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Uniform Fe₃O₄ coating on flower-like ZnO nanostructures by atomic layer deposition for electromagnetic wave absorption

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An elegant atomic layer deposition (ALD) method has been employed for controllable preparation of uniform Fe₃O₄-coated ZnO (ZnO@Fe₃O₄) core–shell flower–like nanostructure. The Fe₃O₄ coating thickness of the ZnO@Fe₃O₄ nanostructure can be tuned by varying the cycle numbers of ALD Fe₃O₄. When served as the additives for microwave absorption, the ZnO@Fe₃O₄-paraffin composites exhibit higher absorption capacity than the ZnO–paraffin composites. For ZnO@500-Fe₃O₄, the effective absorption bandwidth below −10 dB can reach 5.2 GHz and the RL values below −20 dB also cover a wide frequency range 11.6–14.2 GHz when the coating thickness is 2.3 mm, suggesting their potential application in treatment of the electromagnetic pollution problem. On the basis of experimental observations, a mechanism has been proposed to understand the enhanced microwave absorbing properties of the ZnO@Fe₃O₄ composites.

Introduction

Serious electromagnetic (EM) pollution problems from the extensive use of electronic equipment and wireless devices have called upon an urgent development of microwave absorption material (MAM). Indeed, great advances have been achieved on model absorbers, and insights into the correlations of the materials morphology, size as well as chemical composition and absorption characteristics are crucial for not only understanding of EM wave absorbing mechanism, but also generating new concepts to guide the rational design of practical microwave absorbers. Sun et al. found that the absorption peaks could be controlled by varying the intersectional angles of alignedCNT films and the maximum reflection loss (RL) could be further increased by increasing the stacked number of alignedCNT films. Xiao et al. reported that hydrogenation successfully turned inactive TiO₂ into an excellent microwave absorber with an innovative collective-movement-of-interfacial dipole mechanism. Recently, it has also been confirmed that the integration of the dielectric–magnetic composition and unique morphology into the unique core-shell structure is an effective strategy to acquire high-performance microwave absorbers due to intensified polarization at interfaces and its associated relaxation loss, which provides an elegant method for MAM innovations and inspires further developments of other exciting MAMs. For example, Yuan et al. fabricated novel 3-D ordered arrays of core–shell microspheres consisting of Fe₃O₄ cores and ordered mesoporous carbon shells, which showed excellent microwave absorption performances with maximum RL of up to −57 dB at 8 GHz, and large absorption bandwidth (7.3–13.7 GHz, < −10 dB). Yu et al. found that FeCo nanoparticle embedded nanoporous carbon composites exhibited a maximum RL of −21.7 dB at a thickness of 1.2 mm.

ZnO has been widely investigated as a major annexing agent of microwave absorbers due to its low cost, non-toxic nature, long-term stability, semiconductive, and piezoelectric features. A core problem in exploiting new types of functional ZnO absorption materials is how to enhance their EM wave absorbing efficiency. Many studies demonstrated that modifying ZnO could improve its absorption properties by controlling its structure, compositing with other materials or introducing other constituents into the lattice. For example, Wang et al. prepared ZnO/PVDF composites via a simple hot-press method and found that the RL of the composite with a filler content of 10 wt% had two peaks that could reach −15.90 dB at 6.60 GHz and −25.44 dB at 16.48 GHz. The mechanism for the increase in absorption properties could be explained by the Debye relaxation theory. Lu et al. reported the synthesis of multi-wall carbon nanotubes decorated with ZnO nanocrystals by a mild solution-process and investigated its high temperature microwave absorption properties. Their results showed that the absorbing frequency of the composites almost covers the full X-band for RL ≤ −10 dB. Despite these great developments in the synthesis of ZnO based MAMs, the facile synthesis of ZnO composites with well-defined core–shell structure including the coating thickness and uniformity remains a challenge.

