Synthesis of Zn(II)-Doped Magnetite Leaf-Like Nanorings for Efficient Electromagnetic Wave Absorption

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We report the thermal annealing-induced formation of ring-like structure of Zn(II)-doped magnetite from iron alkoxide leaf-like nanoplate precursor. The phase, structure and morphology of magnetite nanorings were comprehensively characterized by powder X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscope, scanning electron microscope, and transmission electron microscope. The obtained Zn(II)-doped magnetite nanorings are of 13–20 nm in edge width, 70–110 nm in short axis length and 100–150 nm in long axis length. The growth mechanism was possibly due to a combined effect of decomposition of the organic component and diffusion growth. Zn(II)-doped magnetite nanorings delivered saturation magnetization of 66.4 emu/g and coercivity of 33 Oe at room temperature. In addition, the coatings containing Zn(II)-doped magnetite nanorings as fillers exhibit excellent microwave absorption properties with a maximum reflection loss of −40.4 dB and wide effective absorbing band obtained in coating with thin thickness of 1.50 mm.

Electromagnetic wave absorbing (EMA) materials are at the core of electromagnetic interference (EMI) prevention and radar concealing (RC) technology1. So far, many kinds of EMA materials including ferrites, metallic powders, ceramics powders, carbon fibers, etc., have been studied in the past a few decades to meet the ever-increasing requirements from EMI prevention and RC technology2–9. Among these materials, magnetite is a good candidate as they present unique electromagnetic (EM) properties6–9. The electromagnetic properties of magnetite are very sensitive to their compositions, microstructures, shapes and dimensions10–12. In general, the morphology and microstructure will affect the conductivity, electric polarization and magnetic properties of magnetite, which will then influences the complex permeability and permittivity in microwave band.

Many efforts were inspired to tailor the microstructure and morphology of magnetite, aiming to optimize the permittivity, permeability and the EM matching. Specifically, a lot of attention has been focused on magnetite nanostructures in recent years6–12. Magnetite nanostructures, including nanoparticles, nanospheres, nanowires, nanorings, nanoporous structures and nanoplatelets, have been prepared by a variety of synthetic methods involving chemical co-precipitation, electrochemical, solvothermal method and iron compound decompositions, etc. In particular, nanorings have attracted strong interests because of their novel structure and properties6–12. Jia et al.13 first synthesized magnetite nanorings via a reduction process. The synthesized magnetite nanorings have the single-vortex magnetic state and could hold the information storage in the circulating magnetization. Chen et al.14 synthesized necklace-like magnetite nanorings by a one-step solvothermal method. Xing et al.15 reported the formation of magnetite ring-like nanostructures through oriented attachment of magnetite nanocrystal building blocks via a hydrothermal process. Fan et al.16 developed a new universal template route to fabricate Fe3O4 nanorings through a simple thermal transformation method, which have great potential in biomedicine and biomagnetic applications.

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Although significant efforts have been exerted to prepare Fe$_3$O$_4$ nanorings, there are only a few reports on the EMA properties of Fe$_3$O$_4$ nanorings. Recently, Tong's group$^{10}$ investigated the EMA properties of elliptical Fe$_3$O$_4$ nanorings. The coating using Fe$_3$O$_4$ nanorings as fillers presented maximum reflection loss ($RL_{max}$) of −58.9 dB at 17.7 GHz, revealing the superiority of Fe$_3$O$_4$ nanorings for EMA applications. The ring-like structure is believed to contribute to the high dielectric/ferromagnetic loss, suggesting the feasibility to obtain enhanced EMA efficiency. However, main EMA peaks appear at high frequency band in the study, which then partially restrict the application of this catalog of materials. It is thus a challenge to obtain enhanced EM properties in Fe$_3$O$_4$ nanorings, which is crucial for extending the EMA application into low frequency band such as C or X band.

