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Metal-semiconductor Zn/ZnO Core-Shell Nanocables: Facile and Large-scale Fabrication, Growth Mechanism, Oxidation Behavior, and Microwave Absorption Performance

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A new and facile synthetic route has been developed for the fabrication of metalsemiconductor Zn/ZnO core-shell nanocables in large scale. Zn/ZnO nanocables were grown by heating a ball-milled mixture of boron and ZnO powders at 1300 °C under ammonia atmosphere. The structure and chemical composition of the as-prepared products were characterized by a variety of techniques including powder X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and X-ray photoelectron spectroscopy. The nanocables were approximately 30-200 nm in diameter and tens of microns in length. The core was a Zn single crystal and the shell was an epitaxially grown ZnO layer of 3-10 nm in thickness. It was found that the Zn/ZnO nanocables transformed into mace-like nanostructures or ZnO nanotubes when oxidized at 300 °C in air. The formation mechanism of the Zn/ZnO nanocables as well as the oxidized products have been clarified based on the experimental observations. The Zn/ZnO nanocable-paraffin composites showed good microwave absorption property, and the reflection loss could reach -23 dB at 13.22 GHz. The mechanism for the enhanced absorption performance is discussed.

Introduction

One dimensional (1D) zinc oxide (ZnO) related nanomaterials have attracted tremendous attention in the past three decades due to their exceptional properties. ZnO nanowires and nanotubes are the most extensively studied ZnO nanostructures and have been demonstrated to exhibit superior mechanical toughness, higher luminescence efficiency, temperature dependent piezotronic effect, and a lowered lasing threshold.¹⁻⁴ Due to these advantageous properties, ZnO nanowires and

nanotubes have been widely used as light-emitting diodes,⁵ thermal-field emitters,⁶ and gas sensors.^{7, 8} To further enhance multi-functionality, a number of unique ZnO-related coaxial nanocables have been designed and fabricated. For example, ZnO/HfO₂:Eu nanocables were prepared by a radio frequency sputtering method and enhanced white-light emission was observed in these nanocables.⁹ ZnO/Zn_xCd_{1-x}Se nanocables were synthesized and were demonstrated to be promising photoelectrodes for photoelectrochemical solar cells.10 ZnO/BeO nanocables have been fabricated using a two-step method and improved optical properties were achieved.¹¹ In addition, the nanocables made of ZnO/ZnGa₂O₄,¹² ZnO/Eu₂O₃,¹³ ZnO/SiO₂,¹⁴ Zn_{0.96}Mn_{0.04}O/ZnO,¹⁵ ZnO/ZnSe,¹⁶ ZnO/ZnS and ZnO/CdS,^{17, 18} SnO/ZnO,^{19, 20} ZnSb₂O₄/ZnO,²¹ In₂O₃/ZnO₃²² and ZnO/CdTe/CdS₂²³⁻²⁶ have also been reported. These ZnO related nanocables exhibit either novel properties or enhanced performances and can find a variety of potential applications in electronics, optics and sensors.

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Zn/ZnO core-shell nanocables with metallic Zn core and semiconducting ZnO shells represent another type of ZnOrelated nanocables which are able to transport electrical signals much quicker than other 1D semiconducting materials and thus can be used as essential building blocks for nano-scaled electronic devices.²⁷ Up to now, only a few chemical strategies have been reported for the preparation of Zn/ZnO core-shell nanocables.²⁷⁻³¹ For example, Kim et al. fabricated coaxial Zn/ZnO nanocables through controlled thermal oxidation of Zn nanowires, yielding various cross-sectional areal fractions of Zn core and ZnO shell.²⁷ Zhang et al. fabricated Zn-ZnO core-shell nanobelts by oxidizing Zn powder in the reaction atmosphere with different oxygen contents.31 Kong et al. synthesized Zn/ZnO core-shell nanobelts via a solid-vapor decomposition process using pure ZnO powders as source material.³² These pioneering works not only discovered the novel Zn/ZnO coreshell nanocables, but also demonstrated that these nanostructures exhibit unique properties that can find applications in many fields. However, it is generally noticed that the synthetic methods of the Zn/ZnO nanocables are complex while the yields remain relatively low. From a practical perspective, it is still necessary to develop novel methods for the large scale production of Zn/ZnO core-shell nanocables.