Herein, we synthesized the interesting Fe₃O₄-coated ZnO (ZnO@Fe₃O₄) core–shell composite materials by an atomic layer deposition (ALD) technology and investigated the dielectric and microwave absorption properties of composites. The results show that ZnO@Fe₃O₄ is an excellent MAM candidate benefiting from the...
uniform core-shell structure which induces the intensified interfacial polarization enlarged microwave absorption.

Experimental

Preparation of ZnO. The ZnO used in this work was synthesized by a hydrothermal method as reported previously. Typically, 40 mL of 20 mmol L$^{-1}$ zinc acetate aqueous solution was mixed with a NaOH aqueous solution (0.3 mol L$^{-1}$) of the same volume under vigorous magnetic stirring at room temperature. The mixture solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and was kept at 160 °C for 5 h. The resultant white solid product was centrifuged, washed with distilled water, and dried at 45 °C in a vacuum.

Synthesis of ZnO@Fe$_{3}$O$_{4}$. The ALD process was carried out in a home-made, closed type, hot-wall ALD reactor. Prior to ALD, the ZnO was dispersed in ethanol by ultrasonic agitation and then dropped onto a quartz wafer. After being air-dried, the Fe$_{3}$O$_{4}$ coatings were deposited by sequential exposure of the ZnO to Ferrocene (FeCp)$_2$ and O$_2$. The temperature of FeCp$_2$ precursor was maintained at 100 °C and the deposition was conducted with a substrate temperature of 250 °C. Finally, after the ALD process, the sample was transferred to a furnace and reduced at 450 °C in 5% H$_2$/Ar atmosphere for 2 h. The sample was collected and was denoted as ZnO@n-Fe$_{3}$O$_{4}$, where n means the cycle number of the Fe$_{3}$O$_{4}$ ALD.

Sample characterization. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer using a Cu Ka source ($\lambda = 0.154056$ nm). Scanning electron microscopy (SEM) images were obtained using a HITACHI S-3000N microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a JEOL-2100 microscope instrument at an acceleration voltage of 200 kV. The composition and elemental maps of the samples were analyzed by energy-dispersive X-ray (EDX) spectroscopy using an EDX attachment to the SEM instrument. Raman spectroscopy was performed on a Renishaw inVia Reflex Raman microscope using 532 nm green laser excitation. The chemical compositions of the samples were determined by atomic absorption spectroscopy (AAS, TAS-990 Super AFG). The specimens for measuring the EM properties were prepared by uniformly mixing 60 wt% ZnO or ZnO@Fe$_{3}$O$_{4}$ with paraffin and pressing the mixture into a cylindrical shape. Then the cylinder was cut into a toroid of 7.00 mm outer diameter and 3.04 mm inner diameter for measurement. The relative permeability and permittivity values of the mixture were determined and obtained by measuring the S$_{11}$ and S$_{11}$ parameters between 2 and 18 GHz with an AV3629D network analyzer by using the transmission/reflection coaxial line method.

Results and discussion

The morphologies and microstructures of the starting ZnO used in this study were characterized by using SEM (Fig. 1a) and TEM (Fig. 1b). It can be seen that ZnO presents a flower-like hierarchical structure assembled by the ZnO nanorods with a diameter of 100–400 nm and a length of up to a few microns. The HRTEM image (Fig. 1c) and FFT diffraction pattern (inset to Fig. 1c) confirm that the flower-like ZnO is the hexagonal phase of zincite. The well-defined crystalline lattice spacing of 0.19 and 0.28 nm can be indexed as (102) and (100) crystal planes of ZnO, respectively.

![Fig. 1 SEM, (b) TEM and HRTEM images of ZnO.](image1)

![Fig. 2 TEM and HRTEM images of (a)–(c) ZnO@500-Fe$_{3}$O$_{4}$ and (d)–(f) ZnO@1000-Fe$_{3}$O$_{4}$.](image2)