The magnetic and electromagnetic properties of magnetite can be tuned significantly upon doping with metal elements. Specifically, the saturation magnetization ($M_s$) and the coercivity ($H_c$) depend on the category and location of metal ion-dopants. Liu et al.$^{11}$ successfully adjusted the $M_s$ and $H_c$ of Zn-doped Fe$_3$O$_4$ nanoparticles by controlling the Zn doping amounts. On the other hand, the substitution of Fe$^{2+}$ by metal ions may lead to enhanced permittivity/permeability. Shimada et al.$^{18}$ observed that the permeability increases with increasing Zn concentration in Ni–Zn ferrite films. On the basis of the above literatures, we could speculate that Zn ion doping can be an effective method to tailor the magnetic and EM properties of Fe$_3$O$_4$ nanorings.

In this work, Zn(II)-doped magnetite nanorings were prepared by thermal decomposition of the solvothermal iron alkoxide precursor. The possible formation mechanism of ring-like structure was proposed based on time-dependent experiments. Furthermore, the magnetic and microwave absorption properties of Zn(II)-doped magnetite nanorings were evaluated. Benefiting from zinc ion-dopants and ring-like structures, the obtained magnetite nanorings exhibit excellent microwave absorption property in lower frequency.

**Results and Discussion**

The crystal structure and phase of iron alkoxide precursor and magnetite products were examined by XRD (Fig. 1). The strong XRD peak at around 10° is a typical feature from the coordination and alcoholysis of EG with the center metal ions$^{12}$. The FTIR spectrum of the precursor is shown in Figure S1. The peak at 2500–3000 cm$^{-1}$ could be attributed to the characteristic of the C–H stretching mode. Except the δ($\text{H}_2\text{O}$) vibration at 1620 cm$^{-1}$, the bands located below are assigned to Fe–O, C–O, C–C, and CH$_2$ bonds$^{20}$. The solvothermal precursor is thought as a kind of iron alkoxide$^{21}$.

DSC was performed to determine the calcination temperature of iron alkoxide precursor. As shown in Figure S2, the precursor decomposed at the temperature range from 300 to 400°C. Black products were obtained when the precursor was annealed at 350°C for 1 h in argon atmosphere. XRD pattern of the calcined products is shown in Fig. 1. All diffraction peaks can be indexed to a face-centered cubic phase ($Ia3d$) of magnetite (JCPDS No. 65–3107). No evident peaks of impurity phase are detected, indicating the high purity of the final products. The average crystalline size of products was evaluated to be 21.1 nm based on the (311) diffraction peaks of magnetite (JCPDS No. 65–3107). No evident peaks of impurity phase are detected, indicating the high purity of the final products.

Figure 1. XRD patterns of iron alkoxide precursor and magnetite products. The low panel shows standard diffraction patterns of magnetite (JCPDS No. 65–3107).

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noted that the adding of slight amount of zinc plays a critical role in controlling the leaf-like nanoplate morphology, which has been discussed in detail in our earlier work. The leaf-like nanorings shaped up after the precursors were calcined at 350 °C for 1 h in argon atmosphere, as shown in Fig. 4a and b. The obtained magnetite nanorings still kept the leaf-like configuration, and their edge width, short axis length, and long axis length were 13–20 nm, 70–110 nm, and 100–150 nm, respectively. TEM image (Fig. 4c) clearly indicates the obtained sample was leaf-like nanorings. Fig. 4e shows a high-magnification TEM image of an individual ring, demonstrating that the nanoring was composed of numerous nanoparticles. Selected-area electron diffraction (SAED) pattern of the leaf-like nanorings is presented in Fig. 4d. The concentric ring characteristic indicated the polycrystalline structure of the as-prepared magnetite nanorings. The strong rings observed in SAED pattern were indexed to the (220), (311), (400), (422), and (511) planes of the face-centered cubic magnetite, respectively. SAED results agree with that from the XRD analysis fairly well. Concurrently, the clear lattice fringes with interplanar distance of 0.29 nm were observed in the HRTEM image (Fig. 4f) of the nanorings (the red rectangle in Fig. 4e), which can be indexed as the (220) planes of the magnetite.