In this work, we report a new facile method to fabricate Zn/ZnO core-shell nanocables in comparatively large scale by simply heating a mixture of boron and ZnO powders at 1300 °C via chemical vapor deposition (CVD). The structure and chemical composition of the as-prepared products were characterized by a variety of techniques. The formation mechanism of the products was clarified on the basis of the experimental observations. The oxidation behavior of the Zn/ZnO nanocables was investigated. Moreover, the dielectric property and microwave absorption performance of the Zn/ZnO nanocable-paraffin composites are discussed.

Experimental Section

Materials and methods

All the solvents and chemicals used in this study were analytical grade or better and were used as purchased. Zn/ZnO nanocables were grown by means of an ordinary tube furnace (80 mm in diameter) which allowed chemical vapor reaction of precursor gases. In a typical procedure, boron (10.8g, 1mol) and ZnO (81g, 1mol) powders were ball-milled for 1 hour using agate jars with agate grinding media in an ethanol medium. The mixture was oven dried and charged into an alumina boat. The boat was mounted into a tube furnace chamber which was then sealed. The furnace was heated to a temperature of 800 °C under argon, and further heated to the ultimate temperature of 1300 °C under ammonia. The heating rate was about 10 °C min⁻¹ and the holding time at the ultimate temperature was 3 hours. After the reaction, the furnace was allowed to cool to room temperature under argon atmosphere. The products were found at the outlet of the tube furnace and were directly used

for characterization without further treatment. The experimental setup and the temperature distribution of the furnace were schematically illustrated in Figure 1. In order to investigate the oxidation behavior of the Zn/ZnO nanocables, the oxidized sample was prepared. An alumina boat loaded with the asprepared Zn/ZnO nanocables was heated up to 300 °C in air atmosphere with holding time of 1 hour. After cooling to the room temperature, the oxidized sample was collected from the boat for further characterization.



Figure 1. Schematic illustration of the experimental setup and the temperature distribution along the furnace tube.

Characterization Techniques

The morphology, crystal structure, and chemical composition of the products were characterized by a variety of techniques including X-ray powder diffraction (XRD, Rigaku D/max-yB X-ray diffractometer with Cu K radiation ($\lambda = 0.154178$ nm)), scanning electron microscopy (SEM, TESCAN VEGA II), high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 equipped with energy-dispersive X-ray (EDX), and Tecnai F30 FEG equipped with electron energy loss spectroscopy (EELS)), X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700 ESCA System with a PC-ACCESS data analysis system), Fourier transformation infrared spectroscopy (FTIR, Nicolet 380 by using pressed KBr disks), and Raman spectrum (Renishaw invia). Thermal analysis was conducted on a Netzsch STA449C system and the data were obtained by heating the samples under argon gas from room temperature to 1400 °C at a heating rate of 10 °C min⁻¹. To investigate the dielectric properties (dielectric constant and dielectric loss tangent) and the microwave absorption properties of the products, specimens were prepared by uniformly mixing 30 wt.% Zn/ZnO nanocables with paraffin and pressing the mixture into a torus with a 7.00 mm outer diameter and a 3.04 mm inner diameter for measurement. The dielectric constant

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and dielectric loss tangent of the composites were estimated by the transmission/refection coaxial line method in the frequency range from 2 to 18 GHz using a microwave network analyzer (Agilent N5245A).

Results and discussion

Preparation and Characterization of Zn/ZnO Nanocables

The phase and purity of the as-synthesized products were examined by XRD, as shown in Figure 2. All the visible diffraction peaks can be indexed to the hexagonal Zn with the lattice constant of a=2.665 Å and c=4.947 Å (JCPDS card No. 04-0831), and the hexagonal ZnO with the lattice constant of a=3.250 Å and c=5.207 Å (JCPDS card No. 36-1451). No peaks related to other phases are found, revealing that the products are composed of Zn and ZnO phases.



Figure 2. XRD pattern of the as-prepared Zn/ZnO nanocables.