Fig. 2a and b show low-magnification TEM images of ZnO@Fe$_{3}$O$_{4}$ obtained by applying 500 ALD cycles of Fe$_{3}$O$_{4}$ deposition. It is clearly seen that the surface of ZnO nanorod is covered with a very uniform Fe$_{3}$O$_{4}$ shell with a thickness of about 10 nm. The HRTEM image shows the well-defined crystalline lattice spacing of 0.25 nm, corresponding to the (110) crystal plane of rhombohedral phase Fe$_{3}$O$_{4}$ (Fig. 2c). The thickness of Fe$_{3}$O$_{4}$ coating can be easily tuned by adjusting the cycle numbers of the Fe$_{3}$O$_{4}$ ALD process. Fig. 2d and e show TEM images of the product after 1000 Fe$_{3}$O$_{4}$ ALD cycles. The formed ZnO@Fe$_{3}$O$_{4}$ core-shell structures are clearly visible due to their different contrasts. The thickness of Fe$_{3}$O$_{4}$ shells increases with the increase of ALD cycles and amounts to about 20 nm, which corresponds to a growth rate of about 0.2 Å per cycle. The lattice fringes from HRTEM images (Fig. 2f) also reveal the features of rhombohedral phase Fe$_{3}$O$_{4}$.

The flower-like ZnO@Fe$_{3}$O$_{4}$ core-shell structures can be readily obtained by annealing ZnO@Fe$_{3}$O$_{4}$ at 450 °C for 2 h under a mixture...
of Ar/H\textsubscript{2} flow in a tube furnace. After a reduction process, the colour of products changed from yellow to black. As shown in Fig. 3a and b and Fig. 3d and e, it can be seen that the ZnO@Fe\textsubscript{3}O\textsubscript{4} core-shell nanostructures have similar morphology and size with the ZnO@Fe\textsubscript{2}O\textsubscript{3}. In comparison to ZnO@Fe\textsubscript{2}O\textsubscript{3}, the average thicknesses of Fe\textsubscript{3}O\textsubscript{4} shells measured by TEM images are also about 10 and 20 nm for the ZnO@500-Fe\textsubscript{3}O\textsubscript{4} and ZnO@1000-Fe\textsubscript{3}O\textsubscript{4}, respectively. The negligible variation in shell thickness should be ascribed to that only approximately 3.33 wt% shrinkage was produced from the release of oxygen anions in the reduction treatment (from Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}). The well-defined crystalline lattice spacing of 0.30 and 0.49 nm are observed, corresponding to the (220) and (111) crystal planes of Fe\textsubscript{3}O\textsubscript{4} (Fig. 3c and f), respectively. The energy dispersive X-ray spectroscopy (EDS) elemental maps of Zn, O and Fe demonstrate that the Fe element is equally distributed on the surface of ZnO and maintains a consistent flower-like morphology, which furthermore indicates the perfect core–shell configuration (Fig. 4).

The phase composition and structure of the as-synthesized products are also investigated by XRD analysis. Fig. 5a presents the XRD patterns of ZnO, ZnO@500-Fe\textsubscript{3}O\textsubscript{4} and ZnO@1000-Fe\textsubscript{3}O\textsubscript{4} products. All of the strong reflection peaks can be readily indexed to those of the hexagonal phase of zincite with the lattice parameters of a = 3.242 Å and c = 5.176 Å, which are consistent with the reported values (Joint Committee on Powder Diffraction Standards (JCPDS), powder diffraction file no. 01-1136). Due to the low content of Fe\textsubscript{3}O\textsubscript{4} (Fig. S1), only two relatively weak peaks at 2θ = 43.0° and 53.5° associated with the planes (400) and (422) of the face-centered cubic crystal structure of Fe\textsubscript{3}O\textsubscript{4} (JCPDS card 01-1111) for the ZnO@500-Fe\textsubscript{3}O\textsubscript{4} and ZnO@1000-Fe\textsubscript{3}O\textsubscript{4} are found from the enlarged XRD pattern (Fig. 5b and c). The XRD analysis is in good agreement with both the HRTEM and EDS results.