To investigate the formation mechanism of Zn(II)-doped magnetite nanorings, time dependent experiments were conducted with other reaction conditions were set same as typical experiment. The products (named as intermediate) prepared with different calcining time of 15, 30, and 45 min were characterized by TEM (Fig. 5). From the TEM image shown in Fig. 5a, it is interesting that the "pores" arise in the surface of leaf-like nanoplates.
As the calcining time was prolonged to 30 min (Fig. 5b), there are some small fragments due to thermal decomposition, and the “pores” of the leaf-like nanoplates surface become larger. When the calcining time was further prolonged to 45 min, the leaf-like nanorings were formed gradually, as shown in Fig. 5c. When the calcining time was further prolonged to 1 h, precursors were completely converted and leaf-like nanorings of 13–20 nm in edge width were obtained, as shown in Fig. 4. In addition, by closer observation of Figs 4e and 5a–c, it can be found that the edge width of the products increases with increasing calcination time.

Based on the above results, we propose the possible formation process of Zn(II)-doped magnetite nanorings, as schematically illustrated in Fig. 6. First, leaf-like precursor nanoplates of iron alkoxide were solvothermally synthesized using the mixture of EG and trace amount of water as solvent. The presence of trace amount of
water may facilitate the decomposition of urea to create a weak alkaline condition for the formation of the iron
alkoxide precursors. Then, the subsequent calcining process is performed to remove the organic component
and to achieve Fe3O4 phase, not tune the morphology of the products. Upon calcination in inert atmosphere, the
iron alkoxide precursor decomposes to form Fe3O4 nuclei and simultaneously release a mass of gases (e.g.,
CO2, CO, and H2O), which would generate in-situ pores in the nanobelts. Thus, at the beginning of the calcin-
ning process, porous leaf-like nanobelts are obtained (Fig. 5a). The as-generated pores in thin nanobelts would
induce the stress concentration. In order to decrease the stress concentration, the bigger pores have to grow up
via swallowing the smaller ones. Simultaneously, to minimize the interfacial energy, the as-formed Fe3O4 nuclei
located in the interior of nanobelts will diffuse outwards and aggregate along the edge of the nanobelts. Such
changes caused the morphological evolution from nanobelts to nanorings. Eventually, Zn(II)-doped magnetite
nanorings of 13–20 nm in edge width are obtained. Based on the above discussion, the morphological evolution
of nanorings from nanobelts is achieved by a combined effect of decomposition of the organic component and
diffusion growth of the newly formed nanocrystals.

We further investigated the effects of Zn(Ac)2 on the formation of Fe3O4 nanorings. As previously observed, the
products were a mixture of Fe3O4 nanospheres and iron alkoxide precursor nanobelts if no Zn(Ac)2 was
added. Once few Zn(Ac)2 (0.04 g) was added into the reaction system, the solvothermal precursors were nan-
oblates with 110–340 nm in long axis, 50–150 nm in short axis (Fig. S4a). As the amount of Zn(Ac)2 was
increased to 0.24 g, nanobelts with 210–340 nm in long axis and 110–210 nm in short axis were produced, as
shown in Figure S4b. XRD patterns of all products were no detectable difference when varied amounts of Zn(Ac)2
were added, regardless the difference in morphology (Figure S5). TG/DSC results (Figure S6) revealed that the
precursors prepared via process using different amounts of Zn(Ac)2 decomposed and converted completely
when annealed at 350 °C, but the products present different morphologies. The products prepared with 0.04 g
of Zn(Ac)2 translated to nerve-like nanowires (Figure S7a) after calcined at 350 °C for 1 h in argon atmosphere
(named as Fe3O4 nanowires (Zn0.04)). While the precursors prepared with 0.24 g of Zn(Ac)2 translates to nanor-
obelts, as shown in Figure S7b. SEM observation suggested that these rings are 25–40 nm in edge width, 75–150 nm
in short axis and 120–300 nm in long axis (named as Fe3O4 nanoring (Zn0.24)). All products are Fe3O4 as XRD
analysis indicates (Figure S8), regardless the difference in morphology. The XPS analysis shows that Zn content
in the products prepared with 0.04 and 0.24 g of Zn(Ac)2 was 0.48 at% and 3.45 at%, respectively (Figure S9). The
above results clearly suggest that the introduction of moderate Zn2+ is indispensable for the formation of Fe3O4
nanorings.