The digital photograph displayed in Figure 3(a) shows the macroscopic aspect of the as-prepared Zn/ZnO nanocables. Felt-like products could be clearly observed in the inner wall of the alumina tube with a diameter of about 80 mm, demonstrating the success of our large-scale synthesis of Zn/ZnO nanocables. Typically, 0.4-0.6 gram of Zn/ZnO nanocables could be obtained in one batch, but the process should be easily scalable to larger amounts. SEM images of the as-synthesized products at different magnifications are shown in Figures 3(b)-(e). Most of the 1D nanostructures possess a serpentine geometry shape with smooth surfaces and are 30 to 200 nm in diameters, dramatically different from ZnO nanowires that are straight³³ or ZnO nanobelts that form helical shapes^{34, 35}. The serpentine shape of these Zn/ZnO nanocables could be attributed to the change in growth directions among the crystallographically equivalent axes³², and/or the difference in the thickness ratio between Zn and ZnO when there is a fixed lattice mismatch between Zn and ZnO.



Figure 3. (a) A typical macroscopic digital photograph of the as-prepared Zn/ZnO nanocables. Typically, the Zn/ZnO nanocables could be obtained on gram scale; (b)-(e) representative SEM images of the Zn/ZnO nanocables taken at different magnifications.

The as-prepared products were dispersed on carbon coated copper grids to perform TEM analysis. TEM observation further revealed that the products were composed of two types of nanocables with different diameters. Figures 4(a)-(b) show low-magnification TEM images of the thinner type, from which a one dimentional (1D) nanostructure with average diameter of 30-50 nm was observed. The high-resolution TEM (HRTEM) image displayed in Figure 4(c) shows clear contrast along the radial direction of the 1D nanostructures, suggesting that the products are coaxial nanocables composed of shells and cores. Normally, the shielding layers are uniform with thickness of 3-10 nm and the cores are 30-50 nm in diameter. The fringe spacing of the shell is 0.52 nm which can be indexed to the (0001) planes of hexagonal ZnO crystal, while the fringe spacing of the core is 0.49 nm which can be indexed to the (0001) planes of hexagonal Zn crystal. Figures 4(d)-(e) show the low-magnification TEM images of the other type of Zn/ZnO nanocables. It is evident that these nanocables have larger diameters (100-200 nm) than the other type of nanocables. Moreover, a series of small protuberances can be observed on the surface of these nanocables. To further confirm the core-shell structure, the nanocables were analyzed by the HRTEM technique. HRTEM images taken from the regions marked in (e) are shown in Figures 4(f)-(g). The fringe spacing of the core is 0.49 nm which matches well with that of the (0001) planes of Zn, while the fringe spacing of the shell is 0.52

nm which corresponds to the (0001) planes of ZnO. This clearly demonstrates the core-shell structure as well as the growth directions of the nanocables.

Figure 4(h) shows a typical selected-area electron diffraction (SAED) pattern taken from an isolated nanocable, which can be indexed to hexagonal ZnO crystal (JCPDS card No. 36-1451). In addition to the sharp spots from (0001) and (10-10) planes of the outer ZnO shell, another set of diffraction spots which are indexed to the (0001) and (10-10) planes of a hexagonal Zn crystal (JCPDS card No. 04-0831) can be clearly identified from this pattern. This implies the presence of both Zn and ZnO in the isolated nanocable and also confirms the core-shell structure of the products. A typical EDX spectrum collected from the single Zn/ZnO nanocable displayed in Figure 4(e) is shown in Figure 4(i), which clearly suggests that the nanocable consists of Zn and O elements. The Cu signals came from the copper grid and no other elements were detected. EDX analysis further demonstrates that the single nanocable indeed contains Zn and O elements, suggesting the nanocable exhibits a possible Zn/ZnO core-shell structure.



Figure 4. (a)-(b) Representative low-magnification TEM images and (c) high-resolution TEM image of Zn/ZnO nanocables with diameters around 50 nm; (d)-(e) representative low-magnification TEM images of Zn/ZnO nanocables with diameters around 100 nm; (f)-(g) high-resolution TEM images taken from the regions marked in (e) and the insets show the corresponding fast Fourier transform (FFT) patterns; (h) typical SAED pattern and (i) EDX spectrum of the Zn/ZnO nanocables.

Electron-energy filtered TEM (EFTEM) analysis was further conducted to track the compositional distribution within both types of Zn/ZnO nanocables, as shown in Figure 5. Figure 5(a, e) are zero energy loss images. Figure 5(b, c, f, g) depict Zn and O elemental maps, which were obtained with the energy loss windows centered at the Zn L-edge of 1021 eV and the O K-edge of 532 eV, respectively. The composite images were shown in Figure 5 (d, h). These images intuitively suggest the layered core-shell structure of the Zn/ZnO nanocables.



