Effect of ultrasonic treatment on morphology and microwave absorption performance of ZnO spheres

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Abstract. ZnO spheres were prepared by hydrothermal method, following calcination process and ultrasonic treatment. Effect of ultrasonic treatment on morphology and microwave absorption properties of ZnO spheres were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and vector network analyzer (VNA). The results show that sea urchin-like ZnO spheres (with ZnO whiskers on the surface) can be obtained by ultrasonic treatment. The microwave absorption properties are improved as the number of ZnO whiskers increases.

1. Introduction
With the development of high technology such as radar detection, satellite communication, aerospace and electronic countermeasure, especially the rise of anti-electromagnetic interference, stealth technology and microwave anechoic chamber in recent years, more and more attention has been paid to the research of electromagnetic wave absorbing materials [1, 2]. With the rapid development of modern electronic industry and information industry, the number of electronic products that produce electromagnetic waves has increased dramatically, which leads to serious electromagnetic radiation and new environmental pollution. Therefore, the study of electromagnetic shielding technology and electromagnetic wave absorbing materials is of great significance in both national defense industry and civil industry [3, 4].

In recent decades, remarkable progress has been made in the synthesis of ZnO. The results show that the piezoelectric, photocatalytic, gas-sensitive and pressure-sensitive properties of ZnO with different morphology are obviously different [5]. In addition, ZnO has the ability to absorb electromagnetic wave, visible light and infrared ray, so it has the potential of multi-band stealth [6-8]. As a special kind of ZnO material, nano-ZnO whiskers can produce quantum size effect and tunneling effect, so they have excellent absorbing properties. There are two main methods for preparing ZnO whiskers [9, 10]: (1) Gasification of zinc powder at high temperature and phase oxidation in an oxygen atmosphere. (2) The zinc powder is mixed with carbon powder and heated in the atmosphere. The first method is the instantaneous oxidation of zinc. The high concentration of zinc oxide and the sharp increase in the number of nuclei results in the poor regularity and low yield of zinc oxide whiskers. The second method is to use the reducibility of carbon to consume oxygen in the surrounding air to meet the growth regulation of whiskers, but in the specific implementation process, a large number of ZnCO₃ will be produced to reduce the purity of products. In this paper, spherical ZnO was prepared by hydrothermal method and calcination process from zinc acetate and ammonium bicarbonate. The
effects of subsequent physical ultrasound on the morphology and microwave absorption properties of surface whiskers were studied.

2. Experimental section

2.1 Preparation of ZnO sphere
A typical preparation of ZnO sphere was as follows: 0.05 mol Zn(CH$_3$COO)$_2$ and 0.15 mol NH$_4$HCO$_3$ were dissolved in 400 ml distilled water respectively, and stirred for 0.5 h. After all the solvents were totally dissolved, they were transferred to a 500 ml teflon-lined stainless-steel autoclave and heated at 100 °C for 10 h. The resultant products were washed with distilled water for several times, and dried at 60 °C for 4 h (The precursor was ZnCO$_3$). ZnO spheres were obtained by calcination of ZnCO$_3$ at 450 °C for 4 h with a heating rate of 10 °C/min. In order to investigate the effect of ultrasonic process, ZnO spheres were irradiated in an ultrasonic reactor for 20 min and 40 min, respectively. For convenience, without ultrasound treatment, 20 minutes with ultrasound treatment and 40 minutes with ultrasound treatment were named S1, S2 and S3, respectively.

2.2 Characterization and measurement
The structure and morphology of ZnO spheres were studied by employing X-ray diffractometer (XRD, Japan Rigaku D/MAX-cA) using a CuKa radiation (\(\lambda=1.5406 \ \text{Å}\)) and scanning electron microscopy (SEM, Hitachi H-800). The complex permittivity and complex permeability of samples in the frequency range 2-18 GHz were tested by a network analyzer (VNA, N5242A, Agilent) for simulation of reflection loss. The sample was mixed with paraffin at a ratio of 20%. All the tests were carried out at room temperature without special conditions.

To study the microwave absorption properties of ZnO spheres, the reflection loss (\(R_L\)) values was calculated using complex permittivity and complex permeability at a range of 2-18 GHz based on the transmit line theory, which was summarized as the following equations [11]:

\[
R_L = 20 \log_{10} \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (1)
\]

\[
Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tan[h \left( \frac{2\pi df}{c} \sqrt{\mu_r \varepsilon_r} \right)] \quad (2)
\]

Among them, \(\varepsilon_r\) and \(\mu_r\) are complex permittivity and complex permeability, \(c\) is the speed of light in vacuum, \(f\) is microwave frequency, \(d\) is the thickness of absorber, \(Z_{in}\) is the input impedance of absorbing material, and \(Z_0\) is the impedance of free space.