We also employed Raman spectroscopy to further characterize the surface functionalities of the samples qualitatively. Fig. 6 shows the Raman spectra of ZnO@Fe\textsubscript{3}O\textsubscript{4} by comparison to that of pristine ZnO. For ZnO, two dominant Raman bands at 99 and 655 cm\textsuperscript{-1} are observed, which correspond to the E\textsubscript{2} (low) and E\textsubscript{2} (high) mode, indicating that the product has perfect crystallinity. The slightly weak peak at 384 cm\textsuperscript{-1} can be attributed to A\textsubscript{1} (TO) mode. For ZnO@Fe\textsubscript{3}O\textsubscript{4}, the weaken E\textsubscript{2} (low) and E\textsubscript{2} (high) mode imply that the thin layer of Fe\textsubscript{3}O\textsubscript{4} shell possibly exists on the surface of the ZnO, as Raman is more sensitive to the sample surface. As shown in Fig. 6, Three fundamental Raman scattering peaks for Fe\textsubscript{3}O\textsubscript{4} are observed.
at 315, 512, and 663 cm\(^{-1}\) corresponding to the \(E_g\), \(T_{2g}\) and \(A_{1g}\) vibration modes, respectively.\(^{36}\) The Raman scattering result unambiguously confirms that the as-prepared core-shell structures observed in the TEM measurements are ZnO@Fe\(_3\)O\(_4\), which is consistent with the XRD results.

\[
Z_{in} = Z_o (\mu_r / \varepsilon_r)^{1/2} \tanh\left[ j (2\pi f d/c) (\mu_r \varepsilon_r)^{1/2} \right] \tag{1}
\]

\[
RL = 20 \log \left( \frac{Z_{in} - Z_o}{Z_{in} + Z_o} \right) \tag{2}
\]

where \(Z_{in}\) is the input impedance of the absorber, \(Z_o\) the impedance of free space, \(\varepsilon_r\) the relative complex permittivity, \(\mu_r\) the complex permeability, \(f\) the frequency of microwaves, \(d\) the thickness of the absorber, and \(c\) the velocity of light. A RL value of \(-10\) dB is comparable to 90% microwave absorption. In general, materials with RL values of less than \(-10\) dB absorption are considered as suitable EM wave absorbers.

Fig. 7 shows the three-dimensional RL values of ZnO–paraffin and ZnO@Fe\(_3\)O\(_4\)–paraffin composites with different thicknesses (1.5–3.0 mm) in the frequency range of 2–18 GHz. Pristine ZnO exhibits poor RL characteristics, hardly less than \(-10\) dB which means 90% absorption efficiency in the range of 1.5–3.0 mm. For ZnO@500-Fe\(_3\)O\(_4\), the absorption bandwidth for RL values below \(-10\) dB is in the range of 12.5–16.6 GHz with a thickness of only 2.0 mm, corresponding to a bandwidth of 4.1 GHz. When the thickness is 2.3 mm, the sample achieves the best microwave absorption performance. The effective absorption bandwidth below \(-10\) dB can reach 5.2 GHz (10.3–15.5 GHz) and the RL values below \(-20\) dB (99% absorption) also cover a wide frequency range 11.6–14.2 GHz. Moreover, the minimum RL value reaches \(-28.6\) dB at 13.1 GHz. Obviously, the microwave absorption properties ZnO@500-Fe\(_3\)O\(_4\) are substantially enhanced relative to the pristine ZnO. Compared with ZnO-based absorption materials reported recently,\(^{27,29,31–33,40}\) the present ZnO@500-Fe\(_3\)O\(_4\) also has a broader bandwidth with a smaller coating thickness. For ZnO@1000-Fe\(_3\)O\(_4\), although the minimum RL value is merely \(-13.0\) dB at 16.8 GHz, the microwave absorption values less than \(-10\) dB is obtained in the range of 15.5–18.0 GHz with a thickness of only 1.5 mm.