Figure 5. Energy filtered TEM analysis of the two types of Zn/ZnO nanocables reflecting compositional distribution. (a, e) Zero-loss image; (b, f) Zn maps; (c, g) O maps; and (d, h) Composite images (Zn and O are shown by green and red colors). All scale bars represent 20 nm.

The elemental composition and the purity of the products were examined by X-ray photoelectron spectroscopy (XPS). Figure 6 shows the survey spectrum of the as-prepared Zn/ZnO nanocables, from which a series of peaks can be identified. The peak located at 284.62 eV is attributed to the carbon atoms from the CO_2 adsorbed on the surface of the sample. The peak located at 531.36 eV corresponds to the binding energy of oxygen atoms, and the peak at 977.84 eV is ascribed to O KLL Auger line. All the other peaks originate from Zn element and can be assigned to Zn2s, Zn2p, Zn3s, Zn3p, Zn3d, or Zn LMM Auger lines, as marked in Figure 6. The survey spectrum clearly suggests the presence of both Zn and O elements in the sample. Quantitatively analysis of the Zn2p and O1s peaks shows that the atomic ratio of Zn:O is around 0.92:1, which is close to the stoichiometric ratio of ZnO. The fine spectrum of the Zn2p2/3 peak shown in the inset of Figure 6 can be decomposed in to two components. The peak at 1022.09 eV can be attributed to ZnO, while the other peak at 1021.40 eV results from Zn beneath the thin ZnO shells.³⁶ XPS analysis further confirms the core-shell structure of Zn/ZnO nanocables.

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Figure 6. XPS analysis of the as-prepared Zn/ZnO nanocables. Inset: Zn2p2/3 fine spectrum.

Vibrational analysis was performed to clarify the bonding characters of the Zn/ZnO nanocables. Figure 7(a) shows the Raman spectrum of the as-prepared products. The broadened and asymmetric peak at ~430 cm⁻¹ is red shifted relative to the E_2 mode of ZnO (~437 cm⁻¹).³⁷ This is caused by the strain at the Zn/ZnO interface, which weakens the Zn-O bonds and therefore lowers their vibrational frequency. The peaks at around ~ 323 cm⁻¹ can be ascribed to the $3E_{2L}$ (316 cm⁻¹) and E_{2H}-E_{2L}(331 cm⁻¹) modes of ZnO.^{38, 39} The Raman spectrum of the ZnO nanocables is similar to that of the ZnO nanotubes. Clearly, the Raman spectrum reveals that the as-prepared products are composed of ZnO. It should be noted that Raman analysis cannot be used to characterize metals, thus the existence of Zn cannot be reflected in the Raman spectrum. Atomic vibrational modes were also examined by FTIR spectroscopy, as shown in Figure 7(b). A broad band around 400-650 cm⁻¹ corresponds to the stretching mode of Zn-O.⁴⁰ The band centered at 1629.2 cm⁻¹ is bending vibrational mode of hydroxyl group of the chemisorbed and/or physiosorbed water molecules. A prominent band at 1115.3 cm⁻¹ observed in our case corresponds to the bending vibration of V_{Zn}-H_{ABOI}. A broad band around 3000-3700 cm⁻¹ corresponds to the O-H bond stretching local vibrational modes (LVM) of ZnO nanophases.41



Figure 7. (a) Raman and (b) FTIR spectra of the as-prepared Zn/ZnO nanocables.