The magnetic properties of products prepared with different amounts of Zn(Ac)2 were measured at 5 and
300 K (Fig. 7). The saturation magnetization (Ms) of the obtained magnetite increased with the increasing Zn
concentration, while Zn0.16 (66.4 emu/g) and Zn0.04 (66.0 emu/g) have lower Ms than that of Zn0.24 (71.3 emu/g)
at 300 K (Fig. 7a). As shown in Fig. 7b, Ms for Zn0.04 samples was 73.3 emu/g at 5 K and slightly increasing Ms
was observed at Zn0.16 (74.8 emu/g). As for Zn0.24, with highest Zn content, Ms reached at 81.2 emu/g at 5 K. The Hc
of Zn0.04, Zn0.16 and Zn0.24 samples were 12.33 and 36 Oe at 300 K, respectively (Fig. 7c), much lower than that of bulk
magnetite (115–150 Oe). The lower Hc of the Zn(II)-doped magnetite may be attributed to small particle size of
magnetite. The fine crystalline size (specifically, ~21.1 nm for Zn0.16) could cause spin frustration on the surface,
resulting in ferromagnetic behavior. The Hc of Zn0.04, Zn0.16 and Zn0.24 samples were 56.2, 436 and 493 Oe at 5 K,
respectively (Fig. 7d). It can be found that the Ms and Hc increases when the temperature decreases. As reported
Liu et al., it attributed this to thermal fluctuations as well as the hysteresis feature disappears.

The magnetic transition was investigated by measuring zero-field cooled curves (ZFC) and field cooled (FC),
and the results are shown in Figure S10. For Zn0.04 and Zn0.16 samples, the ZFC and FC curves don't intersect at
all. So the blocking temperature (Tb) of Zn0.04 and Zn0.16 samples are above the room temperature, unlike those
for Zn0.24 samples (Tb ≈280 K) can be deducted (Figure S10). As the previously reports, no intersections between
ZFC and FC curves could occur because only a slight amount of zinc was doped into the magnetite.

The electromagnetic properties of composite specimen containing products prepared with different amounts
of Zn(Ac)2 as fillers were also measured on a vector network analyzer (VNA) in 2–18 GHz. Fig. 8 shows
the frequency dependence of the complex permittivity and complex permeability of the specimen. As seen from
Fig. 8a, ε′ and ε″, a dielectric relaxation is observed at the range of 6–12 GHz, as a descending of ε″ together with
a peak of ε′ is observed. Compared with the previous research, the dielectric relaxation is much more
intense in the current study, which is believed to be originated from to enhanced charge polarization. The num-
ber of defective sites that serve as polarized centers increases significantly after zinc ions adoption, which thus
enhances the space charge polarization. Moreover, the presence of numerous nanoparticles (Fig. 4e) brings
up large interface area, which will induce enhanced over-all interface polarization. Hence, the substitution
of Fe3+ by Zn2+ leads to enhanced polarization which then contributes to increased permittivity. On the other
hand, plenty of nanorings build a conductive network for electrons hopping and migrating, which could lead
to increased conductivity and thus contributed enhanced electric polarization. As previously reported by Tong
et al. ring-like configuration of Fe3O4 exhibit four effective paths that corresponding to four Debye relaxation
processes, as confirmed by Cole–Cole plots. A segment contains four superimposed semicircles similar to that in ref.10 was also observed in the present study (Figure S11), revealing the effect of conducting networks. Apart from the relaxation, a resonance was observed at about 11.5–12.5 GHz as shown in Fig. 8c and e, but not in Fig. 8a. Specifically, the resonance observed in Fig. 8c was more intense than that in Fe3O4 nanorings (Zn0.16). The resonance is believed to be related to the nanorings morphology of Zn(II)-doped magnetite. When used as fillers, the tubular distribution and the leaf-like morphology of Fe3O4 nanorings would tend to induce current when exposed to electromagnetic wave, leading to dielectric resonance in the curve of permittivity38. The diversity in resonance intensity may be related to the difference in nanorings’ size. As discussed above, zinc ion-dopants and ring-like structure could facilitate multiple dielectric losses.