3. Results and discussion

3.1. XRD analysis
The crystallographic structure and phase composition of ZnO were identified by the XRD. As shown in Fig.1, All the diffraction peaks of samples were measured to be \(2\theta = 31.8^\circ, 34.6^\circ, 36.6^\circ, 47.9^\circ, 57.1^\circ, 63.2^\circ, 68.2^\circ\) and corresponded to (110), (002), (101), (102), (110), (103), (112) planes respectively, which can be readily indexed as the hexagonal wurtzite phase with space group P63mc and lattice parameters of \(a = 3.25 \ \text{Å}\) and \(c = 5.21 \ \text{Å}\) according to JCPDS card no.36-1451. No impurity peaks were observed, indicating that the purity of the synthetic ZnO was very high. It is noteworthy that the intensity of diffraction peaks of ZnO decreases with the prolongation of ultrasonic treatment time, which indicates that the crystallization degree of the surface of ZnO spheres decreases gradually.
3.2 Morphology analysis

In order to observe the surface morphology of ZnO spheres, SEM were carried out and the results were illustrated in Fig.2. It can be seen that the diameter of the prepared ZnO spheres is about 8-12\(\mu\)m, without obvious agglomeration, and the surface is smooth. Subsequent ultrasonic treatment has a significant effect on the surface morphology. When the time of ultrasonic treatment was 20 minutes, the surface of ZnO sphere began to dissociate and the debris increased. When the time of ultrasonic treatment is 40 minutes, all the debris on the surface of ZnO sphere is broken into whiskers. This structural evolution from sphere to urchin reduces the crystallization of ZnO surface, which is consistent with the previous XRD analysis.

In addition, a large number of studies have shown that the absorbing properties of materials are closely related to their structures [12, 13]. Compared with S1 and S2, S3 has the largest specific surface area, more defects and vacancies for the sea urchin-like structure, and can provide a large number of scattering sites, which may be conducive to electromagnetic wave absorption.
3.3. Microwave absorption properties

As a microwave absorbing material, ZnO has very low magnetic loss and belongs to dielectric loss material. Therefore, the dielectric properties of ZnO are mainly analyzed in this paper. It can be seen from Fig.3 (a) (b) that the complex permittivity of ZnO increases with the time of ultrasonic treatment, which indicates that its polarization and loss capacity increase gradually. The dielectric loss tangent (tan \( \delta_E = \varepsilon''/\varepsilon' \)) was calculated based on the data of EM parameters which can be observed in Fig.3(c). The dielectric loss of S1 and S2 varies with frequency in a similar way, with significant differences only at 3.2 GHz, 9.3 GHz and 15.8 GHz. This is because S1 and S2 have similar morphology. After 40 minutes of ultrasonic treatment, the dielectric loss ability of ZnO has been improved significantly. This is due to the fact that the structure of sea urchin S3 has a large number of whiskers, and the charges can gather at the tip of the needle to form multiple polarization centers, which can cause scattered reflection of electromagnetic waves.

The phenomenon can also be explained by the Debye dipolar relaxation model [14]:

\[
\varepsilon \cdot \varepsilon_\infty = \frac{\varepsilon_S - \varepsilon_\infty}{[1 + (j \omega \tau_0)^{1-\alpha}]} \tag{3}
\]

In the formula, \( \tau_0 \), \( \alpha \), \( \varepsilon_\infty \), \( \varepsilon_S \) are respectively the relaxation time, parameter variable, optical frequency dielectric constant, and static dielectric constant. The complex permittivity \( \varepsilon \) can be expressed by the following formula [15]:

\[
\varepsilon = \varepsilon' - j \varepsilon'' = \frac{1}{j \omega \varepsilon_\infty Z} = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + 2\pi f \tau} \tag{4}
\]

The complex permittivity real part \( \varepsilon' \) and imaginary part \( \varepsilon'' \) can be expressed as:

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (2\pi f \tau)^2} \tag{5}
\]

\[
\varepsilon'' = \frac{2\pi f \tau (\varepsilon - \varepsilon_\infty)}{1 + (2\pi f \tau)^2} \tag{6}
\]

According to the real part (\( \varepsilon' \)) and imaginary part (\( \varepsilon'' \)) of complex permittivity, the Debye dipole relaxation equation can be expressed as:

\[
\left( \frac{\varepsilon' - \varepsilon_\infty}{2} \right)^2 + (\varepsilon'')^2 = (\varepsilon_S - \varepsilon_\infty)^2 \tag{7}
\]

According to this formula, We can make the Cole-Cole curve of S3 as shown in Fig.3(d). The frequency dependence of \( \varepsilon' \) and \( \varepsilon'' \) in S3 can be approximated as a large number of semicircles. Each semicircle corresponds to a Debye relaxation. The Debye semicircle can reflect the spectral
characteristics of the dielectric polarization and the extent to which the dielectric deviates from the Debye relaxation. For these reasons, the strong dielectric loss ability of S3 can be determined as multiple relaxation.

![Graph](attachment:image.png)
Formulas (1) and (2) can be used to calculate the reflective loss of a material at a specific thickness. The simulated reflection losses for the different samples of ZnO spheres in paraffin matrix with the coating thickness of 3.0 mm on a perfect conductor are displayed in Fig.4. As the ultrasonic time increases, the surface whiskers increase, and the absorbing properties of the ZnO spheres increase steadily. S3 has the best absorbing performance, the minimum reflection loss can reach -13.4 dB, and the effective bandwidth ($RL < -10$ dB, equivalent to absorbing 90 % of electromagnetic waves) can reach 1.8 GHz.

Figure 3. Electrical loss analysis for ZnO : (a) the real permittivity, (b) the imaginary permittivity, (c) dielectric loss tangent and (d) Cole-Cole curve of S3 in the range of 2-18 GHz

Figure 4. Reflection Loss Diagrams of Different Samples at 3 mm

4. Conclusion
Effect of ultrasonic treatment on morphology and microwave absorption performance of ZnO spheres have been investigated systemically in the present work. From the above results, conclusions are as following. With increases of ultrasonic time, the number of nano-ZnO whiskers on the surface also increases, leading to the microwave absorption properties are improved due to the multiple relaxation losses caused by a large number of whiskers. The work will be helpful for the future development of microwave absorption materials with high absorption properties by ultrasound treatment.

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