Formation Mechanism of Zn/ZnO Nanocables

Thermogravimetric and differential scanning calorimetry (TG-DSC) analyses were performed from room temperature to 1400 °C under argon to investigate the thermal behavior of the ZnO+B reaction mixture (molar ratio ZnO:B=1:1). As shown in Figure 8, a sharp weight loss of about 45 wt% can be observed in the temperature range from 720 to 800°C, which is also accompanied by two exothermic peaks. This indicates that exothermic chemical reactions might occur in this temperature range. Simple thermodynamic calculations show that we found that the enthalpy of the reaction $3ZnO + 2B = Zn + B_2O_3$ (Eq.1) is -169kJ which means the reaction is exothermic. The heat generated from this reaction may cause the evaporation of Zn which is in a liquid state (the melting point of Zn is 419.5°C). Therefore, we can rationally attribute the weight loss in this temperature range to Eq.1. Another broad endothermic peak centered at ~1240 °C appeared in the DSC curve, corresponding to a second weight loss of about 20 wt.% from 920 to 1400°C. Since the boiling point of Zn is 908°C, while that of B₂O₃ is larger than 1500°C, we can ascribe the second weight loss to the endothermic phase transformation of Zn (which is the remainder of Eq.1) from the liquid to gas phase. It is worth noting that the actual experimental conditions of the growth process of the Zn/ZnO nanocables are not exactly the same as those during the TG-DSC analysis, since Ar was replaced by NH₃ at 800°C. Therefore, the TG-DSC analysis is only a guideline for the estimation of the reaction process of the solid mixture.



Figure 8. TG-DSC analysis of the mixture of ZnO and B powders (molar ratio ZnO:B=1:1).

On the basis of the experimental observations as well as the TG-DSC data, the formation mechanism of the Zn/ZnO nanocables can be deduced. The main process can be formulated by the following chemical reactions.

$$2B(s) + 3ZnO(s) = B_2O_3(l) + 3Zn(g)$$
(1)
$$B_2O_3(l) + 2NH_3(g) = 2BN(s) + 3H_2O(g)$$
(2)

 $H_2O(g)+Zn(s)=ZnO(s)+H_2(g)$ (3)

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According to the TG-DSC analysis, the reaction between ZnO and B powders begins at 730°C, and Zn vapor was generated in this process. When the Zn vapor was transferred by the carrier gas (Ar) to the edge area of the furnace tube where the temperature is ~425 °C, Zn atoms tended to crystallize on the surface of alumina tube and grow into Zn nanowires (Figure 9(a)). In the second stage, Ar was replaced by NH₃ which is liable to react with B₂O₃ generated by Eq.1 at temperatures higher than 900 °C to produce solid state BN and gaseous H₂O. The gaseous H₂O was transferred from the central region to the edge region of the furnace where it reacts with Zn nanowires to form core-shell Zn/ZnO nanocables (Figure 9(b)).



Figure 9. Schematic illustration of the formation mechanism of the Zn/ZnO core-shell nanocables. (a) Formation of Zn nanowires; (b) formation of ZnO shell on Zn nanowires.

Oxidation Behavior of Zn/ZnO Nanocables

In order to further regulate the thickness of the ZnO shell of the Zn/ZnO nanocables, we attempted to directly oxidize the nanocables at 300 °C in air atmosphere. To our surprise, instead of the Zn/ZnO nanocables with thicker and uniform ZnO shells which we had expected, we came across two new derivatives of the original Zn/ZnO nanocables. One are the nanocables with ZnO flake protrusions, resembling maces (hereafter referred to as mace-like nanocables); the other are the ZnO nanotubes. Detailed TEM analysis was conducted to reveal the structural characteristics of the two nanostructures. Figures 10(a)-(d) show representative TEM images of the mace-like nanocables. Large amounts of flake-like protrusions can be observed on the surface of the original nanocables. Figure 10(e) further shows a HRTEM image taken from the marked area in Figure 10(d). The inter-plane spacing is about 0.52 nm which matches well with the d-spacing of the (0001) plane of ZnO (JCPDS card No. 36-1451). The inset shows the corresponding FFT images and the patterns can also be indexed to (0001) and (10-10) and (10-11) planes of ZnO. These results strongly demonstrate that the protrusions are ZnO flakes.



Figure 10. TEM analysis of the Zn/ZnO nanocables after oxidation treatment at 300 °C in air atmosphere: (a)-(d) Representative low-magnification TEM images, and (e) high-resolution TEM images of the Zn/ZnO nanocables with ZnO protrusions; (f) representative low-magnification TEM image, (g) SAED pattern, (h) high-magnification TEM image, and (i) high-resolution TEM image of ZnO nanotubes with the diameter of 50 nm. The insets show the corresponding FFT patterns.