Fig. 8b,d and f illustrate the frequency dependence of the complex permeability of the composites. The $\mu'$ decreases apparently in the 2–6 GHz band, while $\mu''$ increases in 2–4 GHz band and reaches at peak at around 4 GHz, as shown in Fig. 8b,d or f, indicating the occurrence of ferromagnetic resonance in the band. According to the previous research39,40, this resonance emerges at 2–6 GHz band is originates from natural resonance. However, it exhibits much higher resonances frequency ($f_r$) to compare with that of the magnetite nanoparticles39. The shift of $f_r$ towards higher frequency is attributed to either the small size effect or high shape anisotropy40. Negative $\mu''$ can be seen when frequency is higher than 8 GHz as shown in Fig. 8b,d and f, which is attributed to left-hand effect related to the asymmetrical ring like structure41,42. Additionally, a resonance is observed at about 11.5 or 12.5 GHz, as shown in Fig. 8d or f. The resonance intensity is also found related to the size of Fe3O4 nanorings. As previously reported10, Fe3O4 nanorings could suppress the eddy current effect for the presence of the center hole. On the other hand, Fe3O4 nanorings, acting as plasmonic structures, induce plasmon resonance and enhance permeability10. Hence, Fe3O4 nanorings generate strong resonance at about 11.5 or 12.5 GHz, which was also attributed to the leaf-like nanorings structure of fillers.

To reveal the EMA properties of magnetite nanowires or nanorings, the reflection loss (RL) of corresponding coatings of various thicknesses was calculated using the measured EM parameters according to the transmit line theory as shown in Fig. 9. Coatings using Fe3O4 nanowires (Zn0.04) as filler present $RL_{max}$ of $-18.3$ dB at 16.5 GHz (Fig. 9a). As shown in Fig. 9b, coatings containing Fe3O4 nanorings (Zn0.16) as fillers exhibit optimized EMA performances, as $RL_{max}$ of $-40.4$ dB is observed at 10.7 GHz when a thin thickness of 1.9 mm is applied. Concurrently, the effective absorbing band (EAB, $RL<-5$ dB) covers the 8–14 GHz band. When slightly increases the thickness to 2.5 mm, an EAB ($RL<-5$ dB) covering 4.2–10.8 GHz band is obtained, suggesting excellent EMA performances in C band. When Fe3O4 nanorings (Zn0.24) was used as fillers, $RL_{max}$ shifts to higher frequency to compare with the case of Zn0.16, as a $RL_{max}$ of $-43.9$ dB at 15.4 GHz was obtained in a very thin coating (1.5 mm). (Fig. 9c). As calculation suggested, Fe3O4 nanorings (Zn0.16) are found excellent candidates for EMA fillers used in...
the highly-concerned C-X band since high RL, thin thickness (around 2 mm) and wide EAB were simultaneously achieved.

The location of $RL_{\text{max}}$ is related to the electromagnetic properties of the coating at set thickness, according to the quarter-wavelength cancellation:

$$\lambda = \frac{\varepsilon \mu}{d} \frac{4\pi}{c}$$

where $d$ is the matching thickness of the coating, equal to $\frac{\lambda_m}{4}$, $\lambda_m$ is the wavelength of microwave, and $c$ is the light speed. According to the above formula (equation (1)) individually, high permittivity and permeability is benefit to compel $RL$ peaks' shifting to lower frequency. The magnetite nanorings that used as EMA fillers in the current study present high permittivity and permeability and thus possess the potential to present excellent EMA efficiency at low frequency when set thickness is applied. Higher $RL_{\text{max}}$, lower $f_m$ as well as wider EAB was obtained when Fe$_3$O$_4$ nanorings (Zn$_{0.16}$) were used as filler, to compare with other coating as shown in Table S1. The zinc ion-dopants and ring-like structures alter the electric polarization and ferromagnetic resonances and thus leads to enhanced permittivity and permeability to compare with other structures of magnetite.

