $\tan\delta_u$.

4. Summary

Under the same hydrothermal technological conditions, different concentrations of surfactant PAM are employed to prepare the chrysanthemum-like ZnO particles. Their morphology, microstructure and electromagnetic properties have been characterised. Comparing the products with PAM with the ones without PAM shows that not only the dielectric properties but also the average values of $\tan\delta_u$ of products with PAM are higher than the ones of the products without PAM. Obviously, the PAM improves the developmental level of the chrysanthemum-like ZnO particles. With the increase of [PAM], the slenderness ratio L_d decreases, and the dielectric properties weaken, while the average value of magnetic loss, tangent $\tan\delta_u$, increases. When the ratio of [PAM] to [Zn^{2+}] is 0.00005%, the dielectric loss, tangent $\tan\delta_e$, of the ZnO product with $L_d = 13.89$ shows the maximum value. However, the maximum average value of magnetic loss, tangent $\tan\delta_u$, is obtained when the ratio of [PAM] to [Zn^{2+}] is 0.0005%, that is to say, the nanostructured chrysanthemum-like ZnO particles not only have good dielectric loss property but also possess good magnetic loss property, which may enlighten us on a new concept in synthesising lightweight and high absorbing level ZnO electromagnetic wave absorber consisting of the same component ZnO with either large $\tan\delta_e$ or large $\tan\delta_u$.

References

[1] Tang X and Hu K A 2007 *Mater. Sci. Eng.* B **139** 119

[2] A Ghasemi, A Hossienpour, A Morisako, A Saatchi and M Salehi 2006 *J. Magn. Magn. Mater.* **302** 429

[3] Li X, Zhai F F, Liu Y, Cao M S, Wang F C and Zhang X X 2007 *Chin. Phys.* **16** 2769

[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] Liu J H, Sun J, Li S M and Chen D M 2004 *Journal of Beijing University of Aeronautics and Astronautics* **30** 822

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

[8] Zhou R F, Qiao L, Feng H T, Chen J T, Yan D, Wu Z G and Yan P X 2008 *J. Appl. Phys.* **104** 094101

[9] Chang P C, Fan Z Y, Wang D W, Tseng W Y, Chiou W A, Hong J and Lu J G 2004 *Chem. Mater.* **16** 5133

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

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

[12] W I Park, D H Kim, S W Jung and G C Yi 2002 *Appl. Phys. Lett.* **80** 4232

[13] Kong Y C, Yu D P, Zhang B, Fang W and Feng S Q 2001 *Appl. Phys. Lett.* **78** 407

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

[15] Yan J F, Zhang Z Y, You T G, Zhao W and Yun J N 2009 *Chin. Phys.* B (Accepted)

[16] Wang Q, Sun Q, Chen Q, Y Kawazoe and P Jena 2008 *Phys. Rev.* B **77** 205411