Figure 10(f) shows representative low-magnification TEM image of the ZnO nanotubes, from which serpentine tubular nanostructures can be observed. SAED pattern taken from these nanostructures can be indexed to (0002), (10-11) and (10-13) planes of ZnO, respectively (Figure 10(g)), and no diffraction spots can be indexed to other phases, suggesting that the tubular nanostructures are composed of ZnO. More detailed properties of the structure can be revealed by the typical high-magnification TEM image shown in Figure 10(h). The average diameter of the ZnO nanotubes is about 50-70 nm and the wall thickness is around 10 nm. Further examination of the ZnO nanotube by HRTEM (Figure 10(i)) suggests that the lattice spacing is 0.26 nm, which corresponds to the spacing of (0002) plane of crystal planes of ZnO. The corresponding FFT image shown in the inset can also be indexed to ZnO.

It is interesting to discuss the formation mechanism of the two derivatives of the original Zn/ZnO nanocables. It is noted that the diameters of the ZnO nanotubes are around 50 nm and are comparable to that of the thinner Zn/ZnO nanocables observed in the SEM and TEM analyses. Similarly, the diameters of the mace-like nanostructures are around 100 nm and are comparable to that of the thicker Zn/ZnO nanocables. From these experimental observations, we may relate the two oxidized derivatives with distinct morphologies to the Zn/ZnO nanocables with different diameters. The mace-like Journal Name

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nanostructures and the nanotubes can be viewed as derivatives of the Zn/ZnO nanocables with larger diameters of 100-150 nm and that with smaller diameters of 30-50 nm, respectively. Although the oxidation temperature is only 300 °C which is lower than the melting pint of Zn, the Zn in the ZnO shells still has the possibility to melt (or sublimate), because the melting points of metals in nanoscale are generally lower than the normal melting points owing to the nanometer size effect. Compared with the Zn in thicker nanocables, the Zn in the thinner ones may have lower melting points. Moreover, the capillarity of a liquid in a tube is also size dependent, and the Zn in the thinner nanocables have more remarkable capillarity. In the meanwhile, it is also possible for sublimation of Zn to occur in the temperature range of 200-300 °C.³²

On the basis of the experimental observations as well as the theoretical considerations, the specific formation process of the two derivatives can be illustrated schematically, as shown in Figure 11. At the oxidation temperature of 300 °C, the Zn in the thinner nanocables melted (or sublimated) first, and then escaped from the nanocables under the capillary forces, leaving only ZnO nanotubes. Because of the higher melting points and/or lower capillary forces, the Zn in the thicker nanocables was retained in the ZnO shells. This may explain why the ZnO nanotubes with diameters comparable to those of the thicker Zn/ZnO nanocables (~100 nm) cannot be observed. During the melting and escaping of liquid Zn in the thinner nanocables, Zn vapor may be generated. The Zn vapor may react with oxygen on the front end of the protrusions on the Zn/ZnO with larger diameters. This causes the growth of the ZnO protrusions on the original thick nanocables into larger ZnO flakes, leading to the formation of the mace-like nanostructures.



Figure 11. Schematic illustration of the formation process of ZnO nanotubes and mace-like Zn/ZnO nanocables. (a) Original Zn/ZnO nanocables with two representative morphologies; (b) Zn vapors evaporated from the thinner nanocables react with oxygen on the surface of the thicker nanocables with small protrusions; (c) final formation of the hollow nanotube and mace-like nanocable.

Dielectric and Microwave Absorption Performances of Zn/ZnO Nanocable-Paraffin Composites

Unique structures always endow nanosized materials with novel physical and chemical properties, including microwave absorbing character. Recently, ZnO related nanostructures have attracted much attraction as microwave absorbing and shielding materials in the high-frequency range.⁴²⁻⁴⁶ Now that the Zn/ZnO nanocables can be fabricated easily in large scale in this study and, more importantly, their microwave absorption property has rarely been reported, it is meaningful to study the microwave absorption property of this distinctive nanostructure. We investigated the dielectric properties as well as the microwave absorption property of the Zn/ZnO nanocableparaffin composite (with 30 wt% nanocables) in the frequency range of 2-18 GHz. Figure 12(a) shows the relative permittivity of the Zn/ZnO nanocable-paraffin composite. The real part of the permittivity \mathcal{E}'_{μ} is around 4-5 and slightly declines with frequency increasing. The imaginary part \mathcal{E}_{r}'' is around 0-0.5 and increase with frequency increasing. The dielectric loss tangent increases with frequency increasing, reaching a maximum at about 12 GHz, and then decreases, as shown in Figure 12(b). A similar strong wide peak at approximately 12 GHz has been reported in ZnO flowers, which was ascribed to the cooperative action of interface scattering, microcurrent attenuation, and dielectric relaxation. 47



Figure 12. (a) The relative permittivity and (b) the dielectric loss tangent of the Zn/ZnO nanocable-paraffin composite.