**Figure 8.** Frequency dependence of complex permittivity and complex permeability in 2–18 GHz range of wax-matrixed specimens containing 75 wt% products (magnetite nanowires or nanorings) prepared with different amounts of Zn(Ac)$_2$: (a,b) 0.04 g; (c,d) 0.16 g; (e,f) 0.24 g.
In summary, we proposed a facile synthetic strategy to prepare Zn(II)-doped magnetite nanorings through thermal annealing of iron alkoxide leaf-like nanoplates, and their application as EMA fillers was evaluated. The formation mechanism of Zn(II)-doped magnetite nanorings was possibly due to a combined effect of decomposition of the organic component and diffusion growth. The saturation magnetization of Zn(II)-doped magnetite nanorings was 66.4 emu/g at room temperature. The doping a slight amount of zinc had little impact on the magnetic properties of magnetite nanorings. Furthermore, the coating using the prepared magnetite nanorings as fillers present excellent microwave absorption property. A $RL_{\text{max}}$ of $-40.4$ dB and wide EAB (8–14 GHz) was achieved in a thin coating (1.5 mm), indicating the superiority of this catalogy of materials used as EMA fillers in C-X band. The excellent EMA performance is attributed to the zinc ion-dopants and ring-like structures, which generate the space charge polarization, electric polarization and dielectric/ferromagnetic loss. The study reveals that Zn(II) doping as well as the ring-like structures present new route for excavating the potential of magnetite as EMA fillers.

**Methods**

**Synthesis of Zn(II)-doped magnetite nanorings.** All the reagents were of analytical grade and were used as received without further purification. First, iron alkoxide precursor nanoplates with leaf-like morphology were prepared by a solvothermal process. 28.0 mL of ethylene glycol (EG) and 1.0 mL of distilled water were used for the mixture solvent. In a typical synthesis, 0.290 g of iron chloride hexahydrate (FeCl$_3$·6H$_2$O), 0.16 g of zinc acetate dihydrate (Zn(Ac)$_2$·2H$_2$O) and 0.600 g of urea ((NH$_2$)$_2$CO) were dissolved into the above-mentioned mixed solution. Then, the solution was sealed into a 40 mL Teflon-lined autoclave, heated at 180 °C for 6 h. The yellow precursors were collected by high speed centrifugation, washed with ethanol and distilled water for several times, and dried at 60 °C in air. The precursors were calcined at 350 °C for 1 h in argon atmosphere to obtain magnetite (named as Fe$_3$O$_4$ nanorings (Zn$_{0.16}$)).

**Characterization.** X-ray diffraction (XRD) analyses were recorded on a Rigaku D/max 2500 diffractometer with Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm). Fourier transform infrared (FTIR) pattern was measured using a Nicolet 60-SXB FT-IR spectrometer. The morphologies and microstructures of samples were examined with a field-emission scanning electron microscope (FE-SEM, FEI Quanta 200 F), and a transmission electron microscope (TEM, JEOL JEM 2100). Thermogravimetry and differential thermal analysis (TG-DSC) was performed in a temperature ramping rate of 10 °C min$^{-1}$ from 25 to 850 °C in N$_2$ atmosphere (SDT Q600 V20.9 Build 20). X-ray photoelectron spectra (XPS) were performed using a K-Alpha spectrometer (Thermofisher Scientific Company). A drop of ethanol containing the magnetite nanorings was placed on a Si substrate, and then naturally dried in air prior to characterization by atomic force microscopy (AFM, Bruker Dimension ICON-PT).

**Static magnetic and electromagnetic measurements.** Magnetic measurements were carried out on Quantum Design physical properties measurement system (PPMS) at 5 and 300 K with the field sweeping from −50 to 50 kOe. Zero-field cooled (ZFC) and field-cooled (FC) magnetization curves were recorded between 5 and 300 K in an applied magnetic field of 100 Oe. Zn(II)-doped magnetite/paraffin composite samples were prepared by uniformly mixing the nanorings in a paraffin matrix and then pressing the mixture into a cylindrical shaped compact. The fabricated cylindrical shaped compact is coaxial toroids with outer diameter of 7 mm, inner diameter of 3 mm, and thicknesses of 3–3.5 mm. The electromagnetic parameters of the microstructures or nanostructures composite samples with 75 wt% of the Zn(II)-doped magnetite were measured in 2–18 GHz range by using an Agilent N5230A vector network analyzer.

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Author Contributions
S.Y., C.-Y.X. and L.Z. conceived and designed the experiments. S.Y. and L.C. performed the experiments. Y.W. measured the magnetic properties. All authors discussed the results and S.Y., C.-Y.X. and J.-T.J. contributed to the manuscript preparation. All authors reviewed the manuscript.

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