It is widely accepted that the dielectric loss and magnetic loss are normally responsible for energy attenuation in microwave absorbing coatings. The RL behaviors of materials are usually associated with the relative complex permittivity (\(\varepsilon_r = \varepsilon' + i\varepsilon''\)) and permeability (\(\mu_r = \mu' + i\mu''\)) determined by their nature, size and microstructure. As shown in Fig. 8, the \(\mu_r\) and \(\varepsilon_r\) of the ZnO–paraffin and ZnO@Fe\(_3\)O\(_4\)–paraffin composites were evaluated at 2–18 GHz in order to study the possible absorption mechanism. It can be seen that the \(\varepsilon'\) values of ZnO@Fe\(_3\)O\(_4\)–paraffin composites increase with the increased thickness of Fe\(_3\)O\(_4\) layer (Fig. 8a), which is higher than that of ZnO–paraffin composites. Both ZnO and ZnO@1000-Fe\(_3\)O\(_4\) display the slow decline of \(\varepsilon'\) values in the whole frequency range of 2–18 GHz, while the \(\varepsilon'\) value of ZnO@500-Fe\(_3\)O\(_4\) keeps to 7.8 from 2.0 to 10.3 GHz, then decreases to 5.2 at 14.6 GHz, and increases to

Fig. 7 Three-dimensional representations of the reflection losses of (a) ZnO, (b) ZnO@500-Fe\(_3\)O\(_4\) and (c) ZnO@1000-Fe\(_3\)O\(_4\).
It is known that the $\varepsilon'$ and $\varepsilon''$ of the complex permittivity correspond to the energy storage and attenuation capability, respectively. The ZnO@500-Fe$_3$O$_4$ shows higher $\varepsilon'$ and $\varepsilon''$ values, suggesting that ZnO@500-Fe$_3$O$_4$ has much higher efficiency in storing and attenuating the electrical energy. We calculated the dielectric loss tangent (tan $\delta$ = $\varepsilon''$/ε') of all the composites, in which the maximum values of tan $\delta$ are 0.26, 0.45 and 0.27 for ZnO, ZnO@500-Fe$_3$O$_4$, and ZnO@1000-Fe$_3$O$_4$, respectively (Fig. S2). The larger tan $\delta$ values for the ZnO@500-Fe$_3$O$_4$ and ZnO@1000-Fe$_3$O$_4$ imply that the coating of Fe$_3$O$_4$ on the surface of ZnO is an efficient strategy to improve the dielectric loss. Dielectric polarizations are mainly composed of the electron polarization, the ion polarization, and the electric dipolar polarization. The electron polarization and ion polarization usually occur at the higher frequency than the infrared frequency. The electric dipolar polarization is well-known dielectric loss mechanism normally responsible for EM wave absorption in the microwave region and might aroused from a heterogeneous interface. Usually, interfacial polarization occurs whenever there is a buildup of a charge at a boundary between two regions or materials.\textsuperscript{15,17,41,42} Therefore, the microwave absorption enhancement in present work should be originated from intensified polarization of the ZnO@Fe$_3$O$_4$ core-shell interfaces and the proper Fe$_3$O$_4$ shell thickness plays an important role to maximize the interface effect. Debye dipolar relaxation is utilized to further understand absorbing mechanisms of the ZnO and ZnO@Fe$_3$O$_4$. Only an obvious Cole–Cole semicircle (Fig. S3) is found for the ZnO@500-Fe$_3$O$_4$, among three samples, which reconfirms that there is the relative intense dielectric relaxation process probably ascribed to the interface polarization. To further give a visual demonstration of the microwave absorption mechanism of ZnO@Fe$_3$O$_4$ composites as discussed above, a schematic is given in Scheme 1.

**Conclusions**

In summary, ZnO@Fe$_3$O$_4$ core-shell structures with controllable shell thickness were successfully synthesized through an atomic layer deposition method. The as-prepared ZnO@Fe$_3$O$_4$ composites with proper Fe$_3$O$_4$ coating show excellent microwave absorption performances including the broad bandwidth and the small coating thickness. The enhanced microwave absorption properties are attributed to the increased relatively complex permittivity and the promoted dielectric loss by the intense interfacial dielectric polarizations.

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Notes and references
Uniform ZnO@Fe$_3$O$_4$ core–shell structure is prepared by an ALD method, which shows great potential for microwave absorption materials.