To evaluate the microwave absorption performance, the reflection loss (RL) of the composites at different assumed coating thicknesses has been calculated according to transmission line theory using Eqs. (4) and (5), in which μ_r and \mathcal{E}_r are the complex permeability and the complex permittivity, respectively. The coefficients, *f*, *d*, *c*, Z_0 and Z_{in} are the frequency, the coating thickness, the velocity of light, the impedance of air, and the impedance of absorber, respectively.⁴⁸

$$RL(dB) = 20\log\frac{|Z_{in} - 1|}{|Z_{in} + 1|}$$
(4)

$$Z_{in} = Z_0 (\mu_r / \varepsilon_r)^{1/2} \tanh[j(2\pi f d / c)(\mu_r / \varepsilon_r)^{1/2}]$$
(5)

As shown in Figure 13, the RL is higher than -3 dB for the composite with a thickness less than 4 mm. It is noticed, however, that as the coating thicknesses increases, the RL increases significantly. The optimal maximum RL of about -23 dB at around 13.22 GHz is obtained with the thickness of 14 mm, which also has a wide effective absorbing band width Δf of about 1.5 GHz (the Δf is generally defined as the width of the band in which the RL exceeds -10 dB). Our results are better than the optimized RL data of the composites containing other ZnO nanostructures reported in the literature.^{42, 47, 49, 50} For example, the optimized RL for the composite containing

ZnO nanowires is -12.28 dB,⁴² that containing polymorphous ZnO complex architectures is -4.9 dB,⁴⁷ that containing cagelike ZnO/SiO₂ nanostructures is -10.68 dB,⁴⁹ and that containing ZnO nanocombs is -12 dB.50 Although the exact mechanism remains to be ascertained by virtue of complex electromagnetic wave equations, it is still meaningful to interpret the microwave absorption property based on the structural characters. The microwave absorption of nanostructures can generally be related with microcurrent attenuation and dielectric relaxation. Owing to the conductive Zn nanowires in the cores of the nanocables, the electric conductivity of the Zn/ZnO nanocables can be increased. Vibrating microcurrent can be excited by alternating electric field and thus microcurrent attenuation may play an important role in the microwave absorption. On the other hand, ZnO itself is a dielectric loss medium and can attenuate microwave by dielectric relaxation (electrons of polar monomers moving back and forth). This effect can be enhanced by rich surfaces or interfaces of samples. It has been reported that when the alternating microwave interacts with the charge multipoles at the interfaces in the composites, strong attenuation of microwave energy tends to occur.42, 47 It is noted that the absorbers used in this study are Zn/ZnO nanocables which possess much richer interfaces (including both paraffin-ZnO interfaces and the ZnO-Zn interfaces) comparing with pure ZnO nanostructures. Therefore, the microwave attenuation caused by the interfacial electric polarization is another factor that contributes to the low RL value of the unique core-shell Zn/ZnO nanocables.



Figure 13. Simulation of the reflection loss of the Zn/ZnO nanocable-paraffin composite with different thicknesses.

Conclusions

In summary, a new method has been developed for the fabrication of novel metal-semiconductor Zn/ZnO core-shell nanocables employing boron powders, ZnO powders and ammonia gas as starting materials. Gram-scale Zn/ZnO nanocables could be typically fabricated in one batch. The

morphology and structure were found greatly altered when the nanocables were oxidized at 300 °C, and novel mace-like Zn/ZnO nanocables and ZnO nanotubes could be obtained. The growth mechanisms of both ZnO nanocables and the oxidized products have been proposed. The dielectric properties and the microwave absorption performance of Zn/ZnO nanocable-paraffin composite have also been investigated. Results showed that the real part of the permittivity \mathcal{E}'_r is around 4-5 and the imaginary part \mathcal{E}''_r is around 0-0.5. The maximum reflection loss of the composite could reach -23 dB at 13.22 GHz, which is outstanding compared with that of composites filled with other ZnO-related nanostructures.

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Zn/ZnO core-shell nanocables have been fabricated in large scale and the formation mechanism and microwave absorption property have been investigated.